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A Review of the Aquatic Environmental Fate of Triclopyr and its Major Metabolites

DAVID G. PETTY[1], K. D. GETSINGER[2], AND K. B. WOODBURN[3]

ABSTRACT

The triethylamine salt formulation of triclopyr was recently registered for use in aquatic sites by the U.S. Environmental Protection Agency for selective control of invasive aquatic and wetland weed species. Research shows that this herbicide and its metabolites have an environmentally compatible degradation scenario, an excellent toxicological profile, and the ability to selectively control a variety of exotic weed species, making it a valuable tool for restoring and managing aquatic ecosystems. Laboratory studies show that photolytic processes rapidly degrade triclopyr, indicating a major role in dissipation from aquatic sites. However, subsequent field studies indicate that photolysis has a more limited role in the aquatic degradation, likely due to sunlight attenuation in natural waters, and show that metabolic degradation processes assume a more important role. Laboratory investigations show aerobic and anaerobic degradation in hydrosoils is a slower process, and hydrolysis plays a minor role in triclopyr degradation. Field studies conducted in California, Georgia, Minnesota, Missouri, Texas and Washington have shown triclopyr and its TCP and TMP metabolites dissipated from water with half-lives ranging from 0.5 to 7.5, 4.2 to 10.0, and 4.0 to 8.8 days, respectively. Sediment dissipation half-lives ranged from 2.7 to 13.3 days for the same compounds. Half-lives for fish and shell fish ranged from 1.6 to 15.1 days. Results from laboratory and field studies indicate dissipation rates of the parent triclopyr and its metabolites are similar and relatively rapid.

Key words: Garlon 3A, Renovate 3, metabolite, toxicology, aquatic plant control, herbicide dissipation.

INTRODUCTION

Triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) is a selective, systemic herbicide used in the control of broadleaf weeds and woody plants on rights-of-way, rangeland and pastures, forests, lawns, industrial sites, and other non-crop areas. It is also used for broadleaf weed control in rice production. Triclopyr is a pyridinecarboxylic acid compound that generally provides selective control of broadleaf (dicot) plants with little injury to most grass (monocot) species. It is absorbed through the roots, stems and leaf tissues, and translocated via apoplastic and symplastic processes, accumulating in the meristematic regions (WSSA 2002).

The triethylamine (TEA) salt formulation of triclopyr, Garlon™ 3A[4], recently received registration by the U.S. Environmental Protection Agency (EPA) for use in aquatic sites under the brand name Renovate™ 3.[5] Research demonstrates it will control invasive aquatic and wetland weeds such as Eurasian watermilfoil (*Myriophyllum spicatum* L.), purple loosestrife (*Lythrum salicaria* L.), waterhyacinth (*Eichhornia crassipes* (Mart.) Solms), alligatorweed (*Alternanthera philoxeroides* (Mart.) Griseb.), American frogbit (*Limnobium spongia* (Bosc) Steudel) and wild taro (*Colocasia esculenta* (L.) Schott), among others (Getsinger and Westerdahl 1984, Langeland 1986, Green et al. 1989, Sisneros 1991, Anderson et al. 1996, Gardner and Grue 1996, Getsinger et al. 1997, Madsen et al. 1998, Nelson and Getsinger 2000).[6] Triclopyr can effectively control these exotic species, causing little or no harm to the native aquatic plants, such as cattails, rushes, reeds, grasses, and submerged monocots.

Upon application to an aquatic system, triclopyr TEA dissociates to triclopyr acid, which subsequently degrades to the primary metabolite, 3,5,6-trichloropyridinol, or TCP. In addition, 3,5,6-trichloro-2-methoxypyridine, or TMP, is a common metabolic degradate. It is uncertain whether TMP is a direct degradate of triclopyr, TCP, or both.

The purpose of this paper is to provide an overview of the aquatic environmental fate of triclopyr and its major metabolites, TCP and TMP. This review is primarily based on results of laboratory and field studies conducted by various Federal Agencies and the registrant to support the US aquatic registration for triclopyr TEA.

