

State of California  
The Resources Agency  
DEPARTMENT OF FISH AND GAME

**HAZARD ASSESSMENT OF THE  
FUNGICIDES BENOMYL, CAPTAN,  
CHLOROTHALONIL, MANEB, AND ZIRAM  
TO AQUATIC ORGANISMS**

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## PREFACE

The California Department of Fish and Game (CDFG) is responsible for the protection and management of fish and wildlife. The CDFG protects fish and wildlife from pesticide hazards through consultation with the California Environmental Protection Agency's Department of Pesticide Regulation (DPR) Pesticide Registration and Evaluation Committee. The State Water Resources Control Board and the Regional Water Quality Control Boards also protect fish and wildlife by promulgating and enforcing water quality standards for pesticides and other toxic materials. In recognition of the need for applicable environmental standards for fish and wildlife, DPR contracted with the CDFG to assess the effects of pesticides on fish and wildlife and to facilitate development of water quality criteria to protect aquatic organisms.

This document is the eleventh in a series of pesticide hazard assessments. Hazard assessments have also been prepared for the herbicides molinate and thiobencarb, and for the insecticides methyl parathion, carbofuran, chlorpyrifos, diazinon, methidathion, methomyl, dimethoate, carbaryl, and malathion.

# Hazard Assessment of the Fungicides Benomyl, Captan, Chlorothalonil, Maneb, and Ziram to Aquatic Organisms

by

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## SUMMARY

Available freshwater and saltwater toxicity data were reviewed for the fungicides benomyl, captan, chlorothalonil, maneb, and ziram. Insufficient monitoring data were available to perform a hazard assessment for California's Sacramento-San Joaquin River system.

Fifty-five tests on the acute and chronic toxicity of benomyl to aquatic animals were reviewed and evaluated. Six of the eight required species were available for calculation of a freshwater Final Acute Value (FAV). The most acutely sensitive freshwater species tested for benomyl was channel catfish *Ictalurus punctatus* with a Genus Mean Acute Value (GMAV) of 41 µg/L. No tests on saltwater species were available. The interim freshwater FAV for benomyl was 17.5 µg/L and the interim Criterion Maximum Concentration (CMC) was 8.8 µg/L. The CMC is the value at which aquatic organisms should not be affected unacceptably if the one-hour average concentration does not exceed the CMC value more than once every three years on the average (EPA 1985). No chronic criteria were calculated due to a lack of data. No monitoring data were available for benomyl in the Sacramento-San Joaquin River system.

Thirty-seven tests on the acute and chronic toxicity of captan to aquatic animals were reviewed and evaluated. Only three of the eight required freshwater species were available, and no acute freshwater criteria were calculated. The most acutely sensitive freshwater species tested for captan was brown trout *Salmo trutta* with a GMAV of 46 µg/L. No saltwater criteria were calculated due to a lack of data. No paired acute-chronic values were available, and no chronic criteria were calculated. No monitoring data were available for captan in the Sacramento-San Joaquin River system.

Twenty-three tests on the acute toxicity of chlorothalonil to aquatic animals were reviewed and evaluated. Only four of the eight required freshwater species were available, and no acute freshwater criteria were calculated. The most acutely sensitive freshwater species tested for chlorothalonil was galaxiid fish *Galaxias auratus* with a GMAV of 21 µg/L. No saltwater criteria were calculated due to a lack of data. The most acutely sensitive saltwater species was eastern oyster *Crassostrea virginica* with a

GMAV of 26 µg/L. No paired acute-chronic values were available, and no chronic criteria were calculated. Chlorothalonil was detected once by the U.S. Geological Service in the San Joaquin River system at a concentration of 0.29 µg/L.

Thirteen tests on the acute toxicity of maneb to aquatic animals were reviewed and evaluated. Only four of the eight required freshwater species were available, and no acute freshwater criteria were calculated. The most acutely sensitive freshwater species tested for maneb was rainbow trout fry *Oncorhynchus mykiss* with a GMAV of 330 µg/L. Only four of the required eight saltwater species were available, and no saltwater criteria were calculated. The most acutely sensitive saltwater species was copepod *Nitocra spinipes* with a GMAV of 110 µg/L. No paired acute-chronic values were available, and no chronic criteria were calculated. No monitoring data were available for maneb in the Sacramento-San Joaquin River system.

Fifteen tests on the acute toxicity of ziram to aquatic animals were reviewed and evaluated. Only four of the eight required freshwater species were available, and no acute freshwater criteria were calculated. The most acutely sensitive freshwater species tested was bluegill sunfish *Lepomis macrochirus* with a GMAV of 9.7 µg/L. Only three of the required eight saltwater species were available and no saltwater criteria were calculated. The most acutely sensitive saltwater species was eastern oyster *Crassostrea virginica* with a GMAV of >1,000 µg/L. No paired acute-chronic values were available, and no chronic criteria were calculated. No monitoring data were available for ziram in the Sacramento-San Joaquin River system.

Monitoring of the Sacramento-San Joaquin River system should be initiated to help assess hazards posed by benomyl, captan and chlorothalonil to aquatic species. Additional acute and chronic tests should be run on freshwater and saltwater species for all five fungicides. Once additional studies become available, the CDFG may reassess the hazards posed by these fungicides to aquatic species. Although current reporting limits or reporting limits currently being developed appear low enough to indicate acute toxicity of these fungicides, it is possible that reporting limits are inadequate to indicate chronic toxicity. Current laboratory methods do not distinguish clearly between ziram, maneb, and other closely related compounds. Monitoring for ziram and maneb should be postponed until more accurate test methods are available.

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## LIST OF ABBREVIATIONS

ACR	Acute-to-Chronic Ratio
ASTM	American Society of Testing and Materials
CCC	Criterion Continuous Concentration
CDFG	California Department of Fish and Game
CDHS	California Department of Health Services
CMC	Criterion Maximum Concentration
DPR	(California) Department of Pesticide Regulation
EPA	(U.S.) Environmental Protection Agency
FACR	Final Acute Chronic Ratio
FAV	Final Acute Value
FCV	Final Chronic Value
FPV	Final Plant Value
FRV	Final Residue Value
GMAV	Genus Mean Acute Value
LOEC	Lowest Observable Effect Concentration
MATC	Maximum Acceptable Toxicant Concentration
NOEC	No Observable Effect Concentration
SMAV	Species Mean Acute Value
USGS	U.S. Geological Survey
WQC	Water Quality Criteria

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## INTRODUCTION

The impact of fungicides on aquatic organisms in the Sacramento – San Joaquin River system has received limited attention in previous studies. Fungicides are used in the Sacramento and San Joaquin Valleys as preventative measures against a variety of fungal organisms. Fungicides are generally used during the rainy season from late fall to early spring, so there is potential for them to run off into waterways. Aerial applications to flooded orchards increase the potential for introduction into surface water. In addition, there is a lack of foliage on the crops during winter and early spring to intercept the fungicides. Hazard assessments were performed for five fungicides commonly used in the Sacramento and San Joaquin Valleys.

Hazards from benomyl, captan, chlorothalonil, maneb, and ziram to aquatic life in the Sacramento-San Joaquin River system could not be evaluated because of the lack of monitoring data for these fungicides. However, toxic effects of these compounds were assessed using available aquatic toxicity tests and environmental fate information. Toxicity tests were evaluated for conformance with specific criteria adapted from the U.S. Environmental Protection Agency (EPA 1985) and the American Society for Testing and Materials (ASTM 1988, 1992). Although toxicity tests were not required to comply with all criteria, tests were rejected if they did not observe fundamental ASTM (1988, 1992) procedures. These include: test results reported as  $LC_{50}$ ,  $EC_{50}$ , NOEC or LOEC, having at least one control, control survival above ninety percent, at least five test concentrations, forty-eight or ninety-six hour acute test duration, acceptable mortality range, and active ingredient above ninety percent. The California Department of Fish and Game's (CDFG) hazard assessments are based on data from accepted tests and procedures adapted from EPA (1985) guidelines (Appendix A).

The U.S. Geological Survey (USGS), the Central Valley Regional Water Quality Control Board, and the Department of Pesticide Regulation (DPR) have not monitored specifically for any of these fungicides.

# BENOMYL

## Use and Environmental Fate

Benomyl is a benzimidazole compound used as a systemic fungicide on fruits, vegetables, nuts and grains, ornamentals, and as a seed treatment. From 1990 to 1995, the reported use of benomyl in California ranged from 123,799 to 580,927 pounds per year (Table 1) (DPR 1990-1995).

**Table 1. Benomyl, captan, chlorothalonil, maneb and ziram use in California (in lbs.), 1990-1995. <sup>a</sup>**

Year	Benomyl	Captan	Chlorothalonil	Maneb	Ziram
1990	233,464	264,290	511,462	1,632,259	934,671
1991	123,799	7,468	666,068	354,023	2,028,905
1992	145,982	296,670	861,252	596,774	1,815,506
1993	580,927	496,331	1,095,651	1,122,084	1,771,370
1994	151,974	618,166	861,603	1,032,686	1,027,380
1995	197,049	754,035	1,152,441	1,309,283	1,639,487

<sup>a</sup> California Department of Pesticide Regulation Pesticide Use Reports 1990-1995

Benomyl decomposes into the relatively stable metabolite carbendazim (methyl 2-benzimidazolecarbamate), which has approximately the same order of toxicity as benomyl (EXTOXNET 1993). In acidic or neutral water, benomyl decomposes within several hours to carbendazim, which has a half life of two months (EXTOXNET 1993) (Table 2). Benomyl's solubility in water is 2 mg/L at pH 9 and 3.6 mg/L at pH 5 (EXTOXNET 1993). Benomyl is strongly bound to soil and has a half-life of six to twelve months when applied to bare soil (EXTOXNET 1993).

**Table 2. Chemical properties of benomyl, captan, chlorothalonil, maneb, and ziram.**

	Hydrolysis t $\frac{1}{2}$	Solubility in H <sub>2</sub> O (mg/L)	Soil t $\frac{1}{2}$	Mobility in Soil
Benomyl	several hrs	2 (pH 9), 3.6 (pH 5)	6-12 mos.	Low
Captan	8.2 hrs	5.1	1-10 d	<4 in
Chlorothalonil	49 d	0.6	N/A	Low
Maneb	Short	7.0	60 d	Low
Ziram	17.67 hrs	18.3	Long	N/A

The estimated bioconcentration factor (BCF) for benomyl ranges from 159 in rainbow trout *Oncorhynchus mykiss* to 460 in bluegill sunfish *Lepomis macrochirus*, indicating that benomyl does not significantly concentrate in living tissues (Howard 1991; National Library of Medicine 1992).

The California Department of Health Services (CDHS) has not set an action level for benomyl or carbendazim in drinking water (Milea 1998).

## Toxicity to Aquatic Animals

Fifty-three tests on the acute toxicity of benomyl to aquatic animals were evaluated (Appendix B). Forty-five tests were accepted (Table B1) and eight tests were not accepted (Table B7).

Genus Mean Acute Values (GMAVs) for benomyl and carbendazim were calculated using data from accepted acute toxicity tests and were ranked in ascending order (Tables 3 and 4). Freshwater benomyl GMAVs ranged from 41 µg/L for channel catfish *Ictalurus punctatus* to >100,000 µg/L for crayfish *Procambarus sp.* No acute toxicity tests were available for saltwater species. Freshwater GMAVs for carbendazim ranged from 26 µg/L for catfish *Ictalurus punctatus* to >3,200 µg/L for bluegill sunfish *Lepomis macrochirus*.

**Table 3. Ranked Genus Mean Acute Values (GMAV) From accepted benomyl acute toxicity tests on freshwater species used to calculate the interim freshwater Final Acute Value (FAV).**

Rank	GMAV (mg/L)	Organism	Genus and species
1	41 <sup>a</sup>	Catfish	<i>Ictalurus punctatus</i>
2	224 <sup>a</sup>	Rainbow trout	<i>Oncorhynchus mykiss</i>
3	750	Amphipod	<i>Gammarus pseudolimnaeus</i>
4	>1,000	Crayfish	<i>Orconectes nais</i>
5	1,194 <sup>a</sup>	Bluegill sunfish	<i>Lepomis macrochirus</i>
6	1,691 <sup>a</sup>	Fathead minnow	<i>Pimephales promelas</i>
7	2,800	Cladoceran	<i>Daphnia magna</i>
8	7,000	Midge	<i>Chironomus plumosus</i>
9	>100,000	Crayfish	<i>Procambarus sp.</i>

<sup>a</sup> GMAV based on a geometric mean of more than one LC<sub>50</sub> or EC<sub>50</sub> for this species.

**Table 4. Ranked Genus Mean Acute Values (GMAV) from accepted carbendazim acute toxicity tests on freshwater species.**

Rank	GMAV (mg/L)	Organism	Genus and species
1	26 <sup>a</sup>	Catfish	<i>Ictalurus punctatus</i>
2	477 <sup>a</sup>	Rainbow trout	<i>Oncorhynchus mykiss</i>
3	>3,200	Bluegill sunfish	<i>Lepomis macrochirus</i>

<sup>a</sup> GMAV based on a geometric mean of more than one LC<sub>50</sub> or EC<sub>50</sub> for this species.

The EPA (1985) guidelines recommend eight freshwater taxa for which data should be available to derive a freshwater Final Acute Value (FAV) and eight saltwater taxa to derive a saltwater FAV (Tables 5 and 6). Usually, the four lowest GMAVs are the most significant determinants in calculating a FAV. The four lowest freshwater GMAVs for benomyl were for the catfish *Ictalurus punctatus*, rainbow trout *Oncorhynchus mykiss*, amphipod *Gammarus pseudolimnaeus*, and crayfish *Orconectes nais*. The interim freshwater FAV for benomyl was 17.5 µg/L. A final freshwater FAV for benomyl will be calculated when data are available for the remaining two categories recommended by the EPA. Acceptable data were available for six of the freshwater and none of the saltwater species. Because of the lack of data, a saltwater FAV value was not calculated for benomyl.

One chronic test on benomyl was accepted and one test was rejected. The Maximum Acceptable Toxicant Concentration (MATC) for rainbow trout *Oncorhynchus mykiss* was 37 µg/L. The Acute-to-Chronic Ratio (ACR) for *O. mykiss* was 6. Two chronic tests on carbendazim were accepted. For carbendazim, MATC values were 2.19 µg/L for channel catfish *Ictalurus punctatus* and 19.34 µg/L for rainbow trout *O. mykiss*. The

ACR values were 8 for *I. punctatus* and 25 for *O. mykiss*. Due to the lack of chronic toxicity tests, chronic criteria were not calculated.

