Effects and persistence of endothall in the aquatic environment

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IN RECENT YEARS the extensive use of highly persistent chemicals for control of certain insects and undesirable plants, not only on agricultural lands, but also in recreational areas, lakes, streams, and marshes, has led to questions concerning the effects of these chemical agents on the ecosystem. There is a great need to know how long these compounds adversely affect aquatic life and water quality. One of the primary goals of this study was to determine the persistence of the aquatic herbicide endothall in water in a field situation. Along with the determination of endothall's degradation and detoxification rate, general observations were also made regarding the effect of endothall on fish and aquatic plants, and on the water chemistry of a treated pond.

The herbicide endothall is a highly active contact weed killer used in weed control programs throughout the country. Although endothall was first found to be herbicidal in 1950, the aquatic uses of this chemical were not discovered until 1953. Endothall has frequenty been called 3,6-endoxohexahydrophthalic acid, but it is properly called 7-oxabicyclo (2.2.1) heptane-2, 3-dicarboxylic acid. Unlike most pesticide and herbicide chemicals, it contains only carbon, hydrogen, and oxygen. Rather than being applied as the free acid, endothall is converted to its inorganic or amine salts. These salts are then applied as water concentrates for aquatic use, making the use of organic solvents or emulsifiers unnecessary. In this study, Aquathol K, the dipotassium formulation of endothall was used. This brown-colored liquid herbicide contains 1.92 kg (4.23 lb) dipotassium endothall (active ingredient), 1.36 kg (3.0 lb) endothall acid, per 3.8 l (gal). It contains 40.3 percent dipotassium salt of endothall (28.6 percent acid equivalent) and 59.7 percent inert ingredients.

This study used two ponds located at the Delafield Station of the Wisconsin Department of Natural Resources, Delafield, Wis., which are supplied with water from the 371-ha (917 acres) Lake Nagawicka, via the Bark River. One treatment pond of 0.32 ha (0.78 acres) and one control pond of 0.43 ha (1.07 acres) were used. Each pond has an average depth of approximately 1 m (3 ft) with a maximum depth of 1.5 m (5 ft). These ponds were constructed about 65 years ago and were used for largemouth bass and bluegill spawning and rearing.[1] Both ponds were drawn down in late October 1972, and remained drawn down over winter to rid the ponds of any existing fish. Rotenone was applied to the drawn-down treatment ponds to complete the fish eradication prior to filling. The ponds were refilled in early spring of 1973 and no additional water was added during this study.

Aquatic organisms present. At time of treatment, the aquatic plant life in the treatment pond consisted of approximately 80 percent milfoil (*Myriophyllum spicatum*), with the remaining 20 percent being comprised mostly of chara (*Chara* spp.), coontail (*Ceratophyllum demersum*), and elodea (*Elodea canadensis*), with some flat-stemmed pondweed (*Potamogeton zosteriformis*) and sago pondweed (*Potamogeton pectinatus*) present. The vegetation in the control pond at this time consisted of approximately 90 percent chara and 10 percent sago pondweed. In late June, the expanding chara growth seemed to surpass the sago pondweed. However, in late August, the reappearance of some sago pondweed was noticed, along with the appearance of some water star grass (*Heteranthera dubia*).[1] On each sampling date, visual observations of the effects of the herbicide on the morphology and relative abundance of the different species of aquatics were made and recorded.

After the ponds were refilled in early spring of 1973, they were stocked with adult bluegills (*Lepomis macrochirus*) obtained from Lake Nagawicka using Fyke nets, at a rate of 247/ha (100/acre) (50 percent male and 50 percent female). Although the primary purpose of this stocking was a longer-term study of the effects of endothall on fish reproduction and growth, it was of value to this short-term study, because any mortalities caused by direct chemical action would be detected at time of sampling. Fifty bluegills were also placed in a livebox in each pond. Any mortalities in these enclosures would be detected.

