



# **Herbicide Risk Assessment for the Aquatic Plant Management Final Supplemental Environmental Impact Statement**

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## **Appendix D Volume 2: Endothall**



WASHINGTON STATE  
DEPARTMENT OF  
E C O L O G Y

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# Endothall

## Volume 2, Section 1

### LABEL DESCRIPTION & HISTORY

**56 PAGES**

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## **1.0 REGISTRATION STATUS**

This section describes the historic and current Federal labels and use directions. It also summarizes application rates, weeds controlled, and reports on typical practices undertaken by licensed Washington applicators. The final section describes research underway, including rate and application technology and proposed new labeling.

### **1.1 ENDOTHALL AS AN AQUATIC HERBICIDE**

#### **1.1.1 Registration Requirements**

In order to register a pesticide with the EPA for use in the United States, the active ingredient and its formulations must be tested for mammalian toxicity, physical chemistry, environmental fate, effects on ground water, and eco-tox effects. Work must also be done to demonstrate the expected magnitude of residue on edible products and residues in water. After this data is generated, it is submitted to various branches of EPA for review. If EPA finds that the product does not pose significant risk to man, livestock, or wildlife and has a favorable environmental persistence and degradation profile, a registration will be granted. With that registration, the manufacturer has permission to sell the product in the United States. However, each state may have its own separate registration process which may be more stringent than the EPA's registration process.

Washington State's registration procedure follows the EPA registration: It requires that the applicant submit a copy of the EPA approved label and a copy of the confidential statement of formula. The Washington State Department of Agriculture reviews these submittals for compliance with state and Federal requirements. If these requirements are filled, the product will be registered by the state unless it presents an unusual hazard to the environment.

Studies conducted for submission to EPA since 1987 must be conducted on compliance with Good Laboratory Practice (GLP) regulations as specified in 40 CFR (Code of Federal Regulations) 160. These regulations were designed to improve the quality of records keeping and prevent fraud. They specify what records must be kept and how long they must be kept. They also specify how long analytical standards must be kept, how often they must be re-characterized and storage conditions. Furthermore they provide guidelines on how to determine how long organic and inorganic reagents, solvents and biological samples can be kept, and under what conditions they should be stored. Also, GLPs provide guidance on how the integrity of the biological samples can be determined. For practical purposes, GLPs insures the integrity of the data. They allow for the reconstruction and interpretation of data within the study.

The Washington State Departments of Agriculture and Ecology have approved Aquathol® and Aquathol® K for use in control of aquatic macrophytes (plants) in lakes and ponds. Aquathol® K has also been approved for control of aquatic macrophytes in irrigation canals. Aquathol® Super K has received a Federal Registration for control of aquatic macrophytes in lakes and ponds but as of January 2000 had not received registration for use in Washington State.

Hydrothol® 191 (liquid) and Hydrothol® 191 (granular) have received Federal registration for control of algae and aquatic macrophytes in canals, lakes and ponds.

They do not currently have a registration in the state of Washington for the control of aquatic algae and weeds.

### **1.1.2 1992 Environmental Impact Statement and Effects of State Senate Bill 5424**

In the State of Washington, all applications of aquatic herbicides and algaecides are performed under a state permit system. Ecology manages this system and uses a 1992 Environmental Impact Statement (EIS) for endothall, copper compounds, glyphosate, diquat and fluridone as well as manual, mechanical and biocontrol methods as its basis for writing permits for aquatic weed and algae control in this state (Ecology, 1992). Hydrothol® 191 is registered by EPA for national use; however, its use is not allowed in Washington based on the current EIS (Ecology, 1992). The permitting system is a result of six agencies working together to develop a statewide integrated pest management system for the managing aquatic plants and noxious emergent vegetation. The goal is to ensure that the most effective and least environmentally damaging management alternatives will be used in the managing agencies respective areas of regulatory or land management responsibilities.

Ecology is responsible for issuing short-term modifications (STMs) to the water quality standards. These are required for management activities such as use of pesticides, or mechanical or other control methods that might cause excess turbidity or violate other provisions of the water quality standards. Ecology is also responsible for ensuring consistency of proposals with rules and regulations designed to protect groundwater, shorelands, wetlands, air quality, and other elements of the environment.

