ment.

RESULTS AND DISCUSSION

When six repeated analyses using the HPLC system for each of 2.5, 5.0, and 10.0 ng of glyphosate were measured as areas (in.^{2}), the mean values, standard deviations, and percent deviation were 1.04 ± 0.06, 5.8%, 1.63 ± 0.05, 3.2%, and 3.3 ± 0.3, 7.7%, with an average of 5.6% deviation.

When five repeated recoveries at each level of 0.05, 0.10, and 0.25 ppm through the described procedure were analyzed, the mean ppm, standard deviation, coefficient of error, and percent recovery were as follows: 0.046 ± 0.004, 8.7%, and 92.0% ± 8.0; 0.083 ± 0.014, 16.9%, and 83.0% ± 14.0; 0.200 ± 0.034, 17.0%, and 80.0% ± 14.0. These data, calculated by the standard statistical procedure, indicate that the method has good precision and accuracy as shown by the recovery data.

Wauchope (1976) determined the acid dissociation of glyphosate to be $pK_1 = 2.32 \pm 0.03$, $pK_2 = 5.86 \pm 0.03$, $pK_3 = 10.86 \pm 0.03$. During the cleanup procedure it is very important that the pH of the eluate from the cation ion be maintained near the pK_1 value and that the pH of the sample be adjusted to near the pK_3 value before addition to the anion column for obtaining adequate recoveries from these resin columns.

Residues of glyphosate on blackberries harvested 81 days after application of the herbicide postplant resulted in less than 0.05 ppm on all treated samples as well as control samples.

This high-performance liquid chromatographic procedure including the rapid crop cleanup method is easy, accurate, and precise. Other crops could also be analyzed with little or no modification of the method.

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Registry No. Glyphosate, 1071-83-6.

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Determination of Extractable and Nonextractable Radioactivity from Small Field Plots 45 and 95 Weeks after Treatment with [^{14}C]Dicamba, (2,4-Dichloro[^{14}C]phenoxy)acetic Acid, [^{14}C]Triallate, and [^{14}C]Trifluralin

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The degradation of ring-labeled [^{14}C]dicamba (2-methoxy-3,6-dichlorobenzoic acid), ring-labeled [^{14}C]-2,4-D [(2,4-dichlorophenoxy)acetic acid], [2-^{14}C]triallate [*S*-(2,3,3-trichloroallyl) diisopropylthiocarbamate], and ring-labeled [^{14}C]trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) was studied under field conditions at rates of 1 kg/ha in small sandy loam plots. Duplicate plots were sampled to a depth of 10 cm after 45 and 95 weeks and extracted with aqueous acetonitrile to determine amounts of extractable radioactivity. The extracted soils were then oxidatively combusted to determine nonextractable, or bound, radioactivity. After 45 weeks, soluble radioactivity recovered from the dicamba-, 2,4-D-, triallate-, and trifluralin-treated plots was <1, 2, 50, and 77% of that applied, while the nonextractable activity accounted for 2, 10, 15, and 10% of that applied. After 95 weeks, <1, 1, 16, and 38% of the applied radioactivity were, on the average, extractable from the dicamba-, 2,4-D-, triallate-, and trifluralin-treated plots, while 3, 6, 30, and 22%, respectively, remained in a solvent nonextractable form.

The herbicides dicamba (Figure 1, **1**), 2,4-D (Figure 1, **2**), triallate (Figure 1, **3**) and trifluralin (Figure 1, **4**) are among the more commonly used herbicides in western Canada. In 1979, approximately 90% of land sown to cereal and oilseed crops in Saskatchewan received treatments with these chemicals for weed control (Smith, 1982).

Persistence of the four herbicides has been studied in prairie soils under labatory (Smith, 1973, 1974, 1978; Smith and Muir, 1980) and field (Smith and Hayden, 1976) conditions. It has been concluded (Smith, 1982) that whereas dicamba and 2,4-D are rapidly lost from treated soils, triallate and trifluralin are moderately persistent, so that residues can be carried over in the soil from one crop year to the next.