Treatment of ponds. The 0.32 ha (0.78 acre) pond was treated with endothall on May 31, 1973. At the time of treatment, the pond water was slightly colored, with a bottom temperature of 17.7°C, and a surface temperature of 18.3°C. The pond, having a total volume of 2,960 cu m (2.4 acre/ft), was treated at the maximum recommended dosage of endothall for weed control, 5.0 mg/l (a.i.). Following the recommended (label) treatment rate of 12.1 l (3.2 gal) of endothall/1,230 cu m (1 acre/ft) at 5.0 mg/l (a.i.), 29.1 l (7.7 gal) of the herbicide were applied to the pond using a gasoline-operated centrifugal pump which sprayed a diluted mixture of the treatment chemical in a fairly even distribution over the entire surface of the pond. A 16–24 km/hr (10–15 mph) wind at the time of treatment aided in mixing of the chemical in the pond. There was no water flow through the pond.

Description of sampling. One-l water samples were collected at both the surface and the bottom of the deepest portion of both ponds with a plastic water sampler, placed in polyethylene containers, and analyzed later at the Department of Natural Resources Water Chemistry Laboratory at Delafield for pH, alkalinity, conductivity, nitrite, nitrate, ammonia, organic nitrogen, total nitrogen, total phosphorus, dissolved phosphorus, sulfate, chloride, calcium, magnesium, sodium, and potassium. Secchi disc, temperature, and dissolved oxygen (DO) readings were taken at each time of sampling. Water samples were

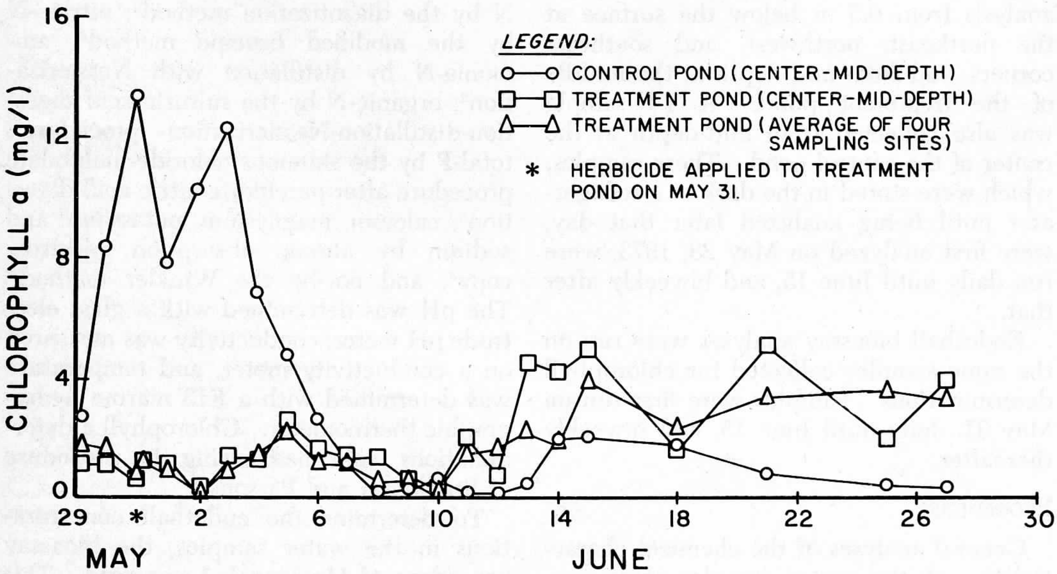

FIGURE 1.—The effect of endothall treatment on chlorophyll.

