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ENVIRONMENTAL FATES AND IMPACTS OF MAJOR FOREST USE PESTICIDES

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PREFACE AND ACKNOWLEDGEMENTS

This compendium of environmental fate and impact profiles for major forestry pesticides is one output of the Forest Use Chemicals Project, a multi-contractor/grantee study sponsored by the Office of Pesticides and Toxic Substances (OPTS) of the U.S. Environmental Protection Agency and aimed at developing guidance for the timber production industry and public on comparative risks and benefits of various chemical and non-chemical approaches to pest management. Those on the TRW project staff wish to express their gratitude to the EPA Project Officer, Mr. Michael Dellarco, for his advice and guidance during the course of the program. Special thanks are also due to a number of EPA technical and management staff, specially to Mrs. Jan Auerbach, Chief of the Regulatory Support Branch, Special Pesticide Review Division of OPTS, who reviewed program progress and provided constructive suggestions and guidance.

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The First Party III

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TABLE 1. PESTICIDES ADDRESSED IN THE PROJECT

Common Name	Major Trade Names
Herbicides	
Amitrole	Amitrole T, Cytrol Amitrole-T, Weedazol
Atrazine	AAtrex 80W, 90W, 4L, 4CL
Dalapon	DOWPON, DOWPON M, DOWPON C, Radapon
Dicamba	Banvel
2,4-D	Weedone LV-4, Esteron 99 Concentrate, Weedar
Fosamine Ammonium	Krenite Brush Control Agent, Krenite S Brush Control Agent
Glyphosate	Roundup
Hexazinone	"Velpar" "Gridball" Brush Killer, "Velpar" Weed Killer, "Velpar" L Weed Killer
MSMA	Ansar, Bueno, Daconate
Picloram	Tordon, Amdon
Simazine	Princep
Triclopyr	Garlon 3A, Garlon 4
Insecticides	
Acephate	Orthene
Carbaryl	Sevin-4-Oil; Sevin 50WP, 80WP, 80S
Trichlorfon	Dylox 1.5 Oil, Dylox 4
Biologicals	
Bacillus thuringiensis	Dipel, Thuricide
Nucleopolyhedrosis viru	s Gypcheck, TM-Biocontrol-1
Pheromones	(various)

Common Name:

Glyphosate

Chemical Name:

N-(phosphonomethyl)glycine

Major Trade Name:

Roundup

Major Applications in Forestry:

Glyphosate is used for site preparation, conifer release, post directed sprays, and tree injection.

SUMMARY

Being a relatively new pesticide, the environmental fate and potential ecological effects of the use of glyphosate in forests have not yet been adequately studied. The limited data which are currently available are almost entirely from greenhouse and laboratory studies with agricultural systems and laboratory animals and have been largely generated by the manufacturer. These data indicate high effectiveness, short persistence in soil and water environments, and very low toxicity to animals for glyphosate. Because of these features, a great potential exists for future large-scale use of glyphosate in forestry.

Glyphosate is absorbed almost exclusively via plant foliage and is translocated throughout the plant. Less than one percent of the glyphosate in the soil is absorbed via the roots. Glyphosate is apparently not metabolized to a significant degree in plants and its mode of action is believed to involve inhibition of aromatic amino acid synthesis. It is rapidly and strongly adsorbed to soil particles; this strong adsorption by soil accounts for the observed lack of mobility and leaching tendency of glyphosate in soil and its "unavailability" for root uptake. Adsorption to soil is believed to be through the phosphonic acid moiety, since phosphate level in the soil influences the quantity of glyphosate adsorbed and glyphosate adsorption is greater in soils saturated with Alith and Feith than with Na and Cait.

Dissipation of glyphosate in soil is fairly rapid (half life about 2 months) and is primarily due to microbial degradation. The principal soil metabolite of glyphosate is aminomethylphosphonic acid (AMPA), which itself is also highly biodegradable. Glyphosate is subject to biodegradation in natural waters and has an estimated half-life of 7 to 10 weeks.

Under normal application rates, Roundup herbicide (the commercial formulation of glyphosate) should not be toxic to forest fauna at recommended application rates. Bioassay tests on several aquatic invertebrates and fishes have indicated 96-hr LC50 values ranging from 2.3 mg/L for fathead minnows to 43 mg/L for mature scuds. Aquatic tests comparing toxicities of the technical grade glyphosate, Roundup herbicide and the surfactant used in Roundup herbicide have indicated that the surfactant and not the glyphosate is the primary toxic agent in Roundup. Animal feeding studies with glyphosate have indicated low toxicity to rat, mallard duck and quail and little or no potential for bioaccumulation.

