

Figure 7. Proposed mechanism for the conversion of oxycarboxin to 2-(vinylsulfonyl)acetanilide involving the surface of a glass container.

by a similar reaction reported for the ring-opened form of carboxin (Corbeil et al., 1973). It is proposed that the silanol groups available at the glass surface act as a base to catalyze the ring-opening step.

The results of this study provide significant impact on analysis of oxycarboxin in general. It is apparent that the glass-catalyzed decomposition of oxycarboxin is rapid enough to cause great variation in recovery levels in metabolism and environmental fate studies. It is possible, for example, that one could misinterpret the absence of oxycarboxin residues as losses occurring in the sample matrix rather than attributing the loss to storage conditions used during isolation or extraction steps, while the presence of 2-(vinylsulfonyl)acetanilide could be misinterpreted as a real product of biological or environmental decomposition. At this point, there are no data available to suggest that the losses noted here have a significant

effect on studies involving much more concentrated solutions of oxycarboxin such as would be encountered in standard assay procedures. However, it is clear that the storage of calibrated standard solutions of oxycarboxin in glass containers for extended periods of time is a questionable practice that should be accompanied by periodic analysis to confirm solution integrity.

Registry No. III, 5259-88-1; $\text{CH}_2=\text{CHSO}_2\text{CH}_2\text{CONHC}_6\text{H}_5$, 75983-69-6; H_2O , 7732-18-5; CH_3OH , 67-56-1; CH_3CN , 75-05-8; CH_2Cl_2 , 75-09-2.

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Residues of Avermectin B_{1a} in Rotational Crops and Soils following Soil Treatment with [¹⁴C]Avermectin B_{1a}

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[¹⁴C]Avermectin B_{1a} was applied twelve times to muck and sandy loam soils and three times to sandy soil at 0.025-0.030 lb/acre per application. These applications simulated the intended use of avermectin B_{1a} on celery, vegetables, and cotton, respectively. Following three aging periods in each soil type, sorghum, lettuce, and carrot or turnip seeds were planted and harvested at one-fourth, half, and full size. Analysis of these crops by oxidative combustion demonstrated that crops grown in muck, sandy loam, and sandy soils contained radiolabeled residues ranging from below the limit of quantitation (BLQ) to 7.4 μg/kg of avermectin B_{1a} equivalents, BLQ to 11.6 μg/kg, and BLQ to 3.54 μg/kg, respectively. There was a general trend of decreasing residue concentrations with increasing preharvest intervals in crops grown in all soils. The radioactivity present in muck and sandy loam soils disappeared with half-lives ranging from 103 to 267 days and from 102 to 132 days, respectively.

Avermectins are a class of macrocyclic lactone pesticides that have been under investigation as acaricides/insecti-

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cides in citrus, orchard, and field crops (Price, 1983; Schuster and Everett, 1983; Wright, 1984; Reed et al., 1985; Burts, 1985). Abamectin (MK-0936) is currently being developed as a miticide/insecticide to control red imported fire ants and several phytophagous pests on horticultural and agronomic crops.

Since the use of a pesticide on a crop may lead to the presence of the pesticide or its degradation products in the soil, the potential exists that crops planted in that soil at a later date (rotational crops) might take up some of these residues. The present study was designed to determine the uptake and accumulation of [¹⁴C]avermectin B_{1a} (the major component of abamectin) and all radiolabeled residues in rotational crops following soil treatment with the

radiolabeled parent compound. The three soils (muck, sandy, sandy loam) and the four different crops (sorghum, lettuce, carrots, turnips) selected for this study characterize three different uses for which abamectin is being developed. These vegetable and grain crops are typically grown in these soils following the harvest of celery treated with abamectin (muck soil), the harvest of cotton treated with abamectin (sandy soil), and the harvest of vegetables treated with this pesticide (sandy loam soil).

Several preplanting intervals (the time from the last application of [^{14}C] avermectin B_{1a} to the time of rotational crop planting) were selected to examine the effects of increasing intervals on subsequent accumulation in these crops of residual [^{14}C] avermectin B_{1a} or its radiolabeled breakdown products. Likewise, crops were harvested at various maturities (one-fourth, half, full size) to determine the effect of crop maturity on residue levels.

