

GLYPHOSATE

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Herbicide Basics

Chemical formula: N-(phosphonomethyl) glycine

Herbicide Family:
None generally recognized

Target Species: most annual and perennial plants

Forms: salts

Formulations: SL, EC

Mode of Action: amino acid synthesis inhibitor

Water Solubility:
900,000 ppm

Adsorption potential: high

Primary degradation mech:
slow microbial metabolism

Average Soil Half-life:
47 days

Mobility Potential: low

Dermal LD50 for rabbits:
>5,000 mg/kg

Oral LD50 for rats:
5,600 mg/kg

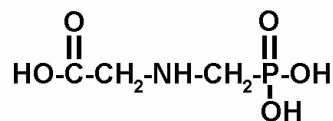
LC50 for bluegill sunfish:
120 mg/L

Trade Names: RoundUp[®], RoundUp-Pro[®], Rodeo[®], GlyPro[®], Accord[®], Glyphomax[®], Touchdown[®]

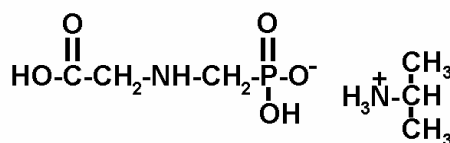
Manufacturers: Monsanto, Cenex/Land O'Lakes, Dow AgroSciences, Du Pont, Helena, and Platte.

Synopsis

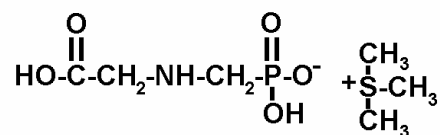
Glyphosate is a non-selective, systemic herbicide that can control most annual and perennial plants. It controls weeds by inhibiting the synthesis of aromatic amino acids necessary for protein formation in susceptible plants. Glyphosate is strongly adsorbed to soil particles, which prevents it from excessive leaching or from being taken-up from the soil by non-target plants. It is degraded primarily by microbial metabolism, but strong adsorption to soil can inhibit microbial metabolism and slow degradation. Photo- and chemical degradation are not significant in the dissipation of glyphosate from soils. The half-life of glyphosate ranges from several weeks to years, but averages two months. In water, glyphosate is rapidly dissipated through adsorption to suspended and bottom sediments, and has a half-life of 12 days to ten weeks. Glyphosate by itself is of relatively low toxicity to birds, mammals, and fish, and at least one formulation sold as Rodeo[®] is registered for aquatic use. Some surfactants that are included in some formulations of glyphosate, however, are highly toxic to aquatic organisms, and these formulations are not registered for aquatic use. Monsanto's patent for glyphosate expired in 2000, and other companies are already selling glyphosate formulations.



Glyphosate acid



Glyphosate isopropylamine salt



Glyphosate trimethylsulfonium salt

Herbicide Details

Chemical Formula: N-(phosphonomethyl) glycine

Trade Names: Monsanto discovered and held the patent for glyphosate, and was for many years, the only company that manufactured and sold this herbicide. The patent expired in 2000, however, and already several other companies are making and selling glyphosate formulations. Some of the current trade names include: Roundup Ultra[®], Roundup Pro[®], Accord[®], Honcho[®], Pondmaster[®], Protocol[®], Rascal[®], Expedite[®], Ranger[®], Bronco[®], Campaign[®], Landmaster[®], and Fallow Master[®] by Monsanto; Glyphomax[®] and Glypro[®] by Dow AgroSciences; Glyphosate herbicide by Du Pont; Silhouette[®] by Cenex/Land O'Lakes; Rattler[®] by Helena; MirageR[®] by Platte; JuryR[®] by Riverside/Terra; and Touchdown[®] by Zeneca. As of November 2001, Rodeo[®] (previously manufactured by Monsanto) is now being manufactured by Dow AgroSciences and Monsanto is now producing Aquamaster[®].

Manufacturers: Current manufacturers include Monsanto, Cenex/Land O'Lakes, Helena, Platte, Riverside/Terra, Dow AgroSciences, and Zeneca.

