Gaughan, L. C.; Casida, J. E. *J. Agric. Food Chem.* **1978**, *26*, 525.
Helmuth, D. W.; Ghiasuddin, S. M.; Soderlund, D. M. *J. Agric. Food Chem.* **1983**, *31*, 1127.
Khan, S. U.; Hamilton, H. A. *J. Agric. Food Chem.* **1980**, *28*, 126.
Ohkawa, H.; Nambu, K.; Miyamoto, J. *J. Pestic. Sci.* **1980**, *5*, 215.
Roberts, T. R. In "Progress in Pesticide Biochemistry"; Hutsou, D. H.; Roberts, T. R., Eds.; Wiley: London, 1981; Vol. 1, Chapter 3.
Roberts, T. R.; Standen, M. E. *Pestic. Sci.* **1981**, *12*, 185.
Ruzo, L. O.; Casida, J. E. *J. Agric. Food Chem.* **1979**, *27*, 572.
Saleh, M. A.; Marei, A. E. M.; Casida, J. E. *J.* Agric. *Food Chem.* **1980**, *28*, 592.
Unai, T.; Casida, J. E. *J. Agric. Food Chem.* **1977**, *25*, 979.

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Fate of Glyphosate in an Oregon Forest Ecosystem

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Glyphosate herbicide residues and metabolites were evaluated in forest brush field ecosystems in the Oregon Coast Range aerially treated with 3.3 kg/ha glyphosate. Deposits were recorded at various canopy depths to determine interception and residues in foliage, litter, soil, streamwater, sediments, and wildlife for the following 55 days. The half-life of glyphosate ranged from 10.4 to 26.6 days in foliage and litter and twice as long in soil. The treated stream peaked at 0.27 mg/L and decreased rapidly; concentrations were higher in sediment than in water and persisted longer. Coho salmon fingerlings did not accumulate detectable amounts. Exposure of mammalian herbivores, carnivores, and omnivores and retention of herbicide seemed to vary with food preference; however, all species had visceral and body contents at or below observed levels in ground cover and litter, indicating that glyphosate will not accumulate in higher trophic levels. (Aminomethyl)phosphonic acid was found at low concentrations but degraded rapidly. *N*-Nitrosoglyphosate was nondetectable.

Glyphosate herbicide is used in two predominant ways for managing forest vegetation (Newton and Knight, 1981). It is aerially applied (1) at rates of 1.7–3.3 kg/ha to remove herbs, shrubs, and hardwoods to prepare sites for planting conifers and (2) at rates of 0.82–1.24 kg/ha to selectively control competing vegetation once conifers are established. Environmental behavior of the chemical is presumed to be the same for both uses.

This paper reports the findings of an investigation on the distribution and fate of glyphosate aerially applied at the maximum registered-use rate to two hardwood communities in the Oregon Coast Range. Specific study objectives were to determine (1) glyphosate deposits in various strata of forest vegetation after aerial application and its persistence in these strata, in litter, and in soil, (2) glyphosate concentrations in streamwater, sediments, and fish after direct application to open streams, (3) glyphosate exposure and retention levels in various forest mammals, and (4) occurrence and persistence of (aminomethyl)-phosphonic acid, the major identifiable metabolite of glyphosate, and of *N*-nitrosoglyphosate, a trace impurity in glyphosate.

EXPERIMENTAL SECTION

Primary Study Site. The first site selected (primary site) was an 8-ha unit, roughly rectangular (about 200 × 400 m), about 12 km west of Summit, OR, in the Oregon Coast Range (Figure 1a). A small perennial stream flows through the site lengthwise. At the time of spraying, the flow rate was estimated at about 50 L/min, probably the lowest flow rate for the year.

Within the site are two large, shallow, beaver ponds. The terrain is moderately dissected, varying in elevation about 50 m. Bedrock is deeply weathered, horizontally stratified, Tyee sandstone. Soils are mostly of the Slickrock series, a very deep, loamy, forest soil of residual and colluvial origin that is common to the area. Soil pH is 4.0–4.7 and organic matter content approximately 3.8–5.2%. Soils of this type are highly productive for Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco], and the site was a typical one for conversion to conifers.

The climate in the area is characterized by mild summers and winters. Rainfall is estimated at about 230 cm annually, 87% of which occurs between Oct 1 and April 30 (Johnsgard, 1963).

Originally covered by Douglas fir, the site was burned by wildfire in the 1850s and later occupied by Douglas fir intermingled with red alder (*Alnus rubra* Bong.) and numerous small deciduous hardwood and shrubs. The salable conifers were removed in about 1955, leaving a deciduous stand ranging in age from 20+ to over 100 years. This stand is dominated by red alder and bitter cherry (*Prunus emarginata* Dougl. ex Eaton) and has an understory comprising two major shrub species, vine maple (*Acer circinatum* Pursh.) and salmonberry (*Rubus spectabilix* Pursh.), and one abundant fern, the swordfern [*Polystichum munitum* (Kaulf.) Presl.]. Younger hardwoods averaged about 22 m in height, with scattered older alder as tall as 35 m.

Pretreatment Sampling. Before herbicide treatment, samples of each type of material were collected as controls to ensure an adequate background basis against which treated samples could be compared. Samples were taken of vegetation (primarily leaves), of soil that was both covered (with litter) and uncovered (litter removed) at 0–7.5 cm, and of litter. Streamwater was sampled on the downstream edge of the site, where 300 coho salmon fin-