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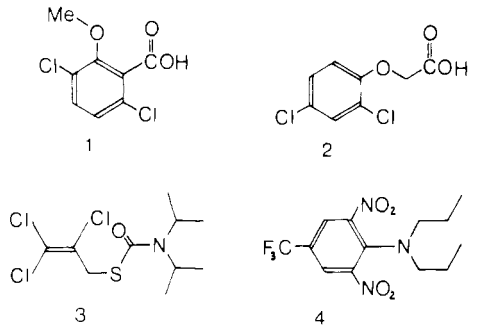

Figure 1. Structures of herbicides.

In recent years, a greater emphasis has been placed on characterizing soil transformation products formed from herbicides. Soil studies involving ^{14}C-labeled herbicides can yield information regarding the nature of solvent-extractable and solvent-nonextractable, or bound, radioactivity. Such studies have been conducted under laboratory conditions with [^{14}C]triallate (Anderson, 1981), [^{14}C]trifluralin (Kearney et al., 1976; Helling and Krivonak, 1978; Nelson et al., 1983), and [^{14}C]-2,4-D (Wilson and Cheng, 1978; Smith and Muir, 1980; McCall et al., 1981; Stott et al., 1983) with the amounts of extractable and nonextractable soil radioactivity being determined. However, of the four herbicides under discussion, only the fate of [^{14}C]trifluralin has been studied under field conditions (Probst et al., 1967; Golab et al., 1979).

In the work to be described, the fate of ring-labeled [^{14}C]dicamba, ring-labeled [^{14}C]-2,4-D, [2-^{14}C]triallate, and ring-labeled [^{14}C]trifluralin was studied in small sandy loam field plots under western Canadian conditions. The treated soils were sampled after 45 and 95 weeks to analyze and assess solvent extractable radioactivity and to determine the amounts of nonextractable soil bound ^{14}C products associated with the humic and fulvic soil fractions.

MATERIALS AND METHODS

Soil. Field plots were situated on a sandy loam soil of the Asquith Association classified as a Dark Brown Chernozemic, Orthic Dark Brown. The soil contained 10% clay, 25% silt, 65% sand, and 4.6% organic matter. Moisture content at field capacity was 20%. Soil pH (in a 1:1 soil–water slurry) was 7.6.

Chemicals. 2-Methoxy-3,6-dichloro[*ring*-U-^{14}C]benzoic acid with a specific activity of 6.47 mCi/mmol and radiochemical purity in excess of 98% was obtained from the Velsicol Chemical Corp., Chicago, IL. (2,4-Dichloro-[*ring*-U-^{14}C]phenoxy)acetic acid was purchased from Amersham Corp., Oakville, Ontario, Canada, with a specific activity of 4.40 mCi/mmol and radiochemical purity of 99%. *S*-(2,3,3-Trichloro[2-^{14}C]allyl) diisopropylthiocarbamate with a specific activity of 10.23 mCi/mmol and radiochemical purity greater than 98% was provided by Monsanto Co., St. Louis, MO. α,α,α-Trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-[*ring*-U-^{14}C]toludine was obtained from Eli Lilly and Co., Indianapolis, IN, and had a specific activity of 4.11 mCi/mmol and radiochemical purity over 98%.

The radioactive herbicides were diluted with unlabeled materials and solutions prepared, in methanol, containing 0.5 mg of the respective chemicals/mL.

Field Studies. Applications of [^{14}C]dicamba and [^{14}C]-2,4-D were made by zig-zagging the herbicide solutions (2.0 mL, 1.0 mg) from a pipet over the surface of small (10 by 10 cm) field plots. To reduce wind erosion, the chemicals were carefully mixed into the top 1 cm of the soil with a small fork. After incorporation, the soil surface was tamped down firmly. This procedure was similar to that described for field studies with [^{14}C]diclofop-methyl (Smith, 1979). Since triallate and trifluralin are both soil-applied herbicides, treatments involving [^{14}C]triallate and [^{14}C]trifluralin were achieved by applying the solutions (2.0 mL, 1.0 mg) as above to the surface of the 10 by 10 cm field plots. The chemicals were then thoroughly mixed into the top 5 cm of the soil for 2 min as noted (Smith, 1971). Following incorporation, the soil was firmly tamped. These rates, equivalent to 1.0 kg/ha, were within the range normally recommended for weed control in Saskatchewan.

