

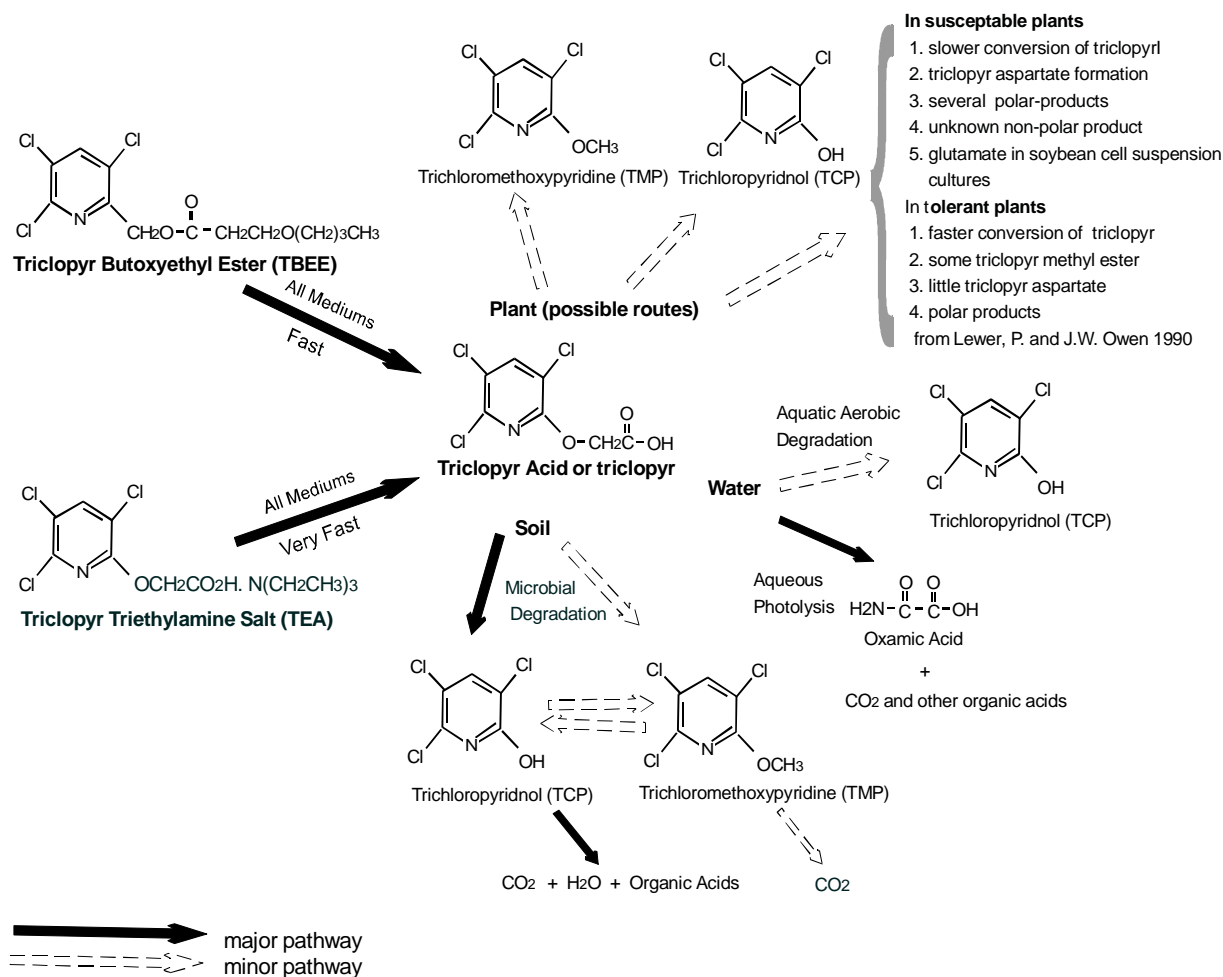
ENVIRONMENTAL FATE OF TRICLOPYR

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(January 2, 1997)

This document reviews all routes of environmental fate for triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) with an emphasis on plant uptake and plant metabolism under forest conditions. Triclopyr is a pyridine-based herbicide that comes in two formulations: the triethylamine salt (TEA) (in Garlon® 3A) and the butoxyethyl ester (TBEE) (in Garlon® 4).

Triclopyr Degradation



Triclopyr butoxyethyl ester (TBEE)^a

Molecular weight ^b	356.67
Water solubility (near 25 °C)	6.81 ppm
Vapor pressure (at 25 °C)	3.60x10 ⁻⁶ mmHg
Henry's constant	2.50x10 ⁻⁷
Hydrolysis half-life (in natural water at pH 6.7 and 25 °C) ^b	0.5 days
Octanol-water coefficient (Kow) ^c	12,589
Anaerobic half-life	26.45 days
Field dissipation half-life	39 days

Triclopyr triethylamine salt (TEA)^a

Molecular weight ^b	357.67
Water solubility (at 25 °C)	234,000 ppm
Vapor pressure (at 25 °C)	3.60x10 ⁻⁷ mmhg
Henry's constant	6.00x10 ⁻¹⁰
Soil adsorption coefficient (Koc) (range of data collected for four soil types)	24.0 to 144 cm ³ /g
Octanol-water coefficient (Kow)	1.23
Anaerobic half-life	1600 days
Aerobic half-life (Average of two samples, two soil types)	12.75 days
Field dissipation half-life	139 days

a- Data from Kollman and Segawa (1995).

b- Data from data package AMB-106279-E. DPR# 51566-001.

c- Personal communication from Vanelle Carrithers, Dow Elanco October 15, 1996.

