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Aquatic dissipation of the herbicide triclopyr in Lake Minnetonka, Minnesota

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Abstract: A study of the aquatic fate of the triethylamine salt of triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) was conducted in three bays of Lake Minnetonka, Minnesota. Triclopyr is under review by the US Environmental Protection Agency as a selective aquatic herbicide. The primary purpose of this study was to determine dissipation rates of the parent active ingredient, triclopyr, and its major metabolites, 3,5,6-trichloropyridinol (TCP) and 3,5,6-trichloro-2-methoxyppyridine (TMP) in selected matrices including water, sediment, plants, finfish and shellfish. Two 6.5-ha plots dominated by the weedy species Eurasian watermilfoil (*Myriophyllum spicatum* L) were treated with triclopyr-triethylammonium at a rate of 2.5 mg AE liter⁻¹ (2.5 ppm) on 21–23 June 1994. A third 6.5-ha plot was established as an untreated reference. Water and sediment samples were collected from within the plots and at selected locations up to 1600 m outside of the plots through six weeks post-treatment for chemical residue analysis. In addition, residue samples were collected from the target and non-target plants and other non-target matrices, including game and rough fish, clams and crayfish. All test animals were sequestered in cages located in the center of each plot and samples were collected through four weeks post-treatment. Half-lives for dissipation of triclopyr and TCP in water ranged from 3.7 to 4.7 days and from 4.2 to 7.9 days, respectively, with trace amounts of TMP found. Peak triclopyr sediment values ranged from 257 to 335 ng gram⁻¹, with a mean half-life of 5.4 days, while peak TCP sediment levels ranged from 27 to 65 ng gram⁻¹ (mean half-life = 11.0 days). Trace levels of TMP were detected at one treatment site at one sampling event. Triclopyr and TCP accumulated and cleared from animal tissues proportionately to concentrations in the water (triclopyr dissipation half-lives < 11 days, TCP < 14 days). TMP levels were two to three times higher than those of the other compounds, particularly in visceral tissue. In all cases, residues of these compounds were higher in the inedible portions of the animals, and were usually higher in bottom-feeding fish species.

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Keywords: aquatic plant management; aquatic herbicide environmental fate; *Myriophyllum spicatum*; Eurasian watermilfoil; TCP; TMP

1 INTRODUCTION

1.1 Background

Triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) is a selective, systemic herbicide registered for use in the control of broad-leaf weeds and woody plants on rights-of-way and non-crop areas including rangeland and pastures, forests and industrial sites. It is also registered for use on ornamental turf and in rice production. Presently, Federal registration is being sought for the triethylamine (TEA) salt of triclopyr

(ISO-approved name triclopyr-triethylammonium), with the product name Renovate[®], for the control of invasive aquatic species such as Eurasian watermilfoil (*Myriophyllum spicatum* L), purple loosestrife (*Lythrum salicaria* L), water hyacinth (*Eichhornia crassipes* (Mart) Solms) and alligatorweed (*Alternanthera philoxeroides* (Mart) Griseb). Triclopyr is an auxin-type compound with a mode of action and spectrum of weed control similar to that of phenoxy herbicides. Triclopyr is taken up through the roots, stems and leaf tissues of

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plants. It is transported via symplastic processes and accumulates in the meristematic regions. Death of triclopyr-sensitive plants usually occurs over a 7- to 14-d period.

Triclopyr-triethylammonium forms a dilute solution of triclopyr anion upon injection into lake water and subsequently degrades to 3,5,6-trichloropyridinol (TCP). In addition, 3,5,6-trichloro-2-methoxypyridine (TMP) is a common metabolic degradate found in terrestrial uses, but it has not previously been found in aquatic applications of triclopyr. It is uncertain whether TMP is a degradate of triclopyr, TCP, or both.

Photolysis can be a significant route of triclopyr and TCP degradation in the environment. Triclopyr photodegrades at the 313nm wavelength, and is further metabolized to carbon dioxide, water, and various organic acids by aquatic organisms.¹ Woodburn *et al*² examined the aqueous photolysis of triclopyr in both buffered and natural river water under artificial and natural lights at 25°C. In the sterile, buffered system, triclopyr degraded with an average half-life of 0.5 days with 5-chloro-3,6-dihydroxy-2-pyridinyl-oxyacetic acid as the only significant photoproduct. Natural river water degradation yielded a half-life of 1.2 days, generating oxamic acid as the major photoproduct. If TCP is formed in the environment by either aerobic or anaerobic processes, it is also readily photodegradable. The photochemical half-life of TCP has been reported to be 2h at a depth of 1m in river water under 40° north latitude midsummer sunlight.³

Hydrolysis is not a significant route of degradation for triclopyr. Cleveland and Holbrook,⁴ and Hamaker⁵ observed no significant hydrolytic degradation in a month-long study conducted at pH 5, 7, and 9. A study of triclopyr under aerobic aquatic conditions yielded a slow degradation rate of 4.7 months, with TCP as the only significant degradate.⁶ Laskowski and Bidlack⁷ showed that triclopyr is slowly degraded under anaerobic conditions, such as those which exist in deeper waters and associated sediments. In that study, triclopyr degraded to TCP with a half-life of about 3.5 years.

Some aspects of the aquatic dissipation of triclopyr have been investigated previously.⁸⁻¹¹ Results of these investigations indicate that triclopyr and its pyridinol metabolite undergo rapid dissipation in the aquatic environment, as opposed to predictions based on laboratory studies.

In an aquatic dissipation study in Lake Seminole, GA,¹¹ triclopyr had an average dissipation half-life of 0.5 to 3.6 days after being applied at a concentration of 2.5mg litre⁻¹. The dissipation half-life for TCP in Lake Seminole was less than 0.5 days. No accumulation of triclopyr or TCP was observed in the sediment. Only trace amounts of these compounds were found in fish, and the half-lives of triclopyr in plants, crayfish and clams were 3.4, 11.5 and 1.5 days, respectively.