**Table 5. Eight families of freshwater aquatic animals recommended by EPA (1985) for use in deriving the freshwater FAV, representative species for which benomyl acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. One Salmonid	Rainbow trout	-----
2. Another family in class Osteichthyes	Bluegill	-----
3. Another family in phylum Arthropoda or Chordata	Fathead minnow	-----
4. One family not in phylum Arthropoda or Chordata	N/A <sup>a</sup>	Rotifer
5. One insect family or any phylum not already represented	N/A	Stonefly
6. One planktonic crustacean	Cladoceran	-----
7. One benthic crustacean	Amphipod	-----
8. One insect	Midge	-----

<sup>a</sup>N/A = Species not available.

**Table 6. Eight families of saltwater aquatic animals recommended by EPA (1985) for use in deriving the saltwater FAV, representative species for which benomyl acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. Two families in phylum Chordata	N/A <sup>a</sup>	Sheepshead minnow
2.	N/A	Longnose killifish
3. One family not in phylum Arthropoda or Chordata	N/A	Eastern oyster
4. Three other families not in phylum Chordata	N/A	Dungeness crab
5.	N/A	Blue crab
6.	N/A	Grass shrimp
7. A mysid or penaeid	N/A	Mysid
8. One other family not already represented	N/A	Rotifer

<sup>a</sup>N/A = Species not available.

## Toxicity to Aquatic Plants

No data were available to analyze the toxicity of benomyl or carbendazim to aquatic plants.

## Hazard Assessment

Freshwater species were available for six of the eight freshwater and none of the eight saltwater taxa recommended by EPA (1985) (Tables 5 and 6). The data shows that fish are more sensitive than invertebrates to benomyl. Because the taxa missing are invertebrates, it is likely that the additional 2 categories will not significantly change the interim freshwater FAV. Therefore, an interim freshwater FAV was calculated, but tests on two taxa are required to complete the eight taxa. These categories would be an insect or an un-represented phylum, and a family not in Phylum Arthropoda or Chordata. The species suggested to fill these categories are stonefly *Plecoptera sp.* and rotifer *Brachionus sp.* It is possible that the FAV may change when these two categories are filled. Eight acute toxicity tests using saltwater species such as those suggested in Table 5 are required to determine saltwater quality criteria using EPA methods. In order to calculate freshwater and saltwater FCVs, paired acute-chronic tests are needed for fish and invertebrates. Calculation of the freshwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive freshwater species. Calculation of the saltwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive saltwater species.

The EPA (1985) guidelines specify that a WQC consists of two concentrations, the Criterion Maximum Concentration (CMC) to protect against acute toxicity and the Criterion Continuous Concentration (CCC) to protect against chronic toxicity. The CMC is equal to one-half the FAV. The CCC is equal to the lowest of three values: the Final Chronic Value (FCV), the Final Plant Value (FPV), or the Final Residue Value (FRV) (Appendix A). The FRV is intended to prevent pesticide concentrations in commercially or recreationally important species from affecting marketability because of exceeding action levels and to protect wildlife which consume aquatic organisms (EPA 1985).

The interim freshwater FAV for benomyl is 17.5 µg/L and the interim CMC is 8.8 µg/L. EPA (1985) methods for establishing a CCC could not be followed because sufficient chronic toxicity data were not available.

No monitoring data were available for benomyl in the Sacramento-San Joaquin River system. Benomyl can be detected in water in concentrations as low as 1 µg/L (Cooper 1998). The lowest GMAV for benomyl is 41 µg/L, and for carbendazim, 26 µg/L. These values and the interim FAV and CMC are higher than the 1 µg/L reporting limit. Therefore, the reporting limit for benomyl should be low enough to determine if water is acutely toxic to aquatic organisms, but may not be adequate to determine chronic toxicity for more sensitive aquatic species.

# CAPTAN

## Use and Environmental Fate

Captan is a carboximide compound used as a protective, eradicating fungicide on fruits, vegetables, ornamentals, and as a seed treatment. From 1990 to 1995, the reported use of captan in California ranged from 7,468 to 754,035 pounds per year (Table 1) (DPR 1990-1995).

Captan's solubility in water is 5.1 mg/L at 20 to 25°C (Wauchope et al. 1992) (Table 2). At 23°C in distilled water, the hydrolysis  $t_{1/2}$  is 8.2 hours (Chevron n.d.). Captan has a low leaching potential (Chevron n.d.). Movement is usually less than four inches through the soil (Chevron n.d.). Captan degrades rapidly in soil with a half-life of one to ten days in most soil environments (EXTOXNET 1993).

An unpublished bioaccumulation study found no captan residues after thirty-three days in any of the test organisms or accumulation in fish, and concluded that it does not persist in water or biomagnify in the food chain (EPA 1975).

The CDHS has set an action level of 350 µg/L for captan in drinking water (Milea 1998).

## Toxicity to Aquatic Animals

Twenty-nine tests on the acute toxicity of captan to aquatic animals were evaluated (Appendix B). Eighteen tests were accepted (Table B3) and eleven tests were not accepted (Table B8).

Genus Mean Acute Values (GMAVs) for captan were calculated using data from accepted acute toxicity tests and were ranked in ascending order (Tables 7 and 8). Freshwater captan GMAVs ranged from 46 µg/L for brown trout *Salmo trutta* to 164 µg/L for fathead minnow *Pimephales promelas*. Saltwater GMAVs ranged from >10,000 µg/L for zoal and juvenile crab *Cancer magister* to >100,000 µg/L for adult crab *Cancer magister*.

Table 7. Ranked Genus Mean Acute Values (GMAV) from accepted captan acute toxicity tests on freshwater species.

Rank	GMAV (mg/L)	Organism	Genus and species
1	46 <sup>a</sup>	Brown trout	<i>Salmo trutta</i>
2	54 <sup>a</sup>	Char	<i>Salvelinus namaycush</i>
3	74 <sup>a</sup>	Salmon (New World)	<i>Oncorhynchus clarki</i> (SMAV = 56) <i>O. kisutch</i> (SMAV = 128) <sup>a</sup> <i>O. mykiss</i> (SMAV = 73) <i>O. tshawytscha</i> (SMAV=57)
4	78	Catfish	<i>Ictalurus punctatus</i>
5	120	Perch	<i>Perca flavescens</i>
6	141	Bluegill sunfish	<i>Lepomis macrochirus</i>
7	164 <sup>a</sup>	Fathead minnow	<i>Pimephales promelas</i>

<sup>a</sup> GMAV based on a geometric mean of more than one LC<sub>50</sub> or EC<sub>50</sub> for this species.

**Table 8. Ranked Genus Mean Acute Values (GMAV) from accepted captan acute toxicity tests on saltwater species.**

Rank	GMAV (mg/L)	Organism	Genus and species
1	>10,000 <sup>a</sup>	Crab zoeae (juvenile)	<i>Cancer magister</i>
2	>100,000 <sup>a</sup>	Crab (adult)	<i>Cancer magister</i>

The EPA (1985) guidelines recommend eight freshwater taxa for which data should be available to derive a freshwater Final Acute Value (FAV) and eight saltwater taxa to derive a saltwater FAV (Tables 9 and 10). Usually, the four lowest GMAVs are the most significant determinants in calculating a FAV. The four lowest freshwater GMAVs for captan were for brown trout *Salmo trutta*, lake trout *Salvelinus namaycush*, salmonids *Oncorhynchus spp.*, and channel catfish *Ictalurus punctatus*. The two lowest saltwater GMAVs for captan were zoeae and juvenile crab *Cancer magister* and adult crab *C. magister*. Acceptable data were available for only three of the freshwater and one of the saltwater taxa. Because of the lack of data, freshwater and saltwater FAV values were not calculated for captan.

Eight chronic toxicity tests were evaluated; all were rejected.

**Table 9. Eight families of freshwater aquatic animals recommended by EPA (1985) for use in deriving the freshwater FAV, representative species for which captan acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. One Salmonid	Rainbow trout	-----
2. Another family in class Osteichthyes	Bluegill	-----
3. Another family in phylum Arthropoda or Chordata	Fathead minnow	-----
4. One family not in phylum Arthropoda or Chordata	N/A <sup>a</sup>	Rotifer
5. One insect family or any phylum not already represented	N/A	Midge
6. One planktonic crustacean	N/A	Cladoceran
7. One benthic crustacean	N/A	Amphipod
8. One insect	N/A	Stonefly

<sup>a</sup>N/A = Species not available.

**Table 10. Eight families of saltwater aquatic animals recommended by EPA (1985) for use in deriving the saltwater FAV, representative species for which captan acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. Two families in phylum Chordata	N/A <sup>a</sup>	Sheepshead minnow
2.	N/A	Longnose killifish
3. One family not in phylum Arthropoda or Chordata	N/A	Eastern oyster
4. Three other families not in phylum Chordata	Dungeness crab	-----
5.	N/A	Blue crab
6.	N/A	Grass shrimp
7. A mysid or penaeid	N/A	Mysid
8. One other family not already represented	N/A	Rotifer

<sup>a</sup>N/A = Species not available.

## Toxicity to Aquatic Plants

Six tests on the toxicity of captan to aquatic plants were evaluated (Appendix D) to derive a Final Plant Value (FPV). Five tests were accepted. The FPV is the lowest concentration of a pesticide that demonstrates a biologically important toxic endpoint (EPA 1985). The lowest biologically toxic endpoint for captan was an EC<sub>50</sub> value of 160 µg/L for alga *Skeletonema costatum* (Table D-1). The FPV for captan is 160 µg/L. Current data indicates that this fungicide is less toxic to aquatic plants than to freshwater aquatic animals. It is likely that freshwater criteria that will protect aquatic animals will also protect aquatic plants, but more data are necessary before this can be determined conclusively.

## Hazard Assessment

Acute captan toxicity data were available for only three of the eight freshwater and one of the eight saltwater taxa recommended by EPA (1985) (Tables 9 and 10). No toxicity values for freshwater invertebrates were available. This is too large of a data gap to justify calculating interim FAVs. Five additional acute toxicity tests using freshwater species such as those suggested in Table 9 are required to calculate freshwater criteria using EPA methods. Seven acute toxicity tests using saltwater species such as those suggested in Table 10 are required to determine saltwater criteria using EPA methods. In order to calculate freshwater and saltwater FCVs, paired acute-chronic tests are needed for fish and invertebrates. Calculation of the freshwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive freshwater species. Calculation of the saltwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive saltwater species.

No monitoring data were available for captan in the Sacramento-San Joaquin River System. Captan can be detected in water at concentrations as low as 0.5 µg/L (Cooper 1998). The reporting limit is probably sufficiently low to be able to indicate acute toxicity. However, no invertebrate toxicity values and chronic values were available. The adequacy of the reporting limit should be reconsidered when more toxicity values are available.

# CHLOROTHALONIL

## Use and Environmental Fate

Chlorothalonil is a nitrile compound used as a preventative fungicide on fruit, vegetables, ornamentals, and grasses. From 1990 to 1995, the reported use of chlorothalonil in California ranged from 511,462 to 1,152,441 pounds per year (Table 1) (DPR 1990-1995).

Chlorothalonil is relatively stable to hydrolysis with a hydrolysis half-life of 49 days (DPR 1994) (Table 2). Aerobic and anaerobic half-life values are 35 days and 8 days, respectively (DPR 1994). Chlorothalonil is almost insoluble in water (0.6 mg/L at 25°C) (EXTOXNET 1993). It is immobile in most soil types, but moderately mobile in sandy soil (EPA n.d.). Chlorothalonil's soil absorption coefficient ( $K_{oc}$ ) is 1,787 cm<sup>3</sup>/g (DPR 1994). Chlorothalonil is highly lipophilic, which would allow for rapid uptake and bioconcentration, but it has a low, estimated bioconcentration factor of 425 (Gallagher et al. 1992, EXTOXNET 1993).

The CDHS has not set an action level for chlorothalonil in drinking water (Milea 1998).

## Toxicity to Aquatic Animals

Twenty-three tests on the acute toxicity of chlorothalonil to aquatic animals were evaluated (Appendix B). Eighteen tests were accepted (Table B4) and five tests were not accepted (Table B9).

Genus Mean Acute Values (GMAVs) were calculated using data from accepted acute toxicity tests and were ranked in ascending order (Tables 11 and 12). Freshwater chlorothalonil GMAVs ranged from 21 µg/L for galaxiid fish *Galaxias spp.* to 64 µg/L for cladoceran *Daphnia magna*. Saltwater GMAVs ranged from 26 µg/L for eastern oyster *Crassostrea virginica* to 320 µg/L for pink shrimp *Penaeus duorarum*.

Table 11. Ranked Genus Mean Acute Values (GMAV) from accepted chlorothalonil acute toxicity tests on freshwater species.

Rank	GMAV (mg/L)	Organism	Genus and species
1	21 <sup>a</sup>	Galaxiid fish	<i>Galaxias auratus</i> (SMAV = 29) <i>G. maculatus</i> (SMAV = 16) <i>G. truttaceus</i> (SMAV = 19)
2	21 <sup>a</sup>	Rainbow trout	<i>Oncorhynchus mykiss</i>
3	52	Catfish	<i>Ictalurus punctatus</i>
4	55	Carp	<i>Cyprinus carpio</i>
5	62	Bluegill sunfish	<i>Lepomis macrochirus</i>
6	64 <sup>a</sup>	Cladoceran	<i>Daphnia magna</i>

<sup>a</sup> GMAV based on a geometric mean of more than one LC<sub>50</sub> or EC<sub>50</sub> for this species.

**Table 12. Ranked Genus Mean Acute Values (GMAV) from accepted chlorothalonil acute toxicity tests on saltwater species.**

Rank	GMAV (mg/L)	Organism	Genus and species
1	26	Oyster	<i>Crassostrea virginica</i>
2	32	Spot	<i>Leiostomus xanthurus</i>
3	320	Pink shrimp	<i>Penaeus duorarum</i>

The EPA (1985) guidelines recommend eight freshwater taxa for which data should be available to derive a freshwater Final Acute Value (FAV) and eight saltwater taxa to derive a saltwater FAV (Tables 13 and 14). Usually, the four lowest GMAVs are the most significant determinants in calculating a FAV. The four lowest freshwater GMAVs for chlorothalonil were for galaxiid fish *Galaxias* spp., rainbow trout *Oncorhynchus mykiss*, channel catfish *Ictalurus punctatus*, and carp *Cyprinus carpio*. The three lowest saltwater GMAVs for chlorothalonil were for oyster *Crassostrea virginica*, spot fish *Leiostomus xanthurus* and pink shrimp *Penaeus duorarum*. Acceptable data were available for only four of the freshwater and three of the saltwater taxa. Because of the lack of data, freshwater and saltwater FAV values were not calculated for chlorothalonil.

Due to the lack of chronic toxicity tests, chronic criteria were not calculated.