Tolerances

eggs	0.05 ppm
Meat, fat and meat byproducts (except liver and kidney) of cattle, goats, hogs, horses, and sheep	0.05 ppm
Meat, fat and meat byproducts (except kidney) of poultry	0.1 ppm
Milk	0.01 ppm
Liver and kidney of cattle, goats, hogs, horses, and sheep	0.5 ppm
Rice, grain	0.3 ppm
Rice, straw	10.0 ppm

Toxicity

Triclopyr Acid	
Rat (oral, acute)	LD ₅₀ 713 mg/kg
Mallard duck (oral, acute)	LD ₅₀ 1,698 mg/kg
Mallard duck 8-day (oral)	LC ₅₀ >5,000ppm
Bobwhite quail 8-day (oral)	LC ₅₀ 2,934
Bluegill sunfish (96 hrs)	LC ₅₀ 148 ppm
Rainbow trout (96 hrs)	LC ₅₀ 117 ppm
<i>Daphnia magna</i> (48 hrs)	LC ₅₀ 132 ppm
Honeybee	LD ₅₀ 60.4 µg/bee
TBEE (96 hrs)	
Bluegill sunfish (96 hrs)	LC ₅₀ 0.36 ppm
Rainbow trout	LC ₅₀ 0.74-2.7 ppm

Data compiled by Jon Shelgren-Registration Branch, Department of Pesticide Regulation

Mode of action

Triclopyr is a pyridine-based herbicide used for the control of woody plants and annual and perennial broadleaf weeds. There are three products sold for forestry use in the United States: Garlon® 3A, a water-based concentrate containing three pounds of triclopyr per gallon as the triethylamine salt (TEA); Garlon® 4, an emulsifiable concentrate containing four pounds of triclopyr per gallon as the butoxyethyl ester (TBEE); and as Pathfinder® II, a ready-to-use dilute ester formulation (TBEE) (DowElanco meeting, 1996; U.S.D.A., 1984). TBEE and TEA convert to triclopyr acid. It is the triclopyr acid (known simply as triclopyr) that causes phytotoxicity (Lewer and Owen, 1990). Triclopyr is absorbed by leaves and roots and is moved throughout the plant. Lab experiments indicate that foliar uptake is fast with 90% of applied TBEE penetrating vegetation in about 12 hours (McCall and Gavit et al., 1986). Triclopyr can damage plants due to root uptake but does not work effectively that way (Newton et al., 1990). Triclopyr acts as a synthetic auxin, giving a plant an auxin overdose 1000 times natural levels, which disrupts the hormonal balance and interferes with growth. The effects occur at the cellular level first, then exterior effects are seen. Ethylene and protein production in the plant increases first then after

about one week, epinasty, abnormal leaf formation and stem swelling occur. Sometimes plants may resprout and then die (DowElanco meeting, 1996). Unlike the susceptibility of broadleaf plants, triclopyr has low phytotoxicity to grasses. Triclopyr, however, can cause injury to conifers at high application rates (Ghassemi et al., 1981). According to the label for Garlon®4, when applications are made as suggested for California, sprays may cause discolored needles and temporary growth suppression of some conifers. Since triclopyr is rapidly degraded by soil microorganisms, there is not enough residue left to injure plants the next growing season (Ghassemi et al., 1981).

Physical Chemical Properties and Environmental Fate of Triclopyr

Air: Both TBEE and TEA have low vapor pressures and thus volatilization occurs only to a minor extent. Low Henry's Law Constants (2.5×10^{-7} and 6.00×10^{-7} atm-m³/mol at 25 °C, respectively) indicate both formulations have little escaping tendency from an aqueous solution. With the exception of spray drift which can be avoided with proper application techniques, triclopyr is not expected to be found in air.

Water: TEA converts to triclopyr acid in seconds (DowElanco meeting, 1996). TBEE rapidly converts to triclopyr acid by hydrolysis in both natural water and soil in less than a day (Somasundarm and Coats, 1991; Bidlack, 1978). In sunny conditions, photolysis of TBEE may occur more quickly than hydrolysis (McCall and Gavit et al., 1986) and microbial degradation occurs as well (Woodburn, et al., 1993b). Since the conversion of TBEE and TEA to triclopyr is rapid, triclopyr is the focus of fate research. Unlike TBEE, triclopyr has little tendency to hydrolyze (T_{1/2}= 270 days in Linders et al., 1994), and photolysis is the main degradation pathway in natural water (Woodburn et al., 1993a; McCall et al., 1986). In river water, the half-life of triclopyr was determined to be 1.3 days in artificial and natural light. In natural water, oxamic acid is the main photodegradation product with low molecular-weight organic acids as minor products (Woodburn et al., 1993a). Kollman and Segawa (1995) report the solubility of TBEE as 6.81 ppm, and TEA is listed as 234,000 ppm. TBEE is not soluble in water, while TEA is very soluble. Triclopyr is in between at 440 ppm (Royal Society of Chemistry, 1990).

