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Brightwell, B., and J. Malik. 1978. Solubility, volatility, adsorption and partition coefficients, leaching, and aquatic metabolism of MON 0573 and MON 0101: Report No. MSL-0207. Final rept. Unpublished study received June 12, 1978 under 524-308; submitted by Monsanto Co., Washington, DC; CDL:234108-A.

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CONCLUSIONS:

Degradation - Hydrolysis

1. This portion of the study is scientifically valid.
2. [¹⁴C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) and aminomethylphosphonic acid were stable in sterile buffered water at pH 3, 6, and 9 during 35 days of incubation in the dark at 5 and 35 C. Slight degradation of [¹⁴C]glyphosate was observed in two of three sterile, natural waters treated with [¹⁴C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid), at 0.1 ppm, and incubated in the dark at 30 C for 35 or 49 days. Aminomethylphosphonic acid was detected at maximum concentrations of 25.3 and 17.2 % of the applied 35 days posttreatment in the Cattail Swamp (pH 6.2) and Ballard Pond (pH 7.3) waters, respectively. No degradation was observed in Sphagnum Bog water (pH 4.2).
3. This portion of the study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of glyphosate and the glyphosate degradate aminomethylphosphonic acid in sterile, buffered water at pH 3, 6, and 9 at 5 and 35 C.



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Metabolism - Aerobic Aquatic

1. This portion of the study is scientifically valid.
2. [¹⁴C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) degraded in three natural waters at pH 4.2, 6.2, and 7.3, with 39-49% of the applied remaining at 49 days, 51-61% at 63 days, and 58-69% at 35 days, respectively. Respective aminomethylphosphonic acid concentrations increased steadily at each sampling interval, reaching maximum concentrations in the Sphagnum Bog, Cattail Swamp, and Ballard Pond waters of 26.2, 30.2, and 23.1% of the applied radioactivity. A maximum of 29, 14.6, and 11.4% of the applied radioactivity evolved as ¹⁴CO₂ in the pH 4.2 (day 63), pH 6.2 (day 63), and pH 7.3 (day 35) waters, respectively. Addition of sediment to the system increased the dissipation of glyphosate and aminomethylphosphonic acid from water via adsorption to sediment. Evolution of ¹⁴CO₂ was not affected. All samples were maintained at 30 C in the dark.
3. This portion of the study does not fulfill EPA Data Requirements for Registering Pesticides because the test waters were not mixed with sediment or soil (Experiment 1), complete water characteristics were not provided, and data on the characterization of radioactivity were not provided for all sampling intervals.

Mobility - Adsorption/Desorption

1. This portion of the study is scientifically valid.
2. [¹⁴C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) was adsorbed to Drummer silty clay loam, Ray silt, Spinks sandy loam, Lintonia sandy loam, and Cattail Swamp sediment with Freundlich K values of 62, 90, 70, 22, and 175, respectively. The maximum percentages of applied glyphosate desorbed were 5.3, 3.7, 3.6, 11.5, and 0.9%, respectively. *Cited all but Cattail Swamp*
3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the adsorption/desorption of glyphosate in silty clay loam, silt, and two sandy loam soils. Data pertaining to the Cattail Swamp sediment do not contribute to data requirements because the characteristics were incompletely provided.

Mobility - Column Leaching

1. This portion of the study is scientifically valid.
2. [¹⁴C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) was slightly mobile to relatively immobile with <7% of the applied ¹⁴C detected in the leachate from 30-cm silt, sand, clay, sandy clay loam, silty clay loam, and sandy loam soil columns eluted with 20 inches of water. Aged (30 days) [¹⁴C]glyphosate residues were relatively immobile in silt, clay, sandy clay loam soils with <2% of the radioactivity detected in the leachate following elution with 20 inches of water. Both glyphosate and amino-

methylphosphonic acid were detected in the leachate of aged and unaged soil columns.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of glyphosate (unaged) in sand, silt, clay, sandy clay loam, silty clay loam, and two sandy loam soils and on the mobility of glyphosate residues (aged) in silt, clay, and sandy clay loam soils.

