

TRICLOPYR

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Herbicide Basics

Chemical formula: [(3,5,6-trichloro-2-pyridinyl)oxy] acetic acid

Herbicide Family:
Pyridine (Picolinic acid)

Target Species: Broadleaf herbs and woody species

Forms: salt & ester

Formulations: EC, SL

Mode of Action: Auxin mimic

Water solubility: 430 ppm (acid), 23 mg/L (ester), 2,100,000 mg/L (salt)

Adsorption potential:
Intermediate (higher for ester than salt)

Primary degradation mech:
Microbial metabolism, photolysis, and hydrolysis

Average Soil Half-life: 30 days

Mobility Potential: Intermediate

Dermal LD50 for rabbits:
>2,000 mg/kg

Oral LD50 for rats:
713 mg/kg

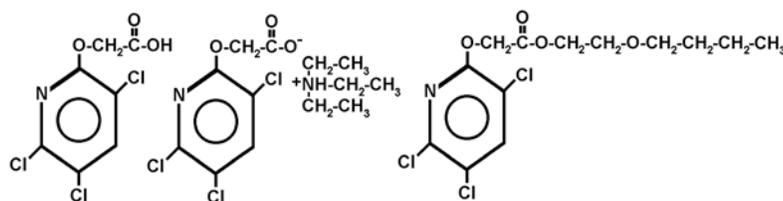
LC50 for bluegill sunfish:
148 mg/L

Trade Names: Garlon® and Access®

Manufacturers: Dow Agro-Sciences and Platte

Synopsis

Triclopyr is a selective systemic herbicide used to control woody and herbaceous broadleaf plants along right-of-ways, in forests, and in grasslands and parklands. It has little or no impact on grasses. Triclopyr controls target weeds by mimicking the plant hormone auxin, causing uncontrolled plant growth. There are two basic formulations of triclopyr - a triethylamine salt, and a butoxyethyl ester. In soils, both formulations degrade to the parent compound, triclopyr acid. Degradation occurs primarily through microbial metabolism, but photolysis and hydrolysis can be important as well. The average half-life of triclopyr acid in soils is 30 days. Offsite movement through surface or sub-surface runoff is a possibility with triclopyr acid, as it is relatively persistent and has only moderate rates of adsorption to soil particles. In water, the salt formulation is soluble, and with adequate sunlight, may degrade in several hours. The ester is not water-soluble and can take significantly longer to degrade. It can bind with the organic fraction of the water column and be transported to the sediments. Both the salt and ester formulations are relatively non-toxic to terrestrial vertebrates and invertebrates. The ester formulation, however, can be extremely toxic to fish and aquatic invertebrates. Because the salt cannot readily penetrate plant cuticles, it is best used as part of a cut-stump treatment or with an effective surfactant. The ester can be highly volatile and is best applied at cool temperatures on days with no wind. The salt formulation (Garlon 3A®) can cause severe eye damage.



Triclopyr acid

Triethylamine salt

Butoxyethyl ester

Herbicide Details

Chemical Formula: [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid

Trade Names: There are two basic formulations of triclopyr: a triethylamine salt (triclopyr amine or salt), and a butoxyethyl ester (triclopyr ester). The amine formulation is sold under the trade name Garlon 3A[®] and is marketed in garden shops and hardware stores as Turflon Amine[®] or as Brush-B-Gone[®]. The ester formulation is sold under the trade name Garlon 4[®] and is marketed in garden shops and hardware stores as Turflon Ester[®]. Other trade names include Access[®], Crossbow[®], ET[®], PathFinder II[®], Redeem[®], and Remedy[®]. These products also may be mixed with picloram or 2,4-D to increase their versatility.

Manufacturers: Dow Agrosiences (formerly known as DowElanco or Dow Chemical), Platte

Use Against Natural Area Weeds: Triclopyr is used to control broadleaf herbs and woody species (WSSA 1994). It is particularly effective at controlling woody species with cut-stump or basal bark treatments. Susceptible species include the brooms (*Cytisus* spp., *Genista* spp., and *Spartium* spp.), the gorses (*Ulex* spp.), and fennel (*Foeniculum vulgare*). Triclopyr ester formulations are especially effective against root- or stem-sprouting species such as buckthorns (*Rhamnus* spp.), ash (*Fraxinus* spp.), and black locust (*Robinia pseudoacacia*), because triclopyr remains persistent in plants until they die.