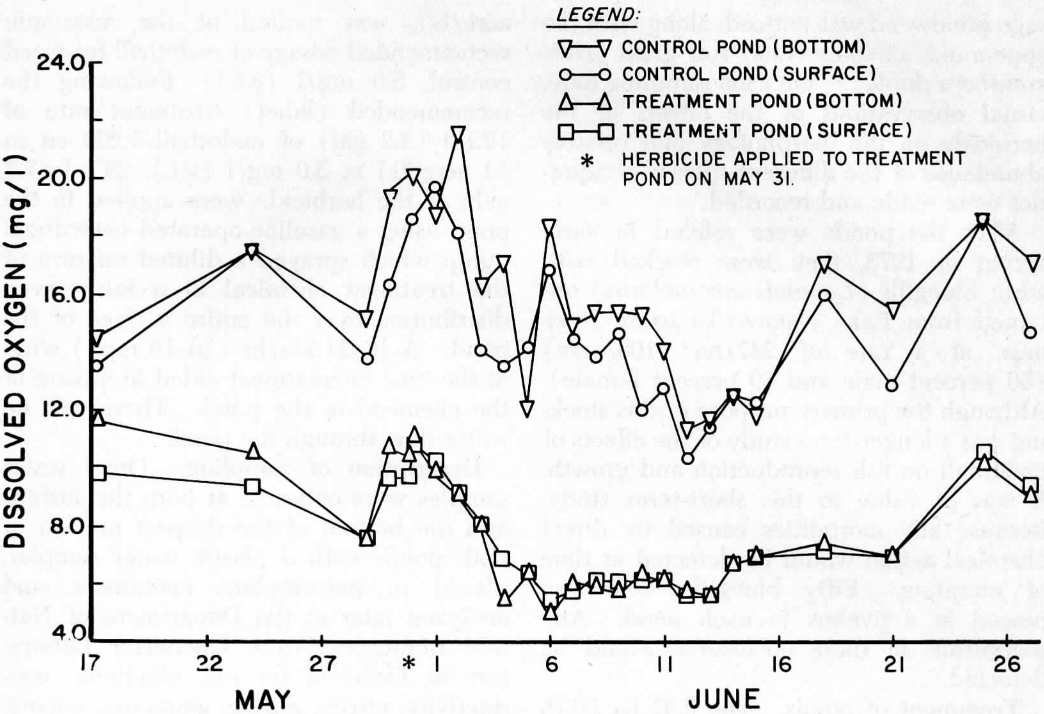

FIGURE 2.—The effect of endothall treatment on dissolved oxygen.

taken periodically before treatment, daily 1 wk before and 2 wk after treatment, and biweekly thereafter.

One l water samples were also collected in polyethylene containers for chlorophyll analysis from 0.5 m below the surface at the northeast, northwest, and southeast corners, and from mid-depth at the middle of the treatment pond. A 1-l sample was also collected from mid-depth at the center of the control pond. These samples, which were stored in the dark in a refrigerator until being analyzed later that day, were first analyzed on May 28, 1973, were run daily until June 15, and biweekly after that.

Endothall bioassay analyses were run on the same samples collected for chlorophyll determinations. Samples were first run on May 31, daily until June 15, and biweekly thereafter.

PROCEDURES

General analyses of the chemical characteristics of the water samples were performed by the following procedures: total alkalinity by the potentiometric method; dissolved phosphorus by the stannous chloride-molybdate procedure; sulfate by the turbidimetric method; chloride by the mercuric nitrate titration procedure; nitrite-N by the diazotization method[2]; nitrate-N by the modified brucine method[3]; ammonia-N by distillation with Nesslerization[2]; organic-N by the sulfuric acid digestion-distillation-Nesslerization procedure[4]; total-P by the stannous chloride-molybdate procedure after perchloric-nitric acid digestion[5]; calcium, magnesium, potassium, and sodium by atomic absorption spectroscopy[3]; and DO by the Winkler method.[2] The pH was determined with a glass electrode pH meter, conductivity was measured on a conductivity meter, and temperature was determined with a F13 marine hydrographic thermometer. Chlorophyll a determinations were made using the procedure of Strickland and Parsons.[6]

To determine the endothall concentrations in the water samples, the bioassay procedure of Massengale[7] was used. This method is based on the endothall-induced inhibition of germinating flax seed root growth, which varies directly with herbicide concentration. In initial runs to determine the optimum conditions for the method, it was found that the greatest sensitivity was achieved when the flax seeds were incubated in the dark for 96 hr at 25°C. With each series of unknowns, standards were run to assure conformance to the standard curve. Four replicates were run on both the standards and samples, and yielded a limit of detection of approximately 0.1 mg/l.

