ENVIRONMENTAL FATE OF GLYPHOSATE

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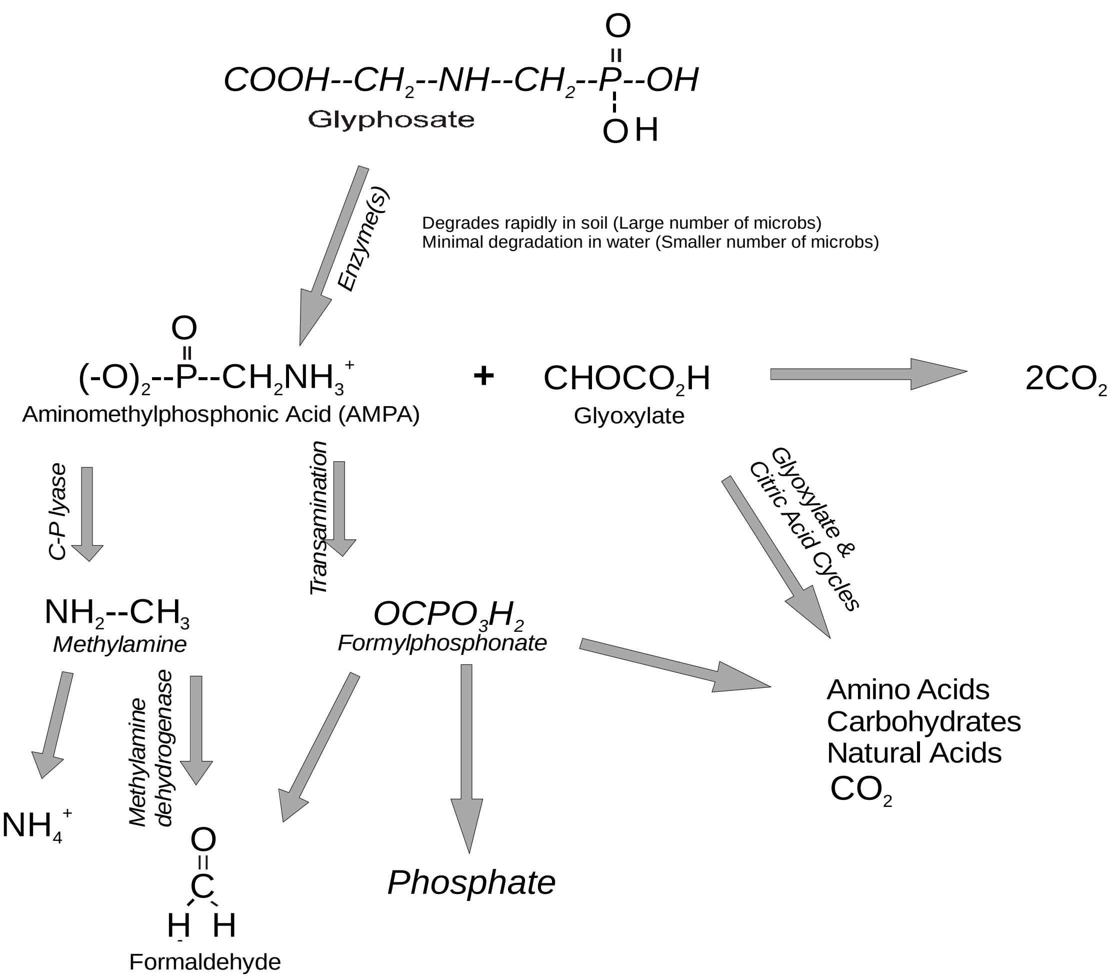
This document reviewed all routes of environmental fate for glyphosate (N-(phosphonomethyl)glycine) with an emphasis on plant uptake and plant metabolism under forest conditions.

Glyphosate Degradation Pathway



Molecular weight*	169.08 g

Water solubility	11,600 ppm (at 25EC)
Vapor pressure	7.5x10^{-8} mm Hg
Henry's constant	<1.44x10^{-12} atm-m^3/mole
Hydrolysis half-life (average over several pH levels and temperature)	>35 days
Soil adsorption coefficient (Kd) (average over several pH levels and soil)	61 g/m^3
Octanol-water coefficient log (Kow)	-3.5
Anaerobic half-life	22.1 days
Aerobic half-life (average of five samples with different soil types)	96.4 days
Field dissipation half-life (average of two samples with different soil types)	44 days

*from The 1993 Agrochemicals Handbook, other data from DPR PestChem Database (Kollman and Segawa, 1995).