Even though offsite movement of triclopyr acid through surface or sub-surface runoff is a possibility, triclopyr is one of the most commonly used herbicides against woody species in natural areas. Bill Neil, who has worked extensively on tamarisk/saltcedar (*Tamarix* spp.) control, concluded that Pathfinder II[®], a triclopyr ester formulation by DowElanco, is the most cost effective herbicide for combating saltcedar. On preserves across the U.S., triclopyr has provided good control of tree-of-heaven (*Ailanthus altissima*), salt cedar (*Tamarix* spp.), glossy buckthorn (*Frangula alnus*), common buckthorn (*Rhamnus cathartica*), sweet fennel (*Foeniculum vulgare*), Brazilian peppertree (*Schinus terebinthifolius*), and Chinese tallow tree (*Sapium sebiferum*). TNC preserves in Hawaii have successfully used triclopyr to control blackwood acacia (*Acacia melanoxylon*), bush honeysuckle (*Lonicera maackii*), Chinese banyan (*Ficus microcarpa*), corkystem passionflower (*Passiflora suberosa*), eucalyptus (*Eucalyptus globulus*), Florida prickly blackberry (*Rubus argutus*), Mexican weeping pine (*Pinus patula*), Monterey pine (*Pinus radiata*), strawberry guava (*Psidium cattleianum*), tropical ash (*Fraxinus uhdei*), and velvet leaf (*Miconia calvescens*). Triclopyr can also be used in forest plantations to control brush without significant impacts to conifers (Kelpsas & White). Spruces (*Picea* spp.) can tolerate triclopyr, but some species of pine (*Pinus* spp.) however, can only tolerate triclopyr during the dormant fall and winter months (Jotcham et al. 1989).

Mode of Action: Triclopyr is an auxin mimic or synthetic auxin. This type of herbicide kills the target weed by mimicking the plant growth hormone auxin (indole acetic acid), and when administered at effective doses, causes uncontrolled and disorganized plant growth that leads to plant death. The exact mode of action of triclopyr has not been fully described, but it is believed to acidify and “loosen” cell walls, allowing cells to expand without normal control and

coordination. Low concentrations of triclopyr can stimulate RNA, DNA, and protein synthesis leading to uncontrolled cell division and growth, and, ultimately, vascular tissue destruction. Conversely, high concentrations of triclopyr can inhibit cell division and growth.

Dissipation Mechanisms:

Summary: Both the ester and amine formulations are degraded by sunlight, microbial metabolism, and hydrolysis. In soils, both the ester and amine formulations will degrade rapidly to the parent compound, triclopyr acid. The acid and ester formulations bind well with soils, and therefore, are not likely to be mobile in the environment. The salt however, does not readily adsorb and can be mobile. The ester can be highly volatile (T. Lanini, pers. com.).

Volatilization

Ester formulations of triclopyr can be highly volatile, and care should be taken in their application. The potential to volatilize increases with increasing temperature, increasing soil moisture, and decreasing clay and organic matter content (Helling et al. 1971).

Photodegradation

Both the ester and salt formulations are degraded readily in sunlight to the parent compound, triclopyr acid, which is also photodegradable. A study of photolysis found the half-life of triclopyr acid on soil under midsummer sun was two hours (McCall & Gavit 1986). Photodegradation can be particularly important in water. Johnson et al. (1995) found triclopyr acid dissolved in water had a half-life due to photolysis of one to 12 hours.

Microbial Degradation

Microbial metabolism accounts for a significant percentage of triclopyr degradation in soils. In general, warm, moist soils with a high organic content will support the largest microbial populations and the highest rates of herbicide metabolism (Newton et al. 1990). Johnson et al. (1995a) found that microbial degradation of triclopyr was significantly higher in moist versus dry soils, and higher at 30° C than at 15° C (DT50 is 46 days versus 98 days in dry soils, and 57 days versus 199 days in moist soils, respectively). Additionally, the presence of sunlight plays a role in the rates of microbial metabolism of triclopyr. Johnson et al. (1995a) found that microbial metabolism was slowed when soil was deprived of light.

Chemical Decomposition

Hydrolysis of both the salt and ester to the acid form occurs readily in the environment and within plants (Smith 1976). McCall and Gavit (1986) reported that the ester was converted to an acid with a half-life of three hours, and that the rate of hydrolysis in water increased with an increase in pH.

Adsorption

Adsorption temporarily or permanently immobilizes triclopyr, but adsorption is not degradation. Adsorption is more important for the immobilization of the ester than of the salt formulation. The ester binds readily with the organic component of the soil, with adsorption rates increasing as organic content increases and soil pH decreases (Pusino et al. 1994; Johnson et al. 1995a). The salt form is soluble in water and binds only weakly with soil (McCall & Gavit 1986). The

strong bond between the ester and soils accounts for the relatively low mobility of the ester in soils, whereas the salt form is much more mobile (McCall & Gavit 1986). In practice, however, both compounds are degraded rapidly to triclopyr acid, which has an intermediate adsorption capacity.

