Aerobic Soil Metabolism and Residue Uptake in Plants of an Organophosphorus Carbamate Insecticide

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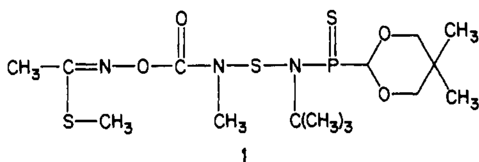
An experimental organophosphorus carbamamate insecticide, methyl *N*-[[[[[(1,1-dimethylethyl)(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)amino]thio]methylamino]carbonyl]oxy]ethanimidothioate, was synthesized with ^{14}C in the thiophosphoramide and carbamate portions of the molecule. The radiolabeled insecticide had a half-life of 6.1, 1.9, and 0.5 days in aerobically aged sandy loam, sandy clay loam, and silty clay loam soils, respectively. The insecticide was degraded to thiophosphoramide and methomyl. The methomyl was further metabolized to CO_2 and bound residue while the thiophosphoramide metabolite was metabolized to an oxophosphoramide metabolite that accumulated in the soil. Changing the soil composition affected the rate of carbamate degradation but the degradation products remained the same. The oxophosphoramide metabolite was absorbed from greenhouse soil by spinach and radish plants without further metabolism but oat plants degraded the oxophosphoramide.

The experimental organophosphorus carbamate (1) is an effective foliar insecticide for the control of lepidopterous larvae. Also, the carbamate insecticide has shown



excellent crop tolerance and is less toxic to mammals and beneficial anthropods than many existing insecticides. This report describes studies to assess the fate of the carbamate insecticide in soil and its soil residue uptake in plants.

MATERIALS AND METHODS

Materials. All solvents were analytical grade and purchased from Burdick & Jackson Co. The 1-(methylthio)[U-^{14}C]acetaldoxime and 2-(*tert*-butylamino)-5,5-dimethyl-2-thioxophosphorinan-*5-methyl*-^{14}C were purchased from Amersham and New England Nuclear, respectively. The sandy loam, sandy clay loam, and silty clay loam soils were obtained from cooperators in Tifton, GA, Donna, TX, and Bard, CA, respectively. The soils were analyzed by the Michigan State University Soil Laboratory (Table I). Thin-layer plates (250 μm) and X-ray film were purchased from Analtech and Kodak Co., respectively.

Methods. A Packard TriCarb Model 3255 scintillation spectrometer and a Beckman Biological oxidizer were used to analyze the soluble and bound ^{14}C samples. Soil moisture was determined with an Ohaus moisture determination balance. TLC plates were automatically scraped with an Analabs, Inc, Multi-Vial Zonal TLC plate scraper. HPLC data were obtained on a Du Pont Model 820 HPLC with a LDC 254-nm detector (Model 1203), a Zorbax ODS column (4.6 mm × 25 cm), and a Valco injection loop (20 μL). Gas chromatographic analyses were obtained on a MT-220 Tracor instrument, which was equipped with a sulfur and phosphorus flame photometric detector (Model FPD-100 AT, Melpar, Inc.) and a 4-ft hi-efficiency 3% 8-BP column. Compounds were analyzed with the detector in the phosphorus mode. The column, inlet, and detector temperatures were set at 170, 180, and 190 °C, respectively. The mass spectra were obtained on a LKB-9000 GC–mass spectrometer that was equipped with a 2-ft 1% OV-1 column at 120 °C. Spinach, mustard, and oat plants were grown in a greenhouse under normal environmental conditions.

Soil thin-layer plates were prepared by the procedures of Helling et al. (1974). Sieved (2.0 mm) soil was moistened with deionized water until moderately fluid and then applied to TLC plates (12 × 12 in.) with a Camag TLC spreader. The plates were allowed to dry overnight.

