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CHEM 036101 Trifluralin

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FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00131137 CONTENT CAT 01
Golab, T., W. Althaus, and H. Wooten. 1978. Fate of ¹⁴C trifluralin in soil. Unpublished study received Sep. 20, 1983 under 1471-70; submitted by Elanco Products Co., Div. of Eli Lilly and Co., Indianapolis, IN; CDL;251257-C.

FICHE/MASTER ID 00125328 CONTENT CAT 01
Golab, T., and J. Occolowitz. 1978. Soil degradation of trifluralin: mass spectrometry of products and potential products: Pre-RPAR Review Submission #25. Unpublished study received Nov. 30, 1978 under unknown admin. no.; submitted by Elanco Products Co., Div. of Eli Lilly and Co., Indianapolis, IN; CDL:249282-D.

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Two hardcopies were reviewed for this study. One hardcopy (00125328) contained the MS analyses of the degradation products and the other hardcopy (00131137) contained the experimental procedures, analytical methods, and results.

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This portion of the study is scientifically valid.
2. [¹⁴C]Trifluralin (99% pure) at 0.84-6.72 kg/ha dissipated in the top 0-15 cm layer of a silt loam soil with 14, 4, and 1.5% of applied remaining 1, 2, and 3 years, respectively, after application. Approximately 30 minor degradates were identified and quantified; none of which represented >2.8% of applied.

3. This portion of the study does not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not an end-use product, there was no pretreatment sampling, field test data were incomplete, and the plot size was not representative of actual use conditions.

Confined Accumulation - Rotational Crops

This portion of the study is scientifically invalid because quantitative data were not presented to support the stated conclusion. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the study was conducted with a degradate of trifluralin, and the field test data were incomplete.

Metabolism - Anaerobic Soil

This portion of the study cannot be validated because the application rate was not confirmed, and quantitative data provided were insufficient to accurately assess the degradation of the test substance or its degradates in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the soil incubation temperature was not reported, and the treated soil was not aged prior to inducing anaerobic conditions.

Metabolism - Aerobic Soil

This portion of the study cannot be validated because the application rate was not confirmed, and the quantitative data provided were insufficient (one sample) to accurately assess the degradation of the applied trifluralin degradate in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the soil incubation temperature was not reported and the study was conducted with a degradation product, not with the parent compound.

Degradation - Photodegradation on Soil

This portion of the study is scientifically invalid because dark controls were not used, the sampling protocol and method of analysis were not described, and quantitative data were not provided. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the intensity and wavelengths of the light were not reported, the test was not conducted on soil, degradation products were not detected or quantified, and the test was conducted with a degradate of the test substance.

MATERIALS AND METHODS:

The trifluralin used in these studies was 99% pure from the Lilly Research Laboratories, and was either mixed labeled [¹⁴C]trifluralin (15% ring and 85% CF₃) with specific activities of 1.0 and 3.0 μCi/mg, or uniformly ring-labeled [¹⁴C]trifluralin with specific activities



of 2.5 and 8.5 $\mu\text{Ci}/\text{mg}$. Ring-labeled [^{14}C] α,α,α -trifluorotoluene-3,4,5-triamine (TR-9), and [^{14}C]2,2-azoxybis-(α,α,α -6-nitro-N-propyl-p-toluidine) (TR-28) were similarly prepared.

Field Dissipation - Terrestrial

[^{14}C]Trifluralin (specific activity unspecified) at 0.84-6.72 kg/ha was incorporated into the top 7.5 cm of plots (0.60 m²) of silt loam soil (34.4-38.4% sand, 5.6-16.4% clay, 54.2-60.0% silt, 0.9-1.3% organic matter, pH 6.6-6.8, CEC 10.0-10.2 meq/100 g). Plots were delineated with a 91-cm diameter galvanized pipe extending 40 cm below and 20 cm above the soil surface, and were fertilized (560 kg/ha 6-24-24 fertilizer) prior to treatment. Soybeans were planted after treatment. Soil samples taken immediately after treatment and after 4, 8, 14, 22, 30, 42, 52, 68, 104, 121, and 156 weeks at depths of 07.5 and 7.5-15 cm. Samples were also taken to a depth of 38 cm and divided into 2.5 or 7.5-cm segments.

