Aquatic Dissipation of Triclopyr in Lake Seminole, Georgia

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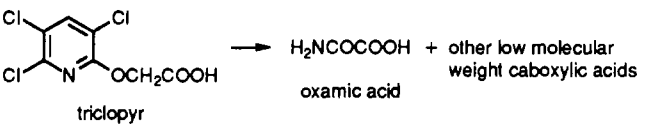
A field study was conducted to evaluate the environmental dissipation of triclopyr herbicide under aquatic-use conditions. Three 4-h plots in Lake Seminole, Georgia, were selected for use: one control, one aerial plot, and one subsurface plot; both applications were at the maximum aquatic-use rate of 2.5 mg/L. Water, sediment, plants, fish, clams, and crayfish were all analyzed for residues, and water temperature, oxygen levels, pH, and conductivity were monitored. The half-life for aqueous-phase triclopyr ranged from 0.5 to 3.6 days, and the dissipation in surface and bottom waters was equivalent. The intermediate decay product of triclopyr, 3,5,6-trichloro-2-pyridinol (TCP), had an observed aquatic half-life of less than 1 day. No accumulation of triclopyr or TCP on sediment was observed. The half-life of triclopyr metabolized by aquatic plants averaged 4 days. Fish species did not exhibit any bioconcentration of triclopyr or TCP, with only trace amounts of either compound found in fish tissue. Both clams and crayfish contained detectable residues of triclopyr. The elimination of triclopyr from clam tissue was more rapid, with an observed half-life of 1.5 days, vs 12 days for crayfish; retention of triclopyr in the crayfish carcass (carapace, chelopeds, and gills) may have been an important mechanism. There was no detectable decline in water quality in either treatment plot.

INTRODUCTION

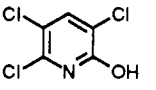
Triclopyr is a frequently used herbicide for postemergence control of a wide range of annual and perennial terrestrial broadleaf weeds and woody plant species. The compound is also under development for use as an aquatic herbicide, formulated as the triethylamine salt in Renovate and Garlon 3A herbicides. As such, the chemical is active against a wide range of introduced aquatic nuisance species, such as Brazilian pepper, purple loosestrife, and Eurasian watermilfoil, but does not control desirable native plant species such as rushes and cattails. The development of triclopyr for aquatic plant control requires study of the aquatic dissipation and fate of the compound under actual-use conditions; several authors have previously evaluated the use of triclopyr for control of Eurasian watermilfoil (Getsinger and Westerdahl, 1984; Green et al., 1989; Netherland and Getsinger, 1992). The objective of this experiment was to evaluate the environmental fate and distribution of triclopyr under aquatic field conditions.

The main degradative mechanism for triclopyr in aquatic ecosystems is photodegradation. McCall and Gavit (1986) estimated the midday, midsummer photolysis half-life for triclopyr in sterile, pH 5, buffered water to be less than half a day at 40° N latitude. Solomon et al. (1988) constructed limnocorrals in a northern Ontario bog lake (50° N latitude) and observed an approximate 4-day summer half-life for triclopyr in the natural water. Little triclopyr adsorption to particles was observed, and dissipation within the limnocorral was largely attributed to photodegradation. Woodburn et al. (1993) recently reported an average first-order half-life of 1.2 days for midsummer photolysis of triclopyr in river water (~40° N latitude, 25 °C), with oxamic acid as the principal photoproduct:



triclopyr — oxamic acid

Triclopyr will also undergo biodegradation in aquatic environments, with an observed half-life of approximately 40 days in a darkened aerobic soil/water system (Woodburn and Cranor, 1987; Grant, 1992). The major degradation product was 3,5,6-trichloro-2-pyridinol (TCP); this compound is also the major soil metabolite (Norris et al., 1987) and a major fish metabolite (Lickly and Murphy, 1987):



3,5,6-trichloro-2-pyridinol (TCP)

In water, TCP is extremely photolabile, with a measured photolysis half-life of less than 1 h in midsummer surface water at 40° N latitude (Dilling et al., 1984). The observed bioconcentration (BCF) value for TCP in mosquito fish is less than 3 (Hedlund, 1972).