Behavior in the Environment

Summary: In soils, both formulations are degraded by photolysis, microbial metabolism, and hydrolysis to the parent compound, triclopyr acid. Triclopyr acid has an intermediate adsorption potential, limiting movement of the acid in the environment. The acid degrades with an average half-life of 30 days. In water, the salt will remain in the water column until it is degraded, which can occur in as little as a few hours under favorable conditions. The ester formulation, however, is not water-soluble and can take significantly longer to degrade in water. Within plants, both the salt and ester formulations are hydrolyzed to the acid form, and transported through the plant. Residues can persist in the plant until the tissues are degraded in the environment.

Soils

Both the ester and salt formulations degrade rapidly in soils to triclopyr acid, and thereafter, behave similarly in soils. Adsorption, photodegradation, microbial metabolism, and volatility, can all play a role in the dissipation of triclopyr from soils. The reported half-life of triclopyr in soils varies from 3.7 to 314 days, but averages 30 days, depending on the formulation applied and the specific soil and environmental conditions. If soil conditions are warm and moist, microbial metabolism can be the primary means of degradation (Newton et al. 1990).

Johnson et al. (1995a) reported an average half-life of triclopyr acid in four laboratory soils of 138 days, but this time varied significantly with soil temperature. At 15°C half-lives ranged from 64-314 days, while at 30°C half-lives were 9-135 days (Johnson et al. 1995). In Southwest Oregon, Newton et al. (1990) found 24-51% of triclopyr residues remained after 37 days in a dry and cool climate. Following an increase in warmth and moisture, however, dissipation increased dramatically and triclopyr residues exhibited a half-life of 11-25 days. In a study of triclopyr persistence in soil and water associated with rice production, triclopyr had a half-life of less than ten days in the three soil types tested (Johnson et al. 1995b). In a pasture near Corvallis, Oregon, the half-life of triclopyr acid was estimated to be 3.7 days (Norris et al. 1987).

Because of the importance of photodegradation and a decrease in the size of microbial populations with soil depth, triclopyr located deeper in the soil column (>15 cm) degrades more slowly than residues near the surface (Johnson et al. 1995a). Traces of triclopyr residues have been found at soil depths of 45 cm as late as 477 days after application (Newton et al. 1990). Sandy soils that are highly permeable may therefore, retain triclopyr longer. Most studies, however, found that triclopyr generally does not tend to move in significant quantities below the top 15 cm of soil (Norris et al. 1987; Newton et al. 1990; Stephenson 1990; Johnson et al. 1995a).

Water

In water, the two formulations can behave very differently. The water-soluble salt is degraded in the water column through photolysis and hydrolysis (McCall & Gavit 1985). The ester, however, is not water-soluble and can be persistent in aquatic environments. The ester binds to organic particles in the water column and precipitates to the sediment layers (McCall & Gavit 1986). Bound ester molecules will degrade through hydrolysis or photolysis to triclopyr acid (Smith 1976), which will move back into the water column and continue to degrade. The rate of degradation is dependent on the water temperature, pH, and sediment content.

Triclopyr acid has an intermediate soil adsorption capacity. Thus, movement of small amounts of triclopyr residues following the first significant rainfall are likely (McCall & Gavit 1986), but further leaching is believed to be minor (Newton et al. 1990; Stephenson et al. 1990; Thompson et al. 1991). Movement of triclopyr through surface and subsurface runoff in areas with minimal rainfall is believed to be negligible (Newton et al. 1990; Stephenson et al. 1990). In southwest Oregon, Norris et al. (1987) found that neither leaching nor long-distance overland water flow contributed significant amounts of the herbicide into a nearby stream, and concluded that the use of triclopyr posed little risk for non-target organisms or downstream water users. Triclopyr can, however, enter waterways via aerial drift and inadvertent overspray. When the acid was applied to rice paddy fields, residues remained in the water column and were not found in significant amounts in the soil (Johnson et al. 1995b). Degradation in water was rapid and showed a half-life of four days.

Vegetation

Both the ester and salt formulations are hydrolyzed to the acid after entering plant tissue. The acid tends to remain in plants until they die or drop leaves and begin to decay (Newton et al. 1990). Newton et al. (1990) reported that triclopyr in evergreen foliage and twigs showed remarkable persistence. Although concentrations of triclopyr in the soil will decrease quickly and remain low through the winter, levels can rise again in the spring if a new supply of contaminated foliage falls from defoliating crowns (Newton et al. 1990). The residues of some herbicides in fruit have been shown to persist up to one month (Holmes et al. 1994). There is therefore a potential for long-term exposure of triclopyr to animal species that eat wild fruit. In non-target plants, triclopyr soil residues can cause damage via root uptake (Newton et al. 1990).