MATERIALS AND METHODS:

Degradation - Hydrolysis

Three buffered (pH 3, 6, and 9) waters containing 0.05% formalin as a mold inhibitor, were treated with filtered (Millipore 0.45 μ m) [14 C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 25 and 250 ppm. Aliquots (1 ml) were transferred to vials, and incubated in the dark at 5 and 35 C. Samples were taken at 0, 7, 14, 21, and 35 days posttreatment.

Additionally, water from three field sites, Cattail Swamp, Sphagnum Bog, and Ballard Pond (pH 6.2, 4.2, and 7.3, respectively), was collected, treated with [14 C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0.1 ppm, sterilized (Millipore filter 0.45 μ m), and incubated in the dark at 30 C. Aliquots (20 ml) were taken immediately after treatment and at 7, 21, 35, and 49 days (Cattail Swamp only) posttreatment.

All samples, in duplicate, were analyzed for radioactivity by LSC. Samples were analyzed for glyphosate and aminomethylphosphonic acid by TLC and HPLC. The material balance was >90% for all samples. Detection limits were not reported.

Metabolism - Aerobic Aquatic

Experiment 1

Three natural waters (see hydrolysis study), in 250 ml flasks fitted with Ascarite traps, were treated with [14 C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0.1 ppm. The flasks were incubated at 30 C in the dark for 9 weeks. Aliquots (size not specified) were taken at 0, 1, 3, 5, 7, and 9 weeks posttreatment. The 14 C 14 O $_2$ evolved was trapped and quantified directly by LSC. Water samples were analyzed for glyphosate and the glyphosate degradate aminomethylphosphonic acid, by HPLC and TLC. Total radioactivity recovered ranged from 92 to 108%. Detection limits were not reported.

Experiment 2

Sediments and waters (100 ml:100 ml) from two Wisconsin sites, the Cattail Swamp and Sphagnum Bog (see Table 1 and hydrolysis study for characteristics) were added to Erlenmeyer flasks fitted with Ascarite towers to trap the $^{14}\text{CO}_2$. Each flask was treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0.1 ppm, and incubated in the dark at 30 C for 7 weeks. Soil and water samples were taken at 3, 7, 21, 35, and 49 days posttreatment. The $^{14}\text{CO}_2$ evolved was trapped, and quantified directly by LSC. The contents of the flasks were separated by centrifugation. The sediment fraction was extracted (3x) with 0.5 N NaOH. Water samples and sediment extracts were analyzed for ^{14}C by LSC, and glyphosate and degradate were determined by column chromatography. Water samples and sediment extracts from the last sampling interval (49 days) were also analyzed by HPLC. To determine the radioactivity in sediment not extracted with NaOH, the sediment was lyophilized, combusted, and the $^{14}\text{CO}_2$ evolved directly quantified by LSC. Detection limits were not reported. Total radioactivity recovered ranged from 83 to 102 and 88 to 113% of the applied radioactivity in the Sphagnum Bog and Cattail Swamp, respectively.

Mobility - Adsorption/Desorption

Silty clay loam, silt, two sandy loam soils, and a swamp sediment (Table 1) were air-dried and sieved (0.5 mm). Duplicate 2.5-g portions of each soil were mixed with 0.01 N CaSO_4 solutions (10 ml) containing [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0, 0.1, 1.0, 10, and 20 ppm. The samples were shaken on a vortex mixer and then mixed mechanically for 4 hours at 25 C. Samples were then centrifuged, and the radioactivity in the supernatant was quantified using LSC.