**Table 13. Eight families of freshwater aquatic animals recommended by EPA (1985) for use in deriving the freshwater FAV, representative species for which chlorothalonil acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. One Salmonid	Rainbow trout	-----
2. Another family in class Osteichthyes	Bluegill	-----
3. Another family in phylum Arthropoda or Chordata	Carp	-----
4. One family not in phylum Arthropoda or Chordata	N/A <sup>a</sup>	Rotifer
5. One insect family or any phylum not already represented	N/A	Midge
6. One planktonic crustacean	Cladoceran	-----
7. One benthic crustacean	N/A	Amphipod
8. One insect	N/A	Stonefly

<sup>a</sup>N/A = Species not available.

**Table 14. Eight families of saltwater aquatic animals recommended by EPA (1985) for use in deriving the saltwater FAV, representative species for which chlorothalonil acute toxicity data were available, and suggested species to provide the necessary data.**

<b>Family</b>	<b>Available Species</b>	<b>Suggested Species</b>
1. Two families in phylum Chordata	Spot	-----
2.	N/A <sup>a</sup>	Sheepshead minnow
3. One family not in phylum Arthropoda or Chordata	Eastern oyster	-----
4. Three other families not in phylum Chordata	Pink shrimp	-----
5.	N/A	Blue crab
6.	N/A	Grass shrimp
7. A mysid or penaeid	N/A	Mysid
8. One other family not already represented	N/A	Rotifer

<sup>a</sup>N/A = Species not available.

## **Toxicity to Aquatic Plants**

No data were available to analyze the toxicity of chlorothalonil to aquatic plants.

## **Hazard Assessment**

Acute chlorothalonil toxicity data were available for only four of the eight freshwater and three of the eight saltwater taxa recommended by EPA (1985) (Tables 13 and 14). This is too large of a data gap to justify calculating interim FAVs. Four additional acute toxicity tests using freshwater species such those suggested in Table 13 are required to calculate freshwater acute criteria using EPA methods. Five additional acute saltwater toxicity tests using saltwater species such as those suggested in Table 14 are required to determine saltwater criteria using EPA methods. In order to calculate freshwater and saltwater FCVs, paired acute-chronic tests are needed for fish and invertebrates. Calculation of the freshwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive freshwater species. Calculation of the saltwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive saltwater species.

Chlorothalonil has never been specifically monitored in the Sacramento-San Joaquin River system. However, in 1994, when monitoring for diazinon in the San Joaquin River, the USGS's test methods coincidentally detected chlorothalonil at 0.29 µg/L. There were no other detections during the remainder of 1994 (Dubrovsky 1998). Chlorothalonil concentrations can be quantified in water at concentrations as low as 0.10 - 0.48 µg/L, and the USGS has recently raised the reporting limit for chlorothalonil to 0.48 µg/L (Riggs 1998; Dubrovsky 1998). The reporting limit is sufficiently low to be able to indicate acute

toxicity. No chronic toxicity values were available; however, given the acute values, it is unlikely that chronic toxicity values are below the reporting limit.

## MANEB

### Use and Environmental Fate

Maneb is a carbamate compound used as a fungicide on vegetables, nuts, ornamentals, and grains. From 1990 to 1995, the reported use of maneb in California ranged from 354,023 to 1,632,259 pounds per year (Table 1) (DPR 1990-1995).

Maneb is unstable in the environment and degrades rapidly to ethylenethiourea (ETU) in water and soil (EXTOXNET 1993). Maneb degrades completely in water in one hour under anaerobic conditions (EXTOXNET 1993). Maneb's solubility in water is 7.0 mg/L at 25°C (Wauchope et al. 1992) (Table 2). Although maneb's half-life in soil is 60 days, it is unlikely to leach into groundwater because of high binding potential to soil and low solubility in water (EXTOXNET 1993). ETU does biodegrade, but is more stable and soluble in water and less binding to soil, and therefore may be more likely to leach and enter groundwater (EPA 1988). ETU degrades rapidly in soil under aerobic conditions, with a half-life of less than 2 days, but a half-life of up to 149 days under anaerobic conditions (EPA 1988).

The CDHS has not set an action level for maneb or ETU in drinking water (Milea 1998).

### Toxicity to Aquatic Animals

Thirteen tests on the acute toxicity of maneb to aquatic animals were evaluated (Appendix B). All tests were accepted (Table B5).

Genus Mean Acute Values (GMAVs) were calculated using data from accepted acute toxicity tests and were ranked in ascending order (Tables 15 and 16). Freshwater maneb GMAVs ranged from 330 µg/L for rainbow trout fry *Oncorhynchus mykiss* to 3,700 µg/L for guppy *Poecilia reticulata*. Saltwater GMAVs ranged from 110 µg/L for copepod *Nitocra spinipes*, to 3,800 µg/L for pink shrimp *Penaeus duorarum*.

Table 15. Ranked Genus Mean Acute Values (GMAV) from accepted maneb acute toxicity tests on freshwater species.

Rank	GMAV (mg/L)	Organism	Genus and species
1	330 <sup>a</sup>	Rainbow trout (fry)	<i>Oncorhynchus mykiss</i>
2	520	Freshwater fish (bleak)	<i>Alburnus alburnus</i>
3	1,000	Cladoceran	<i>Daphnia magna</i>
4	2,978 <sup>a</sup>	Rainbow trout (egg)	<i>Oncorhynchus mykiss</i>
5	3,700	Guppy	<i>Poecilia reticulata</i>

<sup>a</sup> GMAV based on a geometric mean of more than one LC<sub>50</sub> or EC<sub>50</sub> for this species.

**Table 16. Ranked Genus Mean Acute Values (GMAV) from accepted maneb acute toxicity tests on saltwater species.**

Rank	GMAV (mg/L)	Organism	Genus and species
1	110	Copepod	<i>Nitocra spinipes</i>
2	>1,000	Oyster	<i>Crassostrea virginica</i>
3	1,600	Killifish	<i>Fundulus similis</i>
4	3,800	Pink shrimp	<i>Penaeus duorarum</i>

The EPA (1985) guidelines recommend eight freshwater taxa for which data should be available to derive a freshwater Final Acute Value (FAV) and eight saltwater taxa to derive a saltwater FAV (Tables 17 and 18). Usually, the four lowest GMAVs are the most significant determinants in calculating a FAV. The four lowest freshwater GMAVs for maneb were for rainbow trout *Oncorhynchus mykiss* eggs, freshwater fish *Alburnus alburnus*, cladoceran *Daphnia magna*, and rainbow trout fry *O. mykiss*. The four lowest saltwater GMAVs for maneb were for copepod *Nitocra spinipes*, eastern oyster *Crassostrea virginica*, killifish *Fundulus similis*, and pink shrimp *Penaeus duorarum*. Acceptable maneb data were available for only four of the freshwater and four of the saltwater taxa. Because of the lack of data, freshwater and saltwater FAV values were not calculated for maneb.

No chronic toxicity tests were available for maneb.

**Table 17. Eight families of freshwater aquatic animals recommended by EPA (1985) for use in deriving the freshwater FAV, representative species for which maneb acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. One Salmonid	Rainbow trout	-----
2. Another family in class Osteichthyes	Freshwater fish (Bleak)	-----
3. Another family in phylum Arthropoda or Chordata	Guppy	-----
4. One family not in phylum Arthropoda or Chordata	N/A <sup>a</sup>	Rotifer
5. One insect family or any phylum not already represented	N/A	Midge
6. One planktonic crustacean	Cladoceran	-----
7. One benthic crustacean	N/A	Amphipod
8. One insect	N/A	Stonefly

<sup>a</sup>N/A = Species not available.

**Table 18. Eight families of saltwater aquatic animals recommended by EPA (1985) for use in deriving the saltwater FAV, representative species for which maneb acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. Two families in phylum Chordata	Longnose killifish	-----
2.	N/A <sup>a</sup>	Sheepshead minnow
3. One family not in phylum Arthropoda or Chordata	Eastern oyster	
4. Three other families not in phylum Chordata	Copepod	-----
5.	Pink shrimp	-----
6.	N/A	Dungeness crab
7. A mysid or penaeid	N/A	Mysid
8. One other family not already represented	N/A	Rotifer

<sup>a</sup>N/A = Species not available.

## Toxicity to Aquatic Plants

Three tests on the toxicity of maneb to aquatic plants were evaluated and one was accepted (Appendix D) to derive a Final Plant Value (FPV). The FPV is the lowest concentration of a pesticide that demonstrates a biologically important toxic endpoint (EPA 1985). The lowest biologically toxic endpoint for maneb was an EC<sub>50</sub> value of 3,200 µg/L for green alga *Chlorella pyrenoidosa* (Table D-1). The FPV for maneb is 3,200 µg/L. Current data indicates that this fungicide is generally less toxic to aquatic plants than to aquatic animals. It is likely that freshwater criteria that will protect aquatic animals will also protect aquatic plants, but more data are necessary before this can be determined conclusively.

## Hazard Assessment

Acute maneb toxicity data were available for only four of the eight freshwater and four of the eight saltwater taxa recommended by EPA (1985) (Tables 17 and 18). This is too large of a data gap to justify calculating interim FAVs. Four additional acute toxicity tests using freshwater species such as those suggested in Table 17 are required to calculate freshwater criteria using EPA methods. Four additional acute toxicity tests using saltwater species such those suggested in Table 18 are required to determine saltwater criteria using EPA methods. In order to calculate freshwater and saltwater FCVs, paired acute-chronic tests are needed for fish and invertebrates. Calculation of the freshwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive freshwater species. Calculation of the saltwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive saltwater species.

No monitoring data are available for maneb in the Sacramento-San Joaquin River system. Maneb can be detected in water in concentrations as low as 9 µg/L (Miller 1998). The reporting limit is sufficiently low to be able to indicate acute toxicity. As no chronic toxicity values were available it is not known whether the reporting limit is adequate to indicate chronic toxicity. Currently, there is one test method for maneb, which is non-specific. This method screens for a large group of chemicals and it remains problematic to distinguish between maneb and other similar compounds, such as ziram and mancozeb.

## ZIRAM

### Use and Environmental Fate

Ziram is a carbamate compound used as a fungicide on fruits, nuts and ornamentals. From 1990 to 1995, the reported use of ziram in California ranged from 934,671 to 2,028,905 pounds per year (Table 1) (DPR 1990-1995).

Ziram is toxic to bacteria, so biodegradation may be slow in soil (EXTOXNET 1993) (Table 2). Ziram's solubility is 18.3 mg/L in 20°C distilled water (ABC 1985). The photolysis  $t_{1/2}$  of ziram in aqueous solution is 7.84 days (ABC 1985). Hydrolysis  $t_{1/2}$  values at pH 5, 7, and 9 are 10.4 minutes, 17.67 hours, and 6.31 days, respectively (Piccirillo 1998).

The CDHS has not set an action level for ziram in drinking water (Milea 1998).

### Toxicity to Aquatic Animals

Fifteen tests on the acute toxicity of ziram to aquatic animals were evaluated (Appendix B). Eleven tests were accepted (Table B6) and four tests were not accepted (Tables B10).

Genus Mean Acute Values (GMAVs) were calculated using data from accepted acute toxicity tests and were ranked in ascending order (Tables 19 and 20). Freshwater ziram GMAVs ranged from 9.7 µg/L for bluegill sunfish *Lepomis macrochirus* to 1,700 µg/L for rainbow trout *Oncorhynchus mykiss*. Saltwater GMAVs ranged from >1,000 µg/L for eastern oyster *Crassostrea virginica* to 6,400 µg/L for longnose killifish *Fundulus similis*.

Table 19. Ranked Genus Mean Acute Values (GMAV) from accepted ziram acute toxicity tests on freshwater species.

Rank	GMAV (mg/L)	Organism	Genus and species
1	9.7	Bluegill sunfish	<i>Lepomis macrochirus</i>
2	40	Harlequin fish	<i>Rasbora heteromorpha</i>
3	82 <sup>a</sup>	Cladoceran	<i>Daphnia magna</i>
4	90	Guppy	<i>Lebistes reticulatus</i>
5	300	Goldfish	<i>Carassius auratus</i>
6	750	Guppy	<i>Poecilia reticulata</i>
7	1,700	Rainbow trout	<i>Oncorhynchus mykiss</i>

<sup>a</sup> GMAV based on a geometric mean of more than one LC<sub>50</sub> or EC<sub>50</sub> for this species.

Table 20. Ranked Genus Mean Acute Values (GMAV) from accepted ziram acute toxicity tests on saltwater species.

Rank	GMAV (mg/L)	Organism	Genus and species
1	>1,000	Oyster	<i>Crassostrea virginica</i>
2	>5,000	Pink shrimp	<i>Penaeus duorarum</i>
3	6,400	Longnose killifish	<i>Fundulus similis</i>

The EPA (1985) guidelines recommend eight freshwater taxa for which data should be available to derive a freshwater Final Acute Value (FAV) and eight saltwater taxa to derive a saltwater FAV (Tables 21 and 22). Usually, the four lowest GMAVs are the most significant determinants in calculating a FAV. The four lowest freshwater GMAVs for ziram were for bluegill *Lepomis macrochirus*, harlequin fish *Rasbora heteromorpha*, cladoceran *Daphnia magna*, and guppy *Lebistes reticulatus*. The three lowest saltwater GMAVs were for oyster *Crassostrea virginica*, pink shrimp *Penaeus duorarum*, and killifish *Fundulus similis*. Acceptable data were available for only four of the freshwater and three of the saltwater taxa. Because of the lack of data, freshwater and saltwater FAV values were not calculated for ziram.

No chronic tests were available for ziram.

**Table 21. Eight families of freshwater aquatic animals recommended by EPA (1985) for use in deriving the freshwater FAV, representative species for which ziram acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. One Salmonid	Rainbow trout	-----
2. Another family in class Osteichthyes	Bluegill	-----
3. Another family in phylum Arthropoda or Chordata	Guppy	-----
4. One family not in phylum Arthropoda or Chordata	N/A <sup>a</sup>	Rotifer
5. One insect family or any phylum not already represented	N/A	Midge
6. One planktonic crustacean	Cladoceran	-----
7. One benthic crustacean	N/A	Amphipod
8. One insect	N/A	Stonefly

<sup>a</sup>N/A = Species not available.

**Table 22. Eight families of saltwater aquatic animals recommended by EPA (1985) for use in deriving the saltwater FAV, representative species for which ziram acute toxicity data were available, and suggested species to provide the necessary data.**

Family	Available Species	Suggested Species
1. Two families in phylum Chordata	Longnose killifish	-----
2.	N/A <sup>a</sup>	Sheepshead minnow
3. One family not in phylum Arthropoda or Chordata	Eastern oyster	-----
4. Three other families not in phylum Chordata	Pink shrimp	-----
5.	N/A	Dungeness crab
6.	N/A	Grass shrimp
7. A mysid or penaeid	N/A	Mysid
8. One other family not already represented	N/A	Rotifer

<sup>a</sup>N/A = Species not available.