RESULTS

Aquatic organisms. On June 2, two days after herbicide treatment, many of the coontail plants were beginning to drop to the bottom, and several small pieces were observed on the pond surface. By June 3, the tips of the milfoil plants, which were red before treatment, were blackened, and on June 4, the flat-stemmed pondweed was blackened and down and the sago pondweed down. By June 9, except for the chara, elodea, and several milfoil plants, most of the vegetation was down. On June 11, the elodea and chara were noticed growing up through the downed milfoil. However, on June 21, the elodea began turning brown, and large clumps were noticed floating on the pond surface. Eventually, the elodea all but disappeared, and the whole pond was taken over by a dense growth of chara, with a few sago pondweeds appearing in late August.

No bluegill mortalities were detected in either the free population or the enclosed (livebox) population in the treatment pond. There were also no fish mortalities in the free bluegill population in the treatment pond. A few bluegills died in the control livebox during the first week of June, but this was assumed to be because of crowded conditions in the enclosure.

Chlorophyll content. The chlorophyll a concentrations in the control and treatment pond are given in Figure 1. The chloro-

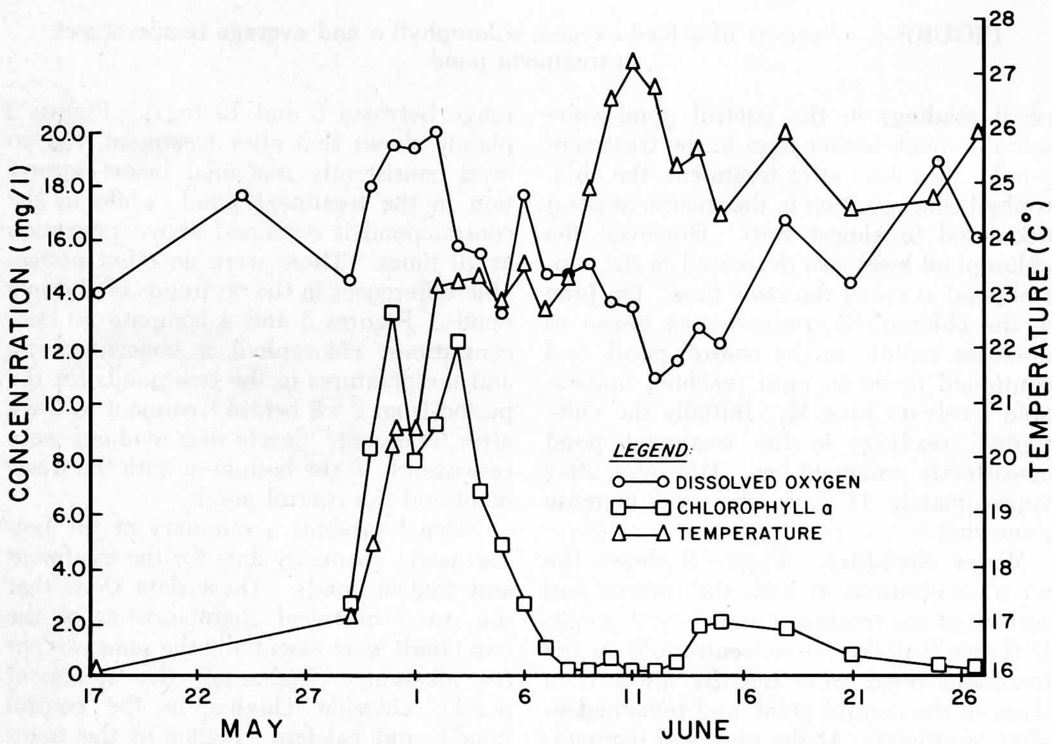

FIGURE 3.—Average dissolved oxygen, chlorophyll a, and average temperatures in control pond.