Soil: In soil, TBEE rapidly hydrolyzes to triclopyr acid with a half-life of three hours (Bidlack, 1978). The major route of triclopyr dissipation in soil is microbial degradation. Increases in temperature and moisture, cause microbial activity and degradation to increase (DowElanco meeting, 1996). Aerobic degradation in soil produces the metabolites 3,5,6-trichloro-2-pyridinol (TCP), 3,5,6-trichloro-2-methoxypyridine (TMP) and CO₂ (Cryer et al., 1993). The relative amounts of these products in a lab soil-column study at 54 days were 4% triclopyr, 88% TCP, and 15% TMP for triclopyr acid treated soil, and 6% triclopyr, 88% TCP and 7% TMP for TBEE treated soil (Lee et al., 1986). Unlike microbial degradation, soil photolysis is a minor route of dissipation (Swann and Unger, 1981). Another study performed in anaerobic soil conditions found that TBEE hydrolyzed to triclopyr within one day and then slowly converted to TCP (Laskowski and Bidlack, 1984). Both TCP and TMP eventually convert to CO₂ (Ghassemi et al., 1981).

TBEE has a tendency to adsorb to organic matter and is relatively immobile. It was found to have a Koc of 6,000 cm³/g (McCall and Gavit et al., 1986). According to Kollman and Segawa (1995), TEA has Koc(s) ranging from 24.0 to 144 cm³/g indicating mobility. However, TBEE and TEA rapidly convert to triclopyr. Studies conducted for Dow Chemical found that the Koc of triclopyr ranged from 19-78 cm³/g with an average of 27 cm³/g. It was noted that triclopyr has a similar mobility as 2,4-D and should be classified as mobile in the Helling classification system (Hamaker, 1975). Linders et al. (1994), however, lists triclopyr as “slightly mobile”. Triclopyr sorption to soil increases with time, decreasing the potential for leaching (Buttler et al., 1993). This may be the reason why studies indicate that triclopyr has low mobility. When 2.5 cm of simulated precipitation was leached every two days through soil columns treated with triclopyr, the application stayed within the top 10 cm of the soil column and was not found in the eluates (Lee et al., 1986). In a soil study conducted on a right-of-way in California, triclopyr (6.4 lb. active ingredient (ai)/acre TBEE) stayed within the upper six inches of a bare soil plot during a 36 week period. Triclopyr was detected once below 6 inches but was not due to vertical movement. (Buttler et al., 1993). Triclopyr is only somewhat prone to lateral movement. In a runoff study, runoff samples from a treated plot contained less than 1 ppb triclopyr from one to 105 days after treatment at 2.7 lbs. ai/ac (Stephenson et al., 1990). Furthermore, adsorption of triclopyr was found to increase as the amount of organic matter increases in soil (Ghassemi et al., 1981). The breakdown products are also not mobile. TMP is listed as “very slightly mobile” and TCP is listed as “slightly mobile” (Linders et al., 1994). Most of the TCP is expected to stay in the top one to two inches of soil (Hamaker, 1974).

Triclopyr is listed as “fairly degradable” in soil at reported half-lives ranging from 12 to 27 days (Linders et al., 1994). In a cold climate triclopyr has persisted for one to two years due to a lack of microbial degradation (U.S.D.A., 1984). TCP is listed as “slightly degradable” with half-lives ranging between 12 and 229 days, and TMP as “very slightly degradable” at 50 to 450 days (Linders et al., 1994).

Biota: Few studies have been conducted to determine metabolites and mechanisms of tolerant and non-tolerant plants. One study found that the ability to metabolize triclopyr is probably a selective mechanism. Triclopyr aspartate, several unknown polar-products, and an unknown non-polar product were the metabolites formed in susceptible plants. Tolerant plants converted triclopyr more quickly to some triclopyr methyl ester with very little triclopyr aspartate and polar products (Lewer and Owen, 1990).

Most studies were conducted to determine the metabolites, not the mechanisms. In several grass studies conducted by DowElanco, some TCP and very low levels of TMP were detected (Dixon-White, 1990; McKellar, 1981). However, these studies were conducted assuming the plant metabolites may be the same as the soil metabolites. In another DowElanco study of all possible triclopyr metabolites in rye grass and grass seed, no TCP or TMP was detected but some triclopyr methyl ester was found. As the study progressed, radio labeled residues became more difficult to extract. The unextractable radioactivity was found in rye grass cellulose and lignin (Yackovich et al., 1993). The half-life of triclopyr in plant tissues listed in the studies summarized in this paper range from four to 291 days (McKellar 1980, and Newton et al., 1990).

According to classification by the U.S. EPA, TBEE was found to be “highly toxic” to bluegill in a flow-through study by DowElanco (Woodburn, Hugo and Kirk, 1993). In a worst case scenario where TBEE is directly applied to surface water, TBEE may cause toxicity. However, since the TBEE half-life is less than a day in water and in soil, when probably applied it should not pose a problem. Triclopyr is much less toxic than TBEE. Triclopyr is listed as “slightly toxic” to crustaceans and “very slightly toxic” to fish (Linders et al., 1994). TBEE has a Kow of 15,589 (pers. comm. V. Carrithers, 1996). This is high, however, TBEE breaks down rapidly to triclopyr, which has a low accumulation potential. TEA has a low Kow of 1.23 (Kollman and Segawa, 1995). Triclopyr is classified by Linders et al., (1994) as “slightly accumulating” with a bioconcentration factor (BCF) of 0.02 and the metabolite TCP has a low BCF of 18. Due to low bioaccumulation, fish would have an equivalent triclopyr concentration as the surrounding water (U.S.D.A., 1984). Triclopyr is approved by the U.S. EPA for use in pastures and rangeland areas where domestic livestock may graze. A U.S.D.A. Forest Service Report (1984) found that triclopyr is rapidly absorbed by animals and then excreted by the kidney. Triclopyr is excreted primarily in the unmetabolized form. Since it is rapidly excreted, it was estimated that only 10 percent of the ingested triclopyr is incorporated into the tissues of deer and rabbit. They calculated at an application of 3.0 lbs/acre, the concentration in deer tissue and rabbit tissue would be 2.2 and 1.7 ppm, respectively. One study showed that burning firewood containing residues of triclopyr would decompose residues if temperatures reached 500°C to more than 1000°C, which is generally the temperature of a fireplace or wood stove fire (Bush, et al., 1987).

