Dissipation of Glyphosate and Aminomethylphosphonic Acid in North American Forests

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Residues of glyphosate (*N*-phosphonomethylglycine) and its metabolite aminomethylphosphonic acid (AMPA) were followed on three forested sites in Oregon, Michigan, and Georgia. Eight-hectare residual stands of low-quality hardwoods were treated with 4.12 kg/ha glyphosate ae applied aerially in late summer. Residues were highest in upper crown foliage. Overstory reduced exposure of understory vegetation and streams. Residues in streams were close to the detection limit or undetectable in 3–14 days. Residues in soils were highest where cover was sparse and where litter was removed. No residues were detectable in soil 409 days after treatment; movement below 15 cm was negligible. AMPA appeared at low levels in all degrading matrices, including sediments, soon after deposition of glyphosate. In pond sediments, both glyphosate and AMPA remained bound and inactive. Residue concentrations in foliage, water, and soil were below levels known to be biologically active in nontarget fauna.

Keywords: *Glyphosate; aminomethylphosphonic acid (AMPA); water contamination; soil residues; litter; foliage; sediments; degradation*

INTRODUCTION

Glyphosate is being used increasingly in temperate regions worldwide to manage vegetation selectively and restore productivity and species composition in cutover forest lands (Lund-Hoie, 1984). Forest conditions warranting herbicide use are widespread in the northeastern United States and Canada (Newton et al., 1987), in the Pacific Northwest, including British Columbia (Walstad et al., 1987; Ackhurst, 1989), and in the southeastern United States (Gjerstad and Barber, 1987) and have been reported in other temperate countries.

Continued registration in the United States of any product regulated by agencies such as the Environmental Protection Agency requires that information about residues be obtained in environments approximating those where the product is used. This paper is a synopsis of experiments in the three major forest regions of the United States where glyphosate is used. It expands and complements data on residues in vegetation, water and soils in the Pacific Northwest (Newton et al., 1984) to elucidate further how environment can influence residue behavior. We also analyze the dissipation of aminomethylphosphonic acid (AMPA), the only known metabolite of glyphosate in which the initial product is recognizable, in the same environments.

We explore the following specific questions: (1) What are residue levels in overstory foliage, understory vegetation, litter, soil, and water immediately after applications of maximum rates of glyphosate to a forest at normal times of application? (2) At what rates do residues dissipate during the 12–14 months following application? (3) What is the pattern of AMPA accumulation and dissipation during the dissipation of glyphosate? (4) Does residue behavior differ in the major climatic zones of the forested United States?

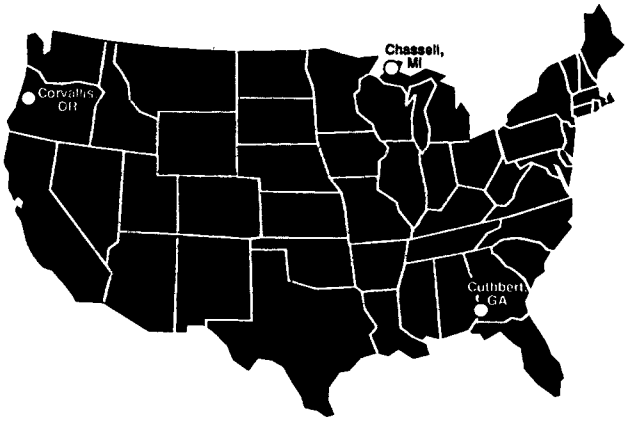

Figure 1. Locations of field sites.

PROCEDURES

Site Descriptions and Application Procedures. These experiments were conducted simultaneously at three forested sites representing distinct degradation environments in the United States (Figure 1): near Corvallis, OR, in the foothills of the Oregon Coast Range; near Chassell, MI, not far from Lake Superior; and near Cuthbert, GA, close to the southwest corner of that state. Conifers had previously occupied or been prominent in management at each site. On all sites, chemical site preparation for establishment of conifers would be routine, but no glyphosate had yet been applied.

The Oregon site is characterized by mild, rainy winters with no sustained freezing temperatures and by warm summers with negligible rainfall. Microbial activity should be maximal in the moist fall and spring; at other times, soils are generally too cool or too dry. The Michigan site has severe winters, with heavy snow cover, and moderate, wet summers. Microbial activity is probably high during the summers but slow or negligible from October through April. The Georgia site has cool, moist winters with infrequent frosts and warm, humid summers with moderately heavy rainfall. Microbial activity is probably very high in spring, summer, and fall, and moderate in winter.

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Table 1. Cumulative Precipitation during 409 Days following Application of Glyphosate at Three Study Sites

DAT[a]	cumulative rainfall (mm) at Oregon	Michigan	Georgia
0	0	0	0
1	0	0	0
3	0	0	0.5
7	0	8	2.5
14	0	51	6
28–30	1	94	6
58–63	1	197	18
120–122	371	297	226
180–187	617	562	496
321–346	951	810	944
398–409	972	1010	1180

[a] Dates of initial application: Oregon, Aug 28, 1987; Michigan, Aug 31, 1987; Georgia, Sept 16, 1987.

Annual precipitation at the Oregon and Georgia sites is about 1250 mm; the Michigan site receives about 1000 mm, of which perhaps a third is as snow. In both Michigan and Georgia, rainfall has a weak summer maximum, whereas Oregon has a Mediterranean climate with a strong winter maximum. The actual cumulative rainfall on the sites during the 14 months of the study (Table 1) was very close to average for each region.