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1.0 INTRODUCTION

Glyphosate is a broad-spectrum and relatively non-selective herbicide introduced in 1971 (1). Its primary uses are in agriculture and on noncrop areas such as industrial and recreational areas, irrigation canals and rights-of-way (2). The use of glyphosate in forestry is relatively new and has been primarily in the Pacific Northwest for control of brush species such as bigleaf maple, vine maple, alder, salmonberry, thimbleberry, hazel, and bracken fern (3). Specific forestry applications include preplant nursery uses for pine seedlings, site preparation, and conifer release and seed orchards and seed production areas (4). In 1979, approximately 4100 1b of glyphosate was used in U.S. Forest Service Regions 5 and 6 (more specifically, in the Pacific Northwest); of this, about 3600 lb were used for conifer release, and the remainder was used for general weed control, including right-of-way applications (5). According to the Oregon Department of Forestry (6), use of glyphosate is now an integral part of that state's vegetation management; about 3000 to 5000 acres of state-owned forest land are annually treated with glyphosate, primarily for conifer release. In the Pacific Northwest, glyphosate has proved considerably more effective than 2,4,5-T for the control of certain specific weed species (e.g., salmonberry and thimbleberry). For these applications, glyphosate may be overall more cost-effective than 2,4,5-T, despite its higher per acre treatment cost (estimated at about \$50/acre). No quantitative data are available on the extent of usage of glyphosate by private timber companies, although such uses are reported to be "major" (3). Limited uses of glyphosate have also been reported in the northeastern United States, primarily in connection with Christmas tree production and in experimental site preparation/conifer release plots. In Maine, 6,000 lb of glyphosate were used for these purposes in 1979, and Georgia Pacific treated 2,400 acres of its forest plantation in Maine with glyphosate in 1979 (8).

Both ground and aerial application methods have been used in connection with forestry uses. When applied aerially, use of "raindrop" nozzles significantly reduces potential for drift. A typical application rate for conifer release is 1 to 1.5 quarts of Roundup herbicide per 10 gallons of solution per acre; somewhat higher rates (about 3-4 quarts of Roundup herbicide per 10 gallons of solution) have been used for site preparation (6).

Glyphosate is manufactured by Monsanto Co. and the commercial formulation, Roundup, is a mixture containing a surfactant and the isopropylamine salt of glyphosate (24). The role of the surfactant is to increase absorption and translocation of the herbicide in plants.

2.0 PHYSICAL/CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

Glyphosate is the common name for N-(phosphonomethyl)glycine. Its structural formulation is:

It is a white odorless solid with a melting point of 200°C. The solubility in water is 1.2 percent at 25°C and the solubility in other solvents is reported as "none" (11). The vapor pressure of glyphosate is reported as "negligible".

3.0 ENVIRONMENTAL FATE

3.1 UPTAKE AND METABOLISM BY PLANTS

Field and greenhouse studies have indicated that the basic mechanism for the uptake of glyphosate is through the plant foliage; some root uptake may also take place, depending on the soil type. Although the mechanism of glyphosate action is not fully elucidated, it is believed to involve blockage of aromatic amino acid biosynthesis (12).

Humidity and the presence of surfactants significantly increase the absorption of glyphosate by the foliage. Foliar absorption experiments conducted in a greenhouse by Gottrup, et al. (13), using Canada thistle (Cirsium arvense) and leafy spurge (Euphorbia esula) indicated maximum absorption under conditions of high humidity when glyphosate was applied with surfactant. Under conditions of low relative humidity (ambient glasshouse conditions), each species absorbed about 27 percent of the applied herbicide after one week. Under high relative humidity (plants in plastic bags), absorption was about 85 percent after one week. Both low and high humidity experiments were conducted in the presence of surfactants.

Wyrill and Burnside (14) also conducted foliar absorption experiments on field and greenhouse plants. Tests were conducted on common milkweed

(Asclepias syriaca) and hemp dogbane (Apocynum cannabinum). The tests found that neither wax removal, subcuticular cell damage, nor surfactant significantly increased diffusion of glyphosate across common milkweed or dogbane cuticles. Removal of epicuticular wax with chloroform did not appreciably increase absorption of glyphosate in either species.

The hydrophobic epicuticular wax is probably an effective barrier to the polar, negatively charged glyphosate molecule. However, since wax removal had little effect on glyphosate absorption, it appears that the cuticle is also an effective barrier to glyphosate absorption. Wyrill and Burnside (14) noted that this was possibly because glyphosate was repelled by negatively charged cuticle components. Based on the finding that an effective surfactant did not increase glyphosate diffusion across the cuticles of either species, Wyrill and Burnside (14) postulated that the main influence of the surfactant may be on the plasma membrane and not the leaf cuticle.

Sprankle, et al. (15) investigated the absorption of glyphosate via roots. Greenhouse studies found that soybean and corn grown in Spinks sandy loam soil absorbed less than 0.8 percent of the glyphosate applied to the soil. However, glyphosate was readily absorbed from a nutrient solution by wheat seedlings. This suggests that the absence of glyphosate effect when applied to the soil is probably due to the unavailability of glyphosphate in soil for absorption by the roots (see Section 3.2.1) (15).

Once absorbed by plants, glyphosate is translocated to all plant parts including the underground propagules of perennial species, thus preventing their regrowth (11). Studies of the metabolism of glyphosphate by Canada thistle, leafy spurge, milkweed and hemp dogbane have indicated no significant degradation in these plants up to 20 days after treatment (13,14). No data have been reported on persistence in plants over longer time periods. In one study using ¹⁴C-glyphosate on Canada thistle and leafy spurge foliage and roots, the examination of autoradiographs of thin layer plates containing plant extracts indicated the presence of intact ¹⁴C-glyphosate in both species with no detectable amount of metabolites of ¹⁴C-glyphosate one week after treatment (13).

3.2 FATE IN SOIL

Dissipation of glyphosate in soil is considered to be relatively rapid.

