

Persistence of Trifluralin in Small Field Plots as Analyzed by a Rapid Gas Chromatographic Method

Allan E. Smith

A simple and rapid method is described for the gas chromatographic determination of trifluralin residues in soils using an electron-capture detector. Recoveries of 89 to 99% are obtained from three soil types treated at the 0.1- to 1.0-ppm level. Small field plots 18 × 18 cm in size were treated with trifluralin at rates equivalent to 1.4 kg/ha at

two locations in Saskatchewan. After a 5-month growing season, the residues remaining in the 0- to 5- and 5- to 10-cm levels of soil were determined. Between 11 and 21% of the applied herbicide was found in the top 5 cm of the soil, while less than 2% of the trifluralin was detected at the 5- to 10-cm levels.

Trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) is a selective preemergence soil-incorporated herbicide used for the control of a variety of grasses and broad-leaved weeds. The herbicide is volatile and must be incorporated into the soil to prevent undue loss after application (Piecarka *et al.*, 1962).

Investigations have shown that trifluralin can undergo degradation in both sterile and nonsterile soils (Messersmith *et al.*, 1971; Petrosini *et al.*, 1970; Probst *et al.*, 1967). Trifluralin is strongly adsorbed by soils (Parka and Tepe, 1969; Petrosini *et al.*, 1970; Hollist and Foy, 1971) and resists leaching in the field (Parka and Tepe, 1969).

Schweizer and Holstun (1966) have reported that phytotoxic residues of trifluralin were not detectable in silt loam samples collected approximately 6 months after application in Mississippi. Probst *et al.* (1967) found that extractable ^{14}C -trifluralin in field plots was reduced to 39% of the original activity after 29 days and to 20% after 43 days. Analysis of soil samples from 107 locations across the United States (Parka and Tepe, 1969), following continuous applications of trifluralin for 1 to 4 years, has indicated that the herbicide can be carried over at the end of the growing season. In general, such carryover is less than 10% of the applied chemical.

Trifluralin is being increasingly used in Saskatchewan for the control of weeds in rapeseed. In view of the possible carryover of the herbicide from one season to the next, persistence studies were undertaken at two locations in the province. Normally with field persistence studies plots are sprayed and residues determined by analysis of soil cores. This method does not give accurate data due to uneven herbicide application and the difficulties of sampling. Thus the technique used in these studies was to apply known amounts of trifluralin to small plots, as has already been described for similar persistence studies with triallate (Smith, 1970, 1971).

Several procedures based on gas chromatography have been described for the analysis of trifluralin in soils (Tepe and Scroggs, 1967; Harrison and Anderson, 1970; Petrosini *et al.*, 1970). The procedure to be described here was developed for the routine analysis of soil-based trifluralin residues obtained from persistence studies. The method is simple, very rapid, and gives excellent recoveries from a variety of soils with the minimum of cleanup.

EXPERIMENTAL

Soils. The composition and physical characteristics of the soils used in these studies are shown in Table I.

Reagents. The benzene was glass-distilled, whereas other chemicals were reagent grade. The Nuchar Attaclay used for cleanup was obtained from Varian Aerograph, Walnut Creek, Calif.

Gas Chromatography. The gas chromatograph used was a Varian 204-2C equipped with glass-lined injector ports and a tritium foil electron-capture detector operated at 90 V in a dc mode. The glass column was 5-ft × $\frac{1}{16}$ -in. i.d. and packed with 5% Dow Corning high vacuum grease (ethyl acetate extract) on 80-100 mesh Chromosorb W, AW, DMCS. The column was conditioned by heating for 24 hr at 220°C under a flow of nitrogen carrier gas at 50 ml/min. For the determination of trifluralin, typical operating conditions were: injector port, 230°C; oven, 160°C; and detector, 200°C. The flow of carrier gas was maintained at 50-60 ml/min. Under these conditions trifluralin had a retention time of 3.2 min.

Standards and samples were injected as benzene solutions. The calibration curve of peak height *vs.* nanograms of trifluralin injected was linear over the range 0.04 to 1.2 ng. Trifluralin present in the samples was calculated by comparing sample peak heights with those of appropriate standards.