Synthesis of the [^{14}C]METH-carbamate (Figure 1). The fluorocarbamoyl thiophosphoramide (140 mg, 0.41 mmol) was dissolved in CH_3CN (1.0 mL) by warming, and the resulting solution was cooled to room temperature, before adding Et_3N (60 μL) and the 1-(methylthio)[U-^{14}C]acetaldoxime (41 mg, 0.39 mmol, sp act. = 13.0 mCi/mmol). After being stirred for 5 h under N_2, the mixture was quenched with water and the resulting white solid was filtered. The white solid was dissolved in CH_2Cl_2–acetone (49:1) and chromatographed on a silica gel column (1.5 × 22 cm) with CH_2Cl_2–acetone (49:1). Fourteen fractions (10 mL) were combined after TLC analysis, EtOAc–hexane (1:1). The solvents were removed in vacuo, and the solid was recyrstallized from methanol to yield 95 mg (57%) of colorless crystals: sp act. = 13.5 mCi/mmol; mp 166–168 °C [lit. mp (Nelson, 1982) 167–168 °C]; TLC, SiO_2, R_f 0.5 (EtOAc–hexane, 1:1); MS m/z (rel intensity) 429 (17, m^+), 373 (64, M − C_4H_8), 325 (4, M − C_3H_6NOS), 268 (25, M − $C_5H_9N_2O_2S$), 211 (100, M − $C_9H_{18}N_2O_2S$), 165 (70, M − $C_9H_{18}N_3O_2S_2$).

Synthesis of the [^{14}C]TPA-carbamate (Figure 1). The title compound was synthesized in a one-step procedure by dissolving the 2-(*tert*-butylamino)-5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinane-*5-methyl*-^{14}C (118.5 mg, 0.5 mmol, sp Act. = 9.76 mCi/mmol) and the carbamyl fluoride (95.7 mg, 0.6 mmol) in CH_2Cl_2 (1.0 mL) and cooling the solution to −10 °C under N_2, before adding Et_3N (97.4 μL, 0.7 mmol) in CH_2Cl_2 (300 μL), dropwise, over a period of 15 min. The mixture was stirred for an additional 30 min at −10 °C before adding the 1-(methylthio)acetaldoxime (73 mg, 0.7 mmol) and tetraethylammonium chloride (15 mg, 0.1 mmol) in 2 N NaOH (0.5 mL). After the mixture was rapidly stirred for 4 h at 0 °C, additional water and CH_2Cl_2 were added and the layers separated. The organic layer was washed with water, dried (anhydrous Na_2SO_4), and filtered. Removal of the solvents produced an oil that was chromatographed as previously described for the [^{14}C]METH-carbamate. The resulting white solid was recrystallized from methanol to yield 100 mg (47%) of colorless crystals: sp act. = 10.6 mCi/mmol.

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Table I. Soil Analysis[a]

sample site	pH	$^1/_3$-Bar[b] moisture	% sand	% silt	% clay	% organic matter	classification
California	8.1	30.1	17.4	49.1	33.4	4.14	silty clay loam
Texas	7.7	18.4	55.1	15.4	29.4	1.52	sandy clay loam
Georgia	5.6	8.1	75.1	9.4	15.4	1.24	sandy loam
greenhouse	6.9	9.1	70.4	10.0	19.6	10.02	sandy loam

[a] Furnished by the Michigan State Soil Testing Laboratory. [b] Percent by weight.

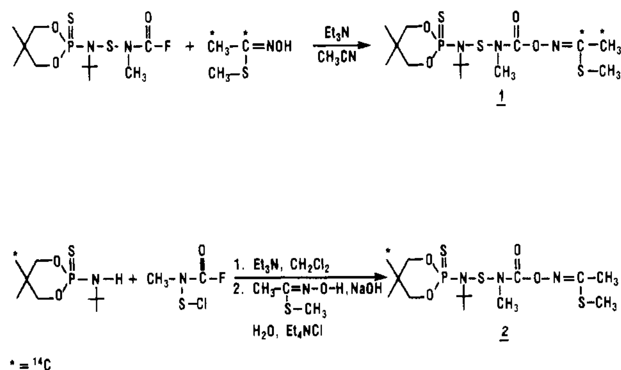

Figure 1. Synthesis of the [^{14}C]METH- (1) and [^{14}C]TPA- (2) carbamates.

