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Aquatic Dissipation of the Herbicide Triclopyr in Lake Minnetonka, Minnesota

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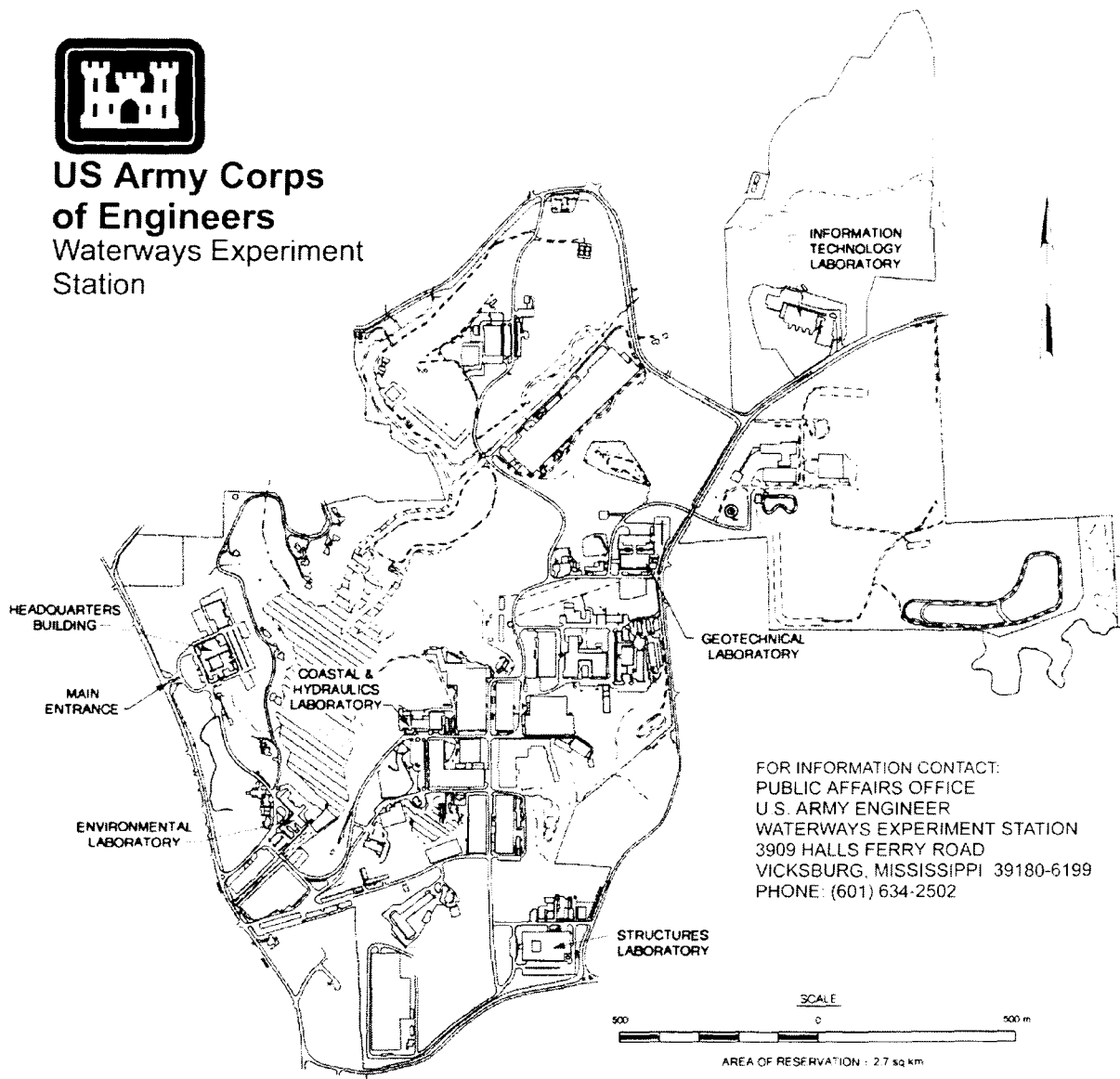
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Preface

The work reported herein was conducted as part of the Aquatic Plant Control Research Program (APCRP), Work Unit 32404. The APCRP is sponsored by the Headquarters, U.S. Army Corps of Engineers (HQUSACE), and is assigned to the U.S. Army Engineer Waterways Experiment Station (WES) under the purview of the Environmental Laboratory (EL). Funding was provided under Department of Army Appropriation No. 96X3122, Construction General. The APCRP is managed under the Center for Aquatic Plant Research and Technology (CAPRT), Dr. John W. Barko, Director. Mr. Robert C. Gunkel, Jr., was Assistant Director for the CAPRT. Program Monitors during this study were Mr. Timothy Toplisek and Ms. Cheryl Smith, HQUSACE. Partial funding for data analyses and report preparation was provided by the Aquatic Ecosystem Restoration Foundation, Inc.

The Principal Investigator for the study was Dr. Kurt D. Getsinger, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL, WES. This study was conducted and the report prepared by Mr. David G. Petty, NDR Research, Drs. Getsinger and John D. Madsen and Mr. John G. Skogerboe, EPEB, Drs. William T. Haller and Alison M. Fox, University of Florida Center for Aquatic Plants (UFCAP), and Mr. Bruce A. Houtman, DowElanco.

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This investigation was performed under the general supervision of Dr. John Harrison, Director, EL; Dr. Richard E. Price, Chief, EPED; and Dr. Robert Kennedy, Acting Chief, EPEB.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Robin R. Cababa, EN.

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1 Introduction

Triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) is a selective, systemic herbicide registered for use in the control of broadleaf weeds and woody plants on rights-of-way, rangeland and pastures, forests, industrial sites, and other noncrop areas. It is also registered for use in rice crop production.

Triclopyr is an auxin-type systemic herbicide 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 plants. It is transported via symplastic mobility processes and accumulates in the meristematic regions.

Investigations have shown that triclopyr can provide aquatic plant managers with a feasible alternative to 2,4-D (2,4-dichlorophenoxy acetic acid) for controlling a variety of nuisance aquatic plants (Getsinger, Turner, and Madsen 1992). Formulated as the triethylamine (TEA) salt, triclopyr can selectively control aquatic weed species such as Eurasian watermilfoil (*Myriophyllum spicatum* L.), purple loosestrife (*Lythrum salicaria* L.), waterhyacinth (*Eichhornia crassipes* (Mart.) Solms) and alligatorweed (*Alternanthera philoxeroides* (Mart) Griseb.), among others (Anderson, Fellows, and Piroosko 1996; Green et al. 1989; Langeland 1986; Getsinger and Westerdahl 1984; Getsinger et al. 1997; Sisneros 1991). Studies conducted by the U.S. Army Corps of Engineers, DowElanco, Tennessee Valley Authority, U.S. Bureau of Reclamation, U.S. Department of Agriculture, and others have shown that triclopyr is rapidly degraded in water and at recommended use rates is not toxic to nontarget organisms (Gersich et al. 1984; Mayes et al. 1984; Gardner and Grue 1996).

Physiochemical Properties of Triclopyr

Triclopyr TEA is a white crystalline solid in appearance and has no discernible odor. It has a molecular weight of 357.67 g, with a melting point between 119 and 121 °C. Triclopyr acid has a molecular weight of 256.5 g/mol, water solubility of 440 mg/L at 25 °C, and a vapor pressure of 1.26×10^{-6} mm Hg at 25 °C.

Environmental Chemistry of Triclopyr

Upon application to an aquatic system, triclopyr TEA quickly hydrolyzes to triclopyr acid (CAS (Chemical Abstract Service) 55335-06-3). This acid subsequently degrades to 3,5,6-trichloropyridinol, or TCP (CAS 6515-38-4). In addition, 3,5,6-trichloro-2-methoxypyridine, or TMP (CAS 31557-34-3), is a common metabolic degradate found in terrestrial uses. It is uncertain whether TMP is a degradate of triclopyr, TCP, or both. TMP has not previously been found in aquatic applications of triclopyr. Figure 1 depicts the structures of triclopyr and its major metabolites.

Photolysis can be a significant route of triclopyr and TCP degradation in the environment. Triclopyr photodegrades at the 313-nm wavelength and is further metabolized to carbon dioxide, water, and various organic acids by aquatic microorganisms (McCall and Gavit 1986). Woodburn et al. (1990) 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 estimated to be 2 hr at a depth of 1 m in river water under 40° north latitude midsummer sunlight (Dilling et al. 1984).

Hydrolysis is not a significant route of degradation for triclopyr. Cleveland and Holbrook (1991) observed no significant degradation in a month-long study conducted at pH 5, 7, and 9. Similar results were observed in a previous hydrolysis study (Hamaker 1975). A study of triclopyr under aerobic aquatic conditions yielded a slow degradation rate of 4.7 months, with TCP as the only significant degradate (Woodburn and Cranor 1987). Laskowski and Bidlack (1984) showed that triclopyr is slowly degraded under anaerobic conditions, such as those that exist in deeper waters and associated with sediments. In that study, triclopyr degraded to TCP with a half-life of about 3.5 years.

The aquatic dissipation of triclopyr has been investigated previously (Getsinger and Westerdahl 1984; Getsinger et al. 1996; Solomon, Bowhey, and Stephenson 1988; Woodburn 1988; Woodburn 1989). Results of these investigations indicate that triclopyr and its pyridinol metabolite undergo rapid degradation in the aquatic environment without adverse effect on the aquatic system. Upon application to an aquatic system, triclopyr degrades and dissipates through chemical, biological, and physical processes.

In an aquatic dissipation study in Lake Seminole, Georgia (Woodburn 1988; Woodburn, Green, and Westerdahl 1993), triclopyr had an average first-order half-life of 0.5 to 3.6 days after being applied at a concentration of 2.5 mg/L. The half-life for the TCP metabolite in Lake Seminole was less than 0.5 days. No accumulation of triclopyr or the TCP metabolite in sediment was observed.

Only trace amounts of these compounds were found in fish, and the half-life of triclopyr in plants, crayfish, and clams was 3.4, 11.5, and 1.5 days, respectively.

A study conducted in Ontario, Canada, showed triclopyr levels in water treated at rates of 0.3 and 120 $\mu\text{g/L}$ to fall below 5 percent of applied within 15 days and to be below detection limits by Day 42 (Solomon, Bowhey, and

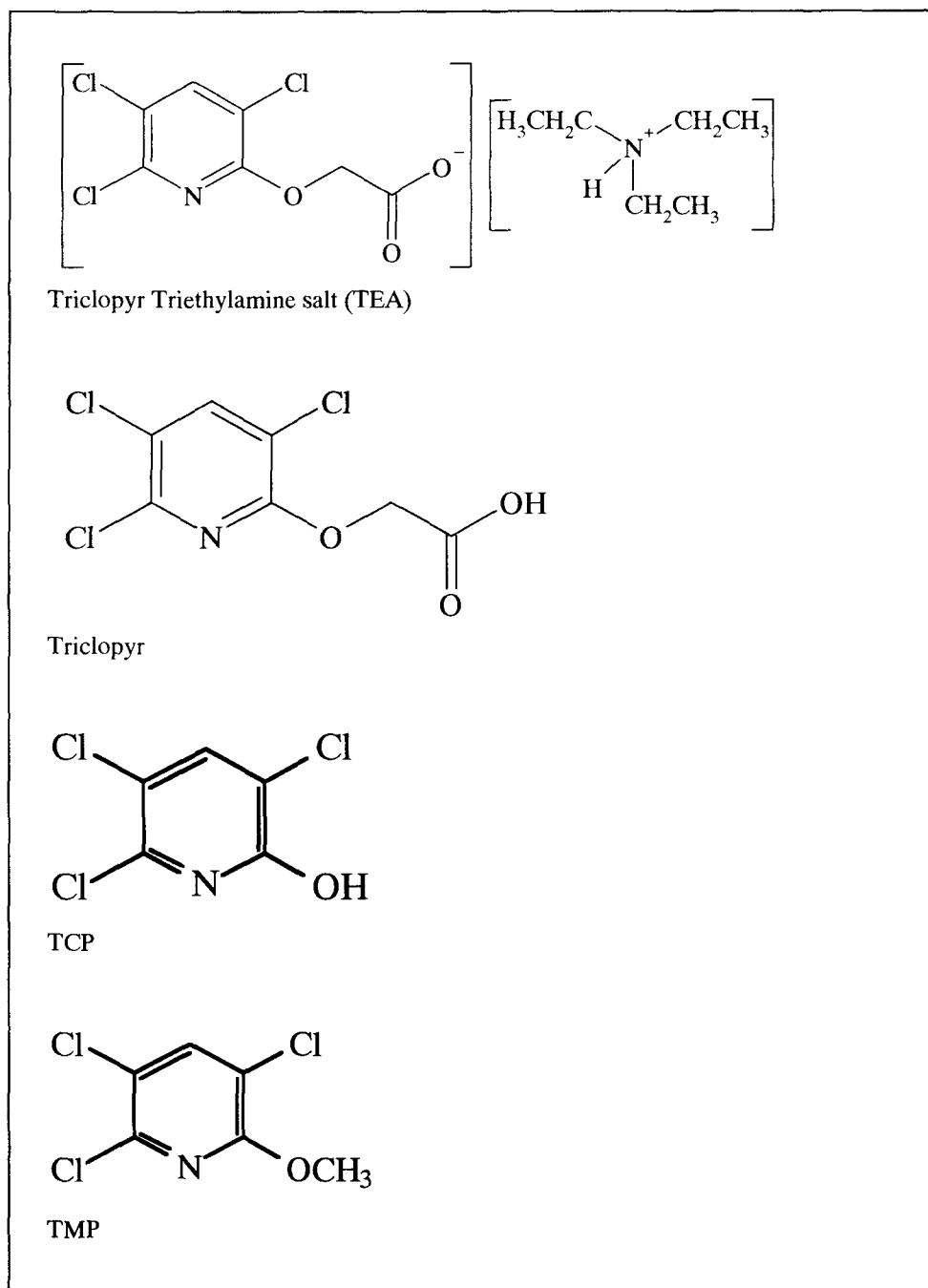


Figure 1. Structure of triclopyr triethylamine, triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP)

Stephenson 1988). 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 (Woodburn 1988) and is thought to be caused by the presence of dissolved organic matter (Woodburn et al. 1990).

A study conducted on the Pend Orielle River, Washington, where triclopyr was applied at a rate of 2.5 mg/L yielded estimated half-lives of 19.4 hr (0.8 days) for a riverine plot, and 52.7 hr (2.2 days) in a protected cove plot with limited water exchange (Getsinger et al. 1996).

Toxicology of Triclopyr

Triclopyr shows a low order of toxicity to microbial communities and higher aquatic organisms, and residue accumulation in sediment, shellfish, and fish is negligible (Getsinger and Westerdahl 1984). Mayes et al. (1984) tested the toxicity of triclopyr TEA salt on fathead minnow and concluded that it is relatively nontoxic and has little cumulative or chronic effect on this species.

The Herbicide Handbook (Humberg 1989) lists LC_{50} values of greater than 200 $\mu\text{g/g}$ for Garlon 3A (the TEA formulation of triclopyr) for trout and almost 900 $\mu\text{g/g}$ for shrimp. The mallard duck 8-day dietary LC_{50} is greater than 10,000 $\mu\text{g/g}$. Triclopyr does not accumulate in any organ of these species, being rapidly excreted.

TCP is minimally concentrated, readily metabolized, and rapidly cleared from the eastern oyster (Holmes and Smith 1991). The 48-hr LC_{50} for daphnia has been measured at 3.13 mg/L, and the 72-hr LC_{50} for fathead minnow has been measured at 14.31 mg/L (Rhinehart and Bailey 1978). Wan, Moul, and Watts (1987) investigated the 96-hr LC_{50} for six species of juvenile pacific salmonids and determined that the values for TCP ranged from 1.5 to 2.7 mg/L.

Wan, Moul, and Watts (1987) also determined 96-hr LC_{50} values on the juvenile salmonids for TMP and reported the range of 1.1 to 6.3 mg/L. The acute mammalian toxicity of 2-methoxy-3,5,6-trichloropyridine (TMP) is relatively low. The oral LD_{50} in male rats is greater than 2,000 mg/kg of body weight, while the acute dermal LD_{50} in rabbits is greater than 795 mg/kg body weight (the highest dose tested) (Vaughn and Keeler 1976). TMP results in only slight eye and skin irritation when tested in rabbits (Rampy, Keeler, and Yakel 1974). Also, TMP is negative in the guinea pig skin sensitization test (Wall 1984). TMP has been tested in repeated-dose dietary studies in rats. A 2-week study was conducted at dose levels of 0 (control), 35, 75, 125, 250, or 500 mg/kg/day. The highest dose level (500 mg/kg/day) resulted in decreased body-weight gain in males and females as well as a slight increase in relative liver weights in males. There were no microscopic changes in the liver of the rats. Males and females at lower dose levels had slightly decreased body-weight gains compared with the control groups (Gorzinski et al. 1982a). A 13-week dietary study in rats was conducted at dose levels of 0 (control), 50, 150, or 500 mg/kg/day.

Decreased body-weight gain and increased relative liver weights were detected in male and female rats treated with 150 or 500 mg/kg/day (Gorzinski et al. 1982b). Male and female rats treated with 50 mg/kg/day had only a minimal decrease in body-weight gain. The no-adverse-effect level was 50 mg/kg/day. The U.S. Environmental Protection Agency (EPA) has reviewed the repeated-dose dietary studies in rats. These data were evaluated as part of the current reregistration process for triclopyr. The Agency has concluded that these mammalian studies indicate that TMP is not more toxic than the parent compound, triclopyr.¹

Control of Eurasian Watermilfoil Using Triclopyr

Eurasian watermilfoil is a submersed perennial, rooting in sediment. Stems of the plant are branched, usually reddish to purple in color, and can grow to lengths of 3 m, often forming extensive mats of vegetation floating at the surface. Leaves are present in whorls of 4 and are pinnately divided into 6 to 16 pairs of threadlike leaflets (Fassett 1957). Although the plant produces seeds, reproduction is usually through vegetative means—by spread of plant fragments and rhizomes (Madsen, Eichler, and Boylen 1988). The plants are essentially evergreen and have no specialized adaptation for overwintering (Aiken, Newroth, and Wile 1979). Some shoots survive the winter, and rapid growth and expansion begin in the spring (Nichols and Shaw 1986). Eurasian watermilfoil inhabits lakes, ponds, streams, and estuaries in both fresh and brackish waters (Grace and Wetzel 1978). It is found throughout North America, as well as Europe and Asia (Smith and Barko 1990).

Eurasian watermilfoil tolerates a broad range of environmental conditions, but is rarely found in acidic waters, preferring waters of about pH 8 (Grace and Wetzel 1978). It grows best in areas of fertile, organic sediment, but will grow as well on a wide range of inorganic sediments (Smith and Barko 1990). Plant growth exhibits a characteristic yearly pattern. Shoots begin to grow rapidly as water temperatures approach 15 °C (Grace and Wetzel 1978). As the shoot lengthens, lower leaves drop off in response to shading, and as the shoot reaches the water surface, it begins to branch profusely, forming a dense floating canopy (Smith and Barko 1990). Dependent upon speed of growth, water and light quality, and water depth, multiple peaks of biomass may occur in a single season. These surface mats can have a severe impact on the functionality of the infested lake or river system, such as maintenance of water quality for wildlife habitat and public health, water storage capacity, navigation, and recreation (Hansen, Oliver, and Otto 1983; Ross and Lembi 1985; Nichols and Shaw 1986).

The timing of Eurasian watermilfoil introduction to the United States is most likely around 1940 (Couch and Nelson 1985), though one author makes claims being made as early as 1881 (Reed 1977). Eurasian watermilfoil is one of many

¹ Personal Communication, July 9, 1997, S. A. McMaster, Registration Manager, DowElanco, Indianapolis, IN.

aquatic plants used in the aquarium trade. By 1985, distribution of Eurasian watermilfoil included 33 U.S. States plus the District of Columbia, and 3 Canadian Provinces (Smith, Barko, and McFarland 1991). By 1996, Eurasian watermilfoil had been identified in 45 U.S. States (Florida Caribbean Science Center 1986). Eurasian watermilfoil is often described as an invasive species, and it is generally accepted that invasions are followed by rapid growth and corresponding displacement of native plant species. A study conducted in Lake George, New York, showed a decline of total aquatic plant species within a Eurasian watermilfoil bed from 30 species to 9 species in a 2-year period (Madsen et al. 1991).

Many methods have been used to control Eurasian watermilfoil, and these include physical, mechanical, biological, and chemical techniques (Madsen 1997).

Physical techniques include drawdown and bottom barriers. Drawdown is the artificial lowering of the water level during cold months so that exposed plants dehydrate and freeze. Although it is possible in lakes with water-level control structures, the cost is usually prohibitive in other lakes. However, under the right circumstances, drawdown can be an effective control measure (Madsen 1997). Bottom barriers can control aquatic plant growth for several years if properly installed and maintained, but are very expensive; their use is restricted to very small areas (<0.1 ha) (Madsen 1997).

Mechanical techniques include harvesting, dredging, and rototilling. While these methods provide immediate favorable results, the effect is short lived, due to Eurasian watermilfoil's growth rate. In fact, these methods all produce vegetative fragments, which help spread the growth of aquatic plants (Madsen 1997). Also, harvesting removes large numbers of macroinvertebrates, semiaquatic invertebrates, forage fishes, juvenile fishes, and even adult game fishes (Madsen 1997). Water quality can be negatively impacted by resuspension of sediment and potential release of bound materials. Mechanical control methods are thought to have negative results in the long term, since Eurasian watermilfoil is known to respond positively to mechanical disturbance (Smith, Barko, and McFarland 1991).

Biological control methods offer the promise of highly specific control with minimal adverse impact on the environment. However, although investigations into control agents continue, few promising candidates have been identified (Smith, Barko, and McFarland 1991). The only operational biological control agent for Eurasian watermilfoil is the white amur (grass carp). The white amur is a poor choice for Eurasian watermilfoil control in most cases due to its preference to eat other, more desirable aquatic plant species (Smith, Barko, and McFarland 1991).

Chemical herbicides are a rapid and easy method for control of aquatic vegetation and under proper conditions can be very effective. Results from concentration/exposure time studies conducted in controlled-environment growth chambers showed that triclopyr provided excellent control of Eurasian watermilfoil under laboratory conditions when exposed to concentrations of 2.5- to

0.25-mg/L acid equivalent (a.e.) triclopyr for 18 to 72 hr (Netherland and Getsinger 1992). In addition, large-scale field studies conducted at various locations around the United States have verified the efficacy of triclopyr against Eurasian watermilfoil. These treatments clearly demonstrated the selective nature of triclopyr applications (i.e., excellent control of Eurasian watermilfoil and minimal impacts on nontarget native vegetation). The study sites included flowing-water situations on the Columbia and Pend Orielle rivers in Washington (McNabb 1993; Getsinger et al. 1996; Getsinger et al. 1997) and more quiescent water conditions in Lake Seminole, Georgia (Getsinger and Westerdahl 1984), and in Guntersville Reservoir, Alabama (Turner, Getsinger, and Burns 1995).

Study Objectives

A study was initiated in June of 1994 by the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, and DowElanco, Indianapolis, IN, to investigate the aquatic dissipation of triclopyr in Lake Minnetonka, Minnesota (Petty 1994). The study protocol was approved by the Registration Division of the EPA, subject to conditions that were addressed in the final study protocol (Taylor 1994). Lake Minnetonka was selected for this study because it is representative of a northern United States Eurasian watermilfoil infestation, the availability of similar yet geographically isolated bays in the same lake, and the cooperative attitude of the residents and local lake management agencies. The primary objectives of this study were to (a) establish the dissipation curves for triclopyr applied to an aquatic environment as the triethylamine salt; (b) follow the formation and decline of its metabolites, TCP and TMP; and (c) establish residue levels of triclopyr and its metabolites found in nontarget aquatic organisms, including fish, clams, crayfish, and plants. This work was conducted according to EPA Guidelines 164-2, Field Dissipation Studies for Aquatic Uses and Aquatic Impact Uses, and 165-5, Field Accumulation Studies of Aquatic Non-target Organisms. Investigations on the efficacy of the treatment, as well as changes in the posttreatment plant community, were also conducted.

2 Test System

Hennepin County

The study was conducted in Lake Minnetonka (44° 56' N Lat., 93° 34' W Lon.), located in Hennepin County, Minnesota. Hennepin County lies in the east-central part of Minnesota and includes part of the city of Minneapolis (Figure 2). The county is irregular in shape, with its boundaries being defined by the Mississippi River and two of its tributaries. Land area within the county is about 139,808 ha, of which 12,442 ha are occupied by 105 different lakes (Lueth 1974). The landscape of Hennepin is gently rolling to steep hills, with extensive lakes and marshes. It was an important dairy farming area, but farming has declined since about 1950, due to residential and industrial expansion.

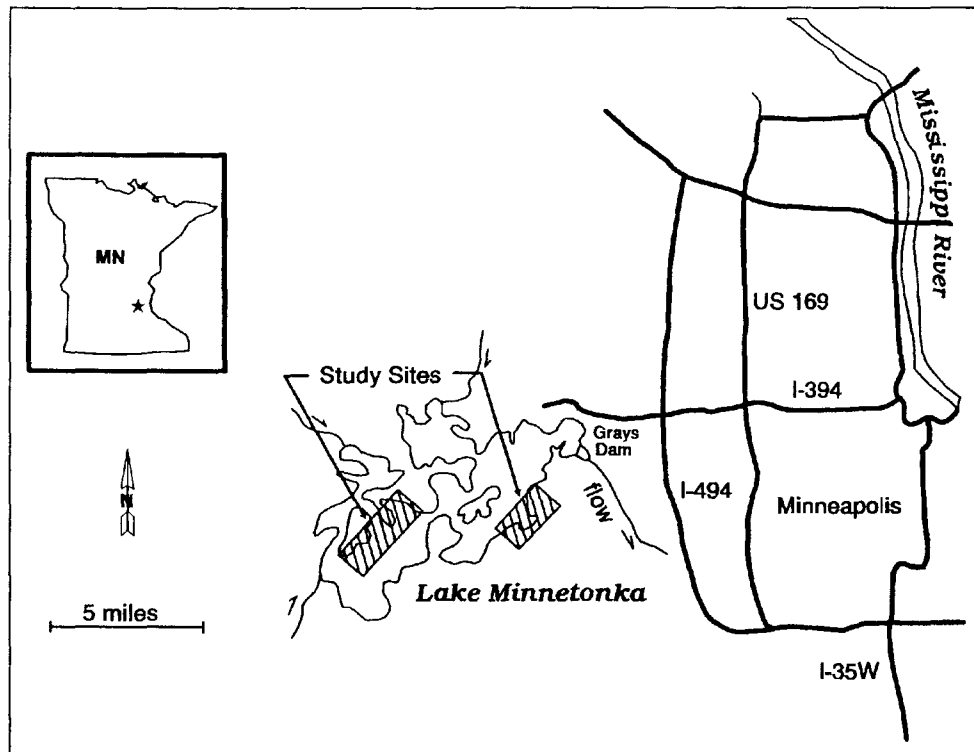


Figure 2. Triclopyr dissipation study site, Hennepin County, Minnesota

Lake Minnetonka

Lake Minnetonka is the largest lake in Hennepin County and is described as “a lake of rare scenic beauty, with many bays and arms” (Lueth 1974). Lake Minnetonka drains the south-central portion of Hennepin County and has its outlet to the Mississippi River through Minnehaha Creek. The lake lies approximately 19.3 km west of the center of the Minneapolis-St. Paul metroplex. The 175 km of shoreline of the lake have been highly developed, mostly as single-family housing units.

Lake Minnetonka is a complex of 15 morphologically distinct basins (Figure 3), with a total area of 5,801 ha (Smith, Barko, and McFarland 1991). The lake has a mean depth of 6.9 m, and a maximum depth of 30.8 m. Total volume of the lake has been calculated to be 400.6 million cubic meters (Smith, Barko, and McFarland 1991). Glacial drifts forming the morainic hills and basins in the watershed of the lake were deposited during the Wisconsin Age of the Pleistocene Epoch. Lake Minnetonka is underlain by a sandy conglacareous red drift, consisting mainly of crystalline igneous and metamorphic rock. The western portion of the watershed had a moraine of gray, claylike drift deposited over the red drift. This gray drift is highly calcareous and contains fragments of limestone and shale. The two drifts can be separated by running a line northwest from Excelsior Bay through Stubbs Bay (Smith, Barko, and McFarland 1991).



Figure 3. Lake Minnetonka, Minnesota, showing three bays used in triclopyr dissipation study: Phelps Bay (treated), Carsons Bay (treated), and Carman Bay (untreated)

Lake Minnetonka has been famous for over a century for the recreational opportunities it provides. Swimming, boating, water-skiing, and fishing (year-round) are among the recreational activities for which the lake is used. This heavy-use pattern provides ample opportunity for the spread of plant species

both within and to other lakes, through the transport of vegetative fragments. There are 14 independently governed cities on the shore of the lake, and its metropolitan nature make it one of the busiest in the State of Minnesota.¹ Aerial surveys of boat density on the lake revealed an average of 1,375 boats per survey flight (Anonymous 1994).

Much of Lake Minnetonka is suitable for rooted submersed aquatic plants, and the lake has supported considerable plant growth for as long as records have been maintained (Smith, Barko, and McFarland 1991). A 1950 survey of plant growth reported rooted vegetation covering about one-sixth of the lake. At the time of this survey, plant species included curlyleaf pondweed (*Potamogeton crispus* L.), coontail (*Ceratophyllum demersum* L.), northern watermilfoil (*Myriophyllum sibiricum* Komarov), Canada waterweed (*Elodea canadensis* L.), sago pondweed (*Potamogeton pectinatus* L.), and water buttercup (*Ranunculus longirostris* Godron) (Moyle 1950).

Climate

The climate of Hennepin County is predominately continental (Lueth 1974). Temperature is varied, and summer precipitation is ample, while winter precipitation is scanty. The National Oceanic and Atmospheric Administration (NOAA) weather station at Maple Plain, located approximately 5 km northwest of the lake, has a recorded 30-year average annual temperature of 6.9 °C. Average long-term temperature for the months of June, July, and August is 16.9 °C. Long-term annual precipitation is 68.4 cm, with 30.5 cm occurring during the same summer months (NOAA 1992).

Eurasian Watermilfoil Infestation

Eurasian watermilfoil was first discovered in Lake Minnetonka in 1986¹ and since has grown to cover a significant portion of the lake. The real extent of the Eurasian watermilfoil infestation fluctuates on a yearly basis, with the estimates of the impacted areas ranging between 600 and 1,200 ha.² Approximately 2,200 ha, over one-third of the lake, are thought to be suitable for Eurasian watermilfoil colonization.¹

¹ Personal Communication, 1995, Lake Minnetonka Conservation District.

² Personal Communication, 1995, C. Welling, Coordinator, Eurasian Watermilfoil Program, Minnesota Department of Natural Resources.

3 Materials and Methods

Test Substance

Triclopyr

Triclopyr TEA salt, formulated as the product Garlon 3A, was the test material used (Table 1). An amount of 3,208 L (790 gal) of lot IC02161106 in 9.5-L (2.5-gal) containers was shipped via ground freight to Braun Intertec, Minneapolis, MN (a local contract research firm), on May 26, 1994. The material was shipped via Roadway Express, Inc. (waybill 321-728502-4), and was received at Braun Intertec on May 31, 1994. An assay was performed on the material on March 24, 1994, and it was found to be 45.0-percent triclopyr TEA (32.3-percent triclopyr a.e.), about 0.5 percent above nominal purity for the product (Hamilton 1995a). The test material was assigned the test substance identification number TSN100421. Upon receipt at Braun Intertec, the test material was placed into a secure storage area under ambient conditions. A record of temperature in the storage area was maintained for the duration of the study.

| | |
|-----------------------------------|---|
| Chemical name | 3,5,6-Trichloro-2-pyridyloxyacetic acid, triethylamine salt |
| Common name | Triclopyr TEA |
| Product name | Garlon 3A herbicide |
| EPA Registration No. | 62719-37 (Garlon 3A) |
| Nominal percent active ingredient | 44.4% |
| Lot No. | IC02161106 |
| TSN | TSN100421 |
| Date of assay | March 24, 1994 |
| Percent active ingredient | 45.0% Triclopyr TEA (32.3% a.e.) |

Prior to application, each bottle of test material was sequentially numbered, and total weight of the unopened bottle was measured and recorded. After each

application, the opened bottles were reweighed and their new weights recorded. The amount of test material applied was calculated from this weight difference. Receipt, use, and disposition logs were maintained for each container of test material. The unused test material and empty containers were returned to DowElanco on August 15, 1994.

Rhodamine WT

The fluorescent dye rhodamine WT was tank-mixed with the triclopyr to monitor the herbicide movement in the water column. Rhodamine WT has been approved for use in potable water at concentrations up to 100 mg/L and can be quantified in situ with the use of a field fluorometer (Getsinger et al. 1996). This dye has also been used to simulate aqueous distribution and dissipation of several herbicides, including triclopyr, used in the control of aquatic plants (Fox, Haller, and Shilling 1991; Fox, Haller, and Getsinger 1992, 1993; Getsinger et al. 1997; Turner, Getsinger, and Netherland 1994; Turner, Getsinger, and Burns 1995). Results from these studies indicate that aquatic herbicide distribution and dissipation can be predicted by monitoring dye movement and concentration. A study conducted by DowElanco (Hamilton 1995b) evaluated the stability and uniformity of a tank mix of Garlon 3A and rhodamine WT dye. This study concluded that the mixture remained stable and uniform throughout.

Two 9.5-L (2.5-gal) containers of rhodamine WT (Lot 087) were hand delivered to Braun Intertec on June 14, 1994, by personnel from the U.S. Army Corps of Engineers (USACE). The dye was placed into storage along with the test material and subjected to the same monitoring. A receipt, use, and disposition log was maintained for each dye container. Remaining dye was returned to the USACE on August 3, 1994.

Test Site Identification and Plot Layout

Plot layout

Three rectangular test plots of approximately 6.5 ha (16 acres) each were established in separate bays of Lake Minnetonka (Figure 3). The plots were selected for similarities in water depth and plant communities, but probable differences in water exchange characteristics. Two of the plots were subsequently treated, with the third plot being used as an untreated reference, or control plot.

Each 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 were established off-plot at 100 m from the edge of the plot, along the off-shore sides of the plot. Additionally, three more off-plot sampling stations were located at 400, 800, and 1,600 m from the plot edge, along what was judged to be the most likely line of chemical movement. Provision was made in the study protocol to add additional offsite residue sampling stations if deemed necessary. The control plot had only a single sampling station

established at plot center. Plot corners and sampling stations were marked with anchored, floating buoys, as described below.

A history of chemical treatments of the test bays is presented in Table 2. These records indicate that no triclopyr was used in any of the study bays. It should be noted that Minnesota aquatic herbicide application permits only identify treatment location by bay and that proximity of previous treatments to the test plots cannot be determined.

Phelps Bay

Plot A, hereafter referred to as Phelps Bay, was established along the west-northwest shore of Phelps Bay, Lake Minnetonka (Figure 4). The plot had a mean water depth of 1.98 m and an estimated water exchange half-life of >17 hr.¹ This plot was subsequently treated via a subsurface injection application, as described below.

Carsons Bay

Plot B, hereafter referred to as Carsons Bay, was established in the back section of Carsons Bay, Lake Minnetonka (Figure 5). This portion of Carsons Bay is a small enclosed arm of the lake, with a mean depth of 1.7 m and with a probability of a water exchange half-life greater than that measured at Phelps Bay. The plot consisted of essentially the entire arm of the bay outside of the emergent zone. This plot was subsequently treated via a surface broadcast application.

Carman Bay

Plot C, hereafter referred to as Carman Bay, was established in the milfoil bed along the northwest shore of Carman Bay, Lake Minnetonka (Figure 6). In August 1993, this plot had a mean water depth of 2.5 m and an estimated water exchange half-life of approximately 8 hr. This plot was used as the control plot.

Markers and buoys

Plot corners at each bay were marked with large, cylindrical buoys, labeled with study and plot identification. Internal and external sampling stations were marked with smaller, round buoys, labeled with the sampling station number. Additionally, the Minnesota Department of Natural Resources (MNDNR) placed their own marker buoys outside the test areas, which indicated a Eurasian water-milfoil research area with restricted entry. For application purposes, small floats were placed into the plot areas to mark off the 0.8-ha treatment segments. Positions of the corner and sampling station buoys were plotted using a global positioning system (GPS).