In 1999, the Washington State Legislature passed legislation (ESBB 5424) requiring an update to the 1992 EIS. From 1992 to present, there has been a considerable amount of research done to support the continuing registration of aquatic herbicides and algaecides containing endothall. As such, the most current data for these materials has not been considered or used in the issuance of permits to perform aquatic weed and algae control in Washington State (Resource Management, Inc., 1999).

In 1955, the Penwalt Corporation first demonstrated the aquatic herbicidal properties of endothall, and endothall was first distributed for aquatic use in 1960. Elf Atochem currently manufactures and distributes the endothall aquatic herbicide line of products. The Aquathol® product line is used primarily to control aquatic macrophytes. This line includes Aquathol® Granular and Aquathol® K. The Aquathol® product line uses the active ingredient dipotassium endothall (dpe), which has a history of being relatively safe to fish (LC50 = usually >100 mg a.e./L where the LC50 = the concentration lethal to 50% of the individuals of the species being tested). See Section 4, Tables 2, 15 and Appendix 2). They are both used widely within the United States to control aquatic weeds (Getsinger, 1999, Personal Communication). Hydrothol® 191 products may also be used safely and effectively for the control of algae in lakes and ponds. However, Hydrothol® 191 is not recommended for use in water bodies where fish kill is not acceptable because of its high toxicity to fish (LC50 = usually >0.3 mg a.e./L). However, due to a number of mitigating factors, Hydrothol® 191 at concentrations of 0.2 mg/L may yield acceptable risk if it is used in irrigation canals. Without the mitigating factors, 30% of the species exposed in irrigation canals to 0.2 mg/L Hydrothol®-191 would be affected. However, due to the short half-life of the extremely toxic dimethylalkylamine component, effects of dissolved organic carbon in reducing the concentration of dimethylalkylamine present, and reduced exposure times under some treatment scenarios, it can be expected that the

ecological effects of Hydrothol® application would therefore be less than without these mitigating factors. Although the limited data available do not support a quantitative risk assessment, if only a two fold increase in the LC50 can be obtained, the acute risk quotient would be lowered from 2.1 to 1.0 which should decrease the percent of sensitive species from 30% to 10%. (Giddings, 1999).

Hydrothol® 191 is currently being used under an experimental use permit (EUP) in Washington to determine its effectiveness for the control of algae, and best application practices.

Formal reports to the EPA by the registrant (Elf Atochem), peer-reviewed literature, and EPA databases were reviewed in order to prepare this risk assessment: 1) The documents used by the registrant to support registration were those documents submitted to EPA in the course of the registration and re-registration process of endothall. They were conducted according to the EPA's current pesticide assessment guidelines and, if conducted after 1987, were also conducted under Good Laboratory Practice Regulations (40 CFR 160). 2) The published articles were found in literature searches for peer reviewed articles written since 1989, using the DIALOG OneSearch. 3) A large portion of the toxicity data was collected from EPA's Brian database or the EPA's ECOTOX database, which are compilations of ecotoxicology data currently in use at EPA to generate and support ecological risk assessments. Information collected on work done before 1989 was collected from general review articles on the toxicity and environmental fate of endothall such as Shearer & Halter (1980) and Ecology (1980, 1989 and 1992).

### **1.1.3 Risk Assessment (For a More Detailed Analysis See Section 4.1.10.2.5)**

Herbicides used for aquatic weed control fall into one or more general categories: 1) Contact herbicides are chemicals that control weeds by direct contact with the foliage and destroy only those portions of the plant (generally the roots survive and plants regrow). 2) Systemic herbicides are applied to the foliage and/or stems of the plant and translocated to the roots or other portions of the plant, eventually resulting in the death of the entire plant. 3) Broad-spectrum herbicides kill most, if not all plants, if the dosage is appropriate. 4) Broadleaf herbicides generally kill dicot plants with broad leaves but there are exceptions; some broadleaf herbicides can kill monocots with broad leaf morphology and certain "narrowleaf" dicots are not harmed at concentrations that typically kill broadleaf plants. 5) Submerged (submersed), emerged (emersed) or floating indicates the way the plant typically grows. i.e., below the water line (submerged), from below the water line to above the waterline (emerged) and on the surface of the water and often un-rooted (floating). Pre-emergent and Post-emergent weed control refers to whether control measures are taken prior to or after germination or first growth of the plant.

Aquathol® and Aquathol® K are post-emergent contact herbicides used primarily to control submerged weeds but they may also be used to control surface weeds. Hydrothol® 191 is typically used for algae control but can be used for submerged and surface weed control on very narrow margins or where some fish kill is acceptable.