The physicochemical data were identical with those of the [^{14}C]METH-carbamate.

Soil Preparation. The analyzed soils (Table I) were allowed to air-dry for 2–3 days and then passed through a 2-mm sieve to remove pebbles and debris. The sandy clay loam and silty clay loam soils were moistened with deionized water to give a 5% moisture content, while the sandy loam soil was moistened to 75% of the 0.33-bar moisture retention level. The soils were allowed to equilibrate for 2 days before treatment with the [^{14}C] carbamates.

Soil Treatment. Soil samples (~600 g) were treated with either [^{14}C]METH- or [^{14}C]TPA-carbamate in acetone (5 mL) to give a carbamate concentration of 1.0 ppm in the soil. The acetone solution was added to the soil in 1-mL increments, and the flasks were frequently shaken and purged with nitrogen after the addition of each 1-mL increment. After treatment, each soil sample was spread out on aluminum foil and quartered. Two samples (~10 g) were taken from each quadrant to determine the uniformity of the carbamate distribution in the soil at zero time. After time zero analysis, the sandy clay loam and silty clay loam soils were moistened to 75% of the 0.33-bar moisture rentention level. The flasks of treated soils were attached to an air flow through apparatus. Carbon dioxide free air (~20 mL/min) was bubbled through deionized water before entering the soil chamber (1-L flask). The off gases were bubbled through consecutive traps containing ethylene glycol and 1 N NaOH.

Sampling of the Treated Soils and Traps. The treated soils were aerobically incubated until >90% of the [^{14}C]carbamate insecticide had been degraded. Soil samples (6–11 g) were taken on days 1, 3, and 7 and every 14 days thereafter. The total incubation time was 70 days for the Georgia sandy loam and Texas sandy clay loam and 14 days for the California silty clay loam soil. The ethylene glycol and NaOH traps were emptied and recharged with fresh solutions on days 1, 3, and 7 and every 7 days thereafter. The volume of solution in the traps was determined, and triplicate aliquots (50 μL) were analyzed by liquid scintillation counting (LSC).

Analysis of the Soil Samples. The soil samples were extracted consecutively with acetonitrile (2 × 50 mL) and 1:1 methanol–water (50 mL). Samples of soil were shaken with acetonitrile and filtered through Celite. The layer of soil was removed and further shaken with methanol–water and filtered through the same Celite. The solvents were removed in vacuo, and the residue was dissolved in acetonitrile (5.0 mL) and methanol (5.0 mL), respectively. Triplicate aliquots (50 μL) of the above extracts were analyzed for carbon-14 by LSC, and the results were calculated in ppm equivalents of [^{14}C]carbamate for 0% moisture soil. The extracted soil was air dried and weighed, and the moisture content of each soil was determined. Triplicate aliquots (200–300 mg) of each extracted soil were analyzed for bound ^{14}C residues by combustion–LSC.

When less than 10% of the [^{14}C]carbamate remained in the soil, the entire soil sample was extracted with acetonitrile (2 × 500 mL), as previously described, and samples (~50 g) of the extracted soil were Soxhlet extracted with methanol overnight. Also, samples (10 g) of the acetonitrile extracted soil were further extracted with 1:1 methanol–water (50 mL), as previously described. After removal of the solvents in vacuo, the acetonitrile residue was reconstituted with acetonitrile (5.0 mL), while the Soxhlet and methanol–water residues were reconstituted with methanol (5.0 mL). Triplicate aliquots (50 μL) of the above solutions were analyzed by LSC. The Soxhlet-extracted soil samples were dried overnight, and triplicate aliquots (200–300 mg) were analyzed for bound ^{14}C residue by combustion–LSC. The results were calculated in ppm equivalents of [^{14}C]-carbamate of 0% moisture soil.

