products. It is our intention to pursue these experiments under actual spray operations to determine whether the same degradation products may be obtained and to confirm that the degradation pathway is also oxidative via the quinones.

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Metabolic Fate of Fenvalerate in Wheat Plants

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The metabolic fate of [*chlorophenyl*-^{14}C]- and [*phenoxyphenyl*-^{14}C]fenvalerate on wheat plants after foliar treatment was examined. The half-life of fenvalerate on foliar surfaces at an exaggerated application rate of 1 lb/acre, under outdoor conditions, was approximately 3 weeks. Systemic movement of [^{14}C]fenvalerate and its metabolite(s) was not observed. The amount of ^{14}C residue in the grain and hull (mature plants harvested 10 weeks posttreatment) was below the limit of reliable measurement (<0.03 ppm). Undegraded [^{14}C]fenvalerate was the major product recovered in the foliage or straw at each sampling interval. Individual degradation products accounting for greater than 1% of the applied radioactivity were not present. Important degradation pathways included decarboxylation and ester cleavage. Formation of water-soluble conjugates was only of minor significance in the wheat plants. The isomeric composition between the [^{14}C]fenvalerate treatment solution and the "aged" parent recovered from the treated plants was unchanged.

Fenvalerate [1, cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate, PYDRIN insecticide, a registered product of Du Pont] is an effective synthetic pyrethroid insecticide possessing excellent insecticidal activity and also favorable environmental stability (Miyamoto and Mikami, 1983). The environmental fate of fenvalerate (Lee, 1985; Caplan et al., 1984; Reed et al., 1983; Ohkawa et al., 1980a; Mikami et al., 1980) and its metabolism in the soil (Mikami et al., 1984; Ohkawa et al., 1978), animals (Lee et al., 1985; Kaneko et al., 1984; Kaneko et al., 1981; Ohkawa et al., 1979), and insects (Soderlund et al., 1983) have been reported. Plant metabolism studies have been conducted with the kidney bean (Ohkawa et al., 1980b) and cabbage (Mikami et al., 1985). The increased wide use pattern of fenvalerate and its extended field residual activity warrant further understanding of its metabolic fate in other crop species, especially in the grain cereals. This report describes the dissipation rate, characterization of the residue distribution pattern, and structural elucidation of significant fenvalerate degradation products in mature wheat plants following foliar application.

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EXPERIMENTAL SECTION

Test Materials and Reference Standards. Radiolabeled fenvalerate and appropriate reference standards were synthesized by the Biological Science Research Center (BSRC), Shell Agricultural Chemical Co. Two preparations of [^{14}C]fenvalerate, one labeled at the chlorophenyl and the other at the phenoxyphenyl moiety, were used. Both compounds had a radiochemical purity of greater than 99.5%, as determined by thin-layer chromatography (TLC), autoradiography, and liquid scintillation counting (LSC). Authentic standards included CPIA [**2**, 4-chloro-α-(1-methylethyl)benzeneacetic acid], 4′-hydroxyfenvalerate [**3**, cyano[3-(4-hydroxyphenoxy)phenyl]methyl 4-chloro-α-(1-methylethyl)benzeneacetic acid], decarb-

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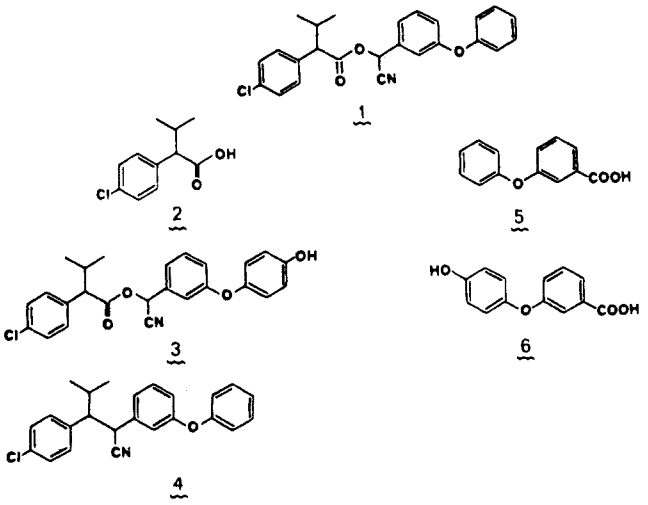

Figure 1. Plant metabolites of fenvalerate.

oxyfenvalerate [4, 2-(3-phenoxyphenyl)-3-(4-chlorophenyl)-4-methylpentanenitrile], PBacid [5, 3-phenoxybenzoic acid], and 4′-OH-PBacid [6, 3-(4-hydroxyphenoxy)benzoic acid]. Chemical structures of these compounds are presented in Figure 1.