Risk Assessment in Section 4 indicates that Aquathol® (dipostassium endothall salt) products may be used safely when most species of fish and invertebrates are present. The Risk Quotient for the most sensitive species is below the acute and chronic levels of concern (0.1 and 1.0, respectively) for protection of the biota. The Acute Risk Quotient

for Aquathol® K using early life-stage walleye, is 0.09 (1.0 ppm a.e./11 ppm a.e.) and the chronic risk assessment, using *Daphnia magna* or rainbow trout, is 0.012 to 0.028 (0.06 to 0.14 ppm a.e./5.0 ppm a.e.). For both acute and chronic risk assessments the levels of concern for protection of the biota are not exceeded. Therefore, it should be possible to use Aquathol® according to the label without significant acute or chronic risk to aquatic animals.

Hydrothol® 191 products, when used in canals at concentrations of up to 0.3 mg a.e. (acid equivalents)/L, should not adversely impact indigenous fish populations (Hydrothol® 191, 1999 and Hydrothol® 191 Granular Labels, 1999 and Eller, 1973 in Finlayson, 1980). However, if lakes are treated at the maximum use rate (5 mg a.e./L), the weighted EEC would be 1.4 mg a.e./L after four days, which is high enough to cause acute risk to the most sensitive invertebrate members of the biota. Since the most sensitive, environmentally relevant species, *Hexagenia* spp. (Mayfly) has an LC50 of 0.12 mg a.e./L Hydrothol® 191, the Acute Risk Quotient is ~12 (RQ = 1.4 ppm/0.12 ppm = 11.7). The criteria value of 0.10 is exceeded, therefore, it is not possible to use Hydrothol® 191 without significant risk to aquatic animals. With the exception of *Uca pugilator* (Fiddler Crab, LC50 = 6.2 mg a.e./L), all invertebrate test species would be affected adversely by Hydrothol® 191; LC50s for the species tested ranged from 0.022 mg a.e./L for *Daphnia magna* (*Daphnia*) to 1.4 mg a.e./L for *Pteronarcys californica* (Stonefly). All of these species would be affected by an EEC of 1.40 mg a.e. A concentration of 0.3 mg a.e./L has the potential to adversely affect both invertebrates (LC50 = 0.022 to 6.2 mg a.e./L) and fish (LC50 = 0.079 to 0.41 mg a.e./L). Therefore, Finlayson (1980) citing Ware and Gorman (1967, Eller (1973)) found limited mortality in green sunfish and common carp in irrigation ditches treated up to 1.0 mg/L. Moore and Amor (1979 in Finlayson, 1980) could not confirm these findings for Channel catfish, threadfin shad, red shiner and mosquito fish with 120 hour irrigation canal exposures of 0.2 to 0.5 mg/L causing extensive loss of these species in hard water. This led Finlayson to conclude weed control requiring treatment rates greater than 0.5 mg/Hydrothol®-191 will cause a great loss of fish. However, the 1998 label indicates that Hydrothol® 191 can be used in lakes and ponds without significant fish kill if the concentration does not exceed 1.0 mg/L.

Endothall in the form of the acid, Aquathol® K (dipotassium endothall salt) or disodium endothall should not chronically affect fish or invertebrates. Since the most sensitive species (Chinook Salmon) has an LC50 of 23 mg a.e./L the predicted NOEC (NOEC = the No Observable Effects Concentration) would be 3.6 mg a.e./L based on a Acute LC50 to Chronic NOEC ratio of 6.4 for the tested species; the value of 3.6 mg a.e./L does not differ significantly from the empirically obtained values of 5 mg a.e./L for rainbow trout and *Daphnia magna*. The chronic EEC ranges between 0.06 and 0.14 mg a.e./L based on the calculations from Ecology (1992) and Section 4.1.10.2.5, respectively. Therefore the chronic risk quotient does not exceed the chronic level of concern of 1.0 (0.06 ppm a.e./3.6 ppm a.e. = 0.017). Therefore, one can anticipate that even the most sensitive species in the biota should not be affected by endothall acid or inorganic endothall salts including Aquathol® K or disodium endothall salt.