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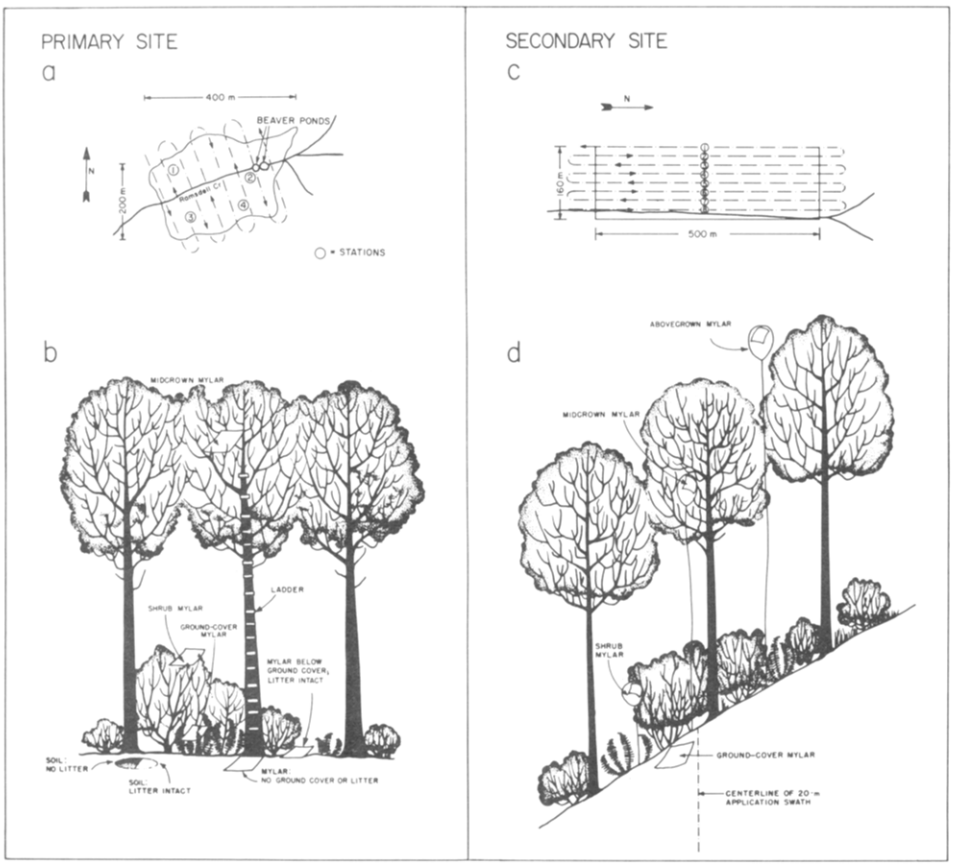

Figure 1. Primary and secondary study sites, showing (a, c) field layout and spray pattern (dashed line) and (b, d) sampling points within each sampling station.

gerlings [*Oncorhynchus kisutch* (Walbaum)] were released to provide an integrated measure of herbicide exposure over time; samples of stream sediment to the 5-cm depth also were collected. Various terrestrial animals, including herbivorous voles (*Microtus* spp.), omnivorous deermice [*Peromyscus maniculatus* (Wagner)], and carnivorous shrews (*Sorex* spp.), were live-trapped. Each animal was identified as to sex and dissected; the weights of internal organs (viscera) and total nonvisceral body were determined. Viscera were packed separately from the remainder of each body for analysis.

Soil arthropods could not be collected in sufficient quantity for analysis at a detection limit of 0.05 mg/kg.

Four sampling stations were chosen for determining herbicide interception patterns of the forest canopy and floor. At each station, mylar sheets (225 cm^2) were placed on the ground, at the top of the ground-cover layer, at the top of the shrub layer, and in the midcrowns of overstory hardwoods (Figure 1b); these sheets, assumed to be estimators of initial deposits at each sampling station, were used as an absolute measure of herbicide penetration. Foliage samples also were taken in the immediate vicinity of the mylar sheets at each sampling level.

Treatment Application. Two loads of glyphosate, 378 L each, were applied Sept 16, 1978, at a rate of 3.3 kg/ha (acid equivalent) by a Hiller 12E turbine-powered helicopter flying at approximately 72 kph (45 mph). Total spraying time was about 15 min. Drop size was not measured in these experiments. The assumption made was that the 45°-angled D-8 nozzles without spinners delivered a distribution of droplets similar to that from D-6 nozzles at 0°, reported by Yates et al (1983) to have a volume median diameter of 900+ μm.

Throughfall water collectors (with openings of about 0.25 m^2) were set out immediately after treatment.

Posttreatment Sampling. After treatment, aquatic and terrestrial samples were collected at each sampling station during the maximum time span over which residues were expected to be collected. Sampling was most frequent immediately after treatment to reflect the assumption that the most rapid decomposition was likely to occur when concentrations were at their highest level.

Terrestrial and animal samples were collected at the time of spraying (day 0) and on days 1, 3, 7, 14, 28, and 55 after treatment. Animals were live-trapped; seven or more animals were collected on each date such that total visceral weights were 26 g or more and whole-body weights 56 g or more. Samples included voles, deermice, shrews, chipmunks [*Eutamias townsendii* (Bachman)], red squirrels [*Tamiasciurus douglasii* (Bachman)], one short-tailed weasel [*Mustella erminea* (Linnaeus)], and one bushy-tailed woodrat [*Neotoma cinerea* (Ord)]; the composition of the catch varied between sampling dates because of the random nature of the trapping.

Liter samples of streamwater were collected at 5-min intervals for the first 90 min after spraying, at 10-min intervals for the next 100 min, and finally at 30-min intervals for the next 5.5 h; additional samples were collected on days 1, 2, 3, 6, 7, 14, 28, and 55. Water samples were collected at the downstream end of the site, where highest herbicide concentrations would be expected. Stream sediment was sampled at the same intervals as foliage. A composite of five bottom samples, mostly silty material, was collected to a depth of 5 cm, also at the downstream end. Coho salmon (10 samples, >10 fish/sample) were collected on each terrestrial sampling date.

All biological samples were frozen within 12 h of collection and were kept frozen until analyzed.

Secondary Study Site. A second site was treated a year later because anomalies appeared in the deposit data

Table I. Average Deposits ± 95% Confidence Intervals of Glyphosate and AMPA on Mylar Sheets and Foliage at Various Levels Immediately after Aerial Application of Glyphosate at 3.3 kg/ha[a,b]

	primary site			secondary site		
level	glyphosate foliage, mg/kg	AMPA foliage, mg/kg	glyphosate mylar, kg/ha	glyphosate foliage, mg/kg	AMPA foliage, mg/kg	glyphosate mylar, kg/ha
top of crown				489 ± 127	2.06 ± 0.25	1.46 ± 0.41
midcrown	84.0 ± 27.8 [5.0][c]	0.23 ± 0.06	0.35 ± 0.23	257 ± 161	0.81 ± 0.27	2.33 ± 0.82
shrub	89.0 ± 30.4 [3.8]	0.13 ± 0.08	0.086 ± 0.03	181 ± 53	0.87 ± 0.24	0.86 ± 0.67
ground cover	20.4 ± 5.3 [3.7]	0.07 ± 0.03	d	28.5 ± 11	0.08 ± 0.04	0.04 ± 0.02
litter	5.0 ± 3.1 [11.0]	0.14 ± 0.08	d			

[a] Glyphosate amount corrected for 90.8% recovery from sevel fortified samples; AMPA corrected for 71.2% recovery. [b] Each observation is a mean of four determinations for the primary site and 16 determinations for the secondary site. [c] Bracketed amounts were recorded after rainfall deposited washoff in litter, day 1. [d] Two of four samples destroyed or contaminated.

