Bull. Environ. Contam. Toxicol. (1985) 35:569–575

Bulletin of Environmental Contamination and Toxicology

Measuring Pesticide Volatilization from Small Surface Areas in the Field

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The volatilization flux of pesticides in the field has frequently been determined from pesticide air concentration profiles by micrometeorological techniques (Parmele et al. 1972; Taylor et al. 1976, 1977). These aerodynamic techniques are not applicable to the small surface areas that might exist at waste dumps and spills, which are too small for concentration gradients to be established and measured accurately (Parmele et al. 1972). An alternative to such "open" sampling is needed.

A field chamber is described here for studying the flux of pesticides at sites too small to allow for more conventional flux measurements. To illustrate use, the flux of trifluralin, a dinitroaniline herbicide, was determined from a soil evaporation bed used for waste disposal. The field chamber flux values were adjusted to approximate the actual flux occurring from the bed. In addition, field chamber flux results were compared to those (1) measured in a laboratory volatilization chamber described previously (Sanders and Seiber 1983) and (2) estimated from high volume air samples collected outside the chamber.

MATERIALS AND METHODS

Analytical trifluralin (99%) was used as a standard. The ethyl acetate was Baker Resi-Analyzed. Amberlite XAD-4 resin (20/50 mesh, Rohm and Haas) was extracted before use as reported previously (Sanders and Seiber 1983).

The field chamber was constructed from a 19 liter Pyrex bottle without the bottom (Figure 1). A ring clamp holder was lined with rubber tubing. Duct tape was used to support a vertical metal rod on the side of the chamber which held flow meters (Dwyer Model RMA-24-SSV) and a Teflon trap. A rubber stopper in the bottle neck held a thermometer, 5 mm I.D. air inlet tube, and 11 mm I.D. air exit tube. The air inlet tube was attached to a steel air

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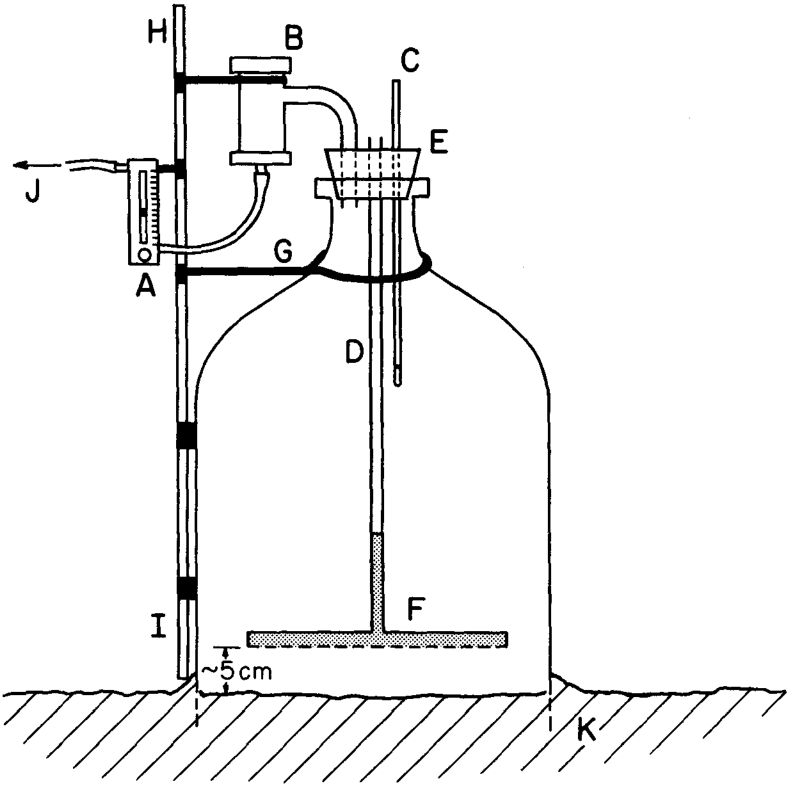

Figure 1. Diagram of Field Chamber. A, flow meter; B, resin trap; C, thermometer; D, air inlet tube; E, rubber stopper covered with aluminum foil; F, air dispersion tube; G, ring clamp; H, support rod; I, duct tape attachment point; J, to intake of air sampler; K, soil.

dispersion tube (chamber A); the tube contained 37 1-mm holes spaced 0.6 cm apart to distribute the air 5 cm above the soil surface. A second chamber (chamber B) used a 10 cm Pyrex funnel instead of the steel tube for air dispersion. For both chambers, exit tubes led to a Teflon vapor trap (Savillex segment #504-37, end cap #501, and transfer cap #501-37). The trap contained a stainless steel screen (100 mesh) and 20 ml of XAD-4 resin. After exiting the trap, the air first went through the flowmeter, then to the intake of a BGI Model U-1/AT air sampler maintained at 30-40 lpm flow rate. Chamber A had an additional trap and flow meter which could be used to pull in background air about 5 cm above the bottle neck.

