LITERATURE REVIEW OF THE EFFECTS OF ENDOTHALL ON FISH

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INTRODUCTION

In January 1992 the Water Quality Program issued the Final Supplemental Environmental Impact Statement (FSEIS) for the Aquatic Plants Management Program for Washington State. The 1992 FSEIS is intended to update and build upon the original EIS issued in 1980. The FSEIS discusses the use of several chemical herbicides as alternatives for the control of "nuisance" aquatic plants. Among these is endothall, manufactured exclusively by Atochem (formerly Pennwalt) for the control of submersed plant species such as Eurasian watermilfoil (*Myriophyllum spicatum*) (Westerdahl and Getsinger, 1988).

Endothall [7-oxabicyclo (2,2,1)heptane-2,3-dicarboxylic acid] is formulated for aquatic use as a disodium or dipotassium salt (Aquathol or Aquathol K) or as an amine salt (Hydrothol 191). Each formulation is water-miscible. Hydrothol 191 is highly toxic to fish and is not recommended for use where fishery resources are important (Pennwalt Corp.).

Aquathol and Aquathol K have been permitted for use by the Washington State Department of Ecology (Ecology) with mitigation measures required to protect human health. However, both the 1980 EIS and the 1992 FSEIS note uncertainties about potential adverse effects to fish, due to a lack of information. In response to this information gap, a literature review has been conducted on the effects of endothall to fish. The objectives of the literature review were to:

- Provide the Water Quality Program with data on the effects of endothall to fish for consideration in their permitting process for aquatic endothall application;

- Identify data gaps on endothall effects to fish; and

- Use the findings as a foundation for designing, conducting, and evaluating studies to fill these data gaps.

RESULTS OF LITERATURE REVIEW

Acute and Chronic Toxicity

Table 1 summarizes the available data on acute toxicity of dipotassium and disodium endothall to a variety of fish species. Toxicity was uniformly low across species and formulations tested. For most species, the median tolerance limit for a 96-hr exposure is between 100 and 200 ppm. This concentration range is 20-to-40 times the maximum recommended application rate for spot treatment in ponds and lakes (Pennwalt Corp.). Only the fathead minnow (*Pimephales promelas*), as tested by Surber and Pickering (1962), falls substantially outside of this range (320-610 ppm). Unfortunately, there are fewer data on salmonids than warm water species such as bluegill (*Lepomis macrochirus*) and largemouth bass (*Micropterus salmoides*). This is probably due, in part, to the predominant historical use of these herbicides in the southern United States.

There are also relatively few data on chronic toxicity of endothall to fish. Most of the available data come from a 1967 study by Hiltibran in which fry of bluegill, green sunfish (*Lepomis cyallenus*), smallmouth bass (*Micropterus dolomieui*), and lake chubsuckers (*Erimyzon succetta*) were exposed to 25 ppm liquid or 10 ppm granular disodium endothall for 8 days (Table 2). None of the fish died in this experiment, therefore tolerance limits could not be established. Small bluegills exposed to 100 ppm liquid or 50 ppm granular endothall in the same experiment also showed no mortality. The only chronic testing done on a species of salmon was that conducted by Ligouri *et al.* (1984) who determined a 14-day LC_{50} of 88 ppm for juvenile chinook (*Oncorhynchus tshawytscha*).

In the case of endothall, acute toxicity tests may be more applicable than chronic tests because of its relatively short half-life in the aquatic environment. After a review of the literature, Reinert and Rogers (1987) estimated the half-life of endothall in ponds and lakes at 1 - 7 days. A recent Ecology survey of endothall persistence in two Western Washington lakes showed that 24-to-48 hours after treatment, concentrations in treated areas decreased to approximately 3% of initial concentrations (Serdar and Johnson, 1993a).

Other aquatic herbicides are generally toxic at concentrations one-to-three orders of magnitude lower than endothall. Diquat, which is used to control similar aquatic plant species as endothall, is about ten times more toxic to rainbow trout (*Oncorhynchus mykiss*) and coho salmon (*O. kisutch*) than endothall (Folmar, 1976; Lorz *et al.*, 1979). Ecology presently does not permit the use of diquat pending availability and review of "critical information" (Ecology, 1992).