MATERIALS AND METHODS

Formulation. [^{14}C] Avermectin B_{1a} (>99% radiochemical purity) in an emulsifiable concentrate (EC) formulation was supplied by Merck, Sharp & Dohme Research Laboratories. The ^{14}C label was located at C3, C7, C11, C13, or C23 of avermectin B_{1a}. All stock solutions contained 18 g of total avermectin/L of EC with a specific activity of 6.5 $\mu\text{Ci}/\text{mg}$ (117 μCi of $^{14}\text{C}/\text{mL}$ of EC) and were diluted with water immediately prior to soil treatment.

Materials and Design. The soils used in this study were acquired from Zellwood, FL (Lauderhill muck); Lake Park, GA (sandy); and Riverside, CA (sandy loam). Twelve galvanized, round tubs (43–45 in. diameter, 23.5-in. depth) with bottom drainage holes were placed within a 30 ft \times 70 ft fenced (7-ft) area located at the Central Florida Research and Education Center, University of Florida, Sanford, FL. Each tub rested on 1 in. \times 2 in. furring strips placed inside wooden catch basins (5-ft square, 1-ft depth) lined with plastic. This arrangement permitted water drainage from the tub into the catch basin as well as reabsorption by the soil of the water that had previously drained from it into the basin.

To prevent flooding of tubs and catch basins caused by rains during the summer of 1984, the entire compound area occupied by the experimental and control tubs was tented with a 6-mil polyethylene film (Monsanto 703, nonultraviolet absorbing film) from Aug 21 to Sept 29, 1984. To protect crops from freezing temperatures, the tubs were covered with plastic film and heated with light bulbs.

[^{14}C] Avermectin B_{1a} Application. Four tubs were filled with muck (celery) soil, four with sandy (cotton) soil, and four with sandy loam (vegetable) soil. Placement of tubs within the compound was randomized for each soil type. One tub of each soil type was designated as an unsprayed (untreated) control tub. The remaining tubs of muck (celery) and sandy loam (vegetable) soil were sprayed once weekly for 12 weeks with a water dilution of [^{14}C] avermectin B_{1a} in EC (3.63 mg/100 mL) at a rate of 0.03 lb of active ingredient/acre (100 mL/tub), 1.5 times the maximum use rate. The spray was evenly applied to the experimental soils with a carbon dioxide pressurized hand-operated applicator. The total amount of avermectin B_{1a} applied to each experimental plot of these two soils was 43.6 mg. The application of radiolabeled avermectin B_{1a} to muck and sandy loam soils extended from July 19 to Oct 4, 1984. The sandy soil received only three applications of [^{14}C] avermectin B_{1a} (3.16 mg/100 mL) at 50-day intervals at a rate of 0.026 lb of active ingredient/acre (100 mL/tub), 1.3 times the maximum use rate, beginning July 31 and ending Nov 8, 1984, according to the same procedure. The total amount of avermectin B_{1a}

applied to each experimental plot of sandy soil was 9.5 mg.

Due to the damage of the sorghum crops from the first planting in muck and sandy loam soils caused by a hard freeze, these parts of the study were repeated with the application of [^{14}C] avermectin B_{1a} in EC (3.0 mg/100 mL) at a rate of 0.025 lb of active ingredient/acre (100 mL/tub), 1.25 times the maximum use rate, from May 8 to July 24, 1985. The total amount of avermectin B_{1a} applied to each experimental repeat plot was 36 mg.

Planting Procedure. After the final [^{14}C] avermectin B_{1a} application to all tubs, each tub was divided into three equal pie-shaped areas (3.76 ft² each). At specific intervals following the final application of [^{14}C] avermectin B_{1a} to each soil [referred to as preplanting intervals (PPINTs)], sorghum, lettuce, and turnip seeds were planted in muck (celery) soil and sorghum, lettuce, and carrot seeds were planted in sandy (cotton) and sandy loam (vegetable) soils, one crop per area. The PPINTs for each soil type were as follows: muck (celery) soil, 14, 123, and 365 days; sandy (cotton) soil, 31, 120, and 365 days; sandy loam (vegetable) soil, 29, 123, and 365 days. Each experimental tub was planted only once during this study. Control tubs were replanted three times, once at the beginning of each planting scheduled for that particular soil.