Determination of the Rate of [^{14}C]Carbamate Disappearance. The acetonitrile extracts from the soils, aerobically aged with [^{14}C]TPA-carbamate, were spotted on individual silica gel TLC plates. After development (10 cm) with ethyl acetate–hexane (1:1), the TLC plates were subjected to autoradiographic analysis. The R_f corresponding to the [^{14}C]carbamate was determined, and each TLC plate was scraped in 5-mm increments and analyzed by LSC. Linear regression analysis was used to determine the depletion rate for the concentration of carbamate left in the soil over time.

Soil Metabolite Identification. The soil treated with [^{14}C]METH-carbamate produced small quantities of one extractable metabolite. The TLC (R_f 0.34, SiO_2, ethyl acetate–hexane, 7:3) and HPLC (retention time 5.6 min, acetonitrile–water, 3:2) behavior of the metabolite was compared to those of authentic standards. Due to the paucity of the metabolite, a California soil sample (500 g) was dosed at 10 ppm with unlabeled carbamate containing tracer amounts of [^{14}C]METH-carbamate. After a 1-day incubation, the soil was extracted with acetonitrile. The extracted metabolite was purified by silica gel column chromatography with ethyl acetate–hexane (1:1) as the eluting solvent. The metabolite was further purified by TLC development with ethyl acetate–hexane (7:3). Identification of the metabolite was accomplished by direct inlet mass spectral comparison with a standard.

The soils treated with [^{14}C]TPA-carbamate produced two acetonitrile-extractable metabolites. Mixtures of the metabolites were compared to standard compounds by TLC analysis with ethyl acetate–hexane (1:1) as the eluting solvent mixture. Further, the gas chromatographic re-

tention times of the metabolites were in good agreement with standard compounds. The metabolites were easily separated by silica gel SiO_2 column chromatography when ethyl acetate–hexane (1:1) and ethyl acetate were used to elute the less polar and more polar metabolites, respectively. The less polar metabolite was further purified by TLC, SiO_2, with hexane–ethyl acetate (9:1) as the eluting solvent. After the metabolite was located by autoradiography, the band was scraped and eluted with ethyl acetate. Similarly, the more polar metabolite was purified by TLC, SiO_2 (ethyl acetate–hexane, 7:3), in the same manner as the less polar metabolite. Both metabolites were identified by GC–mass spectral comparison with standard compounds.

Trap Metabolite Identification. Aliquots (50 μL) of the combined NaOH traps from each soil experiment were analyzed for ^{14}C activity before adding saturated barium chloride solution (Nathan et al., 1958). The mixture was adjusted to pH 8.0–8.5 with 12 N HCl and centrifuged to remove the barium carbonate precipitate. Additional barium chloride solution (1 mL) was added, and the mixture was centrifuged. The supernate was decanted and analyzed for ^{14}C activity.

Fractionation of Bound Soil Residues. The procedures of Ivarson and Stevenson (1964) were used to determine the nature of the bound ^{14}C residues in the soil. The soils were Soxhlet extracted with methanol overnight and dried prior to the hydrolysis and fractionation of the ^{14}C-bound soil residues. The [^{14}C]METH-carbamate-treated silty clay loam soil was hydrolyzed with 12 N hydrochloric acid. After centrifugation, the supernate was fractionated by ion-exchange chromatography.

Soil Thin-Layer Chromatography. A sandy loam greenhouse soil, agricultural sand, and the three soils used in the aerobic soil metabolism study were used to prepare soil thin-layer plates. Both the [^{14}C]METH- and [^{14}C]-TPA-carbamates were applied to the soil plates, and the plates were developed horizontally with deionized water. The water was transferred from a tray to the soil plate with a piece of filter paper. The R_f's were calculated from the autoradiographs of the developed soil plates.

Plant Uptake of the [^{14}C]Carbamate Residues from Aged Soils in the Greenhouse. The greenhouse soil was treated separately with 0.7 ppm of the two radiolabeled carbamates. After aerobically aging for 30 days, the soil was sampled and mustard, radish, and oat seeds were planted in the aged soil. The remaining treated soil was aged for 120 and 365 days before sampling and planting the above crops.