To measure [^{14}C]glyphosate desorption, the supernatant volume was replaced with an equal volume of 0.01 N CaSO_4 solution, shaken for 4 hours with the soil/sediment samples, and again centrifuged. The radioactivity in the supernatant was quantified using LSC. All data were fitted to the Freundlich isotherms. Freundlich K and $1/n$ values were estimated from log-log plots of the amount of [^{14}C]glyphosate adsorbed versus the equilibrium concentration of [^{14}C]glyphosate in the solution. In the Freundlich equation ($x/m = KC^{1/n}$), x/m is the μg of soil adsorbed/g of soil, C is the equilibrium concentration ($\mu\text{g}/\text{ml}$), and K and $1/n$ are constants.

Mobility - Column Leaching

Seven soils (Table 1) were air-dried, sieved (2 mm), and added to glass columns (1.5 inches in diameter x 30 cm in height). The soil moisture contents of three soils (Ray silt, Molokai clay, and Hilo sandy clay loam) were adjusted to 15-20% before treatment. All soil column surfaces were treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 8 lb ai/A. Following treatment, the Ray silt, Molokai clay, and Hilo sandy clay loam soil columns were fitted with traps to collect evolved $^{14}\text{CO}_2$, and incubated (incubation conditions unspecified) for 30 days. The incubated soils were leached

biweekly for 45 days with a total of 20 inches of water added. The other soils were rapidly leached with 20 inches of water.

The leachates from all soil columns were analyzed for radioactivity using LSC. In addition, the leachates from the aged soil columns were combined, concentrated, filtered, and analyzed for glyphosate and aminomethylphosphonic acid by TLC. After the leaching periods, the soil columns were divided into 2-cm segments. Each segment was frozen, lyophilized, combusted, and the $^{14}\text{CO}_2$ evolved was trapped and quantified using LSC. An aliquot (2 g) of the top 2-cm segment of the soil columns was extracted twice with 0.5 N NaOH, the combined extracts concentrated, and analyzed by TLC. Recovery values were >78% of the applied for all soil columns. Detection limits were not reported.

REPORTED RESULTS:

Degradation - Hydrolysis

Neither [^{14}C]glyphosate nor aminomethylphosphonic acid hydrolyzed in sterile, buffered waters (Table 2). The hydrolysis of [^{14}C]glyphosate and aminomethylphosphonic acid was not affected by treatment rate, pH, or incubation temperature. Slight degradation of [^{14}C]glyphosate was observed in two of the three sterile, natural waters (Table 3). Aminomethylphosphonic acid was detected at maximum concentrations of 25.3 and 17.2 percent of the applied 35 days posttreatment in the Cattail Swamp and Ballard Pond waters, respectively. No degradation was observed in Sphagnum Bog water.

Metabolism - Aerobic Aquatic

Experiment 1

[^{14}C]Glyphosate degraded from the Sphagnum Bog, Cattail Swamp, and Ballard Pond waters with half-lives of 49, >63, and >35 days, respectively (Table 4). Aminomethylphosphonic acid concentrations steadily increased at each sampling interval, reaching maximum concentrations in the Sphagnum Bog, Cattail Swamp, and Ballard Pond waters of 26.2, 30.2, and 23.1% of the applied.

Experiment 2

The sum of the glyphosate concentrations in the water, and extract of the sediment of the Cattail Swamp (pH 6.2), was similar to that found in the Sphagnum Swamp (pH 4.2) (Table 5). The partitioning of glyphosate between the water and sediment, however, was quite different. In the Cattail Swamp, glyphosate concentrations in water ranged from 5.9 (day 7) to 3.5% (day 49) of the applied. Glyphosate concentrations in sediment for the same sampling period ranged from 52.1 to 58.7% of the applied. At day 49 of the incubation period, $^{14}\text{CO}_2$ and unextractable radioactivity accounted for 17.1 and 23.0% of the applied. At the end

of the sampling period (49 days), [^{14}C]glyphosate, in sediment extract and water from the Sphagnum Bog (pH 4.2), was detected at 28.3 and 20.0%, respectively, of the applied. $^{14}\text{CO}_2$ and unextractable radioactivity increased during the 7 weeks to maximum concentrations of 21.8 and 22.1% of the applied.