The chronic risk for Hydrothol® 191 is more difficult to predict. There are a number of vertebrate and invertebrate species that would give chronic Risk Quotients that exceed the criterion values if the predicted chronic NOECs are used in the calculations. For example, if the most sensitive predicted environmentally relevant NOEC were used, the values for cutthroat trout would be selected. This predicted chronic NOEC value is 0.012

mg a.e./L for Hydrothol®. Using this value gives a chronic Risk Quotient of >1.0 (RQ = 0.02 ppm/0.012 ppm = 1.67 or 0.01 ppm/0.012 ppm = 0.833 with a geometric mean of 1.18) based on either of the chronic EEC values generated above in Ecology (1991) or the current assessment. However, other species that are chronically sensitive to Hydrothol® 191 include *Hexagenia spp.* (mayfly), *Hyallela azteca* (amphipod) and *Gammarus fasciatus* (scud). Since these sediment associated species should be considered in the Chronic Risk Assessment, the Chronic Risk Quotient is approximately 1.0 for the more sensitive species (RQ = 0.02 ppm/ 0.019 ppm = 1.05 or RQ = 0.01 ppm/0.019 ppm = 0.53 with a geometric mean of 0.53 with a geometric mean of 0.74). Therefore, it is possible that sediment organisms will be chronically impacted by treatment concentrations of 0.3 to 0.5 mg a.e./L. If these sediment associated organisms are eliminated from the chronic risk assessment, the chronic risk quotient becomes less than unity (RQ = 0.02 ppm a.e./0.016 ppm a.e. = 1.25 or 0.010 ppm a.e./0.016 ppm a.e. = 0.625 with a geometric mean of 0.89) using the *Daphnia magna* as the indicator species. Marine and estuarine species were eliminated because they are not environmentally relevant for the purposes of this risk assessment. The values generated in this Chronic Risk Quotient for Hydrothol® 191 are well below the criterion value of 1.0. Therefore, it should be possible to use Hydrothol® 191 and the endothall acid without significant chronic risk to free-swimming fresh water aquatic invertebrates and benthic invertebrates. Furthermore, if the treatment concentration is dropped from 0.3 - 0.5 mg a.e./L to 0.2 mg a.e./L, the chronic risk quotient will drop to below the chronic level of concern for the protection of both fish and invertebrate members the biota of <1.0 (RQ = EEC/NOEC = 0.008 ppm a.e./0.012 ppm a.e. = 0.66 for cutthroat trout).

The effects of both Aquathol® and Hydrothol® 191 on salmon smolts are uncertain, therefore, permits may be written to prohibit use of endothall products when smolts are present or in areas where salmon spawn. Failure to survive seawater challenges after exposure to endothall products at concentrations as low as 3.0 mg a.e. /L for Aquathol® K and 0.2 mg a.e./L for Hydrothol® 191 appears to be due to respiratory distress due to gill hypertrophy.

#### **1.1.4 Registration Labels**

##### **1.1.4.1 Current Labels**

There are currently five formulations of endothall registered for aquatic weed control in the United States. Elf Atochem manufactures all of these formulations. The Washington State University PICOL Database lists two of these as being registered for use in the State of Washington. These formulations are Aquathol® K Aquatic Herbicide (Flowing Water) and Hydrothol® 191 Aquatic Algicide and Herbicide. However, according to Ecology, only Aquathol® and Aquathol® K are registered for aquatic weed control in the State of Washington. Hydrothol® 191 and Hydrothol® 191 Granular are currently not registered in Washington for aquatic algae and weed control but have been used under an Experimental Use Permit (EUP) for the control of aquatic algae in some impounded waterways (i.e., golf-course ponds) and open water ways like Lake Steilacoom. The labels for endothall products currently used in Washington State are attached in Appendix 1.

### 1.1.4.2 Historical Labels

For the purpose of historical significance, two labels from 1988 and 1990 corresponding to the current Washington State registered labels for Aquathol® K and Hydrothol® 191 (liquid) are located in Appendix 2. These historical labels indicate that the formulations, recommended uses and use rates have not changed significantly for Aquathol® K and Hydrothol® 191. However, the new labels have removed the Federal one-day swimming restriction required on previous label. Label restrictions and labeled uses described in this section are given in the specimen labels for Aquathol® (1998), Aquathol® K (1998), Hydrothol® 191 (1999) and Hydrothol® 191 Granular (1999). The labels and permits that govern those restrictions may be periodically changed based on new information submitted to EPA and Ecology.