The soil was analyzed for ^{14}C residues as previously described for the aerobic soil metabolism study. The mature crops were harvested, macerated, and extracted with acetonitrile. The solid material was further extracted with methanol–water (1:1), and the extracts were analyzed for ^{14}C residues. Combustion analysis was used to determine the amount of bound ^{14}C plant residues.

RESULTS AND DISCUSSION

Soil Treatment. Each of the three soils were treated with [^{14}C]METH- and [^{14}C]TPA-labeled carbamates in separate experiments. The experiments were conducted with ^{14}C label at both terminal ends of the carbamate (Figure 1), which provided a basis for following the metabolism of both the methomyl and thiophosphoramide portions of the molecule.

After the treated soils were thoroughly mixed, analysis showed a distributional variance of only 7.0–8.9%. This insured that the accountability data was reliable throughout the sampling period.

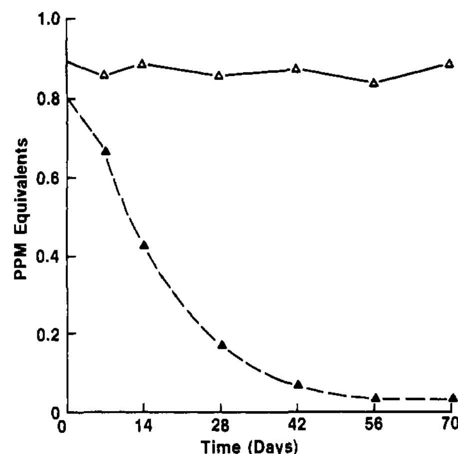

Figure 2. Sandy clay loam soil extractable residues vs. time; soil was treated with [^{14}C]TPA-carbamate (Δ) or [^{14}C]METH-carbamate (▲).

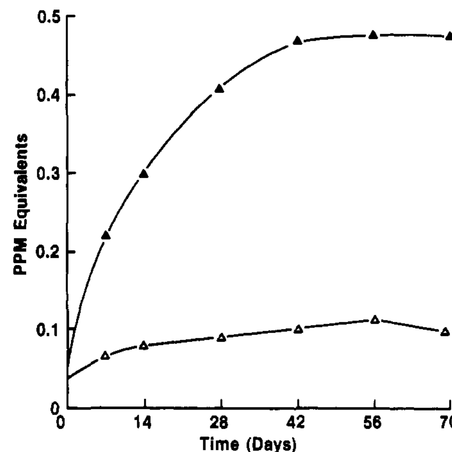

Figure 3. Sandy clay loam bound residues vs. time; soil was treated with [^{14}C]METH-carbamate (▲) or [^{14}C]TPA-carbamate (Δ).

Table II. Metabolism of the [^{14}C]Carbamate in Three Soils[a]

distribution[b] of radioactivity	Georgia sandy loam[c] carbamate [^{14}C]-METH	Georgia sandy loam[c] carbamate [^{14}C]-TPA	Texas sandy clay loam[c] carbamate [^{14}C]-METH	Texas sandy clay loam[c] carbamate [^{14}C]-TPA	California silty clay loam[d] carbamate [^{14}C]-METH	California silty clay loam[d] carbamate [^{14}C]-TPA
carbon dioxide	29.6	3.5	38.3	6.9	42.3	1.6
soil extract	21.2	67.9	2.9	85.7	4.4	79.2
soil bound	31.9	32.3	45.4	11.6	46.9	5.9
total recovery	82.7	103.7	86.6	104.2	93.6	86.7

[a] All soils were dosed with either the [^{14}C]METH- or the [^{14}C]-TPA-carbamate at the 1.0-ppm level. [b] The distribution of radioactivity is calculated in percent of the original treatment. [c] Exposed for 70 days. [d] Exposed for 14 days.