A small-scale field study conducted in Ontario, Canada showed triclopyr levels in water treated at

rates of 0.0003 and 0.120mg litre⁻¹ to fall below 5% of initial concentrations within 15 days, and to be below detection limits by 42 days post-treatment.¹⁰ This study suggests that natural waters may cause a quenching of the photoreaction of triclopyr relative to sterile, buffered waters. This quenching effect has been observed in other field studies, and is thought to be caused by the presence of dissolved organic material.¹¹

A study conducted on the Pend Orielle River, WA, where triclopyr was applied at a rate of 2.5mg litre⁻¹ yielded estimated dissipation half-lives of 19.4h (0.8 days) for a slow-flowing riverine plot, and 52.7h (2.2 days) in a protected cove plot with limited water exchange.⁹

1.2 Study objectives

A study was initiated in June 1994 by the U S Army Engineer Research and Development Center, Waterways Experiment Station, Vicksburg, MS, and Dow AgroSciences, Indianapolis, IN, to investigate the aquatic dissipation of triclopyr within the confines of an operational treatment for control of Eurasian watermilfoil in Lake Minnetonka, MN. The study was required to further characterize the aquatic fate of triclopyr in large lake systems, and the protocol was approved by the Registration Division of the US Environmental Protection Agency (USEPA). Lake Minnetonka was selected for this study because it is representative of a Eurasian watermilfoil infestation, the availability of similar yet geographically isolated bays in the same lake, and the need to more completely document the dissipation of triclopyr in northern US lakes. Specific objectives of this study were to: (1) establish the dissipation curves for triclopyr applied to an aquatic environment as the triethylamine salt; (2) follow the formation and decline of its metabolites, TCP and TMP; and (3) establish residue levels of triclopyr and its metabolites in non-target aquatic organisms, including fish, clams, crayfish and plants. This work was conducted according to USEPA Guidelines 164-2, Field Dissipation Studies for Aquatic Uses and Aquatic Impact Uses, and 165-5, Field Accumulation Studies of Aquatic Non-target Organisms under the conditions of Good Laboratory Practices (GLP). Investigations on the efficacy of the treatment, correlation between triclopyr and a fluorescent dye, as well as changes in the water quality and plant community were also conducted, and have been reported separately.¹²

2 MATERIALS AND METHODS

2.1 Study site

The study was conducted in Lake Minnetonka (44°56'N, 93°34'W), located near the city of Minneapolis, MN (Fig 1). Lake Minnetonka drains the south-central portion of Hennepin county, with its outlet to the Mississippi River through Minnehaha Creek. The 175km of shoreline of the lake has been highly

Figure 1. Lake Minnetonka, Minnesota, showing bays used in the triclopyr dissipation study: Phelps Bay (treated), Carsons Bay (treated) and Carman Bay (untreated).

developed for many years, mostly as single-family housing units, and is a major recreational resource for the region.

The lake is a complex waterbody of 15 morphologically distinct basins, with a total area of 5,801 ha, a mean depth of 6.9 m, and a maximum depth of 30.8 m; its total volume has been calculated to be 400 million cubic meters.¹³

Much of Lake Minnetonka's littoral zone is suitable for rooted submersed aquatic plants, and the lake has supported considerable plant growth.¹³ A 1950 survey reported rooted vegetation covering about one-sixth of the lake, including curlyleaf pondweed (*Potamogeton crispus* L), coontail (*Ceratophyllum demersum* L), northern watermilfoil (*Myriophyllum sibiricum* Komarov), Canada waterweed (*Elodea canadensis* Michx), sago pondweed (*Potamogeton pectinatus* L), and water buttercup (*Ranunculus longirostris* Godron).¹⁴ Eurasian watermilfoil (*M. spiratum*) was first discovered in Lake Minnetonka in 1986, and since has grown to cover a significant portion of the lake. The extent of infestation fluctuates on a yearly basis, with estimates of the impacted areas ranging between 600 and 1200 ha (WellingC, MNDNR, 1995, personal communication). Approximately 2200 ha, over one-third of the lake, is thought to be suitable for colonization by *M. spicatum*.

2.2 Study plots

Three rectangular test plots of approximately 6.5 ha (16 acres) each were established in separate bays of Lake Minnetonka (Fig 1). Plots were selected for similarities in water depth and plant communities, and probable differences in water exchange characteristics. Each herbicide-treated plot was divided into quadrants, and a residue sampling station was established in the center of each quadrant, as well as plot center. Additional sampling stations (one to three) were established at a distance of 100 m away from the edge of the plot (off-plot). Additionally, three more off-plot sampling stations were located at 400, 800 and 1600 m from the plot edge, along what was judged to be the most likely line of chemical drift. The untreated reference plot had only a single sampling station established at plot center.

The Phelps Bay plot was established along the west-northwest shore of the bay (Fig 2). At time of treatment, this plot had a mean water depth of 1.98 m, and an estimated water exchange half-life (based on dye studies) of >17 h. This plot was subsequently treated via a subsurface injection application, as described in Section 2.5. The Carsons Bay plot was established in an enclosed arm of the bay (Fig 2). This plot had a mean depth of 1.7 m, with a probability of a water exchange half-life greater than

Figure 2. (a) Phelps Bay, Lake Minnetonka, Minnesota, treated with triclopyr-triethylammonium at $2.5 \text{ mg AE litre}^{-1}$, 21 June 1994 and (b) Carsons Bay, Lake Minnetonka, Minnesota, treated at $2.5 \text{ mg AE litre}^{-1}$, 23 June 1994. Circled numbers represent residue sampling stations.

that measured at Phelps Bay, due to the enclosed and protected nature of the bay. This plot was subsequently treated via a surface broadcast application, as described in Section 2.5. The Carman Bay plot was established in the *M. spicatum* bed along the northwest shore of the bay. This plot had a mean water depth of 2.5 m, and an estimated water exchange half-life of approximately 8 h. This plot was used as the untreated reference plot. Positions of the plot corners and sampling station buoys were plotted using a satellite global positioning system (GPS) and marked with anchored buoys. To prevent overlapping of treatment swaths, small anchored floats were used to delineate eight 0.81-ha treatment sections in each plot.