¹ Personal Communication, 1994, Kurt D. Getsinger, Biologist, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Table 2
Herbicide Application History for Treatment Sites on Phelps,
Carsons, and Carman Bays, Lake Minnetonka, Minnesota

| Year | Bay | Chemical | Ha Treated | Total Qty | Unit |
|--------------------|---------|------------------|------------|-----------|------|
| 1991 | Carman | 2,4-D ester | 3.23 | 55.92 | kg |
| 1991 | Carman | Hydrothol liquid | 1.36 | 0.61 | L |
| 1991 | Carman | Ortho-Diquat | 3.81 | 31.42 | L |
| 1991 | Carman | Rodeo | 0.14 | 0.95 | L |
| | | | | | |
| 1992 | Carman | 2,4-D ester | 4.66 | 394.95 | kg |
| 1992 | Carman | Aquathol liquid | 1.96 | 58.48 | L |
| 1992 | Carman | Diquat | 4.66 | 67.19 | L |
| 1992 | Carman | Hydrothol | 0.04 | 1.81 | kg |
| | | | | | |
| 1993 | Carman | 2,4-D ester | 5.01 | 398.26 | kg |
| 1993 | Carman | Aquathol liquid | 1.78 | 28.39 | L |
| 1993 | Carman | Diquat | 4.87 | 79.34 | L |
| 1993 | Carman | Hydrothol 191 | 0.05 | 1.81 | kg |
| | | | | | |
| 1994 | Carman | Aqua-Kleen | | 263.09 | kg |
| 1994 | Carman | Copper compounds | | 26.12 | L |
| 1994 | Carman | Copper sulfate | | 110.68 | kg |
| 1994 | Carman | Diquat | | 62.29 | L |
| 1994 | Carman | Hydrothol 191 | | 1.81 | kg |
| 1994 | Carman | Riverdale | | 68.04 | kg |
| | | | | | |
| 1991 | Carsons | Aquathol liquid | 7.02 | 27.37 | L |
| 1991 | Carsons | Ortho-Diquat | 6.56 | 15.14 | L |
| 1991 | Carsons | Other herbicide | 2.63 | | ? |
| | | | | | |
| 1992 | Carsons | Aquathol liquid | 4.53 | 9.84 | L |
| 1992 | Carsons | Diquat | 5.07 | 37.66 | L |
| 1992 | Carson | Hydrothol | 0.87 | 1.63 | kg |
| <i>(Continued)</i> | | | | | |

| Table 2 (Concluded) | | | | | |
|----------------------------|------------|------------------|-------------------|------------------|-------------|
| Year | Bay | Chemical | Ha Treated | Total Qty | Unit |
| 1993 | Carsons | Aquathol liquid | 5.97 | 51.71 | L |
| 1993 | Carsons | Diquat | 6.89 | 63.97 | L |
| | | | | | |
| 1994 | Carsons | Aquathol | | 1.89 | L |
| 1994 | Carsons | Copper compounds | | 37.74 | L |
| 1994 | Carsons | Copper sulfate | | 4.54 | kg |
| 1994 | Carsons | Diquat | | 11.36 | L |
| | | | | | |
| 1991 | Phelps | 2,4-D ester | 1.28 | 65.30 | kg |
| 1991 | Phelps | Aquathol liquid | 0.99 | 4.01 | L |
| 1991 | Phelps | Hydrothol liquid | 0.99 | 9.50 | L |
| 1991 | Phelps | Ortho-Diquat | 1.28 | 21.43 | L |
| | | | | | |
| 1992 | Phelps | 2,4-D ester | 1.67 | 192.78 | kg |
| 1992 | Phelps | Aquathol | 1.17 | 54.43 | kg |
| 1992 | Phelps | Aquathol liquid | 0.83 | 5.75 | L |
| 1992 | Phelps | Diquat | 2.42 | 43.83 | L |
| | | | | | |
| 1993 | Phelps | 2,4-D ester | 1.75 | 195.5 | kg |
| 1993 | Phelps | Aquathol liquid | 2.07 | 70.37 | L |
| 1993 | Phelps | Diquat | 1.46 | 27.63 | L |
| | | | | | |
| 1994 | Phelps | Aqua-Kleen | | 200.04 | kg |
| 1994 | Phelps | Aquathol | | 51.25 | L |
| 1994 | Phelps | Copper compounds | | 10.94 | L |
| 1994 | Phelps | Copper sulfate | | 33.97 | kg |
| 1994 | Phelps | Diquat | | 30.02 | L |

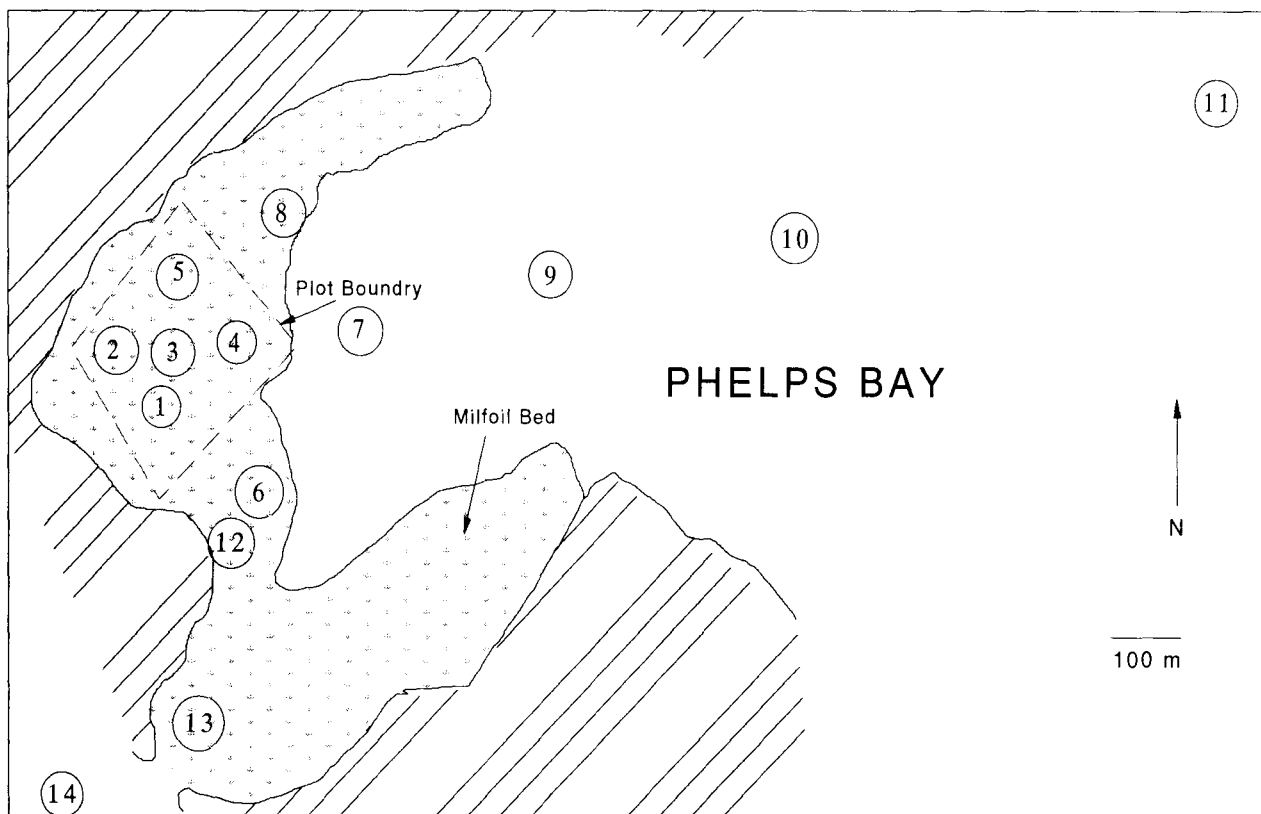


Figure 4. Phelps Bay (Plot A), Lake Minnetonka, Minnesota, treated with Garlon 3A at 2.5 $\mu\text{g/L}$ triclopyr, 21 June 1994 (Circled numbers represent residue sampling stations)

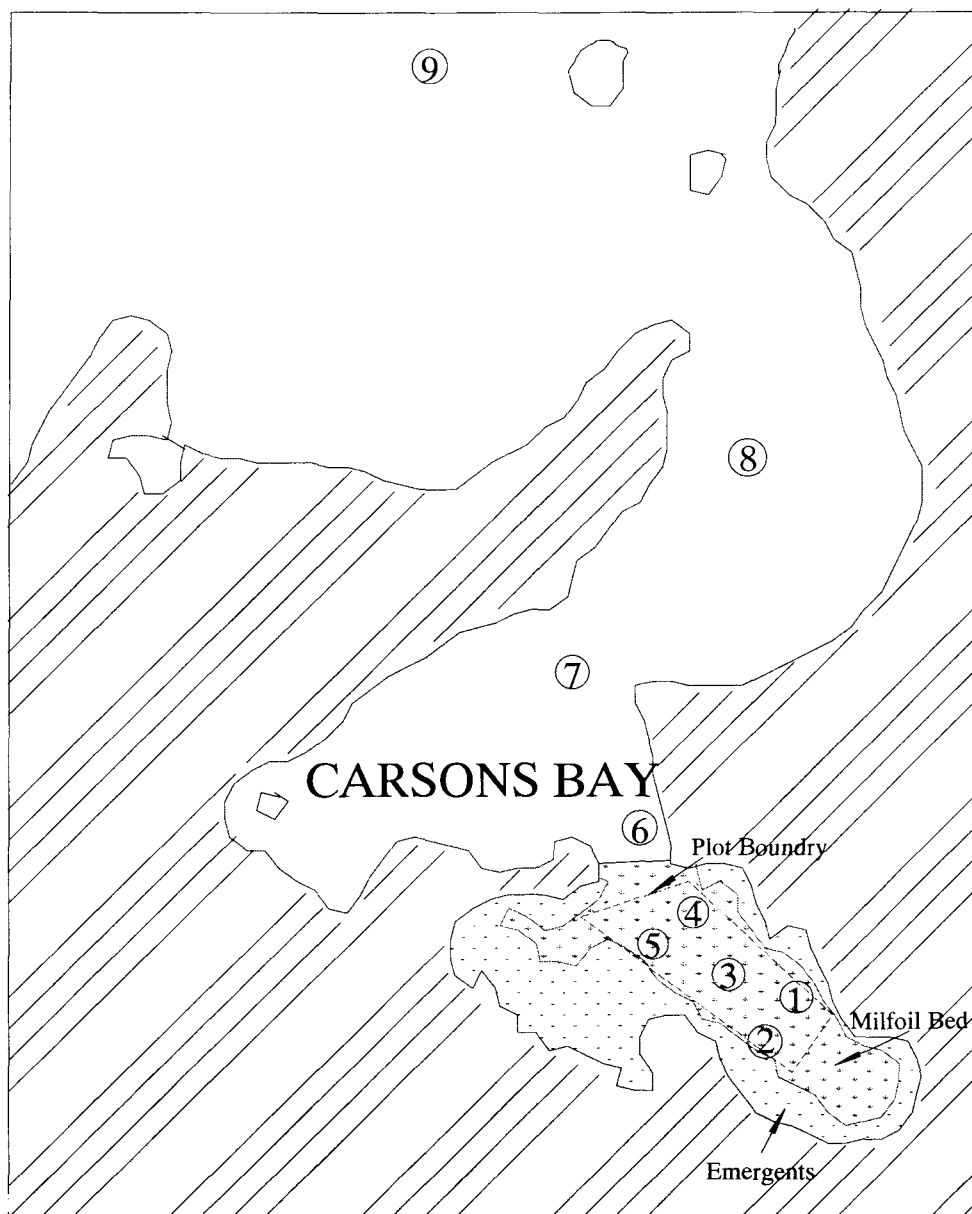


Figure 5. Carsons Bay (Plot B), Lake Minnetonka, Minnesota, treated with Garlon 3A at 2.5 $\mu\text{g/L}$ triclopyr, 23 June 1994 (Circled numbers represent residue sampling stations)

Survey methods

Layout and survey of plot boundaries, sampling stations, and terrestrial landmarks were accomplished through the use of differential GPS survey and interpretation of aerial photographs. GPS is a form of electronic survey that works by triangulation of the measurement device's location in relation to orbiting navigational satellites. The survey instrument receives signals from these orbiting satellites and performs internal calculations of latitude, longitude,

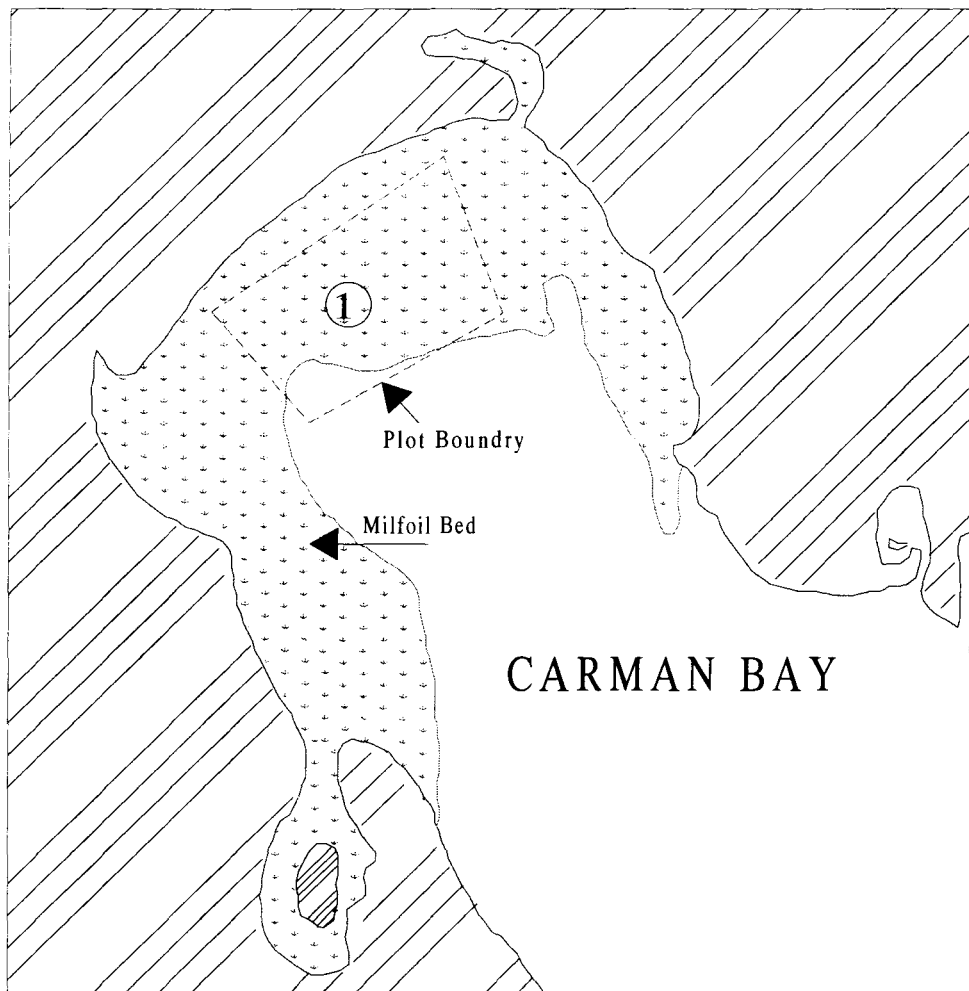


Figure 6. Carman Bay (Plot C), Lake Minnetonka, Minnesota, used as untreated reference plot (Circled number represents residue sampling station)

and elevation. Differential GPS employs a second, stationary receiver, whose measurements are used to provide an error correction offset in the measurements taken with the survey receiver. Navstar Systems (Woodland Hills, CA) model XR4-G GPS receivers were used in the survey.

Aerial photographs of each plot were also taken, and these images were digitized onto existing U.S. Geological Survey (USGS) topographic maps of the region. These photographs were used to correct discrepancies in the existing maps, locate plot features, and to delineate plant beds within the individual test bays.

Meteorological Measurements

Three automated weather stations (Campbell Scientific, Logan, UT) were used to monitor meteorological conditions during the course of the study. Stations were located at each test bay, as close to the water and the actual test plot as possible. Ideally, weather stations should be isolated from terrestrial obstructions that might interfere with the measurements; however, space restraints did not always allow this. It was noted that the stations established at Phelps and Carman bays might fall within the wind and light shadows of nearby trees and structures, which might affect some measurements. The station established at Carsons Bay was constructed at the end of a long dock and was essentially located within the bay itself. Therefore, it was determined that this station would provide the most reliable weather data.

Each station operated continuously throughout the study period, with station records beginning 5 to 6 days prior to application and ending at the conclusion of the 6-week sampling period. Weather stations were powered by internal lead-acid batteries that were continuously trickle charged through the use of an external solar panel. Measurement of all sensors occurred once each second, and stations performed summary statistics at the end of each 1-hr period and again at midnight for the entire the 24-hr period. These final data were transferred to solid state storage modules at the end of each summary period. Storage modules were periodically replaced and the data retrieved and stored electronically.

Each weather station was comprised in part of a Campbell Scientific (Logan, UT) model 21XL micro data logger, which operated the connected sensors and performed summary statistics and error checking on the data collected. The storage module also monitored its internal temperature and available power as part of a self-diagnostic routine.

Measurements made by each station included rainfall, using a Texas Electronics (Dallas, TX) TE525 tipping bucket; air temperature; relative humidity; wind speed and direction, using an RM Young (Traverse City, MI) wind sentry set; solar radiation, using a LiCor (Lincoln, NE) LI200S silicon pyranometer; and net radiation 1 m above the water, using an REBS (Seattle, WA) Q6 net radiometer.

Water Quality Measurements

Water quality was measured from pretreatment (20 June 1994) through 6 weeks posttreatment (3 August 1994) at each plot, at two separate depths using a Hydrolab Corporation (Austin, TX) model Datasonde 3. Measurements of temperature, conductivity, pH, and dissolved oxygen (DO) were made once each hour for the first 4 weeks of the study and then at every 6 hr for the last 2 weeks. The sonde devices were serviced routinely for battery replacement, data collection, and recalibration. Data were collected with a laptop computer through an interface cable. Additional measurements of water quality (temperature, conductivity, pH, and DO) were performed using a portable

submersible Hydrolab device. These depth profiles were taken through the water column in the treatment plots (Phelps and Carsons) at Stations 1 and 3 (center), and in an area of deep (5 to 7.5 m) open water, 100 to 400 m outside of each plot. Water quality profiles were also taken in the reference plot (Carman) at Station 1 (center) and in an area of deep (4 to 5.5 m) open water, 100 m outside of the plot. All water quality profiles were taken between 1000 and 1400 hr.

Light Intensity and Spectral Irradiance

Light intensity, measured as percent of surface light transmitted through the water column, and transparency were measured in the treatment plots (Phelps and Carsons bays) at Stations 1 and 3 (center) and in an area of deep (5 to 7.5 m) open water, 100 to 400 m outside of each plot. Light intensity was also measured in the reference plot (Carman Bay) at Station 1 (center) and in an area of deep (4 to 5.5 m) open water, 100 m outside of the plot. Percent light transmission was measured using a LiCor (Lincoln, NE) Model 1000 meter with a submersible PAR quantum probe and PAR deck (surface) cell, which measured light in the photosynthetically active range (PAR) of 400 to 700 nm; light transparency was measured using a Secchi disk. These light profiles were taken on 19 June (pretreatment) and on the posttreatment dates of 25 and 27 June, and 6 and 18 July between 1000 and 1400 hr.

In order to determine transmission of ultraviolet (UV) solar energy (<400 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 hr.

Nontarget Organisms

Nontarget aquatic organisms used in this study included fin-fish species such as largemouth bass, bluegill, brown bullhead, and sucker and invertebrate species such as clam and crayfish. These nontarget animal species were selected to represent different trophic levels in the aquatic food chain. Bass and bluegill feed in all depths of the water column, while catfish and suckers tend to limit much of their feeding activities to the bottom layers of the water column. Crayfish are omnivorous scavengers, and clams are sedentary filter feeders. Nontarget organisms were obtained from local sources and placed into the lake under permit from the MNDNR. The aquatic animals were kept in floating cages (1.2 by 1.2 by 1.2 m) constructed of nylon mesh and polyvinyl chloride (PVC). The cages included latching covers to prevent escape of, or predation on, the contained animals. The animals were separated by species, and each species was kept in several cages, to minimize population pressures. Small sections (10 to 12 cm) of PVC pipe were placed in the crayfish cages to provide secure hiding places in order to minimize cannibalism. It should be noted that cages did not allow access to the lake bottom, 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. Animals were fed periodically, the feed consisting of such items as pelleted chow and bait leeches, and dead or moribund individuals were recorded and removed from the cages upon discovery. Remaining animals were destroyed and disposed of at the conclusion of the 4-week sampling period. Retainer samples of foodstuff were collected and archived.

Originally, sucker were not one of the protocolled organisms in this study. A power failure at the animal holding facility the night before the cages were stocked resulted in the loss of most of the bullhead species of catfish. Sucker were substituted at the last minute. Later, it was determined that enough bullhead had survived to stock the cages in the control plot (Carman Bay) and one treatment plot (Carsons Bay).

Bass

The bass species used was a largemouth bass (*Micropterus salmoides* Lacepede). The largemouth bass is a member of the sunfish family *Centrarchidae*, which includes 30 species. Members of the sunfish family are characterized by deep, laterally compressed bodies and spiny-rayed fins. The habits and life history of all sunfishes are basically alike. Most are rather sedentary fish, remaining much of the time near submerged cover or in shadows. They generally do not school, but may occur in loose aggregations. Individuals can show an affinity with a specific territory, often spending their entire life within a restricted area. Feeding is primarily by sight, and generally only mobile objects are attractive. Insects, crustaceans, and small fish are the primary foodstuffs. Feeding occurs both at the surface and bottom, and food may be captured by active foraging or by ambush. Feeding generally occurs in early morning and again in late evening.

The largemouth bass is a slender, streamlined sunfish with a large mouth and a distinctive, continuous midside stripe. Adults are commonly 25 to 50 cm long and weigh 0.25 to 2 kg, though individuals weighing up to 3.5 kg are not uncommon. The largemouth bass tolerates varied conditions, but is more characteristic of quiescent rather than flowing waters (Pflieger 1975; Robison and Buchanan 1945).

Bluegill

The bluegill species used was *Lepomis macrochirus* (Rafinesque). The bluegill is also a member of the sunfish family *Centrarchidae* and has habits like that described above for the largemouth bass. The bluegill is a deep and slab-sided sunfish with a rather small mouth and commonly reaches a length of 24 cm and a weight of 350 g. One of the more gregarious of the sunfish, it often moves in associations of 20 to 30 individuals. It feeds by sight, at all levels of the water column. Insects are the staple food for adults, but small fish, crayfish, and snails are also eaten. It may feed on vegetation when other foodstuffs are scarce (Pflieger 1975; Robison and Buchanan 1945).

Bullhead

The bullhead species used was brown bullhead (*Ictalurus nebulosus* Lesueur). Bullheads are a member of the catfish family *Ictaluridae*, which includes 37 species restricted to North America. Catfish have smooth, scaleless skin, four pairs of barbels located near the mouth, and a strong, sharp spine located at the front of the dorsal and pectoral fins. These spines may contain a mild venom that, while not dangerous, does cause a painful reaction. Catfish are most active at night and generally hide in shadowed areas during the daytime. Catfish have abundant external tastebuds, especially on the barbels. Feeding is in direct response to stimulation of these tastebuds. Catfish species are generally bottom-feeders.

The brown bullhead are similar to the black and yellow bullheads, but are distinct in that the back and sides have a strongly mottled rather than uniform coloration. Adults are commonly 18 to 38 cm long and weigh 0.15 to 1 kg (Pflieger 1975; Robison and Buchanan 1945).

Suckers

The species of sucker used in the study was white sucker (*Catostomus commersoni* Lacepede). Suckers are a member of the family *Catostomidae*, which includes about 100 species. They are soft-rayed fishes with toothless jaws, a scaleless head, and a forked tail. Suckers can range in size from 23 cm and 0.23 kg to 90 cm and 36 kg, depending upon species. Suckers feed by sucking material from the bottom. Typically, the mouth is located on the underside of the head and is equipped with fleshy, protruding lips. Typical foodstuff consists of burrowing insects and small mollusks, along with some plant material. Some suckers take in large amounts of sediment from which they extract organic detritus and small animal life.

The white sucker is slender, fine-scaled, and colored a brassy green on the back and sides. The belly is white. Adults are commonly 25 to 40 cm long and weigh 0.23 to .77 kg. The white sucker lives in schools, and although the adults are primarily bottom feeders, the young feed near the surface of the water (Pflieger 1975; Robison and Buchanan 1945).

Clam

The clam species used was first identified as sandshell clam, but later the identification was corrected to be the mussel Fatmucket (*Lampsilis siliquoidea* Barnes).¹ Mussels and clams are a member of the order Pelecypoda. The two valves of the shell are securely attached to each other dorsally by an elastic hinge ligament and gape slightly to permit the protrusion of the foot at the anteroventral margin and the inhalent and exhalent siphons at the posterior margins. There are no tentacles, head, or eyes. The animal lies obliquely with the ventral half buried in the substrate. Food consists of zooplankton, phytoplankton, and

¹ Personal Communication, January 18, 1996, P. Baker, Macalester College, St. Paul, MN.

organic detritus. The feeding process has been specialized for the removal of these suspended microscopic particles from the water by passing a continuous stream of water over the gill structures, where it is entangled in mucous, and then passed on to the mouth structure (Pennak 1978).

The fatmucket is common and widespread throughout the midwestern United States, most often found in lakes and small streams with bottom compositions of mud, sand, or gravel. It is a moderately large, thick-shelled species, colored yellow or tan, with green rays (Cummings and Mayer 1992).

Crayfish

The crayfish species used was either *Oreocnectes virilis* or *O. immunis* (two closely related species). Crayfish are in the order *Decapoda*, which includes the crayfishes and shrimps. Crayfish, also known as crawfish and crawdads, are more or less cylindrical, and the body is heavily sclerotized. The compound eyes are large, stalked, and movable. Crayfish have six distinct abdominal segments, and a fused head and thorax, known as the cephalothorax, covered with a carapace. In general, crayfish are omnivorous and will eat aquatic vegetation and animal matter. Ecologically, they are usually considered scavengers. Adult crayfish usually remain hidden during the daytime and feed during the dark hours. Although they generally crawl along the bottom, many crayfish are strong swimmers and can make use of the entire water column. They usually inhabit shallow waters and tolerate a wide range of temperature and pH conditions (Pennak 1978).

Plants

Samples of target and nontarget plants were collected from each bay for the first 4 weeks of the study or until plants were no longer available for sampling. Plants were gathered from within the defined treatment area, and the indicated species was separated to comprise the sample.

Target plant

Eurasian watermilfoil was the target plant in this study. Characteristics of this plant have been described previously in this report.

Nontarget plants

The species collected as the representative nontarget plant in this study was flatstem pondweed (*Potamogeton zosteriformis* Fernald). This species was widely distributed throughout the study plots. Flatstem pondweed is a common aquatic plant in northern United States lakes, though little has been written about it. It is a submersed plant, firmly rooted in the bottom. Stems are slender and branching, with narrow grasslike leaves (Fink 1994).

Plant Community Biomass and Diversity

A survey of the plant community in each of the test plots was undertaken by a team of self-contained underwater breathing device (SCUBA) divers from the USACE. In the center of each plot, five 100-m transects, with marked intervals every 1 m, were deployed perpendicular to the shore. These transects were separated by a distance of 25 m. Divers recorded the plant species present in each 1-m interval of each transect to determine species distribution and diversity. In addition, four biomass samples were collected in a stratified-random manner from each transect using a 0.1-m² quadrat. These samples were transferred to the laboratory where shoots were sorted into species and dried to a constant weight at 55 °C. All test plots were evaluated 1 week prior to treatment, 6 weeks posttreatment, and 1 year posttreatment.

Application Equipment Calibration

Calibration of both the subsurface and broadcast herbicide delivery systems was accomplished by collecting water delivered by the application rigs into containers and calculating flow rate from the measured amounts. When the desired flow rate was obtained, pressure and revolutions per minute (rpm) settings on the delivery pumps were noted. The calculated flow rates were compared with that measured by an in-line flow meter and found to be in agreement. During application, the in-line flow meter was used to monitor rate of application, and adjustments in boat speed were made according to those observations.

Application of Test Material

Subsurface application

Subsurface application was the delivery method used on Phelps Bay, Plot A of the study. Triclopyr, as Garlon 3A, along with the dye rhodamine WT was applied as a tank mix at nominal rates of 2.5 mg/L and 12 µg/L, respectively, through a spray boom operated from an airboat. The spray boom consisted of three trailing hoses of 1.2, 2.4, and 3.7 m in length. Two airboats were involved in the application, each with a crew of two, an operator and an applicator. Each airboat made application to a marked 0.8-ha segment of the test plot before needing a new tank mix prepared to treat another 0.8-ha plot segment. Upon emptying a tank of test material, the airboat would proceed to the edge of the defined plot and be met by a supply boat loaded with additional containers of triclopyr and dye. Each tank mix was comprised of 113.6 L of Garlon 3A and 1,000 mL of rhodamine WT dye, premeasured into individual bottles. Water was added to bring the total volume of each load to approximately 380 L. A 100-mL sample of each tank mix was collected and stored on ice. The plot size was 6.5 ha; therefore, there were eight 0.8-ha segments, requiring that each

airboat deliver four tank loads of mix to the lake. Application to Phelps Bay began on June 21, 1994, at 0600 hr, and was completed at 0800 hr.

Surface application

Surface broadcast application was the delivery method for Carsons Bay, Plot B of the study. The application device used was a Radiarc sprayer, produced by Waldrum Specialties (Doylestown, PA). The Radiarc is a boomless, low-volume device that applies liquid formulations in a uniform pattern while providing good control of drift. This device was mounted in the bow of the application boats. As on the Phelps Bay application, two airboats were involved in delivering the triclopyr/dye tank mix. Triclopyr (as Garlon 3A) was again applied to make a nominal application rate of 2.5 mg/L, while the dye was applied at 10 µg/L. The same system of 0.8-ha application segments and supply boat was utilized as on Phelps Bay. Each prepared tank mix consisted of 95 L of Garlon 3A, 600 mL of dye, and water to 380 L. The differences in tank mix amounts from Phelps Bay were due to the difference in water depth. Application to Carsons Bay began on June 23, 1994, at 0600 hr and was completed at 0800 hr.

Both application days had fair, moderate weather, with light breezes. Application day temperatures and wind speeds are presented in Tables 3 and 4.

Confirmation of Application Rate

Application rate was confirmed by total weight of formulated material applied to each plot, as well as the early sampling residue results. Each container of formulated test material was labeled with a unique number, and total weight of the unopened container was recorded prior to application. During applications, the mixer/loaders on the supply boat kept records of which containers were used, and postapplication weights of those containers were recorded. Amount of test material applied to the plots was calculated by subtracting the postapplication weights of the containers from the preapplication weights. Calculations show that 1,034.5 kg of test material was applied to Phelps Bay, and 860.7 kg of test material was applied to Carsons Bay.

The average water depth in the Phelps Bay plot was measured to be 1.98 m. The assay of the test material was 32.2 percent triclopyr a.e., so 334.14 kg of triclopyr was applied to a volume of 130,680 m³. This would result in an application rate of 2.6 mg/L. The average water depth in the Carsons Bay plot was measured to be 1.7 m; therefore, 278 kg of triclopyr was applied to a volume of 110,500 m³. This would result in an application rate of 2.5 mg/L. Accordingly, the resultant rates of dye application to Phelps and Carsons bays would be 12.2 µg/L and 8.7 µg/L, respectively.

Table 3
Application Day Weather for Phelps Bay, Lake Minnetonka, Minnesota, June 21, 1994

| Date | Time | Rain cm | Air Temp °C | Max Temp °C | Min Temp °C | %RH | Wind Speed km/hr | Wind Dir | s.d. Dir | Total Rad. KWm ⁻² | Net Rad kWm ⁻² |
|--------|------|---------|-------------|-------------|-------------|-----|------------------|----------|----------|------------------------------|---------------------------|
| 21-Jun | 0100 | 0 | 22.0 | 22.5 | 21.5 | 69 | 3.2 | 299 | 16 | 0 | -306 |
| 21-Jun | 0200 | 0 | 21.1 | 21.6 | 20.8 | 73 | 2.7 | 296 | 17 | 0 | -328 |
| 21-Jun | 0300 | 0 | 20.6 | 21.0 | 20.0 | 74 | 1.7 | 300 | 21 | 0 | -355 |
| 21-Jun | 0400 | 0 | 19.7 | 20.1 | 19.3 | 77 | 1.1 | 301 | 20 | 0 | -339 |
| 21-Jun | 0500 | 0 | 19.0 | 19.4 | 18.6 | 80 | 2.0 | 303 | 17 | 0 | -370 |
| 21-Jun | 0600 | 0 | 18.3 | 18.7 | 18.1 | 81 | 4.0 | 306 | 16 | 42 | -354 |
| 21-Jun | 0700 | 0 | 19.0 | 19.6 | 18.7 | 76 | 6.2 | 322 | 13 | 462 | -167 |
| 21-Jun | 0800 | 0 | 20.0 | 20.7 | 19.6 | 71 | 5.8 | 326 | 14 | 1,079 | 372 |
| 21-Jun | 0900 | 0 | 21.5 | 22.5 | 20.7 | 65 | 3.9 | 328 | 16 | 1,690 | 991 |
| 21-Jun | 1000 | 0 | 23.5 | 24.3 | 22.4 | 55 | 1.4 | 70 | 19 | 2,320 | 1,577 |
| 21-Jun | 1100 | 0 | 24.4 | 24.9 | 24.1 | 47 | 3.2 | 31 | 26 | 2,854 | 2,050 |
| 21-Jun | 1200 | 0 | 24.9 | 25.5 | 24.2 | 42 | 3.2 | 28 | 28 | 3,130 | 2,267 |
| 21-Jun | 1300 | 0 | 25.8 | 26.4 | 24.7 | 40 | 2.0 | 73 | 24 | 3,239 | 2,359 |
| 21-Jun | 1400 | 0 | 26.3 | 27.0 | 25.5 | 42 | 1.6 | 8 | 36 | 3,446 | 2,501 |
| 21-Jun | 1500 | 0 | 26.8 | 27.7 | 26.2 | 41 | 1.9 | 23 | 38 | 3,405 | 2,466 |
| 21-Jun | 1600 | 0 | 26.6 | 27.4 | 25.9 | 40 | 1.8 | 335 | 48 | 1,595 | 2,199 |
| 21-Jun | 1700 | 0 | 26.0 | 26.3 | 25.7 | 41 | 3.1 | 326 | 22 | 133 | 1,797 |
| 21-Jun | 1800 | 0 | 26.0 | 26.2 | 25.8 | 41 | 4.6 | 318 | 20 | 123 | 1,306 |
| 21-Jun | 1900 | 0 | 26.1 | 26.3 | 25.9 | 43 | 5.0 | 328 | 18 | 199 | 758 |
| 21-Jun | 2000 | 0 | 26.5 | 26.9 | 25.7 | 44 | 2.8 | 351 | 17 | 636 | 155 |
| 21-Jun | 2100 | 0 | 24.5 | 25.7 | 23.3 | 54 | 0.5 | 26 | 20 | 74 | -257 |
| 21-Jun | 2200 | 0 | 22.9 | 23.5 | 22.3 | 58 | 0.0 | 297 | 3 | 3 | -339 |
| 21-Jun | 2300 | 0 | 21.8 | 22.5 | 21.2 | 75 | 0.0 | 0 | 0 | 0 | -340 |
| 21-Jun | 2400 | 0 | 20.9 | 21.3 | 20.5 | 84 | 0.1 | 288 | 44 | 0 | -338 |

Table 4
Application Day Weather for Carsons Bay, Lake Minnetonka, Minnesota, June 23, 1994

| Date | Time | Rain cm | Air Temp °C | Max Temp °C | Min Temp °C | %RH | Wind Speed km/hr | Wind Dir | s.d. Dir | Total Rad. kWm ⁻² | Net Rad kWm ⁻² |
|--------|------|---------|-------------|-------------|-------------|-------|------------------|----------|----------|------------------------------|---------------------------|
| 23-Jun | 0100 | 0 | 21.29 | 21.77 | 20.74 | 77.80 | 0.5 | 164 | 17 | 0 | -165 |
| 23-Jun | 0200 | 0 | 20.89 | 21.14 | 20.70 | 81.00 | 0.0 | 153 | 0 | 0 | -134 |
| 23-Jun | 0300 | 0 | 20.61 | 20.82 | 20.51 | 81.40 | 0.0 | 0 | 0 | 0 | -135 |
| 23-Jun | 0400 | 0 | 20.40 | 20.56 | 20.21 | 83.10 | 0.0 | 286 | 71 | 0 | -139 |
| 23-Jun | 0500 | 0 | 20.59 | 21.14 | 20.27 | 83.10 | 0.1 | 71 | 48 | 0 | -141 |
| 23-Jun | 0600 | 0 | 21.29 | 21.41 | 21.12 | 77.70 | 1.9 | 356 | 23 | 11 | -143 |
| 23-Jun | 0700 | 0 | 21.00 | 21.41 | 20.71 | 80.70 | 1.6 | 120 | 27 | 202 | -34 |
| 23-Jun | 0800 | 0 | 21.14 | 21.41 | 21.00 | 81.30 | 1.4 | 118 | 23 | 365 | 100 |
| 23-Jun | 0900 | 0 | 21.89 | 22.30 | 21.36 | 78.70 | 0.7 | 21 | 25 | 724 | 358 |
| 23-Jun | 1000 | 0 | 22.85 | 23.38 | 22.27 | 73.70 | 1.0 | 120 | 16 | 1,057 | 593 |
| 23-Jun | 1100 | 0 | 23.57 | 23.89 | 23.27 | 69.64 | 1.3 | 135 | 16 | 998 | 536 |
| 23-Jun | 1200 | 0 | 23.88 | 24.15 | 23.56 | 62.41 | 1.7 | 135 | 17 | 1,257 | 716 |
| 23-Jun | 1300 | 0 | 24.10 | 24.44 | 23.83 | 56.95 | 3.3 | 119 | 13 | 1,618 | 974 |
| 23-Jun | 1400 | 0 | 24.20 | 24.49 | 23.99 | 57.99 | 2.8 | 137 | 17 | 1,498 | 868 |
| 23-Jun | 1500 | 0 | 24.01 | 24.49 | 23.44 | 57.46 | 3.6 | 141 | 22 | 1,592 | 931 |
| 23-Jun | 1600 | 0 | 23.44 | 23.71 | 23.20 | 62.37 | 5.1 | 137 | 24 | 1,708 | 1,000 |
| 23-Jun | 1700 | 0 | 23.22 | 23.56 | 22.87 | 65.69 | 4.4 | 142 | 26 | 1,366 | 793 |
| 23-Jun | 1800 | 0 | 22.63 | 23.08 | 22.40 | 69.02 | 3.8 | 145 | 27 | 862 | 445 |
| 23-Jun | 1900 | 0 | 22.51 | 22.84 | 22.05 | 69.38 | 3.4 | 138 | 21 | 776 | 371 |
| 23-Jun | 2000 | 0 | 21.77 | 22.11 | 21.49 | 68.48 | 1.7 | 143 | 27 | 255 | 13 |
| 23-Jun | 2100 | 0 | 21.31 | 21.57 | 20.77 | 73.00 | 1.3 | 127 | 26 | 93 | -109 |
| 23-Jun | 2200 | 0 | 20.42 | 20.78 | 20.10 | 77.50 | 0.1 | 140 | 19 | 8 | -164 |
| 23-Jun | 2300 | 0 | 19.76 | 20.34 | 18.79 | 79.00 | 0.6 | 118 | 21 | 0 | -221 |
| 23-Jun | 2400 | 0 | 18.30 | 18.82 | 17.83 | 86.70 | 0.6 | 142 | 19 | 0 | -272 |

Characterization Sampling

Water

Water samples for characterization were collected from one location in each plot during the week prior to application. Samples of approximately 3 L each were collected by pump from two depths, approximately one-third and two-thirds of the total depth of the water column. Samples were collected into metal cans and stored on ice. Samples were immediately shipped to the characterization laboratory in a chilled, unfrozen condition.

Sediment

Sediment for physical characterization was collected in each plot from each of the internal and 100-m external sampling stations. Samples of at least 500 g were collected utilizing a ponar dredge and stored in metal containers. Sediment samples were stored and shipped under ambient conditions. Sampling was conducted during the week prior to application, but method requirements for additional matrix necessitated a second sample collection at the 4-week posttreatment period. Samples were subsequently stored and shipped to the characterization laboratory under ambient conditions.

Residue Sampling

All residue samples were stored in metal cans at the time of collection and placed on ice in a cooler. Preprinted labels were applied to sample containers that included protocol number, unique sample ID number, plot and sample station identification, sample period, matrix, and depth, where appropriate. Disposable gloves were worn during all sample collection and handling activities.

As each sample was collected, data were recorded on a preprinted sampling sheet that contained the same information indicated on the sample label. Additional data recorded at this time included (a) indication the sample was collected; (b) date and time of collection; and (c) depth of sampling, in the case of water samples, along with water temperature and dye reading. Water and sediment were collected for 6 weeks after application. Aquatic animals and plants were collected for 4 weeks, except in those instances where the supply was exhausted. The sampling schedule is presented in Table 5.

Water sampling

Water samples for residue analysis were collected in duplicate from three depths at each sampling station at each indicated water sampling event. Water sampling at the internal and near offsite stations began 1 hr postapplication. Sampling at the offsite stations (400, 800, 1,600 m) did not begin until 3 hr postapplication. At each sampling event, an approximate 400-mL water sample

Table 5
Residue Sampling Schedule for Triclopyr Treatments on Lake
Minnetonka, Minnesota, 1994

| | Water | Sediment | Plants | Fish | Controls |
|--------------|-------|----------|--------|------|----------|
| Pretreatment | X | X | X | X | X |
| 1 Hr | X | | X | X | |
| 3 Hr | X | | X | X | |
| 6 Hr | X | X | X | X | |
| 12 Hr | X | X | X | X | |
| 1 Day | X | X | X | X | |
| 2 Day | X | | | | |
| 3 Day | X | X | X | X | |
| 5 Day | X | | | | |
| 1 Week | X | X | X | X | X |
| 2 Week | X | X | X | X | |
| 3 Week | X | X | X | X | |
| 4 Week | X | X | X | X | X |
| 6 Week | X | X | | | |

was collected at 25 cm below the water surface, at the midpoint of the water column, and at 25 cm above the bottom for all stations located inside the plot. Off-plot water samples were collected at the same depth as the deepest on-plot station, at each plot.

Water was collected by pumping water from the appropriate depth using an uncontaminated, battery-powered bilge pump and drinking-water-quality opaque hose. Two to three pump volumes were expelled prior to collection of the sample, and the sample container was then rinsed with water from the appropriate depth. Water was collected starting with the deepest depth and working toward the water surface. Hoses and pumps were changed after each sampling period to minimize the possibility of sample contamination.

Sediment sampling

Sediment samples were collected from approximately the top 5 cm of the lake bottom at each in-plot and 100-m off-plot sampling station at each indicated sediment sampling event. Sediment was not collected from the 400, 800, and 1,600-m off-plot stations due to the depth of the lake at these points, as well as the unlikelihood of significant residues being found in sediment from these locations. Sediment was collected using a ponar dredge, spread on a section of window screen to drain excess water and remove foreign objects, and sealed in a sample container.

Nontarget organism sampling

Fish and shellfish were sampled from preestablished holding cages by net collection. In general, a sample was comprised of multiple individuals, depending upon size of the individuals collected. Fish and shellfish samples were subsequently rinsed with distilled water in the preparation laboratory prior to initial processing.

Plant sampling

Plant samples were collected from suitable plant stands located near the center of each plot using a garden rake or similar device. Collected plants were separated into the appropriate target and nontarget species and rinsed with distilled water prior to being placed into the sample containers.