Soil Analysis. The soils that were treated with [^{14}C]METH-carbamate showed a decrease in ^{14}C-extractable residues while the same soil treated with [^{14}C]TPA-carbamate showed a minimal decrease in extractable residues over time (Figure 2). Conversely, the concentration of ^{14}C-bound residues increased more rapidly in soil treated with [^{14}C]METH-carbamate than the same soil treated with [^{14}C]TPA-carbamate (Figure 3). Also, analysis of the soils at the termination of the experiments showed predominantly bound ^{14}C residues for the [^{14}C]METH-carbamate treated soils and predominantly extractable ^{14}C residues for the [^{14}C]TPA-treated soils (Table II).

Trap Analysis. The ethylene glycol and NaOH traps were analyzed over time for ^{14}C residues. The ethylene

Table III. Linear Regression Analysis of the Carbamate Depletion in the Soil

soil	slope	rate constant, $days^{-1}$	half-life, days	correlation coefficient
Georgia	-0.049	0.113	6.1	0.959
Texas	-0.161	0.371	1.9	0.960
California	-0.566	1.304	0.5	0.988

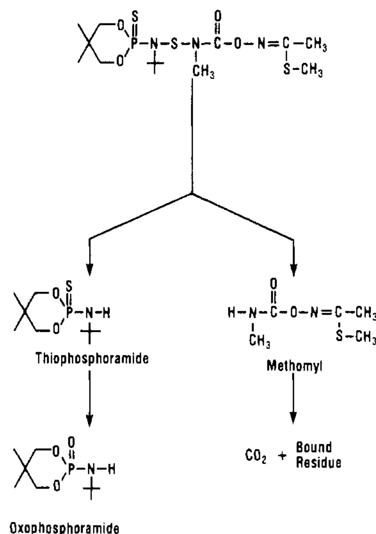

Figure 4. Aerobic soil metabolism of the carbamate insecticide.

glycol traps, which were used to collect volatile ^{14}C organics, had negligible ^{14}C residues throughout all of the soil studies. However, the NaOH traps contained large amounts of $^{14}CO_2$ from the [^{14}C]METH-carbamate-treated soils and much smaller amounts from the [^{14}C]TPA-carbamate-treated soils (Table II). The results indicate that the methomyl portion of the carbamate is degraded to $^{14}CO_2$ and ^{14}C-bound residue while the thiophosphoramide moiety remains in the soil as extractable ^{14}C residues.

Rate of Carbamate Degradation. The rate of carbamate degradation was obtained from the TLC–histogram analysis over time for those soils treated with [^{14}C]TPA-carbamate. The concentration of carbamate remaining in the soil was determined from the TLC–histograms. Linear regression analysis was used to determine the correlation coefficients, rate constants, and half-lives for the depletion of carbamate in three soils (Table III). The data show that the carbamate degraded approximately 12 times faster in the California silty clay loam soil as the Georgia sandy loam soil. The rate difference may be due to the higher concentrations of organic matter and clay in the California soil. Also, the carbamate appeared to degrade by cleavage of the S–N bond. Umetsu et al. (1980) have shown that S–N bond cleavage readily occurred by thiolysis or hydrolysis. Further, experiments with treated sterile soil gave S–N bond cleavage at a rate comparable to unsterilized soil. Therefore, the rate-limiting step in the degradation of the carbamate in soil appears to be chemical rather than microbial.

Soil Metabolite Characterization. The autoradiographs of the extracts from the [^{14}C]METH-carbamate treated soils showed the formation of a ^{14}C metabolite that was more polar than the parent carbamate. Further, the metabolite had an identical TLC R_f, HPLC retention time, and mass spectrum as a methomyl standard (Figure 4).

TLC autoradiogram analysis of the soil extracts over time showed an increase in methomyl concentration with a concomitant decrese in the concentration of the parent carbamate. However, the methomyl concentration also

Table IV. Determination of $^{14}CO_2$ Content in the NaOH Traps[a]

soil	[^{14}C]-carbamate treated	ppm equiv/ 50 mL	ppm equiv/ 50 mL, after pptn	% $^{14}CO_2$	% volatile organics
Georgia	METH	12.50	0.0	100	0
Georgia	TPA	1.74	0.0	100	0
Texas	METH	18.77	0.0	100	0
Texas	TPA	3.66	0.0	100	0
California	METH	54.79	0.71	98.7	1.3
California	TPA	2.01	0.0	100	0

[a] Precipitation of $^{14}CO_2$ as $Ba^{14}CO_3$.