Extraction Procedure. Field samples were air-dried to constant weight, ground in a soil grinder, and thoroughly mixed in a laboratory mixer. Twenty-gram samples were weighed into 125-ml glass-stoppered flasks to which 50 ml of benzene and 25 ml of 2-propanol were added. The flasks were then shaken for 30 min on a wrist-action shaker and, after settling, 35-ml aliquots of the supernatant liquid were pipetted into 250-ml separatory funnels and shaken twice with 25-ml portions of 3% aqueous sodium chloride solution to remove the 2-propanol. The yellow benzene layer was run into a small-stoppered flask and dried over anhydrous sodium bicarbonate. Further cleanup was achieved by the addition of 0.2 g of Nuchar Attaclay to the flasks, followed by shaking for 1 min. After settling, 3- μ l aliquots of the colorless benzene solution were injected directly into the injection port of the gas chromatograph.

Persistence Studies. An emulsifiable concentrate containing 0.4 kg/l. of trifluralin was diluted with benzene and 1.0 ml of this solution, containing 4 mg of the chemical, was applied to 18 × 18 cm field plots with a pipet. Immediately after application the chemical was thoroughly incorporated into the top 5 cm of the soil for 2 min with a small fork. This rate was 2.5 ppm or approximately 1.4 kg/ha. During the first 2 weeks of May, 4 plots were treated at Melfort and 16 were treated at Regina. Throughout the summer the plots were weeded regularly, care being taken to disturb the soil as little as possible.

Canada Department of Agriculture, Box 440, Regina, Saskatchewan, Canada.

Table I. Composition and Physical Characteristics of Soils

Soil type	Composition, %				pH	Field ^a capacity moisture, %
	Clay	Silt	Sand	Organic content		
Regina heavy clay	74.0	22.5	3.5	4.0	7.5	39.7
Oxbow loam	18.0	37.0	45.0	6.5	7.0	28.0
Melfort silty clay	39.0	36.0	25.0	8.8	6.1	35.6

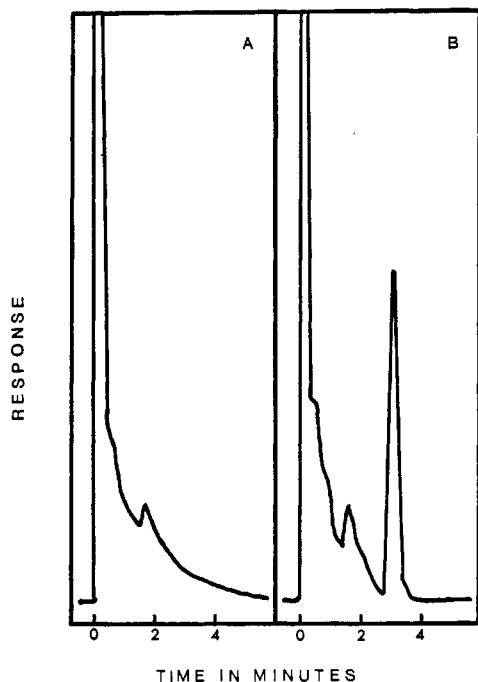
^a Mitchell *et al.* (1947).

Figure 1. Gas chromatograms of Melfort silty clay. A. 20 g of control sample. B. 20 g of control sample fortified with 0.1 ppm of trifluralin

Table II. Recovery of Trifluralin from Soils

Sample	Added, ppm	Found, ppm	Recovery, ^a %	Standard deviation
Regina heavy clay	1.0	0.985	98.5	5.0
	0.5	0.444	88.8	3.4
	0.1	0.094	94.0	2.2
Oxbow loam	1.0	0.937	93.7	2.1
	0.5	0.477	95.4	1.9
	0.1	0.097	97.0	1.4
Melfort silty clay	1.0	0.949	94.9	2.1
	0.5	0.485	97.0	2.7
	0.1	0.089	89.0	1.3

^a Average of six replicates.

During October, the entire soil from the 0- to 5-cm and 5- to 10-cm levels of four plots, at both sites, was removed as previously described (Smith, 1971). After air-drying the samples were ground, mixed thoroughly, and 20-g subsamples analyzed. In addition, at the Regina location, the soil from four plots was sampled 7 and 14 weeks after application so that a measure of the rate of disappearance could be obtained. Rainfall and temperature data were kept for both sites.