Dye sampling

Measurements of dye concentration and water temperature were made concurrently with each water sampling event by pumping water from the appropriate depth through a portable Turner Designs (Sunnyvale, CA) fluorometer. Water temperature and dye concentration data were recorded on the residue sampling sheets.

Additional dye measurements were conducted at random locations surrounding the treated plots. The data collected were used to identify water movement from the plot area and to predict triclopyr movement within the lake. Additional water residue sampling stations were added on the strength of those observations.

Sample Handling

As samples were collected in the field, they were placed into metal cans. Plant and fish samples were rinsed with distilled water to wash away any residual lake water that might contain triclopyr residues. The samples were stored on ice during the sampling procedure. Samples were transported from the study site to a local laboratory, and water, sediment, and plants were logged into frozen storage. Fish samples were refrigerated until the initial preparation was completed, and then were transferred to frozen storage.

Field preparation of fish

Fish samples, including crayfish and clams, were transported to a local laboratory and maintained under refrigerated conditions during the initial sample preparation procedure. Upon receipt in the laboratory, fish were removed from the metal cans they were stored in and rinsed with distilled water to remove excess lake water.

Each fish sample was separated into two new samples, one sample comprising the edible fillet portion of the fish, and the other sample 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 in fresh containers.

Sample shipping

Residue samples were routinely shipped to DowElanco via overnight express. Samples were packaged frozen into insulated shipping boxes along with a supply of dry ice. Appropriate chain of custody forms accompanied the samples. Upon receipt by DowElanco, the condition of the samples was inspected and noted upon the chain of custody forms; samples were logged into the sample tracking system and were placed into frozen storage.

Sample preparation

Samples were prepared by the DowElanco Sample Management Group prior to transfer to the analytical laboratory. Sediment, plant, and fish tissues were ground with dry ice and the prepared sample separated into analytical and long-term storage subsamples. Water underwent no preparation, the duplicate sample serving as the long-term sample.

Analytical Methods

Analysis of water and sediment samples for physiochemical characterization was conducted by A&L Great Lakes Laboratories of Fort Wayne, IN. Residue analysis was conducted by Dow Chemical's Health and Environmental Sciences (H&ES) Group (Midland, MI) and by the DowElanco Analytical Services Group (Indianapolis, IN). Where appropriate, samples were prepared by grinding with a hammermill and stored at -20 °C until analysis.

Water characterization

Lake water was tested for alkalinity, total suspended solids, pH, hardness, conductivity, turbidity, chemical oxygen demand, and for sulfate, sodium, magnesium, and calcium levels.

Sediment characterization

Sediment analyses included pH, cation exchange capacity, organic matter, 1/3 and 15 bar water-holding capacity, and percent proportions of sand, silt, and clay.

Water residue analysis

Water samples were analyzed utilizing DowElanco method GRM 95.18 (Olberding, Foster, and McNett 1996). To analyze water for triclopyr, TCP, and TMP, a 25-mL aliquot of water was transferred into a clean vial. The analytes were extracted into 1-chlorobutane by adding 1 mL of 2 N HCL, 10 g of NaCl, and 6 mL of 1-chlorobutane to the vial. The sample was shaken for 30 min 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 1 mL using nitrogen. A fluoroxypr internal standard was added along with the derivatizing reagent N-(tert-butyltrimethylsilyl)-N-methyltrifluoroacetamide (MSBSTFA), and the final volume was adjusted to 1.0 mL using 1-chlorobutane. The extract was then heated at 60 °C for 1 hr. The samples were then analyzed by gas chromatography/electron impact/mass spectrometry (GC/EI/MS).

Sediment residue analysis

Sediment samples were analyzed for triclopyr, TCP, and TMP using DowElanco method GRM 95.19 (Olberding 1996). Five grams of sediment was extracted with two extractions of a 90-percent acetone, 10-percent 1 N hydrochloric acid solution. The two extractions were combined and the volume adjusted to 40 mL.

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 2 mL under nitrogen, and 20 mL of 0.5 N HCL 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 5 mL of acetonitrile followed by 5 mL of 0.1 N HCL. The sample was loaded into the C₁₈ solid phase column, and the sample vial was rinsed with 2 mL of 0.1 N HCL. This rinse was also loaded onto the column. The column was then rinsed with 3 mL of a 40-percent acetonitrile, 59-percent water, and 1-percent 1 N HCL solution. The sample was eluted with 3 mL of a solution of 80-percent acetonitrile, 19-percent water, and 1-percent 1.0 N HCL. Triclopyr and TCP were extracted by adding 10 mL of 0.1 N HCL, 5 g NaCl, and 5 mL of 1-chlorobutane to the eluant. The sample was then shaken on a mechanical shaker for 30 min. After centrifugation, the 1-chlorobutane layer was transferred to a clean vial. The sample was then extracted a second time with an additional 5 mL of 1-chlorobutane and the extracts combined. The sample was concentrated to less than 1 mL using nitrogen. One hundred microliters of acetone containing the internal fluoroxypr standard was added to the sample, and the final volume was adjusted to 1 mL using 1-chlorobutane. Prior to derivatization, the sample was transferred to a GC vial. The triclopyr and TCP were derivatized to the t-butyltrimethylsilyl ester and ether, respectively, by adding 100 µL of MSBSTFA derivatizing reagent and heating at 60 °C for 1 hr. 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 10 mL of water, 1.0 mL of 2.5 N sodium hydroxide, and 5 mL of hexane. The sample was

shaken for 20 min 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 1 mL using nitrogen. An internal standard was added and volume adjusted to 1 mL using 1-chlorobutane. The sample was then analyzed by GC/MS.

Nontarget organism analysis

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 hydrolyzed using aqueous 0.25 N sodium hydroxide. Following hydrolysis, the sodium hydroxide 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 40-percent acetonitrile, 60-percent butyl chloride, and 0.2-percent acetic acid. The triclopyr and TCP fraction was concentrated to less than 1 mL, 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/MS.

DowElanco Analytical Services' methodology also extracted and hydrolyzed residues of triclopyr, TCP, and TMP from fish using aqueous 0.25 N sodium hydroxide. Following hydrolysis, the sodium hydroxide was acidified and the analytes extracted with ethyl ether. The ethyl ether was passed through an alumina SPE column that retained the triclopyr and TCP, while the TMP was contained in the ethyl ether eluate. For the determination of TMP, the ethyl ether was concentrated and exchanged with 1-chlorobutane. The triclopyr and TCP were eluted from the alumina column with 0.1 N sodium hydroxide, 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.

Plant analysis

Triclopyr and TCP in aquatic plants were determined by adding 20 mL of 0.5 N NaOH in a solution of 20-percent water and 80-percent methanol 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, 20 mL of 1 N HCl was added to the sample. The sample was cleaned up using a C₁₈ solid phase extraction column. After eluting the triclopyr and TCP off the column, the compounds were extracted by adding 10 mL of 0.1 N HCl, 5 g of NaCl, and 5 mL 1-chlorobutane. 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 an additional 5 mL of 1-chlorobutane. 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 1.0 mL with 1-chlorobutane. To complete the derivatization process, the vial was placed into an oven set at 60 °C for 1 hr. After cooling, the samples were placed into GC vials and analyzed by GC/MS.

The aquatic plants were extracted for TMP analysis using three extractions of 0.5 N NaOH in a 20-percent water, 80-percent methanol solution. Extraction in volumes of 20, 15, and 10 mL were each shaken for 30 min, and finally combined in a 50-mL graduated cylinder. Final volume of the combined extracts was 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 10 mL of distilled water and 5 mL of hexane. 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 minutes. 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/MS.

4 Results and Discussion

Meteorological Conditions

The three automated weather stations operated efficiently through the course of the study. In general, the data collected by the stations are in agreement, taking into account the geographical separation between them, and the aforementioned limitations as to ideal placement. This resulted in the station at Carsons Bay, the best placed station, recording higher average wind speeds and total solar radiation than the stations at Phelps and Carman bays. However, the highest total rainfall was recorded at the Phelps Bay station, with total amounts decreasing as measured east across the lake. A comparison of daily rainfall amounts, along with that recorded at Minneapolis International Airport, is presented in Figure 7. These minimal rainfall amounts did not affect the dilution of herbicide applied to the treated plots. A comparison of daily average temperature is presented in Figure 8. Bar graphs of total daily solar radiation and average daily wind speed recorded at Carsons Bay are presented in Figures 9 and 10. A review of the data shows that the weather conditions during the first several days after application were calm and quiet 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. Rainfall amounts and average air temperature as measured during the course of the study were consistent with long-term averages for the area.

Water Quality and Characterization

Water quality standards have been established for many areas of water use, including recreation, public water supply, fish and wildlife, agriculture, and industrial uses. Given the use pattern of Lake Minnetonka, water quality will be discussed in terms of suitability for aquatic life.

The pH values of natural waters are usually in the range of 6.5 to 8.5 (Federal Water Pollution Control Administration (FWPCA) 1968). Higher incident values (pH 9 to 11) may occur due to photosynthetic activities of aquatic plants. The carbonate system is the major buffering system in natural waters, as well as providing the carbon reservoir for photosynthesis.

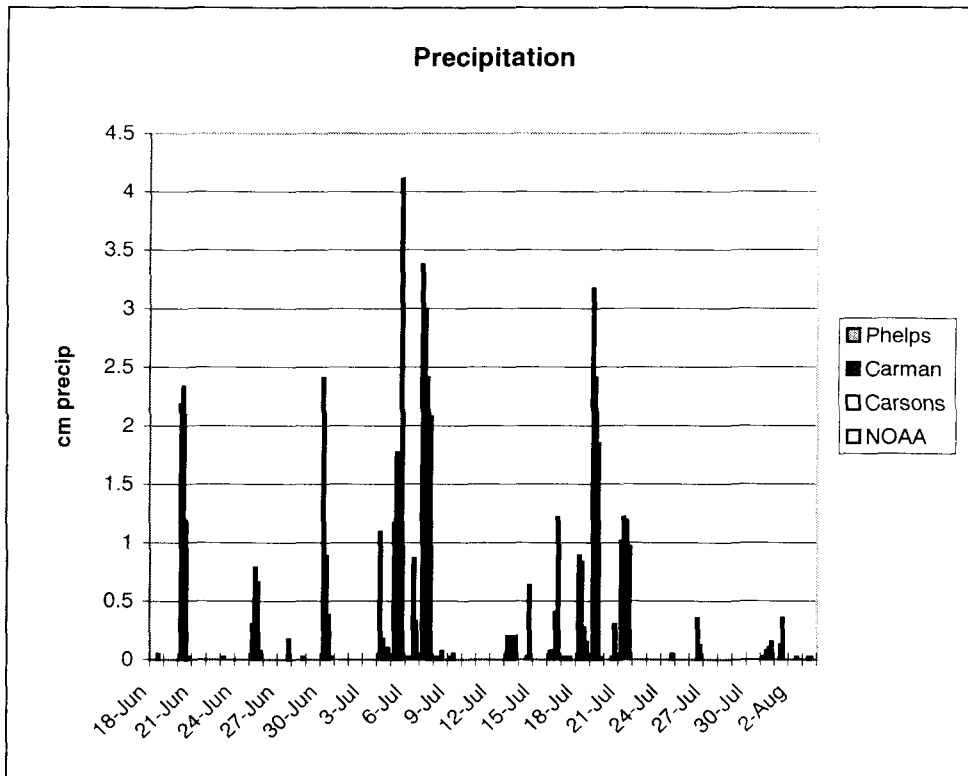


Figure 7. Precipitation comparisons at triclopyr test plots in Phelps, Carsons, and Carman bays on Lake Minnetonka, Minnesota, June-August 1994

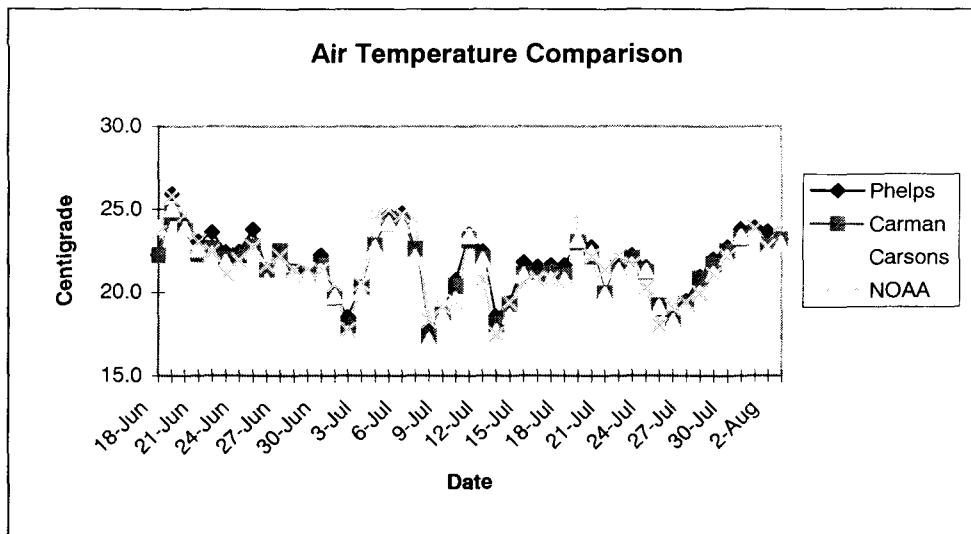


Figure 8. Temperature comparisons at triclopyr test plots in Phelps, Carsons, and Carman bays on Lake Minnetonka, Minnesota, June-August 1994

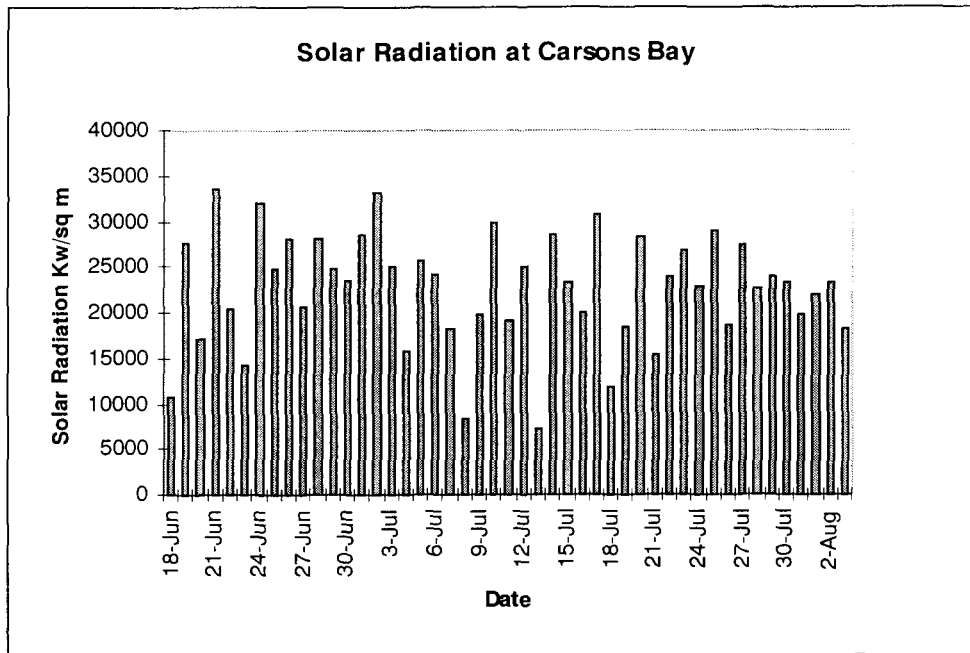


Figure 9. Daily total solar radiation measured at Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

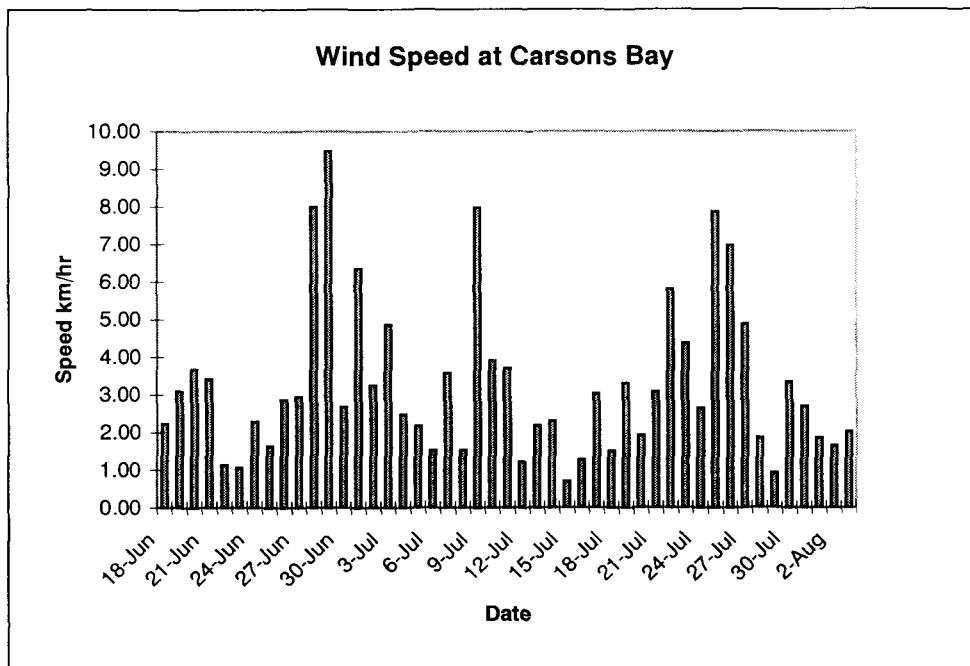


Figure 10. Average daily wind speed at Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994 (TRT – treatment date; ND – no data due to instrument malfunction)

Water hardness is usually attributed to the presence of calcium and magnesium, although other minerals also affect the measure of hardness. Biological productivity is often correlated to water hardness, but there is no direct link. In

fact, some of the contributing factors can be toxic at higher levels, so water hardness is not generally a consistent measure of quality for aquatic life.

Turbidity is caused by the presence of suspended matter, such as clay, silt, organic matter, and minute organisms. Excessive turbidity reduces light penetration and, therefore, photosynthesis by phytoplankton, algae, and submersed plants.

The data generated from water characterization analyses are presented in Table 6. In general, the water in Lake Minnetonka can be characterized as alkaline, somewhat turbid, and having a USGS classification of hard (van der Leeden, Troise, and Todd 1990).

| | Phelps | | Carsons | | Carman | |
|------------------------|--------|-------|---------|-------|--------|-------|
| | Upper | Lower | Upper | Lower | Upper | Lower |
| Alkalinity | 100 | 104 | 137 | 141 | 135 | 135 |
| Total suspended solids | 120 | 132 | 260 | 300 | 154 | 162 |
| pH | 9.5 | 9.1 | 8.5 | 8.2 | 8.9 | 8.9 |
| Hardness | 110 | 124 | 158 | 162 | 152 | 156 |
| Conductivity | 0.29 | 0.31 | 0.38 | 0.39 | 0.39 | 0.33 |
| Turbidity | 129 | 108 | 145 | 156 | 96 | 127 |
| Sulfate | 4 | 2 | 1 | 2 | 2 | 2 |
| Na | 15 | 15 | 19 | 18 | 16 | 15 |
| Mg | 15 | 16 | 17 | 17 | 16 | 17 |
| Ca | 16 | 19 | 31 | 31 | 29 | 30 |
| Chemical oxygen demand | 26 | 32 | 38 | 54 | 30 | 51 |

There were few major differences in water chemistry measured between pretreatment and posttreatment measurements. The semicontinuous water quality factors of temperature, DO, pH, and conductivity measured in each plot are shown in Figures 11 through 16. Generally, diurnal trends in the upper and lower half of the water column were similar for all plots from pretreatment through 6 weeks after application. Greatest deviations occurred with DO in the bottom waters and pH and conductivity in the surface waters of the treated plots (Phelps and Carsons bays).

In both treated plots, but particularly in Carsons Bay, DO levels increased within 1 week posttreatment in the lower half of the water column. Pretreatment levels of DO were essentially nil in the bottom waters of Carsons Bay, but

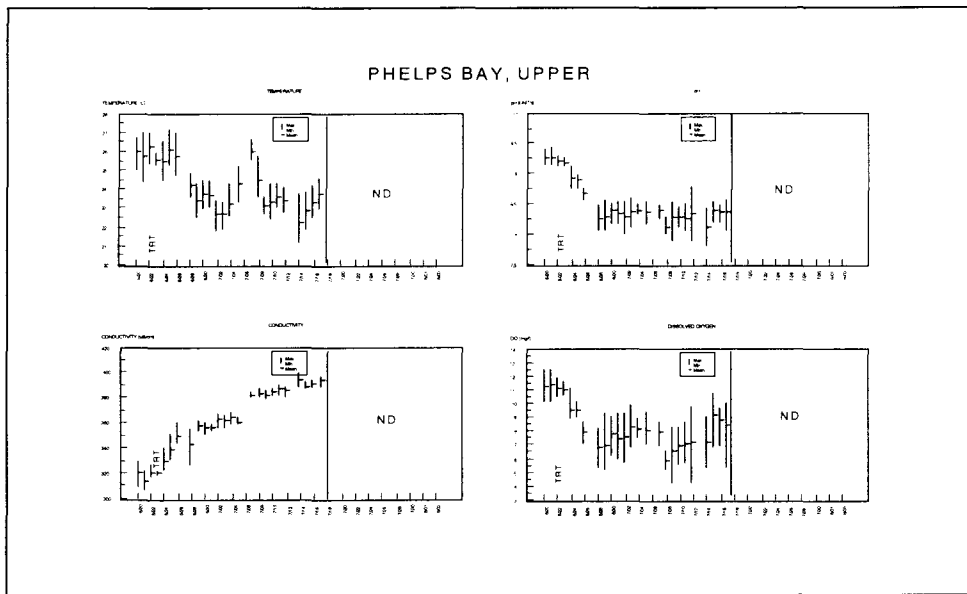


Figure 11. Water quality characteristics of upper water column, Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

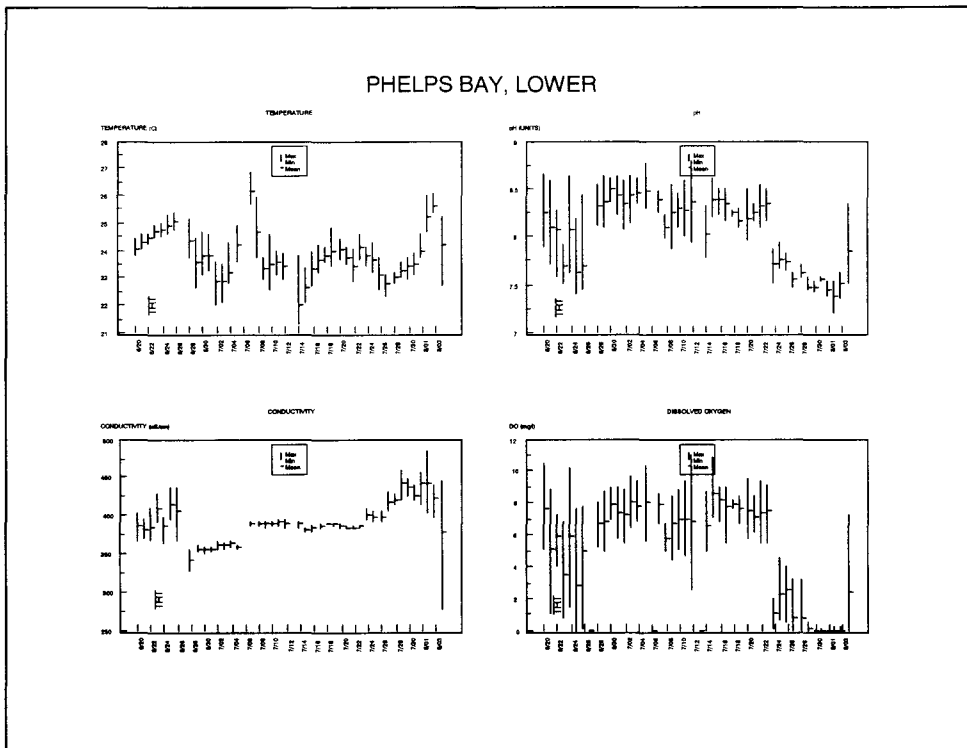


Figure 12. Water quality characteristics of lower water column, Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

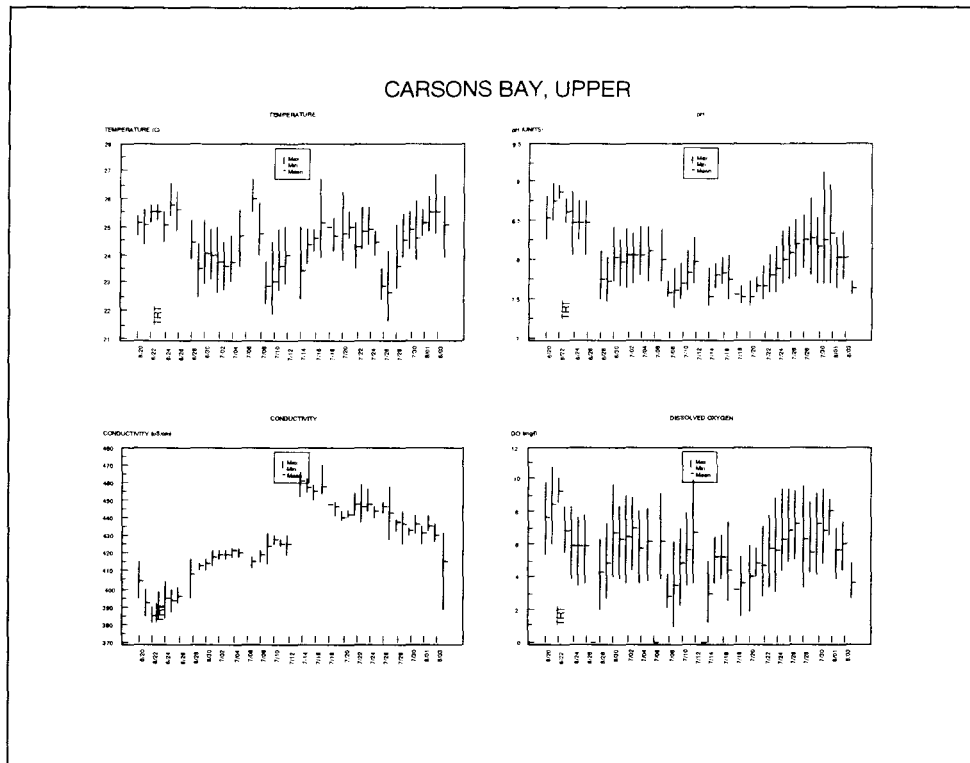


Figure 13. Water quality characteristics of upper water column, Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

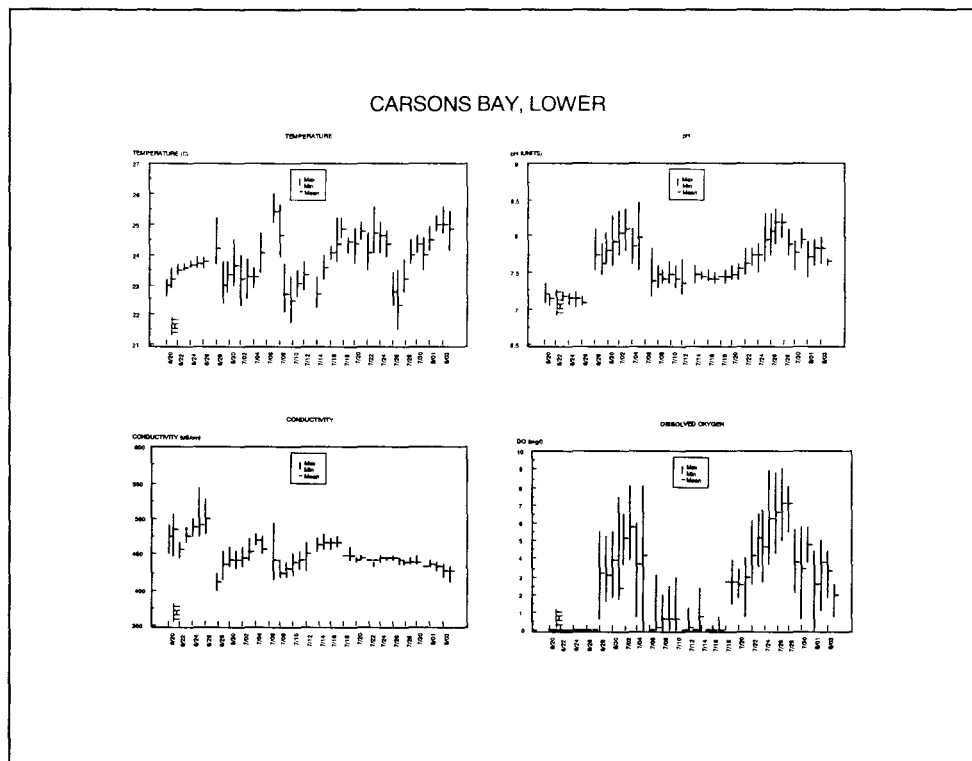


Figure 14. Water quality characteristics of lower water column, Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

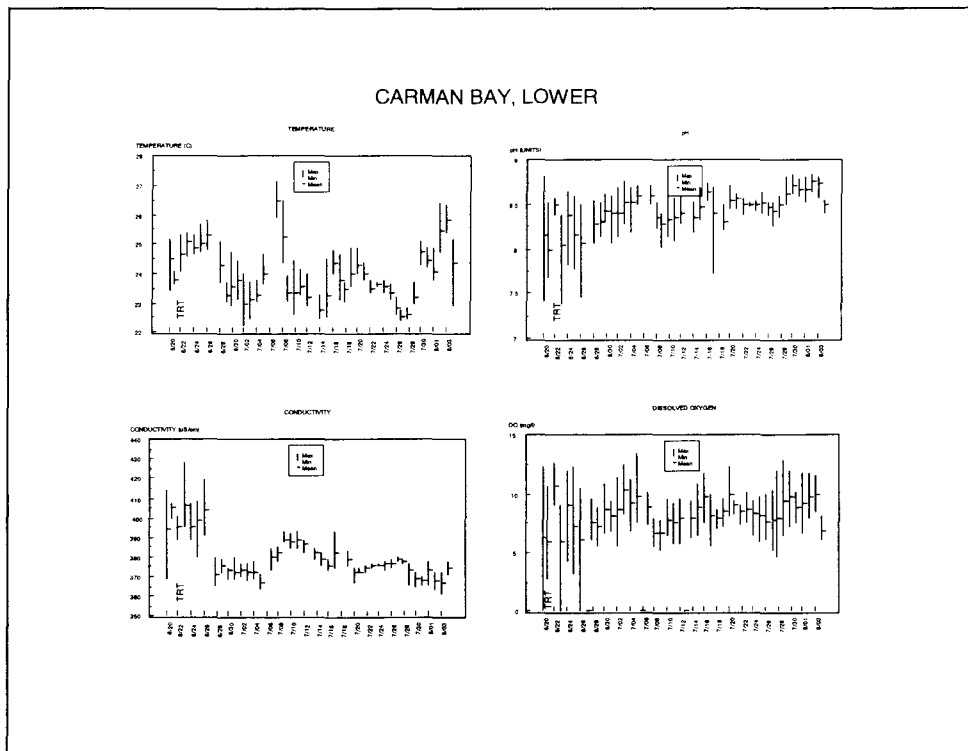


Figure 15. Water quality characteristics of upper water column, Carman Bay, Lake Minnetonka, Minnesota, June-August 1994

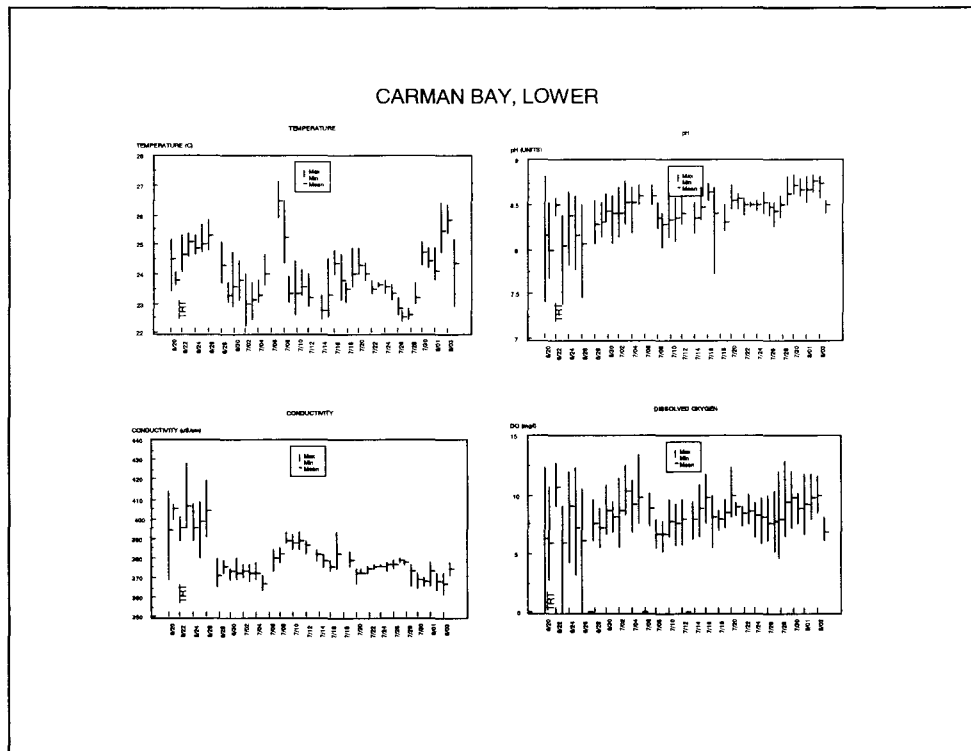


Figure 16. Water quality characteristics of lower water column, Carman Bay, Lake Minnetonka, Minnesota, June-August 1994

reached a peak of 6 mg/L by 2 weeks posttreatment. Prior to removal by the triclopyr applications, dense Eurasian watermilfoil stands in these plots had acted to suppress DO levels in bottom waters by inhibiting circulation and exchange of surface waters, and by contributing greatly to oxygen-consuming respiration processes. Once the target weed was removed, DO levels rebounded. Upon resurgence and growth of nontarget native vegetation, DO began to decline in the bottom waters of Carsons Bay (3 weeks posttreatment) but recovered to higher levels by the end of the evaluation period (6 weeks posttreatment). Dissolved oxygen levels in the bottom waters of Phelps Bay declined during the last 2 weeks of the posttreatment evaluation concomitant with increased growth of native plants during that time. Similar to the pretreatment situation of abundant stands of Eurasian watermilfoil in Phelps Bay, where DO levels were suppressed by restricted water circulation and oxygen consumption by plant respiration near the bottom, the increased abundance of native species in this plot undoubtedly contributed to the low DO levels in the bottom waters at 5 to 6 weeks posttreatment.

By 1 week posttreatment, measurements in the upper half of the water column in the triclopyr-treated plots showed a decline of a full pH unit, 9.25 to 8.25 in Phelps Bay and 8.8 to 7.8 in Carsons Bay. This decline in pH, which stabilized for several weeks and then increased towards the end of the posttreatment evaluation period, reflected the reduced photosynthesis occurring in the surface waters of these two plots following the herbicide removal of the target plant, Eurasian watermilfoil, and the increased photosynthesis that occurred with the growth of native species. Moreover, this posttreatment pH range is consistent with that of healthy and productive natural lakes and provided a more physiologically tolerant environment for most aquatic organisms than did the higher pretreatment pH levels.

Conductivity increased in the upper half of the water column in both treated plots. This slow but steady elevation in conductivity was most likely due to the increased water circulation in the treated plots following removal of the dense stands of Eurasian watermilfoil.

Some differing trends were also detected via the water quality profiles taken between pretreatment and posttreatment time periods (Figures 17 through 28). Most notably, water temperature stratification was reduced within the triclopyr-treated plots (Phelps and Carsons bays) following the removal of Eurasian watermilfoil. This also occurred in the untreated reference plot (Carman Bay), albeit to a lesser extent, and was related to a natural decline of the uppermost shoots of Eurasian watermilfoil in this bay. Trends similar to those observed via the semicontinuous water quality measurement devices, e.g., increases in bottom DO levels and decreases in surface pH levels in the treated plots, were also noted in the water quality profile measurements. Although a record of water quality conditions can be compiled using weekly profiles, it should be cautioned that these data represent a “snapshot” in time compared with the more complete data set provided by the semicontinuous readings reported and discussed above, and as such have limited value per evaluating the significance of water quality variances that occurred during the study period.