Mobility - Adsorption/Desorption

Freundlich K values ranged from 22 for the Lintonia sandy loam (organic matter content 0.7%, CEC 5.1 meq/100 g) to 175 for the Cattail Swamp sediment (organic matter content 1.5%) (Table 6). The percent of applied glyphosate desorbed ranged from 11.5 to 0.9% for the Lintonia sandy loam and Cattail Swamp sediment, respectively.

Mobility - Column Leaching

After leaching the unaged soil columns with 20 inches of water, the percent of recovered radioactivity remaining in the soil columns ranged from 93.4 to 100% (Table 7). Of the radioactivity remaining in all the soil columns (aged and unaged), >95% of the recovered remained in the top 14 cm of the columns. After leaching the aged soil columns with 20 inches of water over a 45-day period, <2% of the radioactivity was detected in the leachate (Table 8). The distribution of the radioactivity in the leachate and the top 2-cm segment of the soil columns between glyphosate and the degrade aminomethylphosphonic acid is presented in Tables 9 and 10, respectively.

DISCUSSION:

Degradation - Hydrolysis

Detection limits were not reported.

Metabolism - Aerobic Aquatic

1. Soil/sediment was not included in the experimental design (Experiment 1).
2. Complete water characteristics, including percent suspended solids and dissolved oxygen content, were not reported.
3. Data were not collected long enough to permit the degradation of glyphosate and the pattern of formation and decline of the degradate MON 0453 to be determined.
4. Complete sediment characteristics for the Cattail Swamp, including textural analysis, pH, and CEC, were not reported.

Mobility - Adsorption/Desorption

1. The soils and sediments were sieved to 0.5 mm, thus removing the coarse sand fraction.

2. The test soil reported to be Ray silt loam is a silt according to the USDA soil textural classification system. The soil textural classifications for the Drummer, Spinks, and Lintonia soils could not be verified because the textural analyses were <100%.

Mobility - Column Leaching

1. Values of soil/water relationships (K_d) were not reported.
2. The test soil reported to be Ray silt loam is a silt according to the USDA soil textural classification system. The soil textural classifications for the Drummer, Spinks, and Lintonia soils could not be verified because the textural analyses were <100%.

Table 1. Soil and sediment characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
	%					
Ray silt ^a	4.6	84.2	10.0	1.2	8.1	10.4
Drummer silty clay loam ^a	2.4	68.8	25.3	3.4	6.2	24.6
Spinks sandy loam ^a	75.1	17.8	4.8	2.4	4.7	11.3
Lintonia sandy loam ^a	86.0	11.0	1.8	0.7	6.5	5.1
Leon sand	94.0	5.0	1.0	1.0	4.8	7.2
Hilo sandy clay loam	54.0	20.0	26.0	9.5	5.7	60.0
Molokai clay	18.0	30.0	52.0	3.0	7.0	20.0
Ballard Pond sediment	18.0	54.0	28.0	0.7	6.0	21.0
Cattail Swamp sediment	--	--	--	1.5	--	--

^a See Discussion #2 under Mobility - Adsorption/Desorption.

Table 2. Concentrations (% of applied) of glyphosate and aminomethylphosphonic acid in sterile buffered solutions incubated for 35 days in the dark after treated with [^{14}C]glyphosate, at 25 and 250 ppm, as determined by TLC and HPLC.

pH	Incubation temperature (C)	Treatment rate (ppm)	TLC	HPLC	
			Glyphosate	Glyphosate	MON 0435 ^a
3	35	25	91.6	94.6	5.4
		250	92.9		
	5	25	91.8	94.2	5.8
		250	92.0		
6	35	25	91.9	93.7	6.3
		250	93.3		
	5	25	92.9	94.1	5.9
		250	92.7		
9	35	25	92.7	94.1	5.9
		250	94.4		
	5	25	93.3	93.7	6.3
		250	93.9		

^a Aminomethylphosphonic acid.

Table 3. Concentrations (% of the applied) of glyphosate and MON 0435 (aminomethylphosphonic acid) in sterile three natural waters treated with [^{14}C]glyphosate, at 0.1 ppm, and determined by HPLC.