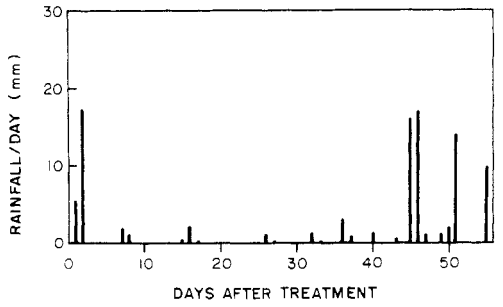

Figure 2. Rainfall pattern at the primary site for 55 days after treatment.

from the primary site. Initial observations on the first site indicated that spray penetration to midcrown was substantially less than the nominal rate released by the helicopter. Furthermore, a 21.0-mm rain within 36 h of application (Figure 2) raised the possibility that glyphosate washoff would bias estimates of interception and degradation. The purpose of the second site was specifically to obtain an improved estimate of deposition pattern.

The secondary site, near Eddyville, OR (10 km from the primary site), was similar in size (about 8 ha), dimensions (about 160 × 500 m), and layout (Figure 1c) to the primary site. The stream was nearly dry, being in a smaller watershed, but soils, topography, history, and vegetation were similar. Aerial application was at the same rate and volume of delivery, with the same pilot and equipment; however, samples were taken at eight, rather than four, stations, each centered on an application swath flown parallel to the stream.

In an attempt to improve our estimate of total herbicide targeting on this site, we collected samples at the top of and above the crown, in addition to the midcrown, shrub, and ground-cover layers; litter was not sampled.

For above-ground estimation, mylar sheets were attached to small, brightly colored, weather balloons filled with helium and tethered with fishing poles and light casting line (Figure 1d). Each station had a stack of three balloons, one above the crown (about 25 m above ground), one at midcrown, and one at the shrub-crown level. A mylar sheet was placed on the ground to determine spray penetration to the forest floor. The pilot was able to see the balloons on which he could center each swath, to ensure that each sample point received a nominal dose.

Foliage samples were collected near the mylar sheets at each balloon location to confirm the basic relation between glyphosate concentration in foliage and absolute amounts intercepted. Foliage was collected on day 0 and again on day 1, to increase sampling precision and determine if measurable amounts of degradation had occurred on day 0. No further samples were taken because the primary site had already provided degradation curves from known initial concentrations. The weakness of the primary site related to our ability to estimate deposition in the presence of rain but not to the kinetics of residual deposits. We therefore did not repeat the degradation phase of the experiment.

Sample Analysis. All samples were frozen immediately after collection, packed with dry ice in insulated containers, and shipped to Monsanto Analytical Laboratories (St. Louis, MO), where all except water were analyzed in duplicate. Some 475 determinations were run each for glyphosate, (aminomethyl)phosphonic acid (AMPA), the major metabolite of glyphosate (Hoagland, 1980; Rueppel et al., 1977), whose presence indicates that degradation is occurring, and *N*-nitrosoglyphosate (NNG), a trace impurity of glyphosate.

The analytical procedures are described by Arras et al. (1984), Beasley et al. (1984), and Daniels et al. (1984), though minor variations, primarily in the type of anion-exchange resin, were occasionally used to optimize recoveries or chromatographic separation. In essence, samples were extracted with deionized water and eluted through an anion-exchange resin: Duolite A101D (Diamond Shamrock) for soil, stream sediment, streamwater, and mammals; AG1-X8 (Bio-Rad) for foliar substrates and fish. The eluate was subjected to repeated evaporation to eliminate the ammonium bicarbonate used in the elution and the residue than applied (in 5 mL of water) to a cation-exchange column (Bio-Rad AG50W-X8) where further cleanup and separation of the three analytes (NNG, glyphosate, and AMPA in order of elution) were effected.

After evaporative concentration, residues of glyphosate and AMPA were determined by gas chromatography and flame photometric detection (GLC/FPD) in fish and by high-performance liquid chromatography with postcolumn ninhydrin detection (HPLC/PCR) in all other substrates. NNG residues were determined in all substrates by HPLC with a Griess reaction postcolumn detection system.

Recovery studies, including fortification with ^{14}C-labeled and cold glyphosate, AMPA, and NNG, were performed on each substrate in conjunction with analysis of each sample set. Control samples were collected on site before application, except for some rodents, which came from outside the study area. All were used in recovery–fortification studies. All residues reported have been corrected for their respective recovery values.

RESULTS

Initial Distribution of Chemical. Nearly all the applied chemical was intercepted by the vegetation, as evidenced by low deposits at ground level (Table I). The secondary site had a somewhat denser stand, hence more total interception. Most of the glyphosate was retained in the tree layers; midcrown foliage averaged 84.0 mg/kg on the primary site and 257 mg/kg on the secondary site. However, some contradictions were apparent on the sec-

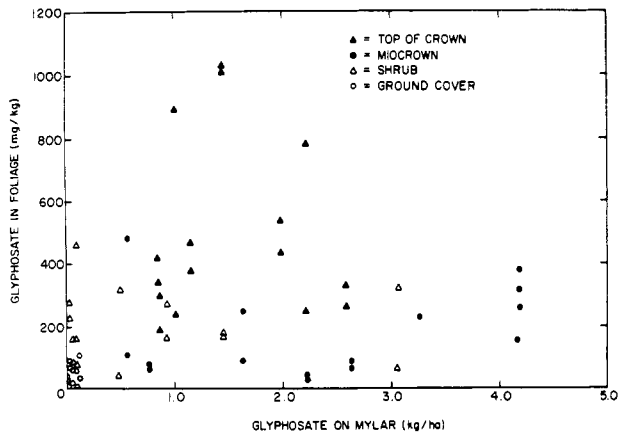

Figure 3. Relation between glyphosate residues on mylar sheets and concentrations on adjacent foliage for the secondary site.