Herbicides were applied on June 18, 1981, in experimental design with four replications. Plots remained fallow and were carefully hand weeded as necessary. Amounts of radioactivity added to the plots were 8.33, 7.12, 5.54, and 10.45 μCi, respectively, of [^{14}C]dicamba, [^{14}C]-2,4-D, [^{14}C]triallate, and [^{14}C]trifluralin.

Duplicate plots of each chemical were sampled on May 3, 1982 (45 weeks), and April 21, 1983 (95 weeks), by removing the soil from the upper 10 cm of each plot. The soils were air-dried at room temperature to constant weight (these ranged from 950 to 1250 g), then ground, and thoroughly mixed. Portions of the soil samples were then subjected to combustion analysis to determine the total radioactivity remaining.

Extraction of Unbound Residues. Duplicate soil subsamples (40 g) were weighed into 250-mL glass-stoppered flasks and shaken for 1 h on a wrist-action shaker with 30% aqueous acetonitrile containing 2.5% glacial acetic acid (100 mL). After shaking, 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. Soil extracts were then centrifuged at 2000*g* for 5 min. Solvent extractable radioactivity was determined by radioassay of the extract (5 mL).

Further portions (25 mL) of the extracts derived from the [^{14}C]dicamba and [^{14}C]-2,4-D treatments were added to 1 N HCl (100 mL) and extracted twice with 50-mL portions of ether as described (Smith and Muir, 1980) Aliquots (5 mL) of the organic and aqueous phases were assessed for radioactivity. Evaporated ether extracts from the 2,4-D-treated plots were then subjected to thin-layer chromatographic and autoradiographic examination as previously reported (Smith and Muir, 1980).

Portions (25 mL) of the extracts derived from the triallate treatments were partitioned between hexane (25 mL) and 5% aqueous Na_2CO_3 solution (100 mL), while extracts (25 mL) obtained from the trifluralin-treated soils were partitioned between dichloromethane (25 mL) and 5% aqueous Na_2CO_3 (100 mL). Aliquots (5 mL) of all phases were checked for radioactivity. Hexane and dichloromethane extracts were also analyzed gas chromatographically to determine amounts of triallate and trifluralin remaining.

Determination of Bound Residues. The soil residues from above, following solvent extraction with aqueous acidic acetonitrile, were collected by vacuum filtration and washed successively with fresh aqueous acidic acetonitrile (100 mL), methanol (100 mL), and acetone (100 mL); all washings were discarded after it was shown that they contained no radioactivity. Each residue was dried for 4 h at 90 °C when samples were combusted to determine nonextractable radioactivity.

Analysis of Nonextractable Radioactivity. The classical procedure involving extraction of the soils with dilute sodium hydroxide solution was used since this procedure has been reported for trifluralin-treated soils

Table I. Extractability of Radioactivity from the Top 10 cm of Field Plots Treated with Ring-Labeled [^{14}C]Dicamba after 45 and 95 Weeks

	% of applied radioactivity[a]			
	45 weeks		95 weeks	
	plot 1	plot 2	plot 1	plot 2
radioactivity from combustion of soil before solvent extraction	3	3	6	2
radioactivity from combustion of soil after solvent extraction	2	2	4	2
difference	1	1	2	0
solvent-extractable radioactivity	<1	<1	<1	<1
radioactivity partitioned into ether from aqueous phase[b]	1 (<1)	1 (<1)	1 (<1)	1 (<)

[a] Average from duplicate analyses. [b] Figures in parentheses represent radioactivity remaining in the aqueous phase after ether extraction.