Fluoridone, which may be effective at controlling a broader spectrum of aquatic plants, is toxic to at least three fish species including rainbow trout at concentrations ten times lower than endothall (EPA, 1986). Lorz *et al.* (1979) observed coho smolt 96 hr LC_{50}s of 0.07 and 0.1 mg/L for acroelin and dinoseb, respectively, both used for weed control along irrigation

Table 1. Summary of acute toxicities of endothall to fish.

Species	Formulation Tested	Exposure Period	LC50 (ppm a.i.)	Reference
Sunfish Family				
Bluegill *Lepomis macrochirus*	dipotassium liquid	96-hr	202	Pennwalt, no date
Largemouth bass *Micropterus salmoides*	disodium liquid	96-hr	200	Surber & Pickering, 1962
Bluegill *Lepomis macrochirus*	disodium liquid	96-hr	160-180	Surber & Pickering, 1962
Largemouth bass *Micropterus salmoides*	disodium	48-hr 96-hr	200 >135	Bond et al., 1960
Bluegill *Lepomis macrochirus*	disodium	96-hr	170-175	Walker, 1963
Bluegill *Lepomis macrochirus*	disodium liquid	96-hr	102-140	Inglis & Davis, 1973
Redear sunfish *Lepomis microlophus*	disodium	96-hr	125	Walker, 1963
Largemouth bass *Micropterus salmoides*	disodium	96-hr	120-125	Walker, 1963
Minnow Family				
Fathead minnow *Pimephales promelas*	disodium liquid	96-hr	320-610	Surber & Pickering, 1962
Carp x Goldfish hybrid	disodium	96-hr	145-210	Walker, 1963
Bluntnose minnow *Pimephales notatus*	disodium	96-hr	110-120	Walker, 1963
Red shiner *Notropis lutrensis*	disodium	96-hr	105	Walker, 1963
Redfin shiner *Notropis umbratilis*	disodium	96-hr	95	Walker, 1963
Salmon Family				
Rainbow trout *Oncorhynchus mykiss*	dipotassium liquid	96-hr	213	Pennwalt, no date
Rainbow trout (fry) *Oncorhynchus mykiss*	not given	96-hr	150	Folmar, 1976
Chinook salmon *Oncorhynchus tshawytscha*	disodium	48-hr	136	Bond et al., 1960
Catfish Family				
Black bullhead *Ictalurus melas*	disodium	96-hr	180-185	Walker, 1963
Yellow bullhead *Ictalurus natalis*	disodium	96-hr	170-175	Walker, 1963

a.i. = active ingredient

Table 2. Summary of chronic toxicities of endothall to fish.

Species	Formulation Tested	Exposure Period	LC50 (ppm a.i.)	Reference
Sunfish family				
Bluegill *Lepomis macrochirus*	disodium liquid disodium granular	12-day 12-day	>100 >50	Hiltibran, 1967
Bluegill (fry) *Lepomis macrochirus*	disodium liquid disodium granular	8-day 8-day	>25 >10	Hiltibran, 1967
Green sunfish (fry) *Lepomis cyallenus*	disodium liquid disodium granular	8-day 8-day	>25 >10	Hiltibran, 1967
Smallmouth bass (fry) *Micropterus dolomieui*	disodium liquid disodium granular	8-day 8-day	>25 >10	Hiltibran, 1967
Sucker family				
Lake chubsucker (fry) *Erimyzon succetta*	disodium liquid disodium granular	8-day 8-day	>25 >10	Hiltibran, 1967
Salmon family				
Chinook salmon *Oncorhynchus tshawytscha*	dipotassium liquid	14-day	88	Ligouri et al., 1984

a.i. = active ingredient

return channels. Hyamine, an algicide, was found to be approximately 100 times more toxic to bluegills and largemouth bass than endothall (Surber and Pickering, 1962).