LABORATORY STUDIES

Woodburn et al. (1993a) studied the photolysis of triclopyr in both buffered and natural waters under natural and artificial sunlight. In this study, ^{14}C-pyridine labeled triclopyr was added to both pH 7 buffered water collected from a domestic water supply, and to natural river water (Midland, MI), which had been centrifuged to remove suspended particles. Triclopyr was added to achieve a nominal concentration of 2.5 mg/L. Each water regime evaluated was exposed to either natural, midsummer (~40°N latitude) sunlight, or artificial sunlight (290 to 400 nm) at 25 C. Buffered triclopyr solution

[1]NDR Research, 710 Hanna St., Plainfield, IN 46168.

[2]U.S. Army Engineer Research and Development Center, Waterways Experiment Station, 3909 Halls Ferry Rd., Vicksburg, MS 39180.

[3]The Dow Chemical Company, Toxicology, Environmental Research & Consulting Laboratory, 1803N Building, Midland, MI 48674. Received for publication February 10, 2003 and in revised form July 31, 2003.

[4]Trademark of Dow AgroSciences, LLC, Indianapolis, IN.

[5]Trademark of SePRO Corporation, Carmel, IN.

[6]Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

(pH 7) was maintained as a dark control. Results from both lighting regimes showed only slight differences in the rate of degradation, and no differences in photoproduct formation. Triclopyr in pH 7-buffered water had an average photolysis half-life of 0.5 days, while dissolving the compound in natural water resulted in a triclopyr half-life of 1.3 days. The natural water photodegradation process resulted in oxamic acid as the major photoproduct, and a number of other low molecular weight acids as minor products. The buffered water degradation produced 5-chloro-3,6-dihydroxy-2-pyridinyloxyacetic acid as the major photoproduct, and minor amounts of oxamic and other low molecular weight acids. No degradation or loss of triclopyr was observed in the dark control samples. The authors stated that the results of this study supported the conclusion that photolysis was the principal degradation pathway for triclopyr in aqueous solution. However, subsequent field studies as discussed below suggest that photolysis may play a more limited role in the aquatic degradation of triclopyr than previously determined under laboratory conditions, likely due to sunlight attenuation in natural waters. Dilling et al. (1984) have examined the aqueous photochemical behavior of TCP and found that the compound is highly labile under mid-summer, 40°N latitude conditions, with a measured photolysis half-life of <2 hr.

Hamaker (1975) investigated the hydrolysis of triclopyr in buffered distilled water. Radiolabeled triclopyr was added to distilled water solutions of pH 5.1, 7.2, and 8.3 at a nominal rate of 3 mg/L. The hydrolysis reaction took place within dark constant temperature cabinets at 15, 25, and 35 C. At the conclusion of 287 days of incubation, there was only a small loss of total radioactivity from the solutions (98.7% triclopyr remaining), with loss increasing with temperature. A small percentage of the triclopyr conversion was estimated to be TCP and TMP. The author concluded that hydrolysis would not be a significant mechanism for dissipation of triclopyr from an aqueous system.

Cleveland and Holbrook (1992) also studied the hydrolysis of triclopyr. Radiolabeled triclopyr was introduced to buffered solutions of pH 5, 7, and 9 to achieve a nominal concentration of 5 mg/L. Samples were incubated at 24 C. After 1 month, triclopyr represented 97.2% of the activity remaining in the samples, confirming that simple hydrolysis would not be an important degradation pathway for triclopyr in the environment.

Woodburn and Cranor (1987) studied the aerobic aquatic metabolism of radiolabeled triclopyr. In this study, triclopyr was introduced into flasks containing aerated, filtered well water, and Mohoun silt loam, a typical rice-production soil. ^{14}C-labeled triclopyr was added to the water to achieve a nominal concentration of 2.6 mg/L, and samples were incubated at 24.5 C in the dark for 30 days. An analysis of total ^{14}C activity after 30 days showed that 85.1% remained as triclopyr, 3.8% was TCP, and the remainder was identified as non-extractable residues. Analysis of water and soil yielded no evidence of TMP, while a small amount of TCP was detected in the water column. The extrapolated first-order aerobic aquatic half-life for triclopyr under these darkened conditions was 142 days.