At each site, glyphosate was applied by helicopter at 4.12 kg/ha ae (the maximum registered rate, about 3 times normal usage), delivered in 92 L total of aqueous spray/ha. No surfactant was present in the glyphosate product or the water-based spray mixture. The lots of glyphosate used for this study ranged from 42.1 to 42.6% glyphosate ae. This mixture was applied to 8.0-ha forest sites supporting degraded stands, largely of residual deciduous vegetation and mixed herbs after clearcut or partial conifer harvest. Application was done by helicopter in the early morning under conditions of still air, relative humidity between 50 and 80%, and temperatures between 10 and 15 °C.

On each site, streams and ponds were included in the spray pattern; each swath was applied directly to the stream or pond and perpendicular to it. All streams were small. The Oregon and Georgia streams each drained less than 100 ha and during the summer flowed at less than 120 L/min. The Michigan stream was perhaps one-sixth the size of the other two. The Oregon stream had a nearly complete canopy of red alder and bigleaf maple 25 m tall. The Georgia stream was covered with an estimated 50% leaf cover, mostly less than 10 m tall. The Michigan stream had relatively little cover, since it was a year-old clearcut with cover less than 1 m tall. Ponds in Oregon and Georgia were true beaver ponds; the pond in Michigan was dammed to simulate a beaver pond. All ponds were less than 1 m deep and 50 m^2 in area and had sediments of highly organic silt.

Sample Collection. Residues on vegetation were sampled at eight stations in each site. At each station, overstory foliage and understory herbage were collected 1–9 days before application of glyphosate; within 10 h of application; and 1, 3, 7, 14, 28, 63, 122, 180, 346 and 409 days after treatment.

Overstory foliage was sampled from the top layer of tree crowns. In Oregon, all crown samples were taken from the tops of bigleaf maple trees 22–28 m tall. Collections were made by cutting a major branch from the upper crown and collecting foliage after the branch fell to the ground. Sampling from crowns in Georgia also required some climbing; Michigan samples were all accessible from the ground. Each sample collected was approximately 1.4 kg and included the foliage pooled from two sampling stations. Thus, there were four samples from the upper crowns on each date at each location. Understory herbage and surface litter (nearly all recently dropped leaves) were sampled similarly in the vicinity of each sampling station on each sampling date to provide an assessment of potential forage residues and litter insect exposures. All vegetation was collected in 8-L polyethylene-lined cloth bags by persons wearing rubber gloves. Gloves were discarded after each sample to prevent cross-contamination. As soon as the sample was collected, the bag was closed and sealed with a drawstring.

At four of the stations, soils were sampled at depths of 0–15 and 15–30 cm, both where litter had been removed to expose soil and where litter remained and was included in the soil sample. Litter on the latter soils was removed before samples were prepared for extraction. As with vegetation, all personnel who handled tubes wore rubber gloves that were discarded after each sample. Soil samples were taken with a contamination-free sampler in which a metal tube (22-mm inside diameter) with a cutting edge at the bottom was inserted 30 cm into the soil. A removable 30-cm plexiglass tube within the sampler received the soil sample as the sampler was inserted into the ground. The tube was then removed from the sampler; labeled with an inventory number; capped with color-coded caps on the upper and lower ends; placed in a plastic-lined cloth bag, which was sealed as soon as the last tube was collected; and labeled with complete site, date, and sample description. Each sample was later divided in half, giving samples representing the 0–15- and 15–30-cm zones. The sampler holding the plexiglass tube was washed with acetone between samples. The four 0–15- and 15–30-cm samples for each site × time interval were pooled to form a composite sample.

Litter samples were collected within a 10-m radius of sample points. Litter consisted of handfuls of loose leaf litter; twigs >1 cm were excluded. Nearly all litter material was leaf-fall from the hardwoods. Samples were placed in 8-L plastic-lined cloth bags, with collections from two sample stations bulked together in the field to make up about 1.5 kg. Bags were sealed after the second-station collections. Sampling intervals for vegetation, litter, and soils were the same.

Soils at each location were taken within short distances from streams and hence were highly variable. At the Oregon site, they were basalt-derived clay loams to coarse sands. In Michigan and Georgia, they were sandy loams but ranged from sands to loams. They varied at each location in organic content. Those with >10% organic carbon often compacted. In such samples, the depth strata were divided in half for analysis, rather than at 15 cm.

Water was sampled from ponds and streams when other samples were taken until 30 days after treatment. Samples from streams were taken at the downstream edge of the spray projects.

As much as possible, pond sediments were collected so that the sediments would have been under water continuously since treatment. However, elevated water at one sampling in Michigan may have led to sampling of soil that had been exposed at the time of spraying. Sediment was sampled at the same intervals as vegetation and soils by collecting by hand (with rubber glove) from the top 15 cm of sediment. Sediment was placed in a 500-mL plastic bottle, which was placed in an 8-L sealed bag. Water was collected in 1-L plastic bottles with unlined screw caps.

All samples were frozen the same day as collected. Each time samples were moved, an inventory sheet describing the samples, collection methods, and date shipped accompanied them; copies remained with the shipper and addressee. All samples were shipped by air freight to Monsanto Analytical Laboratories, St. Louis, MO, and then to A&S Environmental Testing Laboratories, Reading, PA, where all samples were analyzed. All shipments were in dry ice in insulated boxes. All were delivered to the laboratory frozen and received in good condition.

Analytical Procedures. Before analysis, the four samples from each soil depth and the vegetation and litter for each stratum within each site were bulked so that each analysis provided a site mean. General analytical procedures are outlined by Cowell et al. (1986) and Oppenhuizen and Cowell (1991); a synopsis follows. Foliage, litter, and sediments were determined on a wet weight basis, soils on the basis of dry weight, and water as absolute concentration. Subsamples used for analysis of foliage, litter, sediments, and soils were 13.33, 10, 20, and 20 g, respectively.