In the repeat study of muck and sandy loam soils, sorghum seeds were planted 14 days (muck 14 repeat tub) and 30 days (sandy loam 30 repeat tub) after the final [^{14}C] avermectin B_{1a} application to muck and sandy loam soils, respectively. Control sorghum seeds were also planted at these times in the corresponding control tubs.

Two weeks prior to all scheduled plantings, small monitor pots containing the soils corresponding to the tub to be planted were planted with seeds of the crops to be grown in the experimental tubs and placed beside the appropriate tub. Crops grown in these monitor pots were harvested periodically to permit an estimation of the size of each crop growing in the experimental and control tubs prior to actual harvest. Plants were irrigated when signs of water stress were observed, and fertilization was conducted on a regular basis.

The number of seeds planted in each pie-shaped area was approximately that required to grow 84 sorghum plants, 21 lettuce plants, 42 carrot plants, or 21 turnip plants.

Harvesting of Crops. All harvested crop samples were divided into three groups each containing an equal number of plants and stored frozen ($-20\text{ }^\circ\text{C}$) in polyethylene bags until analysis. Both control and experimental crops were harvested at one-fourth, half, and full maturity. Crop parts that were harvested and stored separately included lettuce heads, carrot tops and taproots, turnip tops and taproots, and sorghum leaf stem and grain portions.

Soil Sampling. Soil samples (2.5-cm diameter cores) from the top 30 cm of soil were taken from all tubs (experimental and control) following the final [^{14}C] avermectin B_{1a} application to soils and immediately before planting and from all tubs from which crops were harvested at each harvest time. After the final [^{14}C] avermectin B_{1a} application and immediately before planting, core samples (0.0–7.5-, 7.5–15.0-, 15.0–30.0-cm depth) were taken, one from each pie-shaped area in all tubs, and a polyethylene pipe was then placed in the hole to prevent the collapse of surrounding soil into the hole. Prior to the harvesting of each crop, 2.5-cm-diameter cores from the top (0.0–7.5-cm depth), middle (7.5–15.0-cm depth), and bottom (15.0–30.0-cm depth) soil layers were taken from a single hole in the area in which the crops to be harvested were growing. All soil samples were packaged separately in

Table I. Radiolabeled Residues of [¹⁴C]Avermectin B_{1a} in Fresh Sorghum and Lettuce (μg/kg of Avermectin B_{1a} Equivalents; Mean of Two Groups)

size at harvest	sorghum						lettuce		
	leaf stem			grain			muck	sandy	sandy loam
	muck	sandy	sandy loam	muck	sandy	sandy loam			
First Planting									
preplanting interval	14 days	31 days	29 days	14 days	31 days	29 days	14 days	31 days	29 days
1/4	4.78 [0.98]	<0.85	2.54 [2.08]				6.94	0.92	2.40
1/2	1.74 <0.83	<6.03	11.6 [1.82]				2.52	0.77	0.45
full	7.40 [1.70] ^a	<2.23	(freeze) [1.74]	(freeze) [<4.71]	<4.13	(freeze) [<3.95]	0.44	0.18	0.67
Second Planting									
preplanting interval	123 days	120 days	123 days	123 days	120 days	123 days	123 days	120 days	123 days
1/4	2.73	3.54 ^a	2.19				0.24	0.48	1.49
1/2	6.56 ^a	<0.62	1.60 ^a				0.27	0.33	0.50
full	0.60 ^a	<0.84	1.19	<5.69	<0.99	<1.39	0.15	<0.15	0.16
Third Planting									
preplanting interval	365 days	365 days	365 days	365 days	365 days	365 days	365 days	365 days	365 days
1/4	<0.59	<0.69	0.90 ^a				0.76	<0.43	0.47
1/2	<1.19	<1.86	<1.16				0.72	<0.35	0.50 ^a
full	<2.52	<2.68	1.85 ^a	<3.88	<3.60	<4.13	1.39	<0.52	0.67

^a Value for one group only. Second group had a value BLQ (below the limit of quantitation). Bracketed values are for repeat studies. Values denoted < represent the average of the limits of quantitation for the two samples in a group.

polyethylene bags, labeled appropriately, and stored frozen (-20 °C) until analysis.