## Toxicity to Aquatic Plants

Three tests on the toxicity of ziram to aquatic plants were evaluated and one was accepted (Appendix D) to derive a Final Plant Value (FPV). The FPV is the lowest concentration of a pesticide that demonstrates a biologically important toxic endpoint (EPA 1985). The lowest biologically toxic endpoint for ziram was an EC<sub>50</sub> value of 1,200 µg/L for green alga *Chlorella pyrenoidosa* (Table D-1). The FPV for ziram is 1,200 µg/L. Current data indicates that this fungicide is generally less toxic to aquatic plants than to aquatic animals. It is likely that freshwater criteria that will protect aquatic animals will also protect aquatic plants, but more data are necessary before this can be determined conclusively.

## Hazard Assessment

Acute ziram toxicity data were available for only four of the eight freshwater and three of the eight saltwater taxa recommended by EPA (1985) (Tables 21 and 22). This is too large of a data gap to justify calculating interim FAVs. Four additional acute toxicity tests using freshwater species such as those suggested in Table 21 are required to calculate freshwater criteria using EPA methods. Five additional acute toxicity tests using saltwater species such as those suggested in Table 22 are required to determine saltwater criteria using EPA methods. In order to calculate freshwater and saltwater FCVs, paired acute-chronic tests are needed for fish and invertebrates. Calculation of the freshwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive freshwater species. Calculation of the saltwater FCV requires paired acute-chronic tests from a fish, an invertebrate, and an acutely sensitive saltwater species.

No monitoring data are available for ziram in the Sacramento-San Joaquin River system. Currently, there is one test method for ziram, which is non-specific. This method screens for a large group of chemicals and it remains problematic to distinguish between ziram and other similar compounds, such as maneb and mancozeb. Methods are currently being developed to more specifically detect ziram in water in concentrations of 0.3-0.6 µg/L (Wessmahr et al. in press). The reporting limit currently being developed may be sufficiently low and specific for ziram to be able to indicate acute toxicity. No chronic toxicity values were available, but it is possible that chronic toxicity values are lower than available reporting limits.

## CONCLUSION

Monitoring of the Sacramento-San Joaquin River system should be initiated to help assess hazards posed by benomyl, captan and chlorothalonil to aquatic species. Additional acute and chronic tests should be run on freshwater and saltwater species for all five fungicides (Tables 24 and 25). Once additional studies become available, the CDFG may reassess the hazards posed by these fungicides to aquatic species. Although current reporting limits or reporting limits currently being developed appear low enough to indicate acute toxicity of these fungicides, it is possible that reporting limits are inadequate to indicate chronic toxicity. Current laboratory methods do not distinguish clearly between ziram, maneb, and other closely related compounds. Monitoring for ziram and maneb should be postponed until more accurate test methods are available.

**Table 23. Summary of findings for benomyl, captan, chlorothalonil, maneb, and ziram.**

Fungicide	Lowest Freshwater GMAV or FAV	Lowest Saltwater GMAV or FAV	Reporting Limit	Current Monitoring Program?
Benomyl	41µg/L (GMAV) 17.5 (FAV) (6 species)	N/A (0 species)	1.0 µg/L	No
Captan	46 µg/L (GMAV) (3 species)	>10,000 µg/L (1 species)	0.5 µg/L	No
Chlorothalonil	21 µg/L (GMAV) (4 species)	26 µg/L (3 species)	0.48 µg/L	No (one detection of 0.29 µg/L)
Maneb	330 µg/L (GMAV) (4 species)	110 µg/L (4 species)	9.0 µg/L	No
Ziram	9.1 µg/L (GMAV) (4 species)	>1,000 µg/L (3 species)	developing for 0.3-0.6 µg/L	No

**Table 24. Summary of eight families of freshwater aquatic animals recommended by EPA (1985) for use in deriving the freshwater FAV, and suggested species to provide the necessary data.**

Family	Suggested Species	No Acceptable Tests Available For:
1. One Salmonid	Rainbow trout	-----
2. Another family in class Osteichthyes	Bluegill	-----
3. Another family in phylum Arthropoda or Chordata	Fathead minnow	-----
4. One family not in phylum Arthropoda or Chordata	Rotifer	Benomyl, Captan, Chlorothalonil, Maneb, Ziram
5. One insect family or any phylum not already represented	Midge	Benomyl, Captan, Chlorothalonil, Maneb, Ziram
6. One planktonic crustacean	Cladoceran	Captan
7. One benthic crustacean	Amphipod	Captan, Chlorothalonil, Maneb, Ziram
8. One insect	Stonefly	Captan, Chlorothalonil, Maneb, Ziram

**Table 25. Summary of eight families of saltwater aquatic animals recommended by EPA (1985) for use in deriving the saltwater FAV, and suggested species to provide the necessary data.**

<b>Family</b>	<b>Suggested Species</b>	<b>No Acceptable Tests Available For:</b>
1. Two families in phylum Chordata	Sheepshead minnow	Benomyl, Captan, Chlorothalonil, Maneb, Ziram
2.	Longnose killifish	Benomyl, Captan
3. One family not in phylum Arthropoda or Chordata	Eastern oyster	Benomyl, Captan
4. Three other families not in phylum Chordata	Dungeness crab	Benomyl, Maneb, Ziram
5.	Blue crab	Benomyl, Captan, Chlorothalonil
6.	Grass shrimp	Benomyl, Captan, Chlorothalonil, Ziram
7. A mysid or penaeid	Mysid	Benomyl, Captan, Chlorothalonil, Maneb, Ziram
8. One other family not already represented	Rotifer	Benomyl, Captan, Chlorothalonil, Maneb, Ziram

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## APPENDIX A. Procedure Used By the California Department of Fish and Game to Prepare Hazard Assessments.

The California Department of Fish and Game (CDFG) Pesticides Investigations Unit assesses the hazard of pesticides to aquatic organisms. The hazard assessment procedure includes evaluation of toxicity studies, establishment of the Water Quality Criterion (WQC) and assessment of potential hazards.

Acute and chronic toxicity data are obtained from studies published in scientific literature and laboratory reports required by the U.S. Environmental Protection Agency for pesticide registration. The CDFG evaluates the quality of these data by evaluating the tests for compliance with standards (ASTM 1988, 1992) for test type, method, design, species and for water quality standards and toxicant monitoring and maintenance. Although a study need not comply with every standard, tests are rejected if they do not observe certain fundamental procedures or if several important standards are not met. Studies are also rejected if they do not contain sufficient information to be properly evaluated and the necessary information cannot be obtained from the researcher.

Acute toxicity data from acceptable tests on freshwater and saltwater organisms are used to determine a Final Acute Value (FAV). The EPA (1985) guidelines recommend eight categories of saltwater organisms for deriving freshwater and saltwater FAVs. Generally, these categories of organisms are available, commonly used, and testing procedures are outlined

The FAV is calculated as follows:

1. Species Mean Acute Values (SMAV) are calculated as the geometric mean of LC<sub>50</sub> and EC<sub>50</sub> values from all accepted toxicity tests performed on that species.
2. Genus Mean Acute Values (GMAV) are calculated as the geometric mean of all SMAVs for each genus.
3. The GMAVs are ranked (R) from "1" for the lowest to "N" for the highest. Identical GMAVs are arbitrarily assigned successive ranks.
4. The cumulative probability (P) is calculated for each GMAV as R/ (N+1).
5. The four GMAVs with cumulative probabilities closest to 0.05 are selected. If fewer than 59 GMAVs are available, these will always be the four lowest GMAVs.
6. The FAV is calculated using the selected GMAVs and cumulative probabilities (P), as follows:

$$S^2 = \frac{G [ (\ln \text{GMAV}^2) ] - [ (G (\ln \text{GMAV}) )^2/4]}{G (P) - [ (G (\%P) )^2/4]}$$

$$G (P) - [ (G (\%P) )^2/4]}$$

$$L = [G (\ln \text{GMAV}) - S (G (\%P) ) ]/4$$

$$A = S (\%0.05) + L$$

$$\text{FAV} = e^A$$

Chronic toxicity data from acceptable tests on freshwater and saltwater organisms are used to determine a Final Chronic Value (FCV). If data are available for the eight families, the FCV is calculated using the same procedure as described for the FAV. If sufficient data are not available, the following procedure is used:

1. Chronic values are obtained by calculating the geometric mean of the NOEC and the LOEC values from accepted chronic toxicity tests.
2. Acute-Chronic ratios (ACR) are calculated for each chronic value for which at least one corresponding acute value is available. Whenever possible, the acute test (s) should be part of the same study as the chronic test.
3. The Final ACR (FACR) is calculated as the geometric mean of all mean ACRs available for both freshwater and saltwater species.
4.  $\text{FCV} = \text{FAV} / \text{FACR}$ .

Plant toxicity data from algae or aquatic vascular plants are used to determine a Final Plant Value (FPV). The FPV is the lowest result from a test with a biologically important endpoint.

The EPA guidelines specify that a WQC consists of two concentrations, the Criterion Maximum Concentration (CMC) and the Criterion Continuous Concentration (CCC). The CMC is equal to one-half the FAV. The CCC is equal to the lowest of three values: the FCV, the FPV, or the Final Residue Value (FRV). The FRV is intended to prevent pesticide concentrations in recreational or commercially important species from affecting marketability because of exceedence of applicable action levels and to protect important resident species (EPA 1985).

The WQC is stated as follows: (freshwater / saltwater) aquatic organisms should not be affected unacceptably if the four-day average concentration of (pesticide) does not exceed (CCC value) and if the one-hour average concentration does not exceed (CMC value) more than once every three years on the average (EPA 1985).

Hazard assessment is an iterative process by which new data are evaluated to refine the WQC. Hazard assessments frequently recommend additional toxicity tests with sensitive native species and commonly used test organisms listed by ASTM.

## APPENDIX B. Abstracts of Accepted and Unaccepted Acute Toxicity Tests Reviewed for Hazard Assessment.

**Accepted acute toxicity tests-** The following tests used accepted test methods.

Caldwell (1977) – From 1973 to 1974, 96-h acute static toxicity tests were conducted by the U.S. Environmental Protection Agency with technical grade captan on first instar zoeae, first instar juvenile, and adult dungeness crab *Cancer magister*. Six concentrations were tested in duplicate and water and acetone controls were used. Water quality parameters were: dissolved oxygen at air saturation; temperature of  $13 \pm 1^\circ\text{C}$ ; pH of 7.5-7.8; and salinity of  $25 \pm 0.5$  ‰. The 96-h LC<sub>50</sub> values for *C. magister* were >10,000 µg/L for zoeae, >10,000 µg/L for juveniles, and >100,000 µg/L for adults.

Davies and White (1985) - In 1985, 96-h acute flow-through and acute static toxicity tests were conducted by the Fish Research Group, University of Tasmania, Australia, with chlorothalonil (99%) on rainbow trout *Oncorhynchus mykiss*, common jollytail *Galaxias maculatus*, spotted galaxias *G. truttaceus*, and golden galaxias *G. auratus*. One low-oxygen test was conducted with *O. mykiss* to simulate trout pond conditions during elevated temperatures and restricted water flow. *O. mykiss* was acclimated for three to four days at the low oxygen level. All galaxiids were caught by electrofishing but were acclimated for seven to ten days. Acetone controls were used. Water quality parameters during the flow-through tests were: dissolved oxygen of 8-9 mg/L and temperature of 13-16°C. Water quality parameters during the static tests were: dissolved oxygen of 9 mg/L and temperature of 10°C. Water quality parameters during the low-oxygen flow-through tests on *O. mykiss* were: dissolved oxygen of 5.12 mg/L and temperature of 16°C. Control survival was not reported but a probit program was used to calculate the LC<sub>50</sub> values. The 96-h LC<sub>50</sub> values for *O. mykiss* were 18, 17.1, 14.3 and 10.5 (low oxygen) µg/L. The 96-h LC<sub>50</sub> values were 16.3 µg/L for *G. maculatus*, 18.9 µg/L for *G. truttaceus*, and 29.2 µg/L for *G. auratus*.

Douglas et al. (1991a) - In 1989, a 96-h acute static toxicity test was conducted by Huntingdon Research Centre, Cambridgeshire, England with ziram (98.9%) on rainbow trout *Oncorhynchus mykiss*. Five concentrations were tested in duplicate and water and acetone controls were used. Water quality parameters during the test were: dissolved oxygen of 10 mg/L; temperature of 13°C; and pH of 7.6-7.9. Control survival was 100% and mortality range was acceptable. The 96-h LC<sub>50</sub> for *O. mykiss* was 1,700 µg/L.

Douglas et al. (1991b) - In 1990, a 96-h acute flow-through toxicity test was conducted by Huntingdon Research Centre, Cambridgeshire, England with ziram (98.9%) on bluegill sunfish *Lepomis macrochirus*. Five concentrations were tested in duplicate and water and acetone controls were used. Water quality parameters during the test were: dissolved oxygen of 8.6-8.8 mg/L; temperature of 21°C; pH of 7.5-7.7; and hardness of

350 mg/L as CaCO<sub>3</sub>. Control survival was 100% and mortality range was acceptable. The 96-h LC<sub>50</sub> for *L. macrochirus* was 9.7 µg/L.

Douglas et al. (1991c) - In 1990, a 48-h acute static toxicity test was conducted by Huntingdon Research Centre, Cambridgeshire, England with ziram (98.9%) on first instar cladoceran *Daphnia magna*. Eleven concentrations were tested in duplicate and water and acetone controls were used. Water quality parameters during the test were: dissolved oxygen of 8.6-8.9 mg/L; temperature of 21°C; and pH of 8. Control survival was 100% and mortality range was acceptable. The 48-h EC<sub>50</sub> for *D. magna*, based on immobilization, was 480 µg/L.

Douglas et al. (1992a) - In 1991, a 96-h acute flow-through toxicity test was conducted by Huntingdon Research Centre, Cambridgeshire, England with chlorothalonil (99.18%) on rainbow trout *Oncorhynchus mykiss*. Five concentrations were tested and water and acetone controls were used. Water quality parameters during the test were: dissolved oxygen of 10-10.1 mg/L; temperature of 14 ± 1°C; pH of 7.1; and hardness of 150-200 mg/L as CaCO<sub>3</sub>. Control survival was 100% and mortality range was acceptable. The 96-h LC<sub>50</sub> for *O. mykiss* was 12 µg/L.

Douglas et al. (1992b) - In 1991, a 96-h acute flow-through toxicity test was conducted by Huntingdon Research Centre, Cambridgeshire, England with chlorothalonil (99.18%) on common carp *Cyprinus carpio*. Five concentrations were tested and water and acetone controls were used. Water quality parameters during the test were: dissolved oxygen of 8.7 mg/L; temperature of 21°C; pH of 7.4; and hardness of 150-200 mg/L as CaCO<sub>3</sub>. Control survival was 100% and mortality range was acceptable. The 96-h LC<sub>50</sub> for *C. carpio* was 55 µg/L.

