

Table V. Estimation by Gas-Liquid Chromatography (GLC) and ^{14}C Assay of the Percentage of MBT and Degradation Products in Extract Fractions of Two Walbeck Soil Samples Which Had Been Incubated with [^{14}C]MBT for 6 Months

Soil no.	MBT fraction		Degradation products fraction	
	GLC	^{14}C	GLC	^{14}C
1	91.0	91.9	9.0	8.1
2	95.2	94.6	4.8	5.4

silica gel column followed by acetonitrile to elute the metabolites. The proportion of MBT in the soil extracts, as determined by gas chromatography and by ^{14}C assay, was also found to be over 90% (Table V).

Since most of the ^{14}C in the soil extracts was identified as MBT and the proportion of MBT extracted from the soil whether from an aged sample or a spiked sample was similar, it is unlikely that the 30 to 50% of the ^{14}C not extracted by the proposed method would be in a form or state similar to that of the extractable MBT. Recent studies on the fate of substituted phenylureas and acylanilides have shown that many of these compounds and their degradation products could be tightly bound by soil components and become difficult to be extracted from the soil by the solvent extraction approach (e.g., Hsu and Bartha, 1973). MBT is a substituted urea compound with a benzothiazolyl moiety rather than a phenyl moiety; nevertheless, its behavior and degradation could be analogous to that of phenylureas. Thus, some of the ^{14}C in the aged soil samples could be MBT bound tightly by soil components. Moreover, Cheng et al. (1974) have observed that MBT was partially degraded in these aged soil samples and that considerably more MBT was degraded in soil containing decomposing roots than soil without roots. Therefore, one might expect some portion of the pesticide remaining in the soil to be partially me-

tabolized to product(s) which still retain ^{14}C in the benzothiazolyl moiety of the MBT molecule but in a form that is no longer extractable by the proposed method. More drastic treatments of the soil would be required to remove the remaining ^{14}C from the soil.

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A Simple System to Simultaneously Measure Volatilization and Metabolism of Pesticides from Soils

A new system is described which permits simultaneous measurement of pesticide loss by volatilization and metabolic CO_2 evolution from soils. A polyurethane foam plug effectively trapped volatile dinitroaniline herbicides arising from soil surfaces, while allowing $^{14}\text{CO}_2$ to pass through the plugs and subsequently become trapped in alkali solution. Trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) was more volatile than butralin [4-(1,1-dimethylethyl)-*N*-(1-methylpropyl)-2,6-dinitrobenzenamine] when applied to soil surfaces. Volatilization was the major loss mechanism for trifluralin during the first 3 weeks after application. The distribution of volatile products from trifluralin was drastically altered when exposed to an ultraviolet (uv) lamp.

One mechanism by which pesticides disappear from soil surfaces is volatilization. Due to the volatile nature of most dinitroaniline herbicides, they are incorporated directly into the soil to reduce volatilization and photodecomposition losses. Incorporated dinitroanilines are then dissipated mainly by metabolism and, to a lesser extent, by volatilization.

A number of volatility studies (Bardsley et al., 1968; Ketchersid et al., 1969; Parochetti and Hein, 1973; Spencer and Cliath, 1974) have shown that the greatest loss of trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-

toluidine) occurs from warm, moist soils. These same conditions are conducive for rapid microbial metabolism, and studies with soils (Probst et al., 1967; Otto, 1974) and isolated soil microorganisms (Laanio et al., 1973; Kearney et al., 1974) indicated that under certain situations metabolism might be an important loss mechanism. Under flooded conditions volatility was insignificant and metabolism appears to be rapid (Parr and Smith, 1973). Spencer et al. (1973) have prepared an extensive review of the measurement and soil factors affecting pesticide volatilization. One method employed to measure vapors

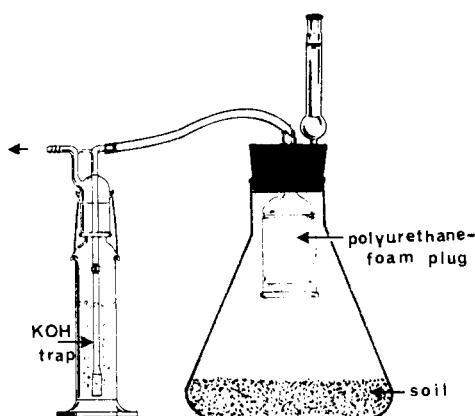


Figure 1. Diagram of system designed to measure volatilization and metabolism of pesticides in or on soils.

of polychlorinated biphenyls and chlorinated hydrocarbon insecticides has been the use of porous polyurethane foam (Bidleman and Olney, 1974a,b).