Bidlack et al. (1977) examined the degradation rate of triclopyr in water-saturated soils. Triclopyr was applied separately to Commerce and Flanagan soils in the laboratory to achieve a nominal soil concentration of 1 mg/kg, and deionized water was added to the soil flasks to provide a 2 cm deep aquatic layer over the soil. These soils are typical agricultural soils, with Flanagan having an organic matter content approximately 2.5 times that of Commerce. Samples were incubated at 25 C in a dark cabinet for 300 days. Triclopyr degraded from the Commerce soil with an extrapolated first-order half-life of 130 days, and from the Flanagan soil with a half-life of 42 days. This indicates that higher organic soils promote more rapid degradation in aquatic conditions. Results of the study indicated that triclopyr degraded to TCP, along with minor amounts of TMP.

The toxicity of triclopyr and its metabolites to aquatic vertebrate and invertebrate species has been evaluated with both acute and chronic assessments. Some of the aquatic toxicity testing has been performed using the triclopyr TEA salt formulation of the compound, in addition to the active ingredient, triclopyr acid. The salt readily dissociates in water to form the triclopyr acid anion (Reim 1993). Barron and Ball (1989) report that the 96-hr LC_{50} value for triclopyr with channel catfish (*Ictalurus punctatus*) was 141 mg/L, while Barron et al. (1989) found the 96-hr LC_{50} with crayfish (*Procambarus clarki*) to be >103 mg/L. For salmonids (salmon, trout, char), Wan et al. (1987) report 96-hr LC_{50} values of 5 to 10 mg/L for triclopyr in low pH water (~5.5) with various salmonids (*Oncorhynchus* sp.), while Gorzinski and Richardson (1990) measured a 96-hr LC_{50} value for triclopyr with rainbow trout of >100 mg/L (water pH ~7.5). Similarly, Mayer and Ellersieck (1986) reported 96-hr LC_{50} values of >100 mg/L for triclopyr acid with rainbow trout (*Oncorhynchus mykiss* Walbaum) and bluegill sunfish (*Lepomis macrochirus* Rafinesque). The reported aqueous pH in these studies was 7.4. Water pH is an important feature in assessing toxicity of triclopyr, as it has an acid dissociation constant (pK_a) of 2.7. As a moderately strong acid, approximately 100 times more triclopyr TEA will be present in solution in a nonionized state at a low pH of ~5.5 (Wan et al. 1987) than at a more neutral pH of ~7.5 (Gorzinski and Richardson 1990; Mayer and Ellersieck 1986). The nonionized chemical is more efficiently transferred across the gill surface as compared to the ionized form of the chemical (Barron 1990), thereby accounting for the greater observed toxicity of the chemical in the low pH waters. A water pH range of 6.5 to 8.5 is generally accepted as optimal for fish habitat (van der Leeden et al. 1990), and the US Department of Interior (DOI) has stated that in most productive, fresh, natural waters, the pH falls within this range (DOI 1968). A 28-day prolonged acute toxicity study with rainbow trout revealed sublethal effects at 89 mg/L (lowest-observed effect concentration or LOEC) and a no-observed effect concentration (NOEC) level of 46 mg/L, producing a maximum allowable toxicant concentration (MATC) of 64 mg/L (Jenkins 1995a). In another chronic experiment, Mayes et al. (1984) reported an MATC for triclopyr to be 91 mg/L in a 31-day, embryo-larval exposure with fathead minnows (*Pimephales promelas* Rafinesque).

Kenaga (1977) determined the 48-hr EC_{50} value for triclopyr with *Daphnia magna* (Strauss) to be 133 mg/L, while Jenkins (1995b) reported the 21-day chronic toxicity of triclopyr with *D. magna*, at pH values ranging rom 7.3 to 8.5. For both prolonged lethality and reproduction the MATC was determined to be 69 mg/L.

The aquatic toxicity of the TCP metabolite has been evaluated by Gorzinski et al. (1991a, 1991b) who reported 96-hr LC_{50} values to be 12.5 and 12.6 mg/L for bluegill and rainbow trout, respectively, and the NOEC ranged from 4 to 8 mg/L. Batchelder (1976) measured the 96-hr LC_{50} values for TMP and a variety of freshwater vertebrate species and found the NOEC levels to be 3.5, 2.5, and 3.3 mg/L, respectively, with fathead minnows, rainbow trout, and bluegill sunfish.