Douglas et al. (1992c) - In 1991, a 48-h acute static toxicity test was conducted by Huntingdon Research Centre, Cambridgeshire, England with chlorothalonil (99.18%) on first instar cladoceran *Daphnia magna*. Nine concentrations were tested in duplicate and water and acetone controls were used. Water quality parameters during the test were: dissolved oxygen of 8.3-8.6 mg/L; temperature of 21 ± 1°C; and pH of 7.1-7.2. Control survival was 100% and mortality range was acceptable. The 48-h EC<sub>50</sub> for *D. magna*, based on immobilization, was 59 µg/L.

EG&G Bionomics (1977) - In 1977, a 48-h acute static toxicity test was conducted by EG&G Bionomics Aquatic Toxicology Laboratory, Wareham, Massachusetts with chlorothalonil (96%) on <24-h cladoceran *Daphnia magna*. Five concentrations were tested in triplicate and water and acetone controls were used. Water quality parameters during the test were: dissolved oxygen of above 60% saturation; temperature of 22 ± 1°C; pH of 7.2; and hardness of 60 mg/L as CaCO<sub>3</sub>. Control survival was 100% and mortality range was acceptable. The 48-h LC<sub>50</sub> for *D. magna* was 70 µg/L.

EG&G Bionomics (1980a) - In 1979, a 96-h acute static toxicity test was conducted by EG&G Bionomics Aquatic Toxicology Laboratory, Wareham, Massachusetts with <24-h chlorothalonil (96%) on year-old bluegill *Lepomis macrochirus*. Seven concentrations were tested and water and acetone controls were used. Water quality parameters during the test were: temperature of  $22 \pm 1^\circ\text{C}$ ; pH of 7.7; and hardness of 44 mg/L as  $\text{CaCO}_3$ . Control survival was 100% for water and 90% for acetone. Mortality range was acceptable. The 96-h  $\text{LC}_{50}$  for *L. macrochirus* was 60  $\mu\text{g/L}$ .

EG&G Bionomics (1980b) - In 1979, a 96-h acute static toxicity test was conducted by EG&G Bionomics Aquatic Toxicology Laboratory, Wareham, Massachusetts with chlorothalonil (96%) on rainbow trout *Oncorhynchus mykiss*. Seven concentrations were tested in replicate and water and acetone controls were used. Water quality parameters during the test were: temperature of  $12 \pm 1^\circ\text{C}$ ; pH of 6.5-6.9; and hardness of 44 mg/L as  $\text{CaCO}_3$ . Control survival was 100% and mortality range was acceptable. The 96-h  $\text{LC}_{50}$  for *O. mykiss* was 47  $\mu\text{g/L}$ .

Ernst et al. (1991) – In 1991, a 96-h acute static toxicity test was conducted by Environment Canada, Nova Scotia, Canada with chlorothalonil (97.8%) on fingerling rainbow trout *Oncorhynchus mykiss*. Four concentrations were tested and water and acetone controls were used. Water quality parameters during the tests were: dissolved oxygen of 8.4 to 11.2 mg/L; temperature of  $12.5\text{-}15.5^\circ\text{C}$ ; pH of 6.5-7.4; and hardness of  $12.3 \pm 3.06$  mg/L as  $\text{CaCO}_3$ . Control survival was 100%. The 96-h  $\text{LC}_{50}$  value for *O. mykiss* was 76  $\mu\text{g/L}$ .

Gallagher et al. (1992), Gallagher (pers. comm.) – In 1992, a 96-h acute static toxicity test was conducted by Ecotoxicology Laboratory, Duke University, Durham, North Carolina with chlorothalonil (99%) on juvenile channel catfish *Ictalurus punctatus*. Five concentrations were tested and an acetone control was used. Water quality parameters during the test were: dissolved oxygen of 5-6 mg/L; temperature of  $23^\circ\text{C}$ ; pH of 7.0-7.2; and hardness of 30 mg/L as  $\text{CaCO}_3$ . Control survival was 100% and mortality range was acceptable. The 96-h  $\text{LC}_{50}$  for *I. punctatus* was 52  $\mu\text{g/L}$ .

Johnson and Finley (1980) – Between 1965 and 1978, 96-h acute static toxicity tests were conducted by the Columbia National Fisheries Research Laboratory of the U.S. Fish and Wildlife Service, Columbia, Missouri with the carbendazim metabolite of benomyl (99%) on rainbow trout *Oncorhynchus mykiss* and channel catfish *Ictalurus punctatus*. At least six concentrations were tested. Water quality parameters during the test were: temperature of  $12^\circ\text{C}$  for *O. mykiss* and  $22^\circ\text{C}$  for *I. punctatus*; pH of 7.2-7.5; and hardness of 40-50 mg/L as  $\text{CaCO}_3$ . The 96-h  $\text{LC}_{50}$  values were 370  $\mu\text{g/L}$  for *O. mykiss* and 16  $\mu\text{g/L}$  for *I. punctatus*.

Linden et al. (1979) – In 1979, 96-h acute static toxicity tests were conducted by the Brackish Water Toxicology Laboratory, Sweden with maneb (85%) on the freshwater fish (bleak) *Alburnus alburnus* and adult copepod *Nitocra spinipes*. At least six

concentrations were tested and controls were used. Water quality parameters during the tests were: dissolved oxygen of 5 mg/L; temperature of 10°C; pH of 7.8; and salinity of 7 ‰. Control survival was not reported but the Litchfield and Wilcoxon (1949) method was used to calculate the LC<sub>50</sub> values. The 96-h LC<sub>50</sub> for *A. alburnus* was 520 µg/L and for *N. spinipes* was 110 µg/L.

Mayer (1987) - From 1961 to 1986, 48-h and 96-h flow-through and static toxicity tests were performed by the Environmental Research Laboratory of the U.S. Environmental Protection Agency, Gulf Breeze, Florida with technical grade chlorothalonil, maneb and ziram on juvenile pink shrimp *Penaeus duorarum*, juvenile eastern oyster *Crassostrea virginica*, juvenile spot *Leiostomus xanthurus* and juvenile longnose killifish *Fundulus similis*. Water quality parameters during the test were: temperature of 20-24°C for *P. duorarum*; 13, 15, and 29°C for *C. virginica*; 11°C for *L. xanthurus*; and 21°C for *F. similis*; and salinity of 27 ‰ for *P. duorarum*; 16, 22, and 27 ‰ for *C. virginica*; 22 ‰ for *L. xanthurus*; and 30 ‰ for *F. similis*. EC<sub>50</sub> effect criteria for *C. virginica* was shell deposition and for *P. duorarum* was immobility. Although control survival and concentrations tested were not given, these tests were accepted because they were deemed acceptable by the EPA. The 96-h and 48-h LC<sub>50</sub> and EC<sub>50</sub> values for these species are listed in tables B-4, B-5 and B-6.

Mayer and Ellersieck (1986) – From 1965 to 1985, 48-h and 96-h acute static toxicity tests were conducted by the Columbia National Fisheries Research Laboratory of the U.S. Fish and Wildlife Service, Columbia, Missouri with benomyl (99%) and captan (90%). The species tested were: cladoceran *Daphnia magna*, amphipod *Gammarus pseudolimnaeus*, crayfish *Orconectes nais* and *Procambarus sp.*, midge *Chironomus plumosus*, rainbow trout *Oncorhynchus mykiss*, fathead minnow *Pimephales promelas*, channel catfish *Ictalurus punctatus*, bluegill *Lepomis macrochirus*, coho salmon *Oncorhynchus kisutch*, chinook salmon *Oncorhynchus tshawytscha*, cutthroat trout *Oncorhynchus clarki*, brown trout *Salmo trutta*, lake trout *Salvelinus namaycush*, and yellow perch *Perca flavescens*. Four or more concentrations were tested in replicate and acetone controls were used. Water quality parameters during the tests are listed in Tables B-1 and B-2. Control survival was acceptable in all tests. The 96-h LC<sub>50</sub> values for these species are listed in Tables B-1 and B-3.

Montedison USA (1977) – In 1977, 96-h acute static toxicity tests were conducted by Montedison USA, Agriculture Division, New York, New York with technical grade ziram on harlequin fish *Rasbora heteromorpha*, guppy *Lebistes reticulatus* and goldfish *Carassius auratus*. The testing temperature was 20-22 °C. Control survival and mortality range was acceptable. The 96-h LC<sub>50</sub> values were 40 µg/L for *R. heteromorpha*, 90 µg/L for *L. reticulatus*, and 300 µg/L for *C. auratus*.

Palawski and Knowles (1986) – In 1985, 96-h acute static toxicity tests were conducted by the Columbia National Fisheries Research Laboratory of the U.S. Fish and Wildlife Service, Columbia, Missouri with technical grade benomyl (99%) on channel catfish

*Ictalurus punctatus* and fingerling rainbow trout *Oncorhynchus mykiss*. The carbendazim metabolite of benomyl (99%) was used on fingerling channel catfish *I. punctatus*, fingerling rainbow trout *O. mykiss* and bluegill fry *Lepomis macrochirus*. Four series of acute toxicity tests were conducted to evaluate the effects of temperature, pH, water hardness and life stage on the toxicity of benomyl and its metabolite carbendazim. Some of these toxicity tests with benomyl on *O. mykiss* and *L. macrochirus* are reported in Mayer and Ellersieck (1986). Four or more concentrations were tested in replicate and acetone controls were used. Water quality parameters are given in Tables B-1 and B-2. Control survival was not reported but the Litchfield and Wilcoxon (1949) method was used to calculate the LC<sub>50</sub> values. The 96-h LC<sub>50</sub> values for these tests are listed in Tables B-1 and B-2.

Van Leeuwen et al. (1985a) – In 1985, 96-h and 48-h acute static toxicity tests were conducted by the Laboratory for Ecotoxicology, Government Institute for Sewage and Waste Water Treatment, Lelystad, Netherlands with maneb and ziram (>90%) on guppy *Poecilia reticulata* and cladoceran *Daphnia magna*. Control survival was not reported, but the Litchfield and Wilcoxon (1949) method was used to calculate the LC<sub>50</sub> values. The maneb 96-h LC<sub>50</sub> was 3,700 µg/L for *P. reticulata* and the 48-h LC<sub>50</sub> was 1,000 µg/L for *D. magna*. The ziram 96-h LC<sub>50</sub> was 750 µg/L for *P. reticulata* and the 48-h LC<sub>50</sub> was 140 µg/L for *D. magna*.

Van Leeuwen et al. (1985b) – In 1985, 96-h acute static toxicity tests were conducted by the Laboratory for Ecotoxicology, Government Institute for Sewage and Waste Water Treatment, Lelystad, Netherlands with maneb (< 90%) on rainbow trout *Oncorhynchus mykiss*. Tests on fertilized eggs, early-eyed eggs, late-eyed eggs, sac fry and early fry were conducted in duplicate. Water quality parameters during the tests were: pH of 7.2 and hardness of 50 mg/L as CaCO<sub>3</sub>. Control survival was not reported but the Litchfield and Wilcoxon (1949) method was used to calculate the LC<sub>50</sub> values. The 96-h LC<sub>50</sub> values were 6,000 µg/L for fertilized eggs at 0-h, 5,600 µg/L for fertilized eggs at 24-h, 1,800 µg/L for early-eyed eggs, 1,300 µg/L for late-eyed eggs, 320 µg/L for sac fry, and 340 µg/L for early fry.

**Unaccepted acute toxicity tests-** The following tests did not use accepted test methods and/or produce acceptable results.

Abedi and McKinley (1967) – In 1967, a 90-minute acute static toxicity test was conducted by the Department of National Health and Welfare, Ottawa, Canada with captan (percent active ingredient not given) on larval zebrafish *Brachydanio rerio*. An unknown number of concentrations were tested and an acetone control was used. Water quality parameters were not given. Control survival was 100%. The 90-minute LC<sub>50</sub> for *B. rerio* was 670 µg/L. This value was not used because the test duration was too short and the percent active ingredient and number of concentrations tested were not given.

Analytical Bio Chemistry Laboratories (1980) – In 1980, a 48-h acute static toxicity test was conducted by Analytical Bio Chemistry Laboratories, Columbia, Missouri with technical grade captan on cladoceran *Daphnia magna*. Two concentrations were tested in triplicate and water and acetone controls were used. Water quality parameters during the test were: temperature of 20 ± 1 °C; pH of 8.2; and hardness of 255 mg/L as CaCO<sub>3</sub>. Control survival was 100%. As there was no mortality in the treatments at the end of the test, the EC<sub>50</sub> for *D. magna* was estimated to be greater than the mean measured concentration of 7.1 mg/L. This test was not used because no EC<sub>50</sub> value was given, too few concentrations were tested, and the mortality range was unacceptable.

Anton et al. (1990) – In 1990, 48-h and 72-h acute static toxicity tests were conducted by the Soil Science and Plant Biology Institute of CSIC, Madrid, Spain, with captan (60.2%) on adult earthworms *Eisenia foetida*. Nine concentrations were tested in replicate and water and acetone controls were used. Earthworms were submerged in a suspension of known doses of pesticides for thirty minutes, then washed with distilled water and placed in petri dishes for the remainder of the test. The 48-h LC<sub>50</sub> for *E. foetida* was 12,120,890 µg/L and the 72-h LC<sub>50</sub> was 6,814,670 µg/L. These values were not used because the percent active ingredient was less than 90% and the test organisms were not continuously exposed to the pesticide for the duration of the test.

Anton et al. (1993) – In 1993, 96-h acute static toxicity tests were conducted by the Ecotoxicology Group, Spanish Council for Scientific Research, Madrid, Spain with captan (60.2%) on goldfish *Carassius auratus*. An unknown number of concentrations were tested and water controls were used. Water quality parameters during the test were a temperature of 20 ± 1°C. The 96-h LC<sub>50</sub> for *C. auratus* was 1,340 µg/L. This value was not used because the percent active ingredient was less than 90%, and the number of concentrations tested were not given.

Clemens and Sneed (1959) – In 1959, 96-h acute static toxicity tests were conducted by the University of Oklahoma Research Institute, Norman, Oklahoma with ziram (76%) on fingerling channel catfish *Ictalurus punctatus*. The 96-h LC<sub>50</sub> for *I. punctatus* was 500 µg/L. This value was not used because the percent active ingredient was less than 90%.