### 1.1.4.3 Label Restrictions and Additional Restrictions from Ecology

#### ▪ Label Restrictions

The label restrictions that are in place as of February 2000 are outlined below. However, label restrictions may change based on new data received by EPA. The current label contains the most up to date restrictions and is the most current label that should be consulted when applying a herbicide.

Application of endothall products must be limited to a portion of the water body at any one time because decaying vegetation can deplete the dissolved oxygen content of the water and aquatic organisms need oxygen to survive. Water containing heavy vegetation should be treated in sections to prevent suffocation of fish and other aquatic animals. Each section should be treated at least five to seven days after the previously treated section. Since Aquathol® products have low toxicity to fish, waterways lightly infested with aquatic weeds may be treated in their entirety for control of these plants. However, due to the high toxicity of Hydrothol® 191 products, not more than 10 percent of a pond or lake should be treated at any one time with Hydrothol® products for the control of aquatic weeds or algae, unless the treatment rate is less than 1.0 mg a.e./L. Hydrothol® 191 may be used at dosages higher than 1.0 mg a.e./L to treat narrow margins or in areas where some fish-kill is acceptable. See sections 1.1.4 and 4.1.10.2.5 for risk assessment information on Aquathol® and Hydrothol® products. However, Ecology may not find any level of fish-kill to be acceptable. For actual size areas recommended for treatment or other restrictions, consult the label and the permit.

Many species of fish are tolerant to Aquathol® products. The acute toxicity (LC50) of Aquathol® K ranges from 82 mg formulation/L (23 mg a.e./L) for Chinook salmon (Penwalt, 1986 in Ecology, 1992) to 740 mg formulation/L (218 mg a.e./L) for bluegill sunfish (Bettencourt, 1993). These toxicity values place Aquathol® K in the US EPA's ecotoxicological category of slightly toxic (LC50 = >10 to 100 mg/L) to practically non-toxic (LC50 = >100 mg/L) (Ebasco, 1993).

Most species of fish show high susceptibility to acute doses of Hydrothol® 191. The acute toxicity (LC50) of Hydrothol® 191 ranges from 0.34 mg formulation/L (0.079 mg a.e. /L) for cutthroat trout (Johnson & Finley, 1980) to 1.7 mg formulation/L (0.40 mg a.e. /L) for bluegill sunfish (Bettencourt, 1994). These toxicity values place

Hydrothol® 191 in the US EPA's ecotoxicological category of very highly toxic (LC50 =<0.1 mg/L) to moderately toxic (>1 mg/L to 10 mg/L) (Ebasco, 1993).

Domestic water use restrictions on the label are 7 days for Aquathol® and 7 to 25-days for Aquathol® K, Hydrothol® 191 and Hydrothol® 191 Granular depending on dosage rate and product used. Please consult the appropriate labels for water use restriction. The water use restrictions are summarized in Table 1. Do not use fish from treated areas for food or feed for three days.

Follow all additional precautionary statements and storage and disposal instructions given in the label.

- **Additional Restrictions from Ecology**

Endothall products must not be applied within a 400 foot radius of open water withdrawal pipes used to obtain water for watering livestock, for preparing agricultural sprays to be used on food crops, or for irrigation. If the water withdrawal pipes are not capped, advanced written permission must be given by those who have filed water claims to withdraw water within a 400 foot radius of the treated area. Domestic water users cannot give permission for treatment within the distance specified in the permit. If no water withdrawal pipe exists or the existing pipe is capped, the conditions of this paragraph do not apply (Ecology, 1992).

If legal permission can be obtained to close an outlet gate, the gate must be closed for the duration of the water use restriction specified on the label. Longer periods of outlet gate closure may be specified in the permit due to local conditions or practices. Up to twice the labeled water use restriction period is recommended (Ecology, 1992).

Do not swim in water at the treatment site for 8-days (Ecology, 1992).

Follow all additional conditions, public notice, posting procedures and chemical restrictions contained in the permit.

#### **1.1.3.4 Labeled Use**

All endothall products are labeled for use in ponds and lakes by the US EPA. Hydrothol® 191 Granular Aquatic Algicide and Herbicide, Hydrothol® 191 Aquatic Algicide and Herbicide (liquid form) and Aquathol® K Aquatic Herbicide (liquid form) are also registered for irrigation and drainage canal applications. Plants with floating leaves (pondweeds) should be treated at the surface with granular or slightly diluted liquid formulations. Subsurface vegetation should be treated as evenly as possible by broadcasting with the granular formulations or with the liquid formulations using surface or subsurface methods. So that drift does not adversely impact non-target or crop species, it is recommended that these herbicides be applied on relatively calm days (Aquathol®, 1998, Aquathol® K, 1998, Hydrothol® 191, 1999, and Hydrothol® 191 Granular label, 1999). All equipment should be calibrated carefully to be sure of spreading the proper amount of herbicide.