ondary site. Midcrown mylar sheets on balloons showed average glyphosate deposits of 2.33 kg/ha and midcrown foliage 257 mg/kg; mylar sheets on balloons above the crown had deposits of 1.46 kg/ha, yet top-of-crown foliage contained 489 mg/kg (Table I). Thus, the targeting rate from a given aerial application was somewhat uncertain on both sites. In both situations, however, foliage samples were more consistent than mylar sheets, and these were used to estimate the degradation rate in serial samples collected at the same locations (Figure 3).

Foliage. Decreases in residues probably resulted largely from degradation or from washing by rain.

On the primary site, foliar glyphosate residues had been in place, dry, for 12 h before rain began. Residues markedly decreased after the rain, dropping from 84.0 to 4.3 mg/kg in the crown during the first 35 h. Residues then decreased from 4.3 to 1.7 mg/kg in 6 days and to 1.1 mg/kg in the next 7 days, based on sampling at three stations (the fourth sample was destroyed). The other sampling strata showed similar patterns. Half-lives ($t_{1/2}$) ranged from 10.4 to 26.6 days in the different foliage levels (Figure 4).

No rain fell on the secondary site, and no change in foliar concentrations was detectable during the first day.

AMPA concentration in most samples averaged 0.4% of initial glyphosate deposits during the first 24 h after application and declined on the following 14 days. NNG was not detected.

Throughfall, Litter, and Soil. All measurable precipitation on the primary site was sampled by throughfall collectors, one at each sampling station of 0.25 m^2. Yet these collectors picked up only 0.72 kg of glyphosate/ha, or about 25% of the nominal application. Throughfall samples showed that the day 1 rain contained 3.99 mg/L glyphosate and the rain between days 27 and 55 ≤0.002 mg/L. This transfer, about twice the rate reported by Norris et al. (1978) with 2,4,5-T, appears to have been the only movement of herbicide from crowns to soil, apart from that in litterfall.

Litter residues were higher at sampling stations where crown residues were lower. Mean residue levels of 5.0 mg/kg were observed on day 0. By day 1, these had doubled, presumably reflecting the rain-induced dripoff from crowns, but decreased rapidly thereafter to 0.2 mg/kg at day 55. Figure 4 illustrates breakdown in litter from the day-1 maximum.

Initial glyphosate deposits on soil varied widely. Exposed soil ranged from 0.2 to 1.24 mg/kg, litter-covered soil from 0.12 to 3.05 mg/kg. Concentrations peaked after the rain on the primary site and then decreased to a low on day 27 (Figure 5). Some stations noted an increase on

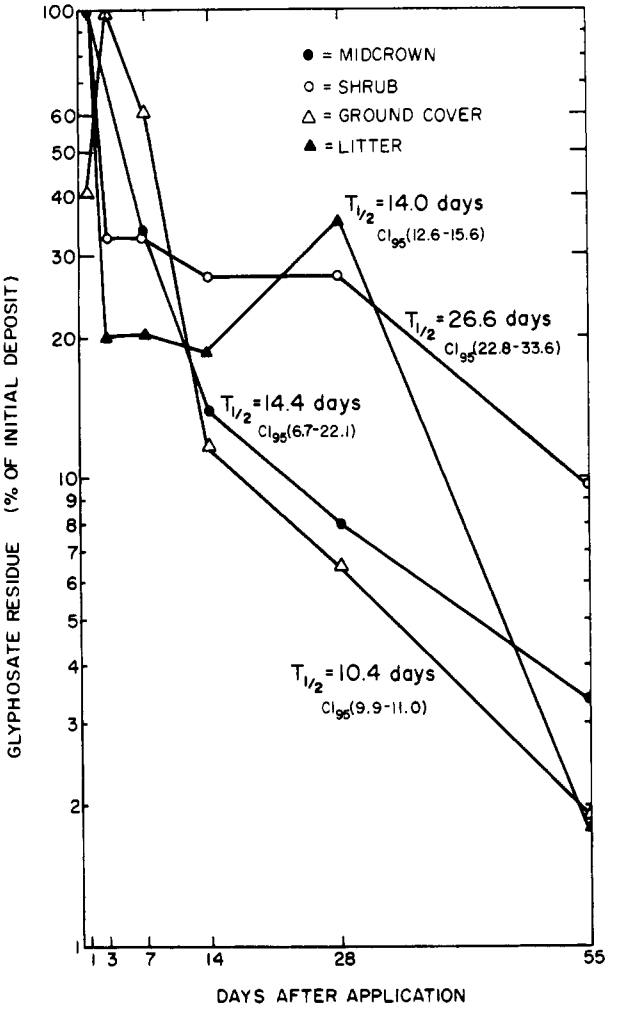

Figure 4. Glyphosate residues decaying over time in foliage and litter on the primary site; $t_{1/2}$ = half-life; CI_{95} (range) = 95% confidence interval (days).

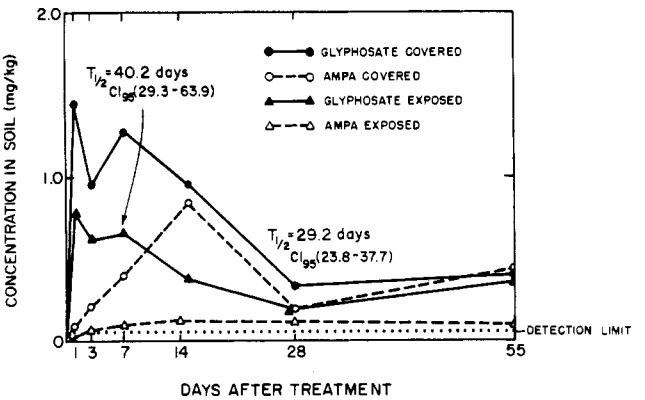

Figure 5. Glyphosate and AMPA concentrations in soil with and without litter cover on the primary site for 55 days after treatment; $t_{1/2}$ = half-life; CI_{95} (range) = 95% confidence interval (days).

day 55, which may have reflected litterfall (not throughfall) additions (Table I). On the basis of classical exponential decay functions, $t_{1/2}$ was 40.2 days for exposed soil and 29.2 days for litter-covered soil. Dependable confidence limits could not be placed around the AMPA decay rate because of (1) lack of fit to classical exponential decay functions and (2) possible additions from litter decay and throughfall.