Ernst et al. (1991) – In 1991, 96-h acute static toxicity tests were conducted by Environment Canada, Nova Scotia, Canada with chlorothalonil (40%) on fingerling rainbow trout *Oncorhynchus mykiss*, threespine stickleback *Gasterosteus aculeatus*, blue mussel *Mytilus edulis*, cladoceran *Daphnia magna* and clam *Mya arenaria*. Four concentrations were tested and water and acetone controls were used. Water quality parameters during the *O. mykiss* tests were: dissolved oxygen of 8.4-11.2 mg/L; temperature of 12.5-15.5°C; pH of 6.5-7.4; and hardness of 12.3 ± 3.06 mg/L as CaCO<sub>3</sub>. Water quality parameters during the *G. aculeatus* tests were: temperature of 9-10°C and pH of 7.7-8.0. Water quality parameters during the *M. edulis* and *M. arenaria* tests were: dissolved oxygen of 8.5-9.9 mg/L; temperature of 10.5-12°C; and pH of 7.3-8. Water quality parameters during the *D. magna* tests were: dissolved oxygen of 9.1-9.3 mg/L; temperature of 20-22°C; pH of 7.8; and hardness of 250 ± 25 mg/L as CaCO<sub>3</sub>. Control survival was 100% in all tests. The 96-h LC<sub>50</sub> values were 69 µg/L for *O. mykiss*, >73 µg/L for *G. aculeatus*, 5,940 µg/L for *M. edulis*, and 34,780 µg/L for *M. arenaria*. The 48-h EC<sub>50</sub> for *D. magna* was 97 µg/L. These values were not used because the percent active ingredient was less than 90%.

Frear and Boyd (1967) – From 1955 to 1960, 26-h acute static toxicity tests were conducted by the Pesticide Research Laboratory, Department of Entomology, Pennsylvania State University with captan and ziram (percent active ingredient not given) on 24-h cladoceran *Daphnia magna*. Four concentrations were tested with 10 replicates each and an acetone control was used. During the test, the temperature was held constant and the water was aerated. The 26-h LC<sub>50</sub> for *D. magna* was 1,300 µg/L for captan and 16 µg/L for ziram. These values were not used because the test duration was too short and the percent active ingredient and control survival were not given.

Graves and Swigert (1993a) – In 1992, a 96-h acute flow-through toxicity tests were conducted by E.I. Du Pont De Nemours & Co., Wilmington, Delaware, with benomyl (50%) on eastern oyster *Crassostrea virginica*. Five concentrations were tested in replicate and water and solvent controls were used. Water quality parameters during the test were: temperature of 21.6-21.9°C; pH of 7.7-7.9; and salinity of 25 ‰. Control survival was 100%. The 96-h EC<sub>50</sub> for *C. virginica*, based on inhibition of shell growth, was >80 µg/L. This value was not used because the percent active ingredient was less than 90%.

Graves and Swigert (1993b) – In 1993, a 96-h acute static toxicity tests were conducted by E.I. Du Pont De Nemours & Co., Wilmington, Delaware, with benomyl (50%) on juvenile sheepshead minnow *Cyprinodon variegatus*. Seven concentrations of benomyl were tested with two replicates per treatment and water and solvent control were used. Water quality parameters during the test were: dissolved oxygen of 7.2-7.3 mg/L; temperature of 22.1-22.9°C; pH of 7.4-7.8; and salinity of 25 ‰. The 96-h LC<sub>50</sub> for *C. variegatus* was 26,000 µg/L. This value was not used because the percent active ingredient was less than 90% and control survival was not given.

Hermanutz et al. (1973) – In 1972, 96-h acute static and flow-through toxicity tests were conducted by the National Water Quality Laboratory of the U.S. Environmental Protection Agency, Duluth, Minnesota, with captan (1.94%) on fathead minnow *Pimephales promelas*, bluegill *Lepomis macrochirus*, and brook trout *Salvelinus fontinalis*. Five concentrations were tested in duplicate and controls were used. Water quality parameters during the tests were: dissolved oxygen of >7.2 mg/L; temperature of 24.9°C; pH of 7.5; and hardness of 45.1 mg/L as CaCO<sub>3</sub>. No clear results were found for the static toxicity tests. For the flow-through tests, the 96-h LC<sub>50</sub> values were 65 µg/L for *P. promelas*, 72 µg/L for *L. macrochirus*, and 34 µg/L for *S. fontinalis*. These values were not used because the percent active ingredient was less than 90%, control survival was not given and no LC<sub>50</sub> values were given.

Holland et al. (1960) – In 1960, 72-h acute static toxicity tests were conducted by the Washington State Department of Fisheries, Olympia, Washington with captan (50%) on rainbow trout *Oncorhynchus mykiss*. Five concentrations were tested and controls were used. Water quality parameters during the tests were: dissolved oxygen of 9.8-9.9 mg/L; temperature of 49-55.5°F; and pH of 7.7-7.8. The 72-h LOEC value for *O. mykiss* was 320 µg/L and 560 µg/L. These values were not used because control survival was not given, the percent active ingredient was less than 90%, and the test duration was too short.

Linden et al. (1979) – In 1979, 96-h acute static toxicity tests were conducted by the Brackish Water Toxicology Laboratory, Sweden with the benomyl metabolite carbendazim (2.5%) and ziram (22.5%), on the freshwater fish (bleak) *Alburnus alburnus* and adult copepod *Nitocra spinipes*. At least six concentrations were tested and controls were used. Water quality parameters during the tests were: dissolved oxygen of 5 mg/L; temperature of 10°C, pH of 7.8; and salinity of 7 ‰. Control survival was not reported but the Litchfield and Wilcoxon (1949) method was used to calculate the LC<sub>50</sub> values. The combined carbendazim and ziram 96-h LC<sub>50</sub> values for *A. alburnus* were 3,000 to 4,000 µg/L and for *N. spinipes* was 400 µg/L. These values were not used because the percent active ingredient was less than 90% and carbendazim and ziram were tested together in a combined formulation.

Mayer and Ellersieck (1986) - From 1965 to 1985, 96-h acute static toxicity tests were conducted by the Columbia National Fisheries Research Laboratory of the U.S. Fish and Wildlife Service, Columbia, Missouri with benomyl (50%). The species tested were: rainbow trout *Oncorhynchus mykiss*, fathead minnow *Pimephales promelas*, channel catfish *Ictalurus punctatus*, and bluegill *Lepomis macrochirus*. Four or more concentrations were tested in replicate and acetone controls were used. Water quality parameters during the are given in Table B-1. Control survival was acceptable in all tests. The 96-h LC<sub>50</sub> values were 310 µg/L for *O. mykiss*, 1,900 µg/L for *P. promelas*, 27.5 µg/L for *I. punctatus* and 1,200 µg/L for *L. macrochirus*. These values were not used because the percent active ingredient was less than 90%.



**Table B-1. Values (mg/L) from accepted tests on the acute toxicity of benomyl to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Salinity/ Hardness <sup>b</sup>	Effect	Values (95% C.L.)	Reference
Amphipod <i>Gammarus pseudolimnaeus</i>	mature	99%	static	96-h	40 mg/L	LC <sub>50</sub>	750 (500-1,100)	Mayer and Ellersieck 1986
Bluegill <i>Lepomis macrochirus</i>	0.9 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	850 (550-1,300)	Mayer and Ellersieck 1986
	0.9 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	560 (410-750)	
	0.9 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	750 (560-1,010)	
	0.9 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	1,300 (960-1,760)	
	0.9 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	1,300 (950-1,780)	
	0.6 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	1,300 (1,000-1,680)	
	0.6 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	1,200 (829-1,736)	
	0.6 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	6,400 (4,185-9,787)	
	0.6 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	1,300 (964-1,752)	
	0.6 g	99%	static	96-h	320 mg/L	LC <sub>50</sub>	2,300 (1,702-3,107)	
	0.8 g	99%	static	96-h	40 mg/L	LC <sub>50</sub>	390 (207-732)	
Channel catfish <i>Ictalurus punctatus</i>	1.20 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	29 (22-37)	Mayer and Ellersieck 1986
	fingerling	99%	static	96-h	44 mg/L	LC <sub>50</sub>	13 (11-15)	
	fry	99%	static	96-h	44 mg/L	LC <sub>50</sub>	24 (19-29)	Palawski and Knowles 1986
	swimup fry	99%	static	96-h	44 mg/L	LC <sub>50</sub>	12 (8.8-16.4)	
	yolk-sac fry	99%	static	96-h	44 mg/L	LC <sub>50</sub>	5.6 (4.6-6.8)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	720 (569-910)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	120 (77-186)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	44 (33-58)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	42 (35-40)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	56 (40-78)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	76 (60-96)	
	fingerling	99%	static	96-h	40 mg/L	LC <sub>50</sub>	47 (36-61)	
	fingerling	99%	static	96-h	320 mg/L	LC <sub>50</sub>	43 (30-62)	
Cladoceran <i>Daphnia magna</i>	1 <sup>st</sup> instar	99%	static	48-h	40 mg/L	EC <sub>50</sub>	2,800 (2,100-3,700)	Mayer and Ellersieck 1986
Crayfish <i>Orconectes nais</i>	early instar	99%	static	96-h	40 mg/L	LC <sub>50</sub>	> 1,000 (N/A)	Mayer and Ellersieck 1986
Crayfish <i>Procambarus sp.</i>	immature	99%	static	96-h	40 mg/L	LC <sub>50</sub>	> 100,000 (N/A)	Mayer and Ellersieck 1986
Fathead minnow <i>Pimephales promelas</i>	0.9 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	2,200 (1,590-3,040)	Mayer and Ellersieck 1986
	0.5 g	99%	static	96-h	45 mg/L	LC <sub>50</sub>	1,300 (880-1,920)	
Midge <i>Chironomus plumosus</i>	3 <sup>rd</sup> instar	99%	static	48-h	40 mg/L	EC <sub>50</sub>	7,000 (5,300-9,200)	Mayer and Ellersieck 1986
Rainbow trout <i>Oncorhynchus mykiss</i>	1.20 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	170 (120-230)	Mayer and Ellersieck 1986
	0.8 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	170 (110-250)	
	0.8 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	200 (140-280)	
	0.8 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	280 (200-390)	
	1.20 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	160 (100-240)	
	1.20 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	190 (120-290)	
	1.20 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	880 (630-1,240)	
	0.6 g	99%	static	96-h	44 mg/L	LC <sub>50</sub>	230 (170-310)	
	0.6 g	99%	static	96-h	320 mg/L	LC <sub>50</sub>	600 (420-850)	
	1.20	99%	static	96-h	44 mg/L	LC <sub>50</sub>	150 (110-200)	
	fry	99%	static	96-h	44 mg/L	LC <sub>50</sub>	120 (90-160)	
	swimup fry	99%	static	96-h	44 mg/L	LC <sub>50</sub>	160 (127-189)	
	yolk-sac fry	99%	static	96-h	44 mg/L	LC <sub>50</sub>	280 (220-360)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	170 (120-270)	

<sup>a</sup> F/T = Flow-through

<sup>b</sup> Water hardness is in mg/L as CaCO<sub>3</sub>.

<sup>c</sup> N/A = Information not available.

**Table B-2. Values (mg/L) from accepted tests on the acute toxicity of carbendazim to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Salinity/ Hardness <sup>b</sup>	Effect	Values (95% C.L.)	Reference
Bluegill <i>Lepomis macrochirus</i>	fry	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	> 3,200 (N/A)	Palawski and Knowles 1986
Channel catfish <i>Ictalurus punctatus</i>	0.8 g	99%	static	96-h	40-50 mg/L	LC <sub>50</sub>	16 (11-23)	Johnson and Finley 1980
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	> 560 (N/A)	Palawski and Knowles 1986
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	140 (91-216)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	32 (23-44)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	23 (18-31)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	14 (11-18)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	23 (18-29)	
	fingerling	99%	static	96-h	40 mg/L	LC <sub>50</sub>	18 (11-28)	
	fingerling	99%	static	96-h	320 mg/L	LC <sub>50</sub>	24 (18-32)	
	yolk-sac fry	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	7 (6-9)	
	swim-up fry	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	12 (9-15)	
	fry	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	10 (8-13)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	19 (13-27)	
Rainbow trout <i>Oncorhynchus mykiss</i>	0.2 g	99%	static	96-h	40-50 mg/L	LC <sub>50</sub>	370 (268-510)	Johnson and Finley 1980
	yolk-sac fry	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	145 (109-192)	Palawski and Knowles 1986
	swim-up fry	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	320 (240-424)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	870 (630-1,190)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	> 1,800 (N/A)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	870 (630-1,190)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	100 (70-140)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	640 (160-900)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	410 (310-550)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	340 (260-440)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	780 (580-1,050)	
	fingerling	99%	static	96-h	40-48 mg/L	LC <sub>50</sub>	880 (640-1,210)	

<sup>a</sup> F/T = Flow-through

<sup>b</sup> Water hardness is in mg/L as CaCO<sub>3</sub>.

<sup>c</sup> N/A = Information not available.

**Table B-3. Values (mg/L) from accepted tests on the acute toxicity of captan to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Salinity/ Hardness <sup>b</sup>	Effect	Values (95% C.L.)	Reference
Bluegill <i>Lepomis macrochirus</i>	1.10 g	90%	static	96-h	44 mg/L	LC <sub>50</sub>	141 (119-167)	Mayer and Ellersieck 1986
Brown trout <i>Salmo trutta</i>	0.7 g 0.6 g	90% 90%	static F/T	96-h 96-h	44 mg/L 314 mg/L	LC <sub>50</sub> LC <sub>50</sub>	80 (63.8-100) 26.2 (21.8-31.3)	Mayer and Ellersieck 1986
Channel catfish <i>Ictalurus punctatus</i>	1.20 g	90%	static	96-h	44 mg/L	LC <sub>50</sub>	77.5 (70.5-85.2)	Mayer and Ellersieck 1986
Chinook salmon fingerling <i>Oncorhynchus tshawytscha</i>		90%	static	96-h	44 mg/L	LC <sub>50</sub>	56.5 (52.3-61)	Mayer and Ellersieck 1986
Coho salmon <i>Oncorhynchus kisutch</i>	0.8 g 0.8 g	90% 90%	static F/T	96-h 96-h	44 mg/L 314 mg/L	LC <sub>50</sub> LC <sub>50</sub>	137 (117-160) 120 (103-140)	Mayer and Ellersieck 1986
Cutthroat trout <i>Oncorhynchus clarki</i>	0.4 g	90%	static	96-h	44 mg/L	LC <sub>50</sub>	56.4 (42.2-75.4)	Mayer and Ellersieck 1986
Dungeness crab zoeae <i>Cancer magister</i>		technical	static	96-h	25 ‰	LC <sub>50</sub>	>10,000 (N/A) <sup>c</sup>	Caldwell 1977
	juvenile	technical	static	96-h	25 ‰	LC <sub>50</sub>	>10,000 (N/A)	
	adult	technical	static	96-h	25 ‰	LC <sub>50</sub>	>100,000 (N/A)	
Fathead minnow <i>Pimephales promelas</i>	0.3 g 0.4 g	90% 90%	static F/T	96-h 96-h	44 mg/L 314 mg/L	LC <sub>50</sub> LC <sub>50</sub>	200 (168-238) 134 (100-178)	Mayer and Ellersieck 1986
Lake trout <i>Salvelinus namaycush</i>	0.42 g 2.30 g fingerling	90% 90% 90%	static static F/T	96-h 96-h 96-h	44 mg/L 162 mg/L 314 mg/L	LC <sub>50</sub> LC <sub>50</sub> LC <sub>50</sub>	49 (40.1-59.9) 63.2 (49.6-80.5) 51 (39.2-66.2)	Mayer and Ellersieck 1986
Rainbow trout <i>Oncorhynchus mykiss</i>	1.0 g	90%	static	96-h	44 mg/L	LC <sub>50</sub>	73.2 (66.6-80.4)	Mayer and Ellersieck 1986
Yellow perch <i>Perca flavescens</i>	1.00 g	90%	F/T	96-h	314 mg/L	LC <sub>50</sub>	120 (97.3-147)	Mayer and Ellersieck 1986

<sup>a</sup> F/T = Flow-through

<sup>b</sup> Water hardness is in mg/L as CaCO<sub>3</sub>.