A 6 x 7 m soil evaporation bed at the University of California West Side Field Station located near Five Points, CA, was chosen for the field study. The soil in the bed was saturated with water, but still provided a firm enough base for the experiments. It had previously been found to contain relatively high concentrations of trifluralin (Winterlin et al. 1984).

For high volume air sampling outside the chamber, two samplers (Bendix #3-1110-18, ca 1 m^3/min) filled with 100 ml of XAD-4 resin were placed in the soil pit facing north (upwind) along the south edge at heights of 18 and 70 cm above the surface. A Casella Meteor No. 4 anemometer was hung nearby at 70 cm height. A background sampler faced upwind away from the pit. Morning (0800-1200) and afternoon (1300-1645) sets of samples were taken on 10-13-83. Much of that day, a dusty NNW wind was blowing across the pit, causing some particulate matter to enter the samplers. Much of this particulate matter came from locations other than the pit itself; the background sampler was used to correct for this. The average wind speed at the height of the upper sampler was 2.5 and 2.1 m/sec for the morning and afternoon, respectively. Ambient air temperatures were continuously recorded using a Weathermeasure Model H313 hygrothermograph.

The first set of field samples was taken overnight (10-12-83, 1715, to 10-13-83, 0715). Chambers A and B were placed in the northwest and northeast quadrants of the bed, respectively. The air flow rate was 30 ± 1 lpm. Only chamber A was used for the remaining two sample sets, which were taken in the morning (0805-1215, southwest quadrant) and afternoon (1300-1730, southeast quadrant) of 10-13-83, using a flow rate of 40 ± 1 lpm. The chambers were firmly pressed into the soil, and some water was applied around the outside edge of the chamber to make a mud seal. Following each experiment, surface soil (top 1 cm) was sampled from the soil that was covered by the chambers. During the overnight run, the outside air temperature was equal to the chamber interior temperature (maximum of 31°C at 1715, minimum of 11°C at 0715). During daylight (sample sets two and three) the chamber temperature was considerably higher than the outside air temperature. Noting a steady increase in the outside air temperature throughout the morning (from 12° to 23°), the interior chamber temperature was assumed to increase in the same manner (from 17° to 31°). In the afternoon, the outside temperature remained constant (25°), while the interior chamber temperature dropped from 34° to 27°. A linear decrease in chamber interior temperature with time was assumed. Despite gusty winds present during the day, no visible particulates were found in the chamber resin.

Soil samples from the evaporation bed were run in a laboratory volatilization chamber described previously (Sanders and Seiber 1983). For this experiment, the model waste dump (crystallizing dish) was nearly filled with clean Reiff sandy loam soil. A 2-4 mm layer of soil from the West Side soil pit was pressed on top so that the dish was filled to the brim. Each sample was run for 24 hours at 50% relative humidity. The flow rate was 20 lpm, and the chamber temperature was 23 ± 2°C.

The soil samples and laboratory and field chamber resin samples were extracted and analyzed as reported previously (Sanders and

Seiber 1983, 1984). Recoveries of trifluralin residue from dry soil and of volatilized trifluralin from the lab chamber were 90±3% and 86 ±6%, respectively (Sanders and Seiber 1983, 1984). Resin (100 ml) from the high volume air samplers was shaken with 250 ml ethyl acetate in a 500 ml Erlenmeyer flask for 1.5 hours. The supernatant and an additional 100 ml washing were filtered and the volume reduced via rotary evaporation for analysis. Recoveries of pesticides using this extraction method have been reported previously (Wehner et al. 1984).

For the field chamber samples, trifluralin flux was calculated by dividing the amount of trifluralin found in the trap (corrected for background levels) by the sampling time and the surface area sampled (0.0592 m^2). For the laboratory chamber samples, the surface area was 0.00709 m^2. To calculate flux from the high volume air samples, the aerodynamic method was used (Taylor et al. 1977). The Richardson number was calculated (Sutton 1955). Concentrations were corrected for background levels. Average windspeeds at the lower height were estimated using a logarithmic adjustment equation (Burns et al. 1982) and a roughness height of 6 mm (Oke 1978). Due to gusty winds, air temperatures at the two heights were assumed to be identical. Average air temperatures for use in the flux calculation were calculated from the hourly ambient air temperatures. For comparison of field chamber, laboratory chamber, and high volume air sampler results, field chamber and high volume air sampler flux values were adjusted to the laboratory sample temperature (23°C). To do this, the vapor pressure for trifluralin at the temperature corresponding to each hour of field sampling was calculated (Spencer and Cliath 1974). The hourly vapor pressures for the desired sample were averaged, and the effective temperature corresponding to that average was also calculated. The field flux values were then adjusted to 23° by altering the flux values in proportion to the vapor pressure change between the effective temperatures of the field measurements and 23°., The effective field chamber sample temperatures were as follows: overnight samples, 21°C; morning sample, 26°; afternoon sample, 31°. Effective high volume air sample temperatures were 19° and 25° for morning and afternoon samples, respectively.

RESULTS AND DISCUSSION

Analysis by GC-mass spectrometry confirmed that trifluralin was present in all soil and air samples from the evaporation bed but, because concentrations were found to vary significantly in different areas of the soil pit (Table 1), results from different samples could not be combined. The concentration range for trifluralin was quite high (86-486 ppm), in agreement with previous investigations (Winterlin et al. 1984).

