

(TDR03B)

DATA EVALUATION RECORD

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4-26-85

CASE GS0178

GLYPHOSATE

STUDY 6

PM 25 06/16/83

CHEM 103601

Isopropylamine glyphosate

BRANCH EFB

DISC 30 TOPIC 050530

GUIDELINE 40 CFR 163.62-10b

FORMULATION 90 - FORMULATION NOT IDENTIFIED

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CONTENT CAT 01

Monsanto Co. 1975. Residue and metabolism studies in sugarcane and soils.
Compilation; unpublished study received July 1, 1976 under 6G1826; CDL:096972-B.

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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact Uses

This portion of the study is scientifically invalid because the test duration and the sampling protocol were inadequate to accurately assess the dissipation of glyphosate and the patterns of formation and decline of degradates in water. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not characterized and soil and sediment samples were not taken.



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Mobility - Leaching and Adsorption/Desorption

1. This portion of the study is scientifically valid.
2. [¹⁴C]Glyphosate (purity unspecified) at concentrations ranging from 0.21 to 50.1 ppm, was highly adsorbed to five soils with organic matter contents ranging from 2.40 to 15.50%. Adsorption of glyphosate ranged from 71% (Soil E, 2.4% organic matter, pH 7.29) to 99% (Soil C, 15.5% organic matter, pH 5.35).
3. This portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because complete soil characteristics were not reported, the study was not run in calcium ion solution, K_d values were not reported, desorption of glyphosate was not assessed, and the test substance was not completely characterized.

Metabolism - Aerobic Soil

This portion of the study is scientifically invalid because the sampling protocol was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the study was not run at a constant temperature, complete analytical methods were not reported, complete soil characteristics were not reported, and the test substance was not completely characterized.

Metabolism - Anaerobic Soil

This portion of the study is scientifically invalid because the sampling protocol was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the study was not run at a constant temperature, complete analytical methods were not reported, complete soil characteristics were not reported, and the test substance was not completely characterized.

MATERIALS AND METHODS:

Field Dissipation - Aquatic and Aquatic Impact Uses

Three irrigation ditches (100 ft x 10 ft; closed at one end and containing full stands of emerged weeds) were treated with glyphosate (Roundup, test substance uncharacterized, source unspecified) at 10 lb ai/A. After 24 hours, water was run into the ditches to a sufficient depth (5 to 8 inches) to induce runoff into irrigation lines.

Water samples were collected 25, 50, 75, and 100 feet along the ditch and at a point 50 feet along the irrigation lines. The samples were cleaned on ion exchange resin columns and fractionated by column chromatography. The appropriate eluate fractions containing glyphosate and aminomethylphosphonic acid were collected. The samples were evaporated, followed by dissolution in trifluoroacetic acid and methylation with

diazomethane. The methylated samples were analyzed by GLC, equipped with a flame photometric detector. The detection limit for glyphosate and aminomethylphosphonic acid was 0.0025 ppm. Recovery values ranged from 67 to 71% and 47 to 90% for glyphosate and aminomethylphosphonic acid, respectively.

Mobility - Leaching and Adsorption/Desorption

Samples (1.0-g) of five Hawaiian soils (Table 2) were treated with [^{14}C]glyphosate (specific activity 9.07 mCi/mM, purity and source unspecified) solution at 0.21, 0.845, 4.92, 9.96, 25.0, and 50.1 ppm. The soil solutions were shaken for three hours and centrifuged. Aliquots of the supernatant were analyzed for radioactivity using LSC.

Metabolism - Aerobic Soil

Experiment 1

Samples (5.0-g) of two soils (Table 3) were placed in flasks and treated with [^{14}C]glyphosate (specific activity 9.07 mCi/mM, purity and source unspecified) at ~10 ppm. Radioactivity evolved as $^{14}\text{CO}_2$ was trapped in ascarite by flushing the system with CO_2 -free air and quantified on a periodic basis (intervals and analytical methods not reported).