Applying the EPA toxicity categories to the above acute exposure results, triclopyr is rated as "practically non-toxic" (the safest category) to catfish, crayfish, rainbow trout and bluegill sunfish, and "moderately toxic" to salmonids at low pH. TCP is "slightly toxic" to bluegill sunfish and trout, and TMP is "moderately toxic" to fathead minnow, rainbow trout, and bluegill sunfish. These data show that triclopyr and TCP pose little toxicological risk to fish populations in waters where it is likely to be used. Due to the low levels of TMP formed in the degradation process, its effects are also of little concern.

FIELD STUDIES

A study of the aquatic dissipation of triclopyr was conducted at Lake Seminole, Georgia from July to August 1986 (Woodburn et al. 1993b). Two plots of approximately 4-ha each were treated with triclopyr TEA to achieve a nominal triclopyr water concentration of 2.5 mg/L. Application to one plot was made 9 July via a boom-equipped helicopter, while application to the second plot was made the same day via subsurface injection by boat. The helicopter-treated plot was somewhat enclosed and sheltered from wind-induced water movement, while the boat-treated plot was more open, and subject to greater water exchange. Both treated plots contained dense stands of submersed aquatic vegetation, primarily hydrilla (*Hydrilla verticillata* (L.f.) Royle) and Eurasian watermilfoil.

Sampling of water, sediment, and submerged aquatic plants was conducted at intervals out to 42 days after treatment, while fish and shellfish were sampled at intervals to 21 days after treatment. Water samples were collected throughout the water column and sediment samples were collected to a depth of 5 to 10 cm. Plant samples were collected with a rake. Wild fish (uncaged) representing both game fish (such as largemouth bass (*Micropterus salmoides* Lacepede) and sunfish (*Lepomis macrochirus* Rafinesque)) and bottom feeders (such as catfish) were periodically collected from the treatment area by electroshocking techniques. Crayfish were contained in cages within the treatment area, and wild (uncaged) clam species were collected from the treatment area.

In the helicopter-treated plot, triclopyr dissipated from water with a half-life of 3.5 days, while the boat-treated plot had a half-life of 0.5 days; the discrepancy in half-lives was most likely due to higher water-exchange processes in the boat-treated plot. Only amounts <0.15 mg/L of TCP were found in water from each plot on the day of application, and were not detected thereafter. Sediment samples from the treated plots contained < 0.1 µg/g triclopyr, and had no measurable TCP residues. Fish and shellfish were analyzed as the whole-organism, though clams were removed from their shells. Fish samples contained <0.1µg/g of triclopyr and TCP. Triclopyr had a half-life in fish of 6.8 days for the helicopter-treated plot, after reaching a maximum concentration of 4.87 µg/g, and a 16 day half-life in the boat-treated plot, after reaching a maximum concentration of 0.24 µg/g. Clams had a triclopyr half-life of 1.6 days in the helicopter-treated plot, after attaining a maximum concentration of 2.49 µg/g on the day of treatment. Clams in the boat-treated plot had a maximum triclopyr concentration of 0.77 µg/g on the day of treatment, and there was insufficient data to calculate a half life. TCP was found at a maximum of 0.07 µg/g in shellfish by day 1 posttreatment. The TMP metabolite was not an analyte in this study.

A study was conducted in late August 1991 on the Pend Orielle River, in northeastern Washington State, using a 6-ha river and a 4-ha cove plot (Getsinger et al. 1997). The river and cove plots were treated with triclopyr TEA using a conventional subsurface injection technique. The river plot was treated at a rate of 2.5 mg/L triclopyr, while the cove plot was treated at variable rates (by depth), averaging 1.75 mg-triclopyr/L for the entire plot. Both plots contained dense surface canopies of Eurasian watermilfoil. Water samples were collected throughout the water column at intervals to 21 days after treatment. Water was subsequently analyzed for triclopyr residues, but not for the major metabolites of triclopyr (TCP and TMP). Triclopyr dissipated from the river plot at a half-life rate of 0.81 days, while dissipation from the cove plot had a longer half-life of 2.2 days. These discrepancies in half-lives were directly influenced by the water exchange rates measured in the treated plots using rhodamine WT dye; 8.4 hours in the river plot, and 52.2 hours in the cove plot (Turner et al. 1994).