Water	pH	Sampling interval (days)	Glyphosate	MON 0435
Cattail Swamp	6.2	21	90.4	9.6
		35	74.7	25.3
		49	80.7	19.3
Sphagnum Bog	4.2	21	94.4	5.6
		35	94.0	6.0
Ballard Pond	7.3	21	83.8	16.2
		35	82.8	17.2

Table 4. Concentrations (% of applied) of glyphosate and aminomethylphosphonic acid (MON 0435) in three natural waters treated with [¹⁴C]glyphosate, at 0.1 ppm, and incubated at 30 C in the dark.

Water	Sampling interval (days)	Radioactivity		TLC		HPLC	
		¹⁴ C ₀₂	H ₂ O	Glyphosate	MON-0435	Glyphosate	MON-0435
Sphagnum Bog	3	1.5	102.5	--	--	--	--
	7	2.3	96.0	--	--	--	--
	21	6.6	87.2	79.4	7.8	--	--
	35	13.5	86.1	71.3	14.8	--	--
	49	22.1	71.7	49.4	22.3	38.9	32.8
	63	29.0	63.1	36.9	26.2	27.9	35.2
Cattail Swamp	3	2.1	95.6	--	--	--	--
	7	3.2	97.1	83.5	13.6	--	--
	21	6.5	96.7	73.8	16.7	--	--
	35	10.8	91.8	68.8	23.0	--	--
	49	12.8	91.7	65.7	26.2	66.9	24.8
	63	14.6	91.2	61.0	30.2	50.9	40.3
Ballard Pond	7	4.0	93.7	76.5	17.2	81.4	18.6
	21	8.3	100.4	78.1	22.3	70.6	29.4
	35	11.4	92.0	68.9	23.1	58.4	33.6

Table 5. Concentrations (% of applied) of glyphosate and aminomethylphosphonic acid (MON 0435) in sediment and water treated with [^{14}C]glyphosate, at 0.1 ppm and incubated aerobically at 30 C in the dark.

Water	Sampling interval (days)	Radioactivity (% of applied)						Total
		$^{14}\text{CO}_2$	H_2O		Sediment			
			Glyphosate	MON 0435	Extractable	Unextractable		
Sphagnum Bog	3	0.87	--	--	--	--	--	--
	7	2.67	--	--	--	--	6.52	93.8
	21	16.91	32.9	4.9	15.8	6.8	5.92	83.3
	35	19.46	19.0	2.7	33.6	13.3	7.15	93.8
	49	21.84	20.0	2.7	28.3	6.7	22.09	102.4
Cattail Swamp	3	0.62	--	--	--	--	--	--
	7	1.87	5.9	1.0	52.1	10.2	25.0	95.1
	21	4.83	4.8	1.1	44.5	18.8	13.8	87.8
	35	15.28	3.7	0.4	45.0	15.1	18.9	97.8
	49	17.11	3.5	0.2	58.7	10.1	23.0	112.6

Table 6. Freundlich K and 1/n for the adsorption of glyphosate on a swamp sediment and four soils.

Soil type	K	1/n	Percent desorbed ^a
Ray silt	90	0.902	3.7
Spinks sandy loam	70	0.944	3.6
Drummer silty clay loam	62	0.951	5.3
Lintonia sandy loam	22	0.782	11.5
Cattail Swamp sediment	175	1.010	0.9

^a Maximum glyphosate desorbed from the four different equilibration concentrations.

Table 7. Distribution of radioactivity (% of recovered) in seven soil columns treated with [^{14}C]glyphosate and rapidly eluted with 20 inches of water.