We investigated using several other models for systematic mathematical evaluation of decay. All have some shortcomings, the principal one being that more than one process may be involved in degradation. There is evidence

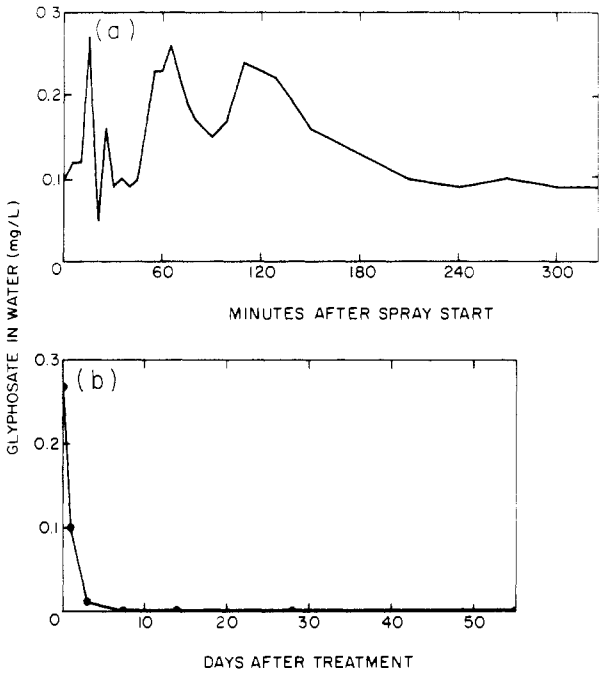

Figure 6. Glyphosate concentrations in streamwater (a) during the first 5.5 h and (b) for 55 days after treatment on the primary site.

that proportional breakdown proceeds more quickly in the first 2 weeks than later, when residues are very low and likely tied up with organic matter and soil colloids. Without definitive evidence for change in processes, we propose that empirical examination of the data points may be more meaningful than rate constants.

Streamwater and Stream Sediments. Patterns of water concentrations (Figure 6) are segregated to illustrate the well-defined changes that occurred during day 1 as a result of dilution and movement. Sampling during the first 2 h (Figure 6a) reflects the movement of concentration peaks downstream as the helicopter made individual swaths across the stream, beginning closest to the first sampling station (see Figure 1a). The smoother pattern later in the day reflects coalescing of peaks during the mixing of the streamwater from natural turbulence and the leveling effect of reservoirs in the two beaver ponds. The extremely smooth pattern late in the day indicates the precision of analysis and high degree of mixing in the streamwater. It is noteworthy that the concentration pattern shows no detection peaks later in the sampling period (Figure 6b), when water from leaching or surface runoff might be expected to carry detectable levels of glyphosate.

Sediments picked up residues much more slowly than water did but reached higher levels. Early stream-bottom samples reflected concentrations found in the streamwater, but later samples showed that even the minute water concentrations occurring below the detection limit may contain enough glyphosate to contribute to adsorption by sediments (Figure 7). By day 558 concentrations had returned to those of day 7 and were decreasing.

Wildlife. Separation of mammal parts into viscera and remainder provides a measure of current intake levels and of retention in body tissue associated with a previously measured exposure period. Segregation of data into food-preference groups permits inferences about the food-chain behavior of glyphosate and its metabolites in the field.

Glyphosate in the viscera of herbivores was roughly equal to or somewhat below concentrations found in litter and ground cover (Table II). These amounts remained above 1 mg/kg for the first 2 weeks after treatment, then decreased to near the minimum detection limit (0.10 mg/kg) by day 55. Glyphosate in the viscera of carnivores decreased rapidly to nondetectable levels by day 55. The omnivores had the highest initial glyphosate intake, but visceral levels decreased the most rapidly.

Concentrations in viscera were always higher than those in the remainder of animal bodies. No particular type of feeding behavior resulted in accumulation to higher levels

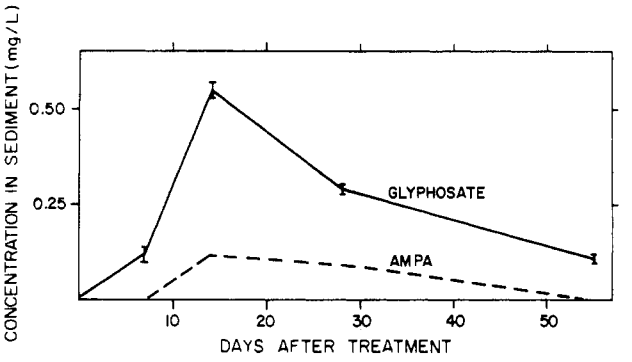

Figure 7. Glyphosate and AMPA concentrations in stream sediment on the primary site for 55 days after treatment. Bars show ranges for two composite samples per sampling date (days 7, 14, 28, and 55).