In many studies conducted on the persistence of dinitroaniline herbicides in soils, quantitative distinction of volatilization and microbial metabolism has been unclear. The present communication describes a simple system for measuring both volatilization and microbial metabolism of the dinitroaniline herbicides in soils. In a larger context, the system would appear to have application for any case of pesticide that is affected by these two processes.

EXPERIMENTAL SECTION

Materials. A diagram of the system is shown in Figure 1. It consists of the following materials: 2.7-l. Fernbach flask, Buchner 60-ml (40 M) sintered glass filter funnel, no. 13 rubber stopper, 125-ml gas washing bottle (with coarse dispersion tube) containing 100 ml of 0.1 M KOH, drying tube filled with Ascarite and Drierite, 4.5 × 4.5 cm o.d. polyurethane foam plug (polyesterurethane, gray type, 2 lb ± 10% cu ft density, ester base, open cell, manufactured by the William T. Burnette, Co., Baltimore, Md.), and two 20-W Westinghouse sunlamps (Model FS20). The system is continuously purged with CO₂ free air by connecting the gas washing bottle to a regulated vacuum source.

Methods. A polyurethane plug was placed into the filter funnel. The filter funnel was covered with aluminum foil, since some discoloration of the plug occurred when exposed to the sunlamp and volatile herbicides coming off the soil surface.

To determine whether CO₂ passed through the polyurethane plug and was trapped in the KOH solution, 0.1 μCi of Na₂¹⁴CO₃ in 10 ml of pH 8 buffer was placed in an empty Fernbach flask. The Na₂CO₃ solution was slowly acidified with 0.1 N HCl. Generation of ¹⁴CO₂ was measured with the plug in the filter funnel and then repeated in the absence of the plug, both at an air flow rate of 25–30 ml/min.

To determine the efficiency of the plug for trapping vapors, 0.1 μCi of [ring-¹⁴C]butralin [4-(1,1-dimethyl-ethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine] in benzene was added to an empty flask; plugs were then replaced and analyzed periodically for 4 weeks. Individual exposure periods varied from 1 to 4 days. At each sampling time, the plug was cut into quarters of ca. 1-cm thick disks and soxhlet extracted for 2 hr with benzene-acetone (1:1, v/v).

For soil studies, 500 g of Matapeake silt loam was placed in the flask and 0.5 mg of butralin plus 0.1 μCi of [¹⁴C]-butralin were added to the soil surface in a benzene solution. Four flasks, two covered with aluminum foil, were

Table I. Vapor and Metabolic Loss of Butralin and Trifluralin from Matapeake Silt Loam^a

Week	Trapped ¹⁴ C as % of total applied					
	Butralin			Trifluralin		
	Plugs	CO ₂	Total	Plugs	CO ₂	Total
1	0.45 (82)	0.10 (18)	0.55	4.42 (95)	0.18 (5)	4.60
2	0.43 (84)	0.08 (16)	0.51	0.86 (81)	0.20 (19)	1.06
3	0.37 (72)	0.15 (28)	0.52	1.16 (69)	0.49 (31)	1.65
Totals	1.25	0.33	1.58	6.44	0.87	7.31

^a Since there was no difference in the amount of ¹⁴C lost as volatile products in the light or dark, the values presented represent averages of four replications. Numbers in parentheses indicate percent ¹⁴C appearing in plugs and CO₂.

then continuously exposed to high-energy uv radiation by the use of a fluorescent light source placed directly against the glass. An identical experiment was also initiated with trifluralin. At weekly intervals, the plugs and CO₂ trapping solutions were assayed for ¹⁴C. Soxhlet extracts of the polyurethane plugs were reduced in volume and separated on silica gel thin-layer chromatographic plates (TLC) by using benzene as a solvent system. Between experiments the polyurethane plugs were cleaned by extracting them with a 1:1 (v/v) hexane-acetone solution for 12 hr in a soxhlet extractor (Gesser et al., 1971). ¹⁴CO₂ trapped in the 0.1 M KOH solution was assayed by standard liquid scintillation methods.

RESULTS AND DISCUSSION

A comparison of the KOH traps revealed no difference in the amount of ¹⁴CO₂ trapped in the presence or absence of the polyurethane plugs. The plugs, therefore, could be used in metabolism studies since they do not impede the generation and alkali trapping of ¹⁴CO₂. Analysis of the plugs divided into four sections showed that 97% of the butralin volatilized from the bottom of the flask was recovered in the first centimeter of the plug and 1% in each of the remaining three 1-cm sections. These results are the average of approximately five runs of various exposure times of the plugs to the vapors of butralin. Extraction of the KOH solutions with ethyl acetate revealed that no butralin had escaped through the plug.