Environmental Toxicity

Birds and Mammals

Triclopyr is regarded as only slightly toxic to birds and mammals. The oral LD50 for rats is 630-729 mg/kg. The LD50s for mallard ducks and bobwhite quail are 1,698 mg/kg and 2,935 mg/kg, respectively. Newton et al. (1990) predicted that triclopyr would not be present in animal forage in doses large enough to cause either acute or chronic effects to wildlife, and concluded that the tendency for triclopyr to dissipate quickly in the environment would preclude any problems with bioaccumulation in the food chain. Garlon 3A[®] can cause severe eye damage to both humans and wildlife, due to the high pH of its water-soluble amine salt base. Care must be taken during mixing and application to prevent accidental splashing into eyes.

In a study of the potential effects of herbicide residues on forest songbirds, sub-lethal doses of triclopyr ester (500 mg/kg in the diet for 29 days) were found to cause weight loss and behavior alterations in zebra finches (Holmes et al. 1994). In a 1987 study of triclopyr metabolism using one cow, all traces of triclopyr were eliminated from the cow's urine within 24 hours, and no residues were detected in its milk or feces. This study, however, did not track whether any triclopyr was absorbed into the cow's tissues, or whether the triclopyr recovered in the urine was still active (Eckerlin 1987).

Aquatic Species

Triclopyr acid and the salt formulation are slightly toxic to fish and aquatic invertebrates. The LC50 of the acid and the salt formulation for rainbow trout are 117 mg/L and 552 mg/L, respectively, and for bluegill sunfish 148 mg/L and 891 mg/L, respectively. The ester formulation is highly toxic to fish and aquatic invertebrates, with an LC50 (96-hour) of 0.74 mg/L in rainbow trout and 0.87 mg/L in bluegill sunfish (WSSA 1994; EPA 1998). The hydrophobic nature of the ester allows it to be readily absorbed through fish tissues where it is rapidly converted to triclopyr acid. The acid can be accumulated to a toxic level when fish are exposed to sufficient concentrations or for sufficient durations.

The extent to which the toxic effects of the ester are reduced by degradation is poorly understood. Studies have shown that the ester formulation degrades rapidly to less toxic forms (Thompson et al. 1991). Kreutzweiser et al. (1994) however, has shown that there is a significant chance of acute lethal effects to fish exposed to low level residues for more than six hours. In addition, delayed lethal effects were seen in fish exposed to high concentrations for a short duration. Considering that Thompson et al. (1991) concluded that organisms subjected to direct overspray were exposed to a high level of herbicide for short periods of time while organisms downstream were exposed to low levels for longer periods, the findings of Kreutzweiser et al. (1994) are of concern.

Nevertheless, most authors including the authors of the fish mortality study have concluded that if applied properly, triclopyr would not be found in concentrations adequate to kill aquatic organisms. As a measure of precaution, however, Kreutzweiser et al. (1991) suggest that some water bodies remain at risk of lethal contamination levels including shallow and slow moving water bodies where dissipation is slow, and heavily shaded streams that experience reduced photodegradation.

Other Non-Target Organisms

Triclopyr inhibited growth of four types of ectomycorrhizal fungi associated with conifer roots at concentrations of 1,000 parts per million (ppm) and higher (Estok et al. 1989). Some evidence of inhibition of fungal growth was detected in bioassays with as little as 100 ppm triclopyr. Typical usage in forest plantations, however, results in triclopyr residues of only four to 18 ppm on the forest floor (Estok et al. 1989).

Application Considerations:**Application Under Unusual Conditions:**

Several natural area managers have found that Garlon 4[®] and 3A[®] are effective when applied in mid-winter as a cut-stump treatment against buckthorns (*Rhamnus cathartica* and *R. frangula*). It is often easier to get to these plants when boggy soils around them are frozen. Randy Heidorn, Deputy Director for Stewardship of the Illinois Nature Preserve Commission (INPC), recommends three protocols to increase the safety of triclopyr ester application in winter:

- (1) use a mineral oil based carrier;
- (2) make sure that at the time of application, no water is at or above the ground surface, and no snow or ice is present that might serve as a route to spread the herbicide following a thaw, and;
- (3) initiate a monitoring program to assess ambient water concentrations of triclopyr ester in communities that seasonally have water at or above the ground surface with little or no discharge (i.e. bogs).

Safety Measures

The salt formulation in Garlon 3A[®] can cause severe eye damage because of the high pH of its water-soluble amine salt base. Care should be taken to prevent splashing or other accident contact with eyes.

Human Toxicology

Because studies into the carcinogenicity of triclopyr have produced conflicting results, EPA has categorized triclopyr as a “Group D” compound, or a chemical that is not classifiable as to human carcinogenicity. The salt formulation in Garlon 3A[®] can cause severe eye damage.

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