Analytical Procedures for Crop and Soil Samples.

Two of the three groups of plant parts and two-thirds of the soil samples were analyzed. With the exception of sorghum seed heads, which were prepared by manual removal of the seeds (grain) from the seed head, each crop part was cut into pieces (1/2-in. long) with scissors. Known amounts of the samples were blended with dry ice and then dried in a hood at 50 °C under an infrared heat lamp for 48 h. The weights of the dried samples were then recorded, and the radioactivity was determined by oxidative combustion of duplicate samples of 200 mg of dried material (Tri-Carb sample oxidizer, Model B306, Packard Instrument Co., Inc.).

Control crop samples harvested from the first planting of all soils and from the repeat studies of muck and sandy loam soils were similarly prepared and analyzed.

The limit of quantitation in micrograms/kilogram of dried sample material for each sample analyzed was determined according to eq 1 and 2, where $\sigma = Bkg_1 + Bkg_2$

$$LQ \text{ (dmp)} = 14.1\sigma/\text{eff} \quad (1)$$

$$LQ \text{ (}\mu\text{g/kg)} = LQ \text{ (dpm)} / [\text{smpl wt combusted (kg)}] \times [\text{sp act. (dpm}/\mu\text{g avermectin B}_{1a})] \quad (2)$$

+ Bkg_3/TN^2 , N = number of background samples, Bkg = cpm of background samples, T = 10-min counting time, and eff = $\text{std (cpm)}/\text{theor std (dpm)}$. Values of microgram/kilogram for dried material were converted to microgram/kilogram for fresh material by dividing the former value by the moisture conversion factor of the sample analyzed (weight of fresh crop/weight of dried crop).

To determine the loss of [¹⁴C]avermectin B_{1a} during the analytical procedure, 100 or 150 μL of a water solution of the applied [¹⁴C]avermectin B_{1a} formulation was added to three weighed portions of each plant part or soil sample taken from control tubs. These fortified samples were then processed as described above (beginning with the blending

step), and the percentage recovery of the added radioactivity was calculated.

RESULTS AND DISCUSSION

Radiolabeled Residues of [¹⁴C]Avermectin B_{1a} in Crops. The total radiolabeled residue concentrations of avermectin B_{1a} (in microgram/kilogram of [¹⁴C]avermectin B_{1a} equivalents) found in all crop parts analyzed ranged from below the limit of quantitation (BLQ) to 9.09 μg/kg for plants grown in muck (celery) soil, from BLQ to 3.54 μg/kg for crops grown in sandy (cotton) soil, and from BLQ to 13.7 μg/kg for crops grown in sandy loam (vegetable) soil. (The ranges of values represent those of all samples analyzed and not the average of two groups as presented in Tables I and II). This small range in values and low levels of residues made the observation of trends and relationships difficult.

Crops grown in sandy soil (sorghum, lettuce, carrots) contained generally lower concentrations of radiolabeled residues of avermectin B_{1a} than the same crops of equivalent harvest size grown in either muck or sandy loam soils (Tables I and II). Sorghum grown in sandy soil was the only crop studied under experimental conditions in which the radioactivity was BLQ in eight out of nine plant part groups analyzed. These findings are most likely related to the smaller amount of [¹⁴C]avermectin B_{1a} applied to this soil (9.5 mg/tub) than to muck and sandy loam soils (43.6 mg/tub in the original study and 36 mg/tub in the repeated sorghum study).