RESULTS AND DISCUSSION

In all recovery experiments 20-g samples of sieved air-dried soils were fortified at the 1.0-, 0.5-, or 0.1-ppm levels by the addition of 20, 10, or 2 μ g of trifluralin in 50 μ l of benzene.

Table III. Residues Recovered from the Top 5 cm of Soil at Two Sites Initially Treated with 4.0 mg (1.4 kg/ha) of Trifluralin

Site	Weeks after application	Recovery, mg/plot ^a	Recovery, % ^b
Regina	7	1.72 \pm 0.2	43 \pm 5
	14	0.96 \pm 0.12	24 \pm 2
	22	0.44 \pm 0.12	11 \pm 3
Melfort	22	0.84 \pm 0.08	21 \pm 2

^a Mean and standard deviation from analysis of four plots. ^b Less than 2% of the applied trifluralin residues at the 5- to 10-cm level.

After thorough mixing the samples were allowed to equilibrate for 24 hr prior to analysis.

Typical gas chromatograms obtained from control samples of Melfort silty clay and samples fortified with 0.1 ppm of trifluralin are shown in Figure 1. In recovery experiments carried out at herbicide concentrations of 0.1, 0.5, and 1.0 ppm, recoveries of 89 to 99% were obtained from all three soil types at all levels (Table II). Analysis also showed that no interfering substances were present in any untreated soils.

This procedure is considerably more rapid than that described by Tepe and Scroggs (1967), in which a methanol extraction, a solvent partitioning, two concentration steps, and a cleanup filtration employing a standardized Florisil column were required before gas chromatographic analysis. Recoveries were in excess of 80%. More recently Harrison and Anderson (1970) have described a method in which soil is extracted with methanol and the trifluralin partitioned into hexane. After concentration the hexane extracts were examined gas chromatographically. This procedure, though shorter than that of Tepe and Scroggs (1967), resulted in only 70% recoveries of trifluralin from treated soils. Recoveries of 90% could be achieved if the methanol-extracted soil were further extracted with hexane.

Using the present procedure, trifluralin can be detected simply, rapidly, and with accuracy down to the 0.1-ppm level.

The effect of moisture on the recovery of trifluralin from the soils at the 0.1-, 0.5-, and 1.0-ppm levels was also investigated. In these experiments, after the addition of the herbicide to the air-dried soils, sufficient water was added to bring the moisture level to 70% of field capacity. The samples were then allowed to equilibrate in sealed jars for 24 hr. On analysis, the recoveries ranged from 89 to 99%, thus confirming the observations of Harrison and Anderson (1970) that moisture does not affect the extraction of trifluralin from soils.

Analysis of treated plots at Regina after 7, 14, and 22 weeks showed a loss of trifluralin with time (Table III). After 22 weeks 11 \pm 3% and 21 \pm 2% of the applied chemical was recovered from plots at Regina and Melfort, respectively. These figures are in good agreement with those reported by Parka and Tepe (1969) for carryover of trifluralin in field soils analyzed 5 to 7 months after application. The temperature

conditions at both locations were similar. At Melfort 32.2 cm of rain was recorded for the duration of the experiment and 12.3 cm was noted at Regina.

At both sites the amounts of residues recovered from each of the four replicated plots were reproducible (Table III), which indicates that removal of entire soil levels from small treated plots is a satisfactory method for the study of herbicide persistence under field conditions.

In all cases less than 2% of the applied trifluralin was detected in the 5- to 10-cm soil levels, thus confirming that trifluralin is not readily leached under field conditions (Parka and Tepe, 1969).

ACKNOWLEDGMENT

Thanks are due to Eli Lilly and Co., Greenfield, Ind., for supplying a sample of trifluralin. The author also wishes to thank B. J. Hayden for technical assistance.