Soil samples (100-200 g) were extracted twice in methanol and once in 50% aqueous methanol, the extracts of which were combined and concentrated, and the aqueous phase partitioned with chloroform and/or ethyl acetate. Aliquots of the organic and aqueous phases were analyzed by LSC for total [^{14}C]radioactivity. Total soil-bound [^{14}C]radioactivity was determined by combustion and quantifying the collected $^{14}\text{CO}_2$. Qualitative and quantitative analyses of organic extracts were performed. TLC analyses using silica gel plates with one or two-dimensional chromatography were performed. The solvent systems used were: 1) benzene: carbon tetrachloride (40:60); 2) benzene; 3) n-hexane:methanol (98:2); 4) n-hexane:methanol (97:3); 5) benzene:ethylacetate (60:40); 6) benzene:1,2-dichloroethane (60:40); 7) benzene: 1,2-dichloroethane (50:50); 8) benzene:ethyl acetate:acetic acid (60:40:1); 9) benzene:methanol (98:2); 10) benzene:methanol (90:10); 11) benzene:methanol (75:25); and 12) carbon tetrachloride. Typical solvent system combinations for two-dimensional analyses were: 7 and 2; 3 and 1; 5 and 6; 9 and 8; 10 and 5; and 11 and 5. GLC, LSC, and radioautography of TLC plates were also performed on organic extracts. Characterization of degradation products were confirmed by MS or a combination of GLC and MS. HPLC was also used, in some cases, for separation and purification prior to MS. Isolated degradates were identified by comparison with appropriate model compounds. When necessary, crude organic extracts were purified and degradates were separated by gravity column chromatography or small bore column chromatography pressurized with nitrogen with silica gel or Florisil as the absorbents. For derivatization of phenol and acids, aliquots of soil were methylated using diazomethane in ether.

Degradation products in the soil not extracted by methanol and aqueous methanol only were further extracted with 0.5 N sodium hydroxide (24 hours at room temperature), centrifuged, the residues washed twice

with 0.5 N sodium hydroxide, recentrifuged, washed with water, centrifuged again, air-dried, and combusted. Radioactivity in the combined supernatant and water washes was quantified by LSC. Portions of the supernatant were adjusted to pH 1, 7, and 13, extracted with chloroform and/or ethyl acetate, and analyzed radiochemically. Another portion of the supernatant was acidified with hydrochloric acid to pH 1 and the precipitated humic acid centrifuged and redissolved in 0.1 N sodium hydroxide. The remaining supernatant containing the fulvic acid was decanted. Both humic and fulvic acid fractions were analyzed for [^{14}C]radioactivity by LSC.

A similar fractionation was performed on soil samples previously extracted with methanol and aqueous methanol using DOWEX A-1 chelating resin as the extractant rather than 0.5 N sodium hydroxide. For each 10 g of extracted soil 20 meq of Na^+ and 200 ml of water were used. Radiochemical analyses was by LSC.

The analytical data were fitted to an exponential equation: $y = ea^{-b(x)}$, where y = calculated percent, a and b = constants calculated from observed values by a least squares method, and x = elapsed time in weeks after initial application. The values were calculated from fitted equations. Recovery values for trifluralin from sandy loam soil fortified with [^{14}C]trifluralin at 5-50 ppm (in methanolic solutions) and incubated at room temperature for 1 hour (dry) and 1 and 72 hours (moist) were 99, 96, and 99%, respectively, after methanol and aqueous methanol extraction.

Confined Accumulation - Rotational Crop

Ring-labeled [^{14}C]2,2-azoxybis-(α,α,α -6-nitro-N-propyl-p-toluidine (TR-28, specific activity 4.64 $\mu\text{Ci}/\text{mg}$, purity unspecified, Lilly Research Laboratories) at 0.112 and 0.224 kg/ha was incorporated into the top 7.5 cm of plots (0.60 m^2) of silt loam soil (see field dissipation portion of the study for soil characteristics, and description and fertilization of plots). Soybeans were planted after treatment. After harvesting the soybeans, wheat was planted, and 1 year after application of TR-28 the wheat was harvested. The [^{14}C]radioactivity in the wheat was determined by combustion analysis.

Metabolism - Anaerobic Soil

Untreated soil (2 kg) from the field plots (see field dissipation study for soil characteristics) was treated with [^{14}C]trifluralin (specific activity 7.55 $\mu\text{Ci}/\text{mg}$, 99% pure, Lilly Research Laboratories) at 1.5 ppm, placed in a 4-l tin container and covered with 5 cm of tap water. The soil was incubated at room temperature (temperature unspecified) for up to 8 weeks, and samples were taken periodically (sampling intervals not provided) to determine [^{14}C]trifluralin degradation and identify extractable degradates. Soil samples were analyzed as in the field dissipation study.