Triclopyr has a hydrolysis half-life of greater than 3 months in darkened, sterile, buffered water (25 °C) at pH 5–9 (Woodburn et al., 1993). The compound is a moderately strong acid, with a pK_a of 2.9, and will therefore exist as an anion in solution at pH greater than 4. Triclopyr exhibits minimal bioconcentration potential in fish, with

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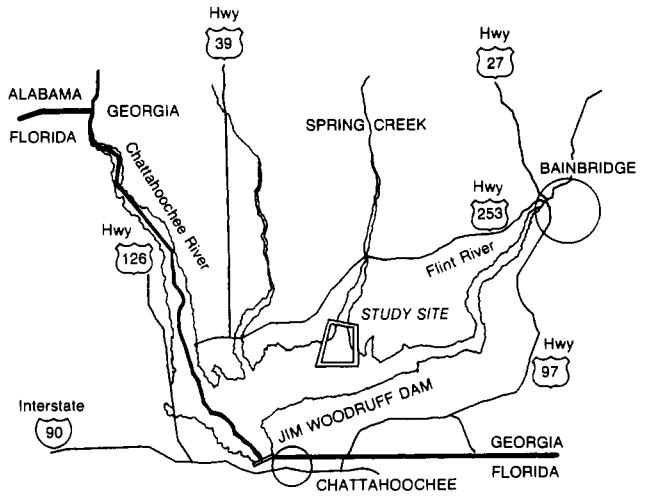

Figure 1. Overview of Lake Seminole, with the study site location noted.

observed BCF values in bluegills of 0.5 and 0.03 for whole fish and edible tissue, respectively (Lickly and Murphy, 1987). The triethylamine salt of triclopyr has a reported octanol/water partition coefficient ranging from 3.3 at pH 5 to 0.1 at pH 9 (Bailey and Hopkins, 1987).

The toxicity of triclopyr (as the triethylamine salt) to aquatic organisms is comparatively low (Wan et al., 1987; Morgan et al., 1991; Janz et al., 1991). Wan et al. (1987) reported acute 96-h LC_{50} values ranging from 267 to 467 mg/L for salmonids, while Morgan et al. (1991) observed a 96-h LC_{50} value of 400 mg/L for rainbow trout. In a study of sublethal threshold concentrations causing avoidance reactions and behavioral responses with rainbow trout, Morgan et al. (1991) found a threshold avoidance reaction at 800 mg/L; the threshold concentration eliciting sublethal responses (loss of equilibrium, etc.) was determined to be 200 mg/L. Janz et al. (1991) found an increase in plasma lactate in juvenile coho salmon exposed to 200 mg/L but observed no corresponding changes in oxygen consumption, hematocrit, or leucocrit values compared to control values.

The aquatic field study described in this paper was a cooperative effort between DowElanco and the U.S. Army Engineer Waterways Experiment Station.

MATERIALS AND METHODS

Study Area. The test and control plots were established in the Spring Creek arm of Lake Seminole, Georgia, in heavy stands of Eurasian watermilfoil (*Myriophyllum spicatum* L.) and hydrilla [*Hydrilla verticillata* (L.f.) Royle]; the treatment area location is shown in detail in Figures 1 and 2. Three 4-ha (10 acre) plots were used in the study. The upstream plot (plot 1 in Figure 2) was selected as the untreated control plot, plot 2 was surface treated by helicopter, and plot 3 was treated by subsurface injection from an airboat. Each plot contained five sampling stations (Figure 2), one in the center of each quadrant and one in the center of the plot. Sampling stations outside the plot were selected approximately 100 m from the center of the plot margins. A sampling station was established about 1.5 km downstream from plot 3. The distance between plots 1 and 2 was approximately 1 km, between plots 2 and 3, ~1.3 km, and between plots 1 and 3, ~2 km.

Vegetation in the three plots differed at the time of treatment. Plot 1 contained (visual estimate) 98% Eurasian watermilfoil and less than 1% hydrilla; almost the entire plot area was covered with aquatic plants. Plot 2 contained ~95% hydrilla and only 5% Eurasian watermilfoil, with approximately 75% of the surface area covered with plants. Plot 3 contained approximately 50% Eurasian watermilfoil and 35% hydrilla; the remaining 15% of the flora was distributed between pondweed (*Potamogeton* sp.) and the alga chara (*Chara* sp.). Approximately 65% of plot 3 was covered with plants.

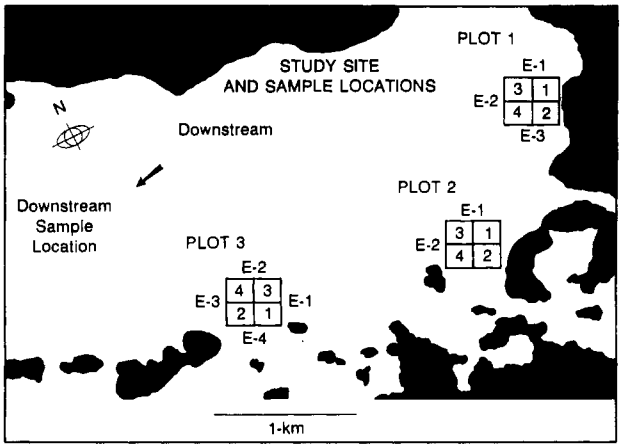

Figure 2. Layout of study site and sampling locations within the Spring Creek arm of Lake Seminole.