A study was conducted under EPA Good Laboratory Practices (GLP) guidelines in June to August 1994 on Lake Minnetonka, Minnesota to further investigate the aquatic dissipation of triclopyr (Getsinger et al. 2000). Two 6.5-ha plots were treated with triclopyr TEA to achieve a nominal water concentration of 2.5 mg/L. The first plot, located in Phelps Bay, was treated by boat using a conventional subsurface injection technique. The second plot was located in a small enclosed arm of the lake, Carsons Bay, and was treated by surface broadcast application from a boat. Both plots were characterized by dense surface canopies of the Eurasian watermilfoil. Winds were light (<10 kph) following application and for several days after. These conditions limited water exchange processes in these treatments, providing for extended triclopyr retention times within the plots, as measured using rhodamine WT dye. The water exchange half-life in Phelps Bay was 3.9 days, and in Carsons Bay was 6.3 days (Fox et al. 2002). Light intensity measurements indicated that ultraviolet (UV) wavelengths, in the spectrum range causing triclopyr degradation (290-313 nm) were essentially extinguished in the top 10 to 15 cm of the water column.

Fish species (bass, bluegill, bullhead (*Ictalurus nebulosus* Lesueur), sucker (*Catostomus commersoni* Lacepede)), clams (*Lampsilis siliquoidea* Barnes), and crayfish were contained in cages within the treatment areas. Fish and shellfish were collected at intervals to 4 weeks post-application; water and sediment samples were collected at intervals to 6 weeks post-application. Water was collected at three discrete depths throughout the water column, and sediment was collected to a depth of 5-10 cm. Fish were divided into the edible fillet, and

the remaining indedible portion. Crayfish were also divided, with the tail meat representing the edible portion, and clams were removed from their shells. Samples were not composited.

The calculated pseudo first-order half-lives for triclopyr, TCP, and TMP in the examined various matrices are shown in Table 1. The half-lives for triclopyr in water were 3.7 days in Phelps Bay, and 4.8 days in Carsons Bay. The half-lives for TCP in water ranged from 4.2 to 7.9 days in Phelps and Carsons Bays, respectively. Triclopyr in sediment displayed half-lives of 5.0 to 5.8 days, while TCP displayed half-lives of 10.7 to 11.3 days in Phelps and Carsons Bay sediments, respectively. Triclopyr in fish and shellfish tissues had half-lives ranging from 3.3 to 10.4 days, while TCP half-lives in these tissues ranged from 2.9 to 13.7 days. The longer fish and shellfish half-lives were observed in Carsons Bay. In this study, fish samples were analyzed for the TMP metabolite, which was found at residue levels up to 2.8 µg/g. The half-life of TMP in fish and shellfish tissues ranged from 2.4 to 11.6 days, with longer half-lives being found in Carsons Bay. After the discovery of TMP in fish tissues, selected water samples were reanalyzed, and the presence of TMP in the water column was confirmed at very low levels (≤0.006 mg/L).

Pond studies were conducted in Elkgrove, California; Columbia, Missouri; and Lewisville, Texas in 1995 (Petty et al. 2001). These GLP studies were conducted in response to an EPA request to provide more geographic representation of the aquatic dissipation of triclopyr, and to better define degradation associated with whole-pond "worst-case" treatment scenarios. In these studies, ponds ranging from 0.1 to 0.3 ha were treated with triclopyr TEA at the nominal rate of 2.5 mg/L. Submerged cages containing bluegill and catfish were placed in each pond prior to treatment. Samples of water, sediment, and fish were collected for a period of 42 days post-treatment. The ponds contained aquatic communities predominated by diverse and widespread populations of submersed plants and algae. Light measurements conducted during the study indicated that, similar to Lake Minnetonka, the UV wavelengths that are required for triclopyr's photodegredation were extinguished in the top 10-15 cm of the water column.