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The same procedure was followed with 1 kg of soil treated with the ring-labeled degradate [^{14}C]TR-28 (specific activity 4.64 $\mu\text{Ci}/\text{mg}$, purity unspecified, Lilly Research Laboratories) at 1 ppm.

Metabolism - Aerobic Soil

Untreated soil (1 kg) from the field plots (see field dissipation study for soil characteristics) was treated with the trifluralin degradate ring-labeled [^{14}C]TR-28 (specific activity 4.64 $\mu\text{Ci}/\text{mg}$, purity unspecified, Lilly Research Laboratories) at 1 ppm, placed in a tin container and maintained at 60% of field capacity at room temperature (temperature unspecified) for up to 8 weeks. Soil samples were taken periodically to determine [^{14}C]TR-28 degradation and identify its degradation products. Soil samples were analyzed as in the field dissipation study.

Degradation - Photodegradation on Soil

The trifluralin degradate [^{14}C]TR-28 (specific activity and purity unspecified, Lilly Research Laboratories) at an unknown concentration was applied to silica gel TLC plates and exposed to combined UV-fluorescent light (light not further characterized) for up to 2 weeks. The method of analysis was not provided.

REPORTED RESULTS:

Field Dissipation - Terrestrial

During the 3 year study the average annual precipitation was ~40 inches, the average temperature was ~52 F with a maximum and minimum of ~78.4 and 10.3 F, respectively, and an average snowfall of ~30-37 inches.

[^{14}C]Trifluralin in the 0-15 cm layer of silt loam soil declined from ~14 to ~4 to ~1.5% of applied at 1, 2, and 3 years after application, respectively (Figure 1, values calculated from fitted equations). Of the total [^{14}C]radioactivity applied 69 and 43.5% was recovered after 1 and 3 years respectively, and 43 and 38% of applied were unidentified [^{14}C]residues after 1 and 3 years, respectively (Table 2). Numerous (~30) degradates were identified (Tables 1 and 2) and quantified, none of which occurred at >3% of applied in any time interval. Identified degradates reached a maximum of 12% of applied between 8 and 52 weeks after application, and declined to 4% after 3 years. [^{14}C]TR-2 was the major degradation product with the maximum detected at 2.8% of applied 4 months after application. The radioactivity remaining following application of [^{14}C]trifluralin (soil incorporated to 7.5 cm) at 1.68 kg/ha was detected mainly in the upper layers of soil, with 98.8, 96, 91, and 92% of recovered [^{14}C]radioactivity in the 0-15 cm layer layer 12, 16, 24, and 36 months posttreatment (Table 3). Three percent or less was detected between the 17.5 and 38 cm soil layers over the 3-year period.

Confined Accumulation - Rotational Crops

Wheat seeded as a rotational crop in the plots after the soybeans were harvested, and harvested 1 year after application of the trifluralin degradate [^{14}C]TR-28 at 0.112 or 0.224 kg/ha, did not contain substantial amounts of [^{14}C]radioactivity in mature straw and grain. Quantitative data were not provided.

Metabolism - Anaerobic Soil

[^{14}C]Trifluralin at 1.5 ppm in flooded silt loam soil degraded with 15 and 5% of applied detected after 3 and 8 weeks of incubation. Unidentified [^{14}C]trifluralin residues increased during incubation from 25% detected in 3 weeks to 50% detected in 8 weeks. Total [^{14}C]radioactivity degraded to ~80% of applied in 8 weeks, and identified degradation products were present at 20-25% of applied at 8 weeks. Twenty-nine degradation products were identified including compounds TR-4 to TR-21, TR-28, TR-32, TR-36, TR-39, and TR-40 (see Table 1 for chemical names). Quantitative data were not provided. The trifluralin degradate [^{14}C]TR-28 at 1 ppm in flooded silt loam soil degraded with ~22 and 5% of applied detected after 3 and 8 weeks, respectively. The major degradation product was TR-32 which was detected at 17 and 5% of applied at 3 and 8 weeks, respectively.