Herbicide Application. In each application, triclopyr was applied as the triethylamine salt using Garlon 3A (32.2% triclopyr acid equivalent, by weight). The experimental-use permit for aquatic applications of Garlon 3A recommends a maximum use rate of 2.5 mg of triclopyr acid equivalent (ae)/L in water. To achieve this concentration in an area with an average water depth of 1.2 m, applications of 94 L/ha (10 gal/acre) each of Garlon 3A were made to plots 2 and 3. The Garlon 3A was aerially sprayed, undiluted, to the surface of plot 2 with a Hughes 500 helicopter using a Simplex 5500 spray system on July 9, 1986. The 10.2-m boom contained 32 Raindrop nozzles operating at a spray pressure of 1.4 kg/cm^2 (20–22 psi), and a swath width of 7 m was produced by running half the nozzles at a time; the speed of the helicopter during application was 72 km/h (45 mph). Plot 3 received an application of Garlon 3A by subsurface injection using an operator-constructed spray system mounted on an airboat; the rate of application was again 94 L/ha (10 gal/acre). The 2-m boom held four nozzles providing a spray pressure of 7.0 kg/cm^2 (100 psi) and a swath width of 4 m. The application date was July 9, 1986, and the speed of the airboat during application was 8–11 km/h (5–7 mph).

Weather conditions at the time of application were an air temperature of 33 °C, clear skies, and a wind speed of <8 km/h. The surface water temperature was ~30 °C, and discharge from the Lake Seminole reservoir was restricted, resulting in a water flow of less than 0.5 km/h.

Water Sampling. One-liter duplicate water samples were taken in and around the treatment and control plots. Samples were taken at the center of each quadrant, the center of the plot, each buffer zone (Figure 2), and the downstream site. Water samples were obtained at two depths, ~0.3 m from the bottom and 0.3 m from the surface. In water 0.75 m deep or less, only a surface water sample was taken. Water was collected using a centrifugal pump connected to a garden hose with a screened intake; the hose was rinsed with water at each new sampling location to prevent contamination. Samples were taken from the outside of the plot (buffer zones), working toward the plot center. The sampling times were pretreatment, 1 h posttreatment (center stations only), 4 h (all stations), 8 h (center stations only), and 1, 3, 8, 14, 21, and 42 days posttreatment.

Sediment Sampling. Sediment samples were taken to a depth of 5–10 cm using a spring-loaded trap door scoop (0.75–1 L), connected to a 3 m × 3 cm (o.d.) steel pipe. Approximately five sediment samples were taken from the center of each quadrant and composited in a stainless steel bowl before a portion of the sample was placed in a 1-L metal can with a metal lid; a similar sampling/compositing procedure was used at the plot center. The time of sampling was pretreatment, 0 days immediately posttreatment, and 1, 3, 8, 14, 21, and 42 days posttreatment.

Aquatic Plant Sampling. Grab samples were taken of submerged plants using a standard garden rake. Samples were taken at each quadrant and the plot center, composited in a stainless steel bowl after they were shaken to remove excess water, and placed in numbered plastic sample bags. Sampling days were pretreatment, 0 days immediately posttreatment, and 1, 3, 8, 14, 21, and 42 days posttreatment. Following day 3 of

treatment, all plant samples from a given plot's four quadrants were composited to a single "quadrant sample".

Fish Sampling. Fish samples were collected using electroshocking, in conjunction with the Georgia Department of Fish and Wildlife. Shocked fish were taken from within the sample plots and the buffer areas. An attempt was made to collect both game fish and nongame fish. Nongame fish included brown bullhead, *Ictalurus nebulosus* (Lesueur); common carp, *Cyprinus carpio* Linnaeus; chain pickerel, *Esox niger* Lesueur; gizzard shad, *Dorosoma cepedianum* (Lesueur); lake chubsucker, *Erimyzon sucetta* (Lacepede); and spotted sucker *Minytrema melanops* (Ratinesque). Game fish included bluegill sunfish, *Lepomis macrochirus* Rafinesque; largemouth bass, *Micropterus salmoides* (Lacepede); redear sunfish, *Lepomis microlopus* (Gunther); and yellow perch, *Perca flavescens* (Mitchill). Each fish was identified and placed in a numbered bag; sampling days were pretreatment, 1 day posttreatment, and 8, 12 (plots 1 and 2), 14 (plot 3), and 21 days.

