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Persistence and Transformation of the Herbicides [^{14}C]Fenoxaprop-ethyl and [^{14}C]Fenthiaprop-ethyl in Two Prairie Soils under Laboratory and Field Conditions

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The experimental herbicidal esters fenoxaprop-ethyl (ethyl 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoate) and fenthiaprop-ethyl (ethyl 2-[4-[(6-chloro-2-benzothiazolyl)oxy]phenoxy]propanoate) both underwent almost complete hydrolysis, within 24 h, to their respective acids in soils with moisture contents greater than 65% of field capacity. In air-dried soils, ester hydrolysis was considerably less. The fate of the two ^{14}C-labeled esters was studied in two soil types under laboratory and field conditions. Each herbicide gave rise to the same transformation products in the laboratory and field studies. [^{14}C]Fenthiaprop acid and its corresponding transformation products (a phenetole, a phenol, and a benzazolone) have a soil persistence of about twice that of [^{14}C]fenoxaprop acid and corresponding transformation products.

The structurally related herbicides HOE 33171, whose proposed common name is fenoxaprop-ethyl (**1**) and HOE 35609, with the proposed common name of fenthiaprop-ethyl (**6**), are currently being evaluated on the Canadian prairies, at rates less than 0.5 kg/ha, as postemergence herbicides for the control of grassy weeds in a variety of broad-leafed crops.

Although these chemicals are applied to the growing crops, some of the herbicidal sprays inevitably come into contact with the soil making it necessary to determine their fate in soil. Currently nothing has been reported regarding fenoxaprop-ethyl and fenthiaprop-ethyl in soils; thus, the studies to be described were undertaken to investigate the rate of hydrolysis of the herbicidal esters to their respective acids in two Saskatchewan soils and to investigate the persistence and transformation of [^{14}C]fenoxaprop-ethyl and [^{14}C]fenthiaprop-ethyl in the two soil types under both laboratory and field conditions.

MATERIALS AND METHODS

Soils. Field plots were situated on a sandy loam of the Asquith Association, classified as a Dark Brown Chernozemic, Orthic Dark Brown, and on a heavy clay of the Regina Association, classified as a Dark Brown Chernozemic, Rego Dark Brown. The composition and physical characteristics of these soils have already been described (Smith and Muir, 1980).

For the laboratory studies, soil samples were collected from the 0–5-cm soil horizons at both locations during the fall of 1982. After screening through a 2-mm sieve, the soils were immediately used for the laboratory experiments.

Chemicals. Fenoxaprop-ethyl (**1**) uniformly labeled with ^{14}C in the chlorophenyl ring, with a specific activity of 28.3 mCi/g and a radiochemical purity of over 99%, was provided by Hoechst Aktiengesellschaft, Frankfurt, Germany, as was the similarly labeled fenthiaprop-ethyl (**6**) which had a specific activity of 22.56 mCi/g and a radiochemical purity in excess of 99%. The radioactive chemicals were dissolved in methanol (10 mL) to prepare solutions containing 8.00 μCi/mL (300 μg/mL) of the oxygenated herbicide and 9.10 μCi/mL (400 μg/mL) of the thio herbicide.

In addition to nonlabeled samples of the two herbicidal esters, samples of the following nonradioactive standards were provided by Hoechst: 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propionic acid (**2**); 2-[4-[(6-chloro-2-benzothiazolyl)oxy]phenoxy]propionic acid (**7**); 4-[(6-chloro-2-benzoxazolyl)oxy]phenetole (**3**); 4-[(6-chloro-2-benzothiazolyl)oxy]phenetole (**8**); 4-[(6-chloro-2-benzoxazolyl)oxy]phenol (**4**); 4-[(6-chloro-2-benzothiazolyl)-oxy]phenol (**9**); 6-chlorobenzoxazolone (**5**); and 6-chlorobenzothiazolone (**10**).

Short-Term Hydrolysis Study. Duplicate samples (20 g) of moist heavy clay and sandy loam at 20%, 65%, and 100% of their field capacity moisture levels were weighed into 125-mL glass-stoppered flasks and treated with 20 μL of a solution containing 1 mg of the respective ethyl ester per mL of methanol. Separate soil treatments were made for each herbicide. This application rate was equivalent to 1.0 ppm herbicide based on moist soil weight. The soils were stirred to distribute the chemicals, before the flasks were sealed and incubated in the dark at 20 ± 1 °C. All soil samples were extracted and analyzed gas chromatographically after 24 h to determine amounts of the ethyl esters remaining.