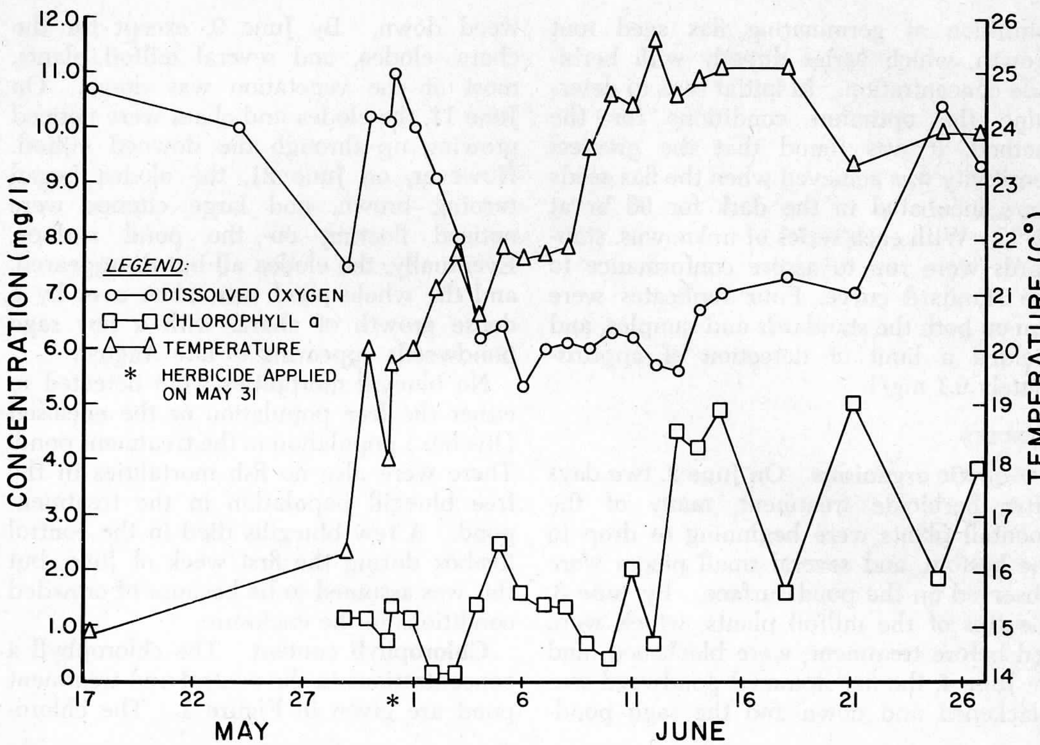

FIGURE 4.—Average dissolved oxygen, chlorophyll a and average temperatures in treatment pond.

phyll readings in the control pond were initially much higher than in the treatment pond. Two days after treatment, the chlorophyll concentration in the treatment pond decreased to almost zero. However, the chlorophyll level also decreased in the control pond at about the same time. On June 4, the chlorophyll concentration began to decrease rapidly in the control pond, and continued to do so until reaching undectable levels on June 11. Initially the chlorophyll readings in the treatment pond consistently remained low. However, after approximately 11 days, they did increase somewhat.

Water chemistry. Figure 2 shows the DO concentrations at both the bottom and surface of the treatment and control ponds. It shows that the DO concentrations in the treatment pond were initially lower than those in the control pond, and remained so after treatment. At the observed temperatures (average of surface and bottom) in the two ponds, the DO saturation values range between 8 and 10 mg/l. Figure 2 plainly shows that after treatment, the DO level consistently remained below saturation in the treatment pond, while in the control pond it remained above saturation at all times. There were no other noticeable differences in the DO trends of the two ponds. Figures 3 and 4 compare DO concentrations, chlorophyll a concentrations, and temperatures in the two ponds for the period from 2 wk before treatment to 4 wk after treatment. Secchi disc readings were consistently at the bottom in both the treatment and the control ponds.

Table I presents a summary of the bottom water chemistry data for the treatment and control ponds. These data show that the water chemical characteristics of the two ponds were essentially the same, except for alkalinity (higher in the treatment pond), chloride (higher in the control pond), and calcium (higher in the treatment pond). There did not appear to be any noticeable changes in the water chemistry parameters of the treatment pond following herbicide application.