Plant Treatment. Spring wheat (cv. Bonanza), four plants per container (6-in. diameter), were planted in the potting soil [mixture of Perlite, peat, and Hanford sandy loam (58% sand, 27% silt, 16% clay, 0.7% organic carbon, 6.1 solid pH)]. Plants were treated 30 days after germination.

Fenvalerate treatment solution for each pot of wheat plants was prepared by the addition of either [*chlorophenyl*-^{14}C]- or [*phenoxyphenyl*-^{14}C]fenvalerate (0.7 mg/0.25 mL of methanol) to 2.75 mL of an aqueous suspension containing 0.1% Tenneco EC formulation, application rate approximately 1 lb/acre. This application rate is approximately 5 times the label-recommended use rate. The specific activities of [*chlorophenyl*-^{14}C]- and [*phenoxyphenyl*-^{14}C]fenvalerate were 25.8 and 36.0 μCi/mg, respectively. After thorough mixing in a 1-oz bottle, the test solution was placed into an atomizer and applied as a fine spray over the entire foliage surface. Control plants were treated with a formulation blank solution. The soil surface of each pot was covered with absorbent paper to minimize soil contamination with the labeled test material. Water was applied as needed only to the soil surface in order to minimize the wash-off of plant surface residues. Treated plants were maintained in the outdoor plant growth enclosure area from Sept 18 to Dec 4, 1984.

Whole immature wheat plants were examined immediately and at various time intervals posttreatment. Mature plants (separated into straw, hull, and grain) were examined 10 weeks posttreatment.

Characterization of Surface Residues. Radioactivity recovered from the treated plants was characterized as surface and plant tissue residues. At each time interval, one pot (four plants each) from the [*chlorophenyl*-^{14}C]- and [*phenoxyphenyl*-^{14}C]fenvalerate treatment group was harvested, and the whole plants were sectioned into an approximately 1-cm-length portions. Surface residues were recovered by the gentle washing (twice) of the sectioned plant tissues with 250 mL of hexane. To characterize the chemical nature of the surface residues, the combined hexane washes were dried over anhydrous sodium sulfate, concentrated, and analyzed by two-dimensional TLC.

"Aged" residues remaining on the leaf surfaces after the initial hexane washes were recovered by a single washing of the sectioned plant parts with 200 mL of methanol. The methanol extract was concentrated to approximately 25 mL, and the final volume was readjusted to 50 mL with 0.01 M acetate buffer (pH 5.0). Radioactivity in this aqueous mixture was recovered after partitioning two times with 100 mL of chloroform. The combined chloroform extract was dried over anhydrous sodium sulfate, concentrated, and analyzed by two-dimensional TLC.

Characterization of Extractable Tissue Residues. The sectioned plant tissues, after the initial hexane and methanol solvent washes, were frozen in dry ice and pulverized with a microanalytical mill (Tekmar Co.) prior to oxygen combustion and LSC.

Extractable residues in the powdered plant tissues were recovered by the two extractions with 200 mL of acetone. The combined acetone extract was concentrated to approximately 50 mL, and the final volume was readjusted to 75 mL with 0.01 M acetate buffer (pH 5.0). Organic-extractable residues were recovered, after partitioning three times with equal volumes of chloroform, and analyzed by two-dimensional TLC. Water-soluble residues in the aqueous phase were quantitated directly by LSC.

Characterization of Unextractable Tissue-Bound Residues. Radioactivity associated with the pulverized plant tissues after the above acetone solvent extraction was considered as tissue-bound residues. A 1-g subsample of the pulverized plant tissues from the mature samples was subjected to the following solvent extractions and enzymatic hydrolysis (in 10-mL final volume): (1) hexane, (2) chloroform, (3) methanol, (4) pH 5 buffer hydrolysis (37 °C, 24 h), (5) cellulase enzyme (type V, Sigma Chemical Co.) hydrolysis (37 °C, 24 h, pH 5), (6) β-glucosidase enzyme (type I, Sigma Chemical Co.) hydrolysis (37 °C, 24 h, pH 5), and (7) acid hydrolysis (pH 1, 85 °C, 2 h).