Table V. Fractionation of ^{14}C Residue Bound to Soil[a]

	soils			
	sandy loam[b]		sandy clay loam,[c]	silty clay loam,[d]
fraction	[^{14}C]-METH	[^{14}C]-TPA	[^{14}C]METH	[^{14}C]METH
volatile[e]	64.0	88.1	73.8	35.1
fulvic acid	8.2	9.0	19.8	4.0
β-humus	14.7	1.6	3.5	0.6
α-humus	4.7	0.3	0.7	1.3
hymatomelonic acid	2.8	0.3	0.7	7.0
remaining bound	5.6	0.7	1.5	52.0[f]

[a] Percentage of the total ^{14}C-bound residue in each soil treated with 1.0 ppm of [^{14}C]METH-carbamate or 1.0 ppm of [^{14}C]TPA-carbamate. [b] Total ^{14}C-bound residue was 0.32 ppm for both the [^{14}C]METH- and [^{14}C]TPA-carbamates. [c] Total ^{14}C-bound residue was 0.45 ppm. [d] Total ^{14}C-bound residue was 0.47 ppm. [e] Percentage of ^{14}C lost during NaOH hydrolysis. [f] Further fractionated into soluble humin (37.2%) and insoluble humin (14.8%).

decreased after depletion of the parent carbamate. The degradation of the methomyl to $^{14}CO_2$ and ^{14}C bound residue is consistent with the results of Harvey and Pease (1973), who studied the aerobic soil metabolism of methomyl. The $^{14}CO_2$ was identified as the only trap metabolite by precipitation as the barium [^{14}C]carbonate (Table IV). Thus, the [^{14}C]METH-carbamate degrades to [^{14}C]methomyl, which is further metabolized to $^{14}CO_2$- and ^{14}C-bound residue. The fractionation of the ^{14}C-bound residue (Table V), showed that the ^{14}C label was distributed throughout the soil fractions as a consequence of reincorporation of the $^{14}CO_2$ into the soil organic matter. Several different methods of trapping the ^{14}C volatiles (Table V) for characterization were tried without success.

The soils treated with [^{14}C]TPA-carbamate produced two ^{14}C-extractable metabolites. One metabolite was less polar and the other metabolite was more polar than the parent carbamate. The less polar metabolite had the same TLC R_f, gas chromatographic retention time, and mass spectrum as a thiophosphoramide standard (Figure 4). Also, the more polar metabolite had the same TLC R_f, gas chromatographic retention time, and mass spectrum as an oxophosphoramide standard (Figure 4). Gas chromatography with phosphorus flame photometric detection provided an excellent method of analysis for the phosphoramide metabolites in both crude and purified soil and plant extracts.

TLC autoradiogram analysis of the soil extracts over time showed that the parent [^{14}C]TPA-carbamate degraded to the less polar [^{14}C]thiophosphoramide, which was further metabolized to the [^{14}C]oxophosphoramide. Thus, after depletion of the parent carbamate, the [^{14}C]thiophosphoramide concentration decreased with a concomitant increase in the concentration of the [^{14}C] oxophosphoramide. The [^{14}C]oxophosphoramide appears to be an end product in the soil and does not undergo further metabolism. Although the rate of degradation of the

Table VI. Residue Determination in Radish, Mustard, and Oats from [^{14}C]METH-Treated Soil

plant	30 day[a] extractable	30 day[a] bound[b]	120 day[a] extractable	120 day[a] bound[b]	365 day[a] extractable	365 day[a] bound[b]
soil	0.217	0.268	0.028	0.275	0.014	0.179
radish bulb	0.153	0.092	0.018	0.016	0	0.002
radish top	0.138	0.200	0.011	0.020	0	0.008
mustard	0.101	0.113	0.022	0.018	0.006	0.005
oat kernels	0.045	0.188	0	0.023		0.029[c]
oat straw	0.309	0.579	0.056	0.053	0.079	0.098

[a] The number of days the [^{14}C]METH soil was aged before sampling and planting the crops. [b] Average ppm equivalents. [c] The oat plants did not produce sufficient oat kernels for the determination of extractable residues. The total residue in the oat kernels is given above.