Table II. Extractability of Radioactivity from the Top 10 cm of Field Plots Treated with Ring-Labeled [^{14}C]-2,4-D after 45 and 95 Weeks

	% of applied radioactivity[a]			
	45 weeks		95 weeks	
	plot 1	plot 2	plot 1	plot 2
radioactivity from combustion of soil before solvent extraction	12	14	8	10
radioactivity from combustion of soil after solvent extraction	8	12	5	7
difference	4	2	3	3
solvent-extractable radioactivity	2	2	1	1
radioactivity partitioned into ether from aqueous phase[b]	2 (<1)	2 (<1)	1 (<1)	1 (<1)
radioactivity in humic fraction	2	3	n.d.[c]	n.d.
radioactivity in fulvic fraction[d]	3 (<1)	3 (<1)	n.d.	n.d.
radioactivity in humin fraction[e]	3	6	n.d.	n.d.

[a] Average from duplicate analyses. [b] Figures in parentheses represent radioactivity remaining in the aqueous phase after ether extraction. [c] Not determined. [d] Figures in parentheses represent ether-soluble radioactivity. [e] Obtained by subtracting amounts of radioactivity in the humic and fulvic fractions from that found in the solvent-extracted soils.

(Helling and Krivonak, 1978; Golab et al., 1979) and for 2,4-D-treated soils (Smith and Muir, 1980; McCall et al., 1981). Thus, samples (20 g) of the extracted soil were shaken on a wrist-action shaker for 24 h with 1 N NaOH solution (50 mL) and separated into a soluble fulvic acid fraction and a humic acid precipitate after acidification to pH 1 of the NaOH extract as described (Smith and Muir, 1980).

A portion of the fulvic acid solution (1 mL) was examined for radioactivity, and the remaining solution was decanted into a separatory funnel containing water (100 mL) and shaken with ether (25 mL), an aliquot of which (5 mL) was checked for radioactivity. The humic precipitate was resuspended in 1 N HCl (25 mL) and recentrifuged, and the supernatant was discarded after it was shown that no radioactivity was being extracted into the acid. Following drying overnight at 70 °C, the humic acid samples were weighed and combusted to liberate any radioactivity as [^{14}C]carbon dioxide.

Radioactivity Determinations. The radioactivity in the various solutions was determined by using a Picker Nuclear Liquimat Model 200 liquid scintillation spectrometer. Scinti Verse (15 mL) was the scintillation solution used. For the determination of counting efficiencies an external ^{137}Cs standard was used.

Radioactivity associated with the soils and humic acid fractions was measured by combustion in a Packard Model 306 sample oxidizer. Prior to oxidation, the samples were mixed with 0.3 mL of Combustaid (Packard Instruments Co., Inc., Chicago, IL) to aid the combustion. The [^{14}C]-carbon dioxide evolved was absorbed in 4 mL of CO_2-M-Met (Amersham Corp., Oakville, Ontario, Canada) and mixed with a xylene-based scintillation solution (12 mL).

Samples were counted in a Beckman 7500 liquid scintillation spectrometer by using an internal channel ratio procedure for quench correction. The efficiency of oxidation of ^{14}C standards to [^{14}C]carbon dioxide was over 95%.

Gas Chromatography. For analysis of triallate and trifluralin a Hewlett-Packard Model 5713A gas chromatograph was used, equipped with a radioactive nickel detector operated at 350 °C. The glass column (1.5 m by 4 mm i.d.) was packed with 5% Dexsil 300 on 80–100-mesh Chromosorb W HP, and all samples were injected directly onto the column packing. Argon containing 5% methane at a flow rate of 40 mL/min was the carrier gas. With a column temperature of 200 °C the retention times for trifluralin and triallate were 2.45 and 4.41 min, respectively. Triallate and trifluralin present in the various solutions were calculated by comparing peak areas with those of appropriate standards.

RESULTS

Recovery of radioactivity from the top 10 cm of the variously treated sandy loam field plots is summarized in Tables I–IV. There was excellent agreement between results from duplicate plots. Also, the data obtained for extractable radioactivity as determined by solvent extraction were, in all cases, very similar to those derived, by difference, from the soil combustion analyses before and after solvent extraction.