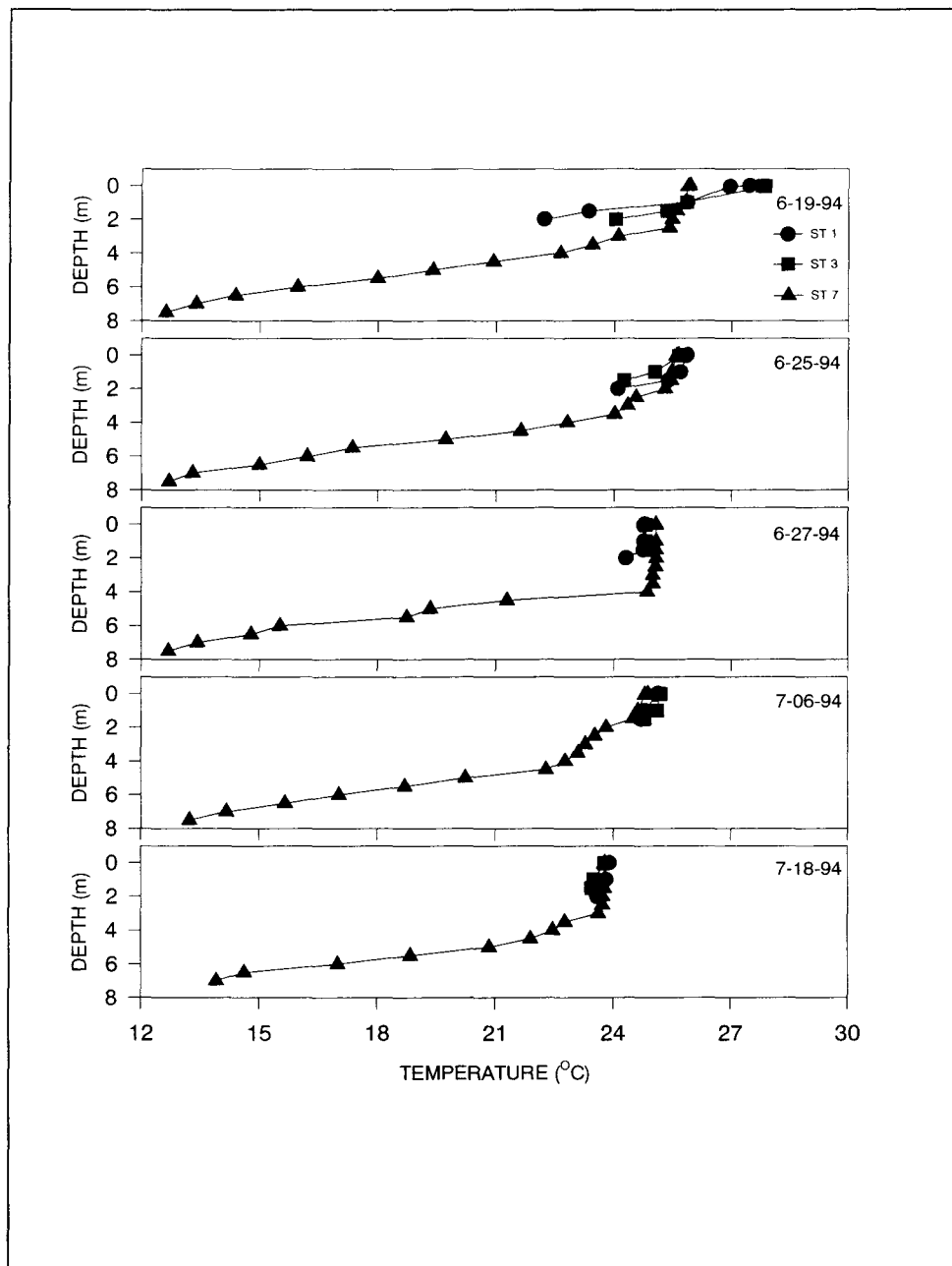


Figure 17. Temperature profiles through depth, Phelps Bay, Lake Minnetonka, Minnesota, June-July 1994

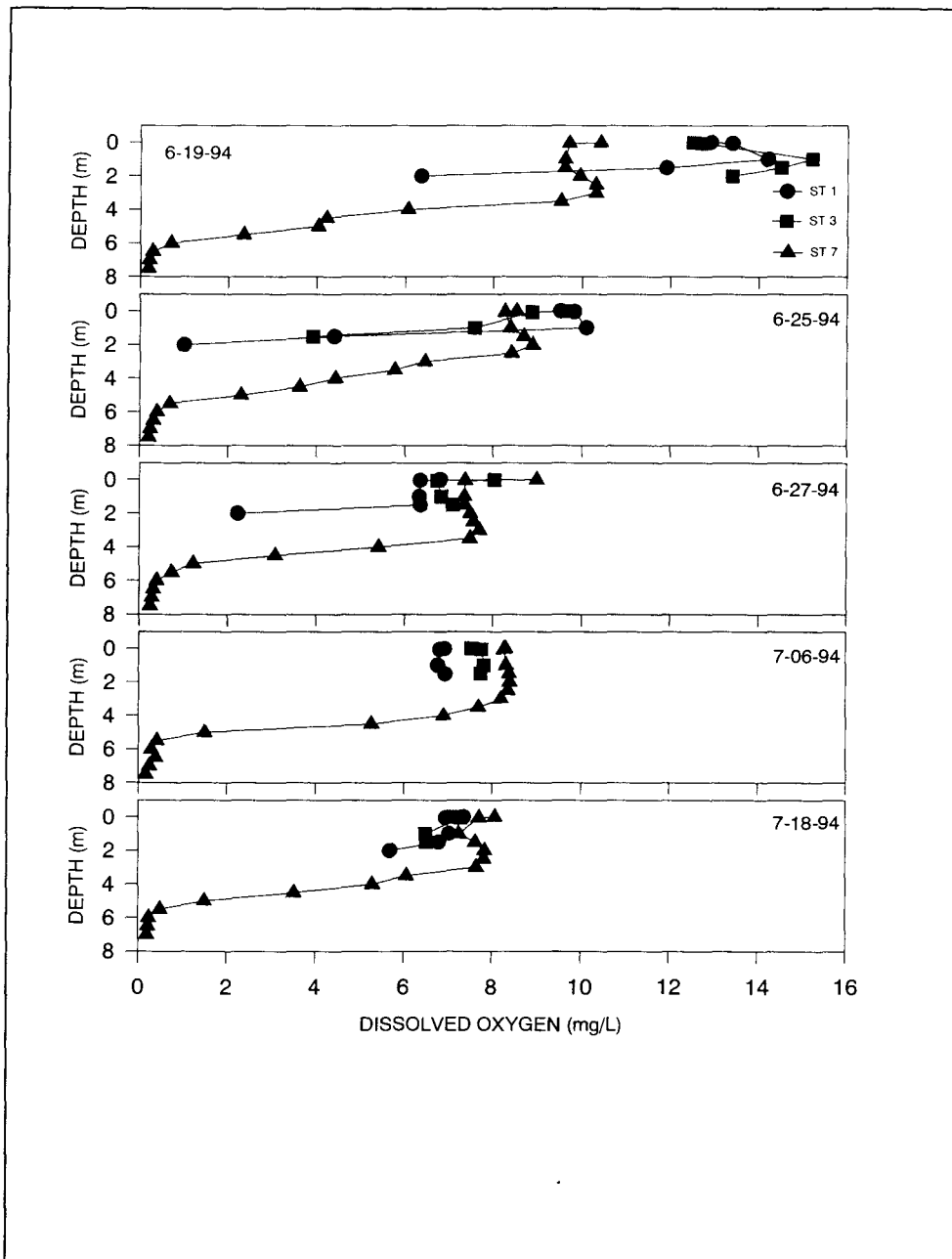


Figure 18. Dissolved oxygen profiles through depth, Phelps Bay, Lake Minnetonka, Minnesota, June-July 1994

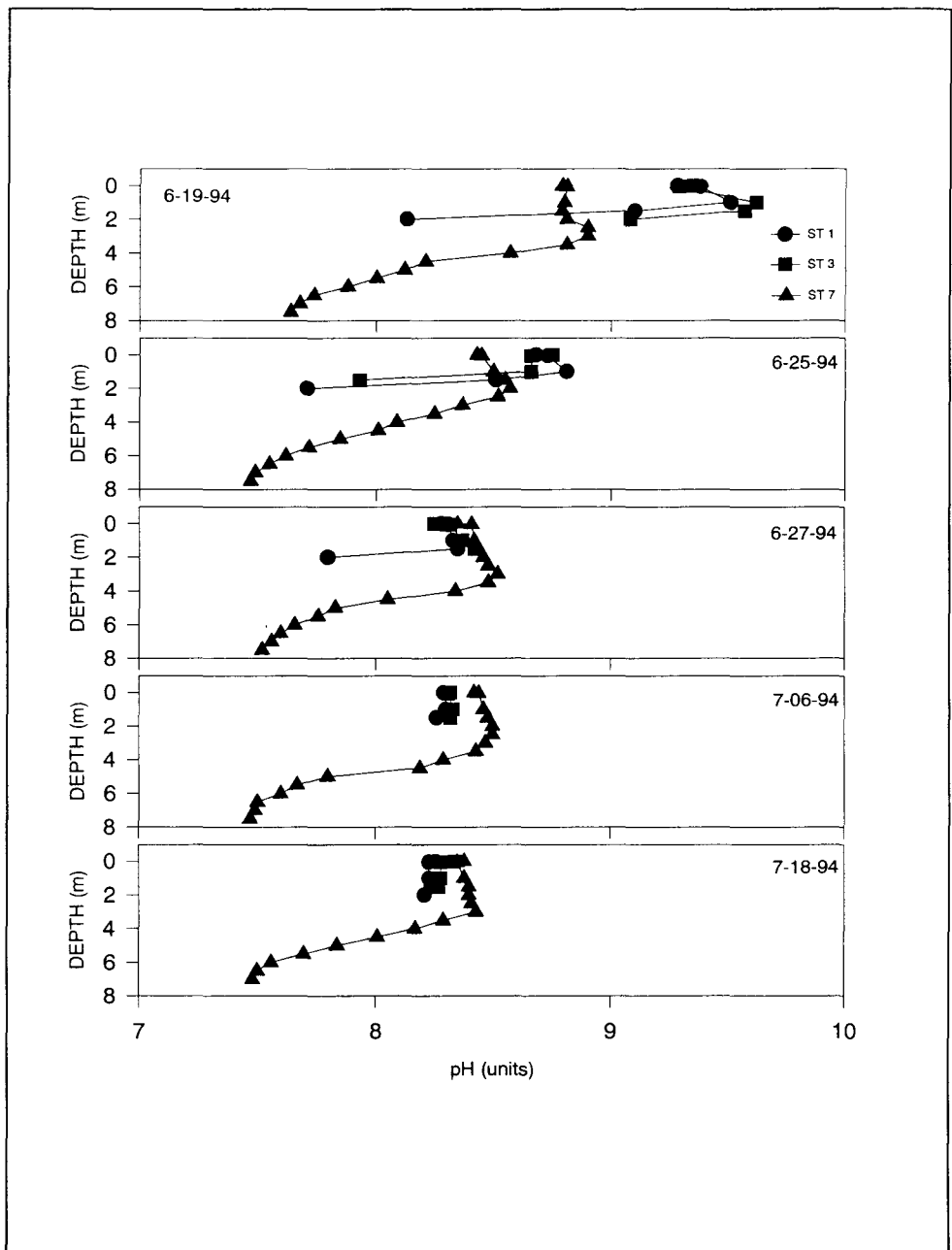


Figure 19. Profiles of pH through depth, Phelps Bay, Lake Minnetonka, Minnesota, June-July 1994

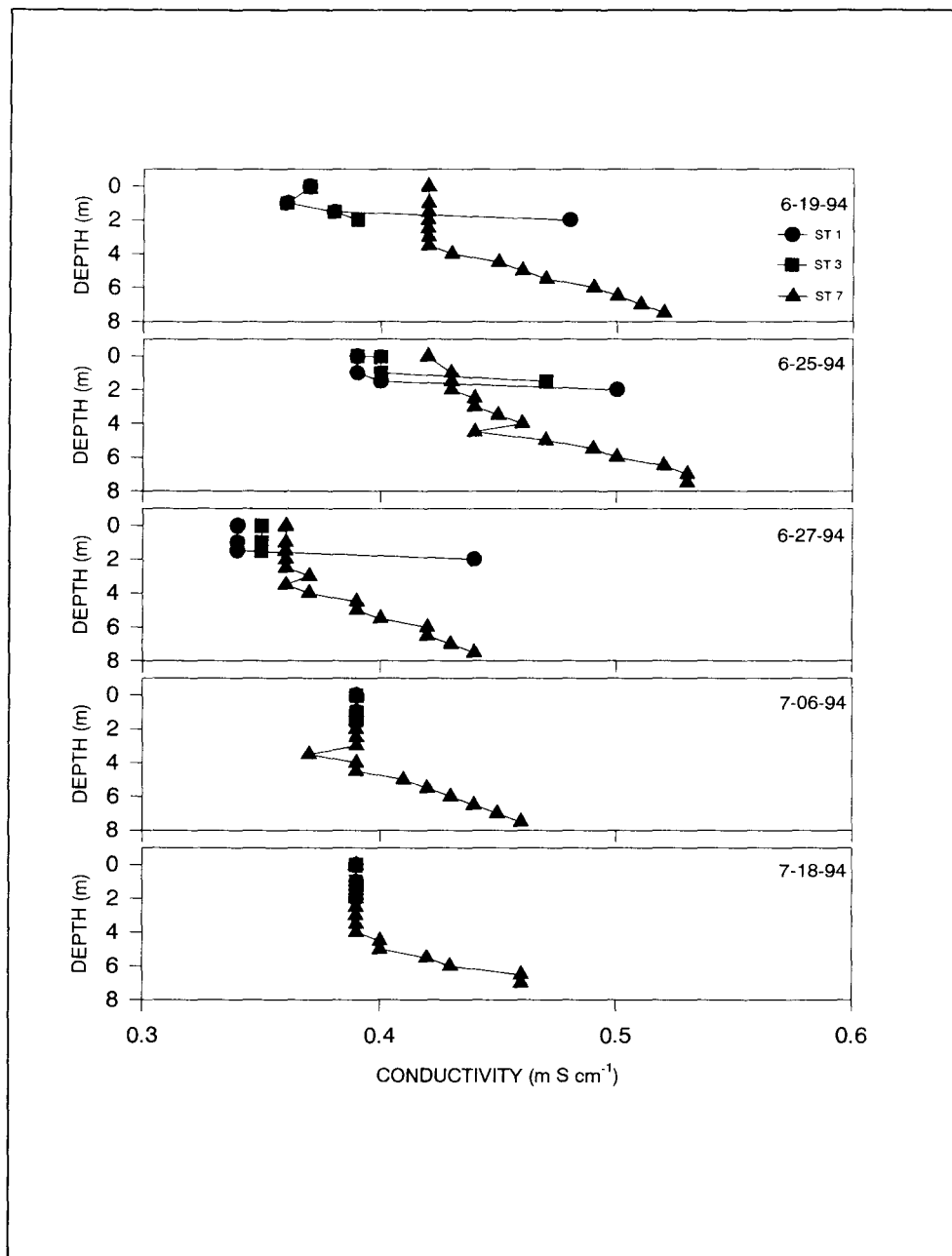


Figure 20. Conductivity profiles through depth, Phelps Bay, Lake Minnetonka, Minnesota, June-July 1994

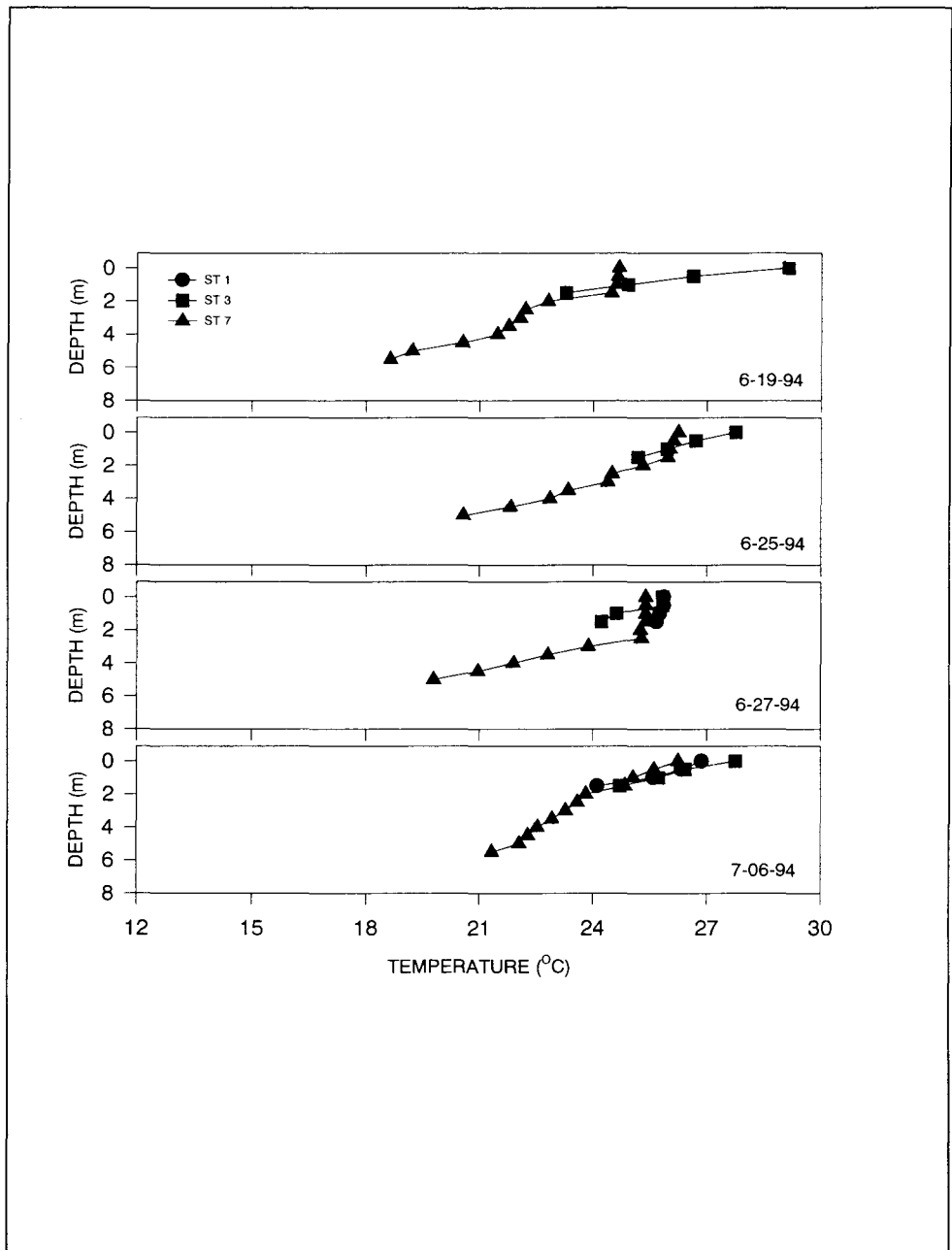


Figure 21. Temperature profiles through depth, Carsons Bay, Lake Minnetonka, Minnesota, June-July 1994

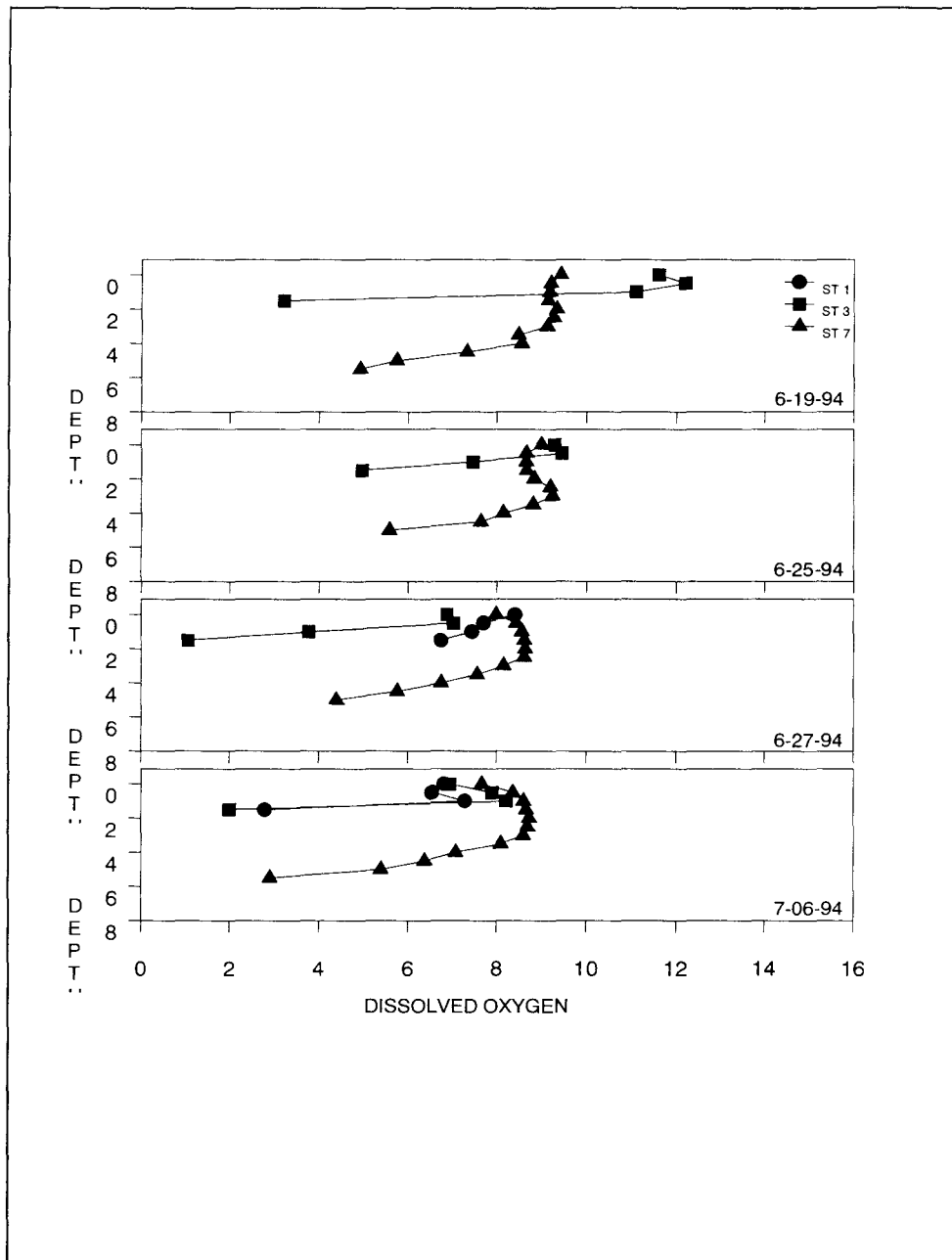


Figure 22. Dissolved oxygen profiles through depth, Carsons Bay, Lake Minnetonka, Minnesota, June-July 1994

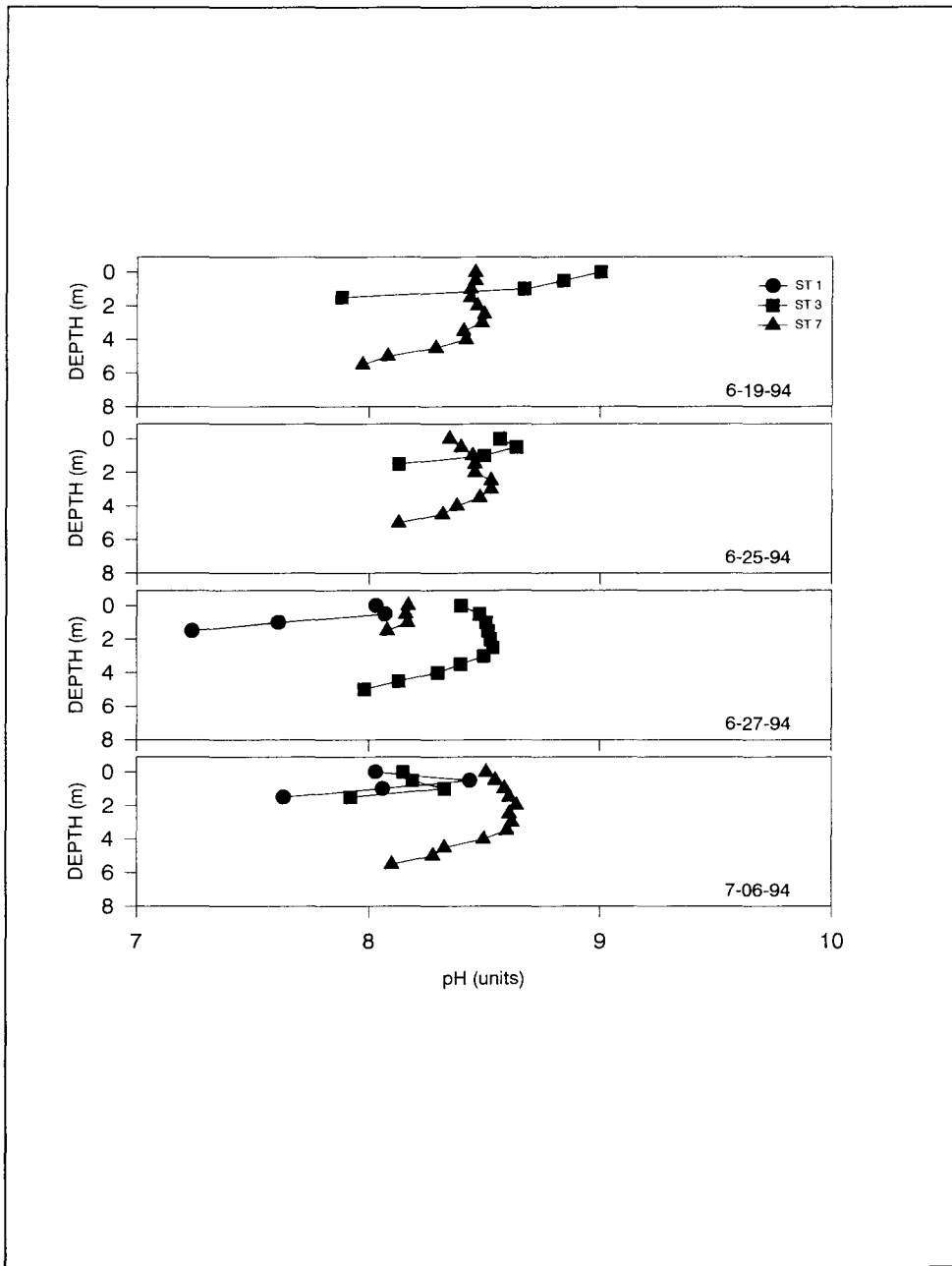


Figure 23. Profiles of pH through depth, Carsons Bay, Lake Minnetonka, Minnesota, June-July 1994

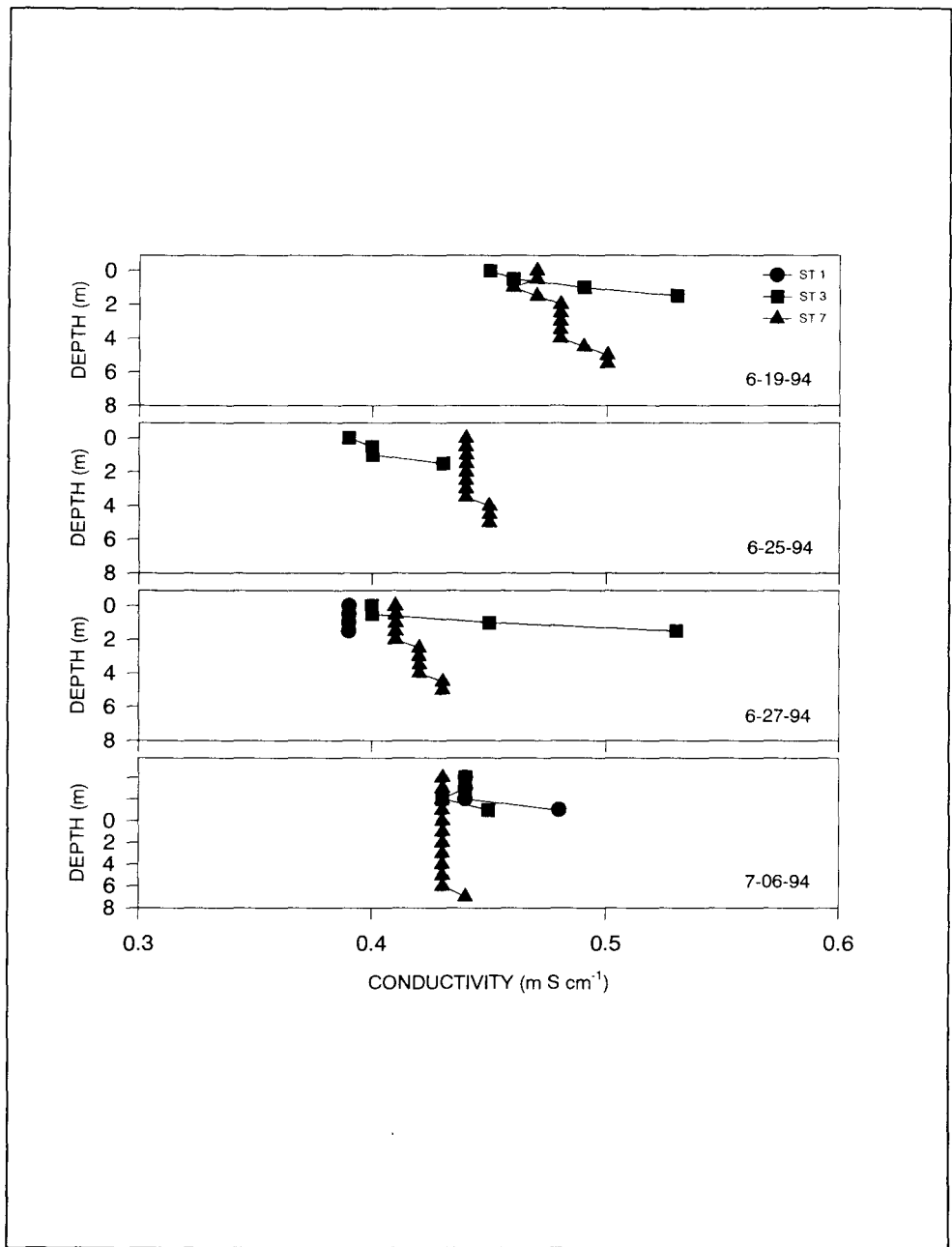


Figure 24. Conductivity profiles through depth, Carsons Bay, Lake Minnetonka, Minnesota, June-July 1994

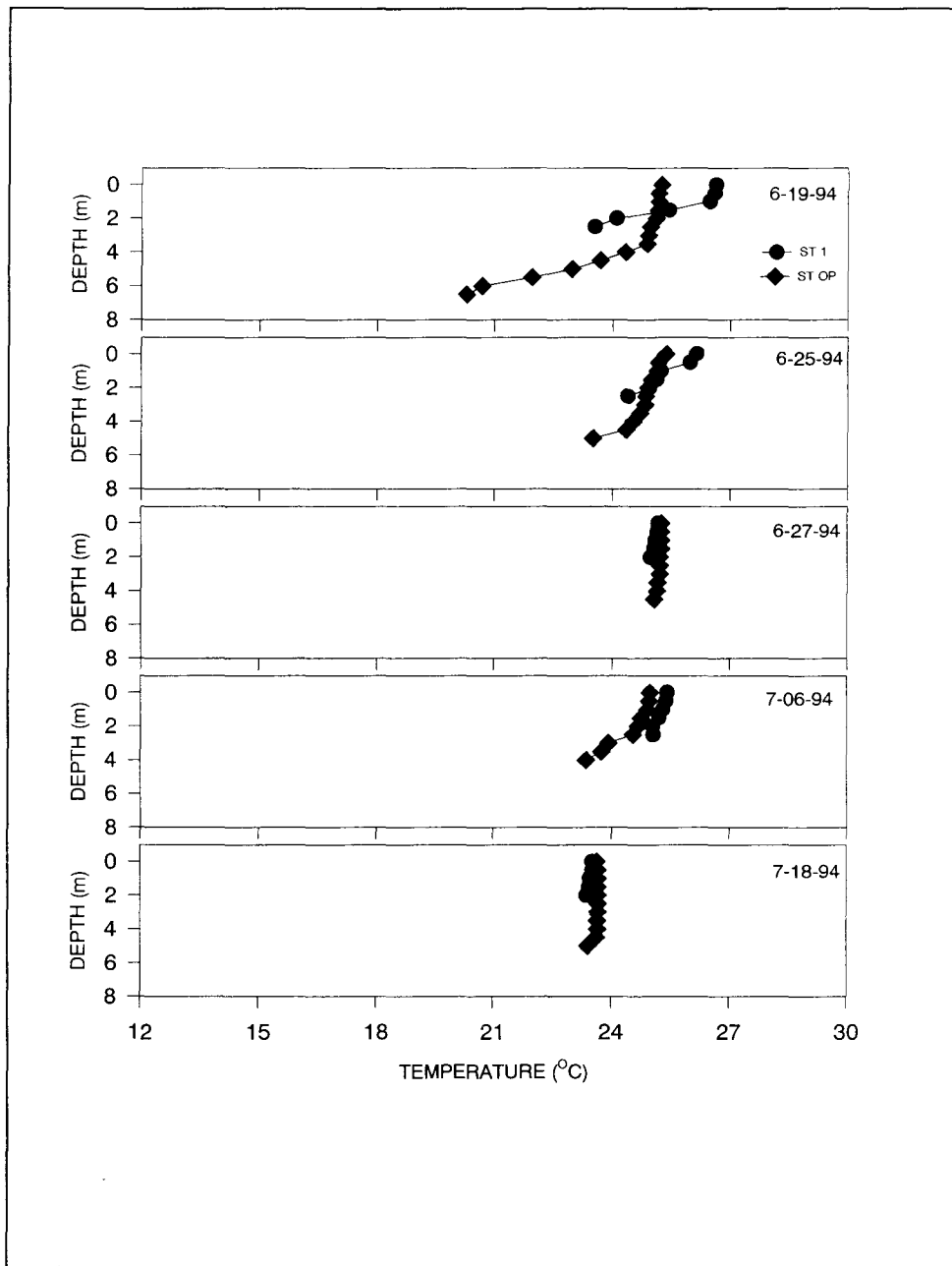


Figure 25. Temperature profiles through depth, Carman Bay, Lake Minnetonka, Minnesota, June-July 1994

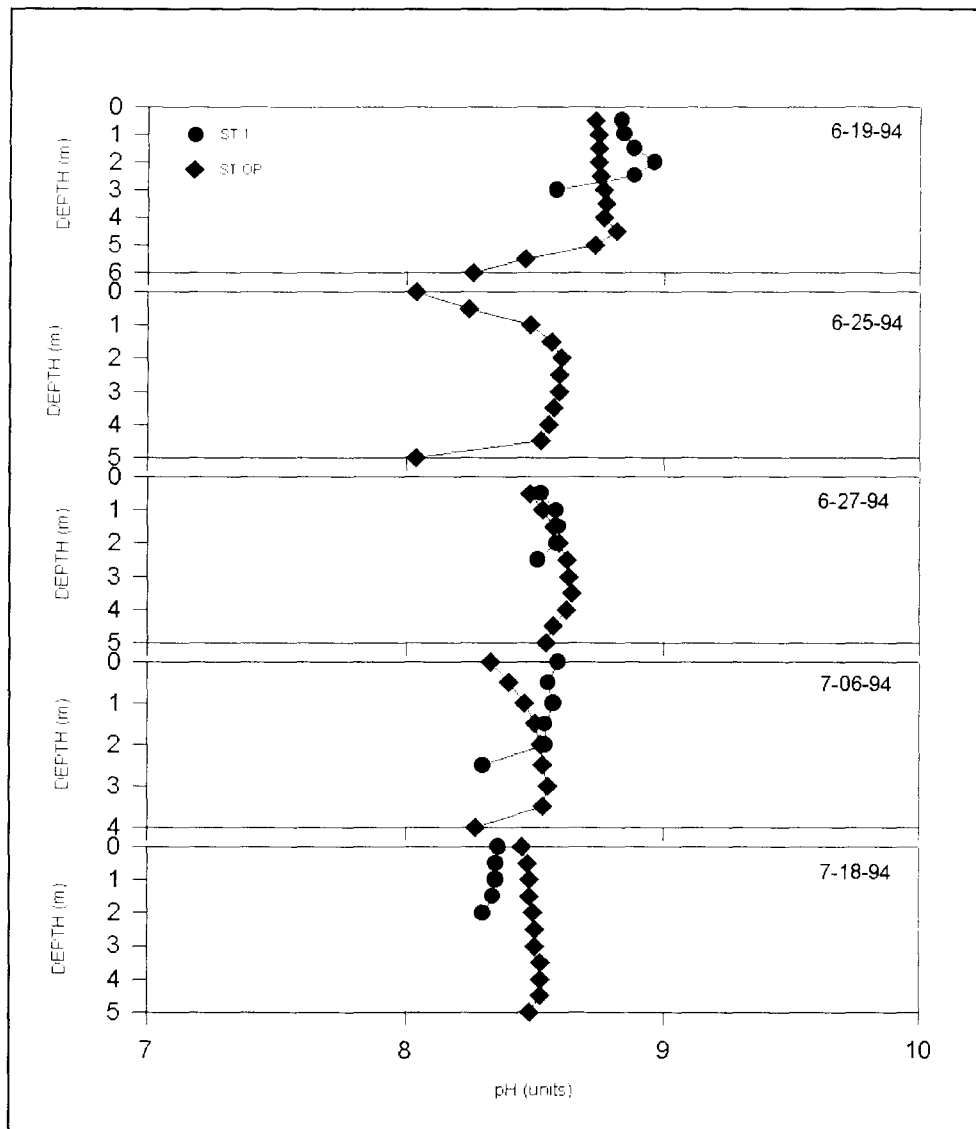


Figure 26. Dissolved oxygen profiles through depth, Carman Bay, Lake Minnetonka, Minnesota, June-July 1994

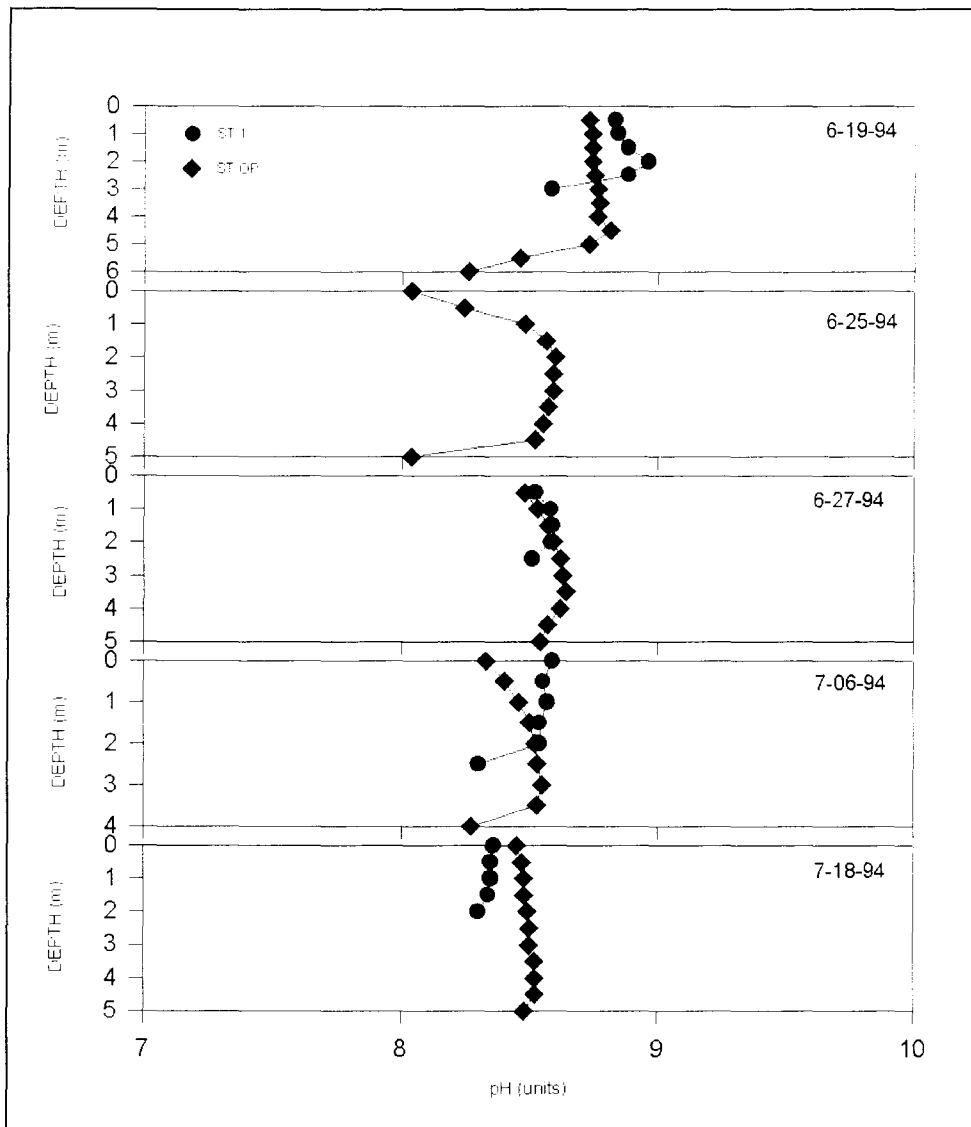


Figure 27. Profiles of pH through depth, Carman Bay, Lake Minnetonka, Minnesota, June-July 1994

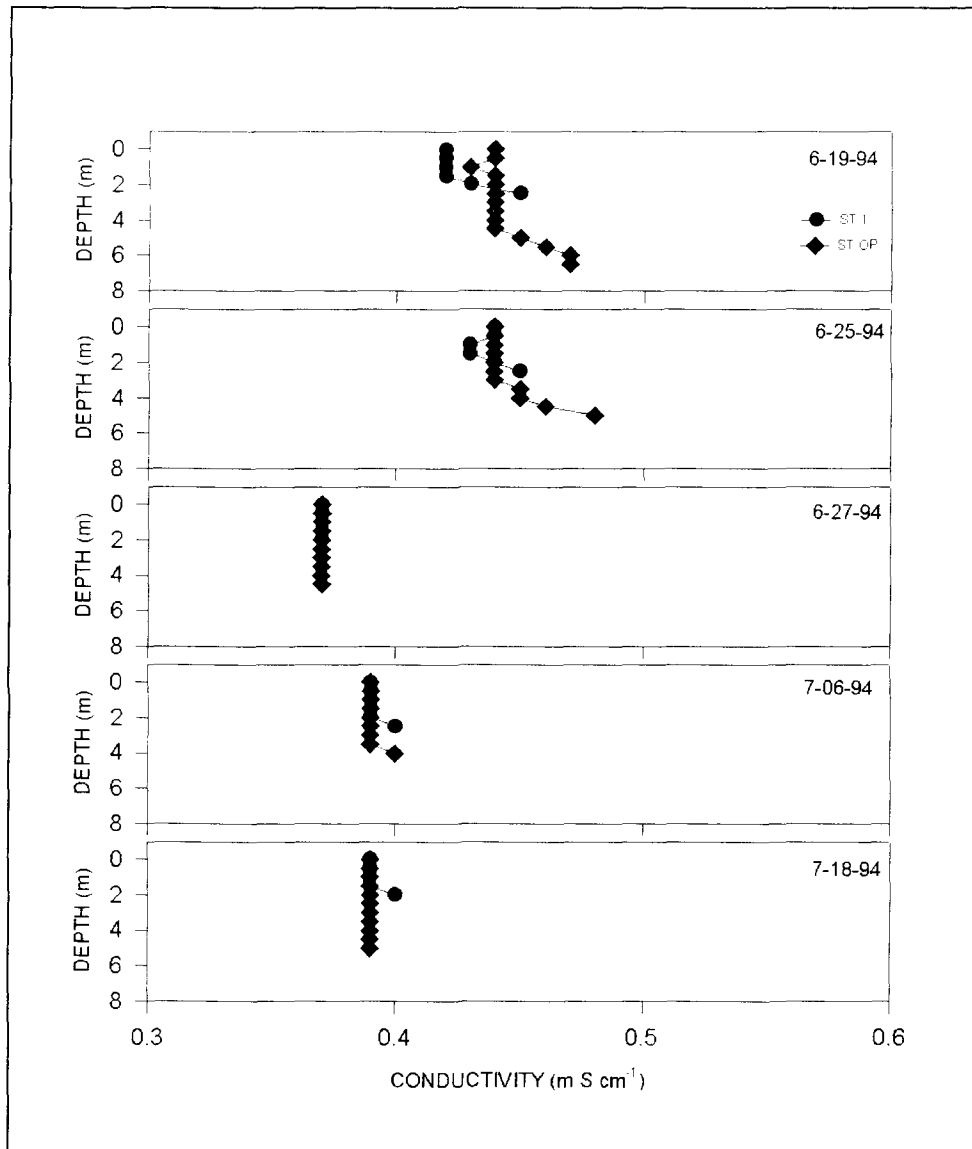


Figure 28. Conductivity profiles through depth, Carman Bay, Lake Minnetonka, Minnesota, June-July 1994