Use Against Natural Area Weeds: Glyphosate is a broad-spectrum, nonselective systemic herbicide that kills or suppresses many grasses, forbs, vines, shrubs, and trees. Care should be taken, especially in natural areas, to prevent it from being applied to desirable, native plants, because it will likely kill them. In terrestrial systems, glyphosate can be applied to foliage, green stems, and cut-stems (cut-stumps), but cannot penetrate woody bark (Carlisle & Trevors 1988). Only certain formulations of glyphosate (e.g., Rodeo[®]) are registered for aquatic use, as glyphosate by itself is essentially non-toxic to submersed plants (Forney & Davis 1981), but the adjuvants often sold with glyphosate may be toxic to aquatic plants and animals.

Glyphosate is one of the most commonly used herbicides in natural areas, because it provides effective control of many species. Natural area weeds that have been controlled with glyphosate include: bush honeysuckle (*Lonicera maackii*), cogon grass (*Imperata cylindrica*), common buckthorn (*Rhamnus cathartica*), glossy buckthorn (*Frangula alnus*), Japanese honeysuckle (*Lonicera japonica*), and smooth brome (*Bromus inermis*). In TNC preserves, glyphosate has been used to control dewberries (*Rubus* spp.), bigtooth aspen (*Populus grandidentata*), and black cherry (*Prunus serotina*) at Kitty Todd preserve in Ohio, sweetclover (*Melilotus officinalis*) in Indiana preserves, leafy spurge (*Euphorbia esula*) and St. John's wort/Klamath weed (*Hypericum perforatum*) in Michigan preserves, and bindweed (*Convolvulus arvensis*) and velvetgrass (*Holcus lanatus*) in Oregon and Washington preserves.

In aquatic or wetland systems, glyphosate has successfully controlled common reed (*Phragmites australis*) in Delaware, Michigan, and Massachusetts preserves, purple loosestrife (*Lythrum salicaria*) in Indiana and Michigan preserves, reed canarygrass (*Phalaris arundinacea*) in Illinois preserves, and glossy buckthorn (*Frangula alnus*) and hybrid cattail (*Typha x glauca*) in Michigan preserves.

Mode of Action: Glyphosate kills plants by inhibiting the activity of the enzyme 5-enolpyruvylshikimic acid-3-phosphate synthase (EPSP), which is necessary for the formation of the aromatic amino acids tyrosine, tryptophan, and phenylalanine. These amino acids are important in the synthesis of proteins that link primary and secondary metabolism (Carlisle & Trevors 1988). EPSPs are present in the chloroplast of most plant species, but are not present in animals. Animals need these three amino acids, but obtain them by eating plants or other animals.

Glyphosate is therefore, relatively non-toxic to animals (Monsanto Company 1985). Certain surfactants or other ingredients that are added to some glyphosate formulations are toxic to fish and other aquatic species (EXTOXNET 1996).

Glyphosate can also act as a competitive inhibitor of phosphoenolpyruvate (PEP), which is one of the precursors to aromatic amino acid synthesis. It also affects other biochemical processes, and, although these effects are considered secondary, they may be important in the total lethal action of glyphosate.

Dissipation Mechanisms:

Summary: Glyphosate is degraded primarily by microbial metabolism. Glyphosate is believed to be susceptible to photodegradation (Lund-Hoie & Friestad 1986), but the extent to which this occurs is uncertain. Glyphosate is not significantly degraded by other chemical mechanisms in the field. Glyphosate is strongly adsorbed to soil, which can slow microbial metabolism but prevents excessive movement in the environment. Glyphosate is non-volatile (T. Lanini, pers. obs).

Volatilization

Glyphosate does not volatilize readily when applied in the field (T. Lanini, pers. obs.).

Photodegradation

Although originally thought to be unaffected by sunlight (Rueppel et al. 1977), later studies found glyphosate to be susceptible to photodegradation (Lund-Hoie & Friestad 1986; Carlisle & Trevors 1988). Lund-Hoie and Friestad (1986) reported a half-life of four days for glyphosate in deionized water under UV light.