Ester Extraction and Analysis. To each flask was added sufficient 20% aqueous acetonitrile containing 2.5% of glacial acetic acid so that the total volume of extractant together with water present in the soils was equivalent to 50 mL. The flask and contents were shaken on a wrist-action shaker for 1 h. Following centrifugation at 3500 rpm for 4 min, 25 mL of the supernatant was added to 5% aqueous sodium carbonate (100 mL) and shaken in a 250-mL separatory funnel with *n*-hexane (25 mL). The organic phase was collected in a 50-mL glass-stoppered tube and dried over sodium chloride, and 5-μL portions examined gas chromatographically for esters remaining.

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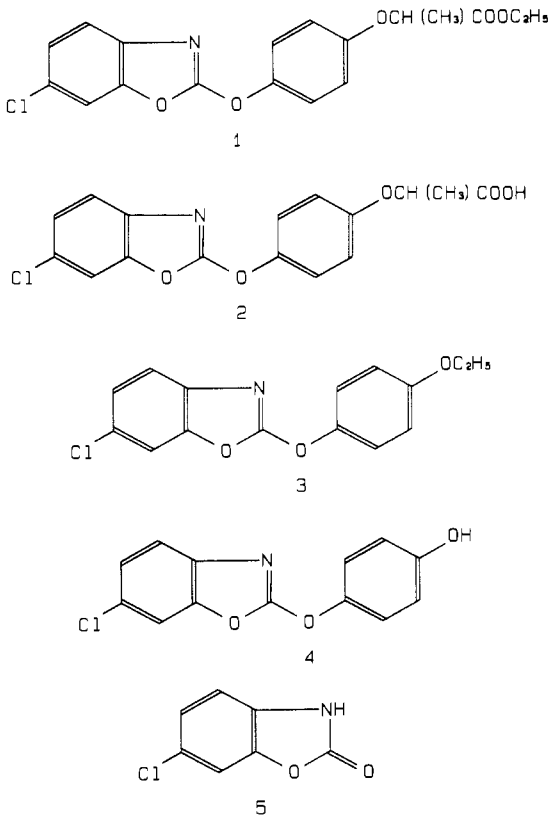
Chart I



1 2 3 4 5 6 7 8 9 10

The gas chromatograph used was a Hewlett-Packard Model 5700A, equipped with an on-column injection port and a radioactive nickel electron-capture detector operated at 350 °C. The glass column (60 cm × 4 mm id) was packed with 2% Apiezon L on 80–100 mesh Gas Chrom Q. Carrier gas was argon containing 5% of methane at a flow rate of 40 mL/min. With a column temperature of 260 °C, the retention times of fenoxaprop-ethyl and fenthiaprop-ethyl were 3.75 and 7.70 min, respectively. Esters present in the extracts were calculated by comparing chromatogram peak areas with those derived from appropriate standards. Extraction of untreated soils confirmed the absence of interfering substances.

Laboratory Degradation Studies. Samples (50 g) of the two soil types, moistened to 85% of their respective field capacities, were weighed into 250-mL capacity styrofoam cartons fitted with loose fitting lids and incubated at 20 ±1 °C for 7 days. Distilled water was added every second day, with stirring, to maintain the moisture contents. After equilibration, [^{14}C]fenoxaprop-ethyl (50 μL, 15 μg) or [^{14}C]fenthiaprop-ethyl (50 μL, 20 μg) was added to the soils. Sufficient nonradioactive ester solutions (1 mg/mL of methanol) were added to each carton to yield a total herbicide content (based on moist soil) of 1.0 ppm. All soils were thoroughly stirred to distribute the chemicals throughout the soils. The cartons were loosely capped to permit circulation of air, but reduce water evaporation, and incubated in the dark at 20 ±1 °C. Duplicate treatments containing fenoxaprop-ethyl were extracted and analyzed after 7, 28, and 49 days while duplicate soil samples treated with fenthiaprop-ethyl were analyzed after 7, 28, and 70 days to determine the amounts of radioactive transformation products present.