Crayfish/Clam Sampling. Crayfish cages were constructed of PVC pipe frames and nylon mesh to hold and maintain crayfish during the test period; the cages were approximately 1 m^3 in volume and constructed to allow free water flow. Native crayfish were obtained in the Lake Seminole area from a local merchant. Small PVC pipe sections were placed in the cages to allow the crayfish hiding locations to minimize cannibalism. The cages were set up at the center of each plot if the water depth was greater than 1 m. If the water depth was less than 1 m, the cages were placed at the point nearest the plot center where water depth exceeded 1 m. The cages were suspended in the water column just beneath the water surface. Forty to fifty crayfish occupied each trap, and duplicate cages were placed within 10–20 m in each plot. Indigenous Lake Seminole clams were collected at the necessary sampling times from within the plots; no clam cages were necessary. At each sampling time, 10–14 clams were harvested from the plot area and 1–4 crayfish were removed from the cages. Samples were placed in a numbered 1-L metal can and number coded. Sampling days were pretreatment, 0 days immediately posttreatment, and 1, 8, 14, and 21 days.

Sample Storage. Water, sediment, plant, fish, clam, and crayfish samples were placed on ice immediately following collection. Within 24 h of sampling, all samples were placed in frozen storage until analyzed.

Water Quality Measurements. Water quality (pH, temperature, specific conductance, and dissolved oxygen) was monitored in all three plots from pretreatment through 21 days; these measurements allowed for a gross evaluation of any decline in water quality arising from triclopyr application. Two submersible, programmable Hydrolab Datasonde I units were placed in the center of each plot, one approximately 30 cm from the lake bottom and one a similar distance from the surface; water quality data were recorded every 30 min, 24 h a day. The Datasonde units were removed from the water every 4–7 days for data retrieval and recalibration and then returned to the plots. For this reason, some short data gaps (1–2 days) exist in the recorded data base. The reported specific conductance measurements were corrected for temperature, and dissolved oxygen (DO) was corrected for conductivity.

ANALYTICAL PROCEDURES

Residue analyses for triclopyr and TCP were performed by DowElanco. Sample preparation and analytical procedures followed DowElanco methods and are summarized here. All samples were analyzed using a Hewlett-Packard 5890 gas chromatograph (GC), equipped with a ^{63}Ni electron-capture detector. The GC capillary column used was an HP1 methyl silicone gum, 5 m × 0.53 mm, 2.65-μm thickness. The initial GC temperature ranged from 145 to 155 °C, with detector and inlet temperatures of 300 and 250 °C, respectively. The carrier gas for the column was helium (7 mL/min), and an argon/methane (9:1) mixture was used for the detector (30–70 mL/min). The chart recorder used was a Hewlett-Packard 7123A. All residues presented are gross values, corrected for recovery from spiked matrices.

Water residue analysis followed DowElanco Method ACR 76.8. For triclopyr residues in water, the aqueous solution was acidified, partitioned (2:1 v/v) with diethyl ether, and methylated [with diazomethane (DAZ)] to form the triclopyr methyl ester; this compound could then be quantified by GC analysis following evaporative concentration. For TCP analysis, the water was acidified, and residues were extracted with benzene (2:1 v/v). This aliquot was then methylated [with *N,O*-bis(trimethylsilyl)-acetamide (BSA)] to form the methylated derivative of TCP, which was analyzed by GC following concentration. These procedures provided analytical validation limits of aqueous triclopyr and TCP of 0.01 and 0.05 mg/L, respectively. Triclopyr levels between 0.005 and 0.01 mg/L were considered to be <0.01 mg/L and levels <0.005 mg/L were considered to be nondetectable. Similarly, TCP levels between 0.025 and 0.050 mg/L were considered to be <0.05 mg/L, and levels <0.025 mg/L were nondetectable. The average recoveries for aqueous triclopyr and TCP were 92 and 96%, respectively.

Sediment residue analysis followed DowElanco Method ACR 84.2. Sediment samples were homogenized and gravity filtered to remove excess water. Triclopyr in the sediment was extracted with methanolic sodium hydroxide; the supernatant was then acidified, saturated with salt, and partitioned into diethyl ether. The aliquots were then methylated (with DAZ) to obtain the triclopyr methyl ester and quantified by GC analysis. TCP in sediment was extracted in a similar fashion to triclopyr, with methanolic sodium hydroxide. The sediment TCP extract was diluted with water, acidified, and saturated with salt, and the TCP was partitioned into benzene. The benzene was then partitioned with sodium bicarbonate; the bicarbonate layer was removed, acidified, and passed through a C_{18} preparatory column. The TCP was eluted with methanol; the methanol was then acidified and diluted with water, and the TCP was partitioned into benzene. An aliquot of the benzene phase is treated with BSA to form the methylated TCP derivative. The derivative was then quantified by GC analysis. These procedures provided analytical validation limits of sediment-absorbed triclopyr and TCP of 0.10 and 0.05 mg/kg, respectively. Triclopyr levels between 0.05 and 0.10 mg/kg were considered to be <0.10 mg/kg, and levels <0.05 mg/kg were nondetectable. TCP concentrations between 0.025 and 0.05 mg/kg were considered to be <0.05 mg/kg, and levels <0.025 mg/kg were nondetectable. The average recoveries for triclopyr and TCP residues in sediment were 84 and 88%, respectively.