Sampling depth (inches)	Soil type						
	Lintonia	Ray	Spinks	Leon	Drummer	Hilo	Molokai
0-2	33.4	24.5	72.1	21.2	80.0	99.5	98.6
2-4	25.3	24.3	24.6	19.8	14.3	0.2	0.9
4-6	17.3	18.0	1.8	15.5	2.4	0.2	0.1
6-8	10.4	14.5	0.4	15.4	0.8	0.1	0.3
8-10	4.8	6.8	0.2	10.4	0.4	0.0	0.0
10-12	2.3	2.4	0.1	6.7	0.3	0.0	0.0
12-14	0.8	1.4	0.1	4.1	0.2	0.0	--
14-16	0.4	0.7	0.1	2.4	0.1	0.0	--
16-18	0.2	0.3	0.1	1.9	0.3	0.0	--
18-20	0.1	0.1	0.0	0.8	0.1	0.0	--
20-22	0.1	0.1	0.0	0.3	0.1	--	--
22-24	0.1	0.1	0.0	0.3	0.1	--	--
24-26	0.1	0.1	0.2	0.2	0.0	--	--
26-28	0.1	0.1	0.0	0.1	0.1	0.0	--
28-30	0.1	0.1	0.1	0.1	0.0	0.0	--
Total recovered in soil column	95.6	93.4	99.9	99.0	99.1	100.0	99.9
Total recovered in leachate	4.4	6.6	0.1	1.0	0.9	0.0	0.1
Total recovered	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Percent of applied	78.7	90.5	95.5	99.9	89.0	98.7	101.7

Table 8. Distribution of radioactivity (% of recovered) in three soil columns treated with [^{14}C]glyphosate, incubated for 30 days, and eluted with 20 inches of water over a 45-day period.

Sampling depth (inches)	Soil type		
	Ray silt	Molokai clay	Hilo sandy clay loam
0-2	30.30	40.39	97.53
2-4	1.07	0.20	0.03
4-6	0.49	0.05	0.03
6-8	0.27	0.07	0.01
8-10	0.24	0.07	0.01
10-12	0.17	0.04	0.01
12-14	0.10	0.04	0.01
14-16	0.12	0.02	--
16-18	0.09	0.02	--
18-20	0.11	0.02	--
20-22	0.08	0.02	0.01
22-24	0.05	0.02	0.01
24-26	0.06	0.02	--
26-28	0.08	0.01	--
28-30	0.04	0.01	0.01
Total recovered in soil column	33.26	41.00	97.66
Total recovered in leachate	1.56	0.22	0.02
Total evolved as $^{14}\text{CO}_2$	65.18	58.78	2.32
Total recovered	100.00	100.00	100.00
Percent of applied	98.40	84.62	98.94

Table 9. Glyphosate and aminomethylphosphonic acid concentration (% of applied) in the leachate of soils treated with [^{14}C]glyphosate at 8 lb ai/A and eluted with 20 inches of water.

Soil	Glyphosate	Aminomethylphosphonic acid
Ray ^a	0.8	0.7
Hilo ^a	--	--
Molokai ^a	--	--
Ray	5.8	0.8
Lintonia	3.9	0.5
Drummer	0.6	0.3
Spinks	--	--
Leon	0.6	0.4
Hilo	--	--
Molokai	--	--

^a Incubated 30 days before being leached over a 45-day period.

Table 10. Distribution of radioactivity (% of extractable) between Glyphosate and aminomethylphosphonic acid in the top 2-cm segment of soil columns treated with [^{14}C]glyphosate, at 8 lb ai/A, and leached with 20 inches of water.

Soil	Radioactivity (% of applied)	% extracted	Aminomethyl- phosphonic acid	
			Glyphosate	(% of extractable)
Ray ^a	30.3	52.4	26	84
Hilo ^a	97.7	8.4	94	6
Molokaia ^a	34.1	47.0	22	78
Ray	234.5	72.3	76	24
Lintonia	33.4	78.9	80	20
Drummer	80.0	77.8	86	14
Spinks	72.1	95.7	90	10
Leon	21.2	99.1	93	7
Hilo	99.5	15.1	94	6
Molokai	98.6	50.3	86	14

^a Incubated 30 days before treatment; leaching period was 45 days.