Table VII. Residue Determination in Radish, Mustard, and Oats from [^{14}C]TPA-Treated Soil

plant	30 day[a] extractable[b]	30 day[a] bound[b]	120 day[a] extractable[b]	120 day[a] bound[b]	365 day[a] extractable[b]	365 day[a] bound[b]
soil	0.52	0.06	0.42	0.08	0.45	0.06
radish bulb	0.23	0.01	0.40	0	0.12	0.0
radish top	2.76	0.02	1.40	0.01	1.94	0.01
mustard	1.96	0.02	2.99	0.03	1.72	0.02
oat kernels	0.07	0.09	0.08	0.07		0.04[c]
oat straw	4.48	2.96	4.32	0.76	1.06	0.57

[a] The number of days the [^{14}C]TPA soil was aged before sampling and planting the crops. [b] Average ppm equivalents. [c] The oat plants did not produce sufficient oat kernels for the determination of extractable residues. The total residue in the oat kernels is given above.

parent carbamate was different in each soil, the metabolic pathway was the same for all three soils.

Soil Thin-Layer Chromatography. The soil thin-layer chromatography study showed that the parent carbamate had no mobility (R_f 0.0) in the California silty clay loam and Texas sandy clay loam soils. However, the carbamate showed some mobility (R_f 0.15) in the greenhouse sandy loam (high organic matter) soil. Further, the carbamate had intermediate mobility (R_f 0.6) in the Georgia sandy loam (low organic matter) and was very mobile (R_f 0.9) in the agricultural sand. Therefore, soils containing clay and/or high concentrations of organic matter appear to inhibit the mobility of the carbamate.

Determination of ^{14}C Residues in Radish, Mustard, and Oat Plants. The radish, mustard, and oat plants had total ^{14}C residues of less than 1.0 ppm when grown in 0.7 ppm of [^{14}C]METH-carbamate treated soil aged for 30 days (Table VI). Further, the total residues decreased to less than 0.1 ppm in plants grown in 120 day and 1 year aged soils. Approximately, 50% of the radioactivity was found in the bound residues of the above crops. The low plant residue levels were consistent with the low levels of extractable ^{14}C residues found in the soil on the days the crops were planted (Table VI).

Conversely, the radish, mustard, and oat plants, grown in 0.7 ppm TPA-^{14}C carbamate treated soil had significant amounts of organic solvent extractable ^{14}C residues (Table VII). The major extractable metabolite in both radish and mustard plants was the oxophosphoramide (Figure 4), which averaged 75 ± 3, 78 ± 3, and 95 ± 1% of the extractable residue in mustard, radish bulbs, and radish tops, respectively. Thus, the oxophosphoramide metabolite from the soil was concentrated in the radish and mustard plants. Also, the oxophosphoramide was stored and not further metabolized in these plants.

However, the oxophosphoramide was extensively metabolized in the oat plant. The oat straw contained 1.0–4.5 ppm equiv of extractable residue that comprised eight minor metabolites that were more polar than the oxophosphoramide.

Registry No. 1, 72542-56-4; [^{14}C]-1, 94483-58-6; 2, 94498-92-7; fluorocarbamoyl thiophosphoramide, 78051-43-1; 1-(methylthio)[^{14}C]acetaldoxime, 94483-59-7; 2-(*tert*-butylamino)-5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinane-[5-methyl-^{14}C], 94498-93-8; (chlorothio)methylcarbamic fluoride, 30933-08-5; 1-(methylthio)acetaldoxime, 13749-94-5.

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