2.3 Light monitoring

Since light can be a prominent mechanism of triclopyr degradation, light intensity and water transparency were measured in the treatment plots and in an area of deep (5–7.5 m) open water, 100–400 m outside of each plot. Percentage light transmission was measured using a LiCor (Lincoln, Nebraska) Model 1000 light meter with submersible quantum probe and deck (surface) cell, which measured light in the photosynthetically active radiation (PAR) range of 400 to 700 nm. These light profiles were taken on 19 June (pre-treatment) and on the post-treatment dates of 25 and 27 June, and 6 and 18 July between 1000 and 1400 h. In order to determine transmission of ultraviolet (UV) solar energy ($<400 \text{ nm}$) in Lake Minnetonka water, spectral irradiance was measured at a depth of 15 cm using a LiCor Model LI-1800UW underwater spectroradiometer. A series of these spectroradiometric readings were taken at Phelps Bay and Carman Bay on 19 June between 1100 and 1300 h.

2.4 Non-target organisms

Non-target aquatic organisms used in this study were

obtained from local sources, and included fin-fish species such as largemouth bass (*Micropterus salmoides* Lacepede), bluegill (*Lepomis macrochirus* Rafinesque), brown bullhead (*Ictalurus nebulosus* Lesueur), and white sucker (*Catostomus commersoni* Lacepede), and invertebrates including the clam species fatmucket (*Lampsilis siliquoides* Barnes) and crayfish (*Oreochelone virilis* Hagen or *O. immunis* Hagen). These non-target animal species were selected to represent different trophic levels in the aquatic food chain that could be susceptible to triclopyr accumulation. Bass and bluegill feed in all depths of the water column, while catfish and suckers limit much of their feeding activities to the bottom. Crayfish are omnivorous scavengers and clams are sedentary filter feeders.

Animals were kept in floating cages ($1.2 \times 1.2 \times 1.2 \text{ m}$) constructed of nylon mesh and polyvinyl chloride (PVC). The cages were fitted with latching covers to prevent escape of, or predation on, the contained animals. Animals were separated by species, and each species was kept in several cages, to minimize crowding. Small sections (10–12 cm) of PVC pipe were placed in the crayfish cages to provide secure hiding places to minimize cannibalism. It should be noted that cages did not allow direct access to the lake sediment, and that all animal species, including bottom feeders and dwellers, were kept suspended in the water column, 0.5 to 0.8 m above bottom. Supplemental foods (eg pelleted chow and bait leeches) were provided to the animals periodically, and dead or moribund individuals were noted and removed from the cages upon discovery.

2.5 Application techniques

Subsurface application was the delivery method used on the Phelps Bay plot. Triclopyr-triethylammonium, as a commercial $360 \text{ g AE litre}^{-1}$ SL (Garlon 3A; Dow AgroSciences, Indianapolis, IN), along with the inert dye rhodamine WT (RWT) (Crompton and Knowles

Table 1. Residue sampling schedule for triclopyr treatments on Lake Minnetonka, Minnesota

	Water	Sediment	Plants	Fish	Controls
Pretreatment	X	X	X	X	X
1 h	X		X	X	
3 h	X		X	X	
6 h	X	X	X	X	
12 h	X	X	X	X	
1 day	X	X	X	X	
2 days	X				
3 days	X	X	X	X	
5 days	X				
1 week	X	X	X	X	X
2 weeks	X	X	X	X	
3 weeks	X	X		X	
4 weeks	X	X		X	X
6 weeks	X	X			
Total samples ^a	1265	160	50	250	

^a Total represents the target total of samples. Slightly more or less may have been collected.

Colors, Reading, PA) were applied as a tank mix to provide nominal rates of 2.5 mg litre⁻¹ and 12 µg litre⁻¹, respectively, through a spray boom operated from an airboat. Approximately 50 depth measurements were made at each plot to determine the average depth. This was multiplied by the plot area to obtain a total plot volume for calculation of the amount of material to be applied. The spray boom consisted of three trailing hoses of 1.2, 2.4, and 3.7 m in length, weighted to sink the hoses at various depths below the surface. The inert dye was added to provide a visual reference during application, and to allow for tracking of chemical drift in real time through the use of field fluorometers. Application to the Phelps Bay plot began on 21, June 1994 at 0600h, and was completed at 0800h.

Surface broadcast application was the delivery method for the Carsons Bay plot. The application device used was a Radiarc sprayer (Waldrum Specialties, Doylestown, PA), a boomless, low volume device that applies liquid formulations in a uniform pattern while providing good control of aerial drift. This device was mounted in the bow of the air boats. Triclopyr was again applied to make a nominal application rate of 2.5 mg litre⁻¹, while the dye was applied at 10 µg litre⁻¹. Application to the Carsons Bay plot began on 23, June 1994 at 0600h, and was completed at 0800h.

Actual application rates were confirmed by total weight of formulated material applied to each plot. Different application techniques were used to compare distribution and fate of the herbicide, as these two techniques will be important commercial-scale application practices for this product.

2.6 Sample collection

All residue samples were stored in appropriately labeled metal cans at the time of collection, and placed

on ice in a cooler. Water and sediment were collected pretreatment and for six weeks after application, as were dye measurements. Aquatic animals and plants were collected pretreatment and for four weeks post-treatment, except in those instances where supplies were exhausted. Table 1 presents the sampling schedule and target sample totals.

Water samples (0.4 litre) for residue analysis were collected in duplicate from three depths at each sampling station at each water sampling time. Water sampling at the internal and near off-site stations began one hour post-application. Sampling at the off-site stations (400, 800, 1600 m) did not begin until three hours post-application. At each sampling event, a water sample was collected in a sequence at 25 cm above the bottom, at the mid-point of the water column, and at 25 cm below the surface for all stations located inside the plot. Off-plot water samples were collected at the same depth as the deepest corresponding on-plot station. Dye was measured concurrently with each water sample, and at additional locations and times during the course of the study. Water was collected by using an uncontaminated, electric bilge pump and drinking water quality opaque hose. Approximately 3 litres of water were expelled prior to collection of the sample, and the sample container was then rinsed with water from the appropriate collection depth. Hoses and pumps were changed after each sampling period to preclude the possibility of sample contamination.