Soil combustion analysis of the top 10 cm of the field plots treated with ring-labeled [^{14}C]dicamba indicated (Table I) almost complete loss during the initial 45 weeks. Solvent-extractable radioactivity at both sampling dates was considerably less than 1% of that applied, and it was thus not possible to characterize this activity by thin-layer chromatographic analysis. Since so little of the applied radioactivity was associated with the soil after 45 and 95 weeks, no attempts were made to determine the amounts of solvent nonextractable radioactivity contained in the fulvic and humic soil fractions.

Extractable radioactivity recovered from the top 10 cm of the sandy loam field plots treated with ring-labeled [^{14}C]-2,4-D accounted for 2% of that applied after 45 weeks, while after 95 weeks 1% of the initial activity re-

Table III. Extractability of Radioactivity and Triallate from the Top 10 cm of Field Plots Treated with [2-^{14}C]Triallate after 45 and 95 Weeks

	% of applied radioactivity[a]			
	45 weeks		95 weeks	
	plot 1	plot 2	plot 1	plot 2
radioactivity from combustion of soil before solvent extraction	57	61	44	44
radioactivity from combustion of soil after solvent extraction	16	15	30	28
difference	41	46	14	16
solvent-extractable radioactivity	50	49	16	16
radioactivity partitioned into hexane from aqueous phase[b]	48 (2)	45 (2)	18 (1)	15 (1)
triallate in hexane by GC analysis	46	47	11	11
radioactivity in humic fraction	2	2	7	7
radioactivity in fulvic fraction[c]	6 (<1)	5 (<1)	11 (<1)	11 (<1)
radioactivity in humin fraction[d]	8	8	12	10

[a] Average from duplicate analyses. [b] Figures in parentheses represent radioactivity remaining in the aqueous phase after hexane extraction. [c] Figures in parentheses represent ether-soluble radioactivity. [d] Obtained by subtracting amounts of radioactivity in the humic and fulvic fractions from that found in the solvent-extracted soils.

Table IV. Extractability of Radioactivity and Trifluralin from the Top 10 cm of Field Plots Treated with Ring-Labeled [^{14}C]Trifluralin after 45 and 95 Weeks

	% of applied radioactivity[a]			
	45 weeks		95 weeks	
	plot 1	plot 2	plot 1	plot 2
radioactivity from combustion of soil before solvent extraction	77	78	53	59
radioactivity from combustion of soil after solvent extraction	11	10	20	23
difference	66	68	33	36
solvent-extractable radioactivity	76	78	35	41
radioactivity partitioned into dichloromethane from aqueous phase[b]	70 (3)	75 (4)	32 (3)	34 (6)
trifluralin in dichloromethane by GC analysis	47	47	10	13
radioactivity in humic fraction	2	2	9	9
radioactivity in fulvic fraction[c]	2 (<1)	2 (<1)	7 (<1)	8 (<1)
radioactivity in humin fraction[d]	7	6	4	6

[a] Average from duplicate analyses. [b] Figures in parentheses represent radioactivity remaining in the aqueous phase after dichloromethane extraction. [c] Figures in parentheses represent ether-soluble radioactivity. [d] Obtained by subtracting amounts of radioactivity in the humic and fulvic fractions from that found in the solvent-extracted soils.

mained (Table II). Most of this radioactivity was in an ether-soluble form and could be partitioned into the organic phase from aqueous solution. This ether solution appeared to contain no discrete ^{14}C-containing compounds as determined by thin-layer and autoradiographic analysis.

After 45 weeks between 8 and 12% of the original radioactivity was nonextractable with 2–3% in the humic acid fraction and 3% in the fulvic acid fraction. None of the radioactivity in the fulvic acid was ether soluble. Alkaline analysis of the ^{14}C in the treated soils after 95 weeks was not carried out since solvent-nonextractable radioactivity was about half that remaining at 45 weeks.