Endothall residues. Table II gives the endothall concentrations remaining in the treated pond at each time of sampling as determined by the flax seed bioassay method. Figure 5 shows that it took approximately 18 days for the endothall to decrease beyond the detection limit (0.1 mg/l) in the treated pond. Although the pond was treated at 5 mg/l, analyses of water samples taken 3 hr after treatment showed that significantly higher concentrations of the herbicide were present. However, samples taken 1 day after treatment showed that the endothall concentration had stabilized at approximately 5 mg/l.

Disappearance of the endothall was slow at first, until about the thirteenth day, when there was an abrupt decrease in concentration. Endothall analyses run on samples from the control pond at 5-day intervals consistently showed nondetectable levels of the herbicide (less than 0.1 mg/l).

TABLE I.—Chemical Characteristics of Ponds Used in this Study.

Parameter	Control		Treatment	
	$\bar{X}$	σ	$\bar{X}$	σ
Temp (°C)	23	3	22	3
NO_2-N (mg/l)	0.005	0.006	0.005	0.006
NO_3-N (mg/l)	0.1	0.1	0.1	0.1
NH_3-N (mg/l)	0.05	0.05	0.05	0.05
Organic-N (mg/l)	0.9	0.2	0.9	0.2
Soluble ortho-P (mg/l)	0.02	0.03	0.02	0.02
Total-P (mg/l)	0.05	0.03	0.06	0.04
pH	9.0	0.4	8.3	0.4
Conductivity (μmhos/cm)	556	52	477	64
Alkalinity (mg/l as $CaCO_3$)	163	17	204	35
Ca (mg/l)	21	8	48	5
Mg (mg/l)	46	10	46	10
Na (mg/l)	47	17	17	5
K (mg/l)	4.1	1.1	3.7	0.8
SO_4 (mg/l)	24	3.5	24	4
Cl (mg/l)	79	14	33	4

$\bar{X}$ = Mean.
σ = Standard Deviation.
Results based on analysis of 80 samples from each pond for the period April 11 through September 28.

TABLE II.—Aquathol K Concentrations at the Various Sampling Sites as Determined by Bioassay Analysis.

Date	Treatment (Center)	Treatment (N.E.)	Treatment (N.W.)	Treatment (S.E.)	Control (Center)
5/31	6.57	5.74	5.80	6.53	<0.10
6/1	5.04	4.54	5.07	4.90	
6/2	5.04	4.83	4.80	5.10	
6/3	4.80	4.97	5.17	4.67	
6/4	5.00	4.20	4.74	4.47	
6/5	4.50	4.47	4.60	4.67	<0.10
6/6	4.74	4.37	4.10	4.44	
6/7	3.00	2.97	3.26	4.23	
6/8	4.10	3.40	3.00	3.87	
6/9	3.47	3.80	3.80	3.47	
6/10	3.50	3.37	3.67	2.97	<0.10
6/11	3.80	3.75	3.72	3.72	
6/12	3.55	3.35	3.30	2.95	
6/13	0.72	1.80	0.57	0.87	
6/14	0.93	0.90	0.56	0.90	
6/15	0.93	0.79	0.88	0.68	<0.10
6/18	<0.10	<0.10	<0.10	0.14	
6/21	0.10	<0.10	<0.10	<0.10	0.18

DISCUSSION

Aquatic organisms. Selectivity of plant control by endothall was shown by the fact that Elodea and Chara were not affected by the herbicide application. However, since the plants which were controlled dropped to the bottom very quickly, it is apparent that endothall works very quickly on susceptible species. Other investigators have also noted the selective toxicity of this herbicide.[8-12]

Since the endothall treatment eliminated certain plant species from the pond while allowing others to thrive and infest the entire area, the value of using such a herbicide can be questioned. In certain cases some plant species may be considered more desirable than others, and selective removal may be desired. However, in this study, Chara was considered a nuisance aquatic plant, yet the desired control for it was not achieved. To achieve total control of all nuisance plants in the pond, it may be possible to use endothall in combination with a second herbicide, one which is toxic to Chara.