Sample Preparation. All vegetation samples were ground frozen in a Hobart chopper or Waring blender with dry ice

added. Samples were stored overnight in a cold room to allow the carbon dioxide to evaporate. The ground vegetation was mixed, subsampled, and extracted by partition extraction, as follows. Ground subsample material was blended for 1 min with 50 mL of chloroform and 150 mL of 0.1 N HCl in a 1-qt Waring blender, transferred to a 250-mL polypropylene centrifuge bottle, and centrifuged at 11 000 rpm for 20 min in a Sorvall refrigerated centrifuge. One hundred twenty-five milliliters of aqueous phase, equivalent to 62.5% of the sample material, was decanted and diluted to a final volume of approximately 400 mL (16-oz bottle, filled to the top). The pH at this point was approximately 2 ± 0.4. The sample (of which 7 mL was eventually used) was then ready for application to a Chelex column.

Soil and sediment samples were analyzed similarly to vegetation and litter except for the extraction procedure. Extraction was done with 0.5 N KOH, rather than HCl/$CHCl_3$, and in a mechanical shaker instead of a blender. Other slight modifications were that 100 mL (instead of 125 mL) was decanted for dilution, and the Chelex column was rinsed with 200 mL of 0.1 N HCl, instead of 100 mL of 0.2 N HCl. Michigan sediment samples were extracted twice with 75 mL of 0.5 N KOH. Soil samples were dried before extraction, and all determinations were based on dry weight.

Water samples (100 mL) were adjusted to pH 2.0 ± 0.4 with 6 N HCl. The samples were then filtered through glass-fiber paper before application to a Chelex column.

Chelex Column Chromatography. Deionized water (7–8 mL) was added to a column (2.2 × 22 cm) plugged with glass wool, followed by 15 mL of Chelex 100 resin in the Fe(III) form. Samples were then transferred to the column and eluted at 6–8 mL/min. After each sample had been eluted, the walls of the column were rinsed with approximately 50 mL of deionized water. The resin bed was rinsed once with 100 mL of 0.2 N HCl as rapidly as possible (stopcock wide open). All of these volumes were discarded.

The glyphosate and AMPA were eluted with 6 N HCl, added so as to disturb the resin bed as little as possible. The stopcock was adjusted to elute the column slowly, approximately 4 mL/min or less. Aliquots of 3 and 4 mL were added sequentially (7 mL total); the effluent was discarded. The next three 5-mL aliquots of 6 N HCl were collected, mixed with 10 mL of concentrated HCl, and applied to an anion-exchange column.

Anion-Exchange Column Chromatography. Deionized water (7–8 mL) and approximately 7 mL of AG 1X8 anion-exchange resin were added to a column (1.7 × 22 cm) plugged with glass wool. The resin bed was adjusted to 5 cm and the column rinsed three times with 6 N HCl (5 mL) shortly before the sample was applied. The samples were applied with the stopcock wide open. The sample container was then rinsed with 2 mL of 6 N HCl, which was applied to the column; just as the last of the sample entered the column, 8 mL of 6 N HCl was applied. Samples were collected in 250-mL recovery flasks.

Samples were concentrated to dryness on a rotary-film evaporator by slowly increasing the temperature of the water bath from 20 to 60 °C. The final traces of moisture were removed with a stream of dry nitrogen if necessary. The residue was dissolved in 2.0 mL of deionized water and filtered through a 0.45-μm membrane filter before application to an HPLC *o*-phthalaldehyde (OPA) postcolumn reactor system.

HPLC OPA Postcolumn Reactor System. Glyphosate and AMPA were analyzed with an HPLC interfaced with a detector specific for compounds that produce a fluorophore upon reaction with OPA and mercaptoethanol (MERC). Glyphosate was oxidized with calcium hypochlorite, and the product (glycine) and AMPA were coupled with the OPA–MERC. The resulting fluorophores were detected by a fluorometer with excitation at 340 nm; emission was measured at 455 nm.

The HPLC was equipped with a precolumn RP-18 Spheri-10, 3.6 cm × 4.6 mm i.d., guard column system (Brownlee Labs, Inc.). The late-eluting peaks found in most of the samples were diverted to waste through a two-column switching device consisting of an air-actuated six-port valve controlled by a digital valve sequence programmer, hooked up to short (10 cm) and long (30 cm) Aminex A-9 columns. When the last peak of interest had entered the 30-cm analytical column, the valve was switched to waste before the late-eluting peaks could enter the analytical column.

Table 2. Analytical Recoveries (Mean ± SD) of Glyphosate and AMPA from Fortified Samples of Matrices

matrix	location	*N*	recovery (% of fortified) glyphosate	AMPA
pond water	MI, OR, GA[a]	11	97.08 ± 4.31	94.72 ± 2.87
stream water	MI, OR, GA[a]	9	105.10 ± 5.87	100.23 ± 4.13
pond sediment	OR	5	79.59 ± 6.96	76.28 ± 9.24
	MI	8	51.05 ± 7.33	59.52 ± 10.29
	GA	6	93.66 ± 6.48	85.05 ± 3.41
stream sediment	OR	6	89.80 ± 6.34	86.34 ± 5.40
	MI	6	79.64 ± 4.07	79.12 ± 5.21
	GA	6	89.96 ± 5.77	85.80 ± 5.66
soil	OR	17	72.89 ± 7.20	72.06 ± 6.03
	MI	32	73.77 ± 7.79	70.99 ± 7.48
	GA	32	91.41 ± 10.50	89.60 ± 9.06
foliage, overstory	MI, OR, GA	14	92.77 ± 7.15[b]	86.73 ± 8.58
herbaceous vegetation	MI, OR, GA	18	94.09 ± 6.11	90.67 ± 7.82
leaf litter	MI, OR, GA	22	84.36 ± 6.49	86.59 ± 5.41

[a] Water samples from all locations were combined for recovery studies. [b] Thirteen recoveries were averaged for this value.