Light Intensity and Spectral Irradiance

Light profiles for selected stations within and outside the study plots are shown in Figures 29 through 31. Pretreatment measurements indicate that light transmission decreased substantially by the 1-m-depth level due to the dense submersed canopy of Eurasian watermilfoil growing in the study plots. Light intensity (percent surface light transmitted) generally increased through the water column during the 4-week posttreatment period in both tricopyr-treated plots (Phelps and Carsons), while light intensity remained relatively constant in the untreated reference plot (Carman). This increase in light transmission in the treated plots corresponded with the substantial decrease in Eurasian watermilfoil biomass following herbicide application in those plots. Light intensity in the

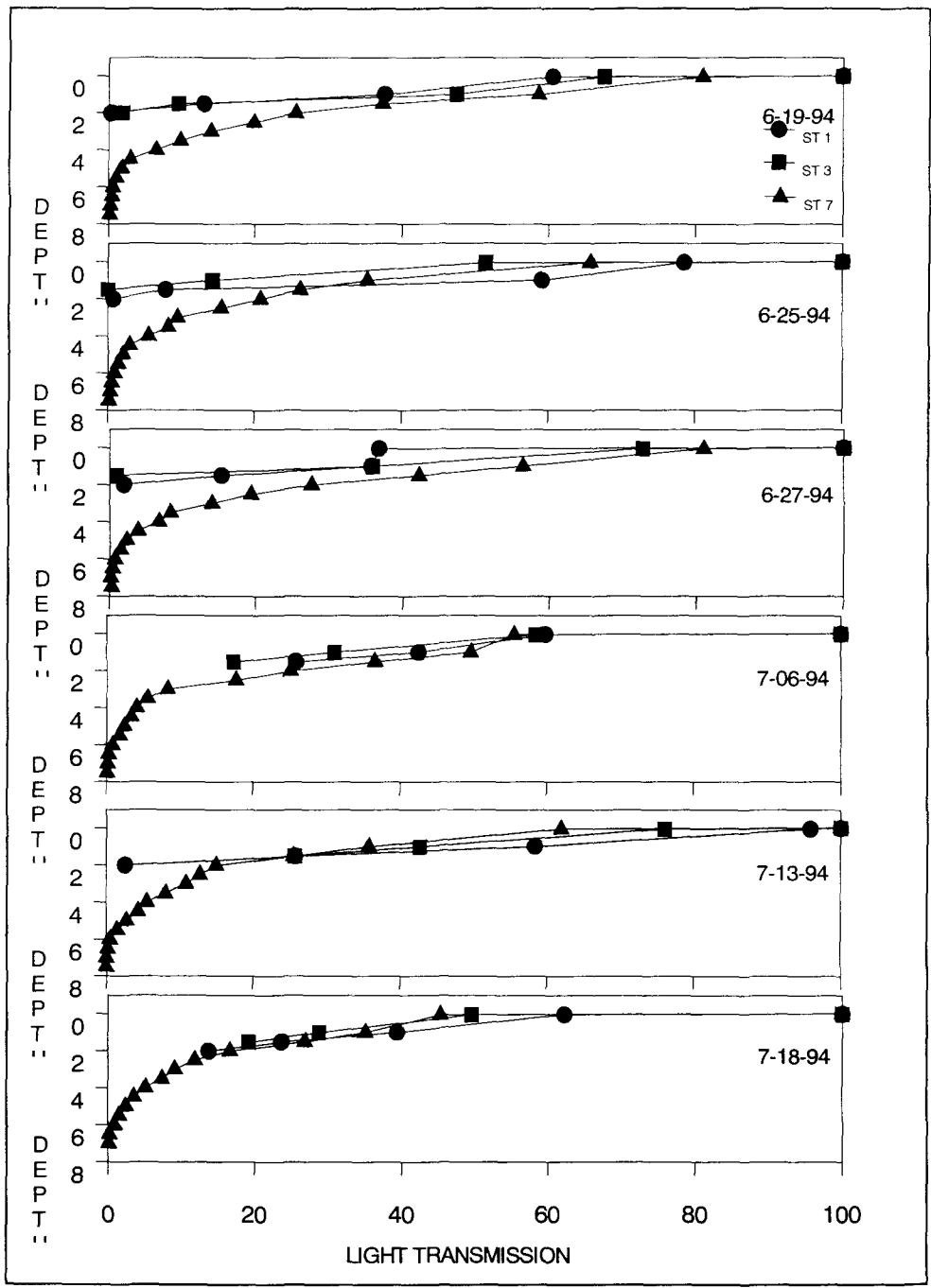


Figure 29. Percent light transmission profiles for Phelps Bay, Lake Minnetonka, June-July 1994

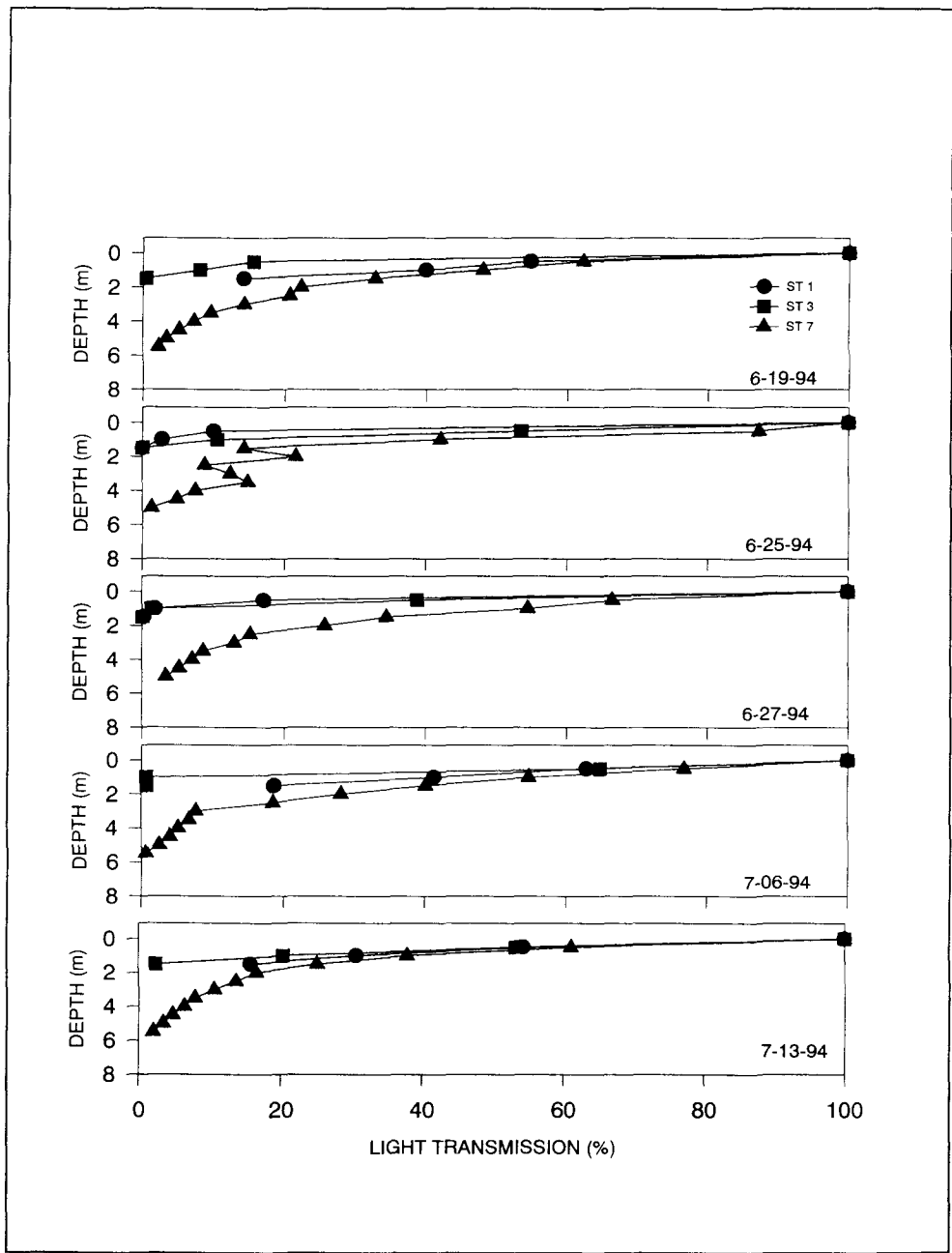


Figure 30. Percent light transmission profiles for Carsons Bay, Lake Minnetonka, June-July 1994

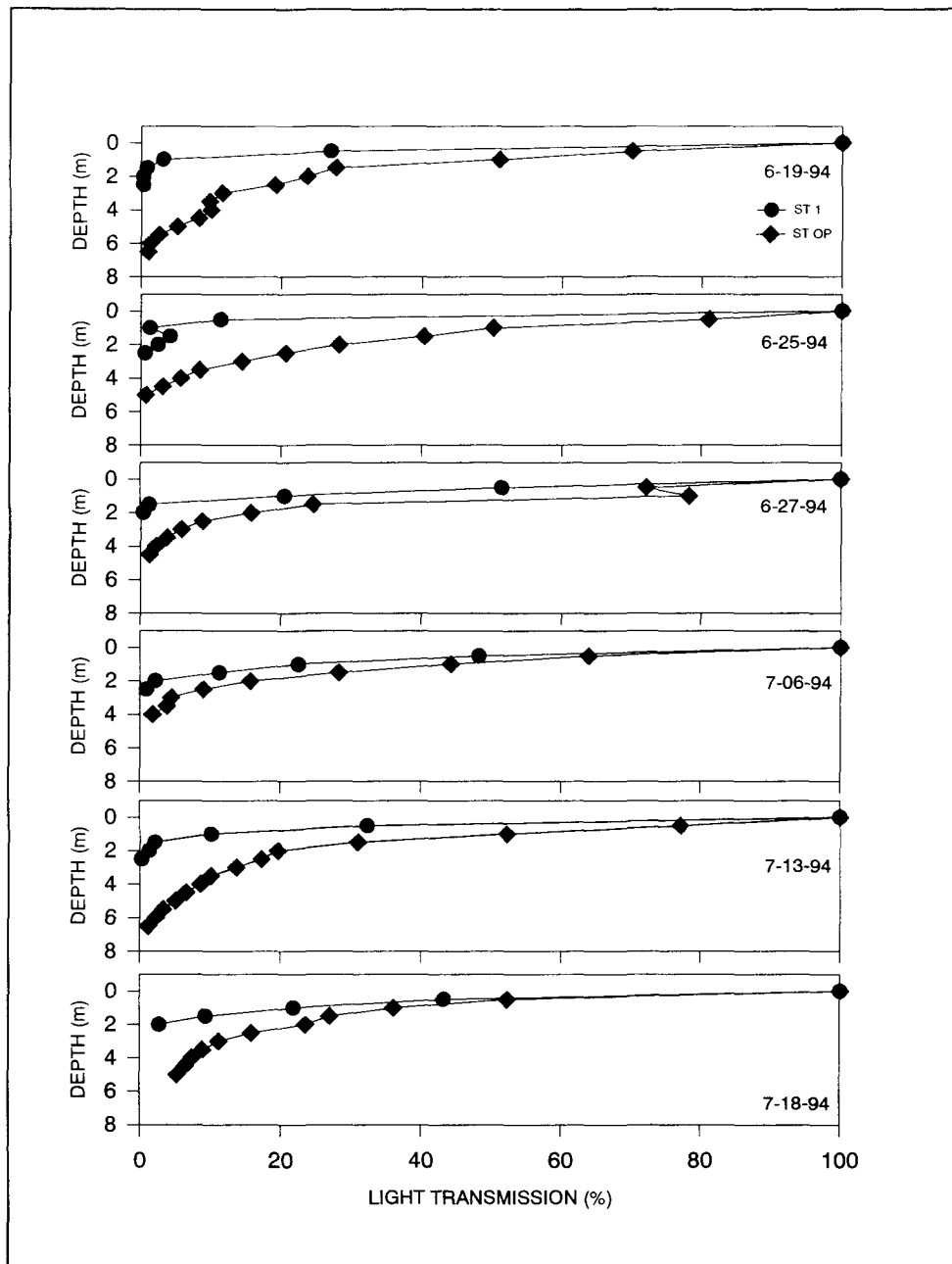


Figure 31. Percent light transmission profiles for Carman Bay, Lake Minnetonka, June-July 1994

deep open water stations (outside the plot boundaries) decreased slightly over time in Phelps and Carman bays and remained fairly constant in Carsons Bay.

Secchi disk transparency values are provided for all plots in Figure 32. No significant changes in Secchi transparency occurred during the measurement period. Secchi readings were relatively stable at Phelps Bay during the evaluation period, with a slight increase observed for the internal stations by 4 weeks

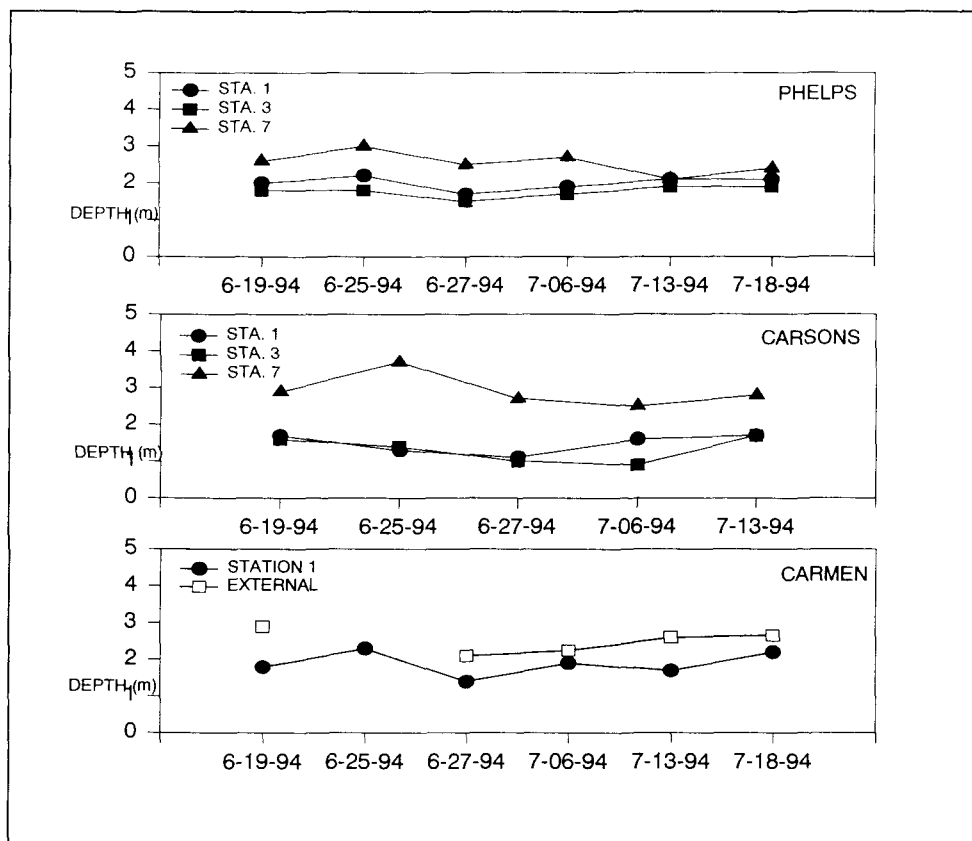


Figure 32. Secchi disk transparency values for Phelps, Carsons, and Carman bays, Lake Minnetonka, Minnesota, June-July 1994

posttreatment. Transparency decreased somewhat in the internal stations at Carsons Bay by 4 weeks posttreatment, and less so at Carman 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 (Figures 33 and 34). This rapid quenching of UV light typically occurs in natural waters due to dissolved organic compounds and other suspended particles that can greatly increase UV absorption (Wetzel 1975). Since the photolysis of triclopyr and TCP primarily occurs at the 313-nm wavelength (McCall and Gavit 1986), limited photodegradation of triclopyr and its TCP metabolite would be expected to occur in depths below 15 cm in the Lake Minnetonka test system.

Sediment Characterization

Results of the physical characterization of sediment are presented in Table 7. These data indicate that the sediment of all three bays was a high-organic muck, probably due to the continuous annual decomposition of plant material. The high levels of organic matter are significant in that they greatly increase the

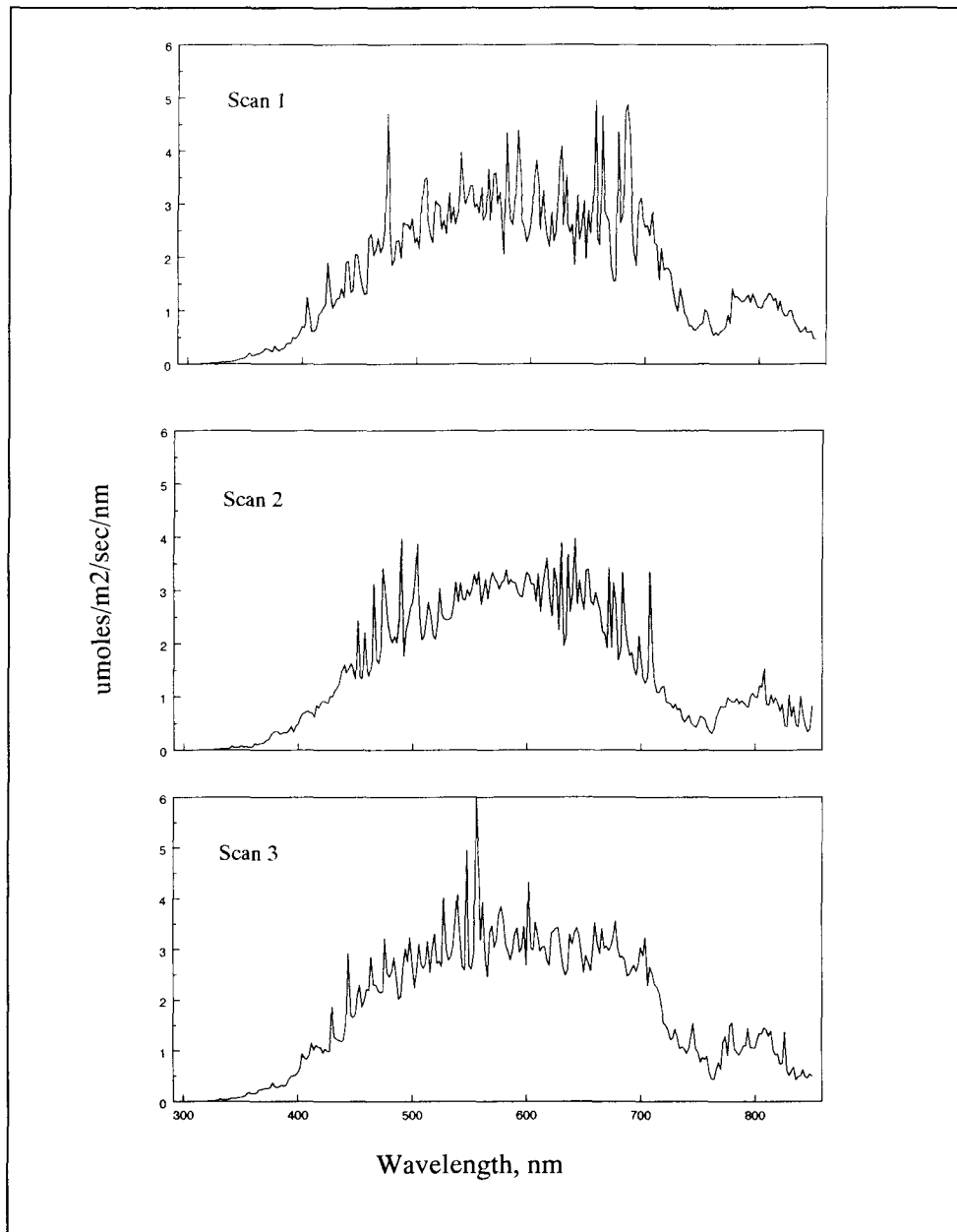


Figure 33. Spectral irradiance measurements at 15-cm depth from three separate scans on June 19, 1994, for Carman Bay, Lake Minnetonka, Minnesota

water-holding capacity of these sediments, which might result in sediment herbicide residues appearing higher than expected, due to the presence of triclopyr-laden water in the samples. Although the mineral soil component of the sediment was insignificant compared with organic matter, the mineral component is generally a silt loam or sandy loam.

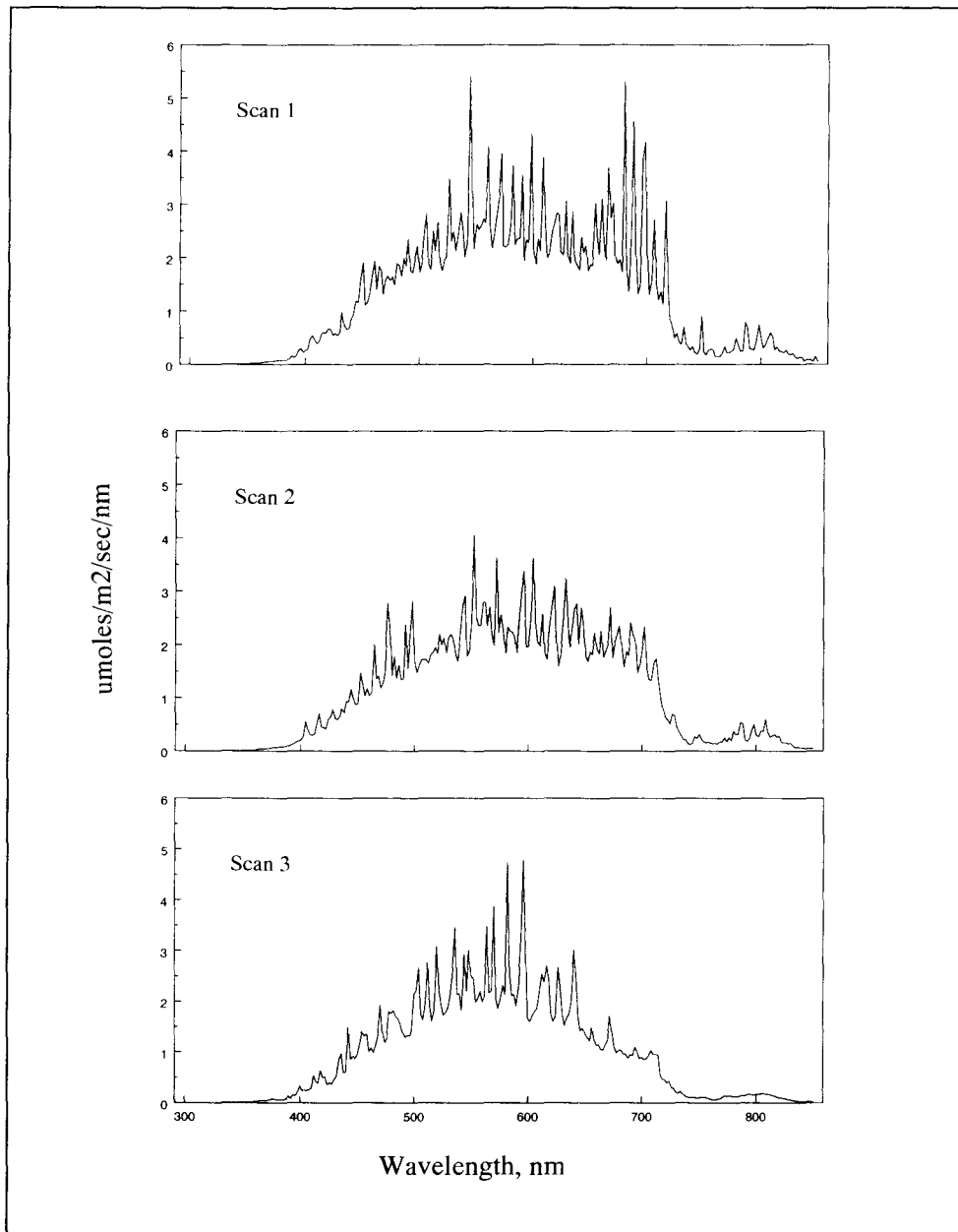


Figure 34. Spectral irradiance measurements at 15-cm depth from three separate scans on June 19, 1994, for Phelps Bay, Lake Minnetonka, Minnesota

Plant Community

Species present

A total of 21 species were observed from quantitative samples collected in Lake Minnetonka (Table 8). Of these species, 13 were monocots (12 native, 1 exotic), 6 were dicots (5 native, 1 exotic), and 2 were macroalgae (charophytes). Using a sum of all transect data, two of five most common species

Table 7
Sediment Characterization Results for Lake Minnetonka, Minnesota, June 1994

| Plot | Stn | pH | CEC | pre %OM | post %OM | 1/3 Bar | 15 Bar | Sand | Silt | Clay | Classification |
|---------|-----|-----|------|---------|----------|---------|--------|------|------|------|-----------------|
| Phelps | 1 | 7.6 | 34.9 | 15.8 | 20.1 | 89.0 | 45.7 | 19.2 | 56 | 24.8 | Silt loam |
| Phelps | 2 | 7.7 | 33.3 | 18.8 | 22.1 | 90.5 | 45.8 | 25.2 | 52 | 22.8 | Silt loam |
| Phelps | 3 | 7.7 | 32.0 | 15.7 | 17.9 | 82.4 | 41.7 | 19.2 | 56 | 24.8 | Silt loam |
| Phelps | 4 | 7.7 | 28.0 | 10.3 | 17.3 | 67.7 | 37.2 | 21.2 | 62 | 16.8 | Silt loam |
| Phelps | 5 | 7.8 | 27.5 | 14.6 | 16.8 | 81.2 | 37.1 | 13.2 | 56 | 30.8 | Silty clay loam |
| Phelps | 6 | 7.7 | 36.2 | 16.7 | 21.3 | 84.4 | 44.7 | 17.2 | 62 | 20.8 | Silt loam |
| Phelps | 7 | 7.3 | 46.1 | 17.3 | 21.7 | 75.0 | 57.1 | 67.2 | 24 | 8.8 | Sandy loam |
| Phelps | 8 | 7.7 | 35.3 | 16.5 | 17.6 | 73.9 | 40.4 | 27.2 | 54 | 18.8 | Silt loam |
| Carsons | 1 | 6.9 | 66.2 | 39.9 | 43.0 | 114.9 | 93.8 | 67.2 | 26 | 6.8 | Sandy loam |
| Carsons | 2 | 6.5 | 64.9 | 40.7 | 44.5 | 118.8 | 91.5 | 57.2 | 38 | 4.8 | Sandy loam |
| Carsons | 3 | 7.3 | 55.8 | 39.5 | 41.7 | 114.3 | 88.4 | 57.2 | 34 | 8.8 | Sandy loam |
| Carsons | 4 | 7.4 | 52.8 | 34.5 | 36.8 | 110.9 | 77.5 | 47.2 | 42 | 10.8 | Loam |
| Carsons | 5 | 7.5 | 53.3 | 37.2 | 34.0 | 99.5 | 67.9 | 61.2 | 32 | 6.8 | Sandy loam |
| Carsons | 6 | 7.9 | 23.9 | 16.1 | 20.4 | 74.5 | 36.7 | 27.2 | 54 | 18.8 | Silt loam |
| Carman | 1 | 7.7 | 31.0 | 13.7 | 15.4 | 69.1 | 33.0 | 27.2 | 58 | 14.8 | Silt loam |

Table 8
Plant Species Observed in Quantitative Samples from Lake Minnetonka, Minnesota

| Species | Common Name | Native (N) or Exotic (E) | Dicot (D) or Monocot (M) | Transect Frequency of Occurrence |
|--------------------------------|-----------------------|--------------------------|--------------------------|----------------------------------|
| <i>Ceratophyllum demersum</i> | Coontail | N | D | 56.0 |
| <i>Chara</i> sp. | Muskgrass | N | * | 1.0 |
| <i>Elodea canadensis</i> | Elodea | N | M | 18.0 |
| <i>Heteranthera dubia</i> | Water stargrass | N | M | 3.0 |
| <i>Myriophyllum sibiricum</i> | Northern watermilfoil | N | D | 0.1 |
| <i>M. spicatum</i> | Eurasian watermilfoil | E | D | 55.0 |
| <i>Najas minor</i> | Bushy pondweed | N | M | 2.0 |
| <i>Nitella</i> sp. | Nitella | N | * | 5.0 |
| <i>Nymphaea odorata</i> | White waterlily | N | D | 0.5 |
| <i>Potamogeton amplifolius</i> | Wideleaf pondweed | N | M | 3.0 |
| <i>P. crispus</i> | Curlyleaf pondweed | E | M | 25.0 |
| <i>P. obtusifolius</i> | Narrow pondweed | N | M | 5.0 |
| <i>P. pectinatus</i> | Sago pondweed | N | M | 5.0 |
| <i>P. praelongus</i> | Muskyweed | N | M | 0.1 |
| <i>P. pusillus</i> | Narrow pondweed | N | M | 1.0 |
| <i>P. richardsonii</i> | Richard's pondweed | N | M | 2.0 |
| <i>P. robbinsii</i> | Robbin's pondweed | N | M | 1.0 |
| <i>P. zosteriformis</i> | Flatstem pondweed | N | M | 18.0 |
| <i>Ranunculus longirostris</i> | Water crowfoot | N | D | 1.0 |
| <i>Utricularia vulgaris</i> | Common bladderwort | N | D | 3.0 |
| <i>Vallisneria americana</i> | Water celery | N | M | ** |

Note: * = Alga.
 ** = Observed in lake, but not collected in transect.

were exotic submersed plants (curlyleaf pondweed, 25 percent; Eurasian watermilfoil, 55 percent). The dominant native submersed species were coontail (56 percent), elodea (18 percent), and flatstem pondweed (18 percent).

Biomass

As shown in Figure 35, Eurasian watermilfoil pretreatment mean biomass was substantially higher at the Carman Bay reference site (270 g m^{-2}) than at the two triclopyr treatment sites: Phelps Bay (57 g m^{-2}) and Carsons Bay (42 g m^{-2}). However, biomass at the reference site did not significantly change during the evaluation period; whereas, a significant reduction in biomass occurred at both treatment sites following triclopyr application. In fact, no Eurasian watermilfoil biomass was found 6 weeks posttreatment at either the Phelps or Carsons bays sites. At 1 year posttreatment, Eurasian watermilfoil had recovered to approximately 25 percent of the pretreatment level in Phelps Bay, but low levels of biomass were present at Carsons Bay. The Eurasian watermilfoil found in these bays at 1 year posttreatment consisted of small, rooted stem fragments that had drifted into the plots from other sites on the lake. Fewer fragments were found in Carsons Bay because of the restricted water entrance into that bay, as opposed to the more open-water conditions at Phelps Bay.

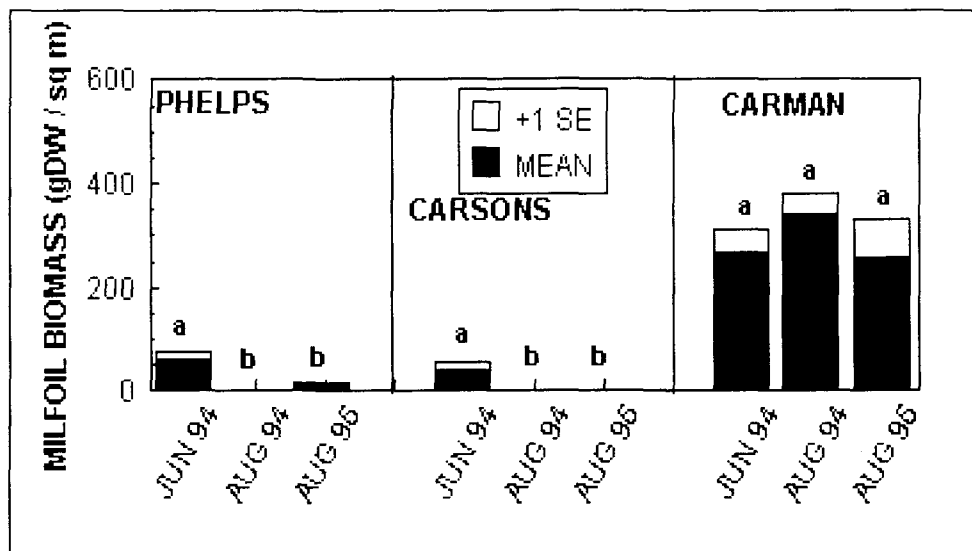


Figure 35. Biomass (g DW m^{-2}) of Eurasian watermilfoil pretreatment, 6 week posttreatment, and 1 year posttreatment at two treatment sites (Phelps, Carsons) and untreated reference (Carman) site (Different letters above bars indicate a significant difference between pretreatment and posttreatment at $p = 0.05$ level using a one-way ANOVA, Bonferfoni LSD test)

Measured native plant mean biomass increased at Phelps Bay after triclopyr treatment (Figure 36), but the increase was not statistically significant. However, the native submersed plant community at Carsons Bay did show a significant decrease in mean biomass following triclopyr application at 6 weeks. The longer

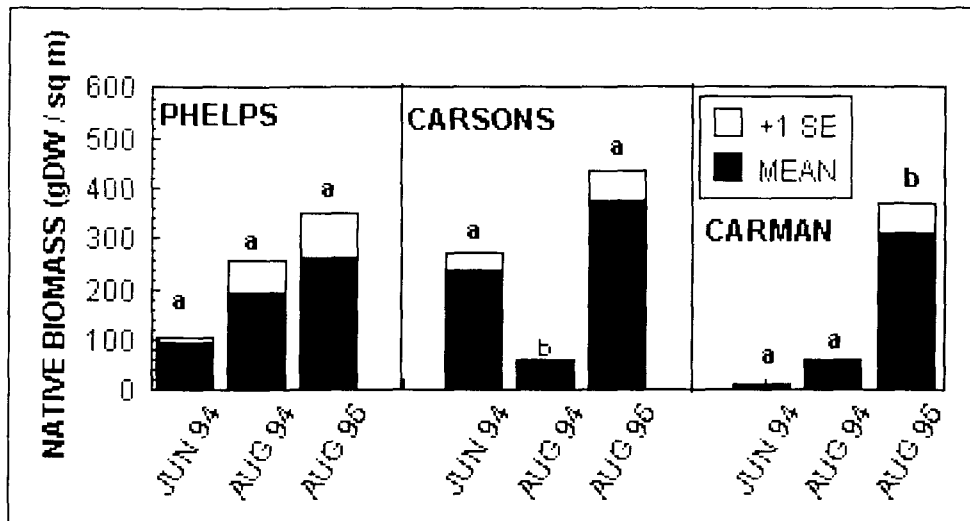


Figure 36. Biomass (g DW m⁻²) of native plants pretreatment, 6 week post-treatment, and 1 year posttreatment at two treatment sites (Phelps, Carsons) and untreated reference (Carman) site (Different letters above bars indicate a significant difference between pretreatment and posttreatment at p = 0.05 level using a one-way ANOVA, Bonferfoni LSD test)

Carsons Bay triclopyr exposure period probably caused the higher degree of native plant damage that was measured in that site. Although native plant biomass decreased following triclopyr application, it was not completely eliminated and had recovered by 1 year posttreatment. Carman Bay, with low native mean biomass at the pretreatment evaluation period, showed no significant increase in native plant biomass as the season progressed. However, native species biomass increased by 1 year posttreatment, although this primarily consisted of one species, coontail.

Transect data

Transect frequency data give more complete information on the distribution and diversity of plants than do biomass data. Eurasian watermilfoil distribution decreased significantly at both treatment sites, from approximately 70 percent before treatment to 0 percent 6 week posttreatment (Figure 37a). In fact, no rooted Eurasian watermilfoil was observed at either Phelps or Carsons bays after triclopyr treatment, although floating Eurasian watermilfoil fragments that had drifted into the plots from untreated areas on the lake were observed at both sites. By 1 year posttreatment, Eurasian watermilfoil had increased to over 50 percent of pretreatment levels in Phelps Bay, but only 15 percent of pretreatment levels in Carsons Bay. This recovery of Eurasian watermilfoil was due to fragments floating into the treated plots from other sites on the lake. In comparison, the distribution of Eurasian watermilfoil at the Carman Bay reference site actually increased and was similar to pretreatment levels by 1 year posttreatment.

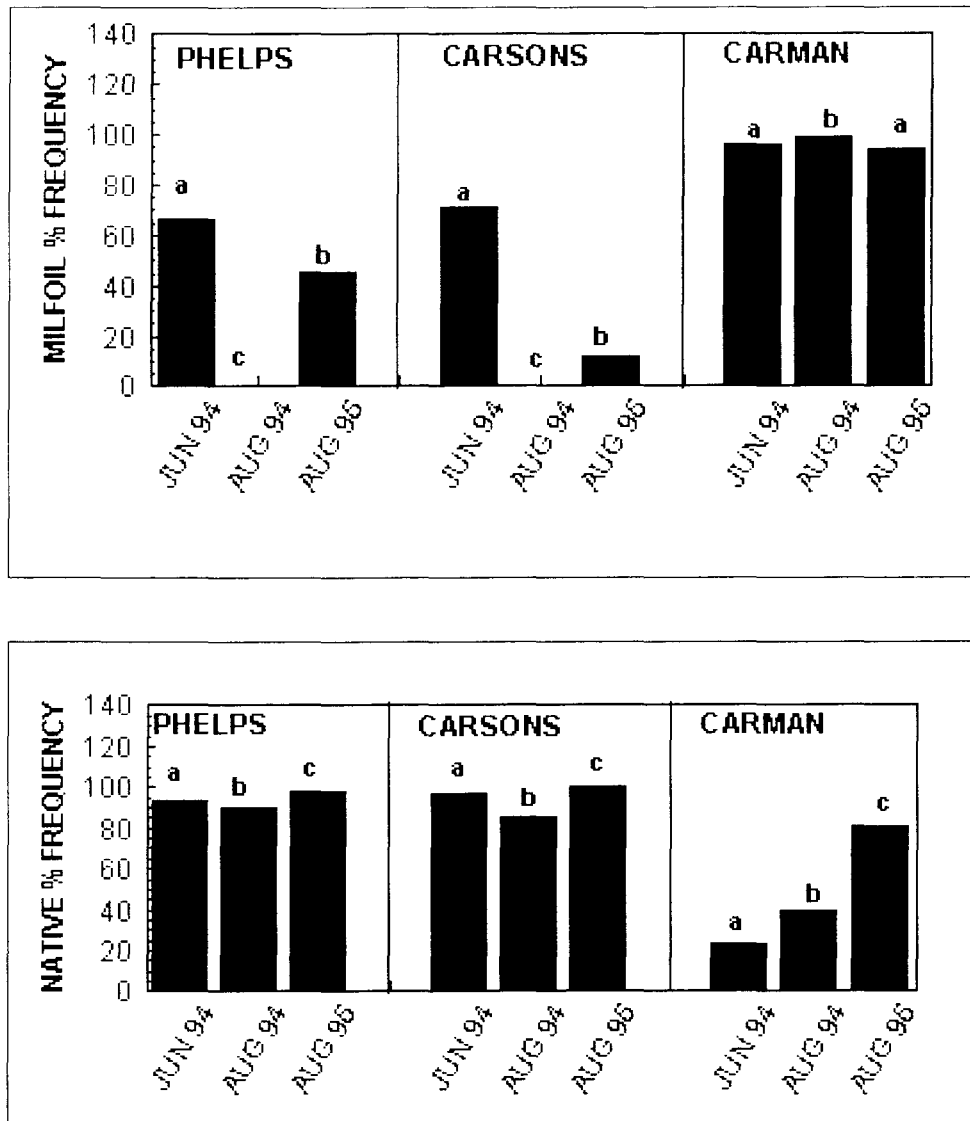


Figure 37. Percent frequency of observance along transects pretreatment, 6 week posttreatment, and 1 year posttreatment at two treatment sites (Phelps, Carsons) and untreated reference (Carman) site: total plant cover, Eurasian watermilfoil cover (a), and native plant cover (b) (Different letters above bars indicate a significant difference between pretreatment and posttreatment at $p = 0.05$ level using a chi-square test on a two-by-two table)

Native plant coverage also decreased at both triclopyr-treated sites, but only by 5 to 10 percent (Figure 37b). In contrast, native plant coverage decreased from 60 percent in June 1994 to 30 percent in August 1994 at the untreated reference site, without any herbicide application. The apparent contradiction with the increase in native plant biomass (Figure 36) at this site may be explained through a significant increase in biomass of a few species locally (e.g., coontail) and mortality of individual plants that occurred throughout the bay. The decrease in native plant cover caused by the application of triclopyr was

substantially less than that observed in the untreated site. Native plant coverage was significantly higher in all three plots by 1 year posttreatment, although the untreated reference plot, Carman Bay, was still dominated by Eurasian watermilfoil

Native plant diversity, as measured by average number of species per transect interval, decreased by almost 1.0 at both Phelps and Carsons bays (Figure 38) at 6 weeks posttreatment. However, the diversity levels at these sites were both above 1.0 after triclopyr treatment, while the Carman Bay reference site with dense stands of Eurasian watermilfoil had average diversity of less than 0.5. Treatment with triclopyr at the full label rate of 2.5 $\mu\text{g/L}$ may have caused the mortality of some native species, particularly in Carsons Bay where water exchange was slow and triclopyr dissipation was reduced. However, by 1 year posttreatment (August 1995), native plant diversity had recovered to near pretreatment levels in Phelps and Carsons bays and continued to increase in Carman Bay.