Radioactivity released after the above solvent extractions or enzymatic hydrolysis was recovered by chloroform extraction and characterized by LSC and TLC.

Chromatography and Radioassay. Radioactivity was quantitated in 15 mL of Aquasol-2 scintillation solution (New England Nuclear) on a Packard Model 300 Liquid scintillation system. The radioactive area of the TLC plate, after solvent development and autoradiography (Kodak SB-5 single-coated X-ray film), was removed by scraping and analyzed in an Aquasol-2/water (11:4 mL) gel system. ^{14}C residues in various plant tissues (straw, hull, grain) were analyzed by combusting subsamples (100 mg) in a Packard 306 sample oxidizer. Background and combustion efficiency of individual plant parts were determined with control samples and [^{14}C]fenvalerate as the calibration standard. All LSC quantitations were corrected for combustion efficiency and quenching.

Extractable ^{14}C residues were analyzed by two-dimensional TLC (silica gel F-254, 0.25 mm, E. Merck). The R_f values of fenvalerate and the reference standard in several TLC solvent systems and mass spectral data have been reported (Lee, 1985; Lee et al., 1985).

RESULTS AND DISCUSSION

Foliar Systematic Properties. To simulate field conditions, [^{14}C]fenvalerate formulated in an aqueous solution was appied to the wheat foliage by surface spraying. The foliar systemic properties of fenvalerate were qualitatively evaluated by whole-plant autoradiography. Immediately after treatment, uniform coverage of the applied radioactivity on the foliage was observed. However, at various time intervals posttreatment, radioactivity was found to remain at the site of deposit and translocation of radioactivity to the new growth or other plant parts was not observed. This lack of systemic movement had been

Table I. Summary of the Distribution of the Total [*chlorophenyl*-^{14}C]- and [*phenoxyphenyl*-^{14}C]Fenvalerate Equivalent Residues in the Mature Wheat Plants 10 Weeks Posttreatment

	level of ^{14}C residues, ppm	
	[chlorophenyl-^{14}C]	[phenoxyphenyl-^{14}C]
whole plant	1.70	1.75
straw	2.18	2.38
hull	<LRM[a]	<LRM
grain	<LRM	<LRM

[a] ^{14}C Residues below the limit of reliable measurement (<0.03 ppm).

demonstrated previously in other plant species (Mikami et al., 1985; Ohkawa et al., 1980b).

Dissipation Rate and Distribution of Radioactive Residues. In the mature wheat plant, harvested 10 weeks after treatment, the majority of the radioactivity (>99.5%) was found in the straw. Even at the exaggerated application rate of 1 lb/acre, the amount of [^{14}C]fenvalerate equivalent residues in the hull and grain, from both the [chlorophenyl-^{14}C]- and [phenoxyphenyl-^{14}C]-labeled fenvalerate, was below the limit of reliable measurement (<0.03 ppm; Table I). This observation confirmed the lack of translocation of [^{14}C]fenvalerate or its metabolites from the application site to other plant parts.

In this study, radioactivity was characterized as surface residues, extractable plant tissue residues, and unextractable bound residues. Distribution data, expressed as the percent of the applied radioactivity, are summarized in Table II. Surface ^{14}C residues (recovered by hexane and methanol washings) readily decreased with time along with an initial increase and then plateau of the tissue residues. The total plant ^{14}C residues declined from approximately 7.2 ppm equivalent immediately after application to approximately 1.7 ppm at the 10-week sampling interval. This residue reduction could be mainly due to growth dilution and loss by environmental factors.

Characterization of Surface Residues. Radioactivity deposited on the leaf was characterized as surface residues that could be readily removed by hexane solvent washing and aged residues that were removed subsequently with methanol. Aged residues could be interpreted as ^{14}C materials absorbed into the epicuticle of the leaf surfaces and, thus, not removed by the simple washing with hexane.