Recovery Validation. Recoveries of glyphosate and AMPA varied among soil types and among locations (Table 2). Reliability of the analytical procedures for each matrix and component is expressed in Table 2 on the basis of residue recovery from the known fortification samples, which were fortified along with each analytical set. Fortification of water ranged from 0.001 to −25.0 mg/L; fortification was extended to 2000 mg/kg in some plant matrices because of the high residues present.

RESULTS

Vegetation and Litter. Upper canopy foliage was the dominant receptor at each location and, therefore, was the most consistent medium for comparing deposition among the three sites. The initial concentrations of glyphosate in this layer (Table 3; Figure 2) represent what actually landed at the sampling stations, although glyphosate was applied at an equal rate at the three sites. They therefore represent the initial condition for dissipation at the specific vegetation and soil sites; water and pond samples, however, reflect the integration of the total application pattern through which they flowed.

Because dissipation of residues in both overstory and herbaceous vegetation started from very different levels at the three sites, proportional decreases in concentrations, as given in Table 3, are more useful to compare than absolute rates. On all sites, overstory residues dissipated rapidly, but patterns in early samplings (Table 3; Figure 2) were not identical. By 30 days after treatment (DAT), 96% of the residues had dissipated at all sites. A tall cover of large hardwoods with approximately 70% cover at the Oregon site intercepted much of the spray, reducing concentrations of glyphosate on ground vegetation and in litter; glyphosate residues in litter increased dramatically as the desiccated overstory foliage fell on the ground. Figure 2 illustrates the absolute decreases in residues on upper canopy foliage, herbaceous vegetation, and leaf litter as

Table 3. Proportional Decrease (Percent Loss; 100% = No Detectable Glyphosate) in Glyphosate Concentration in Upper Foliage[a] and Herbaceous Vegetation[b] during 13 Months following Aerial Application at 4.12 kg/ha at Study Sites in Oregon, Michigan, and Georgia

	upper foliage			herbaceous vegetation		
DAT	Oregon	Michigan	Georgia	Oregon	Michigan	Georgia
0	0	0	0	0	0	0
1	19.6	84.8	79.4	−5.4	70.0	70.6
3	9.1	86.0	89.0	17.7	79.2	59.7
7	20.9	96.9	55.6	−77.8	85.0	53.3
14	77.2	98.5	93.4	−30.9	95.1	86.8
28−30	97.3	99.6	96.1	25.1	96.4	94.8
56−63	98.0	—[c]	99.3	38.0	—[c]	99.2
120−122	—[c]	—[c]	—[c]	99.4	—[c]	—[c]
180−187	—[c]	—[c]	—[c]	98.0	—[c]	—[c]
321−346	—[c]	99.98	100.0	99.4	100.0	100.0
398−409	—[c]	—[c]	—[c]	—[c]	—[c]	—[c]

[a] Initial concentrations were 652 mg/kg in Oregon, 1273 mg/kg in Michigan, and 760 mg/kg in Georgia. [b] Initial concentrations were 27 mg/kg in Oregon, 629 mg/kg in Michigan, and 360 mg/kg in Georgia. [c] Samples were not collected if there were no leaves on the upper canopy because of either defoliation or winter conditions in deciduous forests.

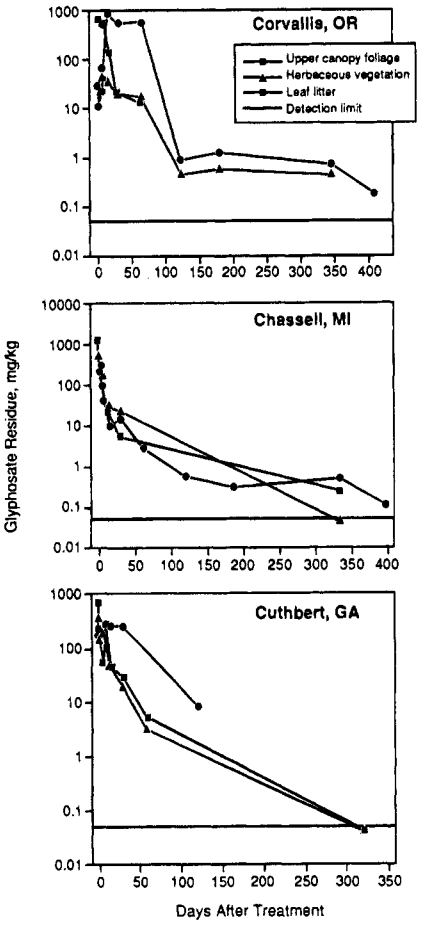

Figure 2. Glyphosate residues in leaf matrices, fresh weight basis. Values below the detection limit do not signify presence.

long as foliage samples could be collected. Deciduous species, which lose foliage in the fall, did not retain sufficient material for sampling after leaf-fall.

In litter, concentrations of glyphosate began to decrease rapidly, but leaf-fall 3−14 days after treatment caused a major increase in leaf litter residues on both sites (Oregon and Georgia) where there was a substantial overstory (Table 4; Figure 2). Concentrations peaked 14−63 days after treatment, except where significant rain occurred. This reflects some continued

Table 4. Concentrations (Milligrams per Kilogram, Wet Weight Basis) of Glyphosate in Forest Litter during 13 Months after Aerial Application of Glyphosate at 4.12 kg/ha at Three Study Sites

DAT	Oregon	Michigan	Georgia
0	28.98	322.4	254.69
1	11.28	210.18	182.88
3	22.35	369.47	54.16
7	63.98	39.78	194.70
14	791.25	10.02	256.51
28−30	557.40	13.85	262.11
56−63	590.07	2.81	94.74
120−122	0.86	0.56	8.41
180−187	1.21	0.30	—[a]
321−346	0.71	0.47	—[a]
398−409	0.19	0.11	—[a]

[a] Bulldozing precluded collection of these samples.