Since no noticeable bluegill mortalities occurred in the treatment pond, it appears that 5.0 mg/l endothall is a sublethal dos-

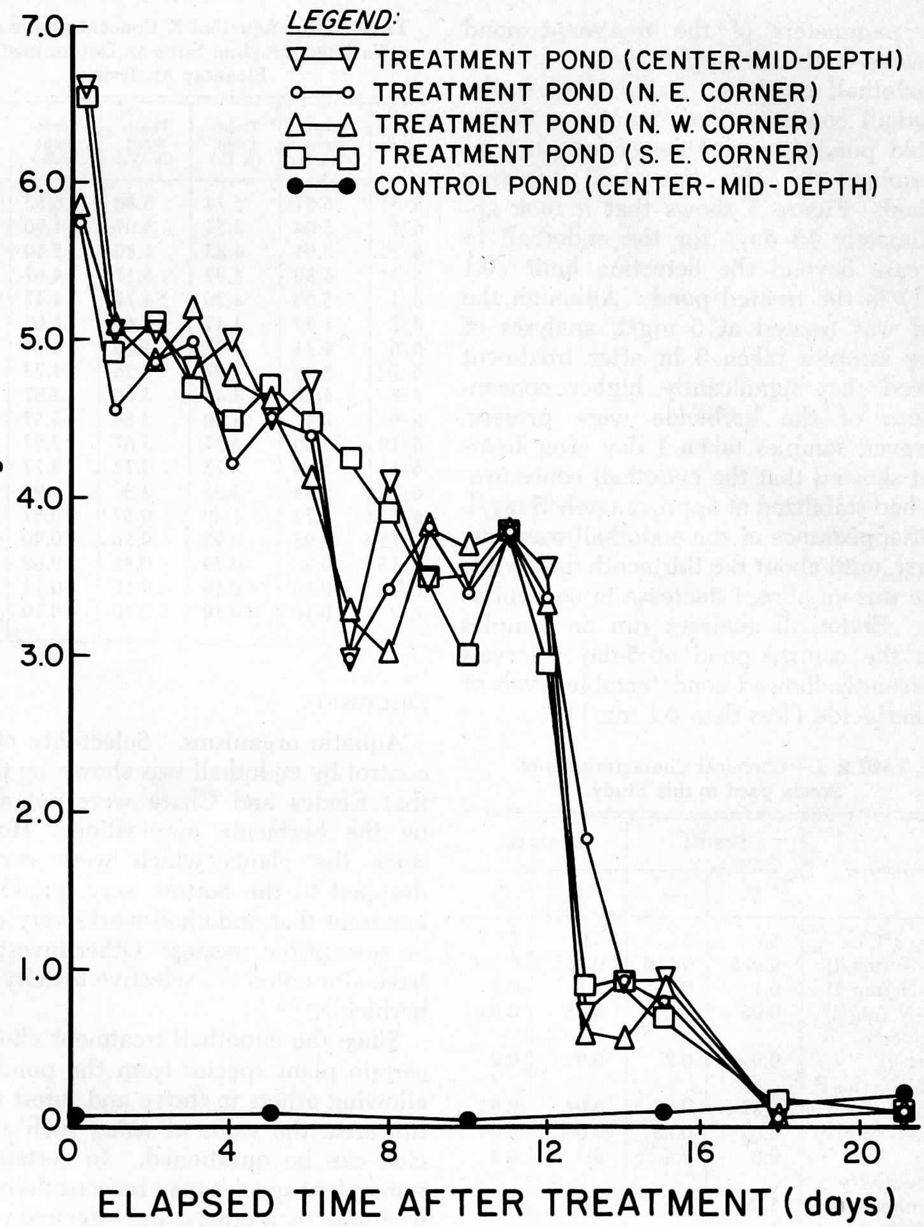

FIGURE 5.—Bioassay determination of residual endothall in ponds.

age for these fish. This is in general agreement with the conclusions drawn by other investigators on the toxicity of endothall to fish.[8-9, 11-15]

Chlorophyll content. It is difficult to make a comparison between the chlorophyll contents in the treatment and control pond water. Even prior to treatment there was a wide discrepancy between values from the two ponds. It appeared that the rapid increase in chlorophyll content in the control pond was due to a microscopic algae bloom. However, soon after this bloom began, Chara began to infest the area and soon was the major plant species in the pond.[1] At this time the chlorophyll content dropped drastically, which may have been because of the removal of available nutrients from the water by the Chara, causing a decrease in the amount available to the phytoplankton. There appeared to be a decrease in chlorophyll content in the treatment pond within a few days of treatment, which was probably due to the endothall killing chlorophyll-bearing phytoplankton.