Sediment samples (300 g) collected from approximately the top 5 cm of the lake bottom at each in-plot and 100-m off-plot sampling station at each sediment sampling event. Sediment was not collected from the 400, 800, and 1600-m off-plot stations due to the depth of the lake at these points, as well as the low likelihood of significant residues being found in sediment from these locations. Sediment was collected using a ponar dredge, deposited and spread on a section of fine mesh screen to drain excess water and remove foreign objects, and sealed in a sample container.

Fish and shellfish were sampled (>50 g) from pre-established holding cages by net collection. In general, a sample was composed of multiple individuals, depending upon the size of the individuals collected. Fish and shellfish samples were subsequently rinsed with distilled water in the preparation laboratory prior to initial processing.

Plant samples were collected from suitable vegetation stands located near the center of each plot using a rake type device. Collected plants were separated into the appropriate target (*M. spicatum*) and non-target (flatstem pondweed (*Potamogeton zosteriformis* Fernald)) species, and rinsed with distilled water prior to being placed into the sample containers.

Samples were transported from the study site to a local laboratory, and water, sediment, and plants were immediately frozen. Fish samples were refrigerated until the initial preparation was completed, and then were transferred to frozen storage.

2.7 Sample preparation and residue analysis

Each fish sample was separated into two distinct sub-samples, one sub-sample comprising the edible fillet portion of the fish, and the other subsample comprising the inedible viscera, including skin. Crayfish were similarly processed, the edible portion comprising the tail meat, and the remainder making up the inedible portion. Clams were removed from the shell to produce only edible samples. The prepared fractions were stored frozen in clean containers.

Samples were shipped on dry ice, and prepared by the Dow AgroSciences Sample Management Group prior to transfer to the analytical laboratory. Sediment, plant, and fish tissues were ground frozen, and the prepared sample separated into analytical and long-term storage sub-samples. Water underwent no preparation, the duplicate sample serving as the long-term sample. Analyses were conducted on Hewlett Packard Model 5989, 5890, and 5971 Gas Chromatograph/Mass Spectrometers. Laboratory spiking was conducted with each sample set, and only recoveries between 70 and 120% were accepted. Analyses were corrected for average sequence recovery.

2.7.1 Water samples

Water samples were analyzed for triclopyr, TCP and TMP by first transferring a 25-ml aliquot of water into a clean vial. The analytes were extracted into 1-chlorobutane by adding hydrochloric acid (2M; 1 ml), sodium chloride (10g) and 1-chlorobutane (6ml) to the vial. The sample was shaken for 30min on a mechanical shaker, and the 1-chlorobutane was removed and placed into a clean vial. This extraction procedure was repeated, and the organic extracts were then combined, and concentrated to less than 1ml under nitrogen. A fluoroxypryl internal standard was added along with the derivatizing reagent *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MSBSTFA), and the final volume was adjusted to 1ml using 1-chlorobutane. The extract was then heated at 60°C for 1h. The samples were then analyzed by gas-chromatography (GC) electron impact (EI) mass spectrometry (MS).

2.7.2 Sediment samples

Sediment samples were analyzed for triclopyr, TCP and TMP by extracting 5g of sediment twice with acetone + 1M hydrochloric acid (90 + 10 by volume). The two extractions were combined, and the volume adjusted to 40ml.

Triclopyr and TCP analysis involved transferring an 8-ml aliquot of the original 40-ml extract into a clean vial. The sample was concentrated to less than 2ml under nitrogen, and hydrochloric acid (0.5M; 20ml) was added to the sample. The sample was cleaned up using an automated solid phase extraction system. A C18 solid phase column was conditioned using acetonitrile (5ml) followed by hydrochloric acid (0.1M; 5ml). The sample was loaded into the C18 solid-phase column, and the sample vial was rinsed

with hydrochloric acid (0.1M; 2ml). This rinse was also loaded onto the column. The column was then rinsed with acetonitrile + water + 1M hydrochloric acid (40 + 59 + 1 by volume; 3ml). The sample was eluted with acetonitrile + water + 1M hydrochloric acid (80 + 19 + 1 by volume; 3ml). Triclopyr and TCP were extracted by adding hydrochloric acid (0.1M; 10ml), sodium chloride (5g) and 1-chlorobutane (5ml) to the eluant. The sample was then shaken on a mechanical shaker for 30min. After centrifugation, the 1-chlorobutane layer was transferred to a clean vial. The sample was then extracted a second time with 1-chlorobutane (5ml), and the extracts combined. The sample was concentrated to less than 1ml under nitrogen. One hundred microlitres of acetone containing the internal fluoroxypryl standard was added to the sample, and the final volume was adjusted to 1ml using 1-chlorobutane. Prior to derivatization, the sample was transferred to a GC vial. The triclopyr and TCP were derivatized to the *tert*-butyldimethylsilyl ester and ether, respectively, by adding MSBSTFA derivatizing reagent (100µl) and heating for 1h at 60°C. Final analysis was by GC/MS.

To analyze for TMP, an 8-ml aliquot of the initial extract was transferred into a clean vial. The TMP was twice extracted into hexane by adding water (10ml), aqueous sodium hydroxide (2.5M; 1.0ml) and hexane (5ml). The sample was shaken for 20min on a mechanical shaker, and the hexane was removed and placed into a clean vial. The two hexane extracts were combined, and concentrated to less than 1ml using nitrogen. An internal standard was added, and volume adjusted to 1ml using 1-chlorobutane. The sample was then analyzed by GC/MS. It should be noted that, due to the high organic matter content, the sediment samples contained a high amount of water, which would skew the results.

2.7.3 Fish and shellfish samples

Two slightly different methods were used for analysis of triclopyr in fish and shellfish samples. For those samples analyzed at Dow Chemical H&ES, residues of triclopyr, TCP, and TMP were extracted and hydrolysed using aqueous sodium hydroxide (0.25M). Following hydrolysis, the solution was acidified and the analytes extracted with butyl chloride. The butyl chloride was passed through a silica solid phase extraction (SPE) column that retained the triclopyr and TCP, while the TMP was contained in the butyl chloride eluate. The triclopyr and TCP were eluted from the silica column with a solution containing acetonitrile + butyl chloride + acetic acid (40 + 60 + 0.2 by volume). The triclopyr and TCP fraction was concentrated to less than 1ml, and the internal standard was added. The sample was derivatized with MTBSTFA to form the *tert*-butyldimethylsilyl (TBDMS) derivatives of triclopyr and TCP. The samples were analyzed by capillary GC/MSD.