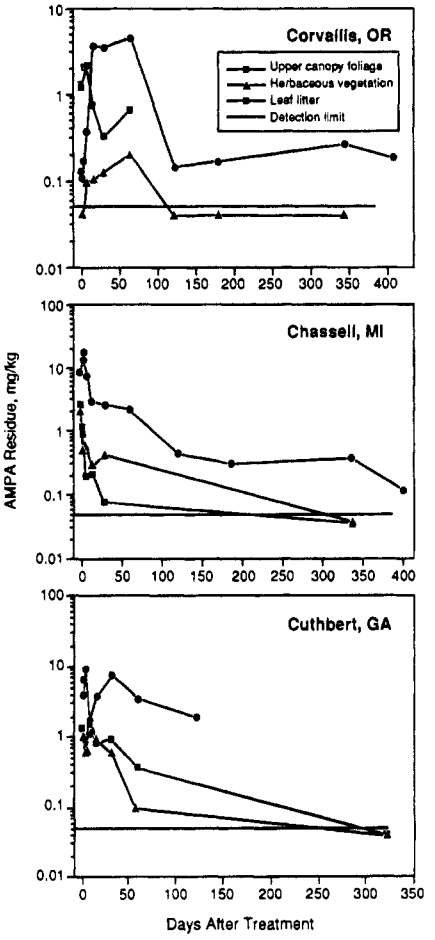

Figure 3. AMPA residues in leaf matrices, fresh weight basis. Values below the detection limit do not signify presence.

deposition while degradation was occurring. Whenever precipitation was >25 mm, residue levels dropped to below 10 mg/kg, suggesting either a high rate of washing to the soil from the litter or the induction of very rapid degradation, but the residues did not appear in covered soils. At the Oregon and Georgia sites, concentrations remained near their peaks until the first rainfall of over 25 mm. At the Michigan site, only 8 mm of rainfall was required to reduce concentrations by nearly 90% between 3 and 7 DAT.

Concentrations of AMPA remained low in foliage and litter samples (Figure 3). AMPA residues were ≤1% of glyphosate residues in all samples containing 50 mg/kg glyphosate or more. As glyphosate decreased, AMPA residues remained substantially lower than those of glyphosate until both were below detection limits (<0.05

Table 5. Residues (Milligrams per Kilogram, Dry Weight Basis) of Glyphosate and AMPA in the Top 15 cm of Exposed and Litter-Covered Soil during 13 Months after Aerial Application of Glyphosate at 4.12 kg/ha to Forest Sites in Oregon, Michigan, and Georgia

	Oregon		Michigan		Georgia	
DAT	glyphosate	AMPA	glyphosate	AMPA	glyphosate	AMPA
			Exposed Soils			
0	<0.05[a]	<0.05	1.96	0.06	0.36	<0.05
1	<0.05	<0.05	0.09	<0.05	1.02	<0.05
3	<0.05	<0.05	2.71	0.19	1.87	<0.05
7	<0.05	<0.05	1.12	0.15	1.87	<0.05
14	0.07	<0.05	4.67	0.17	0.69	0.06
28–30	0.11	<0.05	1.08	0.36	1.29	<0.05
56–63	0.12	<0.05	0.35	0.27	0.26	0.15
120–122	0.15	0.19	0.17	0.14	0.14	0.14
180–187	0.15	0.31	0.49	0.51	<0.05	0.09
321–346	0.08	0.32	0.50	0.28	<0.05	<0.05
398–409	<0.05	<0.05	<0.05	<0.05	<0.05	0.18
			Litter-Covered Soil			
0	<0.05	<0.05	<0.05	0.06	<0.05	<0.05
1	<0.05	<0.05	0.34	0.09	<0.05	<0.05
3	<0.05	0.07	0.62	0.15	<0.05	<0.05
7	<0.05	<0.05	1.40	0.32	<0.05	<0.05
14	<0.05	<0.05	0.30	0.23	<0.05	<0.05
28–30	<0.07	<0.05	0.14	0.68	0.4	<0.05
56–63	0.07	<0.05	0.22	0.30	0.07	0.12
120–122	<0.05	<0.05	<0.05	0.37	0.13	0.20
180–187	<0.05	0.10	0.19	0.56	0.09	0.23
321–346	0.06	0.14	<0.05	0.12	<0.05	<0.05
398–409	<0.05	0.07	0.10	0.12	<0.05	0.13

[a] Not detected at the detection limit of 0.05 mg/kg.

mg/kg). In all instances, AMPA residues remained below 0.88 mg/kg in all vegetation in which glyphosate had degraded to less than 50 mg/kg. Thus, AMPA did not tend to accumulate as an intermediate degradation product but rather was a transient step in complete degradation.

Soil. Glyphosate residues were generally higher in exposed soils than in those where the litter was undisturbed (litter was removed before analysis), despite the apparent lack of retention by litter noted above. Litter did intercept residues (Table 5); hence, residue losses in litter must have been attributable to degradation rather than passage to soil. With the exception of one higher level, glyphosate in exposed soil peaked at or below the amount expected for this application, confined to the top 15 cm of soil with bulk density of about 1.2–1.3. (Maximum concentration in soil with density of 1.3, no interception, and 100% efficiency of application deposition would be 2.75 mg/kg soil.) At the Oregon site, so much glyphosate was intercepted by the canopy that soil levels were never more than about 10% of those found in the other sites; degradation apparently occurred before deposits moved into the soil. Vertical mobility was not observed despite a range of soils and intensity of precipitation. Among all sites and all dates, glyphosate (0.11 mg/kg) was detectable in only one sample (Oregon, exposed soil, 346 DAT) in the 15–30-cm depth zone.