Physical/Chemical Properties: Glyphosate is sparingly soluble in common organic solvents. The alkali metal and amine salts are readily soluble in water. It has a high

Aquatic and Wildlife Toxicity	
Rat (oral)	LD50 4320 mg/kg
Mallard duck 8-day	LC50 >4640 ppm
Bobwhite quail	LD50 >3851 mg/kg
Bobwhite quail 8-day	LC50 >4640 ppm
Bluegill sunfish	LC50 ~78 ppm (96hrs)
Rainbow trout	LC50 38 ppm (96hrs)
Daphnia magna	LC50 930 ppm (48hrs)
Honeybee	LD50 >100 *u* g/bee
Data compiled by Jon Shelgren, Registration Branch, Department of Pesticide Regulation	

soil adsorption coefficient (Kd=61 g/cm^3) and a very low octanol/water coefficient (Kow=0.00033). These numbers suggest that glyphosate has low mobility and only a slight tendency to leach in soil. According to Linders *et al.* (1994), glyphosate is classified as very slightly mobile in soil. Glyphosate is inactivated through soil adsorption; it has low leaching potential and very low volatility (Franz *et al. 1997)*.

Mode of Action: Glyphosate is a broad-spectrum, systemic, post-emergence herbicide that is phloem mobile and is readily translocated throughout the plant (Franz *et al.*, 1997). From the leaf surface, glyphosate molecules are absorbed into the plant cells were they are translocated to meristematic tissues (Laerke, 1995). Glyphosate's primary action is the inhibition of the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS), a chloroplast-localized enzyme in the shikimic acid pathway of plants (DellaCioppa *et al.*, 1986). This prevents the production of chorismate which is required for the biosynthesis of essential aromatic amino acids. These acids are used by plants in protein synthesis and to produce many secondary plant products such as growth promoters, growth inhibitors, phenolics, and lignin (Franz *et al.*, 1997). In forestry, glyphosate is frequently applied to release small coniferous plants from the harmful effects of competition with undesirable vegetation such as grasses, broadleaf weeds, and woody shrubs. Unlike many contact herbicides, phytotoxic symptoms of glyphosate injury often develop slowly. Visible effects on most annual weeds occur within two to four days and may not occur for 7 days or more on most perennial weeds. Extremely cool or cloudy weather following treatment may slow activity of glyphosate and delay development of visual symptoms. Visible effects are a gradual wilting and yellowing of the plant which advances to complete browning of above-ground growth and deterioration of underground plant parts.

Environmental Fate of Glyphosate

Air: The vapor pressure for glyphosate is very low; the fate pathway of this herbicide through volatilization is nonexistent (Franz *et al*. 1997). Glyphosate's low Henry's Law Constant indicates that it tends to partition in water versus air and is readily adsorbed onto soil particles. Aerial drift of the herbicide will cause injury to nontarget plants. The likelihood of drift injury occurring is greatest when winds are gusty or when wind velocities will allow spray drift to occur (Accord® label). Minute quantities of mist, drip, drift or splash of glyphosate onto nontarget vegetation can cause severe damage or destruction to the plants or other areas on which treatment was not intended.

Water: Glyphosate is highly soluble in water (11,600 ppm at 25 ^{O}C Kollman and Segawa, 1995) with a octanol-water coefficient ($\log K_{OW}$) of -3.3. Experiments conducted for US EPA's reregistration eligibility decision (RED) indicate that glyphosate is stable in water at pH 3, 5, 6, and 9 at 35 ^{O}C. It is also stable to photodegradation in pH 5, 7 and 9 buffered solution under natural sunlight. The hydrolysis half-life is >35 days (Kollman and Segawa, 1995). Bronstad and Friestad (1985) also found that glyphosate shows little propensity toward hydrolytic decomposition. Studies conducted in Manatoba Canada (Kirkwood, 1979) suggest that glyphosate's loss from water is through sediment adsorption and microbial degradation. Ghassemi *et al*. (1981) concluded that the rate of degradation in water is generally slower because there are fewer microorganisms in water than in most soils. Studies conducted in a forest ecosystem (Feng *et al*., 1990; Goldsbourough *et al*., 1993; Newton *et al*., 1994) found that glyphosate dissipated rapidly from surface water ponds high in suspended sediment, with first order half-lives ranging from 1.5-11.2 days. In streams, residue was undetectable in 3-14 days. In U.S. Environmental Protection Agency (EPA) tests using water from natural sources, the half-life ranged from 35 to 63 days (U.S. EPA, 1986). For all aquatic systems, sediment appears to be the major sink for glyphosate residue.