Table II. Glyphosate Residues Detected in Visceral and Body Parts of Mammals[a,b]

feed group	days since treatment	glyphosate detected, mg/kg viscera	glyphosate detected, mg/kg body
carnivores			
shrews	pretreatment	<0.10[c]	<0.10
		<0.10	<0.10
	0	1.69	0.41
	1	0.45	0.37
	3	0.19	0.14
	7	0.19	<0.10
	14	0.26	<0.10
	55	<0.10	<0.10
weasel	14	<0.10	<0.10
omnivores			
deermice	pretreatment	<0.10	0.11
		<0.10	<0.10
	0	5.08	0.35
	1	1.00	0.40
	3	0.37	<0.10
	7	0.33	0.15
	14	0.17	<0.10
	28	<0.10	<0.10
	55	<0.10	<0.10
herbivores			
woodrat	pretreatment	<0.10	<0.10
		<0.10	<0.10
squirrel	1	0.37	0.13
vole	3	1.42	0.25
vole	7	1.70	<0.10
vole	14	1.54	<0.10
chipmunk	28	0.44	0.23
chipmunk	55	0.12	<0.10

[a] Glyphosate detection limit was 0.10 mg/kg; AMPA found at 0.13 and <0.16 in two vole samples only, at a detection limit of 0.10 mg/kg; NNG not found at detection limit of 0.04 mg/kg in any samples except deermice viscera, for which the detection limit was 0.05 mg/kg. [b] Glyphosate amounts corrected for analytical recovery of 77.6% and 78.4% in carnivores, 75.0% and 54.5% in omnivores, and 68.4% and 60.0% in herbivores. [c] Each observation is the mean of duplicate analyses run on combined tissues of one to seven animals per sampling interval and animal group. Combining animal tissues precluded estimation of confidence limits.

than in food or in elevated concentrations in meat-eating animals. Furthermore, body concentrations became nondetectable while there was still detectable intake. The animals tested apparently have a sufficiently active elimination system to purge glyphosate several times faster than it can be absorbed at this level of exposure.

AMPA was detected at low levels (0.13 mg/kg at day 1, <0.16 mg/kg at day 14) only in the viscera of two vole samples. Failure to find AMPA in any animal tissue after day 14 suggests either that this compound is absorbed in negligible amounts or that it is formed slowly from glyphosate in wild animals but eliminated rapidly.

The visceral concentrations observed provide a crude approximation of daily intake, much dependent on assumptions. The smaller animals (mice, voles, and shrews) averaged about 30% viscera by weight, the larger mammals (chipmunks, weasel, and wood rats) about 16%. The smaller mammals might be expected to eat perhaps 25% of their body weights each day (shrews higher, voles perhaps lower), or 0.25/0.30 = 0.83 times their visceral weights. If visceral concentrations reflect glyphosate levels in food

$$I_{D_t} = (0.83)(0.3)G_t \quad (1)$$

where I_{D_t} = daily intake, mg/kg, on day t and G_t = glyphosate in viscera on day t. Thus, for example, a determination of 1.42 mg/kg in the viscera of a vole on day 3 (Table II) equates to a daily intake of 0.354 mg/kg on that day. The whole-body concentration of glyphosate, including viscera, would be

$$(1.42 \times 0.3) + (0.25 \times 0.70) = 0.601 \text{ mg/kg} \quad (2)$$

Consumption at this level would require a glyphosate concentration in forage (I_{D_t} divided by the food-intake fraction of body weight) of

$$0.601/0.25 = 2.4 \text{ mg/kg} \quad (3)$$

This is very close to observed levels in ground cover and litter; hence, these data are mutually supportive.

None of the 10 fish collections showed measurable, whole-body levels of glyphosate, AMPA, or NNG at a detection limit of 0.05 mg/kg, despite glyphosate concentrations in streamwater that remained in the detectable range for 3 days and a sink supply in sediments that remained detectable throughout the study.

Metabolites and Contaminants. AMPA was found consistently in foliage and litter and from days 1 to 7 in soil and sediments. One throughfall sample had an AMPA concentration of 0.02 mg/L; 2 of 41 streamwater samples showed traces of 0.01 and 0.05 mg/L. As glyphosate degraded in foliage, AMPA increased and then decreased quickly, indicating that it is a nonpersistent metabolite and a short-lived intermediate in the process of more complete breakdown. Marginally detectable amounts of AMPA were found in viscera, but not bodies, of voles during the peak intake period. Soil showed the presence of AMPA (but not NNG) as long as glyphosate was degrading. In general, the combined totals of glyphosate and AMPA decreased with time.

NNG was found near the detection limit of 0.02 ppm in one of the duplicates of three crown-foliage samples on day 1 and in one litter sample 28 days later. Such low levels may have resulted from formation of NNG in the evaporation procedures used in the glyphosate analysis (Rogers, 1983) and do not necessarily indicate a positive finding here.

DISCUSSION

Our data illustrate that most glyphosate reaches its target, then disappears rapidly in the moist deciduous forest, and does not move to water from soil. There is some transfer from crowns to soil, but the chemical appears to degrade in place at that point. Evidence for degradation is present in the appearance of AMPA (Figure 5).

We are uncertain as to the fate of the herbicide that disappeared from foliage during the rain on the primary site; no more than a fourth of the nominal application appeared in the throughfall water. If breakdown was responsible for the loss, recognizable metabolites or other products would have been expected to leach from leaves but did not; breakdown mechanisms and products in thin layers of water under daylight conditions may warrant investigation. Residues remaining on crown foliage after washoff degraded quickly or were translocated away from foliage. The declines in residues in all three foliage layers (midcrown, shrub, and ground cover) were consistent, though possibly indicating longer degradation times in the lower, shadier, shrub environment (Figure 4).

Foliage falls within 4–6 weeks of treatment in late summer, usually without brownout. Glyphosate obviously transfers to litter at that time. The litter, however, appears not to retain glyphosate from the initial deposit or from throughfall and probably transfers residues to soil, which seems augmented only after rainfall. This behavior contrasts with that of the phenoxy herbicides picloram and triclopyr; these are tied up in dead foliage and litter and give up relatively little to soil in the first month after treatment (Norris et al., 1978; Norris, 1981; Newton et al., 1982). Overall, after glyphosate reaches soil, degradation occurs at rates comparable to those reported in agricultural soils by Rueppel et al. (1977).

Measurements of initial deposits were plagued by variability. The quantity of leaf samples was large enough (≥1 kg) for low and high residue levels to be integrated into individual samples, thus reducing within-sample variability. Concentrations observed in such large foliage samples may be roughly coverted to deposition an area basis (kilograms per hectare) by estimating either leaf area or leaf biomass in a particular stratum.

Observed deposits in the forest canopy showed substantial interception by each foliage layer. Cumulative interception by shrub and crown layers ranged from 70 to 99% (95% average, with all but one station showing more than 93%); crowns of shrub and tree layers in this interception range were visually estimated as having leaf area indices (area of leaves/area of land surface) of about 2–7. This suggests that each incremental unit of leat area index can be expected to intercept spray approximately in the amount

$$I = 100(1 - \tfrac{1}{2}^L) \quad (4)$$

where I = interception, percent of amount applied, and L = leaf area index.