Immediately after application, greater than 99% of the total plant radioactivity was recovered as the intact parent molecule by the hexane washing (Table II). A steady decrease of the hexane-extractable residues was observed. Aged surface residues appeared to be maintained at a steady level of approximately 6% throughout the various sampling intervals.

[^{14}C]Fenvalerate was the major component recovered in the hexane-extractable fraction. Major degradation products accounting for greater than 1% of the applied radioactivity were not present. Decarboxyfenvalerate (**4**), the photodegradation product of fenvalerate (Holmstead et al., 1978; Mikami et al., 1980), accounted for only approximately 0.8% of the applied radioactivity. The two corresponding diastereomers of **4** could be chromatographically separated from the two diastereomers of fenvalerate after six consecutive TLC solvent developments in the hexane/ether (20:1, v/v) solvent system. The TLC R_f values for the corresponding diastereomers of fenvalerate and decarboxyfenvalerate were 0.47, 0.42 and 0.50, 0.38, respectively. The structure of **4** was confirmed by GC/MS.

The isomeric composition of the undegraded [^{14}C]fenvalerate, recovered by preparative TLC (hexane/acetone/acetic acid 25:25:1 v/v/v), was examined by high-performance liquid chromatography (HPLC) using a chiral stationary phase column (Papadopoulou-Mourkidou, 1985; Lee et al., 1987). There are no observable changes in the isomeric composition of fenvalerate before and after exposure (Table III). The four stereoisomers of fenvalerate appeared to be degraded at a similar rate. Photoisomerism or stereoselectivity in the degradation of fenvalerate on wheat foliar surfaces was not observed. This result is consistent with the published data, which showed both racemic fenvalerate and the *S*-acid diastereomers (*SR*, *SS*) dissipated similarly from the treated bean plants (Ohkawa et al., 1980b) and between racemic fenvalerate and the most insecticidally active *SS* isomer in the cabbage (Mikami et al., 1985).

[^{14}C]Fenvalerate was also the major component recovered in the methanol-extractable fraction. Decarboxyfenvalerate (**4**) was not detected, thus indicating that the photolytic decarboxylation reaction occurred only at the leaf surface and **4** did not absorb or penetrate into the leaf cuticles. 4′-Hydroxyfenvalerate (**3**), CPIA (**2**), and PBacid (**5**) were observed as minor degradation products. These minor products and water-soluble conjugates combined to account for 1–2% of the applied radioactivity.

The dissipation half-life of [^{14}C]fenvalerate is approximately 3 weeks. A biphasic dissipation curve was observed. The initial loss of [^{14}C]fenvalerate could be attributed to

Table II. Characterization of Extractable Residues from the Wheat Leaf Surfaces at Various Time Intervals (Weeks) Posttreatment

	% applied radioactivity									
	[chlorophenyl-^{14}C]					[phenoxyphenyl-^{14}C]				
	time	2	4	6	10	time	2	4	6	10
total surface residues	>99	68	54	45	32	>99	65	42	37	26
hexane-extr	99	62	47	38	26	99	58	38	31	20
fenvalerate (1)	97.5	60.8	46.1	36.2	24.5	98.0	57.3	37.3	29.3	17.4
decarboxyfenvalerate (4)				0.6	0.8				0.6	0.7
others[a]	1.5	1.2	0.9	1.2	0.5	1.0	0.7	0.7	1.0	1.9
methanol-extr	<1	6	7	7	6	<1	7	4	6	6
fenvalerate (1)		4.7	5.6	4.9	5.5		5.4	3.0	5.1	4.8
others[a]		1.3	1.4	2.1	0.5		1.6	1.0	0.9	1.2
tissue residues	<1	8	13	11	12	<1	7	15	11	9
acetone-extr	*a*	4	6	6	4		4	5	5	1
unextractable		4	7	5	8		3	10	7	8
total recovery, %	100	76	67	56	44	100	72	57	48	35
total fenvalerate recovery, %	97.5	65.5	51.7	41.0	30.0	98.0	62.7	40.3	34.4	22.2
total ^{14}C residues, ppm	7.34	2.80	1.73	1.43	1.70	7.10	2.87	1.62	1.39	1.75

[a] Including all minor and water-soluble products.