Garlon®4 and Garlon®3A formulations are less toxic to aquatic organisms than the active ingredients alone. In a hazard assessment report on triclopyr, the Department of Fish and Game (DFG) estimated Garlon®4 may be chronically toxic to fish and aquatic invertebrates at levels as low as 0.03 ppm. Based on U.S. EPA procedures, the DFG came up with another estimated chronic toxicity threshold for aquatic organisms of 0.9 ppm. However, the assessment noted aquatic organisms would not likely be exposed to triclopyr for a duration long enough for a chronic exposure. Based on monitoring and toxicity data listed in the report, it was found that the current use of triclopyr in forestry has little toxicological hazard to fish and wildlife. (Menconi and Siepmann, 1994)

Studies Conducted in a Forest Environment

The outcome of studies on triclopyr movement in the forest varies according to the amount and timing of precipitation, application method, herbicide formulation, treatment rate, non-uniform vegetation cover, and for surface water studies, proximity to a stream or river draining a watershed. The following are nine selected studies of the environmental fate of triclopyr. The first five focus on the fate of triclopyr in runoff from forest watersheds. The last four studies concentrate on determining triclopyr fate in the forest environment with particular attention to residues in plants, soil and organic matter.

D. G. Thompson et al. (1995) conducted a study to determine the fate of TBEE and triclopyr in a first order stream (stream with no tributaries/beginning stream). The focus was on sorption to

organic materials and sediments and the determination of effects on aquatic organisms. A small stream was injected at two points at 50 and 15 cm deep with TBEE at an amount equivalent to an application rate of 3.6 lb ai/ac. Samples were collected over several intervals at seven locations. Sediment, drifting and benthic invertebrates, and periphyton were sampled. Nylon bags of degraded hardwood foliage were also placed in the stream at two sites and collected at intervals.

As the pulse moved downstream and time increased, less TBEE and a greater amount of triclopyr was detected. The TBEE degraded to the less toxic triclopyr. TBEE concentrations ranged from an average of 0.32 ppm at sampling points near the injections at 0.02 ppm, 255 m downstream. Total triclopyr residues detected in the sediment were 10 times lower than the levels detected in the stream, but remained longer than in the water. The leaf-pack samples, however, contained a maximum level at both sites 10 and 20 times greater than the maximum level of TBEE in the stream water and lasted four hours longer than residues detected in the water. It was suspected that the sorption process involves TBEE since the K_{ow} of TBEE is greater (1.2×10^4) than that of triclopyr (0.205). Sorption to organic matter may eliminate toxicity by removing TBEE from the water. However, the more persistent concentration of TBEE in organic matter may pose a hazard for organisms that may feed on or inhabit organic matter. The study showed that triclopyr had almost no adverse effects on the drifting and benthic invertebrates. The study did indicate an increase in periphyton growth measured by the amount of chlorophyll-a. It was speculated that the increase may be due to either nutrient enrichment from the phosphate rich components of the triclopyr or the formulation or perhaps the auxin-like properties of the triclopyr stimulated growth. The chlorophyll-a returned to control levels in three months. It was shown that as the pulse moves downstream the triclopyr concentration decreases while the duration of detection increases.

D.G. Thompson et al. (1991). In August of 1987 a study was conducted to determine the fate of TBEE, TCP and triclopyr in a forest watershed in Canada. Stream samples, aquatic vegetation, sediment samples and fathead minnows were collected after 3.4 lb ai/ac of Garlon[®]4 was applied to a 217 ac watershed (no buffer zones). The average concentration of TBEE in the stream ranged from 0.05 to 0.11 ppm in the first 12 to 14 hours after the application. No TCP residues were detected. The maximum amount of triclopyr detected at the downstream site beyond the spray zone was higher than the maximum at the midstream site. This suggests that TBEE degraded to triclopyr acid as it flowed downstream. TBEE degrades to the acid, which is less toxic to aquatic organisms. The concentration of triclopyr acid increased through the sampling period with a maximum level at 0.14 ppm.

Runoff samples were collected during three rain events. Only triclopyr acid was detected in runoff and levels exceeded reportable levels during the first storm 2 days after application. The maximum concentration was 0.09 ppm about six hours after the peak rainfall. Triclopyr acid was not detected beyond 24 hours after rainfall began. Residues were not detected in sediment except on day 30 during the third rainfall event when 0.2 ppm was detected. Only trace levels were found in the water. The sedge and arrowroot sampled from the midstream site were an order of magnitude higher than the plants sampled at the downstream site beyond the treatment boundary. The highest levels detected were 167 ppm for sedge and 128 ppm for arrowroot. Triclopyr half-

lives in these plants ranged from 0.4 to 7 days. At the downstream location, 43.5 ppm was detected in fathead minnows on day zero. The half-life in the fish was less than a day.