The same

Rueppel, et al. (10) conducted greenhouse soil dissipation studies in which glyphosate was applied to soil just prior to the planting of corn. Three different soil types (Drummer silty clay loam, Norfolk sandy loam, and Ray silt loam; organic contents: 6 percent, 1.0 percent, and 1.0 percent, respectively) and two different glyphosate concentrations (4 and 8 ppm corresponding to approximately 4.48 and 8.98 kg/ha application rates) were used. For both application rates, the calculated half-lives were 3, 130, and 27 days for Drummer, Norfolk, and Ray soils, respectively. The relatively rapid dissipation of glyphosate in soil has been substantiated by the results of actual field studies (conducted by Monsanto on eleven different soils covering a full range of soil types and geographic areas) which indicate an average half-life of 2 months. Other investigators have reported half-lives of 17 to 19 weeks for sandy soil and 3 weeks in silt loam (16).

Adsorption on soil particles, which influences the potential for leaching, runoff, and degradation by the action of soil microorganisms are the primary factors in determining the dissipation of glyphosate from soil. Photodecomposition, volatilization and chemical degradation do not appear to make significant contributions to glyphosate losses. (As noted in Section 2, glyphosate is reported to have a negligible vapor pressure. Rueppel, et al. (10) investigated the photodecomposition of ¹⁴C-glyphosate in solution using a Crosby photoreactor and found no loss of ¹⁴C content via volatile degradation products and no change in the composition of the test solution.)

3.2.1 Adsorption, Leaching and Runoff

The strong adsorption of glyphosate on soil has been demonstrated in a number of studies and is considered the initial step in inactivation (i.e., "unavailability" to plant roots) of glyphosate in soil. In a greenhouse study, Sprankle, et al. (15) measured the effect of glyphosate on the growth of 16-day-old wheat plants grown on washed quartz sand, clay loam (3.7 percent organic content) and muck soil (81 percent organic content) treated with glyphosate at application rates of 4.5, 11, and 56 kg/ha. While no reduction in plant yield was observed for the two soils, glyphosate treatment significantly reduced plant growth in the quartz sand, thus indicating that the herbicide was adsorbed to the soils and that adsorption to sand was much less extensive.

Sprankle, et al. (15) also studied the effect of pH and phosphate on the adsorption of glyphosate by soil, using plant yield as a measure of glyphosate inactivation and, hence, adsorption. While no significant pH effect was observed at glyphosate application rates of 4.5 and ll kg/ha, a pronounced effect was observed at an application rate of 56 kg/ha; at this rate, reductions in yield of 20 percent, 7.5 percent, 27 percent, 51 percent and 55 percent were observed at pH levels of 4.6, 5.1, 5.6, 6.1 and 6.7, respectively (see Table 3). These results indicated a decrease in glyphosate adsorption as the pH was raised. Binding of glyphosate to soil was also determined to be influenced by phosphate. Glyphosate applied at 11.2 kg/ha with 98 kg/ha of phosphate gave a significant reduction in plant dry weight, while 11.2 kg/ha of the herbicide alone had no effect. The data also indicated that the initial glyphosate binding was reversible with phosphate anions competing with glyphosate for binding sites.

Glyphosate adsorption to the soil begins immediately after application and increases slowly after one hour (17). Glyphosate rapidly binds to kaolinite, illite and bentonite clays and to muck. Fe and Al saturated clays and organic matter adsorb more glyphosate than Na or Ca saturated clays and organic matter. Based on these observations and the fact that the phosphate level in the soil is the most important factor in determining the quantity of glyphosate adsorbed, it has been concluded that glyphosate is bound to the soil through the phosphonic acid moiety (17).

The strong adsorption of glyphosate to soil reduces its mobility through leaching and surface washout. The mobility of glyphosate in Ray, Norfolk, and Drummer soils (see above) has been examined by Rueppel, et al. (10). Soil thin-layer plates were spotted with $^{14}\text{C-glyphosate}$ and developed twice with water; the distribution of ^{14}C activity relative to the origin was determined by beta camera analysis after each development. The parent compound was so strongly adsorbed by all three soils that 97-100 percent of the ^{14}C activity had an $R_{\rm f}$ of less than 0.09. Similarly, 95-99 percent of the starting ^{14}C activity remained at an $R_{\rm f}$ of less than 0.09 after the second development. In no case was any of the radioactivity of an $R_{\rm f}$ greater than 0.18. These values correspond to a Class 1 pesticide (immobile) in the Helling and Turner pesticide mobility classification system (18). (Class 1, 0.0-0.9; Class 2, 0.1-0.34; Class 3, 0.35-0.64; Class 4, 0.65-0.80; Class 5, 0.90-1.00.)

Comes, et al. (19) investigated leaching of glyphosate from banks of irrigation canals treated with glyphosate. Neither glyphosate nor its primary soil metabolite, aminomethylphosphonic acid (AMPA, see Section 3.2.2), were detected in the first flow of water through two canals following application of Roundup herbicide at 5.6 kg/ha to ditchbanks when the canals were dry. Soil samples collected the day before canals were filled (about 23 weeks after treatment) contained about 0.35 ppm glyphosate and 0.78 ppm AMPA in the 0 to 10-cm layer. Soil column leaching studies conducted by the Monsanto Company have also indicated limited potential for leaching (16). In these studies, soil columns treated with either glyphosate or its sodium salt were aged for 30 days prior to eluting with 1/2 acre inch of water for 45 days; leaching of parent compound was insignificant.