Table III. Isomeric Composition of [*phenoxyphenyl*-^{14}C]Fenvalerate before and after Exposure to the Environment on Wheat Leaf Surfaces

		isomeric ratio,[a] %			
	fenvalerate,[b] %	*SR*[c]	*RS*	*SS*	*RR*
treatment soln	>99	29.5	30.1	20.9	19.5
2 weeks	80	30.5	29.8	20.1	19.6
6 weeks	61	30.8	30.5	19.4	19.4
11 weeks	55	30.1	28.0	22.3	19.6

[a] Determined by fraction collection from the HPLC and LSC. [b] Percent of the applied radioactivity, recovered by hexane, identified as the undegraded [*phenoxyphenyl*-^{14}C]fenvalerate. [c] Asymmetric centers designated at the 2-C in the acid and the α-C in the alcohol moiety.

evaporation or codistillation from the foliar surface.

Characterization of Extractable Tissue Residue. Tissue residues are defined as the radioactivity associated with the plant tissues after the removal of the surface ^{14}C residues by the hexane and methanol washings. Acetone was shown in a preliminary study to be the most effective extraction solvent. Distribution data presented in Table II show acetone extraction recovered approximately 4–6% of the [*chlorophenyl*-^{14}C]- and 1–5% of the [*phenoxyphenyl*-^{14}C]fenvalerate equivalent residues. Tissue residues were not detected when plant samples were analyzed immediately after treatment. Further TLC characterization of the actone extracts showed fenvalerate was the major component. Significant degradation products (greater than 1% of the applied radioactivity) or water-soluble ^{14}C residues (conjugates) were not detected; however, a trace level of CPIA (**2**) was visible.

Characterization of Unextractable Tissue-Bound Residues. Radioactivity associated with the plant tissues after the initial hexane and methanol washes followed by pulverization and acetone extraction was considered as unextractable tissue-bound residue. It accounted for 3–10% of the applied radioactivity at various sampling intervals (Table II). Unextractable tissue-bound residues were not detected when plants were analyzed immediately after treatment.

To further demonstrate the unextractability and to characterize the chemical nature of these ^{14}C residues, additional enzymatic and chemical hydrolysis experiments were conducted with the mature plant tissues sampled 10 weeks posttreatment. Organic solvent extraction of the solid plant materials with hexane or chloroform did not result in the release of detectable ^{14}C residues. Only a trace level of radioactivity was released after methanol extraction.

Approximately 40–50% of the total bound residues (maximum of 5% of the applied radioactivity) was released after incubation with various commerically available enzymes (β-glucosidase and cellulase). β-Glucosidase was not an effective enzyme to hydrolyze the bound residues (38%) since mild buffer hydrolysis (pH 5, 37 °C, 24 h) also released 35% of the bound residues. Cellulase enzyme hydrolysis released approximately 50% of the bound residues; of those residues, 20–50% could be recovered by chloroform extraction. However, TLC analysis of this organic extract was unsuccessful due to the interference by plant pigments and other natural components.

A majority of the radioactivity released after cellulase hydrolysis was water-soluble materials that were subjected to further acid hydrolysis. On the basis of TLC data, ester cleavage products, CPIA (**2**), PBacid (**5**), and 4′-OH PBacid (**6**), were the degradation products found. These products each accounted for less than 1% of the applied radioactivity. Further base hydrolysis of the water-soluble materials after the acid hydrolysis only released trace levels of radioactivity.

CONCLUSION

Results from this and other studies (Ohkawa et al., 1980b; Mikami et al., 1985) have described the metabolic fate of fenvalerate in various plant species. It is clearly evident that fenvalerate and its metabolite(s) have no foliar systemic movement. In the mature wheat plants, ^{14}C residues were not detected (<0.03 ppm) in the grain after foliar treatment of [*chlorophenyl*-^{14}C]- or [*phenoxyphenyl*-^{14}C]fenvalerate, even at an exaggerated application rate of 1 lb/acre. The overall metabolic fate of fenvalerate is consistent with other pyrethroids containing the α-cyano moeity: fluvalinate (Quistad et al., 1982), cypermethrin (Wright et al., 1980), decamethrin (Ruzo and Casida, 1979). Important degradation pathways included the photolytic decomposition of fenvalerate to yield decarboxyfenvalerate (**4**) and ester cleavage to yield corresponding hydrolysis products: CPIA (**2**), PBacid (**5**), and 4′-OH-PBacid (**6**). Hydroxylation of the parent molecule to yield 4′-hydroxyfenvalerate (**3**) was a minor degradation pathway. Undegraded fenvalerate was the major compound recovered. Individual degradation products accounted for only less than 1% of the applied radioactivity. This metabolism study confirmed results obtained from extensive field residue programs that showed, besides the parent molecule, residue level of the various plant metabolites were below the analytical detection limit.