Aquatic plant residue analysis followed DowElanco Method ACR 77.4. Plant samples were drained of excess water, and 10 g of plant material was homogenized, extracted with methanolic sodium hydroxide over a filter, and diluted with water. An aliquot of the filtrate was then acidified and partitioned with diethyl ether/hexane (70:30 v/v). Triclopyr was then extracted with sodium bicarbonate and the organic phase discarded. The bicarbonate phase was then acidified, partitioned into 30/70 diethyl ether/hexane, concentrated by evaporation, and methylated (with DAZ) prior to quantitation by GC analysis.

TCP plant residues were extracted by acidification of the aqueous methanol filtrate and partitioning of the TCP into benzene. The benzene was then passed through an alumina column to adsorb the TCP; TCP was eluted from the column using a pH 6.5 buffer/diethyl ether solution. The TCP in the eluate was partitioned into sodium bicarbonate and the bicarbonate acidified and partitioned into benzene. An aliquot of the benzene phase was methylated (with BSA) and quantified by GC analysis. These procedures provided analytical validation limits of triclopyr and TCP in plants of 1.0 and 0.05 mg/kg, respectively. Triclopyr levels between 0.5 and 1.0 mg/kg were considered to be <1.0 mg/kg, and levels <0.5 mg/kg were considered to be nondetectable. TCP levels between 0.025 and 0.050 mg/kg were considered <0.050 mg/kg, and levels <0.025 mg/kg were nondetectable. The recoveries for triclopyr and TCP residues in aquatic plants were 76 and 101%, respectively.

Fish residue analysis followed DowElanco Methods ACR 77.4S1 for triclopyr and ACR 70.19R for TCP. Fish were prepared for triclopyr analysis by extracting a 10-g portion of the homogenized edible fish tissue with methanolic sodium hydroxide. The extract was then acidified, saturated with salt, and partitioned with 30:70 diethyl ether/hexane. The organic phase was removed and partitioned with sodium bicarbonate, and the organic phase was then discarded. The bicarbonate phase was acidified, saturated with salt, and diluted with methanol. The solution was then repartitioned with 30:70 diethyl ether. The

organic phase was then removed and partitioned again with sodium bicarbonate; the organic phase was discarded. The bicarbonate phase was acidified, salted, and partitioned with diethyl ether. The extract was then reduced in volume and methylated with DAZ, and the triclopyr methyl ester was quantified by GC analysis.

TCP analysis in fish tissue involves an initial extraction of a 10-g tissue homogenate with methanol. The extract was back-extracted with benzene following acidification and saturation with salt. Cleanup of the benzene phase was accomplished using an acidic alumina column and hydrochloric acid eluent. The collected eluate was further acidified and the TCP partitioned into benzene; this phase was then methylated (with BSA) and quantified by GC analysis. These procedures provided analytical validation limits for triclopyr and TCP in fish of 0.10 and 0.05 mg/kg, respectively. Triclopyr levels between 0.05 and 0.10 mg/kg were considered to be <0.10 mg/kg, and levels <0.05 mg/kg were considered to be nondetectable. TCP levels between 0.025 and 0.050 mg/kg were considered to be <0.05 mg/kg, and levels <0.025 mg/kg were nondetectable. The average recoveries of triclopyr and TCP residues from fish tissue were 73 and 70%, respectively.

Clam and crayfish residue analysis also followed DowElanco Method ACR 77.4S1. Whole crayfish (including shell) and clam muscle were homogenized. One-gram portions were extracted with methanolic sodium hydroxide, acidified, saturated with salt, and partitioned with benzene. This phase was then partitioned with sodium bicarbonate and the organic phase discarded. The bicarbonate phase was then acidified, saturated with salt, and repartitioned with benzene. The benzene phase was then methylated and quantified for TCP by GC analysis. The workup of the benzene phase was continued for triclopyr by partitioning with sodium bicarbonate; the bicarbonate phase was acidified, saturated with salt, and partitioned with diethyl ether. This phase was then methylated, reduced in volume, and analyzed for triclopyr methyl ester by GC. These procedures provided analytical validation limits for triclopyr and TCP in clams/crayfish of 0.10 and 0.05 mg/kg, respectively. Triclopyr levels between 0.05 and 0.10 mg/kg were considered to be <0.10 mg/kg, and levels <0.05 mg/kg were considered to be nondetectable. TCP levels between 0.025 and 0.050 mg/kg were considered to be <0.05 mg/kg, and levels <0.025 mg/kg were considered to be nondetectable. An average 82% recovery was obtained for both triclopyr and TCP residues in crayfish and clams.