LITERATURE CITED

- Harrison, R. M., Anderson, O. E., *Agron. J.* **62**, 778 (1970).
 Hollist, R. L., Foy, C. L., *Weed Sci.* **19**, 11 (1971).
 Messersmith, C. G., Burnside, O. C., Lavy, T. L., *Weed Sci.* **19**, 285 (1971).
 Mitchell, J., Moss, H. C., Clayton, J. S., *Soil Surv. Rep. Univ. Sask. Coll. Agr.* No. 12, p 185 (1947).
 Parka, S. J., Tepe, J. B., *Weed Sci.* **17**, 119 (1969).
 Petrosini, G., Tafuri, F., Businelli, M., *Agrochimica* **14**, 123 (1970).
 Pieczarka, S. J., Wright, W. L., Alder, E. F., *Proc. SWC* **15**, 92 (1962).
 Probst, G. W., Golab, T., Herberg, R. J., Holzer, F. J., Parker, S. J., Van der Schans, C., Tepe, J. B., *J. AGR. FOOD CHEM.* **15**, 592 (1967).
 Schweizer, E. E., Holstun, J. T., *Weed Sci.* **14**, 22 (1966).
 Smith, A. E., *Weed Res.* **10**, 331 (1970).
 Smith, A. E., *Weed Sci.* **19**, 536 (1971).
 Tepe, J. B., Scroggs, R. E., "Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives," Vol. V, Academic Press, New York, N.Y., 1967, p 527.

Received for review December 1, 1971. Accepted February 1, 1972

Movement and Fate of Dyfonate in Soils under Leaching and Nonleaching Conditions

E. Paul Lichtenstein,* Kenneth R. Schulz, and Thomas W. Fuhremann

The degradation and movement of ^{14}C -Dyfonate in different soil types was tested in the laboratory under leaching and nonleaching conditions, at different temperatures and various incubation times. Different apparatuses are described which had been especially designed for testing the movement of pesticidal chemicals in soils with and without water. Although Dyfonate did not move to an appreciable extent through an agricultural loam soil, its transport with water through soils was, to a large extent, a function of the soil type. Water, after its percolation

through a silt loam, did not contain measurable amounts of the insecticide, while water after its percolation through a sandy loam soil was toxic to mosquito larvae and contained 4% of the dosage originally applied to the top soil layer. After degradation of ^{14}C -Dyfonate in soils, radiocarbon was lost from the soil by volatilization of the ethoxy moiety and partially by transport of the ring moiety with water. When no water was percolated the insecticide also degraded and moved into untreated soil, but to a lesser degree.

Studies on the persistence and fate of insecticides after application to crops and soils have, to a large extent, been conducted with chemicals of the chlorinated hydrocarbon type. In an attempt to reduce the application of persistent pesticides, more degradable compounds are now being used for insect control. Concurrent with this use, more information is needed as to the fate of these insecticides after application. In addition to persistence and metabolism studies with organophosphorus and carbamate insecticides, problems related to the migration and potential transport of these chemicals with water through soils should be investigated. Concern has particularly been expressed regarding the potential movement of insecticidal residues with water from upper soil strata into uncontaminated soil and ground water below. Lake and river water can undoubtedly be contaminated with runoff water from adjacent agricultural fields. In this case soil particles to which insecticidal residues are adsorbed are being washed off the soil. However, one of the most important questions is whether water in deeper soil strata can be contaminated by insecticidal residues.

To study the movement of pesticide chemicals in soils, various experiments were conducted in the past, primarily

with chlorinated hydrocarbon insecticides (Beran and Guth, 1965; Bowman *et al.*, 1965; Harris, 1969; Lichtenstein and Schulz, 1958). Lichtenstein *et al.* demonstrated in 1967 that water, after its percolation through aldrin- or parathion-treated loam soils, did not contain measurable amounts of aldrin but did contain small amounts of parathion, whose concentration in the water was below the water solubility of the insecticide. The amount of parathion in percolated water, though, was a function of the concentration of the insecticide in the soil.

In the present study, laboratory experiments were conducted with the organophosphorus insecticide Dyfonate (*O*-ethyl *S*-phenyl ethylphosphonodithioate) to study its persistence, metabolism, and potential movement in different soil types under leaching and nonleaching conditions. Dyfonate was selected because it is not as persistent as many of the chlorinated hydrocarbon insecticides (Schulz and Lichtenstein, 1971) but is relatively volatile in comparison to other organophosphorus compounds (Lichtenstein and Schulz, 1970). It has a water solubility of 13 ppm, which is greater than the solubility of most chlorinated hydrocarbon insecticides and smaller than that of most of the organophosphorus compounds. Although these experiments were conducted with one model insecticide, procedures developed and described here could serve as a model for testing the persistence and

*Department of Entomology, University of Wisconsin, Madison, Wisconsin 53706.