Soil: In general, glyphosate is moderately persistent in soil. The primary reason crops can be planted or seeded directly into treated areas following application is that glyphosate exhibits essentially no preemergent activity even when applied at high rates (Franz *et al*. 1997). Soil studies have determined glyphosate half-lives ranging from 3 to 130 days (U.S. EPA, 1990; USDA, 1984). The soil field dissipation half-life averaged 44-60 days (Kollman and Segawa, 1995; WSSA, 1989).

In the soil environment, glyphosate is resistant to chemical degradation, is stable to sunlight, is relatively nonleachable, and has a low tendency to runoff (except as adsorbed to colloidal matter). It is relatively immobile in most soil environments as a result of its strong adsorption to soil particles. Ghassemi *et al*. (1981) found that less than one percent of the glyphosate in the soil is absorbed via the roots. The Accord® label stated that, it is not available for plant uptake and will not harm off-site vegetation where roots grow onto the treatment area or if the soil is transported off-site (Accord® label). Sprankle *et al*. (1975) found that the prime factor in determining the amount of glyphosate adsorbed to soil particles is the soil phosphate level and that glyphosate is bound to soil through the phosphonic acid moiety. Glyphosate competes with inorganic phosphate for soil binding sites and the degree of binding depends on availability of unoccupied phosphate binding sites.

Glyphosate's primary route of decomposition in the environment is through microbial degradation in soil (Franz *et al*. 1997). The herbicide is inactivated and biodegraded by soil microbes at rates of degradation related to microbial activity in the soil and factors that affect this activity (Eriksson, 1975). The biological degradation process is carried out under both aerobic and anaerobic conditions by soil microflora. Rates of decomposition depend on soil and microfloral population types. In nonsterile conditions, as much as 55 percent of ^{14}C-labeled glyphosate is given off as $^{14}CO_2$ within 4 weeks using Lintonia Sandy Loam soil (USDA, 1984; Rueppel *et al*., 1977).

The primary metabolite of glyphosate is aminomethylphosphonic acid (AMPA). Degradation of AMPA is generally slower than that of glyphosate possibly because AMPA may adsorb onto soil particles more strongly than glyphosate and/or because it may be less likely to permeate the cell walls or membranes of soil microorganisms (USDA, 1984).

A study on the effects of glyphosate on microbial biomass (Stratton G. and Stewart K. 1992) found glyphosate generally had no significant effect on the numbers of bacteria, fungi or actinomycetes in forest soil and overlying forest litter. There was no effect of glyphosate on *in situ* respiration in most of the treated systems while the remainder showed a increase in respiration. Muller *et al*. (1981) found that glyphosate degrades at very low temperatures and does not adversely affect nitrogen fixation, nitrification or denitrification activity.

Biota: The major pathway for uptake of glyphosate in plants is through the foliage. Depending upon soil type and conditions, some root uptake may occur. Gottrup *et al*. (1976) demonstrated that the presence of humidity and surfactants increased absorption of glyphosate by plant foliage. Surfactants increased the diffusion rate across the plasma membrane, but not the cuticle (Wyrill and Burnside, 1976). Once absorbed, glyphosate is translocated throughout all plant parts where it prevents regrowth. Glyphosate is not metabolized by plants (Gottrup *et al*., 1976; Wyrill and Burnside, 1976).

Glyphosate's low octanol/water coefficient and low fat (lipids) solubility indicate that it has a low tendency to bioaccumulate. Also limited data available in the early 1980's indicated that glyphosate has little to no potential to bioaccumulate when used in forest systems (Ghassemi *et al*., 1981). Recent studies have found similar results, in a study cited in Franz *et al*., 1997, scientists found that rats excreted 97.5% of an administered dose in their urine and feces. Other metabolism studies have found that glyphosate residues have minimal tissue retention and are rapidly eliminated from various animal species including mammals birds and fish (Franz *et al*., 1997).