Newton et al. (1982) reported deposits in lower crowns of 2–3-m sprout clumps to be approximately $^1/_2$–$^1/_4$ of those observed in the tops of shrub tanoak [*Lithocarpus densiflorus* (Hook & Arm.) Rehd.] crowns; the spaced bushes covered 25–50% of the site and had leaf area indices of 1–3. Harrington (1982) found leaf area indices of 4–8 for tanoak within bushes. The data sets from these two studies approximate the above model (eq 4) with reasonable fit. Although much more precise validation would be desirable, this model provides a first approximation of canopy penetration—hence initial residues—at any canopy depth and density, presumably for any chemical applied as a moderately coarse spray.

The findings of adsorbed glyphosate in stream sediments are of interest to the interpretation of soil data. The ability of sediments to glean moderate amounts of glyphosate

from water when those sediments have much higher glyphosate concentrations than water corroborates reports (Hance, 1976; Hensley et al., 1978) that particulate matter has a high adsorptive capacity for glyphosate. We did not identify retention by sediment soil fraction; should retention in sediments be studied intensively, techniques for separating soil into organic and inorganic components would be needed. Nevertheless, the chemical showed a high affinity for solids even when clean water was running through in substantial excess. The finding of roughly comparable AMPA levels in sediments and upland soils suggest that residues are virtually immobile while being metabolized, even in the presence of substantial leaching opportunity.

The absence of glyphosate in streamwater when streamwater was carrying runoff from the treated site is further evidence of the strong adsorptive capacity of glyphosate on soil and organic detritus. Even in this maximum contamination situation, the very short distance between a heavily treated streambank and flowing water was adequate to protect water from measurable contamination under any normal field procedures other than direct application to the water surface.

Contamination of water by direct spray application was well within the range of safety to stream plants (Christy et al., 1981) and irrigated crops (Comes and Kelley, 1979). No damage to aquatic fauna has been reported at levels of formulated glyphosates below 1 mg/L (Folmar et al., 1979); glyphosate without its surfactant has a much larger safety margin. These data suggest no measurable risk from including forest streams within the spray pattern; there is no effect on water quality from devegetation resulting from the spraying until the following year, at which time dead shade will persist.

The glyphosate application had a pronounced impact on streamside deciduous shrubs, which were replaced by large herbs. The residual standing hardwoods continue to provide considerable shade during the interval in which conifers and seedling shrubs will develop into a protective cover. In an earlier, unpublished study, on a similar site and stream, we observed a 1 °C temperature rise when standing hardwoods were felled and burned, with a much greater degree of stream exposure than occurred here. We therefore anticipate negligible effect, overall, of glyphosate on forest water quality.

Animal exposure could be calculated from estimates of foliar and litter concentrations and verified by examination of visceral and body contents. Day-1 foliar concentrations varied substantially with foliage position in the canopy. Animals that feed on the lowest layers (ground cover or litter) always received concentrations of <30 mg of glyphosate/kg of diet, with an average of 0–11 mg/kg at various times. For example an herbivore that consumed 25% of its body weight per day would take in 0–2.75 mg/kg/day the first few days. If degradation follows the same pattern in animals as in the overstory (see Figure 4), as suggested by these and related data on phenoxy and pyridine herbicides by Newton et al. (1982), daily dosage would decrease steadily, dropping roughly by half every 2 weeks. Residues in animals may remain detectable for several months, but at a very small fraction of initial levels. Detectable intake by small mammals seems limited to the first month after treatment, and elimination systems maintain body levels low enough to suggest that the nonvisceral parts are passively a part of the elimination "pipeline".

A carnivore feeding on herbivores that consume glyphosate-contaminated forage is at less risk than the primary consumer, assuming equal ability to eliminate the chemical and its metabolites. If this model is the general case, and our data contain no exceptions, progression up the food chain will result in successively lower levels of glyphosate intake and body residue. Larger mammals such as deer or elk, which are used for human food, have lower relative visceral weights and would accumulate lower concentrations because of their proportionally lower level of food intake.

The acute and chronic toxicities of glyphosate were reviewed by Newton and Dost (1981), who observed that the acute oral median lethal dose for rabbits is about 3800 mg of glyphosate/kg of body weight and that chronic levels causing no observable effects on dogs and rats are 2000 mg/kg of diet for 90 days. Two-year studies, well beyond the limit of potential persistence of glyphosate, showed that dogs and rats were unaffected by levels of 100 and 300 mg/kg in feed, respectively, and that 300 mg/kg of feed did not affect reproduction during a three-generation test in rats. Forest herbivores are exposed to herbicides at a decreasing rate: the initial dosage—the maximum—decreases to nonmeasurable levels in a matter of several weeks. The typical exposure is therefore neither acute nor chronic but rather intermediate; such exposure, for an acutely toxic substance, would theoretically pose progressively less risk with time.

Maximum body residues of glyphosate were observed 0–3 days after treatment and decreased rapidly as glyphosate in the food supply decreased. After nonvisceral body contents equilibrated with visceral, body concentrations always remained a small fraction of those in viscera and even a smaller fraction of those in litter. Visceral concentrations never persisted for more than a day at >0.001 times the maximum concentrations in feed reported to cause no short-term effects.

Our observation of low exposures and rapid elimination of glyphosate, regardless of feeding preferences of the wild animals tested, is reassuring evidence that mammals, fish, and their food supplies are unlikely to be threatened by glyphosate. Furthermore, the residues at all points in the food chain are low and transient. Humans using game animals for food (a) would have to kill the animal within a few days of spraying for the residue to be detectable and (b) would encounter extremely low or negligible residues in muscle tissue, as suggested in earlier tests with other herbicides (Newton and Norris, 1968). We therefore conclude that the toxicological risk from forest use of glyphosate is probably zero for either wildlife or humans.

The mylar sheets were found to be poor indicators of deposits of aerially applied glyphosate, corroborating Conard's (1982) finding that sampling cards similar in size to our mylar sheets provided a high level of uncertainty. Newton et al. (1982) had better results using cylindrical (Gill) cups for comparing deposits of picloram, trichlopyr, and 2,4-D with tanoak foliage concentrations. We found no consistent relationship between deposits on mylar sheets and foliar concentrations and therefore cannot recommend sheets for quantitative evaluation of aerially applied herbicide.

