Original: Fish Division
cc: Education-Game
Inst. for Fish. Res.
B. Domogalla
K. Mackenthun
A. Gould
Ralph Marks
C. T. Yoder
J. A. Scully

INSTITUTE FOR FISHERIES RESEARCH
DIVISION OF FISHERIES
MICHIGAN DEPARTMENT OF CONSERVATION
COOPERATING WITH THE
UNIVERSITY OF MICHIGAN

ALBERT S. HAZZARD, PH.D.
DIRECTOR

ADDRESS
UNIVERSITY MUSEUMS ANNEX
ANN ARBOR, MICHIGAN

F. F. Hooper
K. G. Fukano

November 21, 1955

Report No. 1461



# LABORATORY AND FIELD EXPERIMENTS WITH NEW ALGAECIDES, 1954-1955

by

F. F. Hooper and K. G. Fukano

For many years copper sulfate (blue vitriol) has been used for control of algal nuisances in lakes, ponds and domestic water supplies. Various objections, some unsubstantiated by good evidence, have been raised against the use of copper sulfate. Hasler (1949) condemns the use of copper sulfate in Wisconsin lakes on the grounds that the copper accumulation in bottom deposits has an unfavorable effect on bottom-living organisms. Hasler presents little or no direct evidence to support his contentions. On the other hand, Mackenthun and Cooley (1952), after study of the bottom muds and benthos of lakes in the vicinity of Madison, Wisconsin treated with copper sulfate for many years, concluded that, although copper was in the mud, the amount was considerably less than that required to have a deleterious effect upon profundal bottom animals. Evidence that repeated copper sulfate treatments have little or no influence upon fish production is presented by Moyle (1949). He found that four Minnesota lakes treated with copper sulfate for the past twenty-six years had a slightly higher average yield of rough fish than five adjacent lakes not treated with copper.

Another objection raised to the use of copper sulfate is that its toxicity to fish varies tremendously from lake to lake depending upon the alkalinity of the water. In soft water, less than 1 p.p.m. may cause a

fish mortality, while in hard water the lethal concentration may be as high as 200 p.p.m. (Nichols et al., 1946). In hard-water lakes there is a large loss of chemical due to its reaction with the carbonate of the water and precipitation as copper carbonate. Only a small fraction of the copper added is actually available to the algae. Hard-water lakes treated with copper sulfate retain their phyto-toxicity for only short periods of time. Several treatments a year may be required to maintain good control. These difficulties encountered in using copper sulfate are compensated for by its low cost and wide-spread availability.

Recently several new organic compounds have been marketed as algaecides for use in fresh-water lakes and ponds. These products are: (1) Cutrine, a copper compound; (2) Delrad (rosin amine d acetate); and (3) Phygon (2,3-dichloronaphthoquinone). Two of these compounds have been used in Michigan. In this report results of field tests with Cutrine and Delrad are summarized and some laboratory experiments with Delrad are reported.

The assistance of other Fish Division personnel in these experiments should be acknowledged. Mr. Ervin Moody, foreman, Hillsdale Rearing Ponds, assisted in treating and mapping the ponds and recorded changes that occurred in ponds following treatment. Mr. Harold Hughes, superintendent, Drayton Plains Hatchery took charge of the mapping and treatment of ponds and the canal sections. J. M. Borglin and Alfred E. Gould of the Hercules Powder Company assisted in the treatments made at the Drayton Plains Hatchery, supplied the Delrad used in all the treatments, and extended many other courtesies. Dr. Bernhard Domogalla, of Applied Biochemists and Associates, cooperated by furnishing a sample of Cutrine for testing.

## CUTRINE

Cutrine is a compound containing ten percent copper in combination with organic substances of unknown composition. The active ingredient is

copper. It is manufactured by Applied Biochemists and Associates, Butler, Wisconsin. It is now prepared as a solid although earlier a liquid form was manufactured. The solid dissolves readily to give a blue solution. Recommended rates of application vary from 0.5 to 1.0 p.p.m. (calculated as metallic copper) depending upon the type of nuisance and other conditions.