Rueppel, et al. (10) also evaluated the runoff potential from Ray, Drummer, and Norfolk inclined soil beds at 7.5° using a rate of 1.12 kg/ha applied uniformly to the upper third of the soil surface. The entire soil surface was then subjected to three artificial rainfalls at 1, 3, and 7-day intervals after treatment. Each time, rainfall was continued through collection of two consecutive 50-ml samples of runoff water and sediment. The water was separated from the sediment by centrifugation and the 14 C content of each determined. In both the sediment and runoff water, the amount of 14 C activity collected was extremely low, ranging from 6.5 x 10 down to 1 x 10 percent of that applied for the water and 3 x 10 to 1 x 10 percent for the sediment. These data correspond to a maximum runoff of less than 2 x 10 kg/ha. The lack of runoff is not surprising in lieu of the tight binding of glyphosate to soil discussed above.

3.2.2 Degradation

Studies conducted by Sprankle, et al. (17) and Rueppel, et al. (10) have indicated that glyphosate degradation in soil is relatively rapid and takes place microbiologically, and not by chemical action. Rueppel, et al. (10) conducted soil/water "shake flask" experiments to investigate, under aerobic and anaerobic, and sterile and non-sterile conditions, the mechanism and rate of glyphosate degradation and the nature of degradation products. Each shake flask contained 4.5 g (dry weight) of soil, 1 mg of a 14 C-glyphosate and 100 ml of distilled water. Three different 12 C-glyphosates were used: N-phosphono-14 C-methylglycine, N-phosphonomethylglycine-1-14 C,

and N-phosphonomethylglycine-2-¹⁴C. Four agricultural soils studied were Ray silt loam, Drummer silty clay loam, Lintonia sandy loam, and Norfolk sandy loam, with organic matter contents of 1.0, 6.0, 1.1, and 1.0 percent, respectively. The results of these experiments and two other experiments using sucrose-¹⁴C and sucrose-¹⁴C plus unlabelled glyphosate are presented in Table 1 for Ray silt loam soil. As shown in the table, all 3 carbons of glyphosate were rapidly degraded at comparable rates in the presence of Ray silt loam. In addition, all three ¹⁴C-labelled compounds were degraded to nearly the same extent and rate as the natural and general metabolite sucrose. From the three ¹⁴C labels, 47-55 percent of glyphosate ¹⁴C was given off as ¹⁴CO₂ in 4 weeks, compared to 57.9 percent for sucrose. Experiments using autoclaved soil/water slurries indicated negligible (less than 1 percent) evolution of ¹⁴CO₂ from the three ¹⁴C-labelled glyphosates and the control sucrose ¹⁴C during a 7-day observation period.

Rueppel, et al. (10) also analyzed the supernatants and soils in shake flasks to determine the distribution of 14C labelled compounds between the two phases and to identify metabolites. The metabolite distribution was similar for both the aerobic and anaerobic shake flasks for a given soil. In general, the same metabolites were observed regardless of the soil type. The principal soil metabolite observed from the N-phosphonic-14C-methyl label of glyphosate was aminomethylphosphonic acid (AMPA); as expected, due to the 14C-label position, this metabolite was not observed radioactively from the two glycine-14C labels. The maximum amount of AMPA detected in the supernatant was 15 per-ent of the starting 14C activity. Several other metabolites were also detected chromatographically in some cases. minor metabolites included N-methylaminomethylphosphonic acid, glycine, N, N-dimethylaminomethylphosphonic acid, hydroxymethylphosphonic acid, and two unknown metabolites; none of these minor metabolites were normally present to an extent greater than 1 percent of the applied radioactivity. No metabolic products containing an intact N-(phosphonomethyl)glycine grouping were detected in these studies.

Analysis of the shake flask soils, carried out by TLC/beta camera analysis of a soil extract obtained by extraction with 0.5 m NH₄OH, indicated that the extractable residue consisted primarily of the parent glyphosate and the major metabolite AMPA. As in the case with the shake flask super-

 $^{14}{\rm Co}_2$ evolution from shake flasks as a function of time and $^{14}{\rm C}$ label for ray silt loam soil (10) TABLE 1.

14c Label	Type of	Pe	Percent 14	cent 16 Released as 14	l as 14 CO ₂		Total 14 _C
	Metabolism	3	7	at nay m 14	21	28	as
N-phosphono 14 C-methy1	A A	13.2	16.7	10.1	4.6	2.2	46.8
Glycine 1^{-14} [*]	A	28.1 12.6	10.1	13.8 18.9	1.9	1.4	55.3 51.4
Glycine 2-14c*	A An	19.0 3.8	16.2 6.8	12.8	4.0 5.9	3.3	55.3 33.5
Sucrose 14 _C	A An	41.5	5.3	4.9	3.0	2.4	57.9 55.3
Sucrose ¹⁴ C plus Unlabelled glyphosate	An	26.7	13.0	11.7	2.2 11.5	2.0 10.8	55.6 61.5

*Labelled N-(phosphonomethyl)glycine.
†Aerobic (A); anaerobic (An).

natants, several minor metabolites were also observed, and the same general distribution was observed on both the aerobic and anaerobic soils. Combustion analysis of the soils after extraction with NH₄OH indicated that from 8.5 to 40.3 percent of the applied ¹⁴C activity was bound to soil. Although the bound residue material could not be identified, the NH₄OH non-extractable residue was considered to represent the extensively metabolized products of glyphosate and AMPA.