Effects of Water Hardness on Toxicity

Several investigations have been conducted to determine if water hardness affects toxicity of endothall to fish, largely because the toxicity of other aquatic herbicides is partially dependent on hardness (Inglis and Davis, 1973; Wan *et al.*, 1989). However, the available data suggest that water hardness has little effect on toxicity of endothall to fish. Surber and Pickering (1962) found that toxicity varied only slightly for bluegills exposed to endothall in soft and hard waters for 96 hours. Median tolerance limits were 160 ppm in soft water and 180 ppm in hard water. For fathead minnows, toxicity appeared to decrease in hard water, but test concentrations were two orders of magnitude higher than the highest recommended application rates (LC_{50}s of 320 ppm for soft water, 610 ppm for hard water).

Other studies have led to the conclusion that water hardness does not alter endothall's toxicity to fish. Inglis and Davis (1973) found that toxicity to bluegills increased with increasing water hardness, but the differences were not statistically significant. Walker (1963) found that harder water tended to reduce toxicity to largemouth bass in 96 hour tests, but the differences were very small (120 vs. 125 ppm).

Toxicity at Early Life Stages

Hiltibran (1967) conducted several experiments to determine toxicity of endothall at the egg and fry stages of life. In the first experiment, all twenty fertilized stoneroller eggs (*Campostoma anomalum*) hatched after being exposed to 50 ppm endothall for 72 hours. In the second experiment, there was no mortality to fry of four species (bluegill, green sunfish, lake chubsucker, and smallmouth bass) following 8-day endothall exposure of either liquid (25 ppm) or granular (10 ppm) disodium endothall. Among the conclusions drawn by Hiltibran was that "endothall appears to be one of the safest herbicides to use during the spawning season."

In a determination of acute toxicity to rainbow trout fry (5 weeks post swim-up), Folmar (1976) calculated a 96-hr LC_{50} of 150 ppm.

Uptake and Distribution

Because of its polar, hydrophobic nature, accumulation of endothall by fish is unlikely (Sikka *et al.*, 1975; Reinert and Rodgers, 1987). Reinert and Rodgers (1987) reported a bioconcentration factor (BCF; ratio of a compound's concentration in fish tissue to water) of approximately 1 in fish, but BCFs ranged from 0.003 to 10 depending on species and environmental conditions. To put these values in perspective, BCFs calculated for thirty seven pesticides used in the Puget Sound basin had a range of 0 - 17,400 with a median of 35 (Tetra Tech, Inc., 1988).

When bluegills were exposed to 2 ppm of ^{14}C-labelled endothall for 96 hours, final whole body burdens averaged 0.17 ppm, and net accumulation of endothall ceased after the initial 12 hours (Sikka *et al.*, 1975). ^{14}C is used to trace the distribution and fate of the labelled compound without altering its chemical nature. Distribution of ^{14}C in various tissues was viscera > scales > flesh > head and fins > skin. Fish force fed [^{14}C]endothall showed a similar distribution in these tissues.

Effect on Fish Behavior

Behavioral changes of fish caused by exposure to certain chemicals may lead to reductions in population, especially if they affect reproductive capacity of a species. Bettoli and Clarke (1992) recently conducted a study to determine if adult male bluegills abandoned their nest more frequently in an area treated with 4 ppm endothall (Aquathol K) compared to an area treated with water. Nest abandonment leads to a decline in reproductive rates because of egg-eating by intruders. They found that 88% of the bluegills in the endothall-treated area (n=8) abandoned their nests compared to 50% for controls (n=6). However, they concluded that the results were not significant due to the small sample size.

Serns (1977) conducted a long-term study on bluegill growth and reproduction over three growing seasons in a pond treated with a single 5 ppm dose of dipotassium endothall. Adult bluegills in the treatment pond showed the same fecundity and timing of spawning as those in a control pond, even though 3 ppm endothall was still present at the time of spawning. Growth, survival, and fecundity of the subsequent generation were monitored and found to be unaffected by the endothall treatment. At the end of the study, bluegill survival in the treatment pond was slightly higher and growth slightly slower than the control pond. The investigators attributed the slower growth rate to the greater overall biomass in the treatment pond.