According to the manufacturers, Cutrine does not precipitate as readily from water as copper sulfate and thus remains in solution longer and has a greater residual effect. Presumably there would be a much slower rate of accumulation of copper in the bottom mud with Cutrine than with copper sulfate. Dr. Domogalla, of Applied Biochemists and Associates, has used Cutrine in several treatments in Michigan lakes. Treatments of Swan Lake, Iron County in 1953 and 1954 (I.F.R. Report 1386) and of Spring Lake, Ottawa County in 1955 were made with Cutrine. The property owners who have stood the cost of these treatments have in general been well satisfied. However, in at least one case treatment has been undertaken at a time when no serious algae problem existed.

Treatment of Rearing Pond No. 1 at Hillsdale, 1955.--This pond has a surface area of 0.74 acre and an average depth of 1.8 feet. It is stocked with trout and open to angling with artificial flies. This is the uppermost pond in the rearing station and probably receives a somewhat richer supply of nutrients than the other ponds because of its proximity to the headwater springs. The pond water is very hard (methyl orange alkalinity 238 p.p.m.). Pond 1 develops heavy mats of filamentous algae at the surface and on the pond bottom each spring. The surface scum interferes with fly fishing so much that the pond is fished very little once the algae appear.

Pond 1 was treated with Cutrine on May 11, 1955. The chemical was dissolved in water and then sprayed over the pond surface with a power sprayer. The concentration used was 0.5 p.p.m. as metallic copper.

Treatment was made on a day with bright sunshine and little or no wind. The water temperature was 57°F. During treatment and for 24 hours afterwards all the inflowing water was diverted around the pond. The treatment produced no noticeable change in the appearance of the algae or the amount of algae present. The patches of green filamentous algae (Spirogyra, Zygnema, Mougeotia) remained on the surface and on the bottom. Because of this failure a second application was made on June 1, 1955. The concentration used was 1.0 p.p.m. expressed as metallic copper (10 p.p.m. Cutrine). Although this treatment was also made under favorable weather conditions, it also appears to have failed. Mr. Moody, Foreman at Hillsdale Rearing Ponds, noted a temporary discoloration. However, the patches of algae on the surface and on the bottom persisted and there was not sufficient improvement to arouse interest in fly fishing the pond. Neither of the Cutrine treatments had any adverse effect upon fish and fish food organisms.

## DELRAD
## (Rosin Amine D Acetate)

Delrad (formerly called Rada) is an organic derivative of rosin manufactured by the Hercules Powder Company, Wilmington, Delaware. It is marketed not only as an algaecide but as a fungicide, bactericide, flotation agent and as a corrosion inhibitor. The compound is sold both as a paste and as a liquid. The liquid is a solution containing fifty percent rosin amine d acetate solids in water and isopropanol. The solution is diluted with water and sprayed over the pond surface. The paste can either be mixed with water to form a slurry which is then diluted and applied by spraying or the solid can be put in burlap bags and towed behind a boat until it dissolves. A third method of applying the paste, recommended for small ponds by the manufacturers, is the suspension of the proper quantity of paste in the pond by means of a small wooden float. A wooden box is ordinarily used as a float. The wooden bottom is removed and

replaced by wire or plastic screen. This allows the paste to dissolve slowly and mix with the pond water.

Laboratory toxicity tests with Delrad.--Tests of the toxicity of Delrad to fish and fish food organisms were made at temperatures ranging from 65° to 75° F. Water having an alkalinity of 100 p.p.m. collected from Whitmore Lake, Livingston County, was used in all tests. In general, experimental conditions and procedures used were those recommended by Duodoroff, et al. (1951). A 96-hour test period was used. The number of hours of the survival of three test animals during this period was recorded. In the case of death of control animals during the 96-hour period, the experimental results were ignored.