Extraction Procedures for Laboratory Studies. The soil from each carton was placed in a 250-mL glass-stoppered flask and covered with sufficient extraction solvent (acetonitrile, water, ammonium hydroxide solution (30% w/v) in the ratio 80:10:10) so that the combined volume of the solvent together with the water present in the soil was equivalent to 100 mL. The flask was shaken on a wrist-action shaker for 1 h when the soil was allowed to remain in contact with the extracting solvent for a further 20 h before being shaken for another 1-h period. The soil extracts were centrifuged at 3500 rpm for 10 min and solvent extractable radioactivity was determined by radioassay of the extract (5 mL).

Further portions of the extracts (20 mL, equivalent to 10 g of moist soil) were evaporated to dryness at 35 °C by using a rotary evaporator. The residue was taken up in methanol (20 mL), aliquots of which (5 mL) were assayed for radioactivity. The remaining methanolic solution was evaporated under reduced pressure to approximately 0.5 mL and examined by using thin-layer chromatographic and radiochemical techniques for the presence of ^{14}C-containing compounds.

Field Studies. Applications of [^{14}C]fenoxaprop-ethyl and [^{14}C]fenthiaprop-ethyl were made by zig-zagging the herbicide solutions (1.00 mL) from a pipette over the surface of small (10 × 10 cm) field plots. To reduce erosion, the herbicides were carefully mixed into the top 1 cm of the soil with a small fork. After incorporation, the soil was firmly tamped down. This procedure was similar to that described for field studies with other ^{14}C-labeled herbicides (Smith, 1979a; Smith and Muir, 1984).

The herbicides were applied on June 17, 1983, with two replications at each site for each herbicide. Plots remained fallow and were hand weeded carefully as necessary. Amounts of radioactivity added to the plots were 8.0 μCi of [^{14}C]fenoxaprop-ethyl and 9.10 μCi of [^{14}C]fenthiaprop-ethyl; these rates were equivalent to 300 μg of the former and 400 μg of the latter compound, thus yielding application rates of 0.30 and 0.40 kg/ha, respectively.

The duplicate plots treated with each chemical were sampled after 43 weeks, on April 16, 1984, by removing the

Table I. R_f Values of Compounds Studied

compd	R_f a	R_f b	R_f c
fenoxaprop-ethyl (1)	0.95	0.97	0.15
fenoxaprop acid (2)	0.04	0.35	0.00
[(benzoxazolyl)oxy]phenetole (3)	0.96	0.97	0.40
[(benzoxazolyl)oxy]phenol (4)	0.71	0.80	0.02
benzoxazolone (5)	0.55	0.65	0.02
fenthiaprop-ethyl (6)	0.97	0.95	0.21
fenthiaprop acid (7)	0.05	0.39	0.00
[(benzothiazolyl)oxy]phenetole (8)	0.92	0.92	0.46
[(benzothiazolyl)oxy]phenol (9)	0.70	0.84	0.03
benzothiazolone (10)	0.60	0.68	0.03

[a] Benzene–acetone (4:1). [b] Toluene–ethyl acetate–acetic acid–water (50:50:1:0.5). [c] Benzene.

soil from the upper 10 cm of each plot. Soils were air dried to constant weight at room temperature (these ranged from about 800 g for the heavy clay treatments to approximately 1100 g for the sandy loam plots), ground, and thoroughly mixed. Portions of the soil samples were then subjected to combustion analysis to determine total radioactivity remaining.

Extraction Procedures for Field Studies. Duplicate soil samples (40 g) were weighed into 250-mL glass-stoppered flasks and shaken with the ammoniated acetonitrile extractant (100 mL) exactly as described above. Following the prolonged extraction, the soil extracts were centrifuged as above and aliquots (5 mL) checked for radioactivity recovered. Further portions (25 mL) of the supernatant (equivalent to 10 g soil) were evaporated to dryness as before, the residue treated with methanol (25 mL), and the radioactivity in an aliquot (5 mL) determined. The remaining solution was evaporated under reduced pressure to 0.5 mL and examined by using thin-layer chromatographic and radiochemical procedures.

The soil residues from above, following solvent extraction, were collected by vacuum filtration and washed successively with methanol (100 mL) and acetone (100 mL). The washings were discarded since no further radioactivity was removed by these solvents. Each soil residue was dried for 4 h at 90 °C and duplicate samples (20 g) were shaken on a wrist-action shaker for 24 h with 1 N sodium hydroxide solution (50 mL) and separated into a soluble fulvic acid fraction and a humic precipitate, after acidification of the alkaline extract to pH 1 as described (Smith and Muir, 1980).