AMPA concentrations in soil tended to be initially lower than those of glyphosate; peaks tended to follow glyphosate maxima by 6 months or more (Table 5). AMPA eventually equaled or exceeded glyphosate concentrations. At the Oregon site, AMPA was obviously generated by rapid conversion of the glyphosate deposited over an extended period through litter-fall. If AMPA is an intermediate for all glyphosate degradation, AMPA at the other sites was never enough to account

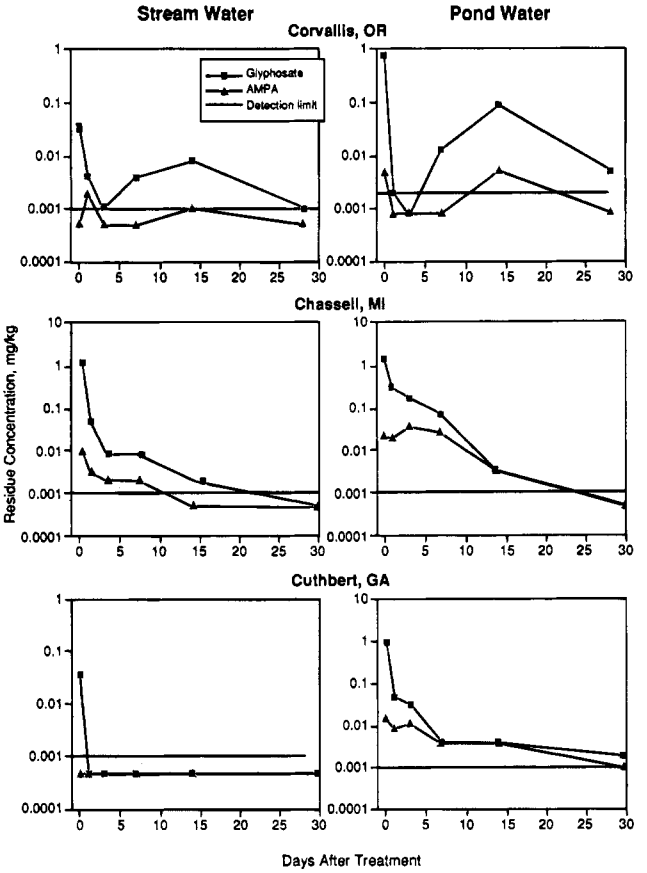

Figure 4. Glyphosate and AMPA residues in aquatic systems on three sites during the 30 days after treatment with glyphosate over water at 4.1 kg/ha. Values below the detection limit do not signify presence.

for the rate of disappearance of the highest residue levels unless (a) the mean residence time for AMPA was much less at those sites or (b) AMPA was somehow bound to soils in Oregon in a temporarily inaccessible form.

Water and Sediments in Streams and Ponds. Previous sampling of water in forest streams showed that residues would be below detection limits within 30 days (Newton et al., 1984; Feng et al., 1989). Water in both streams and ponds on all sites fulfilled that expectation (Figure 4), with the exceptions that 0.001 mg/L was detected in the Oregon stream on day 30 and 0.002 mg/L was detected in pond water at that time in Oregon and Georgia. Both sites had had substantial litter drop in the ponds and upstream channels. The observation in stream water occurred after the concentration dropped below the detection level 3 DAT; glyphosate in the stream was presumably put there by overstory litter drop. Apart from the initial deposits of 0.031 and 0.035 mg/L, all glyphosate concentrations were <0.008 mg/L in Oregon and Georgia, where there was leaf cover over the water (Figure 4). The Michigan site, where the water was fully exposed, had the highest levels of glyphosate, beginning at 1.237 mg/L, decreasing to 0.048 mg/L by day 1, and remaining below 0.008 mg/L for the rest of the sampling period. Only in Georgia was pond water substantially different (greater) in concentration from stream water.

AMPA in water was only marginally detectable in the Oregon stream and undetectable in Georgia. In Michigan, AMPA peaked at 0.010 mg/L on the date of application; all other determinations were ≤0.003 mg/L (Figure 4). As observed in the other matrices except

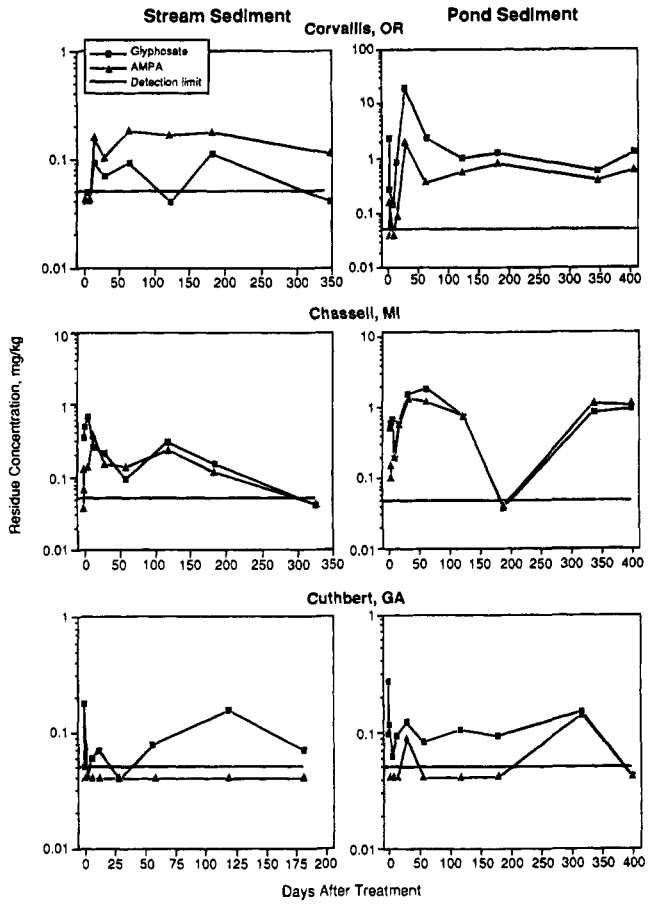

Figure 5. Glyphosate and AMPA residues in stream and pond sediments, wet weight basis. Values below the detection limit do not signify presence.