RESULTS AND DISCUSSION

Water. Initial triclopyr concentrations for the 0 day (1 h) immediately posttreatment samples from plots 2 and 3 were close to the applied dose concentration of 2.5 mg/L. Triclopyr concentrations in the center station of plot 2 were 2.54 (surface water) and 3.37 mg/L (bottom water); the concentrations for plot 3 (center) were 2.44 mg/L at the surface and 1.86 mg/L in the bottom waters. Only a trace (<0.05 mg/L) of TCP was detected at 0-day center sites. The control plot (plot 1) had no detectable residues of triclopyr or TCP on day 0; only minor amounts (<0.02 mg/L) of triclopyr were detected in the control plot during the 42-day study. These residues were probably caused by movement of water along the shore, north from plot 2 to plot 1 (see Figure 2); prevailing winds from the southwest could have caused surface currents to travel north along the shoreline.

The dissipation and persistence of triclopyr residues in water varied considerably among the two treated plots. Triclopyr residues persisted through posttreatment day 21 in plot 2 but only through day 3 in plot 3; the correlation of triclopyr dissipation with first-order kinetics is shown in Figure 3. The first-order half-lives for triclopyr dissipation in the surface and bottom water of plot 2 were 3.3 and 3.5 days, respectively, and 0.4 day in plot 3. The average half-life of 3.4 days in plot 2 is consistent with the 4-day summer half-life for aqueous triclopyr observed by Solomon et al. (1988) in their limnocorral study in northern Ontario.

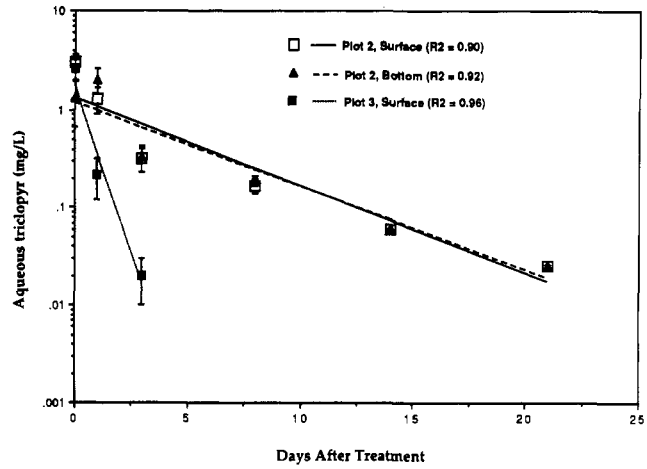

Figure 3. First-order dissipation plot of average aqueous triclopyr residues in plots 2 (surface and bottom) and 3 (surface only). Error bars on data points indicate 1 standard deviation about the mean.

The wide range in half-life values for aqueous triclopyr in plots 2 and 3 demonstrates the variability in persistence and dissipation that can occur among treated areas even within the same body of water. The more rapid dissipation of aqueous triclopyr residues from plot 3 compared to that from plot 2 was probably due to a combination of several interacting factors, i.e., hydrodynamics (water movement and plot depth), vegetative cover, and type of vegetation. Water movement was probably a major factor influencing aqueous triclopyr dissipation. Plot 2 was protected on two sides by land and was 2–3 km from the main channel of the tributary arm, while plot 3 was virtually open on all sides and was less than 1 km from the main channel. Water currents originating from upstream, along with wind-generated mixing patterns, could have dispersed the aquatic residues more rapidly in plot 3 than in plot 2.

The TCP metabolite exhibited very rapid dissipation in water, with an observed first-order half-life of less than 1 day; only trace amounts of TCP (<0.05 mg/L) were found after the 8-h sampling. These results are in agreement with the laboratory data on TCP photodegradation, which reported a half-life of less than 1 h under midsummer sunlight at 40° N latitude (Dilling et al., 1984; unpublished data of The Dow Chemical Co.).

The downstream sampling station showed no detectable confirmed residues of triclopyr or TCP at any sampling time. Flow data indicate that a full day would have been required to transport applied triclopyr ~1.5 km to the downstream location.

Sediment. Triclopyr accumulation and persistence in the sediment was short-lived; residues were generally found only on day 0 in the two application plots (0.10–0.64 mg/kg). Following the day 0 residues, triclopyr residues were sporadically found in sediment on sampling days 1 and 3. Trace amounts (<0.10 mg/kg) were found in six samples, and 0.10 mg/kg was measured in a single sample. No TCP residues were detected in any sediment samples, and neither triclopyr nor TCP residues were observed in control plot sediment.