Of the two crops grown in both muck and sandy loam soils, both sorghum leaf stem portions (from all plantings in the original and repeated studies) and lettuce (from the second planting, preplanting intervals of 123 days) harvested from sandy loam soil usually contained greater or equivalent radiolabeled residue concentrations of avermectin B_{1a} than the same crops of equivalent harvest size and planting periods grown in muck soil (Tables I and II). This finding cannot be directly related to the amount of avermectin B_{1a} applied to these soils, which was the

Table II. Radiolabeled Residues of [¹⁴C]Avermectin B_{1a} in Fresh Carrots and Turnips (μg/kg of Avermectin B_{1a} Equivalents; Mean of Two Groups)

size at harvest	carrots				turnips	
	tops		taproots		tops, muck	taproots, muck
	sandy	sandy loam	sandy	sandy loam		
	First Planting					
preplanting interval	31 days	29 days	31 days	29 days	14 days	14 days
1/4	1.08	2.21	1.49	0.87	0.83	3.45
1/2	0.37	0.62	0.58 ^a	0.42	0.37	0.80
full	<0.66	1.66	<0.37	0.95	<0.96	0.14
	Second Planting					
preplanting interval	120 days	123 days	120 days	123 days	123 days	123 days
1/4	0.47 ^a	1.29	1.05 ^a	1.86	<0.66	1.12
1/2	<0.68	0.99	<1.05	1.01	<1.05	0.18 ^a
full	<1.07	2.62	0.91 ^a	1.93	<0.61	<0.71
	Third Planting					
preplanting interval	365 days	365 days	365 days	365 days	365 days	365 days
1/4	<1.00	1.38	<0.60	1.14	<0.43	<0.44
1/2	<1.18	1.53	<0.80	1.90	<0.69	<0.45
full	<1.02	<1.07	<1.01	0.83 ^a	<0.55	0.37

^a Value for one group only. Second group had a value BLQ (below the limit of quantitation). Values denoted < represent the average of the limits of quantitation for the two samples in a group.

Table III. Preharvest Intervals for Rotational Crops (Days) (Days from Final [¹⁴C]Avermectin B_{1a} Application to Harvest)

size at harvest	sorghum			lettuce			carrots		turnips, muck
	muck	cotton	california	muck	sandy	sandy loam	sandy	sandy loam	
	First Planting								
preplanting interval	14 days	31 days	29 days	14 days	31 days	29 days	31 days	29 days	14 days
1/4	67 [47] ^a	114	99 [63] ^a	67	106	86	114	121	67
1/2	98 [72] ^a	137	117 [84] ^a	80	114	99	127	144	80
full	112 [105] ^a	175	(freeze) [126] ^a	98	127	121	144	163	98
	Second Planting								
preplanting interval	123 days	120 days	123 days	123 days	120 days	123 days	120 days	123 days	123 days
1/4	188	159	167	167	160	167	176	212	173
1/2	219	188	195	176	169	176	201	176	188
full	258	220	231	187	179	187	230	267	204
	Third Planting								
preplanting interval	365 days	365 days	365 days	365 days	365 days	365 days	365 days	365 days	365 days
1/4	398	392	398	407	406	408	434	441	419
1/2	427	448	426	419	414	420	484	470	429
full	484	561	483	429	434	429	547	520	463

^a Repeat.

same for both soils, or to the measured concentrations of radiolabeled residues of avermectin B_{1a} in each of these soils because the concentrations of these residues were consistently greater in muck than in sandy loam soils. It is possible that the availability of avermectin B_{1a} to the plants was lessened in the muck soil.

No radioactivity was detected in any sorghum grain analyzed. Radiolabeled residues of [¹⁴C]avermectin B_{1a} were measurable in sorghum leaf stems grown in muck soil during the first and second planting periods (preplanting intervals of 14 and 123 days, respectively) and in those grown in sandy loam soil during all periods (preplanting intervals of 29, 123, and 365 days, respectively). The mean concentration of radiolabeled residues of [¹⁴C]avermectin

B_{1a} in leaf stem portions of sorghum grown in sandy loam soil during the first planting period of the original study (preplanting interval of 29 days) and harvested at half full size was the highest average concentration (11.6 μg/kg avermectin B_{1a} equivalents) measured in all crops analyzed. The mean concentration of radiolabeled residues found in equivalent samples from the repeat study in this soil was only 1.82 μg/kg. Unlike the sorghum crops in the original study, which required longer growing periods to reach the designated harvest sizes and were stunted in appearance, those in the repeat study exhibited a more typical growth pattern (Table III). The radiolabeled residue concentrations found in crops grown in the repeat study are probably more representative of those concen-