A 1-mL portion of the fulvic acid solution was examined for radioactivity, and the remaining solution was decanted into a separatory funnel containing water (100 mL) and shaken with ether (2 × 25 mL portions). The aqueous phase was discarded after a portion (5 mL) was assayed for radioactivity. The combined ether extracts were evaporated to dryness and the residue dissolved in methanol (10 mL); 1 mL of this extract was checked for ^{14}C. The remaining methanolic solution was evaporated to about 0.5 mL and examined by thin-layer chromatographic and radiochemical analysis.

Thin-Layer Chromatography. Precoated TLC plates (Silica Gel 60F-254) were obtained from E. Merck, Darmstadt, Germany. Following development to a height of 10 cm above the origin, the plates were dried and examined for radioactive compounds by using a PANAX thin-layer radiochromatogram scanner (Panax Equipment Ltd., Redhill, England). Nonradioactive compounds run for comparative purposes were detected by viewing the developed chromatograms under a short wave ultraviolet lamp. The R_f values of the compounds studied in different chromatographic solvent systems are compared in Table I. If peak areas from the chromatogram scans are compared and the amounts of radioactivity extracted from each soil are known, quantification of the various radioactive compounds present was achieved.

Table II. Hydrolysis of Fenoxaprop-ethyl and Fenthiaprop-ethyl in Moist Soils at 20 ± 1 °C after a 24-h Period

soil type	% fenoxaprop-ethyl remaining[a] 20% F.C.	65% F.C.	100% F.C.	% fenthiaprop-ethyl remaining[a] 20% F.C.	65% F.C.	100% F.C.
heavy clay	83	<5	<5	90	<5	<5
sandy loam	75	<5	<5	86	<5	<5

[a] Initial herbicide concentration of 1 ppm. Means of two replicates; less than 5% variation between each replicate extraction and analysis.

The identity of ^{14}C transformation products was assumed providing their R_f values were identical with those of authentic standards in the three solvent systems.

Radioactivity Determinations. The radioactivity in the various solutions was measured by using a Packard TRI-CARB Model 300C liquid scintillation spectrometer. The scintillation solution consisted of an equivolume mixture of toluene and 2-methoxymethanol containing PPO (0.4%) and POPOP (0.1%). Counting efficiencies were determined by using an external [226Ra] source.

Radioactivity associated with the soils was measured by combustion of soils in a Packard Model 306 sample oxidizer.

RESULTS AND DISCUSSION

The results of the 24-h hydrolysis are summarized in Table II, and there was excellent agreement between data from the two replicate analyses. Aqueous acidic acetonitrile was used to recover fenoxaprop-ethyl and fenthiaprop-ethyl from the soils in this study since this extractant has proved most satisfactory for the recovery of other herbicidal esters from soils, including those used in the present work (Smith, 1976, 1977, 1981; Smith and Hayden, 1980). Extraction and analysis of both soil types immediately following herbicide treatments (at the 1.00 ppm level) confirmed that over 90% of the applied ethyl esters were being recovered. This indicated that the extraction procedure was not contributing to the hydrolysis of either ester to carboxylic acid forms.

The results of the hydrolysis study indicate (Table II) that after 24 h less than 5% of the fenoxaprop-ethyl or fenthiaprop-ethyl treatments were recoverable from either soil type moistened at 65% or 100% of their field capacity levels, whereas over 75% of the two ethyl esters were recoverable from the air dry soils at 20% of their field capacities (Table II). It was thus considered that in soils with moistures greater than 65% of field capacity almost complete hydrolysis of fenoxaprop-ethyl and fenthiaprop-ethyl to fenoxaprop acid and fenthiaprop acid had occurred after 24 h. Comparatively, the soil hydrolysis of fenoxaprop-ethyl and fenthiaprop-ethyl is almost as rapid as for the esters of the phenoxyalkanoic acid herbicides to their respective acid anions (Smith, 1976, Smith and Hayden, 1980), and faster than the hydrolysis of diclofop-methyl to its corresponding acid (Smith, 1977).