J. Carlson and H. Fiore (1993). In 1991 triclopyr was applied during the summer in the Eldorado National Forest (ENF) for reforestation. The triclopyr was applied as a tank mix of 1.0% Garlon® 4 (1.0 lb ai/ac TBEE) with 1.5 % Accord® (1.1 lb Glyphosate/ac). During the rainy season eight stream locations were monitored for triclopyr. Sediment samples were collected at all sites since triclopyr can adsorb to soil. During the first and only significant storm runoff about two months after treatment, triclopyr was detected at 0.082 ppm in a sample from a small tributary. The ephemeral headwaters of the tributary ran through a treatment area and was supposed to be surrounded by a buffer zone but was accidentally treated. No triclopyr was detected in the stream at the other sites nor in the sediment samples at reporting limits of 0.001 ppm and 0.01 ppm, respectively.

H. Fiore (1995). In 1992 the Eldorado National Forest sampled again after triclopyr treatments to reforestation areas. Only three runoff water samples were collected because rain never occurred within 90 days of treatment at most sites. Out of the three samples collected, only one was analyzed for triclopyr and no residues were detected.

B.J. Wilcox et al. (1991). New Zealand researchers conducted a study to determine triclopyr levels in runoff, and the persistence of triclopyr in pasture soil and grass. Gorse and pasture grass on a hillside was treated with 3.5 lb ai/ac of TBEE (Grazon® herbicide) by helicopter. Stream water samples were collected with automatic sampling devices at three places continuously for six months after treatment. Grass and soil was collected from sheltered areas beneath bushes and in exposed areas, 3 meters away from any bushes.

It was believed that the first detection in the stream water was due to some TBEE deposited directly into the stream. The second detection was from subsurface flow since little rainfall occurred before sampling. The highest concentration was detected on the third sampling event following rainfall at 41 to 46 days after treatment. Despite rain events, samples collected later yielded no detections. The total mass of the triclopyr in the stream was calculated to be about 103 g or equal to about 2.9 % of the total triclopyr applied. Triclopyr was not detected 400 m downstream. Adsorption to stream sediments and uptake by aquatic plants therefore may have removed some triclopyr from the water. Data from the 0 to 10-cm soil samples yielded half-lives of 107 days in sheltered sites and 97 days in exposed sites. It was noted that soil temperature and the amount and type of organic matter affect the persistence of triclopyr. Half-lives calculated from grass samples were 33 days for the sheltered sites and 29 days for the exposed sites.

S.A. Cryer et al. (1993). In August of 1991, DowElanco commissioned a study to determine the fate of Garlon® 4 (TBEE) in a forest environment up to 13 months. A clear-cut, 65-acre test site was sprayed with 6.0 lb ai/ac by helicopter with buffer zones around the stream. Soil samples were collected from exposed (stripped of litter and vegetation) and unexposed (natural state after

logging) sites. Sediment, pond and stream water, vegetation and litter samples were collected from the treatment area.

The vegetation in the area consisted of mustard, blackberry and thistle. From randomly selected areas in the plots, all three vegetation types were hand harvested and pooled to make composite samples. The samples were collected over time to determine the dissipation pattern of triclopyr and the breakdown products TCP and TMP. Only small quantities of the breakdown products were detected, compared with triclopyr. In one plot for example, TCP and TMP concentrations were about 0.57 and 0.29 percent of the TBEE applied, respectively. The average amount of triclopyr detected on the treatment day was 361 ppm. At two weeks and one month after treatment, 126 and 54.4 ppm was the average residue quantity detected, respectively. At six months and nine months after treatment an average of 7.27 and 1.02 ppm, respectively, was detected. The half-life of triclopyr in vegetation was determined to be 14.9 ± 8.7 days.

Average residues detected in litter samples were 66.1 ppm on the day of treatment, 26.4 ppm two weeks after treatment, 21.4 ppm at one month, and 2.52 ppm at 13 months. Again, the breakdown products were only a small fraction of the triclopyr detected on each sampling date. The dissipation half-life of triclopyr in litter was determined to be 19.7 ± 6.4 days.

Data collected from soil samples indicated that triclopyr remained mainly in the top 6 inches of soil. Even in the exposed soil areas, which represent a worse case scenario, only a fraction of the percent applied was detected at soil intervals below 24 inches at six months after treatment. Less triclopyr was seen at the unexposed site since forest litter and vegetation holds the herbicide at the soil surface where it can be degraded. The average soil half-life for triclopyr was 96.0 ± 9.9 days. The half-life of triclopyr in unexposed soil was shorter than in exposed soil.

M. Newton et al. (1990). Three herbicides, triclopyr, picloram and 2,4-D, were applied to brush in Southwest Oregon to determine the deposition patterns, persistence and mobility in a forest ecosystem. Both triclopyr TEA and TBEE were applied to 100 by 200-m plots by helicopter at 2.0 and 3.9 lb ai/ac for the salt and 1.5 and 2.9 lb ai/ac for the ester. Each treatment was applied to one plot at three different sites. The whole-plot mean was reported for vegetation, litter and soil residues. Tanoak (*Lithocarpus densiflorus*) bushes were selected for vegetation sampling since they were the most abundant and consistent of the plant species in the sampling plots.