Microbial Degradation

Glyphosate is degraded primarily by microbial metabolism. Two steady rates of degradation have been identified (Rueppel et al. 1977). It has been hypothesized that the more rapid rate of degradation represents the metabolism of unbound glyphosate molecules, while the slower rate represents the metabolism of glyphosate molecules bound to soil particles (Nomura & Hilton 1977; Rueppel et al. 1977). The degradation of glyphosate is slower in soils with a higher adsorption capacity. Degradation rate was also affected by the particular microbial community of each soil (Carlisle & Trevors 1988; Malik et al. 1989). The primary metabolite of glyphosate is aminomethylphosphonic acid, which is non-toxic and degraded microbially at a somewhat slower rate than the parent compound (Nomura & Hilton 1977; Rueppel et al. 1977;

Carlisle & Trevors 1988). A number of other minor, biodegradable metabolites have also been identified.

Adsorption

Glyphosate is water-soluble, but it has an extremely high ability to bind to soil particles. Adsorption of glyphosate increases with increasing clay content, cation exchange capacity, and decreasing soil pH and phosphorous content (Sprankle et al. 1975a,b; Hance 1976; Nomura & Hilton 1977; Rueppel et al. 1977; Glass 1987). Glyphosate is adsorbed to soil particles rapidly during the first hour following application and slowly thereafter (Sprankle et al. 1975b). Strong adsorption to soil particles slows microbial degradation, allowing glyphosate to persist in soils and aquatic environments. Because glyphosate rapidly binds to soils, it has little or no herbicidal activity (“killing power”) once it touches soil (Sprankle et al. 1975a; Hance 1976; Nomura & Hilton 1977). Glyphosate can also be inactivated by adsorption if mixed with muddy water.

Adsorption prevents glyphosate from being mobile in the environment except when the soil particles themselves are washed away (Sprankle et al. 1975b; Rueppel et al. 1977; Roy et al. 1989a). Comes et al. (1976) found that glyphosate sprayed directly into a dry irrigation canal was not detectable in the first irrigation waters flowing through the canal several months later, although glyphosate residues remained in the canal soils. In most cases, glyphosate is quickly adsorbed to suspended and bottom sediments (Feng et al. 1990).

Chemical Decomposition

Glyphosate is not readily hydrolyzed or oxidized in the field (Rueppel et al. 1977; Anton et al. 1993; Zaranyika & Nyandoro 1993).

Behavior in the Environment

Summary: Glyphosate binds readily with soil particles, which limits its movement in the environment. It is degraded through microbial metabolism with an average half-life of two months in soils and two to ten weeks in water. In plants, glyphosate is slowly metabolized.

Soils

Glyphosate is highly water soluble, but unlike most water-soluble herbicides, glyphosate has a very high adsorption capacity. Once glyphosate contacts soil it is rapidly bound to soil particles rendering it essentially immobile (Roy et al. 1989a; Feng & Thompson 1990). Unbound glyphosate molecules are degraded at a steady and relatively rapid rate by soil microbes (Nomura & Hilton 1977; Rueppel et al. 1977). Bound glyphosate molecules also are biologically degraded at a steady, but slower rate. The half-life of glyphosate in soil averages two months but can range from weeks to years (Nomura & Hilton 1977; Rueppel et al. 1977; Newton et al. 1984; Roy et al. 1989a; Feng & Thompson 1990; Anton et al. 1993). Although the strong adsorption of glyphosate allows residues to persist for over a year, these residues are largely immobile and do not leach significantly. Feng and Thompson (1990) found that >90% of glyphosate residues were present in the top 15 cm of soil and were present as low as 35 cm down the soil column in only one of 32 samples. Adsorption to soil particles prevents glyphosate from being taken-up by the roots of plants.