Results from the laboratory degradation studies are compared in Tables III and IV; there was excellent agreement between the results from duplicate analyses. For the laboratory (and field) degradation studies, several solvent systems were compared in order to recover the maximum amounts of radioactivity from the treated soils. It was discovered that in the presence of dilute mineral

Table III. Radioactivity Recovered from Heavy Clay and Sandy Loam Soils Treated with 1 ppm [^{14}C]Fenoxaprop-ethyl following Incubation at 20 ± 1 °C and 85% of Field Capacity

	% of applied radioactivity extracted as[a]					
	heavy clay			sandy loam		
	7 days	28 days	49 days	7 days	28 days	49 days
solvent extractable radioactivity	94	27	20	80	18	14
acid (2)	93	19	15	76	15	10
phenetole (3)	<1	<1	<1	<1	<1	<1
phenol (4)	<1	4	1	<1	1	1
benzoxazolone (5)	<1	4	4	4	2	3

[a] Means of two replicates; less than 5% variation between each replicate extraction and analysis.

Table IV. Radioactivity Recovered from Heavy Clay and Sandy Loam Soils Treated with 1 ppm [^{14}C]Fenthiaprop-ethyl following Incubation at 20 ± 1 °C and 85% of Field Capacity

	% of applied radioactivity extracted as[a]					
	heavy clay			sandy loam		
	7 days	28 days	70 days	7 days	28 days	70 days
solvent extractable radioactivity	88	72	63	96	57	49
acid (7)	86	36	22	94	23	10
phenetole (8)	1	3	5	1	3	6
phenol (9)	<1	18	20	1	11	11
benzothiazolone (10)	1	15	16	<1	20	22

[a] Means of two replicates; less than 5% variation between each replicate extraction and analysis.

acid fenoxaprop-ethyl and fenoxaprop acid underwent rapid and complete conversion to the benzoxazolone (5). This hydrolytic conversion did not occur with fenthiaprop-ethyl or fenthiaprop acid, and both these compounds were stable in dilute acidic solutions. Neutral extraction solvents, such as 10% aqueous methanol or 10% aqueous acetonitrile, were much less efficient than the aqueous acidic acetonitrile in recovering the two ethyl esters from the treated laboratory soils; in addition, when hydrolysis of the esters to their respective acids had occurred, radioactivity recovered from both soil types was less than 50% of that applied. After 7 days of incubation under laboratory conditions, aqueous acidic acetonitrile was found to extract less than 70% of the applied radioactivity from any of the soil treatments. This suggested that after formation, the fenoxaprop acid and fenthiaprop acid became strongly adsorbed onto soil organic matter.

The ammoniated acetonitrile extraction solvent used in the laboratory and field studies was selected since it had proved to be an efficient solvent for the extraction of aged residues of atrazine, picloram, and simazine from prairie field soils (Smith, 1981; Smith and Milward, 1983). It was also noted that the extended extraction was necessary, since this procedure recovered up to 25% more radioactivity than did a simple 1-h shaking. This extraction procedure effected complete hydrolysis of the fenoxaprop-ethyl and fenthiaprop-ethyl esters to their respective acids. However, this was not considered important since the results of the hydrolysis experiments, mentioned above, showed that after 24 h in moist soils the hydrolysis of both esters to their acids was complete.

Extraction of [^{14}C]fenoxaprop-ethyl- and [^{14}C]fenthiaprop-ethyl-treated laboratory soils with the ammoniated acetonitrile after 7 days of incubation (Tables III and IV) confirmed that the major products recovered from the soils were the respective ^{14}C acids and that less than 5% of the solvent extractable radioactivity was in the form of other ^{14}C products. This was taken as evidence that the extraction procedure did not directly result in any chemical decomposition of the [^{14}C]fenoxaprop or [^{14}C]fenthiaprop acids to other ^{14}C degradation products.

In the case of soils treated with [^{14}C]fenoxaprop-ethyl, solvent extractable radioactivity decreased with time so that after 49 days 20% of the applied ^{14}C was recoverable from the heavy clay and 14% from the sandy loam. Evaporation of the ammoniated aqueous acetonitrile extracts and subsequent treatment of the residues with methanol resulted in no loss of radioactivity, confirming that no volatile ^{14}C compounds were being solvent extracted from either soil.