At 37 days after application, 24 to 51% of the applied triclopyr was present in the surface soil. Due to no rain during that period, the soil was dry. From 37 to 79 days, the largest decrease in soil residues occurred. This coincided with a warm moist period when the half-life ranged from 11 to 25 days. The herbicide concentration decreased more slowly during the winter. In the spring, the decrease in residues resumed, due to increased soil temperatures and microbial activity. The researchers found that triclopyr was practically immobile in soil-water and therefore would only move a short distance in forest subsurface flow.

Symptoms of the application were noticeable after several weeks and wilting occurred over many months. Tanoak twigs and leaves were composited and dried 0, 18, 37, 79, 153 and 325 days after

application. The triclopyr half-life at the 1.5 lb TBEE-application was 127, 291 and 31 days for the crown, browse and litter, respectively. At the 2.9 lb ester application the half-life in the crown, browse and litter was 74, 202 and 31 days, respectively. Triclopyr amine half-life at the 2.0 lb. rate was 19, 21, and 31; and at 3.9 lbs. the half-life was 29, 56, and 54 days, for the crown, browse and litter, respectively. It was found that triclopyr remains detectable in evergreen brush field ecosystems for up to a year and the herbicide dissipates more quickly in soil and litter than in vegetation. In evergreens, there was rapid early loss of residues, but thereafter the rate of dissipation slowed down. The study showed that residues were held in the vegetation and were not released until the vegetation became litter.

D.G. Thompson et al. (1994) conducted a study on the efficacy, environmental fate and biological significance of three formulations of glyphosate and triclopyr ester (Release®). Each formulation was applied at five different application rates to a site in Canada in September of 1989. The most abundant competitive species in the reforestation area studied were sugar maple (*Acer saccharum*) trees. Foliage samples from the trees were collected from various heights and composited creating one foliage sample per plot. Samples were collected for up to 42 days to assess the dissipation patterns and persistence of the residues in foliage. The half-life of TBEE and triclopyr acid in foliage was calculated to be 1.5 days and 4 days on the average, respectively. The difference noted in the calculated half-life when compared to Newton et al. (1990) was due to differences in plant species, weather, application methods, application site and the different kinetic models used. It was found that residues tend to dissipate in a “biphasic” manner, with a rapid decline followed by a slower degradation rate. At the 90% leaf-drop stage, an average of 46.9 ppm of triclopyr acid was detected in foliage samples. Results from the study indicated that triclopyr acid residues in vegetation dissipated completely by 48 days after application. It was expected that the indirect effects of using these herbicides in the forest, such as habitat alteration due dead vegetation, will affect animals more than actual toxicity. It was found that the time-weighted average concentration of triclopyr acid in foliage each day was 546.5 mg/kg/day, well below the minimum 8-day median lethal dietary concentration of 1,923 mg/kg/day. However, the criterion’s relevance to the biota at the application site was questioned.

D.E.M. Plaumann et al. (1983 a and b). A DowElanco sponsored study of residues of Garlon®4 (2.7 lb. ai/ac) in forest soil and litter found that the rate of triclopyr disappearance in soil is very rapid. The half-life in soil was determined to be about 10 days. Only low levels of triclopyr was found in the litter throughout the 58-day study period (0.18-0.45 ppm). Another study was conducted on a right-of-way using Garlon®4 at 3.4 lb ai/ac in Ontario, Canada. Average detectable levels of triclopyr in grass samples, ranged from 307 ppm on day 1 to 4.4 ppm on day 56. The half-life in grass was determined to be between five and 20 days. Average levels for soil samples ranged from 6.2 ppm on the application day to 0.75 ppm on day 56. Soil was sampled and analyzed on day 274 but no triclopyr was detected. The half-life in soil was determined to be 20 days.

Plant Residues and uptake

The first two studies determined translocation of triclopyr in plant tissue and the mechanism of susceptibility to the herbicide. Subsequent studies determined residue levels of triclopyr and its metabolites in plant tissue.

P. Lewer and W.J. Owen (1990). TBEE was investigated to determine the mechanism of its selectivity by examining triclopyr uptake, translocation and metabolism in several plant species with varying degrees of tolerance. Chickweed (*Stellaria media*) was classified as susceptible, barley (*Hordeum vulgare*) as moderately tolerant and wheat (*Triticum aestivum*) as tolerant. Labeled ^{14}C TBEE was applied to one leaf of replicates of the three species. Whole plants and plant parts were analyzed in different strategies to determine uptake, translocation and metabolism.

It was found that the TBEE uptake was more rapid in wheat and barley compared with chickweed and therefore concluded that inefficient uptake of the herbicide was not the factor that influences tolerance. In the transport research, ^{14}C was found in all parts of each species three days after treatment. ^{14}C accumulated more in the upper leaves and main stem of chickweed, whereas ^{14}C was equivalently distributed in wheat and barley. Transport away from the treatment zone in wheat and chickweed was similar while barley more ^{14}C was transported away from treatment zone. The results were not as expected since barley shows herbicidal effects at the treatment zone but no effects elsewhere in the plant. Furthermore, the herbicide was mobile in both the phloem and xylem in each plant species. Since transport away from the treatment zone for wheat and chickweed were similar, the conclusion was made that differential translocation was not a mode of tolerance or intolerance.