For field plots treated with [2-^{14}C]triallate, solvent-extractable radioactivity recovered from the top 10 cm of soil accounted for approximately 50% of that applied after 45 weeks and 16% after 95 weeks (Table III). The majority of the solvent-extractable radioactivity was partitionable into hexane, with amounts equivalent to less than 2% of that applied to the plots remaining in the aqueous Na_2CO_3 solution. Gas chromatographic analysis of the hexane extracts indicated that all the extractable readioactivity recovered from the soils after 45 weeks was attributable to triallate. After 95 weeks most of the activity extracted from the soils was in the form of triallate, with, perhaps, about 5% of the original activity being in the form of hexane-soluble degradation products.

Approximately 15% of the initial radioactivity could not be extracted from the treated plots after 45 weeks, while after 95 weeks this amount had doubled to about 30%. Alkaline extraction of the solvent-extracted soils suggested that there had been a slow incorporation of the radioactivity into soil organic matter, with greater amounts being noted in all soil fractions after 95 weeks than after 45 weeks. No ether-soluble radioactivity was recovered from any of the fulvic acid fractions.

Solvent-extractable radioactivity recovered from the top 10 cm of sandy loam plots treated with ring-labeled [^{14}C]trifluralin accounted for nearly 80% of that applied after 45 weeks and for 35–40% after 95 weeks (Table IV). Most of this soluble radioactivity could be partitioned into dichloromethane, while 3–6% of the initial activity remained in the aqueous phase in a polar form. Gas chromatographic analysis of the organic extracts indicated that not all of the extractable radioactivity was residual trifluralin and that approximately 25% of the applied activity was in the form of soluble degradation products after 45 weeks and about 20% after 95 weeks. The degradation of ring-labeled [^{14}C]trifluralin in soils is very complex (Probst et al., 1975; Golab et al., 1979), and over 20 degradation products have been identified or postulated. Since pure standards of these breakdown products were not available, detailed analysis of the dichloromethane extracts was not possible. However, it may be presumed in the present study that some of the unaccounted radioactivity occurred as degradation products.

About 10% of the original activity could not be extracted from soil after 45 weeks and about 20% was in a bound form after 95 weeks. Fractionation of the organic matter in these soils indicated that the nonextractable activity was distributed among humic, fulvic, and humin soil fractions. No other soluble radioactivity was recovered from any of the fulvic acid fractions.

DISCUSSION

Given the small size of the plots it was feared that wind and rain erosion might result in significant losses of the

applied herbicides over the 95-week period. To reduce such losses, the chemicals were all incorporated into the soil, which was then firmly tamped down. The fact that over 77% of the applied radioactivity was recovered from the [^{14}C]trifluralin-treated plots after 45 weeks and between 53 and 59% after 95 weeks (Table IV) was an indication that erosional losses from the treatment area were slight and that all losses of radioactivity were due to degradative and volatility processes.

It was considered that after sampling, losses of triallate, trifluralin, and volatile degradation products from treated soils during the drying, grinding, and mixing operations would have been negligible. Under field conditions the plots were alternately moistened with rain and snow and then dried by the action of wind and temperature. Thus, natural volatility losses of herbicides and degradation products over the 45- and 95-week intervals would be much greater than those incurred during the drying, mixing, and grinding of the soils in the laboratory.

Aqueous acidic acetonitrile, together with the extended extraction procedure, was used to recover radioactive residues from the soil since this procedure has proved to be a most effective extractant of acid herbicides, as well as triallate and trifluralin, from aged Saskatchewan soils (Smith, 1981; Smith and Milward, 1983). As has been noted (Smith, 1981), efficient extraction techniques must be used or herbicide residues could be considered to be nonextractable, or bound, when, in fact, they are not being satisfactorily extracted.

Previous studies have indicated (Smith, 1973, 1974) that in soils dicamba is biologically degraded to 3,6-dichlorosalicyclic acid, which undergoes strong soil adsorption. Tracer studies have also shown (Smith, 1974) that dicamba, the salicyclic acid, or both can undergo decarboxylation and ring degradation in soil with slow evolution of carbon dioxide. It would thus appear that in the present study, almost complete loss of the ring carbon atoms of dicamba has occurred so that less than 5% of the originally applied radioactivity remained in the treated field plots after 45 weeks (Table I).