After 35 days of incubation, soil samples were extracted with water and 0.5 N ammonium hydroxide and the extracts were analyzed for total radioactivity by LSC. In addition, aliquots of the extracts were concentrated and spotted on TLC plates. The plates were developed either one dimensionally (using a solution of 1.2 g disodium EDTA: 100 ml 17 N ammonium hydroxide:475 ml water:350 ml 1-propanol:75 ml 1-butanol:2.5 l isobutyric acid) or two dimensionally (using a solution of 37.2 mg disodium EDTA:84 ml 90% aqueous phenol:1-ml glacial acetic acid:16 ml water; followed by the solvent described above) and autoradiographed. Radioactivity remaining in the extracted soil was quantified by combustion analysis.

Experiment 2

Samples (5.0-g) of five soils (Table 4) were placed in flasks and adjusted to ~0.33 bar moisture. Each flask was treated with [^{14}C]glyphosate (specific activity 1.87 mCi/mM, purity and source unspecified) at ~406 ppm. Radioactivity evolved as $^{14}\text{CO}_2$ was captured in ethanolamine:ethylene glycol monomethyl ether (1:2, v:v) trapping solution and quantified by LSC.

The soil samples were analyzed by extraction and LSC, total combustion, and TLC as described in Experiment 1.

Metabolism - Anaerobic Soil

Flasks from Experiment 1 (Metabolism - Aerobic Soil) were flushed with nitrogen gas to establish anaerobic conditions. Radioactivity evolved as $^{14}\text{CO}_2$ and in soil samples, taken at 35 days posttreatment, was analyzed as described in Experiment 1 (Metabolism - Aerobic Soil).

REPORTED RESULTS:

Field Dissipation - Aquatic and Aquatic Impact Uses

Irrigation ditch water, introduced and sampled one day after dry ditch glyphosate treatment at 10 lb ai/A contained a mean concentration of 0.58 ppm (Table 1). Glyphosate was detected in water samples taken from the irrigation lines at 0.0045 ppm (ditch #1) and 0.58 ppm (ditch #3). Aminomethylphosphonic acid was detected at concentrations up to 0.025 ppm in ditch water and at 0.083 ppm in one irrigation line water sample.

Mobility - Leaching and Adsorption/Desorption

[^{14}C]Glyphosate was highly adsorbed to all soils at all concentrations applied (Table 2). Soil E, with the lowest pH and organic matter content had the widest adsorption range of all soils (from 71% adsorbed at 50.1 ppm applied to 92% adsorbed at 0.21 ppm applied).

Metabolism - Aerobic Soil

Experiment 1

Radioactivity evolved as $^{14}\text{CO}_2$ and the radioactivity bound in the extractable and unextractable forms for the two soils are shown in Table 3. Of the radioactivity detected in the soil extracts, 100% was in the form of parent glyphosate for soil G, while in the soil F extracts, 13.3% of the extracted radioactivity was parent glyphosate and 86.7% was aminomethylphosphonic acid.

Experiment 2

Radioactivity evolved as $^{14}\text{CO}_2$ and the radioactivity bound in the extractable and unextractable forms for the five soils are shown in Table 4.

Metabolism - Anaerobic Soil

Radioactivity evolved as $^{14}\text{CO}_2$ and the radioactivity bound in the extractable and unextractable forms are shown in Table 5. All the radioactivity in soil G was identified as parent glyphosate; in soil F, 13.6% and 86.4% was identified as parent and aminomethylphosphonic acid, respectively.

DISCUSSION:

All Studies

The test substance was not completely characterized.

Field Dissipation - Aquatic and Aquatic Impact Uses

1. The test duration (one day) and the sampling protocol (one sampling interval) were inadequate to accurately assess the dissipation of glyphosate and the patterns of formation and decline of degradates in water.
2. The variation of glyphosate detected in three ditches treated at the same application rate (average concentration for ditch 1 was ~0.03 ppm, while the average concentration for ditches 3 and 4 was ~0.61 ppm and 0.85 ppm, respectively) was not explained.
3. The soil and sediments were not sampled.

Mobility - Leaching and Adsorption/Desorption

1. Complete soil characteristics, such as textural analysis and CEC, were not reported. Consequently, a textural class could not be assigned to individual soils.
2. Values of soil/water (K_d) relationships were not reported.
3. The study was not run in calcium ion solution.
4. Detection limits and recovery values were not reported.
5. Desorption of glyphosate was not addressed.