The calculated pseudo first-order half-lives for triclopyr, TCP, and TMP in the examined matrices appear in Table 2. Maximum concentrations in the various matrices are presented in Table 3. As in the Lake Minnetonka study, TMP was detected at low concentrations in the water column (≤ 0.007 mg/L), and was subsequently found in fish tissues at levels up to 2.94 µg/g in the fillet portions and 7.50 µg/g in the inedible portions. Triclopyr had a measured half-life in water of 6.1 to 7.5 days. These slightly increased half-lives (when compared to open water studies) were expected, since the entire ponds were treated, and there was no opportunity for triclopyr to dilute or dissipate from the sampling area by water exchange processes. The water half-lives of TCP ranged from 4.0 to 10.0 days and TMP half-lives in water varied from 4.0 to 8.8 days. Dissipation half-life values in sediment were 2.8 to 4.6 days for triclopyr, and 3.8 to 13.3 days for TCP; no detectable residues of TMP were found in sediment. Half-life values for fish tissues were 2.7 to 12.9 days for triclopyr, 4.8 to 15.1 days for TCP, and 2.5 to 13.3 days for TMP.

Another GLP pond study was conducted in 1996 at Lewisville (Petty et al. 2001) to specifically examine the environmental fate of TMP resulting from an aquatic application of triclopyr. Triclopyr TEA was applied to a 0.3-ha pond at a nominal rate of 2.5 mg triclopyr/L. Water, sediment, sunfish, and catfish were sampled 40 times during a 42-day period. The pond contained a diverse and viable aquatic plant and algae community.

In this study, water half-lives were 6.0 days for triclopyr, which was very similar to the 1995 Texas results, 7.5 days for TCP (within the range of the 1995 Texas results), and 8.8 days for TMP, somewhat higher than the 1995 Texas results (Table 2). The maximum TMP concentrations in water were ≤ 0.007 mg/L (Table 3). Sediment half-lives were 4.5 days for triclopyr (very similar to the 1995 Texas results), and 5.6 days for TCP (about half of that found in the 1995 Texas study). As in the 1995 Texas study, no TMP was detected in sediment samples. In fish tissues, triclopyr half-lives were 4.0 to 5.3 days, TCP half-lives were 4.7 to 11.3 days, and TMP half-lives were 4.2 to 6.9 days.

TABLE 1. SUMMARY OF PSEUDO FIRST-ORDER HALF-LIVES (DAYS) OF TRICLOPYR, 3,5,6-TRICHLOROPYRIDINOL (TCP), AND 3,5,6-TRICHLORO-2-METHOXYPYRIDINE (TMP) IN WATER, SEDIMENT, FISH, AND SHELLFISH FROM LAKE MINNETONKA, MINNESOTA, 1994.

	Carsons Bay			Phelps Bay		
	Triclopyr	TCP	TMP	Triclopyr	TCP	TMP
Water	4.7	7.9	nd[1]	3.7	4.2	nd
Sediment	5.8	10.7	nd	5	11.3	nd
Sunfish Fillet	3.3	7.6	4.9	nd	3.9	3.1
Sunfish Inedible	5.7	11.9	4.4	2.5	6.8	3.5
Catfish Fillet	4.8	5.2	5.8	nd	nd	nd
Catfish Inedible	6.9	nd	5	nd	nd	nd
Sucker Fillet	5.3	nd	7.6	3.6	5.5	4.8
Sucker Inedible	7	nd	5.2	2	4.2	5.4
Bass Fillet	nd	8.9	6	nd	nd	nd
Bass Inedible	5.1	nd	11.6	nd	nd	nd
Crayfish Edible	7.7	10.6	5.1	5.7	5.4	2.4
Crayfish Inedible	8.5	13.7	3.7	9.5	7	2.5
Clam	10.4	nd	5.8	5.2	2.9	3.8

[1]nd = no data - insufficient data for calculation of a half-life.

TABLE 2. SUMMARY OF PSEUDO FIRST-ORDER HALF-LIVES (DAYS) OF TRICLOPYR, 3,5,6-TRICHLOROPYRIDINOL (TCP), AND 3,5,6-TRICHLORO-2-METHOXYPYRIDINE (TMP) IN WATER, SEDIMENT, AND FISH FROM US POND STUDIES CONDUCTED IN 1995 AND 1996.