Water

Because glyphosate binds strongly to soils, it is unlikely to enter waters through surface or sub-surface runoff except when the soil itself is washed away by runoff, and even then, it remains bound to soil particles and unavailable to plants (Rueppel et al. 1977, Malik et al. 1989). Most glyphosate found in waters likely results from runoff from vegetation surfaces, spray drift, and intentional or unintentional direct overspray. In most cases, glyphosate will dissipate rapidly from natural water bodies through adsorption to organic substances and inorganic clays, degradation, and dilution (Folmar et al. 1979; Feng et al. 1990; Zaranyika & Nyandoro 1993; Paveglio et al. 1996). Residues adsorbed to suspended particles are precipitated into bottom sediments where they can persist until degraded microbially with a half-life that ranges from 12 days to 10 weeks (Goldsborough & Brown 1993; EXTOWNET 1996). At least one study found that >50% of the glyphosate added directly to the waters of an irrigation canal were still present 14.4 km downstream (Comes et al. 1976).

Vegetation

Glyphosate is metabolized by some, but not all plants (Carlisle & Trevors 1988). It is harmless to most plants once in the soil because it is quickly adsorbed to soil particles, and even when free, it is not readily absorbed by plant roots (Hance 1976). The half-life of glyphosate on foliage has been estimated at 10.4 to 26.6 days (Newton et al. 1984). Roy et al. (1989b) found 14% and 9% of applied glyphosate accumulated in the berries of treated blueberry and raspberry bushes, respectively. These residues dissipated from the fruit with a half-life of <20 days for blueberries and <13 days for raspberries (Roy et al. 1989b).

Environmental Toxicity

Birds and Mammals

Glyphosate is of relatively low toxicity to birds and mammals (Evans & Batty 1986). The LD50 of glyphosate for rats is 5,600 mg/kg and for bobwhite quail, >4,640 mg/kg. EPA's Re-registration Eligibility Decision states that blood and pancreatic effects and weight gain were noted during subchronic feeding studies with rats and mice (EPA 1993). Other studies show developmental and reproductive impacts to animals given the highest dose.

Newton et al. (1984) examined glyphosate residues in the viscera of herbivores following helicopter application of glyphosate to a forest in Oregon and found residue levels comparable to those found in litter and ground cover (<1.7 mg/kg). These residue levels declined over time and were undetectable after day 55 (Newton et al. 1984). Although carnivores and omnivores exhibited much higher viscera residue levels (5.08 mg/kg maximum), Newton et al. (1984) concluded that carnivores were at lower risk than herbivores due to the lower relative visceral weights and a proportionally lower level of food intake.

Batt et al. (1980) found no effect on chicken egg hatchability or time to hatch when an egg was submerged in a solution of 5% glyphosate. Sullivan and Sullivan (1979) found that black-tailed deer showed no aversion to treated foliage and consumption of contaminated forage did not reduce total food intake. Significant impacts to bird and mammal populations due to large-scale habitat alterations following treatment of forest clearcuts with glyphosate have been reported (Morrison & Meslow 1984; Santillo et al. 1989a,b; MacKinnon & Freedman 1993).

Aquatic Species

Glyphosate itself is of moderate toxicity to fish. The 96-hour LC50 of technical grade glyphosate for bluegill sunfish and rainbow trout are 120 mg/L and 86 mg/L, respectively. Fish exposed to 5 mg/L of glyphosate for two weeks were found to have gill damage and liver damage was observed at glyphosate concentrations of 10 mg/L (Neskovic et al. 1996). The technical grade of glyphosate is of moderate toxicity to aquatic species, and the toxicity of different glyphosate formulations can vary considerably. For example, Touchdown 4-LC[®] and Bronco[®] have low LC50s for aquatic species (<13 mg/L), and are not registered for aquatic use. On the other hand, Rodeo[®] has relatively high LC50s (>900 mg/L) for aquatic species and is permitted for use in aquatic systems. The surfactant in Roundup[®] formulations is toxic to fish, however, Rodeo[®] has no surfactant, and is registered for aquatic use.

