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ANN ARBOR, MICHIGAN

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INSTITUTE FOR FISHERIES RESEARCH

DIVISION OF FISHERIES

MICHIGAN DEPARTMENT OF CONSERVATION

COOPERATING WITH THE

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Report No. 1307 REVIEW OF LITERATURE ON TOXICITY OF SOME HERBICIDES TO FINDECEDVED By FISH DIVISION

Abstract

Observations described in 10 publications are briefly reviewed.

In experimental tanks which contained no plants 2,4-D was moderately toxic to fish when applied at a strength of 100 parts per million. No ill effects were shown by test fish when 25 cc. of 1,000 ppm solution of 2,4-D was sprayed on water hyacinth plants, but when the plants began to die the fish were affected as oxidation lowered dissolved oxygen beyond the toleration limits of the fish. SLI-23 (a modification of 2,4-D) was found to be somewhat more toxic than 2,4-D, although both chemicals did not directly endanger fish life when applied at rates recommended by the manufacturer. For the present at least, prohibitive costs are likely to limit greatly the use of 2,4-D compounds for control of aquatic vegetation.

Pentachlorophenol and sodium pentachlorophenate are highly toxic to fish life. Phenol is much less poisonous than these two chemicals, having been found only 0.003 as toxic as rotenone.

A number of hydrocarbons which can be used in control of vegetation are highly poisonous to fish. This group includes orthodichlorobenzene, trichlorbenzol, dicchlorbenzol, 2,4,5-trichlorbenzene, and naphtha.

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REVIEW OF LITERATURE ON TOXICITY OF SOME HERBICIDES TO FISH

By

Norman O. Levardsen

Within recent years, chemical control of undesirable vegetation has been practiced rather extensively. Destruction of valuable forms of wildlife has sometimes attended this use of chemical substances. Consequently a considerable number of studies have been made on herbicides to learn with some degree of exactitude their toxicity to animal life, and to find safe. practicable methods of application. A number of these investigations have been concerned with fish, and literature on the subject is herein reviewed so that the results will be readily available for reference.

2,4-D and related compounds

King and Penfound (1946) investigated the effects of 2,4-D and SLI-23 (a modified sodium salt of 2,4-D, developed by the Southwestern Louisiana Institute) upon bream (Lepomis macrochirus) and largemouth bass (Micropterus salmoides). The experimental tanks each had 20 liters of tap water. In some were placed 10 water hyacinths. Tanks without plants, besides controls, had 1 and 100 ppm 2,4-D added in solution. Solutions of 1 ppm of 2,4-D showed no significant effect. At 100 ppm the death rates for bream in 3 trials were 0%, 5%, and 15%, on the basis of 20 fish in each trial. For bass in parallel tests,

the death rates were 10%, 10%, and 20%. When 25 cc. of a 1,000 ppm solution of 2,4-D was sprayed over 10 water hyacinth plants, the fish underneath showed no ill effects until the plants began to die and the subsequent oxidation lowered the dissolved oxygen beyond the toleration limits of the fish.

SLI-23 at 100 ppm was found to be quite toxic for both species. At 1 ppm it was appreciably less toxic but a few bass died within 14 days. When used as a spray, the SLI gave results similar to those of 2,4-D. The authors conclude by saying that at recommended rates of the manufacturer, spray applications of 2,4-D will not directly endanger fish life. They do indicate that fish will die if confined under a hyacinth mat which has been sprayed.

In their experiments on toxicity of 2,4-D to fish, Harrison and Rees (1946) used tanks large enough so that each fish had approximately one gallon of water. Water pumps circulated and aerated the water. The fish used were: goldfish (<u>Carassius auratus</u>), sunfish (<u>Lepomis</u> <u>gibbosus</u>), brown bullhead (<u>Ameiurus nebulosus</u>), and killifish (<u>Cyprino-</u> <u>dontidae</u>).

At the outset of the experiments, goldfish appeared to respond erratically, so their use was discontinued. The results, of course, are applicable only under the test conditions and "... refer solely to a 7-day exposure period during which the concentration of 2,4-D was kept at a fixed level." The authors do not state how this level was maintained.

The lethal dose concentrations of 2,4-D:

killifish - 2,000 ppm sunfish - 1,000 ppm bullheads - 2,000 ppm

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The upper safe limits:

killifish - 1,500 ppm sunfish - 500 ppm bullheads - 500 ppm

The authors state that in spraying along and over waterways, the fish inhabiting such waterways will no doubt be exposed to less than the spray concentration. Thus "... testing the effect of a herbicide on fish in the dilution to be used in spraying will indicate the maximum exposure and one which is unlikely to be attained, in actual practice in the waterway treated."

A bibliography of 113 papers is included.

Surber (1949) in a rather broad statement says "... there is no immediate danger to fish from the use of such new herbicides as 2,4dichlorophenoxyacetic acid (2,4-D), its sodium salts and ester, 2,4,5trichlorophenoxyacetic acid (2,4,5-T), 2-methyl-4-chlorophenoxyacetic acid, 0-isopropyl N-phenyl carbamate, and ammonium sulfamate at 10 ppm or less ... In experiments at Leetown, 2,4-D at 50 ppm did not kill bluegill sunfish."