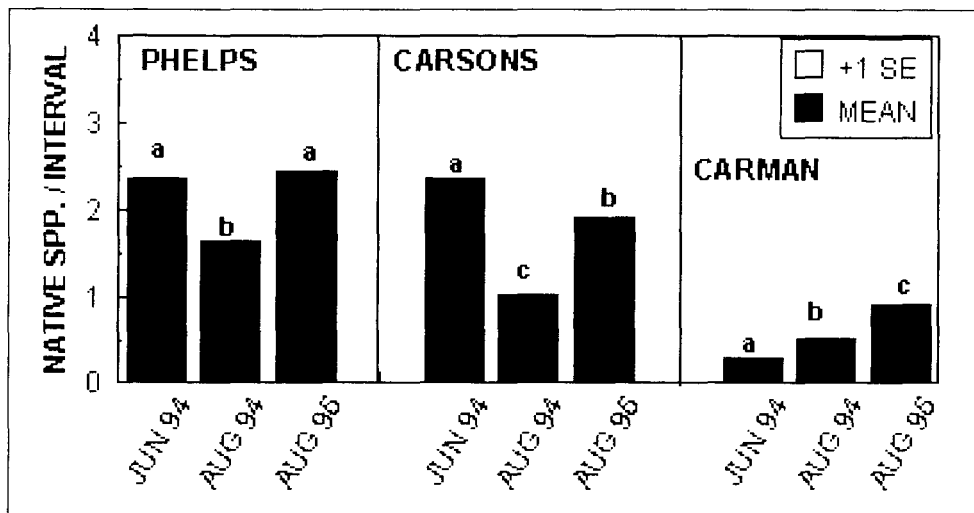


Figure 38. Species richness of native plants as number of species per transect interval pretreatment, 6 week posttreatment, and 1 year posttreatment at two treatment sites (Phelps, Carsons) and untreated reference (Carman) site (Different letters above bars indicate a significant difference between pretreatment and posttreatment at $p = 0.05$ level using a one-way ANOVA, Bonferroni LSD test)

Dye Movement

The rhodamine WT dye proved to be an efficient indicator of water exchange and tracer for triclopyr and its TCP metabolite. In Phelps Bay, dye dissipated at a half-life rate of 3.9 days (Figure 39), while at Carsons Bay, dye dissipated at a half-life rate of 6.3 days (Figure 40). These dye measurements demonstrated that the rate of water movement in the triclopyr-treated plots was minimal with respect to water exchange patterns typically found in embayments of large lakes and reservoirs. In Phelps Bay, the correlation between the dye and triclopyr was

0.99 (Figure 41) and 0.91 for TCP (Figure 42). In Carsons Bay, the correlation was 0.98 for triclopyr (Figure 43) and 0.86 for TCP (Figure 44).

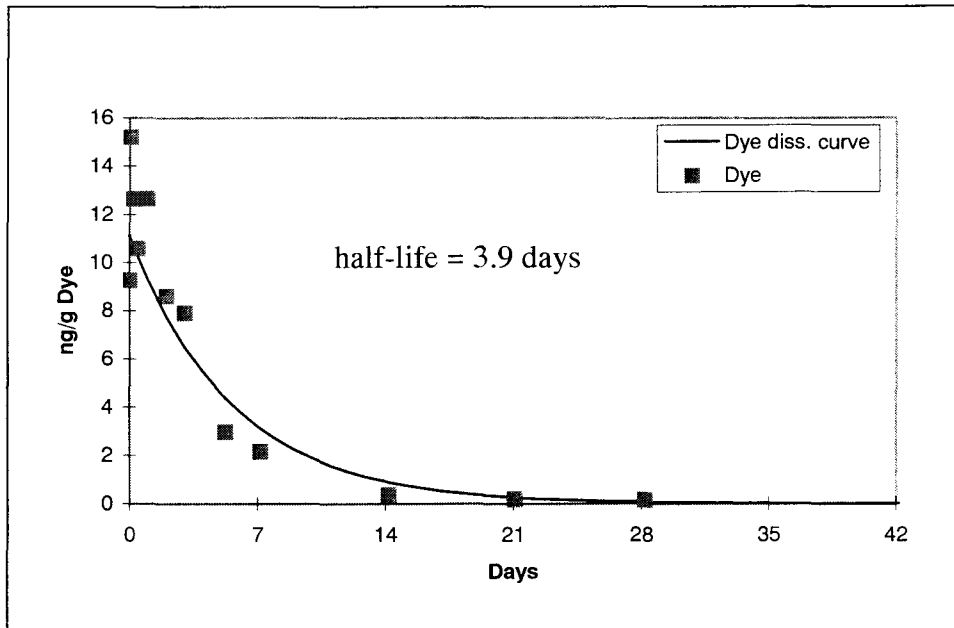


Figure 39. Rhodamine WT dye dissipation in water in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

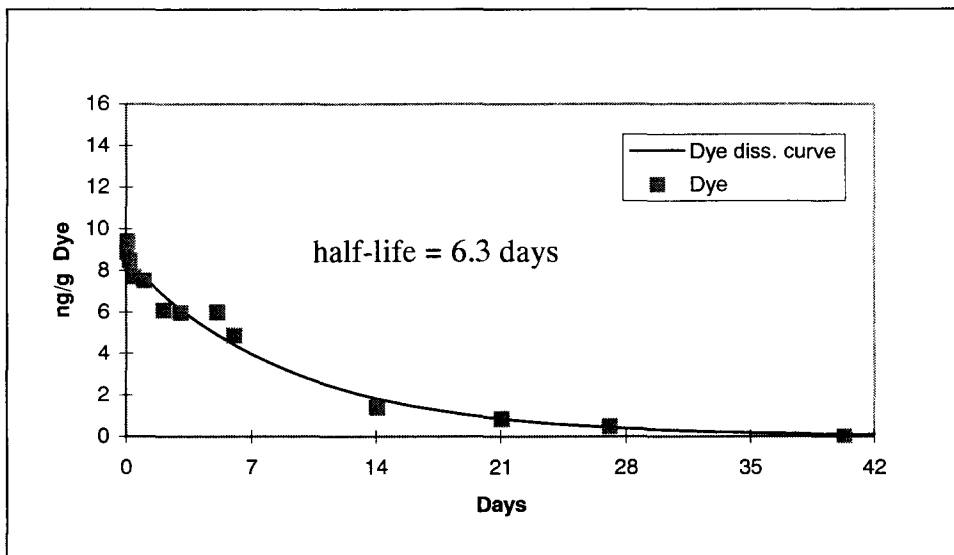


Figure 40. Rhodamine WT dye dissipation in water in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

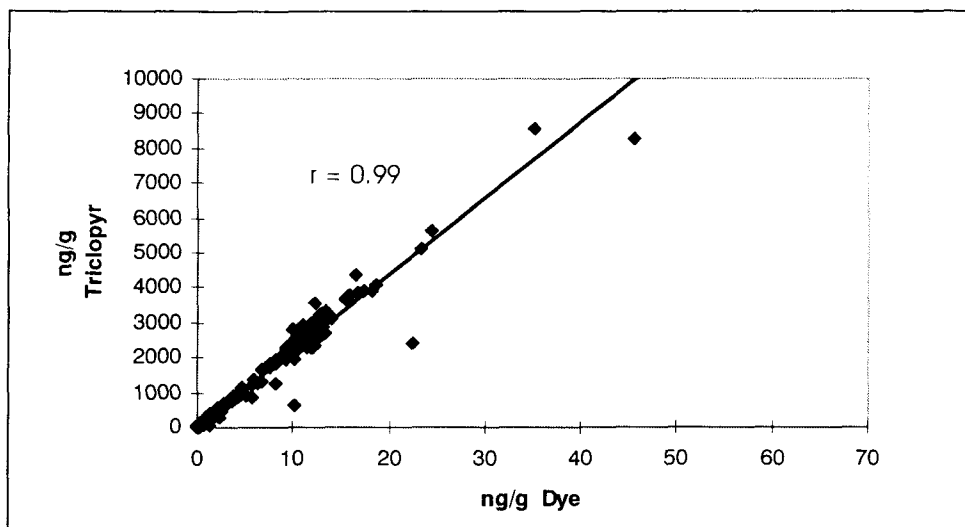


Figure 41. Correlation of triclopyr versus rhodamine WT dye, Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

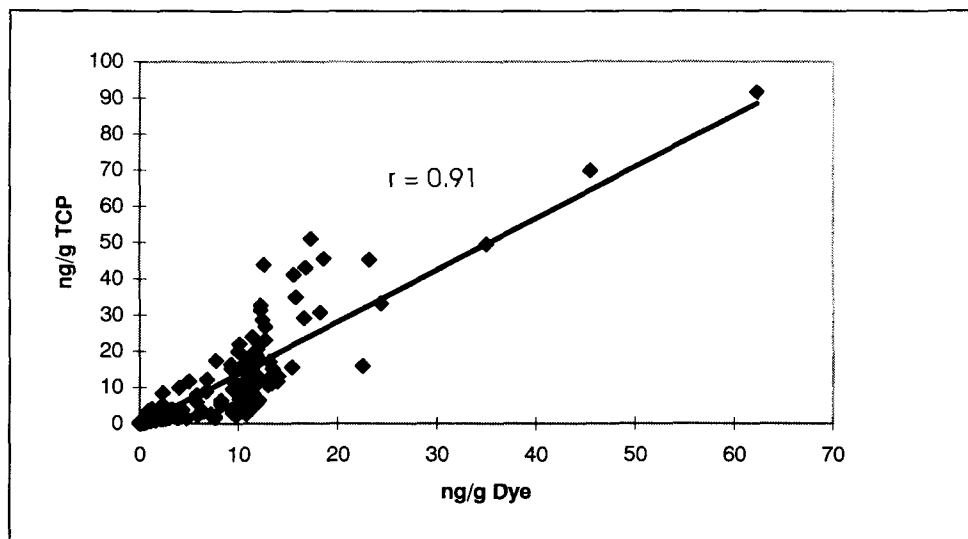


Figure 42. Correlation of 3,5,6-trichloropyridinol (TCP) versus rhodamine WT dye, Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

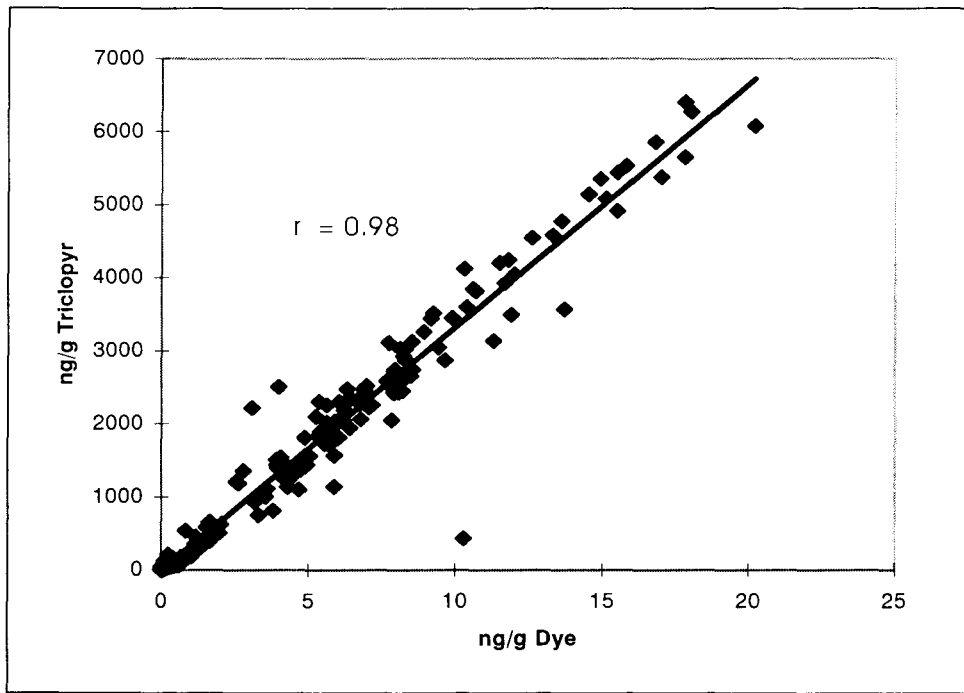


Figure 43. Correlation of triclopyr versus rhodamine WT dye, Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

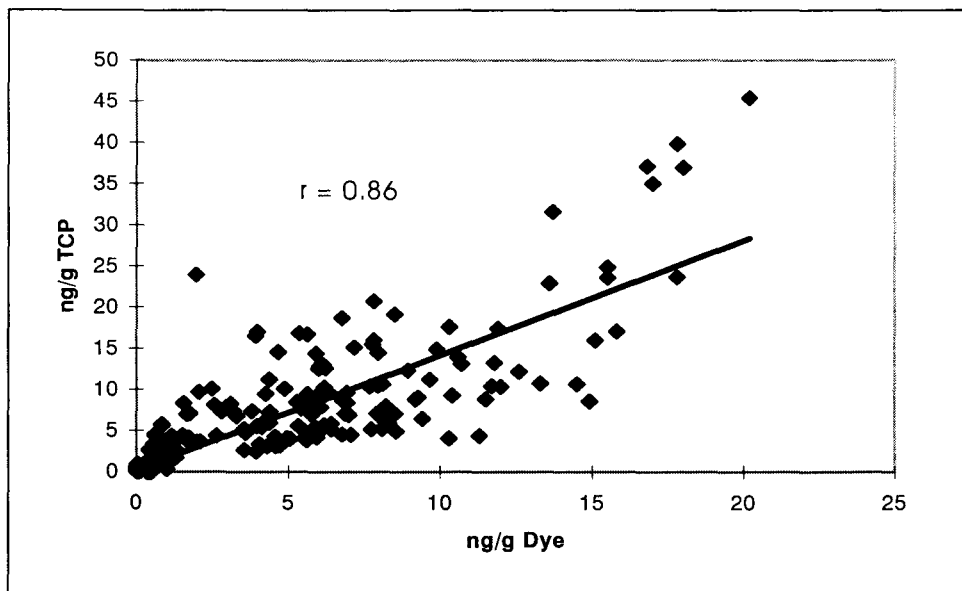


Figure 44. Correlation of 3,5,6-trichloropyridinol (TCP) versus rhodamine WT dye, Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

Dye was first detected outside the Phelps Bay plot 6 hr after treatment at Station 6, which was 100 m southeast of the plot, with a maximum dye concentration in the upper water column of 0.41 $\mu\text{g/L}$. At the same time, dye was visible along the shoreline to the south of the plot. Thus, Station 12 was established 100 m from the plot when there was 3.12 $\mu\text{g/L}$ of dye in the upper water column. Dye movement continued along the southern shoreline and was detected 400 m from the plot in Zimmermans Pass 12 hr after treatment. Dye concentrations were not detectable 800 m from the plot, in West Upper Lake, until 2 weeks after the treatment. Sampling Stations 13, 14, and 15 were established based upon the observed movement. Dye was detected at Station 10, 800 m east of the plot, by 1 week after treatment. Thus, there was an initial movement of dye (and triclopyr residues) from the Phelps Bay plot along the southern shoreline, into West Upper Lake, where it was greatly diluted. Easterly movement of dye through Phelps Bay was initially slower, but less influenced by dilution over 400 m from the plot.

Dye was first detected at Sampling Stations 6 and 7 outside Carsons Bay 12 hr after treatment. Dye was not detected at 800 or 1,600 m from the plot until 2 weeks after treatment.

Triclopyr Dissipation

Results of analysis for triclopyr and its metabolites in the matrices collected in this study have been reported separately (Foster, Blakeslee, and Thomas 1996). A summary of average residue values is reported in Appendix A. The average residue values from the off-plot water sampling stations are summarized in Appendix B. Table 9 lists the reported limits of detection (LOD) and limits of quantification (LOQ) for each sample matrix. Any value falling below the LOD is considered to be nondetectable (ND). A value falling between the LOD and LOQ is considered to be nonquantifiable (NQ) and is referred to as a “trace” value in this report. Calculations of dissipation rates in this report are based on all actual values prior to the ND or NQ interpretation being applied. Data were summarized and summary statistics were applied using commercial spreadsheet software.

Water

Water samples were analyzed for triclopyr and TCP. After the results of fish tissue analyses became available, selected water samples were analyzed for the presence of the TMP metabolite. 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. Calculations of water dissipation at each discrete sampling depth show little variation when examined by depth (Table 10). This indicates that water movement within the treated plots was similar throughout all depths.

Triclopyr and its TCP metabolite dissipated rapidly in this study, in both the open and restricted bays. Figures 45 and 46 represent the dissipation curves of

Table 9
Limits of Detection (LOD, mg/g) and Quantitation (LOQ) for
Residues in Matrices Collected During Triclopyr Treatments on Lake
Minnetonka, Minnesota, June 1994

| | Triclopyr | | TCP | | TMP | |
|---------------------|-----------|-------|-------|--------|------|-------|
| | LOD | LOQ | LOD | LOQ | LOD | LOQ |
| Water | 0.044 | 0.145 | 0.011 | 0.0321 | | |
| Sediment | 3.86 | 12.88 | 2.26 | 7.54 | 2.56 | 8.53 |
| Plants | 3.84 | 12.78 | 1.26 | 4.21 | 1.68 | 5.61 |
| Game fish edible | 4.99 | 16.66 | 4.10 | 13.66 | 2.09 | 6.96 |
| Game fish viscera | 4.22 | 14.05 | 2.51 | 8.36 | 2.06 | 6.87 |
| Bottom fish edible | 2.22 | 7.41 | 1.81 | 6.03 | 4.78 | 15.93 |
| Bottom fish viscera | 3.22 | 10.75 | 9.05 | 30.17 | 3.48 | 11.59 |
| Shell fish edible | 5.52 | 18.41 | 1.78 | 5.96 | 3.56 | 11.87 |
| Shell fish viscera | 2.46 | 8.21 | 2.3 | 7.66 | 1.53 | 5.11 |

Table 10
Triclopyr Dissipation at Different Depths in Water Column, Lake
Minnetonka, Minnesota, June-August 1994

| Level | Avg Depth, m | Half-life, days | r ² |
|--------------------|--------------|-----------------|----------------|
| Phelps Bay | | | |
| Upper | 0.25 | 3.66 | 0.95 |
| Mid | 0.9 | 3.67 | 0.95 |
| Lower | 1.55 | 3.85 | 0.93 |
| Carsons Bay | | | |
| Upper | 0.25 | 4.59 | 0.99 |
| Mid | 0.85 | 4.66 | 0.99 |
| Lower | 1.45 | 4.66 | 0.99 |

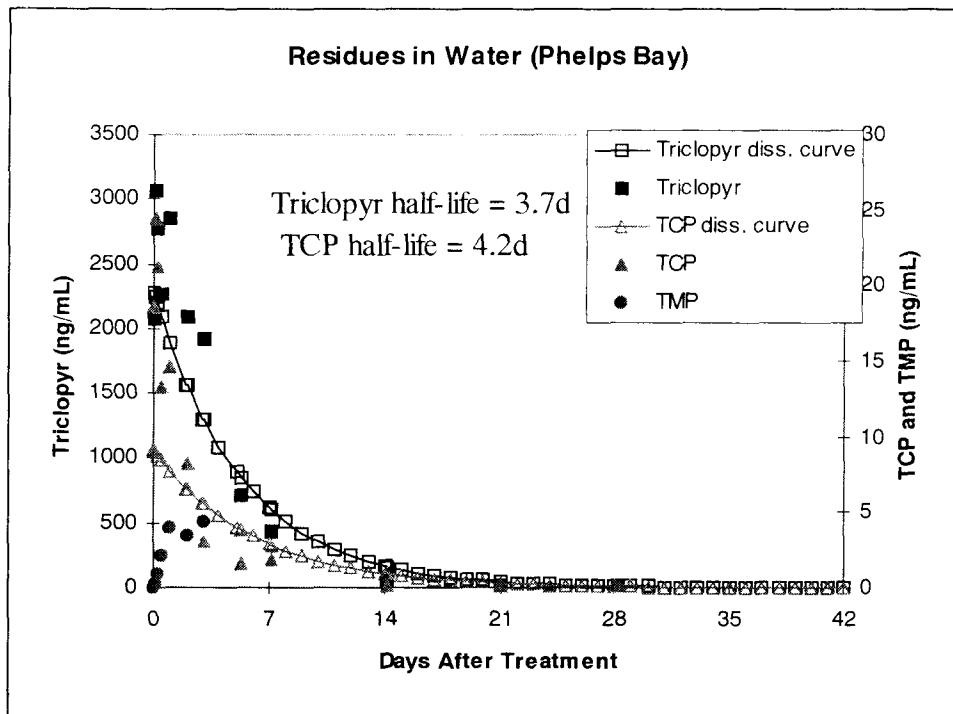


Figure 45. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxy pyridine (TMP) residues in water in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

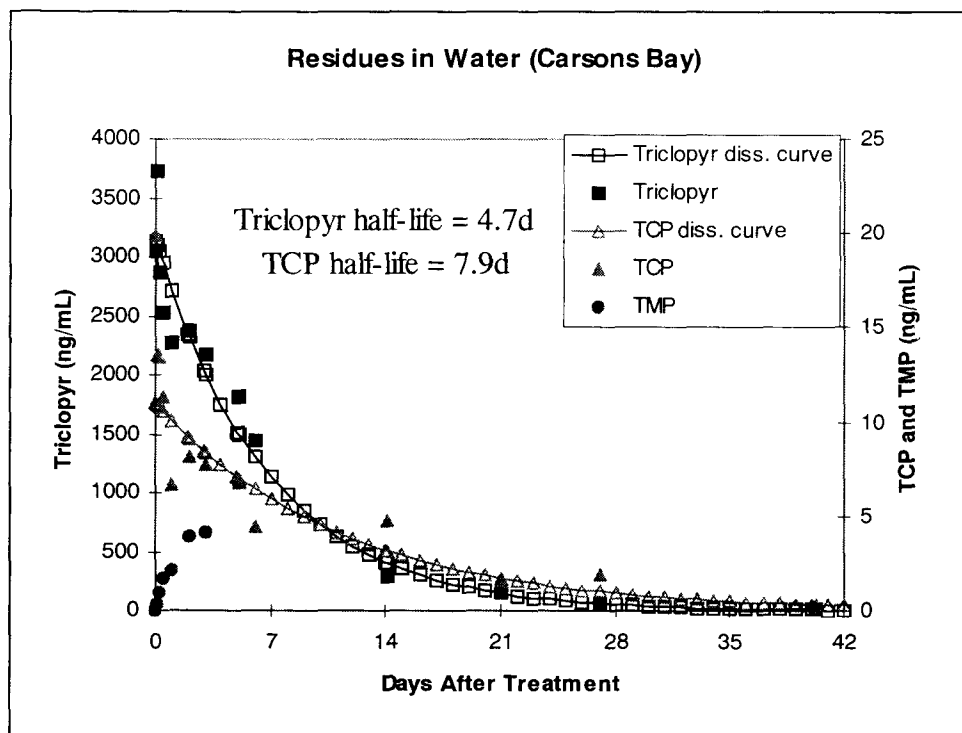


Figure 46. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxy pyridine (TMP) residues in water in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

triclopyr and its metabolites in water from Phelps and Carsons bays. Early residue levels from each bay support the 2.5-mg/L target application rate. In Phelps Bay, triclopyr dissipated in water from the study plot at a half-life rate of 3.7 days, and TCP dissipated at a rate of 4.2 days. At Carsons Bay, triclopyr dissipation in water was calculated at a half-life of 4.7 days and TCP at 7.9 days. The calculated half-lives were consistent with what was expected given the water exchange rates measured in the test bays and the environmental characteristics of triclopyr. These values are consistent with previous studies of triclopyr dissipation in water (Getsinger et al. 1996; Green et al. 1989; Woodburn 1988; Woodburn, Green, and Westerdahl 1993.) Since light levels were low in these plots and bulk water exchange patterns were slow, much of the triclopyr and TCP dissipation measured in this study may be due to microbial degradation.

Residues detected at the off-plot sampling stations strongly support the water exchange patterns provided by the dye movement discussed previously. In Phelps Bay, herbicide movement was primarily to the southwest, through Zimmermans Pass, although detectable levels of triclopyr were found at the remote sampling stations located southeast of the plot. In Carsons Bay, residues were detected at all off-plot sampling stations. In both plots, TCP levels declined below detection sooner than triclopyr. The off-plot data are summarized in Appendix B.

Levels of TMP found in fish tissues prompted the analysis of selected water samples. The compound TMP has not been previously found in water in relation to 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; given that TMP is volatile in nature (vapor pressure = 7.5×10^{-3}), it is likely some material may have been lost from these samples during handling. Given the supposed lipophilic nature of TMP and its estimated bioconcentration 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 four sampling events, with the exception of a triclopyr detection of 0.59 ng/L at the 4-week sampling event. There is no indication that this detection is real, based on the movement/degradation characteristics displayed at the treated bays and the lack of detection of triclopyr in any of the other matrices at Carman Bay. Therefore, it is likely this detection is the result of contamination of the sample.

Sediment

Sediment samples were analyzed for triclopyr and its TCP and TMP metabolites, and the data are summarized in Appendix A. In Phelps Bay, triclopyr was found in sediment with a maximum value of 257 ng/g on Day 3 of sampling and dissipated to below the limit of detection by Week 4. The calculated half-life of triclopyr in this bay was 5 days. The highest level of TCP in Phelps Bay was 27 ng/g at 3 weeks and dissipated at a calculated half-life of 11.3 days. The TMP metabolite was not found at detectable levels. Figure 47 shows the

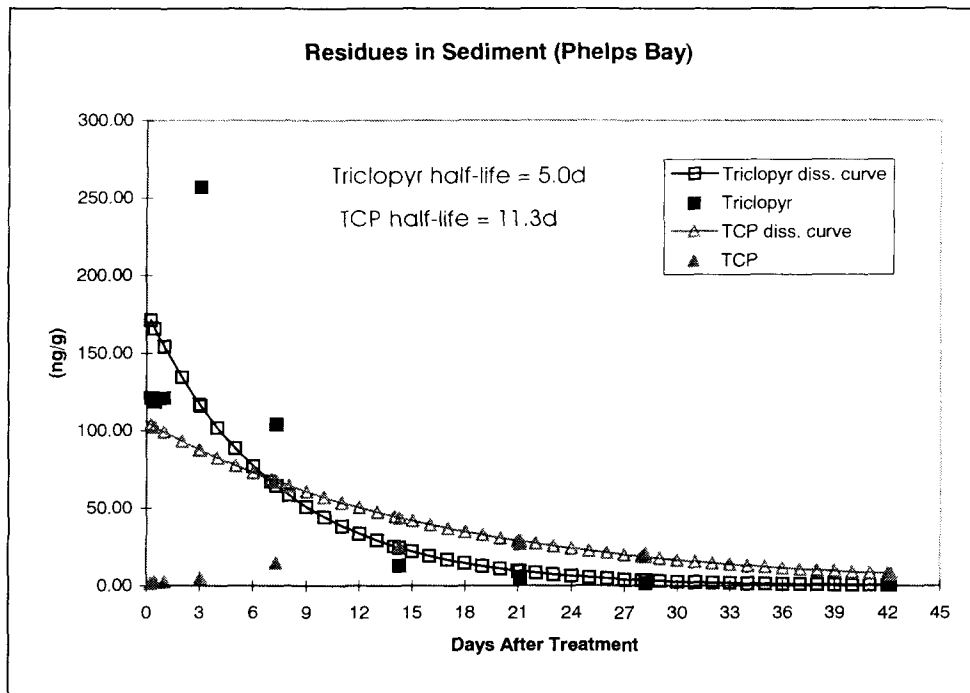


Figure 47. Triclopyr, 3,5,6-trichloropyridinal (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in sediment in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

dissipation curves for Phelps Bay sediment. Samples collected from the three 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 335 ng/g on Day 3 and dissipated with a half-life of 5.8 days to below the level of detection by Week 6. The TCP metabolite had a high value of 65 ng/g at Week 3, and its half-life was 10.7 days. TMP was found at trace levels at the 1-week sampling event. Figure 48 shows the dissipation curves for Carsons Bay sediment.

Samples collected from the single 100-m off-plot station located just outside the constricted entrance to the bay showed levels of triclopyr and TCP dissipating with calculated half-lives of 6.8 and 10.6 days, respectively, similar to the values reported for the within-plot samples.

The Carman Bay control plot tested ND for triclopyr, TCP, and TMP at all three sampling events.

It is likely that the levels of triclopyr and its metabolites found in sediment samples in this study are due to the presence of these materials in the water column in equilibrium with the high moisture content of the sediment, as reported by the characterization analysis; in fact, the sediment results mimic the dissipation rates in water.

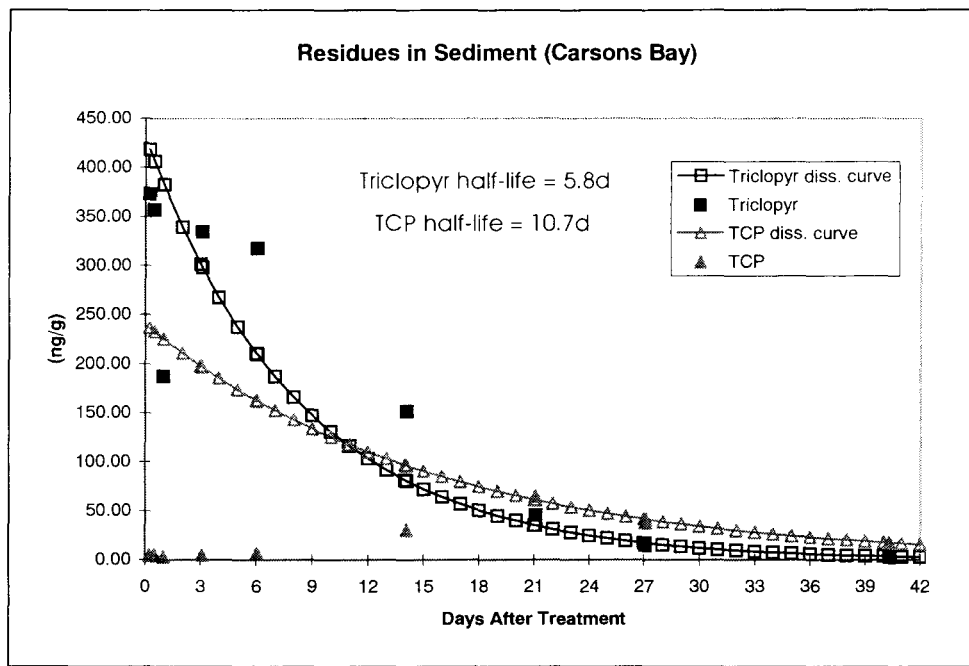


Figure 48. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in sediment in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

Plants

The target plant, Eurasian watermilfoil, accumulated triclopyr steadily until its death. In Phelps Bay, triclopyr accumulated to a level of 19,000 ng/g at Day 3, which was the last sampling event in which sufficient sample could be collected. Levels of TCP and TMP in the plants also accumulated during this period, with final residue values being 205 and 216 ng/g, respectively.

Target plants in Carsons Bay died and decayed around the 1-week sampling period. Residue values were more variable in these samples, with high values occurring early in the sampling scheme. The highest reported values for triclopyr, TCP, and TMP were 23,000, 90, and 107 ng/g, respectively.

The nontarget plant collected in this study showed much less accumulation of triclopyr compared with Eurasian watermilfoil. Figures 49 and 50 represent the dissipation curves for nontarget plants. In Phelps Bay, triclopyr values peaked at 3,580 ng/g and dissipated with a calculated half-life of 2.5 days. The calculated half-life for TCP was 4 days. Residue values for TMP did not support the calculation of a half-life.

In Carsons Bay, triclopyr had a calculated half-life of 3.4 days, from a high value of 4,121 ng/g. TCP dissipation half-life 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 nontarget plants.

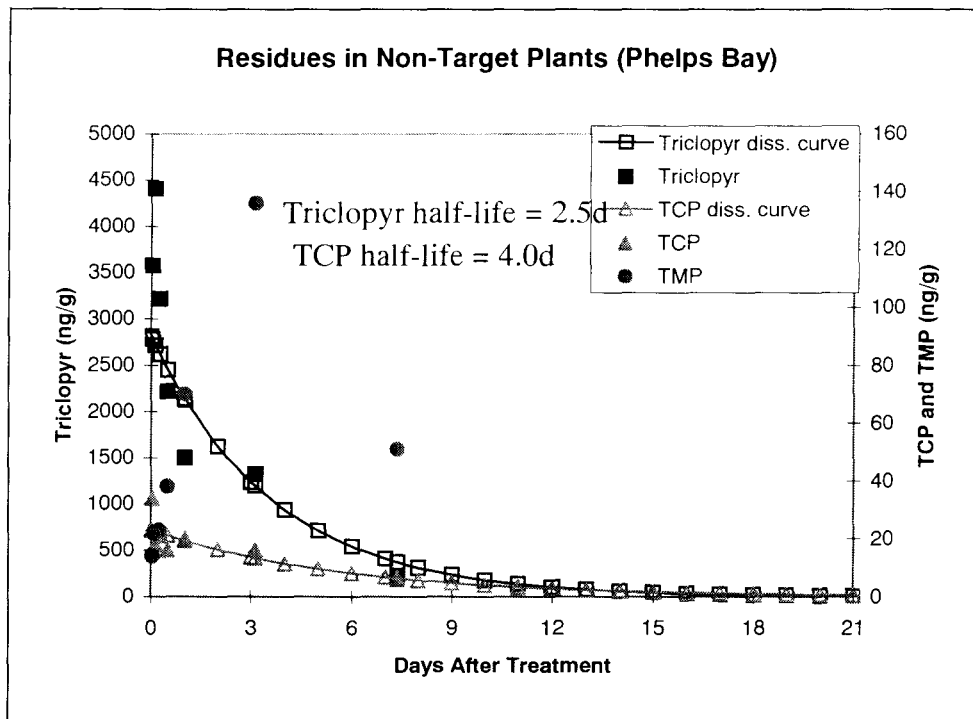


Figure 49. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in nontarget plants in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

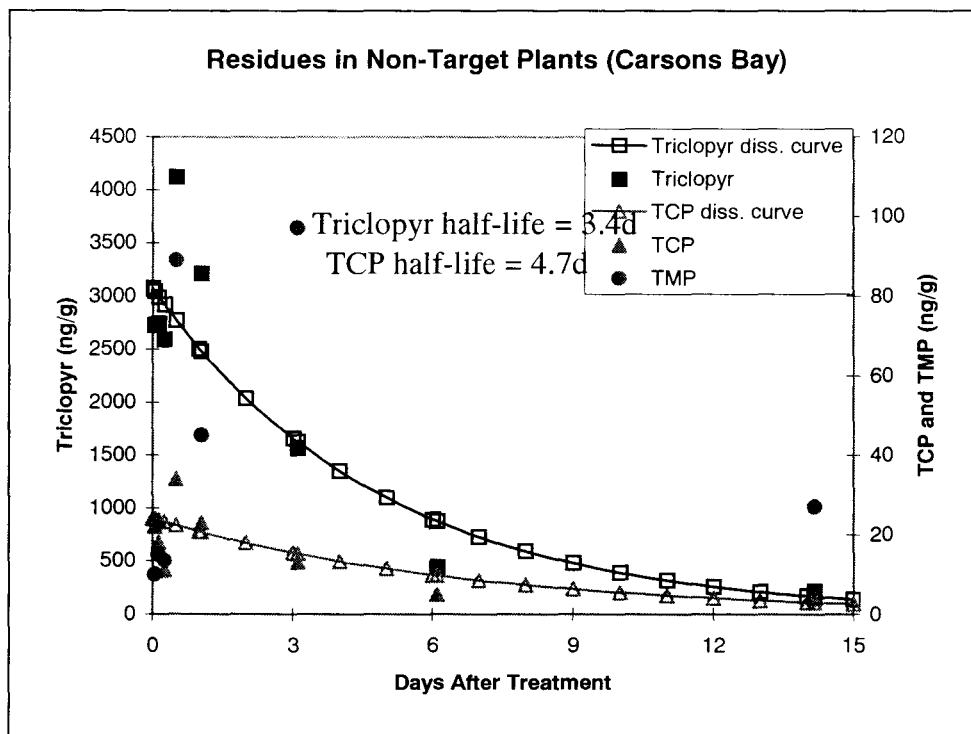


Figure 50. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in nontarget plants in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

Comparison of the levels of triclopyr found in target versus nontarget plants shows the selectivity of triclopyr toward Eurasian watermilfoil. This was supported by the posttreatment plant community data discussed earlier. As in the sediment, levels found in plants are consistent with the dissipation in the surrounding water.

Nontarget aquatic organisms

Triclopyr and its TCP metabolite accumulated and cleared from fish and shellfish tissues in relation to concentrations found in the water column. Residues were generally higher in the inedible viscera portions of the animals. It was also generally true that levels were higher in the bottom-feeding fish (sucker and bullhead) than in the game fish (bass and bluegill). A summary of the calculable half-lives is presented in Table 11. As noted by the summary data in Figures 51 to 60 and Appendix A, triclopyr and its metabolites rapidly accumulated in fish tissues, and clearance was also relatively rapid. Samples of fish and shellfish collected from the untreated reference plot showed no residues of triclopyr and nondetectable or nonquantifiable residues of TCP and TMP, with the exception of a 34-ng/g detection of TCP in a preapplication sample of bluegill viscera and a 29-ng/g detection of TCP in a preapplication sample of crayfish viscera. These isolated detections may be indicative of sample contamination or exposure of these test organisms to the compound prior to stocking of the plots. TCP is a common metabolite of several terrestrial pesticides.

An unexpected discovery was the accumulation of TMP in the tissues of the various fish and shellfish species collected from the triclopyr-treated plots. While TMP is a somewhat common metabolite in terrestrial studies (Petty 1993), 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 triclopyr (Woodburn et al. 1990) or in an aerobic aquatic metabolism study (Woodburn and Cranor 1987). Further, a bluegill metabolism study estimated TMP to comprise only about 0.5 percent of the total activity in the whole fish.¹ Only in one earlier fish metabolism study of bluegill was TMP identified as accounting for a significant metabolite, up to 20 percent of total activity in the fish (Lickly and Murphy 1987). However, these data have fallen under suspicion given the identification of a contaminant in the more current study that duplicated the results of this previous study.¹ Previous studies of TMP reveal it to be of little or no toxicological significance² (Wan, Moul, and Watts 1987).