Metabolism - Aerobic and Anaerobic Soil

1. Complete soil characteristics, such as CEC and textural analysis, were not reported. Consequently, a textural class could not be assigned to the individual soils.
2. The sampling protocol (one sampling interval) was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil.

4. It was not reported whether the flasks were maintained at a constant temperature.
5. Detection limits and recovery values were not reported.

Table 1. Glyphosate and aminomethylphosphonic acid (ppm) detected in irrigation water from ditches treated at 10 lb ai/A.

	Sampling site				
	25	50	50 ^a	75	100
<u>Ditch #1</u>					
Glyphosate	0.0028	0.033	0.045	0.051	-- ^b
AMPA ^c	ND ^d	ND	ND	0.0042	--
<u>Ditch #2</u>					
Glyphosate	0.07	0.18	--	0.52 ^e	1.02 ^e
AMPA	ND	ND	--	0.0049 ^e	0.0093 ^e
<u>Ditch #3</u>					
Glyphosate	0.57	0.64 ^f	0.58	0.89	1.52
AMPA	0.0089	0.0085 ^f	0.0083	0.012	0.025

^a Samples were taken from the 50-foot point of the irrigation lines.

^b Not sampled.

^c Aminomethylphosphonic acid.

^d Not detected; detection limit was 0.0025 ppm.

^e Values represent the average of three samples.

^f Values represent the average of two samples.

Table 2. [^{14}C]Glyphosate adsorbed (% of applied) to five soils^a treated at various concentrations and shaken for three hours.

	Concentration (ppm)					
	0.21	0.84	4.92	9.96	25.0	50.1
Soil A	98	98	98	98	98	98
Soil B	99	98	98	98	98	98
Soil C	99	98	98	98	98	98
Soil D	96	94	93	92	92	93
Soil E	92	86	80	78	72	71

^a Soil A had 5.75% organic matter with a 5.5 pH; Soil B had 10.25% organic matter with a 5.49 pH; Soil C had 15.50% organic matter with a 5.35 pH; Soil D had 2.85% organic matter with a 7.0 pH; Soil E had 2.4% organic matter with a 7.29 pH; no other soil characteristics were reported.

Table 3. Radioactivity detected (% of applied) in two soils^a treated with [¹⁴C]glyphosate at 10.0 ppm and aerobically incubated for 35 days.

	Extractable		Nonextractable	¹⁴ C ₀₂	Total recovered
	Water	Ammonium hydroxide			
Soil F	~0.07	79.9	28.2	1.01	109.2
Soil G	1.37	18.2	5.7	60.9	86.2

^a Soil F contained 7.0% organic matter and had a pH of 7.2; Soil G had 14.0% organic matter with a pH of 5.0; no other soil characteristics were reported.

Table 4. Radioactivity detected (% of applied) in five soils^a treated with [¹⁴C]glyphosate at ~406 ppm and aerobically incubated for 60 days.

	Extractable		Nonextractable	¹⁴ C ₂	Total recovered
	Water	Ammonium hydroxide			
Soil H	4.2	19.2	5.7	65.6	94.7
Soil I	1.8	10.1	8.2	57.7	77.8
Soil J	1.5	40.8	20	35.3	98.2
Soil K	0.02	50.7	33.2	1.2	85.1
Soil L	0.03	66.8	32.1	0.8	99.7

^a Soil H had 4.6% organic matter with a 6.9 pH; Soil I had 8.9% organic matter with a 7.0 pH; Soil J had 14.15% organic matter with a 6.1 pH; Soil K had 14.25% organic matter with a 5.7 pH; Soil L had 17.50% organic matter with a 5.5 pH; no other soil characteristics were reported.

Table 5. Radioactivity detected (% of applied) in two soils^a treated with [¹⁴C]glyphosate at 10.0 ppm and anaerobically incubated for 35 days.

	Extractable		Nonextractable	¹⁴ C ₀₂	Total recovered
	Water	Ammonium hydroxide			
Soil F	~0.03	82.9	23.0	1.75	107.7
Soil G	1.67	22.3	7.3	30.9	62.2

^a Soil F contained 7.0% organic matter with a pH of 7.2; Soil G had 14.0% organic matter with a pH of 5.0; no other soil characteristics were reported.