Dow AgroSciences methodology also extracted and hydrolysed residues of triclopyr, TCP, and TMP from

Table 2. Limits of detection (LOD) and quantitation (LOQ) for residues in matrices collected during triclopyr treatments on Lake Minnetonka, Minnesota, June 1994

	<i>Triclopyr</i>		<i>TCP</i> ^a		<i>TMP</i> ^b	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
	(ng g ⁻¹)					
Water	0.04	0.15	0.01	0.03	–	–
Sediment	3.86	12.9	2.26	7.54	2.56	8.53
Plants	3.84	12.8	1.26	4.21	1.68	5.61
Game fish edible	4.99	16.7	4.10	13.7	2.09	6.96
Game fish viscera	4.22	14.1	2.51	8.36	2.06	6.87
Bottom fish edible	2.22	7.41	1.81	6.03	4.78	15.9
Bottom fish viscera	3.22	10.8	9.05	30.2	3.48	11.6
Shell fish edible	5.52	18.4	1.78	5.96	3.56	11.9
Shell fish viscera	2.46	8.21	2.30	7.66	1.53	5.11

^a 3,5,6-trichloropyridinol.^b 3,5,6-trichloro-2-methoxy pyridine.

fish using aqueous sodium hydroxide (0.25 M). Following hydrolysis, the sodium hydroxide was acidified and the analytes extracted with diethyl ether. The ether was passed through an alumina solid phase extraction (SPE) column that retained the triclopyr and TCP, while the TMP was contained in the ether eluate. For the determination of TMP, the ether was concentrated and exchanged with 1-chlorobutane. The triclopyr and TCP were eluted from the alumina column with sodium hydroxide (0.1 M), which was acidified and purified using a C18 SPE column. The eluate from the C18 SPE was extracted with 1-chlorobutane. For both sample fractions, the 1-chlorobutane was concentrated to less than 1 ml, and an acetone solution containing fluoroxypr analogs as internal standards was added. The sample was derivatized with MTBSTFA to form the TBDMS derivatives of triclopyr and TCP. The sample was analyzed by capillary gas chromatography with mass selective detection.

2.7.4 Plant samples

Triclopyr and TCP in aquatic plants were determined by adding sodium hydroxide solution (20 ml; 0.5 M in water + methanol (20 + 80 by volume)) to 5 g of sample. The sample was loosely capped and heated at approximately 130 °C for 20 min to release any bound compounds. After cooling, the sample was shaken for 30 min on a flatbed mechanical shaker. The extract was then decanted into a 50-ml graduated cylinder. Another 20 ml of extraction solution was added to the sample and it was shaken a second time for 30 min. For the last extraction, 10 ml of extraction solution was added to the sample and it was shaken 30 min. The last extraction was added to other extracts in the 50-ml graduated cylinder and brought to 50 ml with fresh extraction solution.

A 10-ml aliquot of the extraction solution was transferred into a clean vial. This aliquot was dried for 30 min at 40 °C under nitrogen. After drying, hydrochloric acid (1 M; 20 ml) was added to the sample. The

sample was cleaned up using a C18 solid phase extraction column. After eluting the triclopyr and TCP from the column, the compounds were extracted by adding hydrochloric acid (0.1 M; 10 ml), sodium chloride (5 g) and 1-chlorobutane (5 ml). The sample was shaken for 30 min on a mechanical shaker. After centrifugation, the 1-chlorobutane layer was transferred into a clean vial. The sample was extracted a second time with 1-chlorobutane (5 ml). The extracts were combined, and concentrated to less than 1 ml using nitrogen. The internal standard was added to the sample along with the derivatizing solution. The sample was brought to a final volume of 1 ml with 1-chlorobutane. To complete the derivatization process, the vial was placed into an oven set at 60 °C for 1 h. After cooling, the samples were placed into GC vials and analyzed by GC/MSD.

The aquatic plants were extracted for TMP analysis using three extractions with sodium hydroxide (0.5 M in water + methanol (20 + 80 by volume); 20 ml, 15 ml, 10 ml). Each extract was shaken for 30 min, they were combined in a 50-ml graduated cylinder and brought to 50 ml with fresh extraction solution. A 20-ml aliquot of the extraction solution was transferred into a clean vial. The TMP was extracted by adding distilled water (10 ml) and hexane (5 ml). The sample was shaken for 30 min on a mechanical shaker and the hexane removed and placed into a clean vial. Another aliquot of hexane was added and the extract shaken for 30 more min. The hexane layers were combined, and concentrated to approximately 1.5 ml using nitrogen. The hexane was added to a small vial containing 2 ml of chlorobutane, and this solution was evaporated to less than 1 ml using nitrogen. The internal standard solution was added along with derivatizing solution, and the volume adjusted to 1 ml using 1-chlorobutane. Final analysis was by GC/MSD.

2.8 Statistical analysis of data

Table 2 lists the reported limits of detection (LOD) and limits of quantification (LOQ) for the analytical methodology for each sample matrix. Any value falling below the LOD is considered to be non-detectable (ND). A value falling between the LOD and LOQ is considered to be non-quantifiable (NQ), and is considered a 'trace' value. Calculations of dissipation rates are based on all actual values, prior to the ND or NQ interpretation being applied. Data were summarized and summary statistics were applied using Microsoft Excel version 7.0. The data were log transformed, and dissipation half-lives were calculated using the 'linest' function of the software, which uses the 'least squares' method to calculate a line that best fits the data and returns an array that describes the line, including regression statistics.