Rates of degradation observed in foliage and soil corroborate the manufacturer's general statement, based on agricultural data, that glyphosate is broken down quickly (Monsanto Corp., 1980). Conditions of degradation here are likely to have been quite different from those encountered in agricultural studies, suggesting a relative insensitivity of glyphosate degradation to environmental influence and a tendency toward rapid disappearance from both simple and complex ecosystems.

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Registry No. Glyphosate, 1071-83-6; (aminomethyl)-phosphonic acid, 1066-51-9.

LITERATURE CITED

Arras, D. D.; Beasley, R. K.; Conkin, R. A.; Cowell, J. E.; Daniels, R. J.; Kramer, R. M.; Laver, R.; Horner, L. M.; Rogers, P. E.; Taylor, A., Corp., St. Louis, MO, unpublished results, 1984.

Beasley, R. K.; Cowell, J. E.; Daniels, R. J.; Kramer, R. M.; Rogers, P. E.; Lauer, R.; Horner, L. M.; Baszis, S. R., Monsanto Corp., St. Louis, MO, unpublished results, 1984.

Christy, S. L.; Karlander, E. P.; Parochette, J. V. *Weed Sci.* **1981**, 29 (1), 5–7.

Comes, R. D.; Kelley, A. D. *Weed Sci.* **1979**, 27 (6), 658–660.

Conard, S. G. "A preliminary study of the influence of environmental, phenology and application variables on the responses of major conifer and brush species to glyphosate. Final Report"; Department of Forest Science, Oregon State University: Corvallis, OR, 1982.

Daniels, R. J.; Horner, L. M.; Rogers, P. E.; Kramer, R. M.; Cowell, J. E.; Baszis, S. R., Monsanto Corp., St. Louis, MO, unpublished results, 1984.

Folmar, L. C.; Sanders, H. O. Julius, A. M. *Arch. Environ. Contam. Toxicol.* **1979**, *8* (3), 269–279.

Hance, R. J. *Pestic. Sci.* **1976**, *7*, 363–366.

Harrington, T. M. S. Thesis, Oregon State University, Corvallis, OR, 1982.

Hensley, D. L.; Beverman, D. S. N.; Carpenter, P. L. *Weed Res.* **1978**, *18*, 287–291.

Hoagland, R. E. *Weed Sci.* **1980**, *28*, 393–400.

Johnsgard, G. A. "Temperature and the water balance for Oregon weather stations"; Oregon State University Agriculture Experiment Station: Corvallis, OR, 1963; Special Report 150.

Monsanto Corp. "Roundup herbicide bulletin No. 1—Toxicology and environmental review"; Monsanto Agricultural Products Company: St. Louis, MO, 1980.

Newton, M.; Allen, A.; White, D. E.; Loper, B.; Kelpsas, B. R.; Roberts, F. "Deposits and degradation of herbicides in sclerophyll brushfield foliage"; Western Society of Weed Science: Denver, CO, 1982; Abstracts.

Newton, M.; Dost, F. N. "Environmental effects of vegetation management practices on DNR forest lands"; State of Washington, Department of Natural *Resources*: Olympia, WA, 1981.

Newton, M.; Knight, F. B. "Handbook of weed and insect control chemicals for forest resource managers"; Timer Press: Beaverton, OR, 1981.

Newton, M.; Norris, L. A. *Proc. West. Soc. Weed Sci.* **1968**, *22*.

Norris, L. A. *Residue Rev.* **1981**, *80*, 65–135.

Norris, L. A.; Montgomery, M. L.; Troendle, C. A.; Kochenderfer, J. M. "2,4,5-T persistence in a West Virginia watershed"; Weed Science Society of America: Dallas, TX, 1978; Abstracts.

Rogers, P. E., Monsanto Corp., St. Louis, MO, personal communication, 1983.

Rueppel, M. L.; Brightwell, B. B.; Schaefer, J.; Marvel, J. T. *J. Agric. Food Chem.* **1977**, *25* (3), 517–528.

Yates, W. E.; Cowden, R. E.; Akesson, N. B. "Drop size spectra from nozzles in high-speed air streams"; American Society of Agricultural Engineers: St. Joseph, MI, 1983; Paper AA83-005.

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Degradation of Dinocap in Three German Soils

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The degradation of [*ring-U*-^{14}C]dinocap in three German soils was investigated under laboratory conditions using 100 g of soil and uniform distribution of 9 mg of dinocap/kg of soil. The mineralization of the ring carbon was monitored at 15 and 25 °C with 50% of the maximum moisture capacity. Organic amendments in the form of alfalfa meal (0.5 g of dry mass/100 g of soil) stimulated the degradation only during the first 3 weeks of incubation. The degradation rate in a parabraunerde soil was nearly 1 order of magnitude higher than that in two standard soils recommended for degradation studies where only 3.3 or 5.1%, respectively, was mineralized to $^{14}CO_2$ at 25 °C during 100 days. Desorption and solvent extraction studies showed that the dinocap-bound residue fraction increased with incubation time, the highest amount being in soil amended with alfalfa meal. Dinocap and the major metabolite DNOP were identified by HPLC and TLC. In addition, four unknown metabolites were separated.

Fungicidally active compounds reach the soil initially in part during spraying application or are later washed off the plants by precipitations. Once in the soil, they are subject to degradation, rearrangement, and incorporation processes. These processes are dependent upon the physical and chemical behavior of the compound as well as on the multiple reactions in the soil such as sorption, translocation, distribution, and chemical and biochemical degradation. For new fungicides these processes are studied as a prerequisite for registration. However, for some of the organic pioneer compounds that replaced mercury- and sulfur-containing fungicides, comparatively little information is available. Therefore, the degradation behavior was examined for the chemical dinocap (^{14}C labeled) in three soils of the Federal Republic of Germany. In addition to the measurement of the rates of mineralization for up to 100 days at two different temperatures (15 and 25 °C), the influence of an organic amendment (alfalfa meal) on biomass development and hence mineralization

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