Surber states, "Since 5 ppm of 2,4-D and 2,4,5-T are required for effective control of submerged aquatic plants, and the cost of the chemicals is still high when compared with sodium arsenite, there seems nothing to fear at present from their use." Gerking (1948) says "... a concentration of 25 ppm is likely to be effective on most submerged aquatic plants." Surber notes that 2,4-D imparts a disagreeable flavor to fish flesh, making it inedible.

In using the 2,4-D formula of the acid dissolved in the solvents triethanolamine or tributylphosphate with kerosene as a carrier, some care should be exercised in its use near waters. Triethanolamine is

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not toxic to fish, but tributylphosphate at concentrations of 15 ppm will kill fish. Kerosene is also toxic.

Lynch, et al (1947) states "... 2,4-D is non-toxic to fish in concentrations usually employed for hyacinth control. Laboratory experiments ... show that 2,4-D in concentrations less than 100 ppm. is harmless to fish. Higher concentrations will kill some fish, and 1,000 ppm killed all species studied ... Calculations ... show that normal spraying of hyacinth with 2,4-D is unlikely to cause concentrations of the chemical in underlying water greater than 1 ppm."

The abstract of Goodnight's paper (1942) is quoted in full because of its completeness.

"Pentachlorophenol and sodium pentachlorophenate are fatal to the more sensitive species of fish in concentrations above 0.2 ppm although hardier species will survive at 0.4 or 0.6 ppm. In lethal concentrations they increase the metabolism of fish, as evidenced by increased respiratory movements; bleeding results from capillary rupture. Silver-mouthed (silverjaw) minnows are the most sensitive of the fish used in the experiments.

"The toxicity of pentachlorophenol and sodium pentachlorophenate to fish is increased by lowering the pH of the water. Within reasonable limits the size of the fish, the temperature of the water, and its character do not greatly affect the toxicity of the compounds. The number of fish in a solution of given volume does not affect their survival time. Above 10 ppm fish can detect the presence of sodium pentachlorophenate but not below 5.0 ppm.

"Eggs of lake trout are very resistant to these compounds. Lake trout are most sensitive to pentachlorophenol in the yolk sac stage immediately after hatching.

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"Invertebrates such as are used as food are relatively insensitive to pentachlorophenol or sodium pentachlorophenate. The most sensitive invertebrates will live at concentrations at which fish will survive.

"Adsorption by activated carbon, exposure to light in ponds and reservoirs, and natural dilution in flowing water are suggested as alternative solutions to the practical problem of stream pollution by waste waters bearing sodium pentachlorophenate."

The vertebrate species tested in these experiments were Silverjaw minnow (Ericymba buccata), Black fin minnow (Notropis umbratilis), Bluntnose minnow (Pimephales notatus), Doughbelly (Campostoma anomalum), Steel-colored minnow (Notropis whipplii), Horned dace (Semotilus atromaculatus), Top minnow (Fundulus notatus), and Orangespotted sunfish (<u>Lepomis humilis</u>). The invertebrates tested were crayfish, amphipods, cladocera, bloodworms, dragonfly nymphs, damselfly nymphs, and isopods.

This author (Goodnight) did not wish to make as detailed analysis of his observations as Gersdorff (1937) did since he was mainly interested in lethal concentrations. However he does observe, "The different species, ages and sizes of freshwater fish may differ greatly in sensitivity. The young of game fish are in the class of the doughbelly, steel-colored minnow and blackfin minnow. The orangespotted sunfish, tadpole and top minnow are among the hardy species... The insolubility of pentachlorophenol in waters imposes experimental difficulties. Since preliminary studies indicated that its action is similar to that of sodium pentachlorophenate, most of the experimental data, with the exception of the work on the eggs and young of lake trout, have been obtained on the sodium salt."

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Gersdorff (1937) used the goldfish (<u>Carrassius auratus</u>) to compare the relative toxicity of the cresols. He used rotenone for comparison, and included phenol in a number of tests. He wished "... to place a toxicological study of these substances on a quantitative basis." Upon the basis of the tables which he has constructed, he found that phenol was only 0.0030 as toxic as rotenone. M-cresol, the least toxic of the cresols, was slightly less toxic than phenol, while 0-cresol was 1/5th more toxic than phenol. P-cresol, the most toxic of the cresols, was nearly two times as toxic as phenol. This was according to "... the minimum product of concentration and survival time, which measures toxicity at its range of most powerful action. If the compounds were compared according to concentrations necessary to kill under certain conditions the relative toxicity of rotenone becomes 3,000 times that of M-cresol."

A bibliography of 21 papers is included.

Hydrocarbons

Surber (1949) states, "The hydrocarbons such as orthodichlorobenzene, trichlorbenzol and dichlorbenzol, as well as naptha, have proven highly toxic to fish and fish-food animals. It has been shown by experimentation that these chemicals will kill fish and their food before they will kill plants.

Handley (1949) states that in 1946, 2,4,5-trichlorbenzene, sprayed at the rate of 2 to 5 gallons per one-fifth acre, effectively killed <u>Ceratophyllum demersum</u> as well as fish. Orthodichlorbenzene, when sprayed straight, proved to be an excellent vegetation killer. Efforts to reduce the quantity to the point where weeds were killed but not fish were unsuccessful. A chemical mixture obtained from the Michigan Department of Conservation, Fish Division, gave results similar to orthodichlorobenzene. (This substance was a balanced mixture of xylene, trichlorbenzene and solfonated castor oil.)

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