3 RESULTS AND DISCUSSION

Pre-treatment measurements indicated that light transmission decreased substantially (40–50%) by

Table 3. Selected residue levels for the matrices collected during triclopyr treatments, Phelps Bay, Lake Minnetonka, Minnesota, June 1994

Phelps Bay	Triclopyr				TCP				TMP			
	Day 1	Day 3	Day 7	Day 14	Day 1	Day 3	Day 7	Day 14	Day 1	Day 3	Day 7	Day 14
Water ^{a,b}	2.845 (±0.160)	1.913 (±0.212)	0.440 (±0.062)	0.056 (±0.003)	0.015 (±0.001)	0.003 (±0.001)	0.002 (±<0.001)	<0.001 (±<0.001)	0.004 (±0.004)	0.004 (±0.004)	NA ^c	NA
Sediment ^b	121(±45)	257(±97)	104(±12)	13(±2)	NQ ^d	NQ	15(±2)	25(±5)	ND ^e	ND	ND	ND
Target plant	8450	19100	NS	NS	79	205	NS	NS	148	216	NS	NS
Non-target plant	1505	1330	220	NS	20	16	NQ	NS	70	136	51	NS
Bass edible	ND	ND	ND	NS	NQ	18	23	NS	721	931	521	NS
Bass viscera	66	83	25	NS	44	83	183	NS	1611	2365	1670	NS
Bluegill edible	26	ND	ND	ND	NQ	17	NQ	NQ	211	435	111	39
Bluegill viscera	214	100	NQ	NQ	48	127	167	51	1281	2113	1492	196
Sucker edible	51	40	20	ND	35	25	20	NQ	352	232	83	29
Sucker viscera	202	182	42	ND	50	86	42	ND	657	1172	175	96
Clam	147	132	40	NQ	12	12	NQ	ND	52	262	50	17
Crayfish edible	178	162	85	19	11	29	30	NQ	42	118	57	NQ
Crayfish viscera	503	537	347	193	98	161	212	68	70	185	100	6

^a Water concentrations in mg litre⁻¹, all others in ng g⁻¹.

^b Water and sediment concentrations are averages of on-plot samples (±SE). Plant and animal concentrations are from individual samples.

^c NA = Not analyzed.

^d NQ = Not quantifiable.

^e ND = Not detectable.

the 1-m depth level due to the dense submerged canopy of *M. spicatum* growing in the study plots. Light intensity (percentage surface light transmitted) generally increased (by 20–30%) compared to pre-treatment through the water column during the four-week post-treatment period in both triclopyr-treated plots (Phelps and Carsons), while light intensity remained relatively constant over the time course of the study in the untreated reference plot (Carman). This increase in light transmission in the treated plots corresponded with the substantial decrease in milfoil biomass following herbicide application in those plots. Light intensity in the deep open-water stations (outside the plot boundaries) decreased slightly over time in Phelps and Carman Bays, and remained fairly constant in Carsons Bay.

Spectroradiometric data from Phelps Bay and Carman Bay indicated that most of the UV (<400 nm) solar radiation entering the surface waters of Lake Minnetonka was extinguished in the upper 15 cm of the water column. This rapid quenching of UV light typically occurs in natural waters due to dissolved organic compounds and other suspended particles which can greatly increase UV absorption. Since the photolysis of triclopyr and TCP primarily occurs at the 313 nm wavelength, limited photodegradation of triclopyr and its TCP metabolite would be expected to occur in depths below 15 cm in the Lake Minnetonka test system.

Weather conditions during the first several days after application were calm and quiet (winds less than 6 km h⁻¹), and aided in maintaining herbicide contact with the target plant while minimizing water movement within the treated plots and off-plot drift or dilution of the herbicide.

3.1 Residues in water

Complete results of analysis for triclopyr and its metabolites in the matrices collected in this study have been reported separately.¹² Selected residue concentrations for each matrix are presented in Tables 3 and 4. A summary of the calculated half-lives for each matrix is presented in Table 5. Water samples were initially analyzed for triclopyr and TCP, and, subsequently, selected water samples were analyzed for the presence of the TMP metabolite. Comparisons of water dissipation at each discrete sampling depth showed little variation when examined by depth (data not shown). This indicates that water movement within the treated plots was similar throughout all depths. Therefore, water values used in the determination of half-lives are the average values of the samples taken at all in-plot stations, all depths (15 samples total) for each sampling period. It should be noted that TCP is present in the formulated product as an impurity, which accounts for its presence immediately following application.

In Phelps Bay, dissipation half-lives in water were 3.7 and 4.2 days for triclopyr and TCP, respectively (Fig 3). In Carsons Bay, dissipation half-lives in water were 4.7 and 7.9 days for triclopyr and TCP, respectively (Fig 4). Early sampling periods indicate that the application rate was above target rate, but this was an artifact of the time it took for the concentrated material to mix into the water column. Half-lives were consistent with what was expected from the water exchange rates measured in the test bays, and the environmental characteristics of triclopyr were similar to those reported in previous studies of triclopyr dissipation in water.^{9,11,15} Since light levels were low in these plots and bulk water exchange patterns were

Table 4. Selected residue levels for the matrices collected during triclopyr treatments, carsons Bay, Lake Minnetonka, Minnesota, June 1994

Carsons Bay	Triclopyr				TCP				TMP			
	Day 1	Day 3	Day 7	Day 14	Day 1	Day 3	Day 7	Day 14	Day 1	Day 3	Day 7	Day 14
Water ^{a,b}	2.265 (±0.287)	2.170 (±0.166)	1.439 (±0.070)	0.295 (±0.037)	0.007 (±0.001)	0.008 (±0.001)	0.004 (±<0.001)	0.005 (±0.002)	0.002 (±<0.001)	0.004 (±0.001)	NA ^c	NA
Sediment ^b	187(±60)	334(±69)	318(±66)	152(±44)	ND ^e	NQ ^d	NQ	NQ	ND	ND	ND	ND
Target plant	5033	12189	4880	NS	24	43	39	NS	43	171	105	NS
Non-target plant	3210	1563	443	219	23	13	NQ	ND	45	97	NA	27
Bass edible	NQ	24	ND	ND	NQ	17	10	NQ	155	702	208	103
Bass viscera	121	88	53	NQ	21	59	138	161	548	1769	1181	587
Bluegill edible	NQ	NQ	ND	ND	NQ	23	NQ	NQ	227	715	296	254
Bluegill viscera	185	108	139	24	67	143	166	139	807	2800	2067	1445
Bullhead edible	22	13	10	ND	14	32	43	13	59	174	222	86
Bullhead viscera	47	41	66	NQ	56	105	315	90	115	154	965	303
Sucker edible	61	43	43	12	20	21	16	NQ	423	446	175	125
Sucker viscera	225	201	181	80	50	75	86	31	761	1764	1113	217
Clam	153	164	156	55	13	15	20	8	132	344	268	113
Crayfish edible	107	178	156	52	14	31	37	13	83	243	206	49
Crayfish viscera	435	493	687	280	95	184	231	122	157	267	322	36