Shake flask studies of 14 C-labelled AMPA indicated that this major metabolite of glyphosate is also highly biodegradable. Aminomethyl- 14 C-phosphonic acid shake flask studies with Ray silt loam and Drummer silty clay loam soils gave 34.8 and 16.1 percent, respectively, of the applied 14 C as 14 CO₂ in 63 days. The slower degradation of AMPA compared to glyphosate was explained in terms of its possible tighter binding to soil and/or lower permeability through the cell walls of microflora.

Based on shake flask slurry studies and dissipation experiments with moist soil (which confirmed the shake flask results), Rueppel, et al. (10) concluded that glyphosate is clearly a biodegradable compound in the presence of soil microflora and that the rate and extent of metabolism are rapid and complete.

3.3 PERSISTENCE IN WATER

The stability of glyphosate in water has been studied by Monsanto Company in laboratory tests conducted under sterile and non-sterile conditions (25). In these experiments, the sodium salt of glyphosate was incubated in sterile water at pH values of 3.0, 6.0, and 9.0 at 25 and 250 ppm. The solutions were incubated in the dark at 5° and 35°C for 32 days. Samples were taken at 0, 7, 14, 21, and 32 days. In addition, three natural water samples ranging from pH 4 to pH 7.3 were treated with 0.1 ppm and incubated in the dark for 7, 21, 35, and 49 days. Glyphosate was stable in sterile conditions with slow biodegradation occurring in natural water.

The data reported indicate the following half-lives in natural water systems (25): Sphagnum bogs (pH 4.23), 7 weeks; cattail swamp (pH 6.25), 9 weeks; and pond water (pH 7.33), 10 weeks. Monsanto reports that, as with soil, microbial breakdown is the major route of degradation of glyphosate

in water. The material is tightly adsorbed to organic and mineral matter within the aquatic system and then degraded. Rates of degradation are slower than in most soils due to the lower numbers of microbes in the aquatic system (21).

4.0 IMPACT ON NON-TARGET ORGANISMS

4.1 PLANTS

P

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In applications in the Northeast for conifer release, some "browning" of conifers have been observed with glyphosates at normal application rates of 1 to 2 quarts per acre; this browning, however, has been temporary, and the conifers (e.g., Jack and red pines) have gradually recovered (8). Monsanto has conducted field studies on the potential for drift when Roundup herbicide is applied by air. Their results show that at wind speeds of 12 mph, damaging drift is not likely to move more than 200 ft outside the target. With rates of 2 quarts or less per acre, Monsanto recommends a buffer zone of 75 ft. For rates above 2 quarts, 125 ft is recommended; and a general restriction of 200 ft around homesteads and recreational areas is recommended (21).

As discussed previously, once the glyphosate enters soils, it is inactivated relatively rapidly via adsorption and microbial degradation. In agricultural applications, use of glyphosate at proposed rates has been shown to have no injurious effects on crops planted immediately after herbicide treatment (15). In sand cultures where glyphosate adsorption is minimal, high dosages of glyphosate have been shown to reduce height and shoot growth in several crops. The effect of 0.57 kg/ha of glyphosate applied in sand culture on the growth of seven crop species is shown in Table 2. Based on the data in Table 2, a wide spectrum of sensitivity to glyphosate can be expected. Of the species tested, flax is the most sensitive; corn, soybean and bean are less sensitive than flax, while barley, oat and cucumber are the least sensitive of all. Data presented by Sprankle, et al. (15) also indicated that the germination of corn, soybean and wheat is unaffected by glyphosate application rates of as high as 4.5 kg/ha. Table 3 shows that the dry weight of young wheat plants was not affected by glyphosate applied to the soil at rates of 4.48 and 11.2 kg/ha (15). (The highest recommended application rate for forest uses is about 5 kg/ha of glyphosate.)

TABLE 2. THE EFFECT OF 0.56 kg/ha OF GLYPHOSATE* APPLIED IN SAND CULTURE ON THE GROWTH OF SEVERAL CROP SPECIES (15)

Species		Percent of Control	
	Plant Ht.	Shoot Fresh Wt.	Shoot Dry Wt.
Flax	14 a	21 a	20 a
Corn	35 b	48 bc	45 Ъ
Soybean	36 Ъ	42 ab	33 ab
Wheat	56 c	55 bc	52 Ъ
Barley	68 d	72 cd	71 c
Oats	82 e	116 d	100 c
Cucumber	75 de	69 cd	86 c

^{*}Mono(dimethylamine) salt of glyphosate.

TABLE 3. THE EFFECT OF GLYPHOSATE ON THE DRY WEIGHT PER PLANT OF 16-DAY-OLD WHEAT PLANTS FOLLOWING INCORPORATION INTO HILLSDALE SANDY CLAY LOAM AT SEVERAL pH LEVELS (15)

pН			Glyphosa	te* (kg/1	na)		
	0 (mg)†	4.48	(mg)†		(mg)†	56.0	(mg) †
4.6	20 ab	15	å	19	ab	16	ab
5.1	40 de	39	de	42	de	37	cd
5.6	44 c	43	c	.44	c	32	c
6.1	43 de.	43	de	43	de	21	b
6.7	40 de	40	de	40	de	18	ab

^{*} Isopropylamine salt of glyphosate.