Liquid formulations of endothall should be sprayed on the water or injected below the surface and should be distributed as evenly as possible. Liquid formulations of endothall

should be applied as they come in the container or diluted with water depending on the equipment. Some dilution will give better distribution of the material.

Surfactants are not necessary when using endothall products to control submersed vegetation. However, when endothall products are used to control surface or floating weeds, a surfactant at 0.25 to 0.5% by weight should be combined with the slightly diluted liquid formulation to assist with sticking and penetration of the pesticide. This has the effect of reducing both the application rate and the cost of the application. Care should be taken to select a surfactant that has been approved for aquatic use. Surfactants approved for aquatic use will not harm fish. Thickening agents like PolyControl® or one of the organosilicates are often added to herbicide solutions that are applied to the water surface in order to control drift (Kurt Getsinger, Army Corp of Engineers Interview, Appendix 5).

When liquid formulations of endothall are applied by subsurface injection, the use of surfactants is not necessary. However, thickening agents may be used to allow the liquid endothall product to drop lower in the water column where it will be more effective (Kurt Getsinger, Army Corp of Engineers Interview, Appendix 5).

#### 1.1.3.5 Effectiveness Controlling Specific Aquatic Plant Species

Endothall products are broad-spectrum general contact herbicides. Aquathol® Granular Aquatic Herbicide, and Aquathol® K Aquatic Herbicide are effective against a wide variety of aquatic weeds at concentrations of 0.5 to 5.0 mg/L dipotassium endothall equivalents (dpe eq.) (Table 2). According to the label, the Aquathol® products typically control *Potamogeton amplifolius* (bass weed or big-leaf pondweed), *Sparganium spp.* (bur reed), *Ceratophyllum spp.* (coontail) *Hydrilla verticillata* (hydrilla), *Myriophyllum spp.* (milfoil), *Najas spp.* (bushy pondweed, water nymphs or naiads), *P. crispus* (curly-leaf pondweed), *P. zosteriformis* (flat-stem pondweed), *P. natans* (floating-leaf pondweed), *Zannichellia spp.*, (horned pondweed), *P. nodosus* (floating-leaf pondweed), *P. pectinatus* (sago pondweed), *P. diversifolius*, *P. filiformis*, *P. pusillus* (thin-leaf pondweed) and *Heteranthera spp.* (water stargrass). For rates of applications to control these species, consult the Aquathol® and Aquathol® K labels (1998). Robinette (1998-1999) and Westerdahl et al. (1988) list a variety of other species and the relative effectiveness of Aquathol® products to control the growth of these species (Table 2).

Hydrothol® 191 and Aquathol® products have a similar spectrum of activity against aquatic macrophytes. In addition to the macrophytes that Aquathol® products control, Hydrothol® 191 products also control *Elodea spp.* (American waterweed), and *Vallisneria spp.* (water celery). There is no efficacy claimed for Hydrothol® 191 to control water stargrass or bur reed. In addition to macrophytes, Hydrothol® 191 has utility in controlling algae species like *Cladophora spp.* *Pithophora spp.*, *Spirogyra spp.* and *Chara spp.* (muskgrass) (Table 2). For application rates to control these species please consult the Hydrothol® 191 Labels (1999).

Certain species of aquatic macrophytes are of particular interest to Ecology. They are *Myriophyllum spicatum* (Eurasian watermilfoil), *Lythrum salicaria*, (purple loosestrife), *Egeria densa* (Brazilian elodea), *Myriophyllum aquaticum* (parrotfeather), *Cabomba caroliniana* (fanwort), *Hydrilla verticillata* (hydrilla), *Tamarix ramosissima* (saltcedar), *Amorpha fruticosa* (indigobush), *Polygonum sachalinense*, (giant knotweed), *Polygonum*

*cuspidatum* (Japanese knotweed), *Lysimachia vulgaris* (garden loosestrife) and *Phalaris arundinacea* (reed canarygrass).