^a Water concentrations in mg litre⁻¹, all others in ng g⁻¹.^b Water and sediment concentrations are averages of on-plot samples (±SE). Plant and animal concentrations are from individual samples.^c NA = Not analyzed.^d NQ = Not quantifiable.^e D = Not detectable.**Table 5.** Half-life (days) summary for triclopyr and metabolites in examined matrices, Lake Minnetonka, Minnesota, June–August 1994

Phelps Bay	Triclopyr (days) (± SEM)	r ²	TCP ^a (days) (± SEM)	r ²	TMP ^b (days) (± SEM)	r ²
Water	3.7(±0.61)	0.95	4.2(±0.92)	0.87	— ^c	—
Sediment	5.0(±0.99)	0.84	11.3(±0.13)	0.98	—	—
Non-target plant	2.5(±0.38)	0.97	4.0(±0.25)	0.80	—	—
Bass edible	—	—	—	—	—	—
Bass viscera	—	—	—	—	—	—
Bluegill edible	—	—	3.9(±0.81)	0.87	3.1(±0.31)	0.99
Bluegill viscera	2.5(±0.61)	0.92	6.8(±0.50)	0.84	3.5(±0.45)	0.96
Sucker edible	3.6(±0.57)	0.94	5.5(±0.41)	0.93	4.8(±0.28)	0.97
Sucker viscera	2.0(±0.41)	0.97	4.2(±1.18)	0.73	5.4(±0.61)	0.86
Clam	5.2(±0.32)	0.96	2.9(±0.22)	0.99	3.8(±0.41)	0.96
Crayfish edible	5.7(±0.32)	0.96	5.4(±0.61)	0.84	2.4(±0.37)	0.98
Crayfish viscera	9.5(±0.20)	0.95	7.0(±0.24)	0.95	2.5(±0.51)	0.96
Carsons Bay						
Water	4.7(±0.16)	0.99	7.9(±0.35)	0.92	—	—
Sediment	5.8(±0.43)	0.95	10.7(±0.11)	0.98	—	—
Non-target plant	3.4(±0.40)	0.89	4.7(±0.50)	0.78	—	—
Bass edible	—	—	8.9(±0.17)	0.95	6.0(±0.48)	0.85
Bass viscera	5.1(±0.48)	0.84	—	—	11.6(±0.27)	0.83
Bluegill edible	3.3(±0.17)	0.92	7.6(±0.29)	0.91	4.9(±0.52)	0.91
Bluegill viscera	5.7(±0.30)	0.92	11.9(±0.26)	0.86	4.4(±0.63)	0.89
Bullhead edible	4.8(±0.19)	0.88	5.2(±0.08)	0.99	5.8(±0.21)	0.98
Bullhead viscera	6.9(±0.47)	0.85	—	—	5.0(±0.51)	0.90
Sucker edible	5.3(±0.19)	0.98	—	—	7.6(±0.36)	0.89
Sucker viscera	7.0(±0.20)	0.97	—	—	5.2(±0.44)	0.92
Clam	10.4(±0.27)	0.89	—	—	5.8(±0.17)	0.99
Crayfish edible	7.7(±0.34)	0.90	10.6(±0.29)	0.87	5.1(±0.29)	0.97
Crayfish viscera	8.5(±0.39)	0.84	13.7(±0.23)	0.85	3.7(±0.40)	0.96

^a 3,5,6-Trichloropyridinol.^b 3,5,6-Trichloro-2-methoxypyridine.^c — Data insufficient for calculation.

slow, any degradation during the course of this study was likely due to microbial degradation.

Residues detected at the off-plot sampling stations

strongly support the water exchange patterns provided by the dye movement. The correlation between measured dye and triclopyr concentrations was 0.98,

Residues in Water (Phelps Bay)

Figure 3. (■) Triclopyr, (▲) 3,5,6-trichloropyridinol (TCP) and (●) 3,5,6-trichloro-2-methoxypyridine (TMP) residues in water in Phelps Bay, Lake Minnetonka, Minnesota, June–August 1994. (—) Triclopyr and (---) TCP dissipation curves (calculated).

and the dye dissipated at calculated half-lives of 3.9 and 6.3 days in Phelps and Carsons Bays, respectively. A future publication is planned regarding the use of the dye in predicting triclopyr movement and concentrations. In Phelps Bay, herbicide movement was primarily to the southwest, although low levels of triclopyr were found at the remote sampling stations located east of the plot (a peak of $0.0138 \text{ mg litre}^{-1}$ at 1600 m at two weeks post-treatment). In Carsons Bay, residues were detected at all off-plot sampling stations and triclopyr levels peaked at $0.00937 \text{ mg litre}^{-1}$ at 1600 m at two weeks post-treatment. In both sites, TCP levels declined below detection earlier than triclopyr.

The measurements of TMP in fish tissues (see Section 3.3) prompted the analysis of selected water samples. The compound TMP had not been previously found in water following an aquatic application of triclopyr. Those samples analyzed did show small amounts of TMP; however, insufficient samples were analyzed to establish limits of detection and quantification. It was also noted that samples had been thawed and refrozen for previous analyses, and given the volatility of TMP (vapor pressure = 7.5×10^{-3}), it is conceivable that some material may have been lost from these samples during handling. Since TMP is lipophilic and has an estimated bio-concentration factor of 200, the residues of TMP found in fish tissues are likely the result of its being present in the water column. The Carman Bay control plot tested ND for triclopyr and TCP at all sampling events.