Bluegills averaging two inches in length survived for 96 hours in concentrations of 0.3 and 0.6 p.p.m. but died within 24 hours in a concentration of 1.0 p.p.m. Dragonflies of the genus Anax and midges of the genus Tendipes survived for 96 hours in concentrations as high as 1.0 p.p.m. The water flea, Daphnia magna, however survived for only 24 hours in a concentration of 0.6 p.p.m. and for 48 hours in a concentration of 0.3 p.p.m.

The observation that Delrad killed fish at 1.0 p.p.m. in 96 hours agrees with the results obtained by Lawrence (1954) who found that 0.7 p.p.m. killed many species of fish. It should be noted however that a concentration of 1.0 p.p.m. has not killed fish in several of the field tests mentioned below. These differences between the laboratory and field results suggest that the toxicity of Delrad is reduced somewhat when used in natural waters. This perhaps is due to the absorption of the chemical by solid materials in the water itself and by the pond bottom.

## EXPERIMENTAL FIELD TESTS WITH DELRAD

Starr-Cutter Pond, Farmington, Michigan, May 28, 1954.--This pond, located just north of U. S. Highway 16 two miles northwest of Farmington, Michigan,

has an area of about two and one-half acres. It is owned by an automobile parts manufacturing concern. The pond is ornamental in function and fishing is not permitted, although it contains a good population of bass and bluegills. At the time the pond was treated about two-thirds of the surface was covered with yellow patches of filamentous algae. The principal form was Spirogyra, although several other species of filamentous green algae were noted. The pond also had an abundance of Chara and Nitella. The water of the pond was medium hard (alkalinity 82 p.p.m.). On May 28 the pond was sprayed with five gallons of Delrad 50S. The concentration used was 1.02 p.p.m. in terms of the active ingredient. On the morning of May 30 the caretaker at the plant noticed fish in distress ("gasping for air") at the surface. Later about one bushel of small bluegills was picked up around the pond. In two seine hauls made one week after treatment, 120 living bluegills and two bass were captured. This demonstrated that only a part of the fish population had been killed. Since the fish died in the early morning hours when dissolved oxygen is ordinarily lowest, it seems likely that death was due to suffocation rather than the direct effects of the chemical itself. Unquestionably the pond water had a large biochemical oxygen demand (B.O.D.) at the time, brought on by the decay of algae.

One week after treatment the pond was completely free of filamentous algae; much of the Chara had turned white and was beginning to decompose. Qualitative samples of bottom fauna showed that few, if any, fish food organisms had been killed by the treatment. Approximately 3 weeks after treatment a few patches of filamentous algae reappeared. These disappeared promptly when "spot" treatments with Delrad were made by the Starr-Cutter employees. No further trouble with algae was encountered during the summer.

Hillsdale Rearing Pond No. 1, 1954.--This pond was sprayed with one quart of Delrad on June 4, 1954. At the time about one-half of the pond surface

was covered by patches of filamentous green algae. Also large clumps of algae were noted on the pond bottom. A concentration of 0.66 p.p.m. of Delrad was used. The water temperature at the time of treatment was 56° F. During treatment and for twenty-four hours thereafter the inflowing water was diverted around the pond. By June 6 the algae had started to decompose and large clumps had broken loose from the bottom and were floating at the surface. Dead algae temporarily clogged the screens at the outlet on the morning of June 6. The pond remained almost completely free of algae for the remainder of the summer. A second treatment planned for mid-summer was not required.