Toxicity: Single-dose acute oral studies conducted for the U.S. EPA's RED indicate that glyphosate is practically non-toxic to upland birds and only slightly toxic to waterfowl. Tests on warm and cold water fish indicate that technical glyphosate is slightly to practically non-toxic to both types.

A study to determine chronic exposures of mammals to glyphosate observed no cellular changes in mice fed glyphosate at a concentration up to 300 ppm in the diet for 18 months (U.S. Department of Agriculture, 1981). A 2-year chronic study conducted using Sprague-Dawley rats (males) fed 0, 89, 362, and 940 mg/kg/day of glyphosate observed effects only in the high-dose group, indicating that for this study, the no observable effects limit (NOEL) for systemic toxicity is 362 mg/kg/day (8000 ppm), and the lowest observable effects limit (LOEL) is 940 mg/kg/day (20,000 ppm)((Franz *et al.* 1997). When glyphosate is formulated as in Roundup®, Vision®, or Accord®, it becomes slightly more toxic to animal species due to the presence of surfactants. A study by Folmar *et al*., 1979, compared the toxicity of glyphosate and a formulation product to larvae, and found that the formulation was more toxic. The EC_{50} of the formulation was 13 ppm compared to an EC_{50} of 55 ppm for glyphosate. In a study conducted for the U.S. EPA's RED, the formulated product MONO818 was found to be slightly toxic to the invertebrate *Daphnia magna* and moderately toxic to rainbow trout.

The U.S. EPA has set a drinking water Health Advisory (HA) for glyphosate. The lifetime HA for an adult is 800 ppb for effects other than cancer risk. Glyphosate is listed in EPA's group D for cancer risk, which means there is not enough evidence and not enough data to demonstrate that it is a cancer risk (1988).

Studies Conducted in a Forest Environment

The results of environmental fate studies conducted on glyphosate in forest environments vary from study to study. Variations in rates of aquatic dissipation are probably due to factors such as aerobic versus anaerobic conditions (Brightwell *et al*., 1978, Monsanto 1990a and 1990b). Initial residue concentrations in foliage are dependent upon the application rate; persistence in foliage varies with initial concentrations (Thompson *et al*., 1994). Rates of glyphosate degradation also vary considerably in different soils (Torstensson, 1985).

The following are eight studies which describe the environmental fate of glyphosate in the forest environment. The first two studies focus on leaching and runoff from forest watersheds. The other studies include determination of glyphosate dissipation in ponds, residues and persistence in foliage, distribution, mobility, and dissipation in soil, bioaccumulation and chronic toxicity and a study of abundance in birds.

Carlson J. and H. Fiore, 1993. A study was conducted in 1991-1993 by staff of the Eldorado National Forest (ENF) to monitor for glyphosate, triclopyr and hexazinone in water and stream bed sediments. Glyphosate was applied to forest service lands in July and August 1991, as a 2% solution of Accord® at 2.1 lbs active ingredient per acre (ai/acre). Due to the timing of the application, the likelihood for off-site movement from rain runoff was low. By the time the fall rains occurred, glyphosate had probably degraded. Surface water, groundwater and stream bed samples were collected immediately before and after application and during storms and snowmelt runoff. In the 1991-92 study, no glyphosate was detected in any of the background water samples or the two days post-application water samples. Also, no glyphosate was detected in water samples taken during a storm occurring within 90 days of treatment or in any sediment samples.

H. Fiore, 1995. In the 1992-93 study, applications were made between early May and early August 1992 and between early May and late June 1993. Glyphosate was detected at 186 ppb in one background water sample in 1992. ENF staff suspected that the detection was a false positive since it was reported in a pre-application sample. Glyphosate was also detected at 88 ppb in the only sediment sample taken after the first 1992 spring storm. There were no detections in any of the water or sediment samples collected in 1993.