Table IV. Radiolabeled Residues of [¹⁴C]Avermectin B_{1a} in Soils (μg/kg)

time	soil layer	muck, plot 14	sandy soil, plot 31	sandy loam soil, plot 29
final	top	838	18.5	75
applicn	middle	845	BLQ ^a	27.6 ^b
	bottom	229	BLQ	BLQ
preplanting	top	241	16.3 ^b	42.1
	middle	255	BLQ	30.0 ^b
	bottom	356	BLQ	BLQ
¹ / ₄ -size harvest	top	255-833 ^c	BLQ-44.1	12.3-105
	middle	210-761	BLQ-12.7	BLQ-32.2
	bottom	69.4-209	BLQ	BLQ
¹ / ₂ -size harvest	top	389-955	BLQ-14.9	24.1-113
	middle	146-311	BLQ	BLQ-25.0
	bottom	10.8-318	BLQ	BLQ
full-size harvest	top	472-991	13.7-21.7	BLQ-66.9
	middle	263-401	BLQ-11.1	BLQ-31.6
	bottom	61.7-87.9	BLQ	BLQ-8.96

^aBLQ = below the limit of quantitation. ^bValue for one group only. Other group had a value BLQ. ^cRange of concentrations in soils analyzed (range of average concentrations in soils in which each of three crops was grown).

trations that would normally be present.

The highest average radiolabeled residue concentration of avermectin B_{1a} detected in lettuce plants was 6.94 μg/kg and was found in one-fourth size lettuce grown in muck soil during the first planting period (preplanting interval of 14 days). Lettuce grown in muck soil contained the highest concentrations of radiolabeled residues in five of the nine harvests from the three soils. Lettuce grown in sandy soil contained the lowest concentrations of radiolabeled residues in six of the nine harvests (Tables I and II).

The highest average radiolabeled residue concentration in carrots was 2.62 μg/kg and was found in those grown in sandy loam soil during the second planting period and harvested at full size (preplanting interval of 123 days). When carrot residue data are compared, mean residue levels were greater in carrot tops and taproots from plants grown in sandy loam soil than in carrots grown in sandy soil in eight out of nine and seven out of nine harvests, respectively. While radiolabeled residue concentrations were consistently higher in taproots than in tops of carrots grown in sandy soil, there was no such consistent trend in carrots grown in sandy loam soil (Table II).

A residue concentration of 3.45 μg/kg was the highest value measured in turnips grown in muck soil and was found in taproots grown during the first planting period (preplanting interval of 14 days). Taproots of turnips grown in muck soil contained consistently greater concentrations or radiolabeled residues of avermectin B_{1a} than did their corresponding tops.

From the first to the third planting, a general decrease in radiolabeled residue concentrations was observed in all plants grown in all soils where such residues were detectable.

In an attempt to determine whether the radioactivity measured in these crops was avermectin B_{1a}, a chemically similar product, or other materials, acetone extraction of one dried lettuce sample was performed. The resultant extract contained only 4.38% of the total radioactivity of this sample. This suggests that in lettuce the remaining unextractable radioactivity is represented by residues that are not chemically similar to avermectin B_{1a} or which may be chemically similar to avermectin B_{1a} but exist in the plant in a firmly bound form.

The mean limit of quantitation in micrograms/kilogram of avermectin B_{1a} equivalents for dried crop samples was 8.76 (range 8.33-9.66). In the conversion of micrograms/kilograms of dried crop to micrograms/kilogram of fresh crop, the former value was divided by the moisture conversion factor (weight of fresh crop/weight of dried crop). The mean recoveries of [¹⁴C]avermectin B_{1a} added at the 198-888 μg/kg levels to thawed control crops (26-91 g, weight range of crop sample spiked) were 92.2% (range 81.2-105%) for sorghum leaf stems, 102.3% (range 101-104%) for sorghum grain, 67.0% (range 58.3-75.6%) for lettuce, 80.8% (range 78.7-82.3%) for carrot tops, 84.3% (range 83.0-86.6%) for carrot taproots, 78.4% (range 75.3-81.1%) for turnip tops, and 92.1% (range 88.2-95.6%) for turnip taproots. All recovery studies for each plant part were conducted in triplicate.