There is some disagreement on the control of these plants using endothall products. According to Robinette (1998-1999), Westerdahl (1988) and the registered labels (Labels, 1998, and 1999), endothall products control Eurasian watermilfoil, parrotsfeather and hydrilla reasonably well. According to Robinette (1998-1999), Brazilian elodea is not controlled by either Aquathol® products or Hydrothol® products. However, Westerdahl et al. (1998) claims that Brazilian elodea is controlled by the Hydrothol® products and not by the Aquathol® products. According to Getsinger (1999, personal communications), this discrepancy occurred due to a typographical error in Westerdahl et al. (1988) and difficulties in distinguishing between the three species [hydrilla, elodea (*Elodea canadensis*) and Brazilian elodea]. The confusion arises because Aquathol® K provides excellent control of hydrilla, poor control of elodea and very poor control of Brazilian elodea. However, Hydrothol® 191 will provide good control of all three species.

Some species of aquatic plants are known to resist or tolerate Aquathol® products. These species are *Nuphar ssp.* (spatterdock), *Nymphaea spp.* (fragrant water lilies) and *Typha spp.* (cattails) (Shearer and Halter, 1980), *Elodea canadensis* (American waterweed) (Ecology, 1989) and *Chara spp.* (muskgrass) (Serns, 1977). When the biomass of other aquatic species is decreased by endothall use, tolerant species may become dominant and decrease plant diversity in the treated area.

Use of endothall products to control weeds not listed on the label is not recommended. However, these weeds may be controlled incidentally as a result of application of endothall products for the control of species listed on the label.

#### **1.1.4 Maintaining the Current Registration**

Since the last Supplemental Environmental Impact Statement (1992), a number of additional studies compliant with the EPA's FIFRA Pesticide Assessment Guidelines and Good Laboratory Practice Standards have been completed and submitted to the US EPA for review. Studies that are compliant with current regulations not only add to the database but also increase the confidence of regulatory organizations, elected officials and the general public that the data supports the most recent risk assessment (Giddings, 1999) and the Supplementary Environmental Impact Statements (State of Washington 1980, 1989 and 1992). These studies may result in the addition or removal of certain use restrictions depending upon their outcome. The changes brought by the development of new data will be assessed in later sections of this document.

#### **1.1.5 Interviews with Applicators regarding Typical Practices in Washington State**

A set of questions was developed based on specific points of interest outlined by Ecology. The items that were addressed were those that the applicators (Doug Dorling of Allied Aquatics, Inc. and Terry McNabb of Resource Management, Inc.) would have direct knowledge of. Their input was incorporated in the main body of Section 1. The original questions and answers given by the applicators are presented in Appendices 3 & 4. Prior to finalization of the interviews, the respondents were requested to review the

documents, correct any errors and elaborate on points of particular interest or concern to them.

#### **1.1.6 Rate Technologies**

The same set of applicator questions was also asked of Kurt Getsinger of the Army Corp of Engineers. Dr. Getsinger heads up the Chemical Technologies Research Unit at Waterways Experiment Station. Dr. Getsinger is a leading expert and scientist in chemical control technologies. He is the author of many scientific papers in this field and co-author with Howard Westerdahl of the “Aquatic Plant Identification and Herbicide Use Guide (1988). Dr. Getsinger was also asked to discuss his research in rate reduction technology including hardware, products and methods used. Dr. Getsinger’s input was incorporated in the main body of Section 1 and in the assessments and recommendations portions of this document (Section 4). The original questions and answers given by Dr. Getsinger are presented in Appendix 5. Prior to finalization of the interview, the respondent was requested to review the document, correct any errors and elaborate on points of particular interest or concern to him.

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**Table 1: Rate of Application, Effective Concentrations, Comments and Label Restrictions for Endothall Products**