Pond 5A, Hillsdale Rearing Ponds, 1955.--This small pond is located immediately south of Pond 5 on a small tributary stream. It has an area of approximately one acre. Each summer it supports a dense stand of waterweed (Elodea) and Stonewort (Chara). Certain filamentous algae also grow in the pond but they never develop thick mats at the surface or on the bottom as they do in Pond No. 1. Pond 5A was treated with 1.0 p.p.m. of Delrad on May 11. The water temperature at the time was 62° F. The purpose of the treatment was to determine what effect, if any, Delrad has upon rooted aquatic plants (e.g., Elodea) and upon Chara. Two days after treatment much but not all of the Chara had faded and was almost white in color. Elodea also appeared slightly discolored. The pond water appeared brown and turbid, as contrasted to a high transparency noted before treatment. The unusual turbidity and color appear to have resulted from the decay of filamentous algae and Chara in the pond. Duckweed, which was quite abundant at the surface, was unaffected. There were no further signs of action of the chemical on the pond vegetation. By June 1, Elodea had regained its normal color and was growing vigorously; most of the older Chara plants had died but were being replaced by small young plants.

Hillsdale Rearing Pond No. 4, 1955.--This pond was treated with 0.5 p.p.m. of Delrad on May 11, 1955. At the time the pond had only traces of filamentous algae, although it normally develops large surface patches during the summer. A thin mat of filamentous algae was noted on the bottom of the north end of the pond and small patches of scum occurred at irregular intervals at the water's edge. This treatment seemed to have little if any effect. No discoloration could be detected two days after treatment. On June 1 there was considerably more algae in the pond than before treatment.

Canal Treatments, Drayton Plains Hatchery, 1955.--Two sections of the canal supplying the rearing ponds were treated with Delrad by Mr. Harold Hughes, Alfred Gould and J. N. Borglin. A concentration of 1.0 p.p.m. was used on the upstream section (1,370 feet in length) extending from the upper to the middle dam. On the lower section (1,247 feet in length) extending from the middle to the lower dam, a concentration of 0.5 p.p.m. was used. During treatment and for one week afterwards the flow of the Clinton River was diverted around this canal. At the time of treatment algae were not abundant in either section of the canal. Some brown scum was noted on rocks and there were widely scattered small patches of green filamentous algae on the canal bottom. Ten days after treatment (May 19) most of the brown scum over the rocks had disappeared and there was no sign of filamentous algae in either of the canal sections. Elodea and Potamogeton amplifolius were not affected by the treatment.

Drayton Plains Hatchery Pond No. 6, 1955.--This pond was sprayed with a solution of Delrad 50S on May 9, 1955. A concentration of 0.5 p.p.m. was used. The purpose of this experiment was to learn whether or not Delrad could be used to eliminate filamentous algae in a pond without killing Daphnia. Unfortunately at the time of treatment the Daphnia population of the pond was low. A few patches of filamentous algae were present although

it was not abundant.

On May 19, 1955, 45 gallons of water were strained through a #10 bolting silk net. No Daphnia were recovered although the pond water contained midge larvae, Copepods and Cladocera other than Daphnia (Bosmina). Mr. Hughes reported that Daphnia were present at the time but were confined to one location in the pond. His observations after treatment indicated that Daphnia had survived but that the population had remained low. Some algal scum was noted on the pond surface on May 19 showing that the filamentous algae had not been completely eliminated. The results of this test appear somewhat inconclusive and further tests are needed before this question can be answered clearly.

Drayton Plains Hatchery Pond No. 10.--This pond was treated with 1.0 p.p.m. of Delrad on May 9 for the purpose of studying its effect upon Chara. On May 19 there were no definite signs that Chara had been affected. Most of the plants retained their green color, although some had turned white. However there were approximately the same number of clumps of discolored Chara in an adjacent untreated pond (Pond No. 9).

Sylvan Ponds, Washtenaw County.--This series of four ponds is fed mainly by a cold sub-aqueous spring located in the uppermost pond. The water of the ponds is very hard (methyl orange alkalinity 195 p.p.m.) and the bottoms of all ponds are nearly completely covered with Chara. Surface water temperatures varied from about 60° to 75° F. At the time of treatment, the pond had an abundance of pumpkinseeds, sticklebacks, mudminnows and mosquito fish but very few trout. The fish in the pond were considered expendable in as much as the pond was scheduled for treatment with a fish toxicant. This experiment was designed to determine (1) whether or not a high concentration of Delrad (e.g., 1.5 p.p.m.) would kill fish in a hard-water pond

and (2) whether or not such a high concentration would completely eliminate Chara.