Metabolism - Aerobic Soil

The trifluralin degradate [^{14}C]TR-28 at 1 ppm in silt loam soil degraded with 60% of applied detected as [^{14}C]TR-28 after 8 weeks of incubation, 15% detected as unidentified [^{14}C]residues, and 25% detected as degradation products (not characterized in text).

Degradation - Photodegradation on Soil

The trifluralin degradate [^{14}C]TR-28 exposed to combined UV and fluorescent light on silica gel TLC plates was completely degraded 2 weeks after application. Quantitative data were not provided.

DISCUSSION:

Field Dissipation - Terrestrial

1. The test substance used in this study was not an end-use product.
2. The application rate was given as a range of concentrations, and the exact rate for which the results were reported was not provided.
3. Field test data were incomplete and did not include depth of water table, irrigation schedule, or slope of plots. Weather data was reported for an offsite location.

4. Detection limits, extraction efficiencies, and sensitivities of the analytical methods were not provided.
5. Plot size was not representative of actual use conditions.

Confined Accumulation - Rotational Crops

1. This study was conducted with a degradate of trifluralin, not with an end-use formulation of the parent compound.
2. Quantitative data were not presented.
3. It was assumed that the wheat was analyzed by combustion because that the method was used to analyze the soybeans planted immediately after application.
4. Field test data was incomplete and did not include depth of water table, slope of plots, or irrigation schedule. Meteorological data for this portion of the study were the same as in the field dissipation portion of the study.
5. Treatment to planting interval for wheat was not specified.
6. The [^{14}C]trifluralin used was not indicated, and could have been any of those reported in the materials and methods.

Metabolism - Anaerobic Soil

1. Data were reported for 3 and 8 week samples only.
2. The soil incubation temperature was not reported.
3. There was no pretreatment or immediate posttreatment sampling to confirm the application rate.
4. The treated soil was not aged (30-days or one half-life) prior to flooding.

Metabolism - Aerobic Soil

1. Data were reported for 8-week samples only.
 2. The soil incubation temperature was not reported.
 3. The study was conducted with a degradation product, not with the parent compound.
 4. There was no pretreatment or immediate posttreatment sampling to confirm the application rate.
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Degradation - Photodegradation on Soil

1. A dark control was not included and the sampling interval was not described.
2. Degradation products were not identified or quantified.
3. The intensity and wavelengths of the light were not characterized.
4. The test was not conducted on soil.
5. The test was conducted with a degradate not with the parent compound.
6. Quantitative data were not provided.