3.2 Residues in sediment

Sediment samples were analyzed for triclopyr, TCP, TMP. In Phelps Bay, triclopyr was found in sediment with a maximum value of 257 ng g^{-1} on day 3 of sampling, and dissipated to below the limit of detection by four weeks. The calculated half-life of

triclopyr in the sediment of this bay was 5 days (Fig 5). The highest level of TCP in Phelps Bay sediment was 27 ng g^{-1} at three weeks, and dissipated at a calculated half-life of 11.3 days (Fig 6). The TMP metabolite was not found at detectable levels in the sediment. Samples collected from the 100-m off-plot stations showed occasional trace or low-level residues of triclopyr and TCP.

Carsons Bay sediment displayed a maximum triclopyr value of 375 ng g^{-1} on day 1, and dissipated with a half life of 5.8 days to below the level of detection by week 6 (Fig 4). The TCP metabolite had a peak value of 65 ng g^{-1} at week 3, and its half-life was 10.7 days (Fig 4). TMP was found at trace levels at the one week sampling event. Samples collected from the single 100-m off-plot station (#6, Fig 2) located just outside the constricted entrance to the bay showed levels of triclopyr and TCP similar to the values reported for the within-plot samples, with these residues dissipating with calculated half-lives of 6.8 and 10.6 days, respectively.

It is likely that the levels of triclopyr and its metabolites found in sediment samples in this study resulted from the presence of these materials in the water column establishing equilibrium with the sediment, and resulted in dissipation rates, for the sediment, that mimicked those of the water. Moisture analysis of sediment samples resulted in calculated moisture contents between 200 and 1500%, when compared to the dry weight of the sample. Sediments in the Carman Bay control plot tested ND for triclopyr, TCP, and TMP at all sampling events.

3.3 Residues in target and non-target organisms

The target plant, *M. spicatum*, accumulated triclopyr steadily until its death. In Phelps Bay, triclopyr accumulated to a level of 19100 ng g^{-1} at day 3 in the plant, which was the last sampling event in which

Residues in Water (Carsons Bay)

Figure 4. (■) Triclopyr, (▲) 3,5,6-trichloropyridinol (TCP) and (●) 3,5,6-trichloro-2-methoxypyridine (TMP) residues in water in Carsons Bay, Lake Minnetonka, Minnesota, June–August 1994. (—) Triclopyr and (---) TCP dissipation curves (calculated).

sufficient sample could be collected because plants collapsed and decayed from herbicidal effects (Table 3). Levels of TCP and TMP in the plants also accumulated during this period, with final residue values being 205 and 216 ngg⁻¹, respectively. Target plants in Carsons Bay died and decayed around the one-week sampling period. Residue values were more variable in these samples, with high values occurring early in the sampling scheme. The highest reported value for triclopyr was 23 000 ngg⁻¹, 90 ngg⁻¹ for TCP and 107 ngg⁻¹ for TMP.

The non-target plant (*P. zosteriformis*) collected in this study showed much less accumulation of triclopyr compared to *M. spicatum*. In Phelps Bay, triclopyr values in *P. zosteriformis* peaked at 4410 ngg⁻¹, and dissipated with a calculated half-life of 2.5 days. The calculated half-life for TCP was four days. The

relatively low residue values for TMP did not support the calculation of a dissipation half-life. In Carsons Bay, triclopyr had a calculated half-life of 3.4 days, from a high value of 4 121 ngg⁻¹. The dissipation half-life of TCP was 4.7 days. Again, a TMP half-life could not be calculated. Carman Bay, the untreated reference plot, showed no residues of triclopyr, TCP, or TMP in either target or non-target plants.

Comparison of the levels of triclopyr found in target versus non-target plants indicate the affinity of triclopyr toward *M. spicatum*. This selectivity was supported by the post-treatment plant community data presented in Petty *et al*¹² which showed little or no remaining *M. spicatum* and increased abundance of non-target vegetation. As in the sediment, levels found in plants were proportionate with the concentration and dissipation in the surrounding water.

Residues in Sediment (Phelps Bay)

Figure 5. (■) Triclopyr, (▲) 3,5,6-trichloropyridinol (TCP) and (●) 3,5,6-trichloro-2-methoxypyridine (TMP) residues in sediment in Phelps Bay, Lake Minnetonka, Minnesota, June–August 1994. (—) Triclopyr and (---) TCP dissipation curves (calculated).

Residues in Sediment (Carsons Bay)

Figure 6. (■) Triclopyr, (▲) 3,5,6-trichloropyridinol (TCP) and (●) 3,5,6-trichloro-2-methoxypyridine (TMP) residues in sediment in Carsons Bay, Lake Minnetonka, Minnesota, June–August 1994. (—) Triclopyr and (...) TCP dissipation curves (calculated).

Triclopyr and its TCP and TMP metabolites accumulated and cleared from fish and shellfish tissues with a close temporal relationship to concentrations found in the water column. In all cases, residues were nominally higher in the inedible viscera portions of the animals. Although triclopyr and its metabolites rapidly accumulated in fish tissues, clearance was also relatively rapid and complete (Table 5). Triclopyr half-lives ranged from 2.5 to 10.4 days across all species. TCP half-lives ranged from 2.9 to 13.7 days. TMP half-lives ranged from 2.4 to 11.6 days. Samples of fish and shellfish collected from the untreated reference plot showed no residues of triclopyr, and non-detectable or non-quantifiable residues of TCP and TMP.

An important new finding in this study was the accumulation of TMP in the tissues of various fish and shellfish species collected from the triclopyr-treated plots. TMP levels in fish tissue were often two to four times the level of the parent triclopyr. While TMP is a common metabolite in terrestrial settings,¹⁶ it has been thought to be of little significance in the aquatic environment. It was not identified as a metabolite in either an aquatic photolysis study of triclopyr² or in an aerobic aquatic metabolism study.⁶ Further, a bluegill metabolism study estimated TMP to comprise only about 0.5% of the total activity in the whole fish (Woodburn K B 1995, personal communication). In one earlier fish metabolism study (bluegill), TMP was identified as accounting for a significant metabolite: up to 20% of total residues in the fish.¹⁷ However, these data are now considered erroneous, given the identification of a contaminant in a more recent study (Woodburn K B 1996, personal communication).

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