Delrad 50S was diluted with pond water and sprayed over the surface in the usual manner. The upstream pond received a slightly higher dosage than the lower pond since it was diluted more rapidly by inflowing water. The over-all concentration for the series of ponds was 1.5 p.p.m.

The kill of Chara appeared to be almost complete except in the uppermost pond. Here it was killed down the slope of the pond basin to a depth of approximately two feet. Below this depth it was bright green and showed no signs of injury. The sharp line separating dead from living Chara suggested that the algaecide failed to penetrate the colder water of the pond in the vicinity of the springs. Thus only the warmer upper water was actually treated. Although the Chara appeared to be completely killed in the remaining ponds, it grew back rapidly. One month after treatment a new growth of Chara was present in all ponds.

Almost a complete fish kill occurred in the ponds as a result of the treatment. Dead and dying fish of several species were noted throughout the pond three days after treatment. Some of the mosquito fish (Gambusia affinis), the mudminnow (Umbra limi), and the brook stickleback (Eucalia inconstans) are known to have survived. Also there appears to have been a heavy mortality among the invertebrate fish food organisms of the pond. Burrowing mayflies, damsel flies and crayfish were killed. Some dead tadpoles and frogs were also noted.

## CONCLUSIONS AND RECOMMENDATIONS

The sample of Cutrine furnished by the manufacturer for the tests at Hillsdale Pond No. 1 was ineffective as an algaecide. Since it failed to control algae at the dosage rate suggested by the manufacturer, it cannot be recommended until somewhat better algaecidal properties are demonstrated.

The effectiveness of Delrad as an algaecide cannot be questioned. In hard water ponds (methyl orange alkalinity 75 p.p.m. or more), using a concentration of 0.66 p.p.m., it proved to be very effective against filamentous green algae. A lower concentration (0.5 p.p.m.) was effective in some treatments, but gave poor results in others. Although Delrad is known to kill bluegreen algae, none of the treatments clearly demonstrated its effectiveness against a nuisance of this type. At 1.0 p.p.m. it was effective against the Stonewort (Chara), however it failed to kill all plants and a new growth was rapidly established. Delrad is highly toxic to fish life and cannot be safely used in concentrations greater than 1.0 p.p.m. Since it is effective against filamentous algae at 0.66 p.p.m., this concentration rather than 1.0 p.p.m. is recommended because it will give a greater margin of safety in treating ponds containing valuable fish.

Costs should be considered in evaluating chemical treatment methods. The cost of the chemical necessary to treat one acre-foot of water is nearly seven times greater for Delrad than for copper sulfate and eight times greater for Cutrine than for copper sulfate (Table 2). However if fewer treatments are required each year with Delrad or Cutrine than with copper sulfate to maintain good control of algae, the difference in chemical cost would be minimized. However, it seems clear that several copper sulfate treatments could be made at a lower cost than one treatment with either Delrad or Cutrine. Furthermore, at the present time there seems to be little good evidence that Cutrine has a greater residual phyto-toxicity than copper sulfate.

Delrad is somewhat more convenient to apply than copper sulfate. The liquid form (Delrad 50S) can be diluted and sprayed with less effort than copper sulfate. Delrad apparently retains its phyto-toxicity somewhat longer in hard-water lakes than does copper sulfate. Hence it does not need to be dispersed as thoroughly and evenly. Crude methods of dispersal

such as the "drag" and "float" methods can be used. Delrad can be recommended for the treatment of small ponds with a volume less than three or four acre-feet. In such cases the convenience seems to justify the additional expense. It cannot, however, be recommended for treating the shoreline of large lakes where the chemical cost is large as compared to the cost of labor needed to apply the chemical. Copper sulfate probably will continue to be the only practical algaecide for such treatments unless a cheaper organic algaecide is marketed.