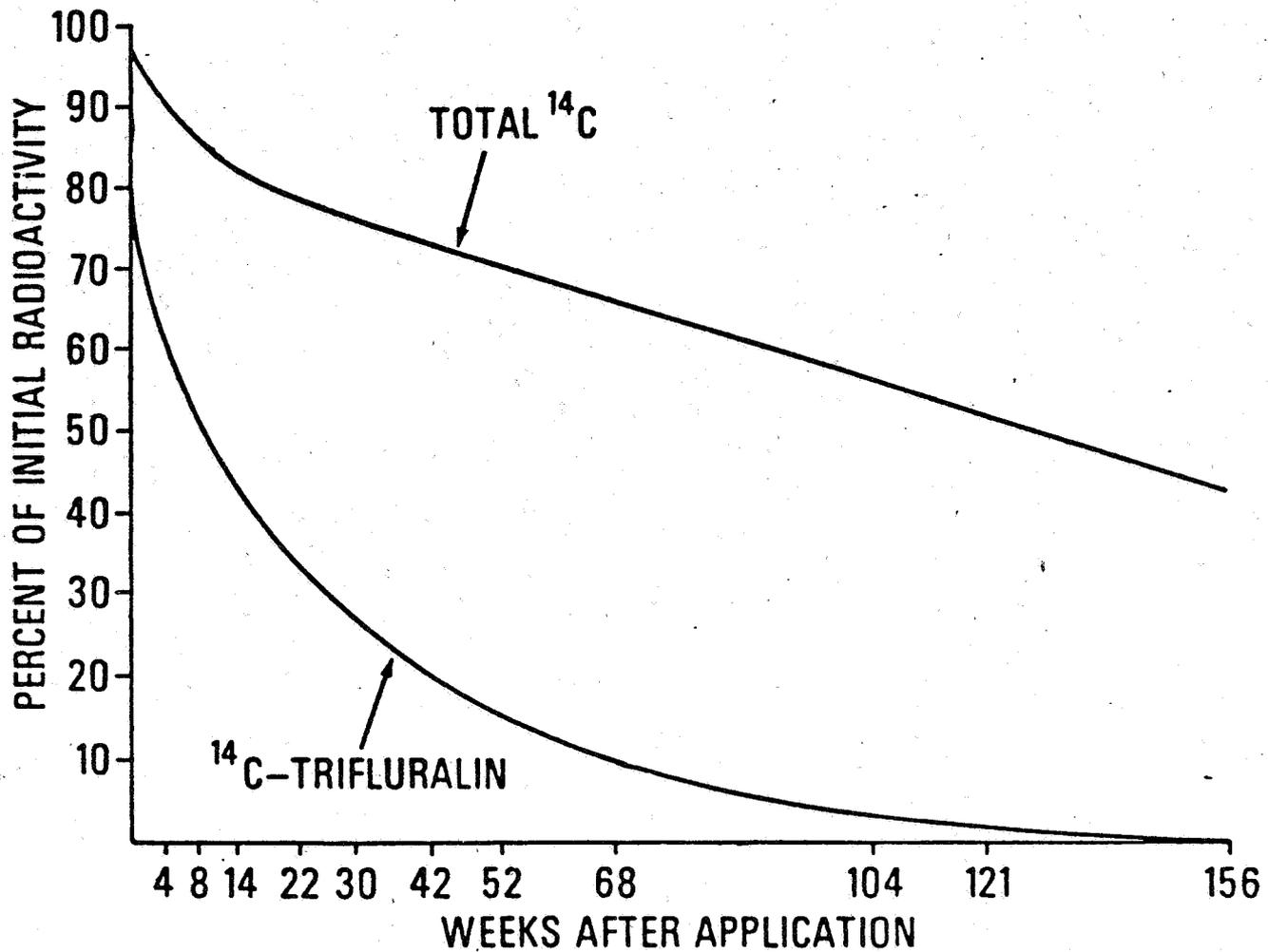


Figure 1. Rate of dissipation (% of applied) of [¹⁴C]trifluralin residues, and total [¹⁴C]radioactivity in silt loam soil at the 0-15 cm depth in field plots treated with [¹⁴C]trifluralin at 0.84-6.72 kg/ha.

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Table 1. Chemical names of trifluralin and its degradates detected and identified in field and laboratory studies.

Code number	Chemical name
TR-1 (Trifluralin)	α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine
TR-2	α,α,α -trifluoro-2,6-dinitro-N-propyl-p-toluidine
TR-3	α,α,α -trifluoro-2,6-dinitro-p-toluidine
TR-4	α,α,α -trifluoro-5-nitro-N ⁴ ,N ⁴ -dipropyltoluene-3,4-diamine
TR-5	α,α,α -trifluoro-5-nitro-N ⁴ -propyltoluene-3,4-diamine
TR-6	α,α,α -trifluoro-5-nitrotoluene-3,4-diamine
TR-7	α,α,α -trifluoro-N ⁴ ,N ⁴ -dipropyltoluene-3,4,5-triamine
TR-9	α,α,α -trifluorotoluene-3,4,5-triamine
TR-10	α,α,α -trifluoro-2'-hydroxyamino-6'-nitro-N-propyl-p-propiontoluidine
TR-11	2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole-3-oxide
TR-13	2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole
TR-14	7-amino-2-ethyl-1-propyl-5-(trifluoromethyl)benzimidazole
TR-15	2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole
TR-16	7-amino-2-ethyl-5-(trifluoromethyl)benzimidazole
TR-17	7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole
TR-18	7-nitro-5-(trifluoromethyl)benzimidazole
TR-19	7-amino-5-(trifluoromethyl)benzimidazole
TR-20	α,α,α -trifluoro-2,6-dinitro-p-cresol
TR-21	4-(dipropylamino)-3,5-dinitrobenzoic acid
TR-28	2,2-azoxybis-(α,α,α -trifluoro-6-nitro-N-propyl-p-toluidine)
TR-29	N-propyl-2,2'-azoxybis-(α,α,α -trifluoro-6-nitro-p-toluidine)
TR-31	2,2'-azoxybis-(α,α,α -trifluoro-6-nitro-p-toluidine)
TR-32	2,2'-azobis-(α,α,α -trifluoro-6-nitro-N-propyl-p-toluidine)
TR-36	α,α,α -trifluoro-4,6-dinitro-5-(dipropylamino)-o-cresol
TR-39	α,α,α -trifluoro-2-hydroxyamino-6-nitro-N,N-dipropyl-p-toluidine
TR-40	α,α,α -trifluoro-2'6'-dinitro-N-propyl-p-propiontoluidine
TR-41	α,α,α -trifluoro-2,6-dinitro-N-(propan-2-ol)-N-propyl-p-toluidine