	CA1[1]	CA2	MO1	MO2	TX1	TX2	TX3		
Water								**Mean[2]**	**RSD[3]**
Triclopyr	6.9	7.5	5.9	6.1	6.5	6.3	6.0	6.5	8%
TCP	4.2	4.5	4.0	5.9	5.7	10.0	7.5	6.0	33%
TMP	5.3	7.7	4.0	4.8	6.5	5.7	8.8	6.1	25%
Sediment									
Triclopyr	3.4	3.6	2.8	3.2	4.6	4.6	4.5	3.8	18%
TCP	5.6	3.8	6.2	7.0	13.3	12.3	5.6	7.7	44%
Sunfish Fillet									
Triclopyr	5.4	2.7	6.7	nd[4]	nd	6.2	5.3	5.3	26%
TCP	nd	nd	nd	nd	nd	15.1	4.7	9.9	53%
TMP	4.4	nd	5.1	5.5	5.3	4.3	4.2	4.8	11%
Sunfish Inedible									
Triclopyr	7.4	5.0	6.0	5.0	8.0	5.6	4.4	5.9	21%
TCP	5.1	12.5	8.8	5.0	8.7	8.5	7.1	8.0	30%
TMP	2.9	2.5	5.6	5.7	11.5	13.3	6.7	6.9	55%
Catfish Fillet									
Triclopyr	nd	nd	5.0	nd	12.9	nd	nd	9.0	44%
TCP	nd	nd	nd	nd	nd	5.2	11.3	8.3	37%
TMP	nd	nd	4.9	5.7	6.5	7.7	6.7	6.3	15%
Catfish Inedible									
Triclopyr	10.2	7.7	8.4	9.5	5.7	3.7	4.0	7.0	34%
TCP	4.9	4.8	7.0	8.6	nd	9.2	7.4	7.0	24%
TMP	nd	nd	4.8	6.9	7.4	8.1	6.9	6.8	16%

[1]CA1 = California pond A, CA2 = California pond B, MO1 = Missouri pond A, MO2 = Missouri pond B, TX1 = Texas pond A, TX2 = Texas pond B, TX3 = Texas 1996 pond.
[2]Mean value of measured half-lives.
[3]Percent relative standard deviation.
[4]nd = no data - insufficient data for calculation of a half-life.

Of note in this study is that the extensive sampling regime allowed for a greater number of values to be used in the half-life calculations, especially for TCP and TMP, the residues of which had to peak and then decline. Accordingly, the calculated half-lives for those compounds are probably a better estimate over the previous studies, although the regression correlation (r^2) for each calculation was generally lower.

SUMMARY AND CONCLUSIONS

Evidence from the laboratory investigations suggests that triclopyr will degrade in natural waters primarily due to the presence of direct sunlight, through the process of photolysis, producing oxamic and other non-halogenated, low molecular weight organic acids as the photoproducts. These results also indicate that in the absence of light, such as conditions of murky natural water, direct shading, or floating vegetation mats, the degradation of triclopyr by microbial action would be quite slow, producing the metabolites TCP and TMP only after several months. In addition, chemical hydrolysis would not be a major route of triclopyr degradation.

However, the evidence from field studies examining triclopyr dissipation in natural waters would seem contradictory to the conclusions which might be drawn from laboratory studies. Field studies indicate that triclopyr in natural waters degrades rather quickly, but at least partially independent of the action of direct photolysis. Applications of triclopyr to the surface of the water, or subsurface below dense plant mats yielded similar dissipation half-lives (Tables 1 and 2), with TCP and TMP being the major degradation products. However, residues of oxamic acid and other low molecular weight acids, the breakdown products of photolysis, would be difficult to measure in aqueous solution and such concentrations have not been determined in field studies.

Measurements of light intensity in the range absorbed by triclopyr (~290 to 313 nm) indicate that these wavelengths are quickly attenuated in surface waters (generally within 10 to 15 cm), limiting the role of photolysis in systems where triclopyr is well mixed within the water column. In fact, water exchange would seem to be the most significant factor affecting the predicted dissipation of triclopyr in open systems, through the action of water exchange. Triclopyr applied to enclosed systems (ponds) degraded at a predictable rate, regardless of geographic location and light intensity, producing measurable residues of the metabolic products TCP and TMP at predictable levels. This would suggest that a major mecha-

Table 3. Summary of maximum concentrations of triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) in water (mg/L), sediment (µg/g), and fish (µg/g) from US pond studies conducted in 1995 and 1996.