soil, AMPA generally was a small fraction of glyphosate levels. Concentrations of AMPA in pond water also decreased very quickly. The Oregon and Georgia ponds received very different initial levels of glyphosate deposit because of the differing levels of sheltering vegetation; both ponds decreased to 5% or less of initial contamination within 1 day. AMPA in the Michigan pond, which was initially contaminated with 1.678 mg/L glyphosate, was 0.018 mg/L AMPA at day 1, 0.035 mg/L at day 3, 0.025 mg/L at day 7, 0.003 mg/L at day 14, and nondetectable at 30 DAT.

Glyphosate residues in stream sediments were very low but more persistent than in water (Figure 5). Residues in Oregon sediments were not detectable (<0.050 mg/kg) until after those in water had decreased to nondetectable levels and then been recontaminated by leaf-fall. Residues never exceeded 0.11 mg/kg. Glyphosate levels in Georgia were comparable, peaking at day 1 at 0.18 mg/kg and fluctuating between the detection limit and 0.15 mg/kg for the remainder of the study. In keeping with initial residue levels in water, residues in sediment samples from Michigan peaked at the highest level (0.69 mg/kg) at 3 DAT and decreased slowly for the remainder of the study, becoming nondetectable by 335 DAT.

AMPA in all sediments had an extended time to accumulate because of the immobile supply of glyphosate. Oregon and Michigan stream sediments showed detectable residues by day 1 in Michigan and by day 14 in Oregon. AMPA was still detectable in Oregon at 346 DAT (the last sample) but was not detectable in Michigan at that date. Georgia stream sediments never had detectable AMPA.

Glyphosate was much higher in pond sediments than in stream sediments in Oregon and Michigan but not in Georgia (Figure 5). Oregon and Michigan peaked at 2.36 and 1.92 mg/kg, respectively; one apparently anomalous sample in Oregon contained 19.42 mg/kg. Georgia pond sediments peaked at 0.26 mg/kg on day 1 and then remained at 0.14 mg/kg or less for the remainder of the study with no clear trend. AMPA peaked in Oregon and Michigan at over 1.3 mg/kg and then continued, at detectable levels but in no clear pattern, for the rest of the study.

DISCUSSION

The patterns observed in Oregon in this study largely corroborated previous studies of glyphosate residues in the Pacific Northwest, including British Columbia (Newton et al., 1984; Feng and Thompson, 1989; Feng et al., 1989). Glyphosate disappeared rapidly in water, overstory foliage, and litter, and penetration of glyphosate below the surface soil was negligible. Substantial interception by the upper layers of canopy prevented most of the potential deposition in understory, litter, or soil. Much of this was later transferred to litter, sometimes reaching higher concentrations than average overstory concentrations (presumably because the heaviest deposits caused early leaf-fall).

Residue levels tended to be highest in upper foliage layers on the Michigan and Georgia sites as well. However, the lower level of crown development in Georgia and the near absence of tall vegetation in Michigan were reflected in much higher residues in herbage, litter, and soil surface layers; these higher residues were not reflected in movement below 15 cm of soil, despite heavy rains. Deposition on upper crown foliage was similar to that recorded by Feng and Thompson (1989) for salmonberry but more than they or Newton et al. (1984) observed in red alder. Presumably interregional differences in initial deposits are attributable to the structure of the forests treated rather than geographical parameters. The proportional decreases in glyphosate residues over time were very close to those reported by Feng and Thompson (1989) for overstory foliage. The most rapid decreases in overstory residues at all sites were associated with high humidity. The rain was too light to have caused appreciable washing and therefore is regarded as associated with humidity levels, which increase microbial degradation or possibly metabolic degradation or export.

None of the sites received appreciable rain for the first 3 days. Thus, we are confident that washable losses were negligible and that decreases observed on foliage are the result of degradation and/or export to stems. Little wilting occurred to decrease water content. Rain, and possibly resulting microbial activity, appeared to be the largest contributing factor in decreasing residues in litter, apart from increasing water content. One would expect that rain would have a similar effect on overstory foliage, as is the case in Oregon and Michigan, but residues declined rapidly to less than 5% of initial levels in Oregon and Georgia despite the absence of significant rainfall. We have no explanation for this anomaly, other than the possibility that absorption and export from foliage vary among species (Lund-Hoie, 1979), leading to differences in observed residues. We also observed some minor transfer from overstory to understory in Oregon in the absence of rain. Presum-

ably, this resulted from fine particles from the overstory being intercepted by understory vegetation, which was mostly swordfern, a species with rather rough leaf texture.

Litter residues are expressed in terms of wet weight. As shown in Table 4 and 1, litter became wet after an initial period of dryness during which change was minor. With the advent of rain, concentration decreased sharply, whether from dilution as litter absorbed water, leaching, or decomposition. We were unable to segregate decomposition from dilution until the next dry season, when residues had all but disappeared. By 4 months after treatment, Oregon and Michigan litters were below 0.2% of their original concentrations, despite late-season fall of heavily contaminated overstory foliage. In Georgia, residues at 120 days were about 3% of those 3 months before. Even if water content was 300% of dry weight (a likely value during winter) and 50% soon after application, total net residues at 120 days were about 0.5% of day 1 residues in Oregon and Michigan and 10% in Georgia, where little rain had fallen.