TABLE 1

SUMMARY OF EXPERIMENTAL TREATMENTS WITH ALGAECIDES, 1954-1955

| Water treated | Date | Algaecide | Concentration p.p.m. (active ingred.) | Kind of plants | Results | Effects on fish |
|---|---|---|---|---|---|---|
| Starr-Cutter Pond | 5/28/54 | Delrad | 1.0 | filamentous green algae | Excellent | Partial mortality [1] |
| | | | | Chara | Good | |
| Hillsdale | | | | | | |
| Pond 1 | 6/4/54 | Delrad | 0.66 | filamentous green algae | Excellent | None |
| | 5/11/55 | Cutrine | 0.5 | filamentous green algae | Failure | None |
| | 6/1/55 | Cutrine | 1.0 | filamentous green algae | Failure | None |
| Pond 5A | 5/11/55 | Delrad | 1.0 | Chara | Good | None |
| | | | | Elodea | Failure | None |
| Pond 4 | 5/11/55 | Delrad | 0.5 | filamentous green algae | Poor | None |
| Drayton Plains | | | | | | |
| Upper canal | 5/9/55 | Delrad | 1.0 | filamentous green algae | Good | None |
| Lower canal | 5/9/55 | Delrad | 0.5 | filamentous green algae | Good | None |
| Pond 6 | 5/9/55 | Delrad | 0.5 | filamentous green algae | Poor | None |
| Pond 10 | 5/9/55 | Delrad | 1.0 | Chara | Poor | None |
| Sylvan Ponds | 6/24/55 | Delrad | 1.5 | Chara | Good | Partial mortality |

[1]- Mortality probably due to oxygen depletion.

TABLE 2

COMPARISON OF TREATMENT COSTS

OF VARIOUS ALGAECIDES

| Algaecide | Current price per pound (in lots of 100 lbs. or more) | Recommended concentration for hard waters (p.p.m.) | Treatment cost per acre-foot of water |
|---|---|---|---|
| Copper sulfate | $0.20 | 1.0 | $0.54 |
| Cutrine | $0.30 | [1] 0.5 | $4.05 |
| Delrad 50S | $0.99 | [2] 0.66 | $3.54 |

[1] - Concentration as p.p.m. metallic copper recommended by manufacturer. This concentration and a concentration twice as high failed to kill algae in our tests.

[2] - Concentration of active ingredient recommended for hard waters on the basis of data in this report.

## LITERATURE CITED

Duodoroff, P., et al. 1951. Bio-assay methods for the evaluation of acute toxicity of industrial wastes to fish. Sewage and Ind. Wastes, 11: 1380-1397.

Hasler, Arthur D. 1947. Antibiotic aspects of copper treatment of lakes. Trans. Wis. Acad. Sci., Arts and Letters, 39: 97-103.

Lawrence, J. M. 1954. Control of a branched alga Pithophora, in farm fishponds. Prog. Fish-cult. 16: 83-86.

Mackenthun, Kenneth M. and Harold L. Cooley. 1952. The biological effect of copper sulphate treatment on lake ecology. Trans. Wis. Acad. Sci., Arts and Letters, 41: 177-187.

Moyle, John B. 1949. The use of copper sulfate for algal control and its biological implications. Limnological Aspects of Water Supply and Waste Disposal. Pub. Amer. Assoc. for the Adv. of Sci., Washington: 79-87.

Nichols, M. S., Henkel, T. and McNall, D. 1946. Copper in lake muds from lakes of the Madison area. Trans. Wis. Acad. Sci., Arts and Letters, 38: 333-350.

INSTITUTE FOR FISHERIES RESEARCH

F. F. Hooper and K. G. Fukano

Approved by A. S. Hazzard

Typed by A. J. Hamilton