The metabolism study showed that only chickweed had detectable triclopyr as the ester, whereas the wheat and barley rapidly hydrolyzed the ester since only triclopyr acid was detected. Triclopyr acid was metabolized most rapidly in wheat, less in barley and the least in chickweed when analyzed three days after application. The peak concentration of triclopyr acid occurred at 12 hours for wheat and barley, while the concentration in chickweed peaked at 24 to 36 hours. Therefore the ability to metabolize triclopyr is probably the selective action mechanism. Further study of metabolites found that wheat and barley metabolize triclopyr to polar products, but chickweed created an additional non-polar product. It was thought that polar products may have impaired transport across the membranes and were more easily metabolized, which most likely contributed to wheat and barley tolerance. The major chickweed metabolite was triclopyr aspartate. The metabolite can be hydrolyzed to release triclopyr again and therefore is not a route of detoxification.

Bovey, R.W. et al. (1986) measured triclopyr in stems at the canopy level and base level of honey mesquite (*Prosopis glandulosa*) to determine translocation of the herbicide in the phloem and xylem tissue. Stems were wrapped with tape to prevent herbicide deposition onto the stem surface then TBEE was applied at 1 lb ai/ac. The stems were collected and the phloem and xylem tissue was separated and analyzed at three and 30 days after treatment. The highest amount of the herbicide detected at three days after treatment was in the upper canopy stem phloem (0.8 ppm wet weight). Mean concentrations in plant parts were very similar at three and 30 days after

treatment. After 22 to 26 months, up to 0.9 ppm of triclopyr was detected in dead stems that fell to the ground. In this study they did not find any strong relationship between concentrations detected and percentage of kill.

Whisenant S. G. and E. D. McArthur (1989). In August of 1996 a study was conducted to determine the persistence of triclopyr in animal forage at two Idaho sites. Terminal twig and leaf segments were sampled for 12 months after ground treatment with TBEE at 2.1 lb ai/ac. The plant species sampled were shinyleaf ceanothus (*Ceanothus velutinus* Dougl. Ex. Hook.), Douglas fir (*Pseudotsuga menziesii* (Mirbel Franco), mountain lover (*Pachistima myrsinites* (Pursh) Raf.), sticky currant (*Ribes viscosissimum* Pursh), snowberry (*Symphoricarpos albus* (L.) Blake), Wood's rose (*Rosa woodsii* Lindl) and grasses. The vegetation samples were collected six times for up to one year after treatment. Shinyleaf ceanothus foliage had the highest triclopyr concentrations with the highest detection at 362 ppm one day after treatment. At one year after treatment, triclopyr was still detected in ceanothus, Douglas fir, mountain lover and grasses at concentrations of 6.7, 1.5, 2.6, and 0.2 ppm, respectively, at one site. On the average, for all species there was a 42% decline in residues after six days, 72% after 28 days and 98% after 365 days after treatment. Several species lost their leaves and were not sampled after 28 days. By comparing this study's data with toxicological data the authors indicated that there is little or no risk to herbivores foraging in areas treated with triclopyr at proper label rates.

Dixon-White, H.E. (1990). Residues of TBEE and its metabolites, TCP and TMP were determined for applications of the ester to green grass and grass dried for hay. At each of 11 sites in different geographical areas, there were three plots that received either 2.0, 4.0 or 6.0 lb ai/ac. Samples were harvested from each plot at 0, 14, and 30 days after application. Hay samples were dried for 1 to 7 days before freezing for sample storage. At approximately 30 days after applications detected residues ranged from 16-88 ppm, 9.6-173 ppm, 34-389 ppm at the 2, 4, and 6 lb. application respectively, for green grass. Residues in hay at the same rates at 30 days ranged 17-140 ppm, none detected-285 ppm, 48-568 ppm. TCP residues at four weeks averaged 43, 88, and 134 ppm at 2, 4, and 6 lbs. per acre for grass. The TCP residues for hay were 72,141, and 246 for the same time period and rates. TMP residues were not detected or were detected very close to the reporting limit of 0.10 ppm.

DowElanco Data package 51566-006, Garlon®3A studies

Grass samples were collected from seven experimental plots at several intervals from day 0 to 385 days following ground or aerial applications of Garlon®3A (TEA) at 9 lb /ac. The samples were analyzed for triclopyr, TCP, and TMP. The average day 0 residue of triclopyr in grass samples was 835 ppm. The detectable levels decreased quickly with a half-life of six days. At approximately one month, triclopyr residues averaged 73 ppm, at two months, residues averaged 27 ppm and at close to one year the residues were detected at levels approaching or under the reporting limit (1 ppm). Residues of TCP were detected at less than 20 ppm and decreased to less than 0.10 ppm or non-detectable. Average residues of TMP were less than 0.30 ppm and were non-detectable after 2 weeks to a month (McKellar, 1981). In another study Garlon®3A was applied at 1.5 lbs/ac to experimental plots. Again, samples were analyzed for triclopyr, however only TCP was analyzed this time. Average levels of triclopyr detected were 165, 37, 20,

8.2, 4.1, 1.4, and <1.0 ppm at 0, 1, 2, 4, 16 weeks and one year, respectively. TCP was detected at less than 3.7 ppm. The average half-life was determined to be 10 days (McKellar, and Jeffries 1980). When applied at 3 lb ai/ac, 297, 54, 60, 19, 10, 2 ppm, and non-detectable were the triclopyr levels detected during the same intervals. The average half-life was determined to be 7 days (McKellar, 1978).