Aquatic Plants. Triclopyr was concentrated in the treated submerged aquatic plants and persisted through posttreatment day 8. On day 0, residues averaged 5.7 and 3.3 mg/kg in plots 2 and 3, respectively. Residue levels fell to below detectable limits (<1 mg/kg) after day 3 in plot 3 and after day 8 in plot 2. Trace amounts of TCP (<0.05 mg/kg) were detected in four plant samples, and no detectable residues of the metabolite were found after posttreatment day 3. In Figure 4, the correlation of

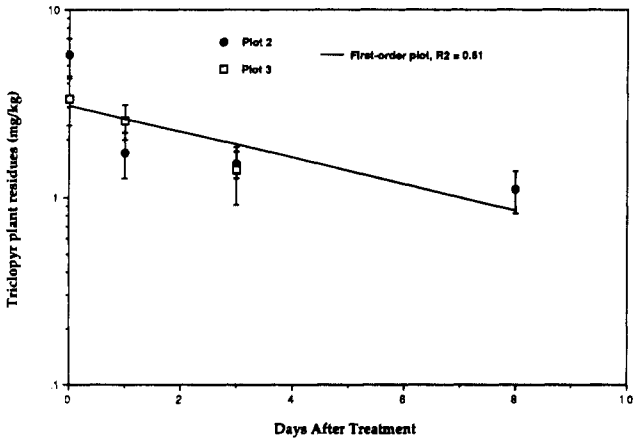

Figure 4. First-order dissipation plot of average triclopyr residues in aquatic plants. Error bars on data points indicate 1 standard deviation about the mean.

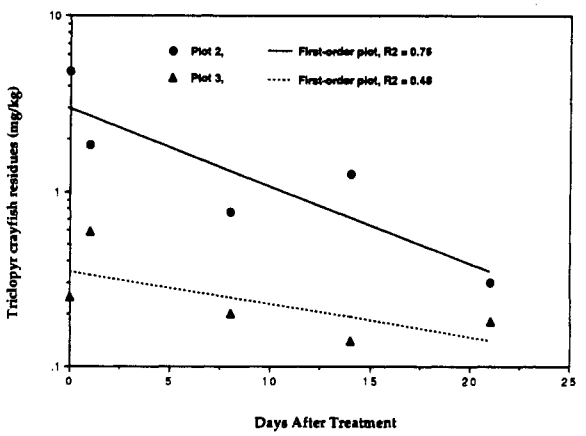

Figure 5. First-order dissipation plot of average triclopyr residues in whole crayfish. The crayfish residue data were taken from composited samples and therefore do not have standard deviation error bars.

triclopyr dissipation in aquatic plants with first-order kinetics is shown, and the agreement with first-order decay is relatively poor. The overall first-order half-life for triclopyr residues in plants from both plots 2 and 3 was found to be ~4 days. These results suggest rapid metabolism/elimination of triclopyr by the plants, and there appears to be little potential for residue release from decaying plants into the surrounding environment. The slight bioconcentration of triclopyr initially seen in the collected plants (bioconcentration factor ~1–2 mL/g) is in agreement with recent work by Hinman and Klaine (1992).

Fish. Triclopyr residues were not detected in excess of the analytical validation limit (0.10 mg/kg) in any of the game and nongame fish collected during the entire study; four fish from days 1 and 8 had residue levels of <0.10 mg/kg. The metabolite TCP was detected in trace quantities (<0.05 mg/kg) in five fish collected during the study. These results are in keeping with the measured triclopyr BCF value of 0.5 mL/g in whole bluegill (Lickly and Murphy, 1987). The data indicate that no adverse effects on the fishery would be expected when triclopyr is applied as small-area treatments in a large water body.

Crayfish. The concentration and persistence of triclopyr were greater in whole crayfish than in fish tissue. The crayfish residue data are shown in Figure 5 and demonstrate a rapid uptake of triclopyr into crayfish in plot 2, with 4.87 mg/kg present on day 0; TCP residues in crayfish were low to nondetectable throughout the study. Triclopyr residues were consistently higher in the crayfish

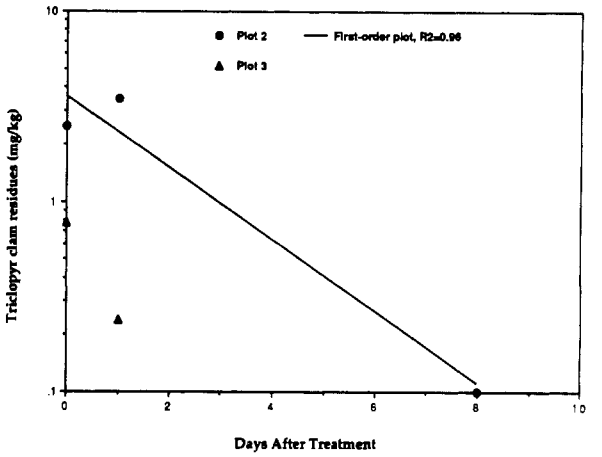

Figure 6. First-order dissipation plot of average triclopyr residues in clam tissue. The clam residue data were taken from composited samples and therefore do not have standard deviation error bars.