Several studies (Haider et al., 1975; Haider and Martin, 1975; Wagner, 1975) have shown that such easily degradable compounds as [^{14}C]glucose and [^{14}C]benzoic acid can undergo rapid decomposition in soil to [^{14}C]carbon dioxide, which is then incorporated into soil organic matter, including the fulvic and humic fractions. This radioactivity slowly dissipates as [^{14}C]carbon dioxide, but small amounts of the original radioactivity can still be detected after 3 years of soil incubation (Wagner, 1975).

It is well-known that in soil, 2,4-D can undergo a facile biological degradation with rapid loss of both side chain and aromatic carbon atoms as carbon dioxide (Foster and McKercher, 1973; Loos, 1975; Fournier et al., 1981; McCall et al., 1981). Therefore, it is probable that this carbon dioxide or small carbon-containing fragments formed by breakdown of 2,4-D will be incorporated into the soil biomass (Wilson and Cheng, 1978). Laboratory experiments tend to confirm this concept. Soil incubation studies carried out with ring-labeled [^{14}C]-2,4-D, for periods up to 150 days, have shown that between 17 and 36% of the applied radioactivity can be converted to a solvent-nonextractable form and that, in general, these levels were reached after a few weeks and then slowly declined (Wilson and Cheng, 1978; Smith and Muir, 1980; McCall et al., 1981). A long-term laboratory study, using ring-labeled [^{14}C]-2,4-D, has indicated (Stott et al., 1983) that, after 1 year, up to 8% of the residual activity was present in the soil biomass in an unextractable form. These latter data are in excellent agreement with those from the present data (Table II) where about 10% of the applied radioactivity was bound to the soil after 45 weeks. About half this amount was present after 95 weeks (Table II), indicating that with time the ring-carbon atoms of 2,4-D are almost completely lost from soil under field conditions.

Triallate is lost from treated soils by a combination of volatility losses and biological degradation (Banting, 1967; Beestman and Deming, 1976; Anderson, 1981; Grover et al., 1981). The laboratory studies by Anderson (1981) have disclosed that, depending upon soil moisture, between 3 and 18% of the radioactivity from [2-^{14}C]triallate can be lost as [^{14}C]carbon dioxide after 10 weeks, while between 32 and 55% of the applied activity could not be solvent extracted from the soil. This, as in the case of 2,4-D, would suggest that at least some of the solvent-nonextractable ^{14}C may be attributed to the incorporation of [^{14}C]carbon dioxide, or perhaps small ^{14}C-containing fragments derived from the [^{14}C]triallate, into the soil organic matter.

In the present study, there appeared to be no significant amounts of solvent-extractable degradation products formed in the plots treated with [2-^{14}C]triallate after 45 and 95 weeks (Table III). The persistence of the herbicide to the extent of almost 50% after 45 weeks is somewhat higher than that normally encountered in prairie soils (Smith, 1982), and this was attributed to edaphic factors. The increase in soil-bound radioactivity from 15% after 45 weeks to 30% after 95 weeks can be explained by further incorporation of ^{14}C fragments from the [2-^{14}C]triallate into soil organic matter. After 95 weeks, about 10% of the initial radioactivity remained in an extractable form (Table III), and once volatility and degradation losses have depleted this remaining residue, a gradual decline in the amounts of soil-bound activity, such as occurs with 2,4-D, would be expected.