DowElanco Data package 51566-006, Garlon® 4 studies

In a similar study, grass samples were collected from two experimental plots at seven intervals for up to one year following an application of Garlon® 4 (TBEE), at 6 and 8 lb ai/ac. Again samples were analyzed for triclopyr and only TCP. The initial average triclopyr concentrations were 193 and 244 ppm for the 6 and 8 lb applications. At one month the average concentrations were 26 and 22 ppm, respectively. At four months the concentrations were 1.2 and 1.4 ppm, and then both were non-detectable at one year. The highest average TCP concentration was detected at the 8 lb ai plot at an average of 0.62 ppm, one week post application. The half-life of triclopyr was determined to be 7 days (Woods, 1980). In another study with Garlon 4® at 4 lb ai/ac, the average levels of triclopyr detected were 90, 22, 15, 5.6, and 1.3 for day 0, 7, 14, 28, and 56, respectively. Again TCP was detected at very low levels or not at all. The half-life was estimated to be four to five days (McKellar, 1980).

H. Siltanen et al. (1981). In 1977 researchers in Finland conducted a study to determine residue levels and the effect of treatment date in wild berries and lichen from controlled ground spray of triclopyr, glyphosate and phenoxyherbicide in forest areas. Cowberry (*Vaccinium vitis-idaea*) and bilberry (*Vaccinium myrtillus*) plots were sprayed with triclopyr acid at rates of 0.22, 0.66 and 2.0 lbs. ai/ac. When the cowberries were sampled 30 days after application, the residues detected were 0.3, 0.8 and 1.9 ppm for each treatment rate, respectively. The bilberries were sampled eight days after treatment. Residues detected were 0.2, 0.8 and 4.0 ppm, respectively. Residues increased with an increase in the application rate in both berry species.

Cowberry and bilberry plots were then treated with triclopyr at 0.66 lb. ai/ac at different times and harvested at the same time in the early fall. Cowberry plants were treated at intervals between six and 98 days before harvest. Residues detected were 2.4 ppm at six days, 0.7 and 1.1 ppm for days 30 and 36. Days 64, 70, 92 and 98 were 0.2 to 0.3 ppm. Bilberry plants were treated at 7, 41 and 69 days before harvest. Residues detected were 0.9, 0.4 and 0.7 ppm, respectively.

Lichen (*Cladonia rangiferina*) from the bilberry plot was sampled 13 months after treatment. The application rates were 0.22, 0.66 and 2.0 lbs. ai/ac. The amount detected increased with the increased application rate and yielded results of 0.15, 1.0 and 1.7 ppm, respectively.

Conclusion

Triclopyr is a selective herbicide used to control woody plants and broadleaf weeds. The herbicide is absorbed by leaves and roots and is moved throughout the plant in both the phloem

and xylem. Triclopyr acts as a synthetic auxin, giving a plant an auxin overdose which interferes with growth.

Since it has a low Henry's Law Constant, except for spray drift, triclopyr is not expected to be found in air. In soil and water the conversion of TBEE and TEA to triclopyr acid is rapid, thus the fate of triclopyr acid is the focus of most fate research. TBEE and TEA hydrolyze quickly in natural water, while triclopyr acid has little tendency to hydrolyze at all. The primary degradation pathway for triclopyr in water is photolysis, producing oxamic acid and low molecular weight organic acids as minor products. Microbial degradation also degrades triclopyr in water. Studies conducted on forest streams found that when applied directly, TBEE and TEA degrade to triclopyr acid as it flows downstream. The only exception is some TBEE may be retained in organic matter such as leaf material and might pose a hazard for organisms that may feed on or inhabit organic matter. In general, once TEA and TBEE convert to triclopyr, there is little toxicological hazard to aquatic organisms and triclopyr does not accumulate to a great extent.

The major route of triclopyr dissipation in soil is microbial degradation, producing the metabolites TCP and TMP and also CO₂. As temperature and moisture increases, microbial activity increases, which in turn increases the rate of degradation. In addition, forest litter and vegetation hold the herbicide near the soil surface where it is degraded more easily than in the soil. Triclopyr has a low K_{oc} which indicates mobility, however studies show that it is only somewhat prone to lateral movement and is practically not prone to vertical movement. In addition, triclopyr was fairly immobile in sub-surface flow. The lack of mobility may be due to increased adsorption to soil with time and to short persistence (T_{1/2} of 10 days at the shortest) in more optimal conditions. With the use of buffer zones around streams and ephemeral drainage routes, forestry applications of triclopyr could be made without harm to nearby streams.

Few studies have been conducted to determine plant metabolites and even less study the mechanisms of tolerance and susceptibility to triclopyr. One study showed that tolerant and non-tolerant plants produce different metabolites. However discovering the metabolites seems problematic and therefore there are many unknown metabolites or unextractable metabolites. Several studies were conducted looking for TCP and TMP, the soil metabolites in plants. Very little TCP was found and less or no TMP was detected. The half-life of triclopyr in plant tissues listed in the studies summarized in this paper range from four to 291 days and in one study triclopyr remained detectable in an evergreen brush field ecosystem for a year. Another study found that on the average, for the species sampled there was a 42% decline in residues after six days, 72% after 28 days and 98% after 365 days after treatment. The herbicide tends to dissipate more quickly in soil and litter than in vegetation. In the environment, triclopyr would cause more damage to animal habitat due to eliminating vegetation, the intended purpose of the herbicide, than due to triclopyr toxicity to animals.

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