Thin-layer chromatographic separation of ^{14}C products contained in the evaporated methanolic solutions, using the three solvent systems (Table I), followed by radiochemical analysis indicated that after 28 and 49 days [^{14}C]fenoxaprop acid was the major transformation product in both soils (Table III). Small amounts of the phenetole (3), the phenol (4), and the benzoxazolone (5) were also recovered from the treated soils, but each accounted for less than 5% of the applied radioactivity. No other ^{14}C-labeled products were observed in either soil.

Solvent extractable radioactivity from the [^{14}C]fenthiaprop-ethyl-treated soils also decreased with time (Table IV), though at a slower rate than was noted for [^{14}C]fenoxaprop-ethyl. Thus, after 70 days, 63% of the applied ^{14}C was recoverable from the heavy clay and 49% from the sandy loam. No volatile ^{14}C compounds were extracted from either soil, since amounts of radioactivity in the acetonitrile extracts were the same after solvent evaporation as before.

Thin-layer chromatographic and radiochemical analysis of soil extracts, using the three solvent systems (Table I), showed that after 7 days the predominant transformation product in both soils was [^{14}C]fenthiaprop acid (Table IV). Only trace amounts of radioactivity (less than 1% of that applied) were attributable to the [^{14}C]phenetole (8), the [^{14}C]phenol (9), or the [^{14}C]benzothiazolone (10). In both soils there was a loss of [^{14}C]fenthiaprop acid over the next 21 days which was accompanied by a considerable increase in the amounts of solvent extractable phenol and benzothiazolone (Table IV); concentrations of the phenetole accounted for less than 5% of the initially applied ^{14}C. After 70 days, amounts of solvent extractable [^{14}C]fenthiaprop acid in the heavy clay and sandy loam had decreased to 22 and 10%, respectively, of the applied radioactivity; however, concentrations of the corresponding [^{14}C]phenetole, [^{14}C]phenol, and [^{14}C]benzothiazolone present in the soils were similar to those recovered after 28 days. No other ^{14}C transformation products were de-

Table V. Radioactivity Recovered from the Top 10 cm of Heavy Clay and Sandy Loam Field Plots 43 Weeks after Treatment with [^{14}C]Fenoxaprop-ethyl

	% of applied ^{14}C[a]			
	heavy clay		sandy loam	
	plot 1	plot 2	plot 1	plot 2
radioactivity from soil combustion before extraction	48	51	60	50
solvent extractable radioactivity	10	10	11	8
acid (2)	7	8	7	5
phenetole (3)	<1	<1	<1	<1
phenol (4)	<1	<1	<1	<1
benzoxazolone (5)	3	2	4	3
radioactivity in fulvic acid fraction	24	22	29	24
ether soluble radioactivity in fulvic acid fraction	8	8	6	6
phenetole (3)	<1	<1	<1	<1
phenol (4)	<1	<1	<1	<1
benzoxazolone (5)	8	8	6	6
radioactivity in humic and humin fractions[b]	14	19	29	18

[a] Means from duplicate samples; less than 5% variation between each analysis. [b] Obtained by subtracting the combined amounts of solvent extractable and fulvic-associated radioactivity from that determined by combustion in unextracted soils.

Table VI. Radioactivity Recovered from the Top 10 cm of Heavy Clay and Sandy Loam Field Plots 43 Weeks after Treatment with [^{14}C]Fenthiaprop-ethyl

	% of applied ^{14}C[a]			
	heavy clay		sandy loam	
	plot 1	plot 2	plot 1	plot 2
radioactivity from soil combustion before extraction	54	45	73	71
solvent extractable radioactivity	36	27	40	33
acid (7)	22	16	25	21
phenetole (8)	1	<1	2	2
phenol (9)	7	6	5	5
benzothiazolone (10)	6	5	8	5
radioactivity in fulvic acid fraction	12	9	7	7
ether soluble radioactivity in fulvic acid fraction	9	6	3	3
phenetole (8)	5	3	3	3
phenol (9)	4	3	<1	<1
benzothiazolone (10)	<1	<1	<1	<1
radioactivity in humic and humin fractions[b]	6	9	26	31

[a] Means from duplicate samples; less than 5% variation between each analysis. [b] Obtained by subtracting the combined amounts of solvent extractable and fulvic-associated radioactivity from that determined by combustion in unextracted soils.

tected in any of the soils on any of the three sampling dates.