<sup>c</sup> N/A = Information not available.

**Table B-4. Values (mg/L) from accepted tests on the acute toxicity of chlorothalonil to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Salinity/ Hardness <sup>b</sup>	Effect	Values (95% C.L.)	Reference
Bluegill <i>Lepomis macrochirus</i>	1-year	96%	static	96-h	44 mg/L	LC <sub>50</sub>	60 (52-78)	EG&G Bionomics 1980a
Carp <i>Cyprinus carpio</i>	1.68 g	99.18%	F/T	96-h	150-200 mg/L	LC <sub>50</sub>	55 (50-60)	Douglas et al. 1992b
Channel catfish <i>Ictalurus punctatus</i>	juvenile	99%	static	96-h	30 mg/L	LC <sub>50</sub>	52 (30-90)	Gallagher et al. 1992
Cladoceran <i>Daphnia magna</i>	1 <sup>st</sup> instar	99.18%	static	48-h	N/A <sup>d</sup>	EC <sub>50</sub>	59 (50-70)	Douglas et al. 1992c
	< 24-h	96%	static	48-h	60 mg/L	LC <sub>50</sub>	70 (34-143)	EG&G Bionomics 1977
Eastern oyster <i>Crassostrea virginica</i>	juvenile	technical	F/T	96-h	27‰	EC <sub>50</sub>	26 (N/A)	Mayer 1987
Golden galaxias <i>Galaxias auratus</i>	7-11 g	99%	F/T	96-h	N/A	LC <sub>50</sub>	29.2 (N/A)	Davies and White 1985
Jollytail <i>Galaxias maculatus</i>	7-10 g	99%	F/T	96-h	N/A	LC <sub>50</sub>	16.3 (N/A)	Davies and White 1985
Pink shrimp <i>Penaeus duorarum</i>	juvenile	technical	F/T	48-h	27‰	EC <sub>50</sub>	320 (N/A)	Mayer 1987
Rainbow trout <i>Oncorhynchus mykiss</i>	6-11 g	99%	F/T	96-h	N/A	LC <sub>50</sub>	17.1 (N/A)	Davies and White 1985
	6-11 g	99%	F/T	96-h	N/A	LC <sub>50</sub>	14.3 (N/A)	
	6-11 g	99%	F/T	96-h	N/A	LC <sub>50</sub>	10.5 <sup>c</sup> (N/A)	Douglas et al. 1992a EG&G Bionomics 1980b Ernst et al. 1991
	6-11 g	99%	static	96-h	N/A	LC <sub>50</sub>	18.0 (N/A)	
	1.27 g	99.18%	F/T	96-h	150-200 mg/L	LC <sub>50</sub>	12 (10-14)	
	1.03 g	96%	static	96-h	44 mg/L	LC <sub>50</sub>	47 (32-68)	
fingerling	97.8%	static	96-h	12.3 mg/L	LC <sub>50</sub>	76 (54-100)		
Spot <i>Leiostomus xanthurus</i>	juvenile	technical	F/T	48-h	22‰	LC <sub>50</sub>	32 (N/A)	Mayer 1987
Spotted galaxias <i>Galaxias truttaceus</i>	8-20 g	99%	F/T	96-h	N/A	LC <sub>50</sub>	18.9 (N/A)	Davies and White 1985

<sup>a</sup> F/T = Flow-through

<sup>b</sup> Water hardness is in mg/L as CaCO<sub>3</sub>.

<sup>c</sup> This tested the effect of low oxygen (53% saturation).

<sup>d</sup> N/A = Information not available.

**Table B-5. Values (mg/L) from accepted tests on the acute toxicity of maneb to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Salinity/ Hardness <sup>b</sup>	Effect	Values (95% C.L.)	Reference
Cladoceran <i>Daphnia magna</i>	N/A <sup>c</sup>	> 90%	static	48-h	N/A	LC <sub>50</sub>	1,000 (800-1,300)	Van Leeuwen et al. 1985a
Copepod <i>Nitocra spinipes</i>	adult	85%	static	96-h	7‰	LC <sub>50</sub>	110 (90-140)	Linden et al. 1979
Eastern oyster <i>Crassostrea virginica</i>	juvenile	technical	F/T	96-h	16‰	EC <sub>50</sub>	<1,000 (N/A)	Mayer 1987
Freshwater fish (bleak) <i>Alburnus alburnus</i>	8 cm	85%	static	96-h	7‰	LC <sub>50</sub>	520 (480-560)	Linden et al. 1979
Guppy <i>Poecilia reticulata</i>	N/A	> 90%	static	96-h	N/A	LC <sub>50</sub>	3,700 (3,200-5,600)	Van Leeuwen et al. 1985a
Longnose killifish <i>Fundulus similis</i>	juvenile	technical	F/T	48-h	30‰	LC <sub>50</sub>	1,600 (N/A)	Mayer 1987
Pink shrimp <i>Penaeus duorarum</i>	juvenile	technical	static	48-h	27‰	EC <sub>50</sub>	3,800 (N/A)	Mayer 1987
Rainbow trout <i>Oncorhynchus mykiss</i>	egg-0-h	< 90%	static	96-h	50 mg/L	LC <sub>50</sub>	6,000 (4,700-7,600)	Van Leeuwen et al. 1985b
	egg-24-h	< 90%	static	96-h	50 mg/L	LC <sub>50</sub>	5,600 (3,200-10,000)	
	early-eyed egg	< 90%	static	96-h	50 mg/L	LC <sub>50</sub>	1,800 (1,400-2,400)	
	late-eyed egg	< 90%	static	96-h	50 mg/L	LC <sub>50</sub>	1,300 (1,000-1,800)	
Rainbow trout <i>Oncorhynchus mykiss</i>	sac fry	< 90%	static	96-h	50 mg/L	LC <sub>50</sub>	320 (180-560)	
	early fry < 90%	static	96-h	50 mg/L	LC <sub>50</sub>	340 (270-430)		

<sup>a</sup> F/T = Flow-through

<sup>b</sup> Water hardness is in mg/L as CaCO<sub>3</sub>.

<sup>c</sup> N/A = Information not available.

**Table B-6. Values (mg/L) from accepted tests on the acute toxicity of ziram to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Salinity/ Hardness <sup>b</sup>	Effect	Values (95% C.L.)	Reference
Bluegill Sunfish <i>Lepomis macrochirus</i>	1.01 g	98.9%	F/T	96-h	350 mg/L	LC <sub>50</sub>	9.7 (8.6-11)	Douglas et al. 1991b
Cladoceran <i>Daphnia magna</i>	N/A <sup>c</sup>	> 90%	static	48-h	N/A	LC <sub>50</sub>	140 (100-180)	Van Leeuwen et al. 1985a
	1 <sup>st</sup> instar	98.9%	static	48-h	N/A	EC <sub>50</sub>	48 (34-68)	Douglas et al. 1991c
Eastern oyster <i>Crassostrea virginica</i>	juvenile	technical	F/T	96-h	22‰	EC <sub>50</sub>	>1,000 (N/A)	Mayer 1987
Goldfish <i>Carassius auratus</i>	3 cm	technical	static	96-h	N/A	LC <sub>50</sub>	300 (260-350)	Montedison USA 1977
Guppy <i>Lebistes reticulatus</i>	2.5-3 cm	technical	static	96-h	N/A	LC <sub>50</sub>	90 (73-120)	Montedison USA 1977
Guppy <i>Poecilia reticulata</i>	N/A	> 90%	static	96-h	N/A	LC <sub>50</sub>	750 (560-1,000)	Van Leeuwen et al. 1985a
Harlequin fish <i>Rasbora heteromorpha</i>	2.5-3 cm	technical	static	96-h	N/A	LC <sub>50</sub>	40 (37-43)	Montedison USA 1977
Longnose killifish <i>Fundulus similis</i>	juvenile	technical	static	48-h	30‰	LC <sub>50</sub>	6,400 (N/A)	Mayer 1987
Pink shrimp <i>Penaeus duorarum</i>	juvenile	technical	static	48-h	27‰	EC <sub>50</sub>	>5,000 (N/A)	Mayer 1987
Rainbow trout <i>Oncorhynchus mykiss</i>	3.22 g	98.9	static	96-h	N/A	LC <sub>50</sub>	1,700 (1,500-2,000)	Douglas et al. 1991a

<sup>a</sup> F/T = Flow-through

<sup>b</sup> Water hardness is in mg/L as CaCO<sub>3</sub>.

<sup>c</sup> N/A = Information not available.

**Table B-7. Values (mg/L) from unaccepted tests on the acute toxicity of benomyl and carbendazim to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Effect	Values (95% C.L.)	Reference	Test Deficiencies <sup>b</sup>
Bluegill <i>Lepomis macrochirus</i>	0.6 g	50%	static	96-h	LC <sub>50</sub>	1200 (900-1,590)	Mayer and Eilersieck 1986	1
Channel catfish <i>Ictalurus punctatus</i>	1.20 g	50%	static	96-h	LC <sub>50</sub>	27.5 (21-34)	Mayer and Eilersieck 1986	1
Copepod <i>Nitocra spinipes</i>	adult	carbendazim 2.5%	static	96-h	LC <sub>50</sub>	400 (300-500)	Linden et al. 1979	1, 6
Eastern oyster <i>Crassostrea virginica</i>	25-50 mm	50%	F/T	96-h	EC <sub>50</sub>	> 80 (62-110)	Graves and Swigert 1993a	1
Fathead minnow <i>Pimephales promelas</i>	0.5 g	50%	static	96-h	LC <sub>50</sub>	1,900 (1,430-2,530)	Mayer and Eilersieck 1986	1
Freshwater fish <i>Alburnus alburnus</i>	8 cm	carbendazim 2.5%	static	96-h	LC <sub>50</sub>	3,000-4,000 (N/A) <sup>c</sup>	Linden et al. 1979	1, 6
Rainbow trout <i>Oncorhynchus mykiss</i>	1.00 g	50%	static	96-h	LC <sub>50</sub>	310 (250-390)	Mayer and Eilersieck 1986	1
Sheepshead minnow <i>Cyprinodon variegatus</i>	juvenile	50%	static	96-h	LC <sub>50</sub>	26,000 (24,000-26,000)	Graves and Swigert 1993b	1, 2

<sup>a</sup> F/T = Flow-through

<sup>b</sup> 1 = Formulation not given or active ingredient less than 90%.

2 = Control survival not given or less than 90%.

3 = Too few concentrations tested, must be five or greater.

4 = No effect criteria values given, such as LC<sub>50</sub> or EC<sub>50</sub>.

5 = Test duration too short.

6 = Test design unacceptable.

7 = Mortality range unacceptable.

<sup>c</sup> N/A = Information not available.

<sup>b</sup> (ASTM 1988)

**Table B-8. Values (mg/L) from unaccepted tests on the acute toxicity of captan to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Effect	Values (95% C.L.)	Reference	Test Deficiencies <sup>b</sup>
Bluegill <i>Lepomis macrochirus</i>	N/A	1.94%	F/T	96-h	LC <sub>50</sub>	72 (47-111)	Hermanutz et al. 1973	1, 2
Brook trout <i>Salvelinus fontinalis</i>	N/A	1.94%	F/T	96-h	LC <sub>50</sub>	34 (22-52)	Hermanutz et al. 1973	1, 2
Cladoceran <i>Daphnia magna</i>	N/A	technical	static	48-h	EC <sub>50</sub>	N/A	ABC 1980	3, 4, 7
	24 hours	N/A	static	26-h	LC <sub>50</sub>	1,300 (N/A)	Frear and Boyd 1967	1, 2, 5
Earthworm <i>Eisenia foetida</i>	adult	60.2%	static	48-h	LC <sub>50</sub>	12,120,890	Anton et al. 1990	1, 6
				72-h	LC <sub>50</sub>	6,814,670		
Fathead minnow <i>Pimephales promelas</i>	N/A	1.94%	F/T	96-h	LC <sub>50</sub>	65 (59-72)	Hermanutz et al. 1973	1, 2
Goldfish <i>Carassius auratus</i>	4.0-8.0 g	60.2%	static	96-h	LC <sub>50</sub>	1,340 (N/A)	Anton et al. 1990	1
Rainbow trout <i>Oncorhynchus mykiss</i>	N/A	50%	static	72-h	LOEC	320	Holland et al. 1960	1, 2, 4, 5
	N/A	50%	static	72-h	LOEC	560		
Zebrafish <i>Brachydanio rerio</i>	larvae	N/A	static	90-min	LC <sub>50</sub>	670 (N/A)	Abedi and McKinley 1967	1, 5

<sup>a</sup> F/T = Flow-through

<sup>b</sup> 1 = Formulation not given or active ingredient less than 90%.

2 = Control survival not given or less than 90%.

3 = Too few concentrations tested, must be five or greater.

4 = No effect criteria values given, such as LC<sub>50</sub> or EC<sub>50</sub>.

5 = Test duration too short.

6 = Test design unacceptable.

7 = Mortality range unacceptable.

<sup>c</sup> N/A = Information not available.

<sup>b</sup> (ASTM 1988)

**Table B-9. Values (mg/L) from unaccepted tests on the acute toxicity of chlorothalonil to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Effect	Values (95% C.L.)	Reference	Test Deficiencies <sup>b</sup>
Blue mussel <i>Mytilus edulis</i>	5.9 cm	40%	static	96-h	LC <sub>50</sub>	5,940 (2,870-9,050)	Ernst et al. 1991	1
Cladoceran <i>Daphnia magna</i>	N/A <sup>c</sup>	40%	static	96-h	EC <sub>50</sub>	97 (81-113)	Ernst et al. 1991	1
Clam <i>Mya arenaria</i>	5.2 cm	40%	static	96-h	LC <sub>50</sub>	34,780 (12,560-57,000)	Ernst et al. 1991	1
Rainbow trout <i>Mytilus edulis</i>	fingerling	40%	static	96-h	LC <sub>50</sub>	69 (53-97)	Ernst et al. 1991	1
Threespine stickleback <i>Gasterosteus aculeatus</i>	N/A	40%	static	96-h	LC <sub>50</sub>	> 73 (N/A)	Ernst et al. 1991	1

<sup>a</sup> F/T = Flow-through

<sup>b</sup> 1 = Formulation not given or active ingredient less than 90%.