Fish and shellfish mortality was quite low in all three plots, with the exception of the sucker species. About 26 percent of the sucker stocked at all three sites died during the course of the study. Death rates were equal at Phelps and Carsons bays, while it was almost double at Carman Bay, the untreated reference plot. These results may indicate that sucker is an unacceptable test species, but it must also be noted that the sucker were stocked at the last moment, after a lengthy overland transport from their rearing site, and likely suffered more stress

¹ Personal Communication, 1995, K. B. Woodburn, DowElanco, Indianapolis, IN.

² Personal Communication, 1997, S. A. McMaster, Registration Manager, DowElanco, Indianapolis, IN.

Table 11
Half-Life (in days) Summary for Aquatic Organisms, Lake Minnetonka, Minnesota,
June-August 1994

| | | | Carsons Bay | | | Phelps Bay | | |
|----------------|----------|-----------|-------------|------|------|------------|------|------|
| | | | Triclopyr | TCP | TMP | Triclopyr | TCP | TMP |
| Bass | Edible | Half-life | * | 8.9 | 6.0 | * | * | *** |
| | | r^2 | | 0.95 | 0.85 | | | |
| | Inedible | Half-life | 5.1 | ** | 11.6 | *** | ** | ** |
| | | r^2 | 0.84 | | 0.83 | | | |
| Bluegill | Edible | Half-life | 3.3 | 7.6 | 4.9 | * | 3.9 | 3.1 |
| | | r^2 | 0.92 | 0.91 | 0.91 | | 0.87 | 0.99 |
| | Inedible | Half-life | 5.7 | 11.9 | 4.4 | 2.5 | 6.8 | 3.5 |
| | | r^2 | 0.96 | 0.86 | 0.89 | 0.92 | 0.84 | 0.96 |
| Brown bullhead | Edible | Half-life | 4.8 | 5.2 | 5.8 | **** | **** | **** |
| | | r^2 | 0.88 | 1.00 | 0.98 | | | |
| | Inedible | Half-life | 6.9 | ** | 5.0 | **** | **** | **** |
| | | r^2 | 0.85 | | 0.90 | | | |
| Clam | Edible | Half-life | 10.4 | *** | 5.8 | 5.2 | 2.9 | 3.8 |
| | | r^2 | 0.89 | | 0.99 | 0.96 | 0.99 | 0.96 |
| Crayfish | Edible | Half-life | 7.7 | 10.6 | 5.1 | 5.7 | 5.4 | 2.4 |
| | | r^2 | 0.90 | 0.87 | 0.97 | 0.96 | 0.84 | 0.98 |
| | Inedible | Half-life | 8.5 | 13.7 | 3.7 | 9.5 | 7.0 | 2.5 |
| | | r^2 | 0.84 | 0.85 | 0.96 | 0.95 | 0.95 | 0.96 |
| Sucker | Edible | Half-life | 5.3 | *** | 7.6 | 3.6 | 5.5 | 4.8 |
| | | r^2 | 0.98 | | 0.89 | 0.94 | 0.93 | 0.97 |
| | Inedible | Half-life | 7.0 | *** | 5.2 | 2.0 | 4.2 | 5.4 |
| | | r^2 | 0.97 | | 0.92 | 0.97 | 0.73 | 0.86 |

Note: * = Not calculable because data consist mainly of values <LOQ or LOD.
 ** = Not calculable because data tend to increase over time, or insufficient decline data.
 *** = Not calculable because data are variable, with no steady decline.
 **** = Brown bullhead not stocked in Phelps Bay.

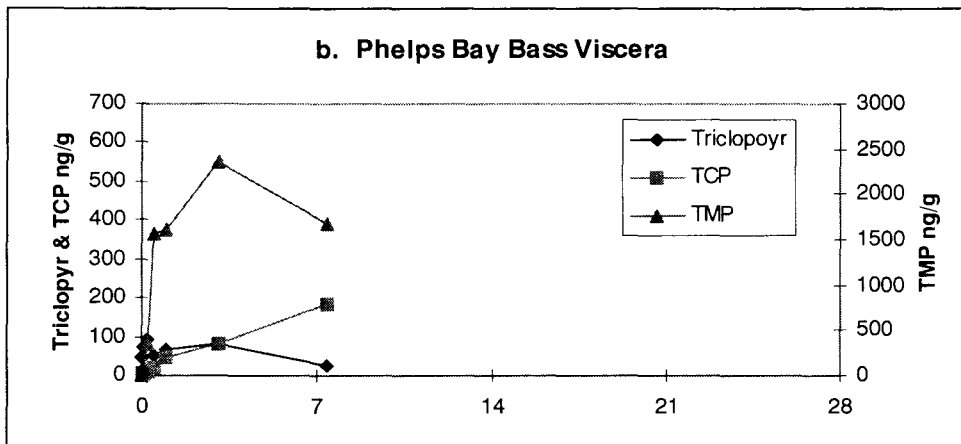
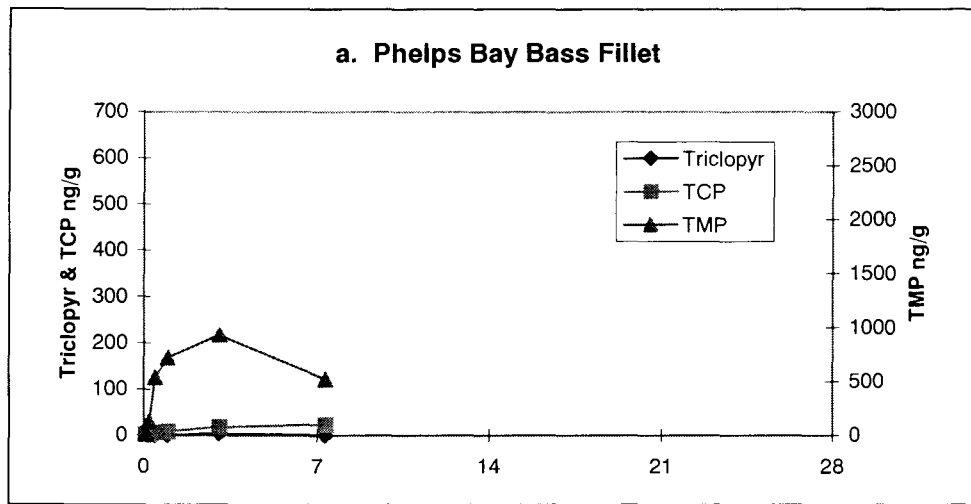


Figure 51. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxy pyridine (TMP) residues in bass fillet (a) and viscera (b) in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

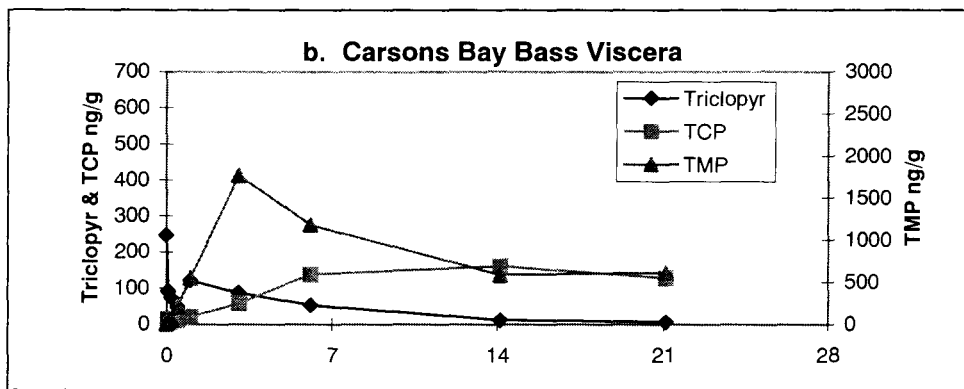
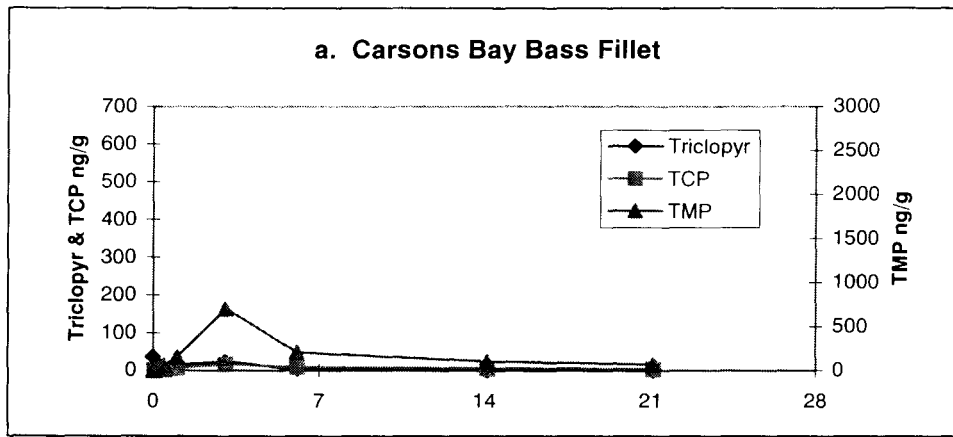


Figure 52. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in bass fillet (a) and viscera (b) in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

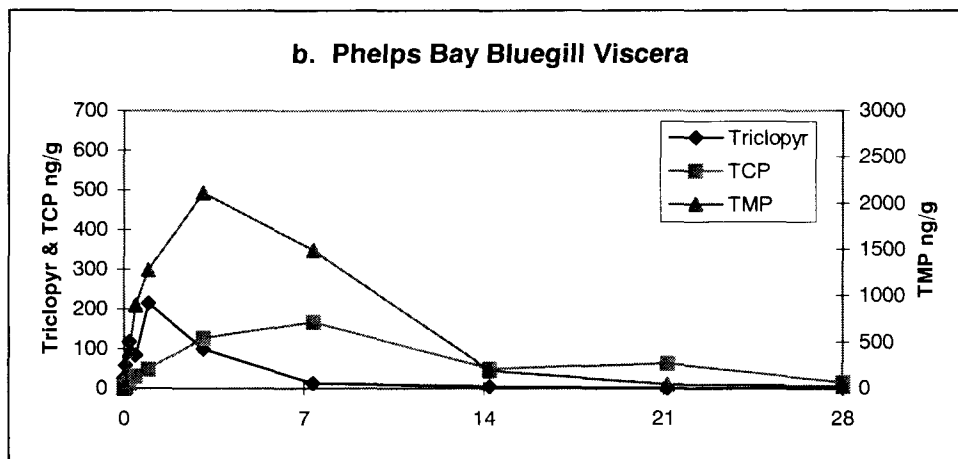
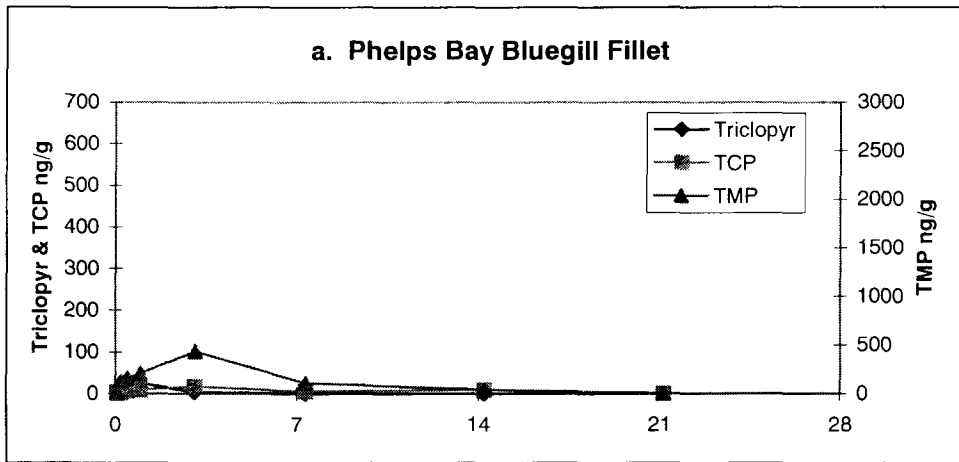


Figure 53. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in bluegill fillet (a) and viscera (b) in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

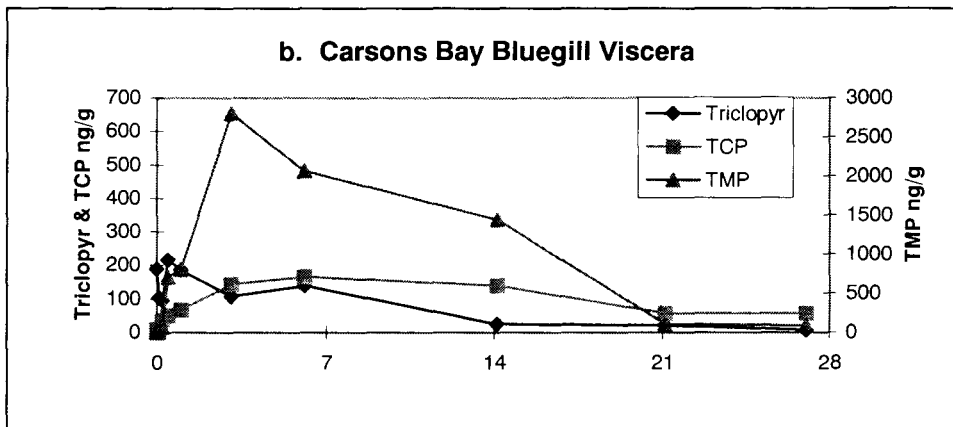
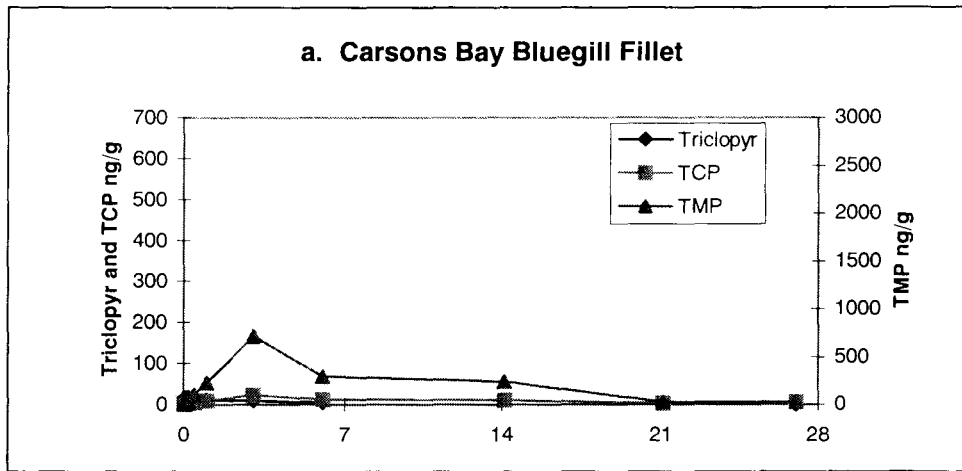


Figure 54. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in bluegill fillet (a) and viscera (b) in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

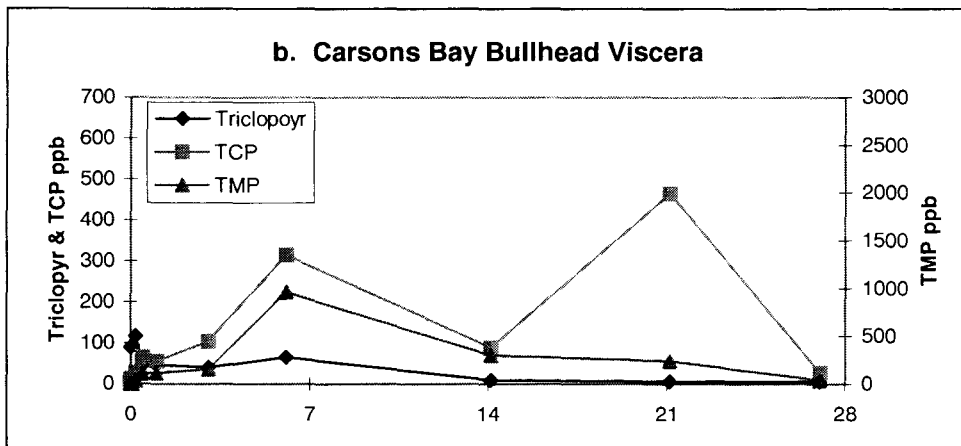
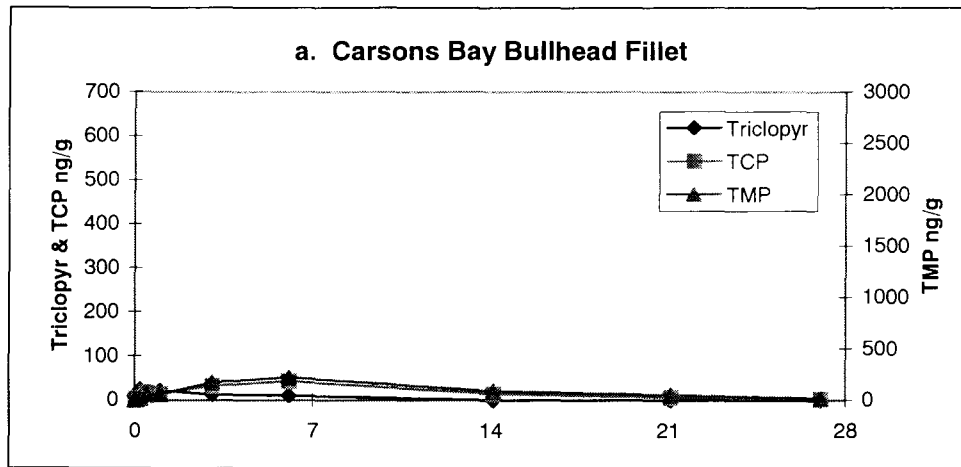


Figure 55. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in bullhead fillet (a) and viscera (b) in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

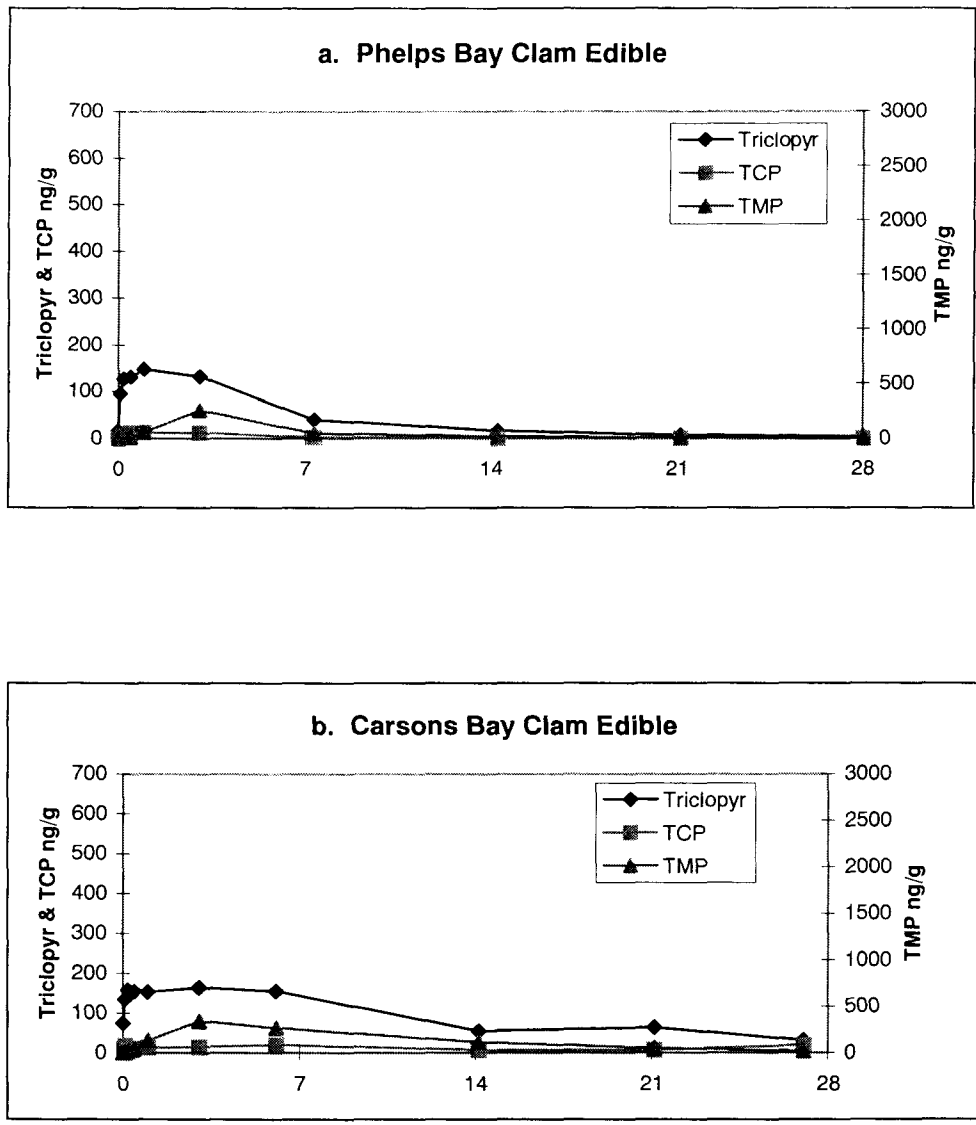


Figure 56. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in clam edible tissue in Phelps (a) and Carsons (b) bays, Lake Minnetonka, Minnesota, June-August 1994

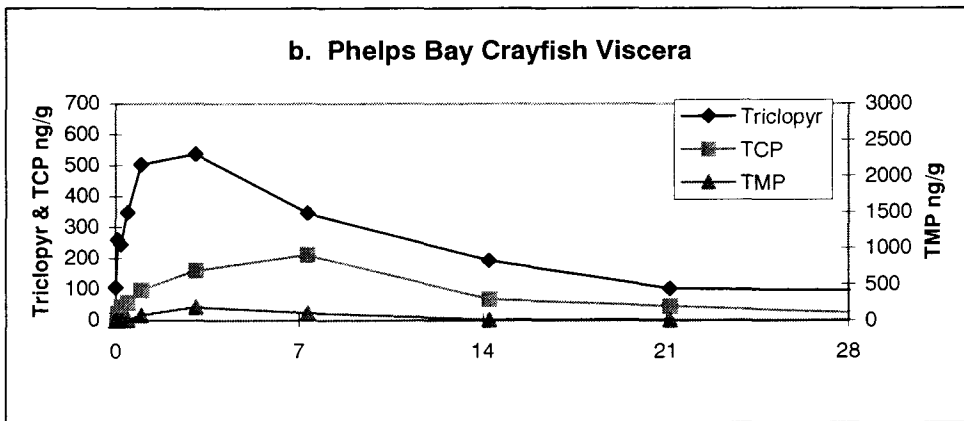
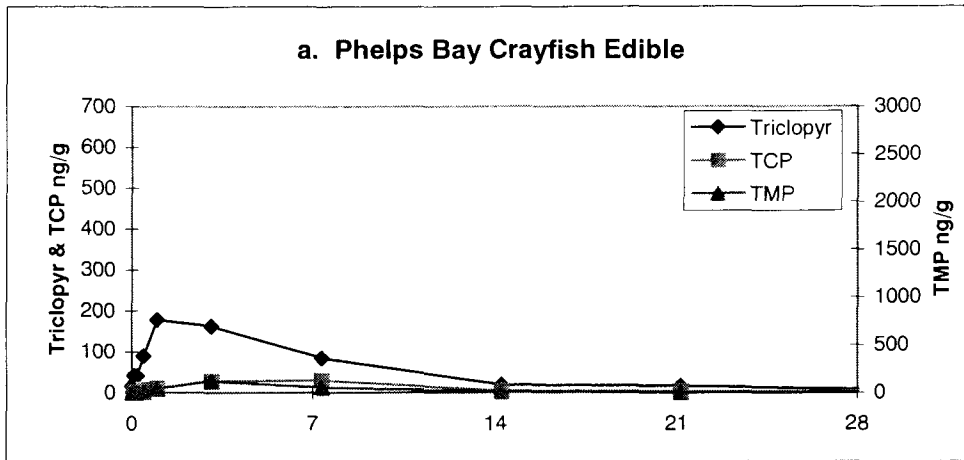


Figure 57. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in crayfish edible (a) and viscera (b) in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

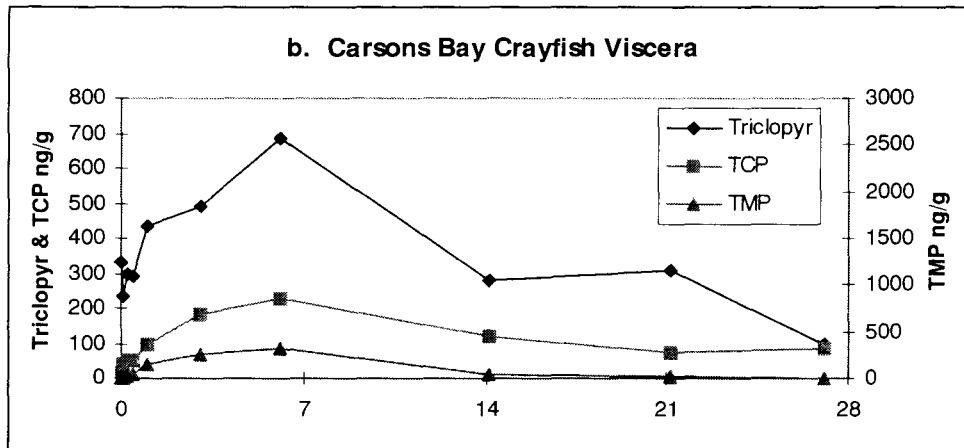
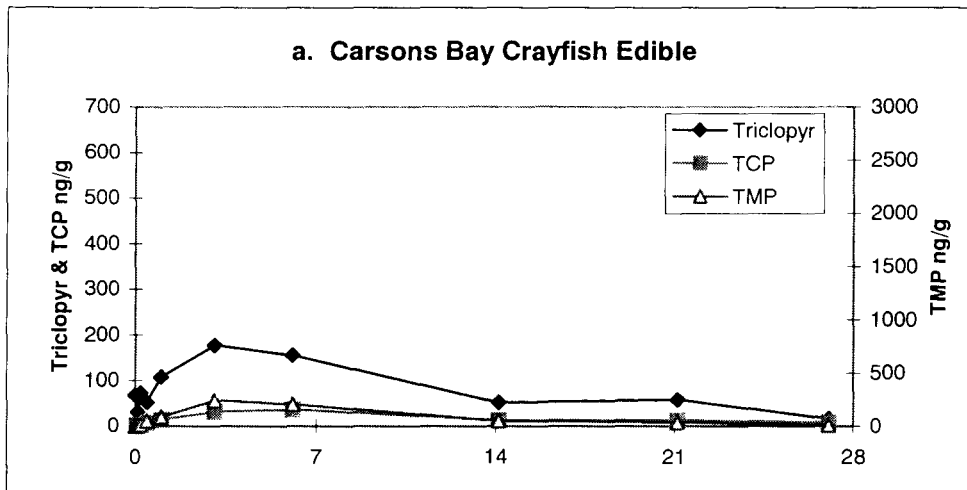


Figure 58. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in crayfish edible (a) and viscera (b) in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

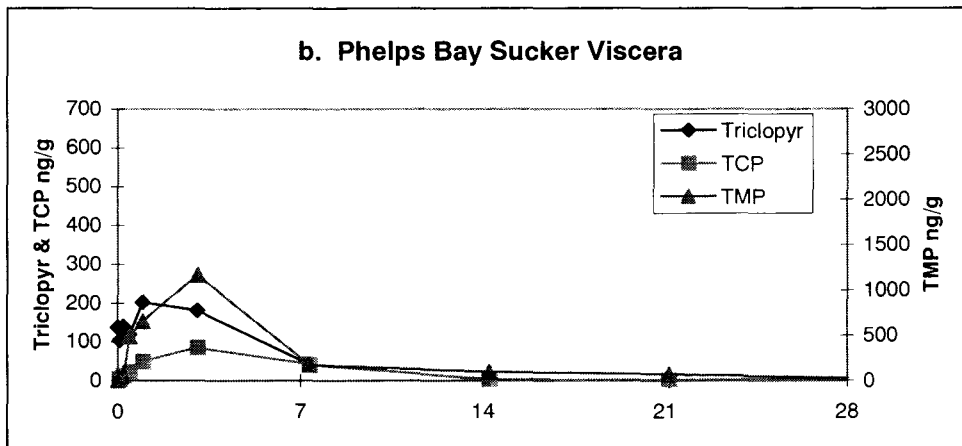
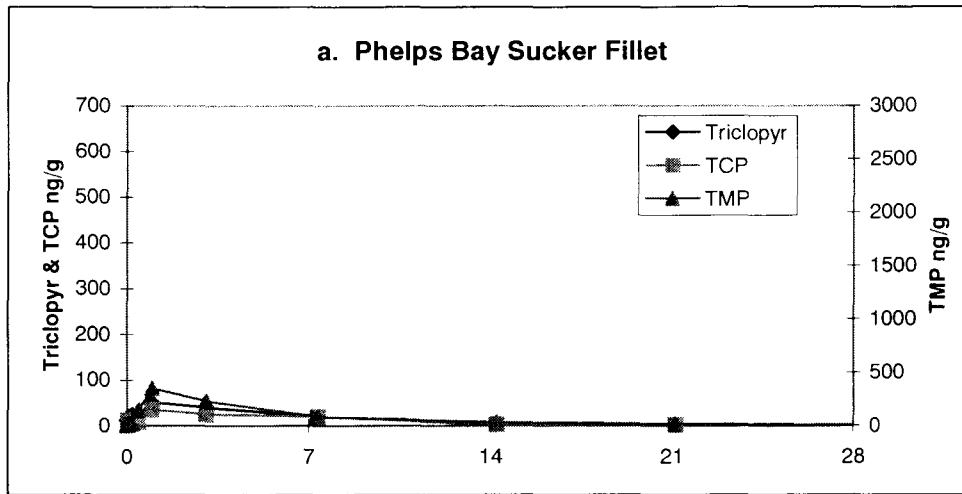


Figure 59. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in sucker fillet (a) and viscera (b) in Phelps Bay, Lake Minnetonka, Minnesota, June-August 1994

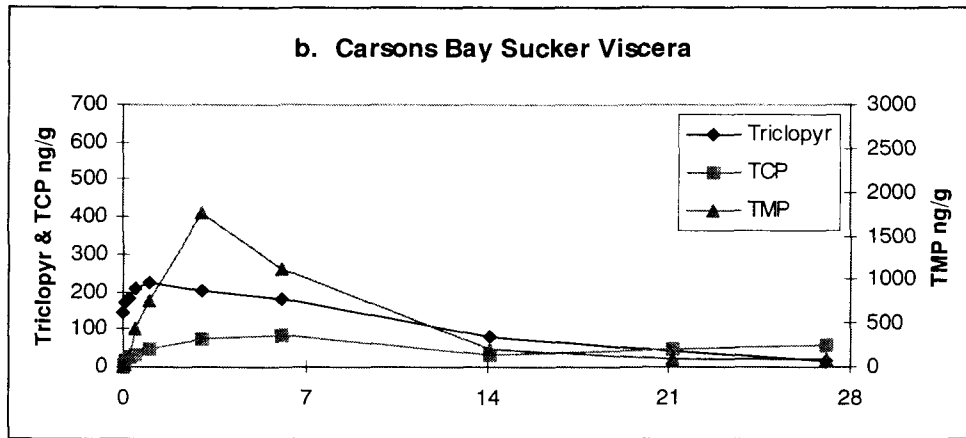
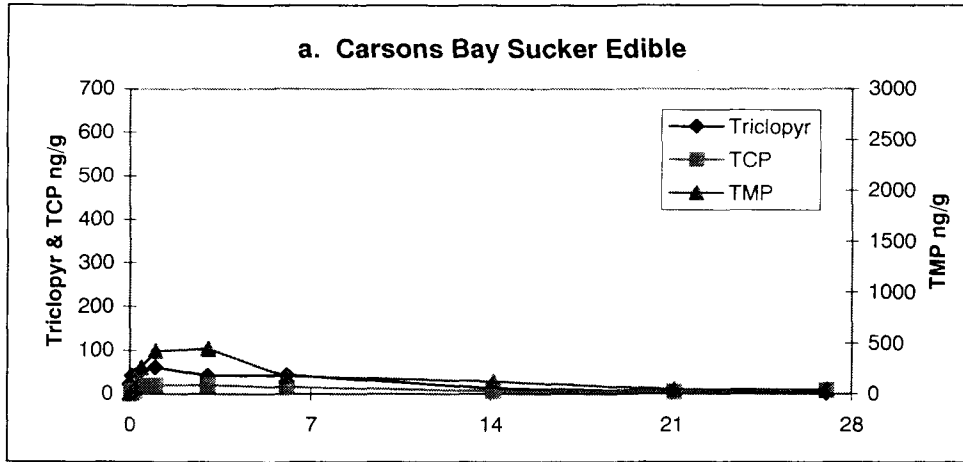


Figure 60. Triclopyr, 3,5,6-trichloropyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) residues in sucker fillet (a) and viscera (b) in Carsons Bay, Lake Minnetonka, Minnesota, June-August 1994

than the other species. Bass suffered 11-percent mortality and bluegill 5 percent. Death rates were slightly higher in Carsons Bay (untreated reference) than the others and can likely be attributed to the observed oxygen sag in that bay. There were no observed deaths of bullhead, crayfish, or clam in any of the plots.

5 Conclusions and Recommendations

Conclusions

Triclopyr, as the herbicide product Garlon 3A, applied to Eurasian watermilfoil stands in Lake Minnetonka rapidly degraded to its metabolites, TCP and TMP. These metabolites, along with the parent triclopyr, were temporarily sequestered by various matrices, such as sediment, fish, shellfish, and plants, in relation to the quantities present in the water column. However, these compounds all dissipated rapidly from all matrices examined. Concentration in the water column was the driving force for accumulation in the other matrices.

Treatment with triclopyr at the full label rate resulted in complete control of Eurasian watermilfoil rooted plants (the target species) in both treatment sites, as evidenced by biomass and transect data. Many native plant species survived, although some were affected by the treatment. Native species distribution and diversity both had small but statistically significant decreases. Native plant biomass was affected at one treated site, but not the other. However, native plant biomass, cover, and diversity remained higher after triclopyr treatment than values for those parameters at the untreated reference plot, which remained infested with Eurasian watermilfoil growth throughout the evaluation period.

No adverse effects on water quality were found following triclopyr applications. Following eradication of the target species, Eurasian watermilfoil, water quality conditions generally improved, particularly with respect to pH and DO levels.

No treatment-related deaths occurred in any of the seven species of fish and shellfish contained in cages in the center of the triclopyr applications.

Although photolysis can be a significant route of triclopyr degradation in the aquatic environment, the results of this study showed that triclopyr applied beneath a dense submersed plant canopy where bulk water exchange is relatively slow and where UV light is quenched in the surface waters also degraded rapidly, possibly due to microbial action. This would indicate that a rapid decline of triclopyr will be observed in waters of various indices of light transmission.

When used according to label conditions, triclopyr provides safe, effective, and selective control of Eurasian watermilfoil, with minimal environmental risk.

Recommendations

Based upon the results of this study, recommendations for the continued evaluation of triclopyr dissipation in aquatic systems are as follows:

- a.* The triethylamine salt formulation of triclopyr should be evaluated in "worst-case" treatment scenarios where the maximum aqueous rate (2.5 mg/L) of the active ingredient is applied to closed, whole ponds that preclude water exchange and dilution.
- b.* Bottom feeding nontarget organisms, such as catfish, should be included in these evaluations and should have direct contact with triclopyr-treated sediments.
- c.* These whole-pond evaluations should be conducted in various geographic regions in the United States, selected to supplement the regions (Florida, Georgia, Minnesota, Washington) previously used in triclopyr aquatic dissipation studies.