After adjusting for temperature, a good correlation was observed between laboratory chamber and field chamber flux measurements (correlation coefficient = 0.994, Table 1). The absolute flux was nearly the same for corresponding laboratory and field chamber

Table 1. Trifluralin flux from the field and laboratory chambers.

Chamber sample[a]	Sample time	Soil conc[b]	Amount in trap (μg)	Flux in field[c]	Flux adj to 23°C[c]	Conc adj flux (23°C)[d]
A (field)	overnight (10/12/83)	398 ± 91	360	434	607	1.5
B (field)	overnight (10/12/83)	486 ± 12	627	756	1058	2.2
A (field)	morning (10/13/83)	86 ± 9	133	539	328	3.8
A (field)	afternoon (10/13/83)	273 ± 38	432	1622	441	1.6
Laboratory		398 ± 91	98		614	1.5
Laboratory		486 ± 12	156		978	2.0
Laboratory		86 ± 9	55		345	4.0
Laboratory		273 ± 38	81		508	1.9

[a] Field and laboratory chambers with identical soil concentrations were from same soil sample.

[b] ppm ± 1 std dev, for 1 cm depth

[c] $\mu g \cdot m^{-2} \cdot hr^{-1}$

[d] $\mu g \cdot m^{-2} \cdot hr^{-1} \cdot ppm^{-1}$

samples, despite some differences in air flow patterns and the flow rate of the two systems. There was no observable difference in results for field chamber B (dispersion funnel) and chamber A (dispersion tube). When normalized to the soil concentrations, three of the samples had similar fluxes (Table 1). For one sample ("morning"), however, a slightly higher volatility for a given soil concentration of trifluralin was observed in both the laboratory and field experiments. Apparently the trifluralin in the southwest quadrant of the bed from which the soil for this sample was taken was less tightly bound than in the other quadrants.

The temperature-corrected field chamber flux values were averaged to give an estimated flux of 600 ± 300 $\mu g \cdot m^{-2} \cdot hr^{-1}$ for trifluralin. Since the bed surface area was approximately 40 m^2, this would correspond to 24 ± 12 mg of trifluralin volatilizing from the pit per hour at a temperature of 23°C. Assuming that averaging samples from each quadrant of the bed is adequate to give a representative flux, the calculated flux would differ from the actual flux occurring from the bed at 23° only because of differences in air flow patterns inside and outside the field chamber. Although not done in this experiment, a study of

Table 2. Trifluralin flux calculated from high volume air samples using the aerodynamic method[a].

Sample time (10/13/83)	Sampler	Amount in trap (μg)	Air conc (μg/m^3)	Flux[b]	Flux adj to 23°C[b]
Morning	lower	146	0.61		
Morning	upper	36	0.15	106	208
Morning	background	8	0.05		
Afternoon	lower	227	1.0		
Afternoon	upper	43	0.19	157	113
Afternoon	background	15	0.07		

[a] Flux is at field temperature through a horizontal plane above the soil surface.

[b] $\mu g.m^{-2}.hr^{-1}$

comparative water volatilization inside and outside the chamber could be used to ascertain this difference.

The surface flux was also calculated from high volume air sample concentration gradients using the aerodynamic method (Taylor et al. 1977) to compare with the chamber-measured flux values. Even though the aerodynamic method is not appropriate for such a small surface area, it yielded a value of 160 $\mu g.m^{-2}.hr^{-1}$ at 23° (Table 2) which was similar to the average field chamber results. It is likely that the small site resulted in systematically low aerodynamic fluxes; the chamber-measured values may thus better reflect the actual flux occurring at the site.

The field chamber is intended for quantifying volatilization losses at sites too small for use of more conventional techniques. It worked well for this purpose. The field chamber air sampler trapped roughly the same amounts of trifluralin as the lower of the two high volume air samplers located outside the chamber and considerably more than the upper air sampler (Tables 1 and 2). The detection limit of the chamber is thus equal to, or perhaps somewhat better than the high volume air sampler when deployed in this manner. An additional advantage of the field chamber is that it provides flux values independent of environmental wind conditions, and can therefore be used in gusty winds which could contribute interfering particulate matter to air samplers placed directly in the environment. The field chamber can also be sealed to a variety of surfaces; we have used it to measure flux above a pesticide spill on an asbestos driveway and it is potentially useful for measuring flux from turf. A disadvantage of the field chamber is that its flux measurement is determined by the surface covered by the chamber, so that several replicates (or a concentration normalization technique as employed in this study) must be employed when working with surfaces of inhomogenous concentrations. The field chamber also artificially modifies the microclimate at the surface requiring adjustment of the measured flux values to conditions which prevail at the open surface.

Acknowledgments. We thank Wray Winterlin for help in designing the field study, and Dwight Glotfelty for advice on the manuscript. This work was supported in part by NIEHS Training Grant ES 07059-06 and a UCD Jastro-Shields research grant.

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Received November 20, 1984; accepted January 9, 1985.