One observable qualitative and quantitative difference in the metabolism of fenvalerate between the wheat, bean, and cabbage plants was the lack of water-soluble conjugated products (less than 2% maximum) generated from the wheat plants. Such species variability could be attributed to the reduced absorption or penetration of fenvelerate into the wheat foliage.

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Comparative Degradation of Organophosphorus Insecticides in Soil: Specificity of Enhanced Microbial Degradation

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Laboratory experiments investigated the comparative degradation of six organophosphorus insecticides in soil as affected by enhanced microbial degradation. The degradation rates and product distributions of chlorpyrifos, fonofos, ethoprop, terbufos, and phorate were not dramatically altered in soils containing microbial populations adapted to rapidly degrade isofenphos. An *Arthrobacter sp.* isolated from soils with a history of isofenphos use rapidly metabolized isofenphos in pure culture but did not metabolize or cometabolize any of the other five organophosphorus insecticides. Likewise, only fonofos was rapidly degraded in soil with a long history of fonofos use. None of the organophosphorus insecticides were rapidly degraded in soil containing carbofuran-degrading microbial populations. Results indicate that the phenomenon of enhanced microbial degradation of soil insecticides may exhibit some degree of specificity.

Organophosphorus and carbamate insecticides are widely used in the Midwest to control such soil-dwelling pests of corn as larval corn rootworms (*Diabrotica sp.*) and cutworms (*Agrotis sp.*). Corn is now the crop receiving the most intensive use of soil-applied insecticides, and in Iowa alone, approximately 6×10^6 acres are treated annually with soil insecticides (Wintersteen and Hartzler, 1987). Although the degradation of individual insecticides in soil has been investigated, few comparative studies of their degradation have been conducted (Fuhremann and Lichtenstein, 1980).

Enhanced microbial degradation is an increasingly important phenomenon affecting the degradation of pesticides in soil (Tollefson, 1986). Enhanced degradation occurs when a population of soil microorganisms, which has adapted due to previous exposure to a pesticide, rapidly degrades a subsequent application of the pesticide. The result of this enhanced degradation is a failure of the pesticide to adequately control the target pests due to dramatically decreased persistence (Felsot et al., 1982). Enhanced degradation of several commonly used soil pesticides has been reported, including carbofuran (Felsot et al., 1981), EPTC (Wilson, 1984), and isofenphos (Racke and Coats, 1987).

Enhanced degradation is, at its core, a pesticide/microbe interaction. The decreased persistence of the pesticide involved results from rapid catabolism by populations of pesticide-adapted soil microorganisms (Fournier et al., 1981; Kaufman and Edwards, 1983; Racke and Coats, 1987). Pesticide catabolism by adapted soil microorganisms usually involves a hydrolysis, with further metabolism and utilization of one or more hydrolysis products as carbon or nutrient sources (Karns et al., 1986; Tam et al., 1987; Racke and Coats, 1987).

The current research was initiated to study the comparative degradation of six organophosphorus insecticides in soil as affected by enhanced microbial degradation. The study focused on determining the specificity of the enhanced degradative phenomenon, with special emphasis on the specificity of enhanced isofenphos degradation.

MATERIALS AND METHODS

Chemicals. The following radiolabeled insecticides, along with model metabolites, were obtained from the respective manufacturers: [*U-ring*-^{14}C]isofenphos, Mobay Chemical Corp., Kansas City, MO; [*2,6-phenyl*-^{14}C]-chlorpyrifos, Dow Chemical Co., Midland, MI; [*U-ring*-^{14}C]fonofos, Stauffer Chemical Co., Mountain View, CA; [*1-ethyl*-^{14}C]ethoprop, Rhone-Poulenc Inc., Monmouth Junction, NJ; [*methylene*-^{14}C]terbufos and [*methylene*-

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