Means within a column with common letters are not significantly different at the 5 percent level by Duncan's multiple range test.

[†]The control is the treatment where 0.8 percent surfactant was applied to the sand.

[†]Means with common letters are not significantly different at the 5 percent level by Duncan's multiple range test.

Yates, Akesson, and Bayer (27) looked at the effects of spray drift on wheat and grape plants. Exposure to plants was measured by measuring the amount of glyphosate deposited on Mylar plates. Previous studies found an excellent correlation between deposit on Mylar plates and residues on alfalfa. The tests found a rather wide band of injury levels as related to deposit levels. For example, some low levels of injury occurred at levels as low as 0.1 to 1 g/ha while some values as high as 10 g/ha produced no injury. The authors state that the data from this study can be used to indicate rough guidelines for the most sensitive conditions. For example, they found that a 10 g/ha exposure on mylar sheets could result in a 70 percent injury on wheat at the 4-leaf stage of growth. For grape plants, the band of injury levels were somewhat lower (i.e., less injury) but similar to the response of wheat plants. The data also showed that the grape plants tended to grow out of the symptoms in time.

4.2 FAUNAL IMPACTS

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Data on the toxicity and limited data on the effects of Roundup on habitat suitability indicate that Roundup can be used in the forest without resulting in toxic effects to forest fauna.

Folmar, et al. (9) conducted several experiments on the effects of glyphosate and glyphosate formulations on aquatic ecosystems. Among the tests conducted were acute toxicity assays for Roundup on several aquatic invertebrates and fishes. As shown in Table 4, the 96-hr LC_{50} values varied from 2.3 mg/L for fathead minnows to 43 mg/L for mature scuds. In Table 5, it can be seen that under "worse case" conditions, the LC_{50} for rainbow trout can be as low as 1.4 mg/L. The toxicities determined for the other organisms were nearer the values for fathead minnows than for the more resistant scuds.

Tests comparing the toxicities of the technical grade glyphosate, Roundup and the surfactant used in the Roundup formulation have indicated that the surfactant, and not the glyphosate, is the primary toxic agent in Roundup (9) (see Tables 5 and 6). As shown in Table 4, the 24-hr LC₅₀ for rainbow trout is 140 mg/l for glyphosate and only 2.1 mg/l for the surfactant. The data in Table 5 also illustrate the effect of pH on aquatic toxicity of Roundup and its glyphosate and surfactant components. Except for the glyphosate which appears to be more toxic at a pH of 6.5 than at a pH of 9.5,

TABLE 4. TOXICITY OF ROUNDUP TO AQUATIC INVERTEBRATES AND FISH (9)

Organisms	Temp.	LC ₅₀ or EC ₅₀ *	(mg/L) and 95% Co	nfidence Limits
	(°C)	24 h	48 h	96 h
Daphnids	22		3.0 (2.6-3.4)	
Scuds	12	100	62 (40–98)	43 (28-66)
Midge larvae	22		18 (9.4-32)	
Rainbow trout	12	8.3 (7.0-9.9)		8.3 (7.0-9.9)
Fathead minnows	22	2.4 (2.0-2.9)		2.3 (1.9-2.8)
Channel catfish	22	13 (11-16)		13 (11-16)
Bluegills	22	6.4 (4.8-8.6)		5.0 (3.8-6.6)

Daphnid and midge toxicities expressed as 48-h EC₅₀ (concentration immobilizing 50 percent of the test organisms).

TABLE 5. TOXICITY OF TECHNICAL GLYPHOSATE AND THE ROUNDUP SURFACTANT TO MIDGE LARVAE AND FOUR SPECIES OF FISH (9)

Chemical and	Temp.	LC50 or EC50*	(mg/L)	and 95% Co	nfidence Limits
Organism	(°C)	24 h		48 h	96-h-
GLYPHOSATE					
Midge larvae	22		55	(31-97)	
Rainbow trout	12	140 (120-170)			140 (120-170)
Fathead minnows	22	97 (79–120)		•	97 (79–120)
Channel catfish	22	120 (110-160)			130 (110-160)
Bluegills	22	150 (120–190)			140 (110-160)
SURFACTANT		*			
Midge larvae	22		13	(7.1-24)	
Rainbow trout	12	2.1 (1.6-2.7)			2.0 (1.5-2.7)
Fathead minnows	22	1.4 (1.2-1.7)			1.0 (1.2-1.7)
Channel catfish	22	18 (8.5-38)			13 (10-17)
Bluegills	22	3.0 (2.5-3.7)			3.0 (2.5-3.7)

Midge toxicity expressed as 48-hr EC₅₀ (concentration immobilizing 50 percent of the test organisms).