2 = Control survival not given or less than 90%.

3 = Too few concentrations tested, must be five or greater.

4 = No effect criteria values given, such as LC<sub>50</sub> or EC<sub>50</sub>.

5 = Test duration too short.

6 = Test design unacceptable.

7 = Mortality range unacceptable.

<sup>c</sup> N/A = Information not available.

<sup>b</sup> (ASTM 1988)

**Table B-10. Values (mg/L) from unaccepted tests on the acute toxicity of ziram to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Effect	Values (95% C.L.)	Reference	Test Deficiencies <sup>b</sup>
Channel catfish <i>Ictalurus punctatus</i>	fingerling	76%	static	96-h	LC <sub>50</sub>	500	Clemens and Sneed 1959	1
Cladoceran <i>Daphnia magna</i>	24	N/A <sup>c</sup>	static	26-h	LC <sub>50</sub>	16 (N/A)	Frear and Boyd 1967	1, 2, 5
Copepod <i>Nitocra spinipes</i>	adult	22.5%	static	96-h	LC <sub>50</sub>	400 (300-500)	Linden et al. 1979	1, 6
Freshwater fish <i>Alburnus alburnus</i>	8 cm	22.5%	static	96-h	LC <sub>50</sub>	3,000-4,000 (N/A)	Linden et al. 1979	1, 6

<sup>a</sup> F/T = Flow-through

<sup>b</sup> 1 = Formulation not given or active ingredient less than 90%.

2 = Control survival not given or less than 90%.

3 = Too few concentrations tested, must be five or greater.

4 = No effect criteria values given, such as LC<sub>50</sub> or EC<sub>50</sub>.

5 = Test duration too short.

6 = Test design unacceptable.

7 = Mortality range unacceptable.

<sup>c</sup> N/A = Information not available.

<sup>b</sup> (ASTM 1988)

## APPENDIX C. Abstracts of Accepted and Unaccepted Chronic Toxicity Tests Reviewed for Hazard Assessment.

**Accepted chronic toxicity tests-** The following tests used accepted test methods.

Baer (1993a) – In 1993, a 79-d chronic flow-through toxicity test was conducted by E.I. Du Pont De Nemours & Co., Newark, Delaware with the carbendazim metabolite of benomyl (99%) on embryo, alevin and fingerling rainbow trout *Oncorhynchus mykiss*. Six concentrations were tested in replicate and water and solvent controls were used. Water quality parameters during the test were: dissolved oxygen above 60% saturation; temperature of 9.6 - 12.8 °C; and pH of 7.0 - 7.5. Controls had 76% hatching success, 98% larval survival from hatching to thinning and 95 and 97% survival from thinning to the end of the test. The 79-d NOEC and LOEC values for early life stage *O. mykiss*, based on embryo survival, were 11 and 34 µg/L, respectively.

Baer (1993b) – In 1993, a 21-d chronic flow-through toxicity test was conducted by E.I. Du Pont De Nemours & Co., Newark, Delaware with benomyl (97.4%) on fingerling rainbow trout *Oncorhynchus mykiss*. Six concentrations were tested in duplicate and water and solvent controls were used. Water quality parameters during the test were: temperature of 11.3 - 11.6 °C; pH of 7.1 - 7.5; and hardness of 80 - 84 mg/L as CaCO<sub>3</sub>. Control survival was 100%. The 21-d NOEC and LOEC values for *O. mykiss* were 26 and 54 µg/L, respectively.

Rhodes et al. (1995) - In 1995, a 41-d chronic flow-through toxicity test was conducted by Analytical Bio Chemistry Laboratories, Columbia, Missouri, with the carbendazim metabolite of benomyl (99.3%) on early life stage channel catfish *Ictalurus punctatus*. Eight concentrations were tested with four replicates and two water controls were used. Water quality parameters during the test were: dissolved oxygen of 6.4 - 7.9 mg/L; temperature of 25.1 - 25.2 °C; pH of 7.85 - 8.51; and hardness of 140 mg/L as CaCO<sub>3</sub>. Control survival was 84.4 and 93.7 %. The 41-d NOEC and LOEC values for *I. punctatus* were 1.5 and 3.2 µg/L, respectively.

**Unaccepted chronic toxicity tests-** The following tests did not use accepted test methods and/or produce accepted results.

Caldwell (1977) – From 1973 to 1974, 18, 69, 36, 80 and 85-d chronic flow-through toxicity tests were conducted by the U.S. Environmental Protection Agency with technical grade captan on zoeal (18-d, 69-d), juvenile (36-d, 80-d) and adult (85-d) dungeness crab *Cancer magister*. Four concentrations were tested in the zoeal test, four in the juvenile test and two in the adult test. The zoeal and juvenile tests were conducted in duplicate and water and acetone controls were used in all tests. Water quality parameters during the zoeal test were: dissolved oxygen of 8.7 mg/L, temperature of 12 to 13 °C, pH of 7.6 to 8.1 and salinity of 15-28 ‰. Water quality parameters during the juvenile test were: dissolved oxygen of 8.0 to 8.7 mg/L; temperature of 13 °C; pH of 7.3 to 8.1; and salinity of 31-35 ‰. Water quality parameters during the adult test were: dissolved oxygen of 6.8 to 8.5 mg/L; temperature of 11 to 15 °C; pH of 7.0 to 8.3; and salinity of 23-34 ‰. These tests could not be used because there was no mention of control survival and no NOEC or LOEC values were given.

Hermanutz et al. (1973) – In 1972, flow-through toxicity tests were conducted by the National Water Quality Laboratory of the U.S. Environmental Protection Agency, Duluth, Minnesota, with captan (1.94%) on fathead minnow *Pimephales promelas*, bluegill *Lepomis macrochirus*, and brook trout *Salvelinus fontinalis*. Five concentrations were tested in duplicate and controls were used. Water quality parameters during the tests were: dissolved oxygen of > 7.2 mg/L; temperature of 24.9°C; pH of 7.5; and hardness of 45.1 mg/L as CaCO<sub>3</sub>. No significant differences between the controls and tested concentrations were found. These test were not used because the test duration was not given, the percent active ingredient was less than 90%, control survival was not mentioned, and no NOEC or LOEC values were given.

Lightner et al. (1996) – In 1996, a 30-d chronic static renewal toxicity test was conducted by the Department of Veterinary Science, University of Arizona, Tucson, Arizona with benomyl (50%) on juvenile Pacific white shrimp *Penaeus vannamei*. Three concentrations were tested in duplicate and controls were used. Water parameters during the test were: temperature of 27.5 to 28.5 °C and salinity of 10 to 12 ‰. Control survival was 94 and 75%. This test was not used because the percent active ingredient was less than 90%, the 75% control survival was too low and no NOEC or LOEC values were given.

**Table C-1. Values (mg/L) from accepted tests on the chronic toxicity of benomyl and carbendazim to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Salinity/ Hardness <sup>b</sup>	Effect	Values	Reference
Channel catfish <i>Ictalurus punctatus</i>	Early Life Stage	carbendazim 99.3%	F/T	41-d	140 mg/L	NOEC LOEC MATC	1.5 3.2 2.19	Rhodes et al. 1995
Rainbow trout <i>Oncorhynchus mykiss</i>	Early Life Stage	carbendazim 99%	F/T	21-d	N/A <sup>c</sup>	NOEC LOEC MATC	11 34 19.34	Baer 1993a
	fingerling	benomyl 97.4%	F/T	21-d	80-84 mg/L	NOEC LOEC MATC	26 54 37.47	Baer 1993b

<sup>a</sup> F/T = Flow-through

<sup>b</sup> Water hardness is in mg/L as CaCO<sub>3</sub>.

<sup>c</sup> N/A = Information not available.

**Table C-2. Values (mg/L) from unaccepted tests on the chronic toxicity of benomyl and captan to aquatic animals.**

Species	Life Stage	Formula	Test Method <sup>a</sup>	Test Length	Effect	Values	Reference	Test Deficiencies <sup>b</sup>
Bluegill <i>Lepomis macrochirus</i>	N/A <sup>c</sup>	captan 1.94%	F/T	N/A	N/A	N/A	Hermanutz et al. 1973	1, 2, 3, 4
Brook trout <i>Salvelinus fontinalis</i>	N/A	captan 1.94%	F/T	N/A	N/A	N/A	Hermanutz et al. 1973	1, 2, 3, 4
Dungeness crab <i>Cancer magister</i>		captan					Caldwell 1977	2, 3
	zoeae	technical	F/T	18-d	N/A	N/A		
	zoeae	technical	F/T	69-d	N/A	N/A		
	juvenile	technical	F/T	36-d	N/A	N/A		
	juvenile	technical	F/T	80-d	N/A	N/A		
	adult	technical	F/T	85-d	N/A	N/A		
Fathead minnow <i>Pimephales promelas</i>	9-day old	captan 1.94%	F/T	N/A	N/A	N/A	Hermanutz et al. 1973	1, 2, 3, 4
Pacific white shrimp <i>Penaeus vannamei</i>	juvenile	benomyl 50%	static	30-d	N/A	N/A	Lightner et al. 1996	1, 2, 3

<sup>a</sup> F/T = Flow-through

<sup>b</sup> 1 = Formulation not given or active ingredient less than 90%.

2 = Control survival not given or less than 90%.

3 = No effect criteria values given, such as NOEC or LOEC.

4 = Test duration too short, or not given.

<sup>c</sup> N/A = Information not available.

<sup>b</sup> (ASTM 1992)

#### **APPENDIX D. Abstracts of Aquatic Plant Toxicity Tests Reviewed for Hazard Assessment.**

Anton et al. (1993) – In 1993, 96-h acute static toxicity tests were conducted by the Ecotoxicology Group, Spanish Council for Scientific Research, Madrid, Spain with captan (60.2%) on microalgae *Chlorella pyrenoidosa*. An unknown number of concentrations were tested and water controls were used. During the test the temperature was  $20 \pm 1^\circ\text{C}$ . The 96-h  $\text{EC}_{50}$  for *C. pyrenoidosa* based on 50% inhibition of algal growth as effect criterion was 73,890  $\mu\text{g/L}$ . This value was not used because the percent active ingredient was less than 90%.

Mayer (1987) - From 1961 to 1986, 48-h static toxicity tests were performed by the Environmental Research Laboratory of the U.S. Environmental Protection Agency, Gulf Breeze, Florida with technical grade captan on algae *Pavlova gyrans*, *P. lutheri*, *Isochrysis galbana*, *Skeletonema costatum* and *Dunaliella tertiolecta*. During the test the temperature was  $20^\circ\text{C}$ .  $\text{EC}_{50}$  effect criteria for algae was population growth. Although control survival and concentrations tested were not given, these tests were accepted because they were deemed acceptable by the EPA. The 48-h  $\text{EC}_{50}$  for *P. gyrans* was 760  $\mu\text{g/L}$ , for *P. lutheri* 550  $\mu\text{g/L}$ , for *I. galbana* 210  $\mu\text{g/L}$ , for *S. costatum* 160  $\mu\text{g/L}$  and for *D. tertiolecta* 2,300  $\mu\text{g/L}$ .

Van Leeuwen et al. (1985a) – In 1985, 96-h, 15-minute and 3-h acute static toxicity tests were conducted by the Laboratory for Ecotoxicology, Government Institute for Sewage and Waste Water Treatment, Lelystad, Netherlands with maneb and ziram (>90%) on green algae *Chlorella pyrenoidosa*, bacteria *Photobacterium phosphoreum* and nitrifying bacteria *Nitrosomonas* and *Nitrobacter*. The algal bioassays were conducted in a temperature controlled room at  $20 \pm 1^\circ\text{C}$ , in triplicate. The minimum inhibiting concentration (MIC) of the nitrifying bacteria was determined using a screening test based on the conversion of ammonia nitrite into nitrate. The maneb 96-h  $\text{EC}_{50}$  for *C. pyrenoidosa* based on inhibition of the average specific growth rate as effect criterion was 3,200  $\mu\text{g/L}$  and for ziram was 1,200  $\mu\text{g/L}$ . The maneb 15-min  $\text{EC}_{50}$  for *P. phosphoreum* based on reduction of bacterial luminescence by 50% as effect criterion was 1,200  $\mu\text{g/L}$  and for ziram was 150  $\mu\text{g/L}$ . The maneb 3-h MIC for *Nitrosomonas* and *Nitrobacter* was 56,000  $\mu\text{g/L}$  and for ziram was 100,000  $\mu\text{g/L}$ .

**Table D-1. Values (µg/L) from accepted tests on the toxicity of captan, maneb and ziram to aquatic plants.**

Species	Formula	Test Length	Endpoint/ Effect	Values (95% C.L.)	Reference
Algae	<b>Captan</b>				Mayer 1987
<i>Dunaliella tertiolecta</i>	technical	48-h	EC <sub>50</sub>	2,300 (N/A <sup>a</sup> )	
<i>Isochrysis galbana</i>	technical	48-h	EC <sub>50</sub>	210 (N/A)	
<i>Pavlova gyrams</i>	technical	48-h	EC <sub>50</sub>	760 (N/A)	
<i>Pavlova lutheri</i>	technical	48-h	EC <sub>50</sub>	550 (N/A)	
<i>Skeletonema costatum</i>	technical	48-h	EC <sub>50</sub>	160 (N/A)	
Green algae	<b>Maneb</b>	96-h	EC <sub>50</sub>	3,200 (N/A)	Van Leeuwen et al. 1985a
<i>Chlorella pyrenoidosa</i>	< 90%				
Green algae	<b>Ziram</b>	96-h	EC <sub>50</sub>	1,200 (N/A)	Van Leeuwen et al. 1985a
<i>Chlorella pyrenoidosa</i>	< 90%				

<sup>a</sup> N/A = Information not available.

**Table D-2. Values (µg/L) From Unaccepted Tests on the Toxicity of Captan to Aquatic Plants.**

Species	Formula	Test Length	Endpoint/ Effect	Values (95% C.L.)	Reference	Test Deficiencies <sup>a</sup>
Bacteria	<b>Maneb</b>	15-min	EC <sub>50</sub>	1,200 (1,200-1,300)	Van Leeuwen et al. 1985a	1
<i>Photobacterium phosphoreum</i>	< 90%					
<i>Nitrosomonas &amp; Nitrobacter</i>		3-h	LOEC	56,000		1
Bacteria	<b>Ziram</b>	15-min	EC <sub>50</sub>	150 (120-190)	Van Leeuwen et al. 1985a	1
<i>Photobacterium phosphoreum</i>	< 90%					
<i>Nitrosomonas &amp; Nitrobacter</i>		3-h	LOEC	100,000		1
Microalgae	<b>Captan</b>	96-h	EC <sub>50</sub>	73,890 (N/A)	Anton et al. 1993	2
<i>Chlorella pyrenoidosa</i>	60.2%					

<sup>a</sup> 1 = Test duration too short.

2 =Formulation not given or active ingredient less than 90%.