Goldsborough, L.G. and A.E. Beck, 1989. This study found that glyphosate dissipated rapidly in small forest ponds. Roundup® herbicide was applied at a rate of 0.59 lb ai/acre to the surface of four small boreal forest ponds and to six *in situ* microcosms contained in polyethylene basins. Each microcosm initially contained 40 L of unfiltered water collected from a nearby stream. Three randomly-selected microcosms contained 0.01 m^3 of intact sediment collected from a nearby pond. Initial glyphosate concentrations in surface water samples collected within 0.5 to 6 hours after application averaged 53 ppb. Levels of AMPA did not exceed 2.2 ppb in any pond water samples and in most cases were at or below the 0.50 ppb detection limit. Glyphosate levels remained at or above the initial treatment concentration in those microcosms containing only water but decreased rapidly in the three microcosms containing pond sediment. The average estimated half-life for glyphosate dissipation in the microcosms containing pond sediment was 5.8 days. Concentrations of AMPA in microcosms were much lower than the levels of glyphosate and did not exceed 20 ppb.

D.G. Thompson *et al*., 1994. A study was conducted by Canadian Forest Service staff to monitor the levels and persistence of glyphosate and triclopyr ester in foliage. Data were used to draw relationships among the chemical fate, efficacy, and environmental toxicology associated with these compounds. Three different formulations of glyphosate were applied to a variety of competitive shrub species, among which sugar maple predominated. The maximum initial foliar residues of 529, 773, and 777 mg/kg were dependent upon the application rate and increased by a similar factor for each kilogram of herbicide applied, irrespective of formulation type. Initial deposit levels were generally consistent with previously published estimates for aerial applications in forestry. The rate of dissipation of foliar residues was dependent upon initial concentration for all glyphosate formulations. The average period for 50% dissipation was 2 days and for 90% dissipation was <16 days. Statistical analysis confirmed that glyphosate residue dissipation was independent of the salt formulation applied.

L.M. Horner, 1990. A forestry dissipation study was conducted by staff of the Monsanto Agricultural Company. Glyphosate (Accord®) was aerially applied at the maximum label rate of 3.75 lb ai/acre to three, 20-acre forestry sites representative of areas of normal silviculture practice in the U.S. The distribution, mobility, and dissipation of glyphosate in the soil were determined. The results of this study found that when used under normal silviculture practices according to label directions, the maximum combined glyphosate and AMPA residue level in soil is less than 5 ppm. The average half-life for the dissipation of glyphosate was 100 days and 118 days for AMPA. It was also determined that under conditions of high rainfall, glyphosate and AMPA are tightly bound to the soil and do not move vertically in the soil profile.

D.N. Roy *et al*., 1989. Roy *et al*. investigated the persistence, movement, and degradation of glyphosate in selected Canadian forest soils. One sandy soil site was selected for persistence and leaching studies and one clay soil site was selected for a mobility study. All dead wood, live brush, and as much vegetation as possible were manually removed from sandy soil site with minimal disturbance of the 5-10 cm soil horizon. For the clay soil test site, dead wood and other matter thought to have a potential for runoff channeling were removed, an application strip at the top of the 8E slope was cleared, and a trench was prepared at the bottom of the slope for the collection of runoff water.

For the sandy soil site, the half-life for glyphosate dissipation was 24 days, and the time required for 90% dissipation was 78 days. With the exception of the 14 day after treatment sampling event, glyphosate was found only in the upper organic layer of the soil. There was no evidence of lateral movement of glyphosate down the 8E slope at the clay soil site. No glyphosate residues greater than or equal to 0.1 ppm were detected at any of the sampling stations located down slope from the application zone or in the runoff water collected in the trench.

Monsanto Co, 1995. This study provided bioaccumulation information pertaining to glyphosate usage in a forest environment. Glyphosate was applied aerially as Roundup® herbicide (360 g/l glyphosate acid) to a 20-acre forest test plot which included a small fish containing stream and its buffer zones. Water, stream sediment and fish biomass samples were collected. Small mammals including voles, mice, shrews, chipmunks, red squirrels and wood rats were live-trapped. The peak concentration of glyphosate in the water on the first day of application was 0.27 ppm, declining to less than 0.002 ppm by day four. No measurable residues of glyphosate were found in fish. Low levels of residue were found in the bodies and viscera of mice and shrews but these levels dissipated to non-detectable in most cases by day 28 and in all cases by day 55. Glyphosate levels found in the mice were far lower than levels found in the foliage, indicating a bioconcentration factor of less than one. The predator, the shrew, did not accumulate more glyphosate than the prey, the mouse.