To some extent, herbicide manufacturers may rely on an avoidance reaction of fish to prevent mortality. For instance, Pennwalt Corp. recommended spot Hydrothol 191 application of up to 5 ppm although the label warns that it is toxic to fish at 0.3 ppm (Pennwalt Corp.). They claimed that fish will be "herded" away from treatment areas and avoid any direct exposure. However, Folmar (1976) found no observable avoidance reaction by rainbow trout to endothall at aqueous concentrations ranging from 0.1 to 10 ppm.

The study by Ligouri *et al.* (1984) includes the only additional behavioral observations found in the literature. They noted that chinook salmon smolts exposed to 88 ppm dipotassium endothall in aquaria stopped swimming after 5 days. After 9 days of exposure, surviving fish refused to eat.

Osmoregulatory Performance

A study conducted by Bouck and Johnson (1979) raised concerns that the transition from freshwater to seawater may be a critical life stage in tolerance of salmonids to endothall.

They exposed coho smolts to 5 ppm endothall (no formulation given) for one hour followed by either an immediate seawater challenge, or return to freshwater for four days and then a gradual introduction to seawater. Survival was 0% in one trial of the immediate seawater challenge, but 100% in another trial. For fish returned to freshwater, there was 96% survival in one trial and 100% in a second trial. The authors of this study did not measure any physiological parameters that may explain these results, but they suggested that the endothall exposure interfered with the smolts' osmoregulatory system which led to the substantial mortality. There was no mortality in the control group (not challenged with seawater) for this experiment.

A similar seawater entry test was conducted by Ligouri *et al.* (1984). They exposed chinook smolts to various dipotassium endothall concentrations (1.5 - 55 ppm acid equivalent) for 4 or 14 days and then challenged then with seawater for up to 10 days. Fish exposed to 3 ppm endothall or more had survival rates of 10 - 50% after 24 hours in seawater, and at 0 - 20% after 72 hours. Fish placed in clean freshwater after endothall exposure had high survival rates (90 - 100%). Mild gill inflammation was observed in endothall-exposed fish and the researchers concluded this as the cause of reduced osmoregulatory capacity.

An investigations of smolts' physiological response to seawater following endothall exposure was recently conducted by Ecology (Serdar and Johnson, 1993b). By measuring blood sodium levels, the authors of this study found that endothall does not interfere with smolts' ability to osmoregulate in seawater after a 4-day treatment at the maximum recommended dosage of endothall (5 ppm acid equivalent).

There are several possible explanations for the disparate results from the three seawater challenge studies. Salmon at the smolting stage are extremely sensitive to changes in environmental conditions. Differences in test conditions, species, and herbicide formulations may have contributed to the various results. However, authors of all three investigations concluded that the seawater challenge tests are a useful and sensitive indicator of marine survival.

Other Considerations

Endothall acts quickly in killing aquatic macrophytes which may then decompose, leading to reduced dissolved oxygen levels. An oxygen sag was observed in a shallow Wisconsin lake a few days after treatment with endothall due to decomposition of affected plants (Holmberg and Lee, 1976). Although this oxygen sag did not create any apparent fish loss, the authors concluded that treatment in a deeper lake with less mixing may cause serious problems. The available literature contains no reports of fish kills due to endothall treatment.

Reduction or elimination of food sources is a potential concern associated with herbicide application. In a survey of macroinvertebrate populations in a pond receiving a 1:1 application of diquat and endothall (final water concentrations were 0.17 ppm endothall and 0.11 ppm diquat), populations of 14 taxa did not decline following application (Berry *et al.*, 1975). Species that were displaced when the aquatic plants they inhabited died off, easily colonized artificial substrates.

CONCLUSIONS

1. Data on acute and chronic toxicity of endothall to fish indicates that the maximum recommended application rate in lakes and ponds provides a substantial margin of safety for fish survival.

2. Water hardness does not appear to have a significant effect on the toxicity of endothall to fish.

3. Bioaccumulation rates of endothall in fish are low compared to other pesticides.

2. Endothall is not highly toxic to several species of fish at the egg or fry stage. Endothall does not appear to affect fecundity or other aspects of reproduction in species tested.

5. The effect of endothall on osmoregulation of smolting salmon is inconclusive, and may be dependent on species and chemical formulations tested. Additional study is recommended to resolve this issue.

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