	CA1[1]	CA2	MO1	MO2	TX1	TX2	TX3
Water							
Triclopyr	2.087	2.663	2.799	2.345	2.389	2.743	3.039
TCP	0.012	0.017	0.011	0.004	0.015	0.020	0.017
TMP	0.004	0.004	0.007	0.007	0.007	0.004	0.003
Sediment							
Triclopyr	0.680	0.860	0.173	0.080	0.264	0.453	0.621
TCP	0.128	0.154	0.071	0.085	0.134	0.159	0.166
TMP	0	0	0	0	0	0	0
Sunfish Fillet							
Triclopyr	0.032	0.037	0.050	0.036	0.031	0.047	0.014
TCP	0.016	0.022	0.024	0.043	0.039	0.026	0.033
TMP	0.546	0.927	0.665	0.522	0.792	0.369	0.657
Sunfish Inedible							
Triclopyr	0.192	0.184	0.296	0.224	0.176	0.205	0.063
TCP	0.287	0.167	0.222	0.320	0.149	0.146	0.230
TMP	3.379	3.771	1.819	0.724	2.430	2.610	6.030
Catfish Fillet							
Triclopyr	<0.004	<0.004	0.018	0.025	0.033	0.053	0.016
TCP	<0.004	<0.004	<0.004	0.012	<0.004	<0.004	0.012
TMP	0.940	0.841	2.062	2.941	1.069	0.629	2.015
Catfish Inedible							
Triclopyr	0.065	0.047	0.136	0.084	0.142	0.210	0.080
TCP	0.076	0.105	0.055	0.030	0.039	0.041	0.040
TMP	1.082	1.595	5.022	5.078	7.503	5.120	6.260

[1]CA1 = California pond A, CA2 = California pond B, MO1 = Missouri pond A, MO2 = Missouri pond B, TX1 = Texas pond A, TX2 = Texas pond B, TX3 = Texas 1996 pond.

nism for the removal of triclopyr from the aquatic environment is microbial degradation, though the role of photolysis likely remains important in near-surface and shallow waters.

Field results indicate that triclopyr and its TCP metabolite have little affinity toward sediments (Tables 1 and 2), with the exception of those with high organic matter content, such as in Lake Minnetonka; and the calculated sediment half-lives for these two compounds were 2.8 to 5.8 days, and 3.8 to 13.3 days, respectively. In these situations, higher residue levels in sediment are likely the result of the high pore water holding capacities of the organic matter, thereby collecting triclopyr-laden water.

Field studies clearly show that triclopyr and TCP are found in fish and shellfish tissues in direct proportion to the residues found in water, and depurate from these organisms at rates roughly equivalent to the dissipation from the water column (typical fish half-lives of 5 to 8 days), indicating a low bioconcentration potential. The TMP metabolite appears to bioaccumulate in certain fish tissues, especially those higher in fat, such as the inedible and visceral tissues. However, this is short-lived, with clearance from fish tissue mirroring the decline of TMP in the water column. Fish half-life values for TMP ranged from 4.6 to 11.6 days.

Triclopyr TEA applied to an aquatic system readily degrades to its primary metabolites, TCP and TMP. These metabolites, along with the parent molecule triclopyr, are temporarily sequestered by various matrices such as sediment and fish, in relation to the quantities present in the water column. However, these compounds dissipate readily from these matrices, and pose little toxicological risk to fish and shellfish in waters where triclopyr may be used. Concentration of these compounds in the water column is the driving force for accumulation in the other matrices.

Finally, results from dissipation studies conducted in open and closed systems indicate that the degradation of triclopyr and its major metabolites is relatively rapid and would be similar throughout the continental US. This environmentally compatible degradation scenario, combined with its excellent toxicological profile, and ability to selectively control exotic weedy species, will make triclopyr a valuable tool for restoring and managing aquatic ecosystems.

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