Whereas leaching would be a logical explanation of the movement of glyphosate residues out of the organic litter, our soil data do not demonstrate receipt of such deposits where litter was undisturbed, with the exception of a partial transfer in the earliest rains in Michigan. The very low residues in covered soils in Oregon and Georgia suggest that the litter layer may be a very efficient decomposition sink for glyphosate residues, dislodgeable only by heavy precipitation soon after application.

Immobility of glyphosate and AMPA in soils was remarkable. Forest soils contain many voids from root channels, worm holes, and burrows. Frequently, the 30-cm sample had only 15 cm of material in it, indicating the low density of the top 30 cm. Nevertheless, segregating the top half of this column from the deeper zone left virtually all residues in the top portion. We consider it highly likely that nearly all of the residues were bound very close to the surface.

AMPA residues demonstrated two moderately distinct patterns with respect to those of the parent glyphosate. In well-aerated substrates, including vegetation and litter, water, and, in Georgia, soils and sediments (i.e., all but pond sediments), AMPA behaved like a transient intermediate in degradation. Initial deposits of glyphosate were followed by a rise in AMPA, which then paralleled the status of glyphosate in the same substrate, finally trailing glyphosate until disappearance. Thus, AMPA dissipated at a rate limited by the presence of its precursor glyphosate, and concentrations of AMPA remained generally a small percentage of the concentration of glyphosate.

Residues of AMPA and glyphosate were more persistent in pond sediments and soils of the northern sites. The appearance of AMPA is *prima facie* evidence that degradation began, but the cessation of change after the first month or two indicates a gross change in status of both compounds. In all aqueous systems, including streams with gravel bottoms, there was a very strong tendency to resist leaching or diffusion into fresh water, despite marked temperature fluctuations and large variations in flow. Once glyphosate entered these sediments, there was an initial conversion to AMPA; availability of either compound for microbial or other dislodgment apparently was reduced to extremely low levels. We interpret this persistence as evidence that both compounds were bound to organic or colloidal clay matrices that held them from either leaching or biological degradation, as reported also by Preston and Trofymow (1989). We regard this as evidence of complete sequestering out of reach of any biological entity.

The soil was the only medium in which it was possible to express residues in terms of per-hectare initial applications, minus dissipation. A concentration of 2.75 mg/kg would be present if 4.12 kg/ha were applied to bare soil with a density of 1.3 g/cm^3. All sites showed increases after application. One observation in Michigan (the site with least cover) exceeded the application level 2 weeks after treatment (4.67 mg/kg). By 120 DAT, the soil was the repository for nearly all remaining residues for all layers, yet residues were down to <4% of all initial deposits. The rise of AMPA in winter months suggests that AMPA may complex with some portion of the soil matrix during cold weather, dissipating completely when warm weather returns.

One observation, in winter pond sediment concentrations from Michigan, was anomalous. The entire area was covered by snow, and the pond level was high. The levels of glyphosate and AMPA were very similar to those nearby in soil; we therefore assume that the soil taken to be sediment had not been under water at the time of treatment. The similarity of observations before and after the winter samples is evidence that the sample does not represent logical change, and our interpretation is that that data point should be ignored in the assessment of degradation in the winter.

It may be argued that the spot sampling in this study does not give full acknowledgment to local heterogeneity of residue deposit. If there had been wild fluctuation within patterns observed, this would have been a concern. However, the anomalous observations were few, and the total number of determinations was very large. Thus, the means and the patterns in which they expressed themselves are undoubtedly reliable indicators of actual residue occurrence and dissipation.

Overall, the evidence from this and other studies indicates that glyphosate and its metabolite behave with reasonable similarity over a wide range of environments. Although conditions of application may differ (e.g., open or closed forest cover, rate of application), those conditions are consistently related to observed concentrations in various ecosystem strata as attenuated by periods of high humidity and temperatures favorable for microbial activity. Most importantly, glyphosate and AMPA residues are depleted or virtually inactivated to levels below any known herbicidal activity within a month of application. Moreover, previous evidence (Newton et al., 1984; Chapman, 1989; Holtby and Baillie, 1989a,b; Kreutzweiser and Kingsbury, 1989; Scrivener and Carruthers, 1989) indicates strongly that neither the terrestrial fauna nor the aquatic fauna shows direct toxic responses to glyphosate at any of the concentrations we found. We therefore conclude that the use of glyphosate to achieve a particular forest management objective poses no measurable toxic hazard in the long or short run, regardless of region of use.

CONCLUSIONS

In a complex forest ecosystem, glyphosate dissipates rapidly through a combination of dilution, translocation, and biodegradation. When all sample systems are examined together, a general and rapid dissipation of glyphosate is observed:

1. Water from both flowing streams and slow-flowing ponds shows rapid dissipation of applied herbicide through dilution and binding to bottom soil sediments, with an observed half-life of 10 h or less for direct inputs.

2. Residues in sediments in slow-flowing ponds from Michigan or Oregon appear to have the lowest rate of dissipation, presumably because of the cooler climate and lower microbial activity. They appear to be very tightly bound and of no biological significance because of their nonavailability.

3. In the stratified forest, there are many instances of a recharge phenomenon resembling, in a sense, multiple applications of herbicide to the various matrixes—for example, leaves or dust falling from trees into ponds or on the litter. Field half-life calculations are seldom applicable for this reason, as well as because of varying environments.

4. Glyphosate binds tightly to the soil, where it dissipates rapidly in place.

5. Foliage residues are highest of all matrixes initially but decline rapidly. Residues in the leaf litter show a dramatic rise at 2 weeks because of the dropping leaves. Moist conditions favor very rapid degradation of glyphosate in organic litter. The degradation rate in organic matter appears to follow humidity fluctuations in the presence of favorable temperature.

6. Regardless of forest region, patterns of use in worst-case situations result in residues below known thresholds of toxic hazard to nontarget species.

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