Losses of trifluralin from treated soils occur by both volatilization and biological processes (Probst et al., 1975; Helling, 1976). In the present study (Table IV), after 45 weeks, 50% of the applied trifluralin was recoverable from the soil and solvent-extractable degradation products accounted for about 25% of the initial activity. Bound residues accounted for 10% of the radioactivity. Over the next 50 weeks further degradation of the trifluralin occurred that was accompanied by a doubling in the amounts of nonextractable radioactivity. Soluble degradation products could still be attributed to nearly 20% of the applied activity. Thus, in the present study there appeared to be formation of greater amounts of soluble degradation products and lesser amounts of nonextractable radioactivity than were reported by Golab et al. (1979) from their field studies. In the latter field study with ring-labeled [^{14}C]trifluralin, after 12 months approximately 15% of the applied herbicide remained in the soil, while degradation products accounted for 8% of the applied ^{14}C and bound residues for 43%. After 24 months, less than 10% of the original trifluralin was present, 4% of the applied radioactivity was in the form of extractable degradation products, and 42% of the initial activity was in a nonextractable, or bound, form (Golab et al., 1979).

The present data tend to agree more with those from laboratory incubation studies. Nelson et al. (1983) reported that after 6 months, when almost 60% of applied ring-labeled [^{14}C]trifluralin still remained in the soil, 15% of the applied radioactivity could be attributed to solvent-extractable degradation products and 10% to nonextractable residues. Helling and Krivonak (1978) have noted that after 7 months in soil under laboratory conditions only 7% of activity from treatments with ring-la-

beled [^{14}C]trifluralin was in a nonextractable form.

The trifluralin ring system does not appear to undergo extensive fission in the soil (Probst et al., 1975), but as mentioned, the fate of trifluralin in soils is very complex and a considerable number of transformation products have been implicated during its degradation (Probst et al., 1975; Golab et al., 1979). It has also been suggested Golab et al., 1979) that certain transformation products of trifluralin may become complexed directly with soil organic matter and thus be rendered nonextractable.

Perhaps with time, more of the unidentified soil transformation products from the present study would have become complexed or otherwise bound to the soil, thus decreasing their amounts in the soil and increasing the quantities of nonextractable residues to the levels reported by Golab et al. (1979).

Of concern is whether after repeated annual applications of herbicides bound residues have phytotoxic significance and are likely to adversely affect soil fertility. The findings from long-term studies conducted at the Agriculture Canada Experimental Farm at Indian Head, Saskatchewan, have indicated that crop fertility, as determined by wheat yields, has not been impaired by 24 repeated annual applications of 2,4-D [cf. Smith (1982)]. Similar long-term field studies carried out at the Weed Research Organization near Oxford, England, with repeated annual applications of triallate have shown no adverse effects on soil fertility as determined by crop yields, organic carbon, and soil pH measurements (Fryer, 1981). Such field data for dicamba and trifluralin have not been reported.

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Registry No. 1, 1918-00-9; [*ring*-U-^{14}C]-1, 89300-29-8; 2, 94-75-7; [*ring*-U-^{14}C]-2, 89300-30-1; 3, 2303-17-5; [2-^{14}C]-3, 89232-81-5; 4, 1582-09-8; [*ring*-U-^{14}C]-4, 89300-31-2.

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Biodegradation of *o*-Phenylphenol in River Water and Activated Sludge

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The compound *o*-phenylphenol (OPP) is widely used in disinfectant formulations and as a fungicide in the fruit packing industry. The biodegradation of [^{14}C]OPP, labeled on the phenolic ring, was examined in both river water and activated sludge. The rates of disappearance of [^{14}C]OPP, appearance of degradation products, and $^{14}CO_2$ formation were monitored. The data showed that a 50% reduction in [^{14}C]OPP concentration from its initial value occurred in approximately 1 week in river water, 24 h in nonacclimated sludge, and 3 h in acclimated sludge. The conversion of [^{14}C]OPP to $^{14}CO_2$ was found to be 50–65% after 16 days in the river water and 48 h in the activated sludge.

The compound *o*-phenylphenol (OPP) is widely used in disinfectant formulations and as a fungicide in the fruit packing industry. The biodegradation of OPP has been studied by several groups. Results of the simple biochemical oxygen demand (BOD) test for OPP indicate rapid and extensive biodegradation (Simmons et al., 1977). Voets et al. (1976) report that OPP (40 mg/L) was 100% degraded in an activated sludge confirmatory test as described by the Organization for Economic Cooperation and Developement (OECD). They also observed 100% deg-

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