The amounts of butralin and trifluralin recovered from the polyurethane plugs and ¹⁴CO₂ in the KOH traps from surface applications to soil and the total amount of ¹⁴C lost by these two mechanisms are shown in Table I. For both herbicides, volatilization was the major mechanism of loss. The amount lost as vapor tended to decrease with time. This was particularly the case with trifluralin, where there was a large decline in the amount lost from the first to the second week. Trifluralin was more volatile than butralin, the loss of trifluralin during the first 3 weeks being 6.44% as compared to butralin's 1.25%. Trifluralin was reported to be more volatile than butralin in a previous study (Parochetti and Heim, 1973). The ratio of pesticide volatilized to pesticide metabolized will depend on a great many factors, including air exchange rate, method of application (surface or incorporated), soil properties, moisture, and others. For comparable results, these factors should be maintained constant.

There was no difference in distribution of the volatile products extracted from the polyurethane plugs between light and dark treatments for butralin. Approximately

90% of the ^{14}C was recovered as butralin (based on TLC evidence). For trifluralin at the first week sampling time, there was a major difference in volatile products recovered between the light and dark flasks. About 90% of the ^{14}C was recovered as trifluralin in the dark, but only 25.3% in the light. Most of the ^{14}C (72.6%) was located in more polar products than trifluralin at or adjacent to the origin on the TLC plate in the uv experiments. At subsequent sampling dates the relative amount of photoalteration decreased with a larger percentage of the volatilized ^{14}C appearing as trifluralin.

This fairly simple system appears to offer a mechanism for simultaneously measuring volatility and CO_2 metabolic loss of pesticides on or in soils. Before the system can be applied to other pesticides, the trapping characteristics of the plugs should be tested. The system was easy to maintain although the soils lost moisture during the time between weekly samplings. The use of humidified air may control or prevent soil moisture loss. Studies on vapor phase photolysis may be feasible in the system, although considerable difficulty was experienced in identifying any trifluralin photoproducts when the plug extracts were examined by GLC-mass spectral analysis.

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Instability of Methyl 1-(Butylcarbamoyl)-2-benzimidazolecarbamate (Benomyl) in Various Solvents

In all the solvents investigated, the conversion of benomyl to MBC proceeds by spontaneous intramolecular catalysis. The observed rate constants show no correlation with the existing empirical solvent parameters but can be explained in terms of solvent-solute interactions. Spontaneous intramolecular catalysis is markedly slowed down by water.

The systemic fungicide, benomyl, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, is unstable in dilute aqueous solutions and is rapidly converted into methyl 2-benzimidazolecarbamate (MBC) by removal of the butylcarbamoyl side chain (Clemons and Sisler, 1969). Benomyl is soluble in some organic solvents (Du Pont de Nemours and Co., 1970; Pease and Holt, 1971) but its stability is not well documented in spite of the work done (Kilgore and White, 1970; Chiba and Doornbos, 1974). The kinetic study we carried out allowed us to elucidate the effect of various solvents on the conversion rate of benomyl.

EXPERIMENTAL SECTION

Apparatus. A Unicam SP 800 recording spectrophotometer, equipped with a thermostated multiple cell compartment, was used for all spectroscopic measurements.

Chemicals. All organic solvents were analytical grade materials. Benomyl was supplied by Du Pont de Nemours-France. MBC was obtained through hydrolysis of benomyl; its chemical characteristics were identical with those reported in the literature.

Uv Spectra. Water-methanol solutions of benomyl and MBC exhibited the following absorptions [λ_{max} nm (log ϵ); s = shoulder]: benomyl, 223 (4.3), 240 (4.0), 255 (3.9), 263 (3.9) s, 285 (4.2) s, 294 (4.3); MBC, 241 (4.0), 281 (4.1) s, 287 (4.2), 294 (3.8) s.

Kinetic Measurements. All reactions were carried out at $25 \pm 0.1^\circ\text{C}$ in tightly stoppered 1-cm quartz cells. The change in optical density of the substrate was followed at suitable wavelengths. Initial repetitive scans of the uv region established that these reactions held tight isobestic points, indicating the absence of intermediates.

The absorbance vs. time plots gave the pseudo-first-order rate constants graphically, using the experimental infinity value. The observed rate constants k_{obsd} were obtained by plotting $\log(A_t - A_\infty)$ vs. time, where A_∞ and A_t are the absorbance readings at infinity and at time t , respectively: $\log(A_t - A_\infty) = \log A_0 - (k_{\text{obsd}}/2.303)t$.

RESULTS AND DISCUSSION

The constants derived from the kinetic study of the solvolysis of benomyl in various solvents at $25 \pm 0.1^\circ\text{C}$ are listed in Table I.

The investigation of the uv spectra recorded at the end