Results from the laboratory studies indicated that the transformation of [^{14}C]fenoxaprop-ethyl in both the heavy clay and sandy loam soils was similar (Table III). [^{14}C]-Fenoxaprop acid was the major degradation product with small amounts of the [^{14}C]phenol (4) and the [^{14}C]benzoxazolone (5) being detected. Even lesser amounts of phenetole (3) appeared to be present in either soil. Laboratory studies also confirmed that the transformation of [^{14}C]fenthiaprop-ethyl was similar in the heavy clay and sandy loam (Table IV). However, in contrast to the oxygenated herbicide, although [^{14}C]fenthiaprop acid was a major transformation product, after 28 and 70 days the phenol 9 and the benzothiazolone (10) were formed to a much greater extent (cf, Tables III and IV). Greater amounts of the phenetole (8) were also noted in soils treated with [^{14}C]fenthiaprop-ethyl than was the case with [^{14}C]fenoxaprop-ethyl. Thus, it would appear that the phenetole, phenol and benzothiazolone derived from fenthiaprop-ethyl (or acid) are more stable in moist soils than are the corresponding products formed from fenoxaprop-ethyl (or acid). In the laboratory studies no attempts were made to characterize solvent nonextractable radioactivity.

Recovery of radioactivity from the top 10 cm of the ^{14}C herbicide-treated heavy clay and sandy loam field plots is summarized in Tables V and VI. There was good agreement between results from the duplicate plots. Given the small size of the plots, it was impossible to prevent erosional losses of the herbicides from the treated soils by wind and rain over the 43-week period. To reduce such losses, the chemicals were lightly incorporated and the soil of the plots tamped down to the same level as the surrounding soil area. The fact that after 43 weeks, approximately 50% of the applied radioactivity could be accounted for in the heavy clay plots and up to 73% in the sandy loam plots was taken as evidence that erosional mechanisms were responsible for losses of less than 50% of the applied ^{14}C. Losses of radioactivity could also have occurred as a result of chlorophenyl ring fragmentation.

Combustion analysis of the soil from field plots treated with [^{14}C]fenoxaprop-ethyl indicated (Table V) that between 48 and 60% of the applied radioactivity was still present in the heavy clay and sandy loam field plots after 43 weeks. In both soils about one-fifth of this ^{14}C was solvent extractable and no volatile ^{14}C transformation products were present. The majority of the solvent extractable radioactivity recovered from both soils was identified by thin-layer chromatographic and radiochemical analysis as [^{14}C]fenoxaprop acid, with the [^{14}C]benzoxazolone (5) being present in amounts that accounted for less than 5% of the original ^{14}C treatment (Table V). Traces of [^{14}C]phenetole (3) and the [^{14}C]phenol (4) were noted but accounted for less than 1% of the initial radioactivity.

Combustion analysis of soils from the top 10 cm of field plots treated with [^{14}C]fenthiaprop-ethyl 43 weeks previously indicated (Table VI) that amounts of radioactivity present in the heavy clay and sandy loam plots were approximately 50% and 70%, respectively, of that applied.

Of this radioactivity, nearly one-half was solvent extractable from each soil type. None of the soil extracts contained volatile ^{14}C transformation products. The major transformation product in both soils was [^{14}C]fenthiaprop acid which accounted for between 16 and 25% of the applied ^{14}C. Traces of the [^{14}C]phenetole (**8**) were recovered from both soils but accounted for less than 2% of the initial radioactivity. In the two soil types about 5–7% of the applied ^{14}C was in the form of the [^{14}C]phenol (**9**) or as the benzothiazolone (**10**) (Table VI).

^{14}C transformation products isolated from treated field plots were identical with those recovered during the laboratory studies. Thus, the respective ^{14}C acids were the major transformation products (Tables V and VI), the phenetoles, phenols, and benzoxazolone (or benzothiazolone) being recovered in relatively minute amounts. As with the laboratory studies, greater amounts of the [^{14}C]fenthiaprop acid, the [^{14}C]phenol, and [^{14}C]benzothiazolone were observed in both soil types than were their oxygen analogues derived from [^{14}C]fenoxaprop-ethyl. This again indicated a greater soil persistence for the former compounds (Tables V and VI).