TABLE 6. EFFECTS OF pH ON TOXICITY OF ROUNDUP, GLYPHOSATE, AND THE SURFACTANT TO RAINBOW TROUT AND BLUEGILLS (9)

Chemicals, Organism, and pH	LC	50 (mg/L) and 24 h	i 95% Confider	oce Limits 96 h
ROUNDUP				
Rainbow trout				
6.5	14	(12-17)	7.6	(6.4-9.1)
7.5	2.4	(2.0-2.9)	1.6	(1.2-2.2)
8.5	2.4	(2.0-2.9)	1.4	(1.2-1.7)
9.5	2.4	(2.0-2.9)	1.4	(1.2-1.7)
Bluegills				
6.5	7.6	(6.4-9.1)	4.2	(3.5-5.0)
7.5	4.0	(3.2-5.0)	2.4	(2.0-2.9)
8.5	3.9	(3.1-4.9)	2.4	(2.0-2.9)
9.5	2.4	(2.0-2.9)	1.8	(1.3-2.5)
GLYPHOSATE				
Rainbow trout				
6.5	240	(200-290)	140	(120-170)
9.5	240	(200-290)	240	(200–290)
Bluegills				
6.5	240	(200-290)	140	(120-170)
9.5	230	(190-280)	220	(170-280)
SURFACTANT				
Rainbow trout				
6.5	7.4	(6.2-8.9)	7.4	(6.1-9.0)
9.5	1.4	(1.2-1.7)	0.65	(0.54-0.78)
Bluegills				
6.5	4.2	(3.1-5.7)	1.3	(1.1-1.6)
9.5	3.0	(2.2-4.1)	1.0	(0.72-1.4)

all three chemicals were less toxic to the species tested at the lower pH value of 6.5.

Folmar, et al. (9) also investigated the effects of temperature on the toxicity of Roundup to two species of fish. The results, shown in Table 7, indicate that Roundup is about twice as toxic to rainbow trout at 17°C than it is at 7°C, and that it is more toxic to bluegills at 27°C than at 17°C.

TABLE 7. EFFECTS OF TEMPERATURE ON THE TOXICITY OF ROUNDUP TO TWO SPECIES OF FISH (9)

Organism and Temp. (°C)	LC ₅₀ (mg/L) and 95% 24 h	Confidence Limits 96 h
Rainbow trout		
7°	14 (11–17)	14 (11-16)
12°	14 (11–17)	7.5 (6.3-9.0)
17°	7.5 (6.3-9.0)	7.4 (6.2-8.9)
Bluegills		
17°	9.6 (7.9-12.0)	7.5 (6.3-9.0)
22°	6.4 (4.8-8.6)	5.0 (3.8-6.6)
27°	4.3 (3.4-5.4)	4.0 (3.2-5.0)

Folmar, et al. (9) also conducted experiments on mayfly avoidance of Roundup and rainbow trout avoidance of the isopropylamine salt of glyphosate. In these tests, rainbow trout did not avoid concentrations of the isopropylamine salt up to 10 mg/L; mayfly nymphs avoided Roundup at concentrations of 10 mg/L but not at 1.0 mg/L.

Folmar, et al. (9) exposed various early life stages of rainbow trout and channel catfish to Roundup. The results of their tests indicated that, for both species, the egg stage was the least sensitive and that the toxicity of Roundup increased in the sac fry and early swim-up stages, but decreased in the fingerling stage as the fish grew larger. Significant reductions in the hatch of trout eggs was observed at 10 mg/L whereas no significant difference was observed at 5.0 mg/L. A significant reduction in the survival of sac-fry was seen at 5.0 mg/L but not at 2.0 mg/L. These data indicate that applications of Roundup could have adverse effects if applied during seasons when young fish are present in the receiving waters (9).

Although many studies have been conducted, very limited data are publicly available on the toxicity of glyphosate to animals (wildlife and beneficial insects). Feeding studies with mallard duck and quail have indicated an LC_{50} of greater than 4600 ppm of glyphosate (in food) (20). Experiments with bees have indicated an LD_{50} of greater than 100 µg per bee (20). The oral rat LD_{50} for glyphosate is 4320 mg/kg (22).

4.3 BIOACCUMULATION

The limited data available indicate that glyphosate has little to no potential to bioaccumulate when used in forest systems. Trout, bluegills, and bass exposed to 10-12 ppm of Roundup for 14 days contained only 0.1 ppm of glyphosate (20). Upon being placed in clear water, the glyphosate in the "contaminated" fish was depleted (20). The octanol/water partition coefficient for glyphosate is reported to be 0.0017 at 20 ppm and 0.0006 at 100 ppm, indicating virtually no tendency to bioconcentrate in living cells (26).

Folmar, et al. (9) exposed rainbow trout for 12 hours to 0.02, 0.2, and 2.0~mg/L of either the isopropylamine salt of glyphosate or Roundup as a simulation of actual field exposures. No residues of glyphosate or the primary metabolite, AMPA, were detected in either the fillets or eggs of fish exposed to the isopropylamine salt. However, in fish exposed to 2.0~mg/L of Roundup, the fillets contained 80 µg/kg of glyphosate and the eggs contained 60 µg/kg. Midge larvae, from both drift and substrate samples, were collected for 7 days after exposure to Roundup in artificial stream studies. No glyphosate residues were detected in the midge larvae (9).

In another study, rabbits were administered a single oral dose of 14 C-glyphosate. Five days after treatment, more than 80 percent of 14 C were found in the feces, 7 to 11 percent in urine, less than 1 percent in expired 14 CO₂ and most of the unrecovered 14 C was found in the colon (16).

4.4 MICROORGANISMS

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Rueppel, et al. (10) investigated the effect of glyphosate on soil microorganisms by measuring the rate of sucrose degradation in treated and untreated soil and by conducting plate counts of treated and untreated soil under aerobic and anaerobic conditions, the rate of degradation of 14 C sucrose to 14 CO $_2$ was similar in both glyphosate-treated and glyphosate-untreated soils. Plate counts appeared to indicate that glyphosate had no adverse effect on the total microflora population. Treatment of Norfolk sandy loam caused a large increase (from 3.8 x 10^{-5} to 62.0 x 10^{-5}) in the total number of microorganisms per gram of soil. These findings are generally consistent with those of Quilty and Geoghegan (23) who found glyphosate to have minimal effect on microflora in peat.