The surfactant X-77 Spreader[®], which is often used in conjunction with Rodeo[®], is approximately 100 times more toxic to aquatic invertebrates than Rodeo[®] alone (Henry et al. 1994). The surfactant MONO818[®] is included in Roundup[®] formulations because it aids the break-down of surface tension on leaf surfaces, but it may also interfere with cutaneous respiration in frogs and gill respiration in tadpoles (Tyler 1997 a,b). In addition, MONO818[®] is highly toxic to fish (Folmar et al. 1979; Servizi et al. 1987). The LC50 of MONO818[®] is 2-3 mg/L for sockeye, rainbow, and coho fry (Folmar et al. 1979; Servizi et al. 1987; Tyler 1997 a,b). The LC50 of Roundup[®] for bluegill sunfish and rainbow trout is only slightly higher at 6-14 mg/L and 8-26 mg/L, respectively. Similarly for *Daphnia*, the 96-hour LC50 of glyphosate alone is 962 mg/L, but the LC50 of Roundup[®] drops to 25.5 mg/L (Servizi et al. 1987). Roundup[®] is therefore not registered for use in aquatic systems.

Despite these toxicity levels, Hildebrand et al. (1980) found that Roundup[®] treatments at concentrations up to 220 kg/ha did not significantly affect the survival of *Daphnia magna* or its food base of diatoms under laboratory conditions. In addition, Simenstad et al. (1996) found no significant differences between benthic communities of algae and invertebrates on untreated mudflats and mudflats treated with Rodeo[®] and X-77 Spreader[®]. It appears that under most conditions, rapid dissipation from aquatic environments of even the most toxic glyphosate formulations prevents build-up of herbicide concentrations that would be lethal to most aquatic species.

Other Non-Target Organisms

Roberts and Berk (1993) investigated the effects of Roundup[®] on chemoattraction of the protozoa *Tetrahymena pyriformis* and found that it significantly interfered with chemoreception but not motility. Doses of glyphosate <10 ppm were stimulatory to soil microflora including actinomycetes, bacteria, and fungi, while concentrations > 10 ppm had detrimental impacts on microflora populations in one study (Chakravarty & Sidhu 1987). While some short-term studies (< 30 days) found glyphosate caused significant impacts to microbial populations, Roslycky (1982) found that these populations rebound from any temporary increase or decrease within 214 days. Similarly, Tu (1994) found that microorganisms recovered rapidly from treatment with glyphosate and that the herbicide posed no long-term threat to microbial activities.

Application Considerations:

Glyphosate can be applied using conventional, recirculating, wet apron, hooded and hand-operated sprayers; controlled drop, rope-wick, roller, and carpet applicators; mistblowers; injectors; and wipe-on devices (Carlisle & Trevors 1988). Feng et al. (1990) found that 10 meter buffer zones limited unintentional effects through chemical drift and off-target deposits into streams during application, while Marrs et al. (1993) concluded that 20 meters was a safe buffer width. Liu et al. (1996) found that increasing the glyphosate concentration was more effective in controlling weeds than increasing the droplet size. Thielen et al. (1995) concluded that the cations of hard water, including Ca^{++} and Mg^{++} , can greatly reduce the efficacy of glyphosate when present in a spray solution. Addition of ammonium sulfate or other buffer can precipitate out heavy elements in “hard” water if added before the herbicide is mixed with water.

When glyphosate is used as an aquatic herbicide, do not treat the entire water body at one time. Treat only one-third to one-half of any water body at any one time, to prevent fish kills caused by dissolved oxygen depletion.

Safety Measures:

Some glyphosate formulations are in EPA toxicity categories I and II (the two highest categories) for eye and skin exposure. Care should be taken and protective clothing worn to prevent accidental contact of these formulations on skin or eyes.

Human Toxicology:

EPA classified glyphosate as a “Group E” carcinogen or a chemical that has not shown evidence of carcinogenicity in humans (EPA 1993).

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