Chronic toxicity to aquatic invertebrates (*Daphnia magna*) was reported. Six groups of 20 *Daphnia magna* were exposed to glyphosate (98.7% pure) at concentrations of 0, 3.0, 9.4, 30, 94.9 and 300 mg/l for 21 days. All daphnids exposed to 300 mg/l died within five days from the start of exposure. No significant mortality was observed in any of the other treatment groups. Another study with five groups of 40 *Daphnia magna* (less than 24-hr old) placed into four replicate chambers per group and exposed to glyphosate (99.7% pure) concentrations of 0, 25, 50, 99, 100 and 397 mg/l for 21 days, observed decreases in the mean number of young/adult/reproductive day in the upper three concentration levels (96, 186, 378 mg/l).

D. Santillo *et al*., 1989. A three year study on songbird abundance in forests was conducted in Maine. Following glyphosate treatment of clearcuts in Maine forests, the total number of birds and the abundance of three common species of birds decreased in comparison to untreated control areas. The decrease in bird abundance was correlated with a decrease in the diversity of the habitat. The study also found the numbers of small mammals were reduced on the glyphosate treated clearcuts in comparison to the untreated controls. Shrews were less abundant on treated clearcuts for three years following treatment, while mice were less abundant for two years. Decreases in small mammal abundance were paralleled by reductions in the amount of plant cover, the amount of plant food, and the number of invertebrates on the plants.

Plant Residues and Uptake

Brecke and Duke (1980) demonstrated that glyphosate penetrates plant cuticles within 4 hours, but is slowly taken up by mesophyll cells. Caseley and Coupland (1985) suggested that glyphosate uptake is a biphasic process with initial rapid penetration followed by slower symplastic uptake. The duration of both steps are dependent on a number of factors, including species, age, environmental conditions, concentration of glyphosate, and concentration of the surfactant. Green *et al.* (1992) demonstrated that foliar absorption of glyphosate was slow in both red maple and white oak with only 37 to 38% absorbed over a period of days and no significant increase in absorption thereafter. Similarly, D'Anieri *et al.* (1990) reported 42% foliar absorption in red maple over 14 days. Green *et al*. and D'Anieri *et al.* suggested that differential foliar absorption played an important role in hardwood tolerance. However, both studies indicated that differential symplastic translocation was an important factor in observed tolerance of red maple.

In a study by Newton *et al.* 1984, glyphosate herbicide residues and metabolites were evaluated in forest brush field ecosystems in the Oregon Coast Range which had been aerially treated with 2.9 lb/acre glyphosate. Deposits were recorded at various canopy depths to determine interception and residues in foliage, litter, soil, stream water, sediments, and wildlife for the following 55 days. There were decreases in residues probably resulting largely from degradation or from washing by rain. Foliar glyphosate residues had been in place, dry, for 12 hours before rain began. Residues markedly decreased after the rain, dropping from 84.0 to 4.3 ppm in the crown during the first 35 hours. Residues then decreased from 4.3 to 1.7 ppm in 6 days and 1.1 ppm in the next 7 days, based on sampling at three stations. The other sampling strata showed similar patterns. The half-life of glyphosate ranged from 10 to 27 days in foliage and litter and twice as long in soil. AMPA was found at low concentrations but degraded rapidly.

N-nitrosoglyphosate, a trace impurity in glyphosate, was not detected.

Conclusion

Glyphosate is a non-selective, non-residual broad-spectrum, foliar applied, post-emergence herbicide that is highly effective against emerged grasses, brush and broad-leaf weeds. The summarized studies indicate that glyphosate is adsorbed to mineral clays and organic matter and is excluded from these sites by inorganic phosphate. Glyphosate has limited preemergence herbicidal activity in most soils because of its tendency to adsorb strongly to soil. A low Koc is an indication that glyphosate will not move readily through soil, and under conditions of the summarized studies, glyphosate would not leach into non-target areas. Glyphosate is inactivated in soil and water by microbial degradation. When applied to foliage, glyphosate is readily absorbed and translocated to various parts of plant via the phloem. Recent data indicate that glyphosate appears to be relatively nontoxic to mammals, birds, and fish and shows no signs of bioaccumulation in the food chain.

Glyphosate herbicide is used predominantly in two ways for managing forest vegetation. A broadcast application by ground equipment is performed to control or partially control woody brush, trees and herbaceous woods for site preparation; a targeted application is made to selectively control competing vegetation once conifers are established.

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