Application of glyphosate to three soils - Drummer silty clay loam, Lintonia sandy loam, and Ray silt loam - at 5 and 25 ppm (1 and 5 times normal dose) showed no apparent significant effects on nitrogen fixation or nitrification by microbes (16). Treatment of the three soils mentioned above with 5 and 25 ppm of glyphosate resulted in no apparent effect on cellulose degradation, starch degradation, protein degradation, or leaf litter degradation (16).

REFERENCES

- 1. Baird, D.D., R.P. Upchurch, W.B. Homesley, and J.E. Franz. Introduction of a New Broad Spectrum Postemergence Herbicide Class with Utility of Herbaceous Perennial Weed Control. Proc. No. Centr. Weed Contr. Conf. 26: 64-68, 1971.
- 2. Farm Chemicals Handbook. Meister Publishing Company, Willoughby, Ohio. 1979.
- 3. Weyerhaeuser Trip Data; Vegetation Problems, Control Methods for Conifer Release. Weyerhaeuser Company, Tacoma, WA. 4 pp. 1979.
- 4. National Forest Products Association, Pesticide Uses for Forestry. Report prepared by the National Forest Products Association, Washington, D.C. March 1980.
- 5. Pest Management Group, University of California at Berkeley, Raw Data on Pesticides Usage on Public Lands (U.S. Forest Service), 1980.
- 6. Personal communication with Mr. Jerry Chetock, Oregon Department of Forestry, June 13, 1980 (to M. Ghassemi of TRW).
- 7. McCormack, M.L. and M. Newton. Aerial Application of Triclopyr, Phenoxies, Picloram and Glyphosate for Conifer Release in Spruce-fir Forests of Maine. Abstracts. Meeting, Weed Science Society of America, February 5-7, 1980.
- 8. Personal communication with Mr. Oscar Selin, Georgia Pacific (Woodland, Maine), May 16, 1980 (to M. Ghassemi of TRW).
- 9. Folmar, L.C., H.O. Sanders, and A.M. Julin. Toxicity of the Herbicide Glyphosate and Several of Its Formulations to Fish and Aquatic Invertebrates. Arch. Environ. Contam. Toxicol. 8: 269-78, 1977.
- 10. Rueppell, M.L., et al. Metabolism and Degradation of Glyphosate in Soil and Water, J. Agric. Food Chem. 25(3): 512-528, 1977.
- 11. Weed Science Society of America, Herbicide Handbook, Fourth Edition, pp. 224-228, 1979.
- 12. Jaworski, E.G. Mode of Action of N-(phosphonomethyl)glycine: Inhibition of Aromatic Amino Acid Biosynthesis. J. Agr. Food Chem. 20(6): 1195-8, 1972.
- 13. Gottrup, O., et al. Uptake, Translocation, Metabolism, and Selectivity of Glyphosate in Canada Thistle and Leafy Spurge. Weed Research 16: 197-201, 1976.

- 14. Wyrill, J.B. and O.C. Burnside. Adsorption, Translocation, and Metabolism of 2,4-D and Glyphosate in Common Milkweed and Hemp Dogbane. Weed Sci. 24(6): 557-566, 1976.
- 15. Sprankle, P., et al. Rapid Inactivation of Glyphosate in the Soil. Weed Sci. 23(3): 224-228, 1975.
- 16. Information provided by EPA, based on a review of registration files by the Ecological Effects Branch. (Most information in this file was originally provided by Monsanto Company.)
- 17. Sprankle, P., et al. Adsorption, Mobility, and Microbial Degradation of Glyphosate in the Soil. Weed Sci. 23(3): 229-234, 1975.
- 18. Helling, C.S. Pesticide Mobility in Soils. Parameters of Thin-Layer Chromatography. Proc. Soil Sci. Soc. Amer. 35: 732-748, 1971.
- 19. Comes, R.D., et al. Residues and Persistence of Glyphosate in Irrigation Water. Weed Sci. 24(1): 47-50, 1976.
- 20. Personal communication with Dr. Frank Serdy, Monsanto Company, June 18, 1980 (to M. Ghassemi of TRW).
- 21. Serdy, F., Monsanto Company. Information provided in a letter to M. Ghassemi of TRW. September 3, 1980.
- 22. National Institute for Occupational Safety and Health, Registry of Toxic Effects of Chemical Substances, 1978.
- 23. Quilty, S.P. and M.J. Geoghegan. University College, Ireland. Private communication. 1976. Cited in Reference 10.
- 24. Monsanto Company. Information provided on Roundup Herbicide label cleared as of April 24, 1979. EPA No. 897.10-000.83/53.
- 25. Brightwed, B.B., and J.M. Malik. Monsanto Agricultural Research Department, St. Louis, Missouri. Data provided by Monsanto Company. In: Environmental Fate File, Glyphosate, U.S. Environmental Protection Agency. Undated.
- 26. Data provided by Monsanto Agricultural Research Department, St. Louis, Missouri. In: Environmental Fate File, Glyphosate, U.S. Environmental Protection Agency. Undated.