Radiolabeled Residues of [¹⁴C]Avermectin B_{1a} in Soils. Table IV presents the radiolabeled avermectin B_{1a} residues (expressed as avermectin B_{1a} equivalents) present in soils at the time of final [¹⁴C]avermectin B_{1a} application, immediately prior to the planting of crops, and at each harvest for the first planting of each of the three soils studied. The lower radiolabeled residue concentrations found in sandy soil relative to those found in muck and sandy loam soils were probably related to the smaller amount (9.5 mg) of avermectin B_{1a} applied to sandy soil. The differences between the residual ¹⁴C radioactivity found in muck and sandy loam soils, both of which received the same amount of avermectin B_{1a} (43.6 mg), must be partly attributed to the physical and chemical differences between these soils (Table V). For example, the high content of organic carbon in muck soil (38.3%) may play a significant role in adsorbing the avermectin B_{1a} parent compound and any hydrophobic degradation products (Table V). Conversely, the low organic carbon content of sandy loam soil (0.14%) indicates that adsorption by this soil component would play a smaller role in the dissipation of these compounds from sandy loam soil. The same relative differences among residual ¹⁴C radioactivity were observed in the second and third plantings of the three soils.

Figures 1 and 2 present dissipation curves of ¹⁴C radioactivity (expressed as the ln of avermectin B_{1a} equivalents (μg/kg)) from top, middle, and bottom layers of muck soil and from top and middle layers of sandy loam soil. (Radioactivity found in bottom layers of sandy loam soil and in all layers of sandy soil was insufficient to pro-

Table V. Characterization of Soils

soil	% organic carbon	particle size, ^a g					total sand, g	% silt	% clay	% moisture
		very coarse	coarse	medium	fine	very fine				
muck	38.32	** ^b	**	**	**	**	**	**	**	56.1 ± 4.5 ^c
sandy	0.66	2.0	13.5	31.0	36.0	6.8	89.3	7.4	3.3	7.71 ± 2.79
sandy loam	0.14	10.0	13.5	12.5	13.9	14.1	64.0	30.3	5.7	9.47 ± 3.72

^a100 g of soil sieved. Soil samples were composed of equal parts of top, middle, and bottom layers. ^bFollowing combustion of muck soil, the amount of residual material was too small to analyze for mineral content and sand particle size. Samples analyzed for percentage organic carbon, particle size, total sand, percentage silt and percentage clay were taken from control tubs on April 11, 1986. Percentage moisture content values represent averaged data from all experimental soils sampled during this study. ^cMean ± standard deviation.

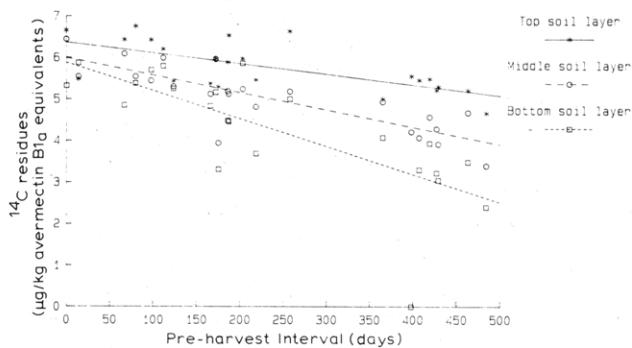


Figure 1. Disappearance of radioactivity from muck soil following treatment of soil with [^{14}C]avermectin $\text{B}_{1\text{a}}$. Radioactivity was measured from the combustion of soil samples and is expressed as equivalents of avermectin $\text{B}_{1\text{a}}$ ($\mu\text{g}/\text{kg}$). Each point represents the average of duplicate combustions of a soil sample.