collected from plot 2 than plot 3, and residues from plot 2 crayfish remained through 21 days after treatment (last sampling). The plot 2 crayfish residue data in Figure 5 fit a first-order elimination/metabolism process moderately well ($R^2 = 0.76$), with a calculated half-life of 7 days. The residues from plot 3 crayfish did not fit first-order kinetics well ($R^2 = 0.48$), and the estimated half-life was 16 days; the overall average half-life of 12 days for triclopyr residues in whole crayfish is in agreement with the results of Barron et al. (1991). It should be noted that triclopyr residues in the Lake Seminole crayfish may have been unrealistically high due to the placement of the crayfish cages just below the water surface and not in sediment, where crayfish are generally located. Crayfish were therefore exposed to short-term elevated water concentrations of triclopyr rather than the much lower sediment levels.

Barron et al. (1991) have determined that crayfish exposed to aqueous ^{14}C-labeled triclopyr (2.5 mg/L) largely accumulate the compound in their carcass (carapace, chelopeds, and gills), as opposed to internal organs and muscle tissue. Greater than 50% of the total ^{14}C activity was found in the carcass, with the remainder of the activity in the hemolymph (30–40%), hepatopancreas (5%), other organs (2%), and tail muscle (2%); the total ^{14}C activity tissue concentration was consistently less than 5 mg/kg (ppm). A majority of the ^{14}C activity in the hepatopancreas was parent triclopyr (~85%), with the taurine–triclopyr conjugate as the major metabolite (~15%). The BCF values for total ^{14}C activity averaged 0.5 and 0.15 in whole crayfish and tail muscle, respectively, values similar to those reported for triclopyr in bluegill (Lickly and Murphy, 1987). The measured laboratory half-lives for total ^{14}C residues in whole crayfish and tail muscle averaged 11 and 12 days, respectively (Barron et al., 1991). An earlier study by Barron et al. (1989) reported the 96-h LC_{50} for triclopyr (acid equivalent) with crayfish to be >103 mg/L. The data of Barron et al. (1989, 1991) indicate that the observed whole organism residues pose no adverse health effects to crayfish exposed to 2.5 mg/L triclopyr applied as small-area treatments in a large water body.

Clams. The clam residue data are shown in Figure 6 and again demonstrate a rapid uptake of triclopyr, with 2.5 mg/kg present in plot 2 clam tissue on day 0; TCP residues in clams were nondetectable throughout the study. As with crayfish, triclopyr residues were consistently higher in clams collected from plot 2 than plot 3. Residues in clam tissue were nondetectable in plot 2 at 14 days and at day 8 in plot 3. The plot 2 clam residue data in

Figure 6 fit a first-order elimination/metabolism process well (R^2 = 0.96), with a calculated half-life of less than 2 days. The data indicate that no adverse effects to the clams would be expected when triclopyr is applied as small-area treatments in a large water body.

Water Quality. Conductivity, dissolved oxygen (DO), pH, and water temperature exhibited diel patterns over the 22-day measurement period (data not presented). The water quality of the treatment plots was virtually identical to that of the control area; the data did not demonstrate any decline in water quality due to treatment. Typical values of conductivity, DO, and pH in the plots were 0.1 mmho/cm, 8 mg/L, and 8.4, respectively.

SUMMARY

An application of triclopyr (as the triethylamine salt) at the prescribed maximum aquatic-use rate of 2.5 mg/L dissipated in the Lake Seminole ecosystem at rates generally anticipated from laboratory experimentation on the material. Aqueous triclopyr residues had average half-lives of 3.6 days in plot 2 and 0.5 day in plot 3; the differences in the dissipation rate are probably due to greater water flow through plot 3. The TCP metabolite of triclopyr had an observed half-life in water of less than 1 day. No accumulation of triclopyr or TCP in sediment was observed. The estimated half-life for triclopyr residues in aquatic plants was 4 days. Neither bottom-feeding nor sport fish species exhibited any bioconcentration of triclopyr or TCP during the study. Crayfish concentrated detectable residues of triclopyr, and the observed elimination half-life from whole crayfish was 12 days. The observed triclopyr half-life in clam tissue was ~1.5 days. There was no detectable decline in water quality in either treatment plot. Overall, triclopyr and the TCP metabolite appeared to undergo rapid dissipation and degradation in the aquatic environment without adverse effect on the ecosystem.

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