The transformation of the two herbicidal esters in soils is very similar to that of the structurally related herbicide diclofop-methyl which also possesses a phenoxypropanoate grouping ($OC_6H_4OCH(CH_3)CO_2CH_3$). Diclofop-methyl undergoes hydrolysis in soils under laboratory and field conditions to the corresponding carboxylic acid (Martens, 1978; Smith, 1977, 1979a). Diclofop acid then undergoes a decarboxylation to a phenetole which, in turn, is transformed to a phenol. Direct cleavage between the oxygen and carbon atom adjacent to the carboxyl moiety of diclofop acid would also give rise to the observed phenolic transformation product (Martens, 1978; Smith, 1977, 1979a). Similar transformation mechanisms can also be envisaged for the [^{14}C]fenoxaprop and [^{14}C]fenthiaprop acids to account for the analogous phenetole and phenol transformation products. Formation of the benzoxazolone (**5**) and benzothiazole (**10**) would result from the soil hydrolysis of the acid, phenetole, or phenol transformation products derived from the two esters.

Alkaline extraction of the solvent extracted heavy clay and sandy loam soils released between 22 and 29% of the applied radioactivity from the [^{14}C]fenoxaprop-ethyl-treated plots into the fulvic acid soil fraction (Table V). Ether extraction of this fraction indicated that about one-third of the radioactivity could be attributed to the [^{14}C]benzoxazolone (**5**), while minute traces of the corresponding phenetole and phenol were also observed (Table V). Since hydrochloric acid was used to precipitate humic acid from the alkaline soil extracts during workup, it is not possible to state whether this benzoxazolone was material actually recovered by the caustic solution that had not been completely extracted by the ammoniated acetonitrile or was formed by acid hydrolysis of [^{14}C]fenoxaprop acid similarly recovered from the soils by the aqueous sodium hydroxide. Radioactivity associated with the humic acid and humin soil fractions were similar in both soil types, being about 15–20% of that initially applied.

Alkaline treatments of the solvent extracted soils originally treated with [^{14}C]fenthiaprop-ethyl indicated that between 7 and 12% of the applied ^{14}C was associated with the fulvic acid fractions. Of this, about one-half was ether extractable and found to consist of small concentrations of the corresponding phenetole and phenol; amounts of the benzothiazolone recovered accounted for less than 1% of the initial ^{14}C (Table VI). Radioactivity associated with the humic and humin soil fractions were greater in the sandy loam (26–31%) than in the heavy clay (6–9%).

Treatment of the solvent extracted soils with 1 N sodium hydroxide for 24 h would result in the extraction of fulvic acid and humic acid soil components containing incorporated radioactivity derived from ^{14}C fragments of the ^{14}C-labeled herbicidal esters. The sodium hydroxide solution could also contain other ^{14}C compounds that were either not or only partially removed from the soils by the ammoniated acetonitrile. It has been noted (Smith, 1979b; Smith and Muir, 1980) that quantities of the acidic compounds benzoylprop acid, flamprop acid, and 2,4-D extracted from fortified soils using sodium hydroxide solutions can be readsorbed onto precipitated humic acids following acidification of the alkaline solutions.

No attempts were made to further characterize the nature of the radioactivity remaining in the aqueous fulvic acid phases following ether extraction. It is possible that some of this ether-insoluble radioactivity could have been due to such water soluble compounds as [^{14}C]2-amino-5-chlorophenol and [^{14}C]2-amino-5-chlorothiophenol (and transformation products therefrom) that were not recovered from the soils by the ammoniated acetonitrile. It is also possible that the above [^{14}C]chlorophenol and [^{14}C]chlorothiophenol could be formed directly from the appropriate [^{14}C]acids, [^{14}C]phenetoles, [^{14}C]phenols, and [^{14}C]oxazolones by hydrolytic ring-opening mechanisms effected by the prolonged treatment with the sodium hydroxide solutions.

In summary, it has been shown that both fenoxaprop-ethyl and fenthiaprop-ethyl undergo rapid hydrolysis in moist soils to their respective acids and that these can then undergo further transformation. Each herbicide yielded identical degradation products under laboratory and field conditions in the two soil types. Of the two herbicides, fenthiaprop acid and its corresponding transformation products were more persistent in soils, both under laboratory and field conditions, than were those of its oxygen analogue fenoxaprop acid.

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