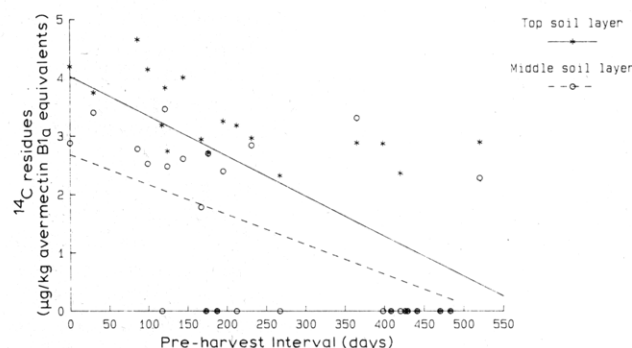


Figure 2. Disappearance of radioactivity from sandy loam soil following treatment of soil with [^{14}C]avermectin $\text{B}_{1\text{a}}$. See Figure 1 for details.

vide meaningful disappearance curves). The data presented in Figure 1 include results from all soil samples analyzed from all three plantings in all three soils and show a gradation of concentrations of radioactivity from the top to the bottom layers in muck soil, with the highest concentrations found in the top layer. This same gradient is also evident from the top to the middle soil layers of sandy loam soils. Assuming a first-order disappearance of radiolabeled residues, $t_{1/2} = 0.693/k$ ($-k = \text{slope}$; $\ln [A] = \ln [A]_0 - kt$) was used to calculate half-life of radiolabeled residues of [^{14}C]avermectin $\text{B}_{1\text{a}}$ in the three layers of muck soil and the two layers of sandy loam soil (Table VI). In muck soil the half-life of radiolabeled residues was longer in the top layer (267 days) and decreased with increasing depth of the soil sampled (165 days, middle layer; 103 days, bottom layer). The converse was true when the top layer (half-life 102 days) and middle layer (half-life 132 days) of sandy loam soil are compared.

The limit of quantitation of [^{14}C]avermectin $\text{B}_{1\text{a}}$ equivalents ranged from 8.28 to 9.14 $\mu\text{g}/\text{kg}$ for dried soil. Studies of the recoveries of [^{14}C]avermectin $\text{B}_{1\text{a}}$ added at the 264–429 $\mu\text{g}/\text{kg}$ levels to 5–10 g of fresh soil samples showed average recoveries (duplicate samples of each soil type) from muck, sandy, and sandy loam soils of 92.9%, 80.1%, and 83.0%, respectively.

Table VI. Half-life of Radiolabeled Residues of [^{14}C]Avermectin $\text{B}_{1\text{a}}$ in Soils^a

soil	half-life, days	soil	half-life, days
muck		sandy loam	
top	267	top	102
middle	165	middle	132
bottom	103		

^a Half-life calculated from $t_{1/2} = 0.693/k$; $\ln [A] = \ln [A]_0 - kt$. Radioactivity in bottom soil layers of sandy loam soil and in all soil layers of sandy soil was insufficient to permit half-life calculations in these layers or soils.

CONCLUSIONS

On the basis of results of this study, the levels of radiolabeled residues derived from avermectin $\text{B}_{1\text{a}}$ were low. The tolerance of avermectin $\text{B}_{1\text{a}}$ in plants will be approximately 5 $\mu\text{g}/\text{kg}$, which is the limit of reliable quantitation for nonlabeled material. Under normal field conditions residue concentrations of avermectin $\text{B}_{1\text{a}}$ in crops and soils would probably be lower than those found in the present study since the amount applied exceeded the maximum use rate by 25–50%. However, the possible effects on the microbial population and the chemical composition and pH of the soils treated with avermectin $\text{B}_{1\text{a}}$ resulting from holding soil in tubs for periods exceeding 465 days must also be recognized when extrapolating the results of the present study to ordinary field conditions. Finally, the observed differences among residue concentrations found in crops grown in different soils may not be the same when these soils are studied in areas with less rainfall than Sanford, FL.

ABBREVIATIONS USED

BLQ, below the limit of quantitation; EC, emulsifiable concentrate; PPINT, preplanting interval; LQ, limit of quantitation; sp act., specific activity; σ , sigma; N , number of background samples; Bkg, cpm of background samples; T , 10-min counting time; $t_{1/2}$, half-life.

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