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Appendix A

Summary of Average Residue Values for All Matrices (ng/g)

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|--------|---------|-----------|-------|------|
| Phelps | Pre | Water | | ND | ND | ND |
| Phelps | 1 Hour | Water | | 2074.80 | 18.53 | 0.00 |
| Phelps | 3 Hour | Water | | 3068.59 | 24.41 | 0.31 |
| Phelps | 6 Hour | Water | | 2770.61 | 21.19 | 0.90 |
| Phelps | 12 Hour | Water | | 2254.20 | 13.24 | 2.18 |
| Phelps | 1 Day | Water | | 2844.56 | 14.55 | 4.03 |
| Phelps | 2 Day | Water | | 2090.54 | 8.25 | 3.43 |
| Phelps | 3 Day | Water | | 1912.90 | 3.03 | 4.34 |
| Phelps | 5 Day | Water | | 718.23 | 1.66 | NA |
| Phelps | 1 Week | Water | | 440.46 | 1.88 | NA |
| Phelps | 2 Week | Water | | 56.39 | 0.19 | NA |
| Phelps | 3 Week | Water | | 18.71 | NQ | NA |
| Phelps | 4 Week | Water | | 8.45 | NQ | NA |
| Phelps | 6 Week | Water | | 2.42 | ND | NA |
| Carsons | PRE | Water | | ND | ND | NA |
| Carsons | 1 Hour | Water | | 3058.44 | 19.90 | 0.00 |
| Carsons | 3 Hour | Water | | 3727.10 | 13.51 | 0.27 |
| Carsons | 6 Hour | Water | | 2862.55 | 13.41 | 0.94 |
| Carsons | 12 Hour | Water | | 2526.35 | 11.33 | 1.72 |
| Carsons | 1 Day | Water | | 2264.82 | 6.68 | 2.16 |
| Carsons | 2 Day | Water | | 2369.92 | 8.18 | 3.93 |
| Carsons | 3 Day | Water | | 2169.66 | 7.73 | 4.18 |
| Carsons | 5 Day | Water | | 1808.65 | 6.74 | NA |
| Carsons | 1 Week | Water | | 1438.99 | 4.46 | NA |
| Carsons | 2 Week | Water | | 295.24 | 4.78 | NA |
| Carsons | 3 Week | Water | | 163.24 | 1.62 | NA |
| Carsons | 4 Week | Water | | 61.95 | 1.90 | NA |
| Carsons | 6 Week | Water | | 8.54 | 0.20 | NA |
| Carman | Pre | Water | | ND | ND | NA |
| Carman | 1 Week | Water | | ND | ND | NA |
| Carman | 4 Week | Water | | 0.59 | ND | NA |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|--------------|---------|-----------|-----|-----|
| Phelps | PRE | Sediment | | ND | ND | ND |
| Phelps | 6 Hour | Sediment | | 121 | ND | ND |
| Phelps | 12 Hour | Sediment | | 119 | NQ | ND |
| Phelps | 1 Day | Sediment | | 121 | NQ | ND |
| Phelps | 3 Day | Sediment | | 257 | NQ | ND |
| Phelps | 1 Week | Sediment | | 104 | 15 | ND |
| Phelps | 2 Week | Sediment | | 13 | 25 | ND |
| Phelps | 3 Week | Sediment | | NQ | 27 | ND |
| Phelps | 4 Week | Sediment | | ND | 21 | ND |
| Phelps | 6 Week | Sediment | | ND | 8 | ND |
| Carsons | PRE | Sediment | | ND | ND | ND |
| Carsons | 6 Hour | Sediment | | 373 | ND | ND |
| Carsons | 12 Hour | Sediment | | 357 | ND | ND |
| Carsons | 1 Day | Sediment | | 187 | ND | ND |
| Carsons | 3 Day | Sediment | | 334 | NQ | ND |
| Carsons | 1 Week | Sediment | | 318 | NQ | ND |
| Carsons | 2 Week | Sediment | | 152 | NQ | ND |
| Carsons | 3 Week | Sediment | | 45 | NQ | ND |
| Carsons | 4 Week | Sediment | | 15 | NQ | NQ |
| Carsons | 6 Week | Sediment | | ND | 30 | ND |
| | | | | | 65 | ND |
| Carman | Pre | Sediment | | ND | 38 | ND |
| Carman | 1 Week | Sediment | | ND | 18 | ND |
| Carman | 4 Week | Sediment | | ND | | |
| Phelps | Pre | Target Plant | | ND | ND | ND |
| Phelps | 1 Hour | Target Plant | | 3170 | 35 | 9 |
| Phelps | 3 Hour | Target Plant | | 10370 | 56 | 43 |
| Phelps | 6 Hour | Target Plant | | 12200 | 64 | 109 |
| Phelps | 12 Hour | Target Plant | | 15100 | 91 | 236 |
| Phelps | 1 Day | Target Plant | | 8450 | 79 | 148 |
| Phelps | 3 Day | Target Plant | | 19100 | 205 | 216 |
| Phelps | 1 Week | Target Plant | | NS | NS | NS |
| Phelps | 2 Week | Target Plant | | NS | NS | NS |
| Phelps | 3 Week | Target Plant | | NS | NS | NS |
| Phelps | 4 Week | Target Plant | | NS | NS | NS |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|------------------|---------|-----------|-----|-----|
| Carsons | Pre | Target Plant | | ND | ND | ND |
| Carsons | 1 Hour | Target Plant | | 23166 | 90 | 69 |
| Carsons | 3 Hour | Target Plant | | 3971 | 20 | 17 |
| Carsons | 6 Hour | Target Plant | | 6859 | 27 | 40 |
| Carsons | 12 Hour | Target Plant | | 14247 | 36 | 94 |
| Carsons | 1 Day | Target Plant | | 5033 | 24 | 43 |
| Carsons | 3 Day | Target Plant | | 12189 | 43 | 171 |
| Carsons | 1 Week | Target Plant | | 4880 | 39 | 105 |
| Carsons | 2 Week | Target Plant | | NS | NS | NS |
| Carsons | 3 Week | Target Plant | | NS | NS | NS |
| Carsons | 4 Week | Target Plant | | NS | NS | NS |
| Carman | Pre | Target Plant | | ND | ND | ND |
| Carman | 1 Week | Target Plant | | ND | ND | ND |
| Carman | 4 Week | Target Plant | | ND | ND | ND |
| Phelps | Pre | Non-Target Plant | | ND | ND | ND |
| Phelps | 1 Hour | Non-Target Plant | | 3580 | 34 | 14 |
| Phelps | 3 Hour | Non-Target Plant | | 4410 | 18 | 22 |
| Phelps | 6 Hour | Non-Target Plant | | 3220 | 21 | 23 |
| Phelps | 12 Hour | Non-Target Plant | | 2220 | 16 | 38 |
| Phelps | 1 Day | Non-Target Plant | | 1505 | 20 | 70 |
| Phelps | 3 Day | Non-Target Plant | | 1330 | 16 | 136 |
| Phelps | 1 Week | Non-Target Plant | | 220 | NQ | 51 |
| Phelps | 2 Week | Non-Target Plant | | NS | NS | NS |
| Phelps | 3 Week | Non-Target Plant | | 10 | ND | NA |
| Phelps | 4 Week | Non-Target Plant | | NS | NS | NS |
| Carsons | Pre | Non-Target Plant | | ND | ND | ND |
| Carsons | 1 Hour | Non-Target Plant | | 2723 | 22 | 10 |
| Carsons | 3 Hour | Non-Target Plant | | 2739 | 18 | 15 |
| Carsons | 6 Hour | Non-Target Plant | | 2590 | 11 | 14 |
| Carsons | 12 Hour | Non-Target Plant | | 4121 | 34 | 89 |
| Carsons | 1 Day | Non-Target Plant | | 3210 | 23 | 45 |
| Carsons | 3 Day | Non-Target Plant | | 1563 | 13 | 97 |
| Carsons | 1 Week | Non-Target Plant | | 443 | NQ | NA |
| Carsons | 2 Week | Non-Target Plant | | 219 | ND | 27 |
| Carsons | 3 Week | Non-Target Plant | | NS | NS | NS |
| Carsons | 4 Week | Non-Target Plant | | NS | NS | NS |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|------------------|----------|-----------|-----|------|
| Carman | Pre | Non-Target Plant | | ND | ND | ND |
| Carman | 1 Week | Non-Target Plant | | ND | ND | ND |
| Carman | 4 Week | Non-Target Plant | | ND | ND | ND |
| Phelps | Pre | Bass | Edible | ND | ND | ND |
| Phelps | 1 Hour | Bass | Edible | ND | ND | ND |
| Phelps | 3 Hour | Bass | Edible | NQ | ND | 10 |
| Phelps | 6 Hour | Bass | Edible | ND | ND | 127 |
| Phelps | 12 Hour | Bass | Edible | ND | NQ | 538 |
| Phelps | 1 Day | Bass | Edible | ND | NQ | 721 |
| Phelps | 3 Day | Bass | Edible | ND | 18 | 931 |
| Phelps | 1 Week | Bass | Edible | ND | 23 | 521 |
| Phelps | 2 Week | Bass | Edible | NS | NS | NS |
| Phelps | 3 Week | Bass | Edible | NS | NS | NS |
| Phelps | 4 Week | Bass | Edible | NS | NS | NS |
| Phelps | Pre | Bass | Inedible | ND | ND | ND |
| Phelps | 1 Hour | Bass | Inedible | 47 | NQ | ND |
| Phelps | 3 Hour | Bass | Inedible | 70 | NQ | 97 |
| Phelps | 6 Hour | Bass | Inedible | 95 | 9 | 357 |
| Phelps | 12 Hour | Bass | Inedible | 52 | 21 | 1576 |
| Phelps | 1 Day | Bass | Inedible | 66 | 44 | 1611 |
| Phelps | 3 Day | Bass | Inedible | 83 | 83 | 2365 |
| Phelps | 1 Week | Bass | Inedible | 25 | 183 | 1670 |
| Phelps | 2 Week | Bass | Inedible | NS | NS | NS |
| Phelps | 3 Week | Bass | Inedible | NS | NS | NS |
| Phelps | 4 Week | Bass | Inedible | NS | NS | NS |
| Carsons | Pre | Bass | Edible | ND | ND | ND |
| Carsons | 1 Hour | Bass | Edible | 37 | ND | ND |
| Carsons | 3 Hour | Bass | Edible | NQ | ND | NQ |
| Carsons | 6 Hour | Bass | Edible | 17 | ND | 25 |
| Carsons | 12 Hour | Bass | Edible | ND | ND | 59 |
| Carsons | 1 Day | Bass | Edible | NQ | NQ | 155 |
| Carsons | 3 Day | Bass | Edible | 24 | 17 | 702 |
| Carsons | 1 Week | Bass | Edible | ND | 10 | 208 |
| Carsons | 2 Week | Bass | Edible | ND | NQ | 103 |
| Carsons | 3 Week | Bass | Edible | ND | ND | 69 |
| Carsons | 4 Week | Bass | Edible | NS | NS | NS |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|----------|----------|-----------|-----|------|
| Carsons | Pre | Bass | Inedible | ND | ND | NQ |
| Carsons | 1 Hour | Bass | Inedible | 247 | 14 | NQ |
| Carsons | 3 Hour | Bass | Inedible | 92 | 9 | 20 |
| Carsons | 6 Hour | Bass | Inedible | 73 | 9 | 52 |
| Carsons | 12 Hour | Bass | Inedible | 49 | 10 | 199 |
| Carsons | 1 Day | Bass | Inedible | 121 | 21 | 548 |
| Carsons | 3 Day | Bass | Inedible | 88 | 59 | 1769 |
| Carsons | 1 Week | Bass | Inedible | 53 | 138 | 1181 |
| Carsons | 2 Week | Bass | Inedible | NQ | 161 | 587 |
| Carsons | 3 Week | Bass | Inedible | NQ | 128 | 616 |
| Carsons | 4 Week | Bass | Inedible | NS | NS | NS |
| Carman | Pre | Bass | Edible | ND | ND | ND |
| Carman | 1 Week | Bass | Edible | ND | ND | ND |
| Carman | 4 Week | Bass | Edible | ND | ND | ND |
| Carman | Pre | Bass | Inedible | ND | ND | ND |
| Carman | 1 Week | Bass | Inedible | ND | ND | ND |
| Carman | 4 Week | Bass | Inedible | ND | ND | ND |
| Phelps | Pre | Bluegill | Edible | ND | ND | ND |
| Phelps | 1 Hour | Bluegill | Edible | NQ | ND | ND |
| Phelps | 3 Hour | Bluegill | Edible | NQ | ND | 13 |
| Phelps | 6 Hour | Bluegill | Edible | NQ | ND | 123 |
| Phelps | 12 Hour | Bluegill | Edible | NQ | NQ | 159 |
| Phelps | 1 Day | Bluegill | Edible | 26 | NQ | 211 |
| Phelps | 3 Day | Bluegill | Edible | ND | 17 | 435 |
| Phelps | 1 Week | Bluegill | Edible | ND | NQ | 111 |
| Phelps | 2 Week | Bluegill | Edible | ND | NQ | 39 |
| Phelps | 3 Week | Bluegill | Edible | ND | ND | NQ |
| Phelps | 4 Week | Bluegill | Edible | ND | ND | ND |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|----------|----------|-----------|-----|------|
| Phelps | Pre | Bluegill | Inedible | ND | ND | ND |
| Phelps | 1 Hour | Bluegill | Inedible | 25 | ND | ND |
| Phelps | 3 Hour | Bluegill | Inedible | 59 | NQ | 24 |
| Phelps | 6 Hour | Bluegill | Inedible | 117 | 13 | 411 |
| Phelps | 12 Hour | Bluegill | Inedible | 84 | 30 | 901 |
| Phelps | 1 Day | Bluegill | Inedible | 214 | 48 | 1281 |
| Phelps | 3 Day | Bluegill | Inedible | 100 | 127 | 2113 |
| Phelps | 1 Week | Bluegill | Inedible | NQ | 167 | 1492 |
| Phelps | 2 Week | Bluegill | Inedible | NQ | 51 | 196 |
| Phelps | 3 Week | Bluegill | Inedible | ND | 63 | 38 |
| Phelps | 4 Week | Bluegill | Inedible | ND | 15 | 22 |
| Carsons | Pre | Bluegill | Edible | ND | ND | ND |
| Carsons | 1 Hour | Bluegill | Edible | NQ | ND | NQ |
| Carsons | 3 Hour | Bluegill | Edible | NQ | ND | 25 |
| Carsons | 6 Hour | Bluegill | Edible | 17 | ND | 20 |
| Carsons | 12 Hour | Bluegill | Edible | NQ | NQ | 104 |
| Carsons | 1 Day | Bluegill | Edible | NQ | NQ | 227 |
| Carsons | 3 Day | Bluegill | Edible | NQ | 23 | 715 |
| Carsons | 1 Week | Bluegill | Edible | ND | NQ | 296 |
| Carsons | 2 Week | Bluegill | Edible | ND | NQ | 245 |
| Carsons | 3 Week | Bluegill | Edible | ND | ND | 29 |
| Carsons | 4 Week | Bluegill | Edible | ND | NQ | 25 |
| Carsons | Pre | Bluegill | Inedible | ND | ND | ND |
| Carsons | 1 Hour | Bluegill | Inedible | 190 | 8 | ND |
| Carsons | 3 Hour | Bluegill | Inedible | 104 | 9 | 12 |
| Carsons | 6 Hour | Bluegill | Inedible | 95 | 34 | 71 |
| Carsons | 12 Hour | Bluegill | Inedible | 216 | 50 | 704 |
| Carsons | 1 Day | Bluegill | Inedible | 185 | 67 | 807 |
| Carsons | 3 Day | Bluegill | Inedible | 108 | 143 | 2800 |
| Carsons | 1 Week | Bluegill | Inedible | 139 | 166 | 2067 |
| Carsons | 2 Week | Bluegill | Inedible | 24 | 139 | 1445 |
| Carsons | 3 Week | Bluegill | Inedible | 20 | 57 | 110 |
| Carsons | 4 Week | Bluegill | Inedible | NQ | 58 | 90 |
| Carman | Pre | Bluegill | Edible | ND | ND | ND |
| Carman | 1 Week | Bluegill | Edible | ND | ND | ND |
| Carman | 4 Week | Bluegill | Edible | ND | ND | ND |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|----------------|----------|-----------|-----|-----|
| Carman | Pre | Bluegill | Inedible | ND | 34 | ND |
| Carman | 1 Week | Bluegill | Inedible | ND | ND | ND |
| Carman | 4 Week | Bluegill | Inedible | ND | ND | ND |
| Carsons | Pre | Brown Bullhead | Edible | 26 | ND | ND |
| Carsons | 1 Hour | Brown Bullhead | Edible | 8 | NQ | ND |
| Carsons | 3 Hour | Brown Bullhead | Edible | 13 | ND | ND |
| Carsons | 6 Hour | Brown Bullhead | Edible | 23 | NQ | NQ |
| Carsons | 12 Hour | Brown Bullhead | Edible | 13 | 18 | 49 |
| Carsons | 1 Day | Brown Bullhead | Edible | 22 | 14 | 59 |
| Carsons | 3 Day | Brown Bullhead | Edible | 13 | 32 | 174 |
| Carsons | 1 Week | Brown Bullhead | Edible | 10 | 43 | 222 |
| Carsons | 2 Week | Brown Bullhead | Edible | ND | 13 | 86 |
| Carsons | 3 Week | Brown Bullhead | Edible | ND | 6 | 49 |
| Carsons | 4 Week | Brown Bullhead | Edible | ND | NQ | 16 |
| Carsons | Pre | Brown Bullhead | Inedible | NQ | ND | ND |
| Carsons | 1 Hour | Brown Bullhead | Inedible | 89 | NQ | ND |
| Carsons | 3 Hour | Brown Bullhead | Inedible | 94 | NQ | ND |
| Carsons | 6 Hour | Brown Bullhead | Inedible | 117 | NQ | 34 |
| Carsons | 12 Hour | Brown Bullhead | Inedible | 45 | 66 | 106 |
| Carsons | 1 Day | Brown Bullhead | Inedible | 47 | 56 | 115 |
| Carsons | 3 Day | Brown Bullhead | Inedible | 41 | 105 | 154 |
| Carsons | 1 Week | Brown Bullhead | Inedible | 66 | 315 | 965 |
| Carsons | 2 Week | Brown Bullhead | Inedible | NQ | 90 | 303 |
| Carsons | 3 Week | Brown Bullhead | Inedible | NQ | 466 | 241 |
| Carsons | 4 Week | Brown Bullhead | Inedible | NQ | NQ | 40 |
| Carman | Pre | Brown Bullhead | Edible | ND | ND | ND |
| Carman | 1 Week | Brown Bullhead | Edible | ND | ND | ND |
| Carman | 4 Week | Brown Bullhead | Edible | ND | ND | ND |
| Carman | Pre | Brown Bullhead | Inedible | ND | ND | ND |
| Carman | 1 Week | Brown Bullhead | Inedible | ND | ND | ND |
| Carman | 4 Week | Brown Bullhead | Inedible | ND | ND | ND |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|--------|----------|-----------|-----|------|
| Phelps | Pre | Sucker | Edible | ND | ND | ND |
| Phelps | 1 Hour | Sucker | Edible | 12 | 12 | ND |
| Phelps | 3 Hour | Sucker | Edible | 19 | NQ | NQ |
| Phelps | 6 Hour | Sucker | Edible | 24 | NQ | 20 |
| Phelps | 12 Hour | Sucker | Edible | 26 | 8 | 148 |
| Phelps | 1 Day | Sucker | Edible | 51 | 35 | 352 |
| Phelps | 3 Day | Sucker | Edible | 40 | 25 | 232 |
| Phelps | 1 Week | Sucker | Edible | 20 | 20 | 83 |
| Phelps | 2 Week | Sucker | Edible | ND | NQ | 29 |
| Phelps | 3 Week | Sucker | Edible | ND | NQ | NQ |
| Phelps | 4 Week | Sucker | Edible | ND | NQ | NQ |
| Phelps | Pre | Sucker | Inedible | ND | ND | ND |
| Phelps | 1 Hour | Sucker | Inedible | 138 | ND | ND |
| Phelps | 3 Hour | Sucker | Inedible | 105 | ND | 17 |
| Phelps | 6 Hour | Sucker | Inedible | 140 | NQ | 58 |
| Phelps | 12 Hour | Sucker | Inedible | 120 | NQ | 488 |
| Phelps | 1 Day | Sucker | Inedible | 202 | 50 | 657 |
| Phelps | 3 Day | Sucker | Inedible | 182 | 86 | 1172 |
| Phelps | 1 Week | Sucker | Inedible | 42 | 42 | 175 |
| Phelps | 2 Week | Sucker | Inedible | ND | ND | 96 |
| Phelps | 3 Week | Sucker | Inedible | ND | ND | 69 |
| Phelps | 4 Week | Sucker | Inedible | NQ | ND | 26 |
| Carsons | Pre | Sucker | Edible | ND | ND | ND |
| Carsons | 1 Hour | Sucker | Edible | 21 | NQ | ND |
| Carsons | 3 Hour | Sucker | Edible | 41 | NQ | NQ |
| Carsons | 6 Hour | Sucker | Edible | 41 | 7 | 58 |
| Carsons | 12 Hour | Sucker | Edible | 53 | 19 | 261 |
| Carsons | 1 Day | Sucker | Edible | 61 | 20 | 423 |
| Carsons | 3 Day | Sucker | Edible | 43 | 21 | 446 |
| Carsons | 1 Week | Sucker | Edible | 43 | 16 | 175 |
| Carsons | 2 Week | Sucker | Edible | 12 | NQ | 125 |
| Carsons | 3 Week | Sucker | Edible | NQ | NQ | 44 |
| Carsons | 4 Week | Sucker | Edible | ND | 10 | 46 |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|--------|----------|-----------|-----|------|
| Carsons | Pre | Sucker | Inedible | 0 | 0 | 0 |
| Carsons | 1 Hour | Sucker | Inedible | 146 | ND | 0 |
| Carsons | 3 Hour | Sucker | Inedible | 172 | NQ | 19 |
| Carsons | 6 Hour | Sucker | Inedible | 184 | NQ | 124 |
| Carsons | 12 Hour | Sucker | Inedible | 210 | 31 | 430 |
| Carsons | 1 Day | Sucker | Inedible | 225 | 50 | 761 |
| Carsons | 3 Day | Sucker | Inedible | 201 | 75 | 1764 |
| Carsons | 1 Week | Sucker | Inedible | 181 | 86 | 1113 |
| Carsons | 2 Week | Sucker | Inedible | 80 | 31 | 217 |
| Carsons | 3 Week | Sucker | Inedible | 45 | 48 | 89 |
| Carsons | 4 Week | Sucker | Inedible | 16 | 57 | 93 |
| Carman | Pre | Sucker | Edible | ND | NQ | ND |
| Carman | 1 Week | Sucker | Edible | ND | NQ | NQ |
| Carman | 4 Week | Sucker | Edible | ND | ND | ND |
| Carman | Pre | Sucker | Inedible | ND | ND | ND |
| Carman | 1 Week | Sucker | Inedible | ND | ND | ND |
| Carman | 4 Week | Sucker | Inedible | ND | ND | ND |
| Phelps | Pre | Clam | Edible | ND | ND | ND |
| Phelps | 1 Hour | Clam | Edible | NQ | ND | ND |
| Phelps | 3 Hour | Clam | Edible | 95 | NQ | NQ |
| Phelps | 6 Hour | Clam | Edible | 126 | 6 | NQ |
| Phelps | 12 Hour | Clam | Edible | 130 | 13 | 14 |
| Phelps | 1 Day | Clam | Edible | 147 | 12 | 52 |
| Phelps | 3 Day | Clam | Edible | 132 | 12 | 262 |
| Phelps | 1 Week | Clam | Edible | 40 | NQ | 50 |
| Phelps | 2 Week | Clam | Edible | NQ | ND | 17 |
| Phelps | 3 Week | Clam | Edible | NQ | ND | NQ |
| Phelps | 4 Week | Clam | Edible | ND | ND | ND |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|----------|----------|-----------|-----|-----|
| Carsons | Pre | Clam | Edible | ND | ND | ND |
| Carsons | 1 Hour | Clam | Edible | 75 | 9 | ND |
| Carsons | 3 Hour | Clam | Edible | 134 | 19 | NQ |
| Carsons | 6 Hour | Clam | Edible | 158 | 13 | 18 |
| Carsons | 12 Hour | Clam | Edible | 154 | 11 | 36 |
| Carsons | 1 Day | Clam | Edible | 153 | 13 | 132 |
| Carsons | 3 Day | Clam | Edible | 164 | 15 | 344 |
| Carsons | 1 Week | Clam | Edible | 156 | 20 | 268 |
| Carsons | 2 Week | Clam | Edible | 55 | 8 | 113 |
| Carsons | 3 Week | Clam | Edible | 64 | 8 | 52 |
| Carsons | 4 Week | Clam | Edible | 32 | 20 | 18 |
| Carman | Pre | Clam | Edible | ND | ND | ND |
| Carman | 1 Week | Clam | Edible | ND | ND | ND |
| Carman | 4 Week | Clam | Edible | ND | ND | ND |
| Phelps | Pre | Crayfish | Edible | ND | ND | ND |
| Phelps | 1 Hour | Crayfish | Edible | NQ | ND | ND |
| Phelps | 3 Hour | Crayfish | Edible | 42 | NQ | ND |
| Phelps | 6 Hour | Crayfish | Edible | 41 | NQ | NQ |
| Phelps | 12 Hour | Crayfish | Edible | 90 | 7 | NQ |
| Phelps | 1 Day | Crayfish | Edible | 178 | 11 | 42 |
| Phelps | 3 Day | Crayfish | Edible | 162 | 29 | 118 |
| Phelps | 1 Week | Crayfish | Edible | 85 | 30 | 57 |
| Phelps | 2 Week | Crayfish | Edible | 19 | NQ | NQ |
| Phelps | 3 Week | Crayfish | Edible | 16 | NQ | ND |
| Phelps | 4 Week | Crayfish | Edible | NQ | ND | ND |
| Phelps | Pre | Crayfish | Inedible | ND | ND | ND |
| Phelps | 1 Hour | Crayfish | Inedible | 106 | NQ | ND |
| Phelps | 3 Hour | Crayfish | Inedible | 260 | 23 | ND |
| Phelps | 6 Hour | Crayfish | Inedible | 244 | 44 | NQ |
| Phelps | 12 Hour | Crayfish | Inedible | 348 | 58 | 6 |
| Phelps | 1 Day | Crayfish | Inedible | 503 | 98 | 70 |
| Phelps | 3 Day | Crayfish | Inedible | 537 | 161 | 185 |
| Phelps | 1 Week | Crayfish | Inedible | 347 | 212 | 100 |
| Phelps | 2 Week | Crayfish | Inedible | 193 | 68 | 6 |
| Phelps | 3 Week | Crayfish | Inedible | 102 | 45 | NQ |
| Phelps | 4 Week | Crayfish | Inedible | 95 | 25 | ND |

| PLOT | PERIOD | Matrix | Portion | Triclopyr | TCP | TMP |
|---------|---------|----------|----------|-----------|-----|-----|
| Carsons | Pre | Crayfish | Edible | ND | ND | ND |
| Carsons | 1 Hour | Crayfish | Edible | 68 | NQ | ND |
| Carsons | 3 Hour | Crayfish | Edible | 32 | ND | ND |
| Carsons | 6 Hour | Crayfish | Edible | 73 | NQ | 12 |
| Carsons | 12 Hour | Crayfish | Edible | 52 | 8 | 49 |
| Carsons | 1 Day | Crayfish | Edible | 107 | 14 | 83 |
| Carsons | 3 Day | Crayfish | Edible | 178 | 31 | 243 |
| Carsons | 1 Week | Crayfish | Edible | 156 | 37 | 206 |
| Carsons | 2 Week | Crayfish | Edible | 52 | 13 | 49 |
| Carsons | 3 Week | Crayfish | Edible | 58 | 13 | 33 |
| Carsons | 4 Week | Crayfish | Edible | NQ | 8 | NQ |
| Carsons | Pre | Crayfish | Inedible | 29 | 14 | 10 |
| Carsons | 1 Hour | Crayfish | Inedible | 334 | 16 | 0 |
| Carsons | 3 Hour | Crayfish | Inedible | 236 | 42 | 0 |
| Carsons | 6 Hour | Crayfish | Inedible | 297 | 51 | 21 |
| Carsons | 12 Hour | Crayfish | Inedible | 293 | 54 | 50 |
| Carsons | 1 Day | Crayfish | Inedible | 435 | 95 | 157 |
| Carsons | 3 Day | Crayfish | Inedible | 493 | 184 | 267 |
| Carsons | 1 Week | Crayfish | Inedible | 687 | 231 | 322 |
| Carsons | 2 Week | Crayfish | Inedible | 280 | 122 | 36 |
| Carsons | 3 Week | Crayfish | Inedible | 311 | 77 | 19 |
| Carsons | 4 Week | Crayfish | Inedible | 98 | 85 | NQ |
| Carman | Pre | Crayfish | Edible | ND | ND | ND |
| Carman | 1 Week | Crayfish | Edible | ND | ND | ND |
| Carman | 4 Week | Crayfish | Edible | ND | ND | ND |
| Carman | Pre | Crayfish | Inedible | ND | 29 | ND |
| Carman | 1 Week | Crayfish | Inedible | ND | NQ | ND |
| Carman | 4 Week | Crayfish | Inedible | ND | ND | ND |

Appendix B Summary of Average Off-Plot Water Residue Values

| Plot | Period | Station | Triclopyr ng/g | TCP ng/g | Distance from Plot |
|--------|---------|---------|-------------------|----------|--------------------|
| Phelps | 1 Hour | 6 | NQ | ND | 100 m |
| Phelps | 3 Hour | 6 | 0.33 | ND | 100 m |
| Phelps | 6 Hour | 6 | 26.82 | 0.12 | 100 m |
| Phelps | 12 Hour | 6 | 240.12 | NQ | 100 m |
| Phelps | 1 Day | 6 | 166.95 | 0.70 | 100 m |
| Phelps | 2 Day | 6 | 121.23 | 0.30 | 100 m |
| Phelps | 3 Day | 6 | 77.53 | 0.13 | 100 m |
| Phelps | 5 Day | 6 | 179.11 | 0.53 | 100 m |
| Phelps | 1 Week | 6 | 95.96 | 0.19 | 100 m |
| Phelps | 2 Week | 6 | 36.55 | 0.17 | 100 m |
| Phelps | 3 Week | 6 | 16.76 | NQ | 100 m |
| Phelps | 4 Week | 6 | 8.08 | NQ | 100 m |
| Phelps | 6 Week | 6 | 2.32 | ND | 100 m |
| Phelps | 1 Hour | 7 | NQ | ND | 100 m |
| Phelps | 3 Hour | 7 | ND | ND | 100 m |
| Phelps | 6 Hour | 7 | 7.74 | ND | 100 m |
| Phelps | 12 Hour | 7 | 2.37 | ND | 100 m |
| Phelps | 1 Day | 7 | 16.87 | NQ | 100 m |
| Phelps | 2 Day | 7 | 17.53 | NQ | 100 m |
| Phelps | 3 Day | 7 | 41.26 | 0.11 | 100 m |
| Phelps | 5 Day | 7 | 61.46 | 0.12 | 100 m |
| Phelps | 1 Week | 7 | 52.42 | 0.24 | 100 m |
| Phelps | 2 Week | 7 | 33.85 | 0.12 | 100 m |
| Phelps | 3 Week | 7 | 14.29 | NQ | 100 m |
| Phelps | 4 Week | 7 | 9.33 | NQ | 100 m |
| Phelps | 6 Week | 7 | 2.28 | NQ | 100 m |

| Plot | Period | Station | Triclopyr ng/g | TCP ng/g | Distance from Plot |
|--------|---------|---------|-------------------|----------|--------------------|
| Phelps | 1 Hour | 8 | ND | ND | 100 m |
| Phelps | 3 Hour | 8 | ND | ND | 100 m |
| Phelps | 6 Hour | 8 | ND | ND | 100 m |
| Phelps | 12 Hour | 8 | NQ | ND | 100 m |
| Phelps | 1 Day | 8 | 2.92 | ND | 100 m |
| Phelps | 2 Day | 8 | 51.39 | 0.19 | 100 m |
| Phelps | 3 Day | 8 | 65.21 | 0.16 | 100 m |
| Phelps | 5 Day | 8 | 52.67 | 0.11 | 100 m |
| Phelps | 1 Week | 8 | 130.87 | 0.63 | 100 m |
| Phelps | 2 Week | 8 | 24.90 | NQ | 100 m |
| Phelps | 3 Week | 8 | 19.02 | NQ | 100 m |
| Phelps | 4 Week | 8 | 9.00 | NQ | 100 m |
| Phelps | 6 Week | 8 | 1.99 | ND | 100 m |
| Phelps | 3 Hour | 9 | ND | ND | 400 m |
| Phelps | 6 Hour | 9 | ND | ND | 400 m |
| Phelps | 12 Hour | 9 | 0.61 | ND | 400 m |
| Phelps | 1 Day | 9 | 6.99 | NQ | 400 m |
| Phelps | 2 Day | 9 | 0.86 | 0.01 | 400 m |
| Phelps | 3 Day | 9 | 8.71 | ND | 400 m |
| Phelps | 5 Day | 9 | 26.10 | ND | 400 m |
| Phelps | 1 Week | 9 | 48.23 | 0.29 | 400 m |
| Phelps | 2 Week | 9 | 24.77 | NQ | 400 m |
| Phelps | 3 Week | 9 | 11.20 | NQ | 400 m |
| Phelps | 4 Week | 9 | 8.90 | 0.11 | 400 m |
| Phelps | 6 Week | 9 | 2.25 | NQ | 400 m |

| Plot | Period | Station | Triclopyr ng/g | TCP ng/g | Distance from Plot |
|--------|---------|---------|-------------------|----------|--------------------|
| Phelps | 3 Hour | 10 | ND | ND | 800 m |
| Phelps | 6 Hour | 10 | ND | ND | 800 m |
| Phelps | 12 Hour | 10 | 0.39 | ND | 800 m |
| Phelps | 1 Day | 10 | NQ | ND | 800 m |
| Phelps | 2 Day | 10 | NQ | ND | 800 m |
| Phelps | 3 Day | 10 | 0.89 | ND | 800 m |
| Phelps | 5 Day | 10 | 12.08 | ND | 800 m |
| Phelps | 1 Week | 10 | 30.03 | 0.20 | 800 m |
| Phelps | 2 Week | 10 | 15.56 | 0.05 | 800 m |
| Phelps | 3 Week | 10 | 11.61 | 0.09 | 800 m |
| Phelps | 4 Week | 10 | 7.15 | NQ | 800 m |
| Phelps | 6 Week | 10 | 2.26 | ND | 800 m |
| Phelps | 3 Hour | 11 | ND | ND | 1600 m |
| Phelps | 6 Hour | 11 | ND | ND | 1600 m |
| Phelps | 12 Hour | 11 | ND | ND | 1600 m |
| Phelps | 1 Day | 11 | ND | ND | 1600 m |
| Phelps | 2 Day | 11 | ND | ND | 1600 m |
| Phelps | 3 Day | 11 | NQ | ND | 1600 m |
| Phelps | 5 Day | 11 | 12.49 | ND | 1600 m |
| Phelps | 1 Week | 11 | 7.56 | 0.12 | 1600 m |
| Phelps | 2 Week | 11 | 13.78 | NQ | 1600 m |
| Phelps | 3 Week | 11 | 5.82 | NQ | 1600 m |
| Phelps | 4 Week | 11 | 5.45 | NQ | 1600 m |
| Phelps | 6 Week | 11 | 1.76 | ND | 1600 m |
| Phelps | 6 Hour | 12 | 361.87 | 1.91 | 100 m |
| Phelps | 12 Hour | 12 | 583.24 | 2.83 | 100 m |
| Phelps | 1 Day | 12 | 557.57 | 2.46 | 100 m |
| Phelps | 2 Day | 12 | 692.28 | 2.57 | 100 m |
| Phelps | 3 Day | 12 | 599.67 | 2.09 | 100 m |
| Phelps | 5 Day | 12 | 751.28 | 3.48 | 100 m |
| Phelps | 1 Week | 12 | 43.98 | 0.32 | 100 m |
| Phelps | 2 Week | 12 | 47.45 | 0.51 | 100 m |
| Phelps | 3 Week | 12 | 15.03 | 0.12 | 100 m |
| Phelps | 4 Week | 12 | 6.13 | 0.12 | 100 m |
| Phelps | 6 Week | 12 | 2.58 | NQ | 100 m |

| Plot | Period | Station | Triclopyr ng/g | TCP ng/g | Distance from Plot |
|--------|---------|---------|-------------------|----------|--------------------|
| Phelps | 6 Hour | 13 | NQ | ND | est. 400 m |
| Phelps | 12 Hour | 13 | 26.33 | 0.16 | est. 400 m |
| Phelps | 1 Day | 13 | 13.56 | NQ | est. 400 m |
| Phelps | 2 Day | 13 | 93.13 | 0.25 | est. 400 m |
| Phelps | 3 Day | 13 | 36.90 | 0.22 | est. 400 m |
| Phelps | 5 Day | 13 | 44.00 | 0.07 | est. 400 m |
| Phelps | 1 Week | 13 | 3.62 | 0.03 | est. 400 m |
| Phelps | 2 Week | 13 | 18.39 | 0.13 | est. 400 m |
| Phelps | 3 Week | 13 | 7.48 | NQ | est. 400 m |
| Phelps | 4 Week | 13 | 4.81 | NQ | est. 400 m |
| Phelps | 6 Week | 13 | 2.56 | ND | est. 400 m |
| Phelps | 12 Hour | 14 | ND | ND | est. 600 m |
| Phelps | 1 Day | 14 | ND | ND | est. 600 m |
| Phelps | 2 Day | 14 | 0.65 | ND | est. 600 m |
| Phelps | 3 Day | 14 | NQ | ND | est. 600 m |
| Phelps | 5 Day | 14 | 0.55 | ND | est. 600 m |
| Phelps | 1 Week | 14 | 0.39 | NQ | est. 600 m |
| Phelps | 2 Week | 14 | 0.79 | ND | est. 600 m |
| Phelps | 3 Week | 14 | 1.78 | ND | est. 600 m |
| Phelps | 4 Week | 14 | 0.99 | ND | est. 600 m |
| Phelps | 6 Week | 14 | 0.62 | ND | est. 600 m |
| Phelps | 2 Week | 15 | 2.66 | ND | est. 800 m |
| Phelps | 3 Week | 15 | 2.05 | ND | est. 800 m |
| Phelps | 4 Week | 15 | 2.46 | NQ | est. 800 m |
| Phelps | 6 Week | 15 | 1.27 | ND | est. 800 m |

| Plot | Period | Station | Triclopyr ng/g | TCP ng/g | Distance from Plot |
|---------|---------|---------|-------------------|----------|--------------------|
| Carsons | 1 Hour | 6 | ND | NQ | 100 m |
| Carsons | 3 Hour | 6 | ND | ND | 100 m |
| Carsons | 6 Hour | 6 | NQ | ND | 100 m |
| Carsons | 12 Hour | 6 | 291.24 | 2.49 | 100 m |
| Carsons | 1 Day | 6 | 147.11 | 0.53 | 100 m |
| Carsons | 2 Day | 6 | 150.46 | 0.58 | 100 m |
| Carsons | 3 Day | 6 | 147.97 | 0.74 | 100 m |
| Carsons | 5 Day | 6 | 44.79 | 0.22 | 100 m |
| Carsons | 1 Week | 6 | 121.49 | 0.83 | 100 m |
| Carsons | 2 Week | 6 | 21.05 | 0.40 | 100 m |
| Carsons | 3 Week | 6 | 42.08 | 0.39 | 100 m |
| Carsons | 4 Week | 6 | 17.34 | 0.19 | 100 m |
| Carsons | 6 Week | 6 | 5.89 | 0.13 | 100 m |
| Carsons | 3 Hour | 7 | ND | ND | 400 m |
| Carsons | 6 Hour | 7 | ND | ND | 400 m |
| Carsons | 12 Hour | 7 | 31.12 | 0.18 | 400 m |
| Carsons | 1 Day | 7 | 10.50 | NQ | 400 m |
| Carsons | 2 Day | 7 | 31.66 | NQ | 400 m |
| Carsons | 3 Day | 7 | 20.88 | 0.13 | 400 m |
| Carsons | 5 Day | 7 | 20.02 | NQ | 400 m |
| Carsons | 1 Week | 7 | 57.55 | 0.37 | 400 m |
| Carsons | 2 Week | 7 | 6.76 | 0.22 | 400 m |
| Carsons | 3 Week | 7 | 18.22 | NQ | 400 m |
| Carsons | 4 Week | 7 | 13.70 | NQ | 400 m |
| Carsons | 6 Week | 7 | 0.65 | NQ | 400 m |

| Plot | Period | Station | Triclopyr ng/g | TCP ng/g | Distance from Plot |
|---------|---------|---------|-------------------|----------|--------------------|
| Carsons | 3 Hour | 8 | ND | ND | 800 m |
| Carsons | 6 Hour | 8 | NQ | ND | 800 m |
| Carsons | 12 Hour | 8 | ND | ND | 800 m |
| Carsons | 1 Day | 8 | 0.69 | ND | 800 m |
| Carsons | 2 Day | 8 | 0.79 | ND | 800 m |
| Carsons | 3 Day | 8 | 6.82 | ND | 800 m |
| Carsons | 5 Day | 8 | 17.82 | NQ | 800 m |
| Carsons | 1 Week | 8 | 17.27 | 0.13 | 800 m |
| Carsons | 2 Week | 8 | 17.59 | NQ | 800 m |
| Carsons | 3 Week | 8 | 13.88 | NQ | 800 m |
| Carsons | 4 Week | 8 | 9.12 | NQ | 800 m |
| Carsons | 6 Week | 8 | 5.01 | ND | 800 m |
| Carsons | 3 Hour | 9 | ND | ND | 1600 m |
| Carsons | 6 Hour | 9 | ND | ND | 1600 m |
| Carsons | 12 Hour | 9 | ND | ND | 1600 m |
| Carsons | 1 Day | 9 | ND | ND | 1600 m |
| Carsons | 2 Day | 9 | ND | ND | 1600 m |
| Carsons | 3 Day | 9 | ND | ND | 1600 m |
| Carsons | 5 Day | 9 | 0.27 | ND | 1600 m |
| Carsons | 2 Week | 9 | 9.37 | NQ | 1600 m |
| Carsons | 3 Week | 9 | 3.72 | ND | 1600 m |
| Carsons | 4 Week | 9 | 1.54 | ND | 1600 m |
| Carsons | 6 Week | 9 | 5.11 | NQ | 1600 m |

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| 13. ABSTRACT (Maximum 200 words) <p>The aquatic fate of the triethylamine (TEA) salt formulation of triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) was studied in Lake Minnetonka, Minnesota. This study determined dissipation rates of triclopyr and metabolites, TCP (3,5,6-trichloropyridinol) and TMP (3,5,6-trichloro-2-methoxypyridine) in water, sediment, finfish, and shellfish.</p> <p>Two plots containing Eurasian watermilfoil-dominated plant communities were treated at 2.5 mg/L triclopyr. The dye rhodamine was applied with triclopyr to provide water-exchange information during the study.</p> <p>Water and sediment residue samples were collected from within and outside of plots. All nontarget animals were caged in the center of each plot. Water and sediment samples were collected through 6 weeks posttreatment, while nontarget organisms were collected through 4 weeks posttreatment.</p> <p>Triclopyr and TCP dissipation half-lives in water were 3.7 to 4.7 days and 4.2 to 7.9 days, respectively. Small amounts of TMP (<5 ng/ml) were measured in the water in treated plots. Triclopyr sediment values were 257 to 335 ng/g (mean half-life = 5.4 days). TCP sediment levels were 27 to 65 ng/g (mean half-life = 11.0 days). TMP was found in sediment at trace levels. An untreated reference plot tested ND for triclopyr, TCP, and TMP in water and sediment.</p> <p style="text-align: right;">(Continued)</p> | | | |
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Triclopyr and TCP cleared from animals in relation to concentrations found in water (triclopyr half-lives <11 days; TCP <14 days) and were generally higher in inedible viscera tissue. TMP levels were two to three times higher than those of triclopyr or TCP in viscera tissue.

Eurasian watermilfoil was controlled in the treatment areas. Native plants recovered, and no adverse effects on water quality were found following treatment.

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