Endothall residues. The initial high concentration of endothall detected in the water 2 hr after treatment is probably because total mixing of the herbicide with the pond water had not yet occurred. After an initial period of slow herbicide degradation, during which a microbial population capable of degrading endothall was building up, the endothall rapidly broke down, and remained near or below the limit of detection.

Water chemistry. It was expected that when vegetation decomposition began to occur in the treatment pond, a gradual oxygen depletion would result. The oxygen concentration decreased and remained low in the treatment pond until approximately 2 wk after treatment.

Although this oxygen sag may be attributed to plant decomposition, a similar decrease in oxygen occurred in the control pond at approximately the same time. Some other factors may have been responsible for the oxygen trends in the 2 ponds. However, it does not appear that changes in chlorophyll content or temperature were responsible for the trends, since Figures 3 and 4 show no correlation among these factors. It is not known why the oxygen concentrations in the control pond were consistently much higher than in the treatment pond, since both ponds had the same water source, were approximately the same temperature, and were equally exposed to the wind and sunlight.

Since a serious oxygen depletion did not occur in the treatment pond, it is assumed that either the nonsusceptible species were able to produce enough oxygen to offset the additional demand from the decomposing plants, or that because the pond was always essentially mixed, enough oxygen was transferred into the pond from the atmosphere to keep the DO concentration at a moderate level. However, in a deeper body of water which is not completely mixed, oxygen depletion could be a major problem.

The herbicide application did not appear to have an effect on the water chemistry of the treated pond. Since plant life was not eradicated from the treatment pond, the nutrients released by the decomposing vegetation may have been incorporated immediately by the growing nonsusceptible species, preventing any noticeable change in the water chemistry.

A concurrent investigation of the zooplankton populations in the ponds by Serns [16] indicated that the endothall treatment had no effect on these organisms, Serns did find an apparent difference in the overall mortality of the bluegills in that there were fewer bluegills surviving in October 1973 in the pond that received the treatment than the control pond. As noted above, there were no differences in the survival of bluegills in the two ponds at the time of and within a few weeks of treatment. Serns indicated that he does not feel that the differences in long term survival between the two ponds were due to the endothall treatment. He has also reported [17] that the reproduction of the bluegills that had been exposed to the endothall treatment was not significantly different from that of the fish not exposed to this treatment.

SUMMARY

The degradation of endothall was followed in a small Wisconsin pond by a bioassay method. The effects of the herbicide treatment on the pond's plant and fish life, chlorophyll content, and water chemistry were also determined.

The results of the bioassay analyses showed that after a period of slow degradation (approximately 12 days), the endothall rapidly broke down, reaching the level of detection (0.1 mg/l) in 18 days. Most weeds which were controlled by the endothall treatment dropped to the bottom of the pond within 7 days. However, Chara, which was unaffected by the treatment, infested the entire area. The endothall application did not appear to cause any

fish mortalities. Although it was difficult to compare the treatment pond with the control pond, it appeared that the endothall application caused a decrease in chlorophyll content. Although the DO level dropped and remained below the saturation level, serious oxygen depletion was not observed. Apparently, oxygen was supplied throughout the pond through mixing at all times. There did not appear to be any noticeable changes in the other water chemistry parameters which could be attributed to the herbicide.

ACKNOWLEDGMENTS

Credits. This investigation was supported in part by the Environmental Protection Agency Training Grant No. T-900114. In addition, support was given this project by the University of Wisconsin Department of Civil and Environmental Engineering. This project was conducted in cooperation with the Wisconsin Department of Natural Resources. The authors wish to thank the DNR personnel who aided in the field work of this study.

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