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Table 2. Recovery (% of applied)^a of trifluralin degradates^b in silt loam soil treated with [¹⁴C]-trifluralin at 0.84-6.72 kg/ha.

Degradation products ^b	Sampling interval (months)							
	0.5	1	2	4	12	16	24	36
TR-2	1.5	1.8	2.6	2.8	1.7	0.8	0.4	0.2
TR-3 & TR-5 ^c	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.05
TR-4	Tr ^d	0.05	Tr	0.05	0.1	0.1	0.07	0.04
TR-10 & TR-11 ^e	ND ^f	0.5	1.5	0.6	ND	ND	ND	ND
TR-13	0.5	1.3	1.2	1.5	2.0	1.6	0.8	0.5
TR-15	ND	0.5	1.0	0.7	1.5	1.1	1.0	0.6
TR-17	0.3	0.9	1.0	0.2	1.0	0.5	0.6	0.4
TR-20	ND	ND	0.7	0.5	1.0	0.5	0.1	0.1
TR-28	0.05	0.5	0.5	0.6	0.5	0.6	0.3	0.3
TR-29	ND	0.05	0.1	0.05	Tr	0.1	0.08	0.07
TR-32	-- ^g	--	--	--	0.1	0.1	0.05	0.04
Other ^h	2.5	5.4	3.4	3.2	3.9	5.3	3.5	2.0
Unidentified RA ⁱ	9.0	14.0	20.0	28.0	43.0	44.0	42.0	38.0
RA in humin	--	--	--	--	11.0	--	11.0	12.0
RA in humic acid	--	--	--	--	15.0	--	14.0	11.0
RA in fulvic acid	--	--	--	--	17.0	--	17.0	15.0
Unaccounted ^e RA	2.0	2.8	0.8	0.6	0.2	1.2	1.5	0.2

^a Percent of applied [¹⁴C]trifluralin. Exact application rate not specified.

^b Chemical names of degradates are in Table 1.

^c Initially compounds were not well separated.

^d Tr = trace amount; <0.01% of applied.

^e Data for both compounds, constant transformation of TR-10, TR-11 occurred on the TLC plates.

^f ND = Not detected; detection limit not reported.

^g -- = Not analyzed.

^h Represents radioactivity corresponding to the following 6 identified degradation products which could not be estimated singly: TR 6, TR 7, TR 8, TR 9, TR 12, TR 14, TR 16, TR 18, TR 19, TR 21, TR 29, TR 31, TR 36, TR 39, TR 40, TR 41.

ⁱ Radioactivity not extracted with methanol and aqueous methanol.

Table 3. [^{14}C]Trifluralin residues (% of recovered)^a in silt loam soil treated with [^{14}C]trifluralin at 1.68 or 6.72 kg/ha.

Sampling depth (cm)	[^{14}C]Trifluralin (Kg/ha)				
	1.68		6.72		
	Sampling interval (months) ^b				
	12	16	24	36	36
2.5	35	21	21	29	44
5.0	47	32	28	34	40
7.5	15	31	27	17	7
10.0	1	9	10	7	2
12.5	0.5	2	3	3	2
15.0	0.3	1	2	2	2
(Subtotal) ^c	(98.8)	(96)	(91)	(92)	(97)
17.5	0.2	1	3	2	2
20.0	0.2	0.6	1.5	2	1
22.5	0.1	0.5	1	1	0.1
25.0	0.1	0.4	1	0.7	
27.5	0.2	0.3	1	0.5	
30.0	0.1	0.4	0.5	0.6	
32.5	0.1	0.3	0.5	0.5	
35.0	0.1	0.3	0.3	0.4	
38.0	0.1	0.2	0.2	0.3	

a Percent of [^{14}C]radioactivity in total soil sample (0-38 cm).

b Sampling interval, months after application.

c Cumulative amount of [^{14}C]radioactivity from the 0-15 cm depth.

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