<b>Herbicide Formulation &amp; Active Ingredient</b>	<b>Comments &amp; Label Restrictions</b>
<p><b>Aquathol® K Aquatic Herbicide</b> Dipotassium salt of endothall (40.3% dpe eq.)<sup>1</sup> (28.6% endothall acid eq.) (Aquathol K Label, 1998)</p> <p><b>Aquathol® Granular Aquatic Herbicide</b> Dipotassium salt of endothall (10.1% dpe eq.)<sup>1</sup> (7.2% endothall acid eq.) (Aquathol® Granular Label, 1998)</p>	<p>For instructions on specific dose level preparation, see Aquathol® K Label (1998). For the control of aquatic weeds, application rates vary from 0.5 to 5 mg dpe eq./L (0.35 to 3.5 mg endothall acid eq./L). Rates vary depending on the target species and treatment conditions.</p> <p>Treat as soon as weeds are present with temperature at least 65°F</p> <p>Restricted water use periods for watering livestock, preparing agricultural sprays for food crops, irrigation and domestic purposes are: 7 days after treatment at 0.5 mg dpe eq./L; 14 days after treatment at 4.25 mg dpe eq./L; 25 days after treatment at 5.0 mg dpe eq./L.</p> <p>Restricted water use period for use of fish for food or feed is 3 days.</p> <p>Washington State swimming restriction is 8-days post treatment.</p> <p>For instructions on specific dose level preparation, see Aquathol® Label (1998). Application rates vary from 0.5 to 5 mg dpe eq/L (0.35 to 3.5 mg endothall acid eq/L for the control of aquatic weeds. Rates vary depending on the target species and treatment conditions.</p> <p>Treat as soon as weeds are present with temperature at least 65°F</p> <p>Restricted water use period for watering livestock, preparing agricultural sprays for food crops, irrigation and domestic purposes is 7 days.</p> <p>Restricted water use period for use of fish for food or feed is 3 days.</p> <p>Washington State swimming restriction is 8-days post treatment.</p>
<p><b>Aquathol® Super K Granular Aquatic Herbicide</b> Dipotassium salt of endothall (63.0% dpe eq.)<sup>1</sup> (44.7% endothall acid eq.)</p>	<p>Currently not registered for aquatic use in Washington State.</p>

**Table 1: Rate of Application, Effective Concentrations, Comments and Label Restrictions for Endothall Products (Continued)**

<b>Herbicide Formulation &amp; Active Ingredient</b>	<b>Comments &amp; Label Restrictions</b>
<p><b>Hydrothol® 191 Aquatic Algicide and Herbicide</b> mono(N,N-dimethylalkylamine) salt of endothall (53% dmaa eq.)<sup>2</sup> (23.36% endothall acid eq.)<sup>3</sup> (Hydrothol® Label, 1999)</p>	<p>For instructions on specific dose level preparation, see Hydrothol® 191 Label (1999). Application rates vary from 0.05 to 5.0 mg endothall acid eq/L for the control of aquatic weeds. Rates vary depending on the target species and treatment conditions.</p> <p>Treat as soon as weeds or algae are present and actively growing.</p> <p>Restricted water use periods for watering livestock, preparing agricultural sprays for food crops, irrigation and domestic purposes are: 7 days after treatment at 0.3 mg endothall acid eq./L; 14 days after treatment at 3.0 mg endothall acid eq./L; 25 days after treatment at 5.0 mg endothall acid eq./L.</p> <p>Restricted water use period for use of fish for food or feed is 3 days.</p> <p>Washington State swimming restriction is 8 days post treatment.</p>
<p><b>Hydrothol® 191 Granular Aquatic Algicide and Herbicide</b> mono(N,N-dimethylalkylamine) salt of endothall (11.2% dmaa eq.)<sup>2</sup> (5.0% endothall acid eq.)<sup>3</sup> (Hydrothol® 191 Granular Label, 1999)</p>	<p>For instructions on specific dose level preparation, see Hydrothol® 191 Granular Label (1999). Application rates vary from 0.05 to 5.0 mg endothall acid eq/L for the control of aquatic weeds. Rates vary depending on the target species and treatment conditions.</p> <p>Treat as soon as weeds or algae are present and actively growing.</p> <p>Restricted water use periods for watering livestock, preparing agricultural sprays for food crops, irrigation and domestic purposes are: 7 days after treatment at 0.3 mg endothall acid eq./L; 14 days after treatment at 3.0 mg endothall acid eq./L; 25 days after treatment at 5.0 mg endothall acid eq./L</p> <p>Restricted water use period for use of fish for food or feed is 3 days.</p> <p>Washington State swimming restriction is 8 days post treatment.</p>

- 1 For Aquathol® products, the label reports the active substance to be the active ingredient (dipotassium endothall).
- 2 dmma eq. = endothall mono(N,N-dimethylalkylamine) salt equivalence.
- 3 For Hydrothol® products, the labels report the active substance to be the acid equivalent [Mono(dimethylalkylamine) salt of endothall].

**Table 2: Species Controlled, Effectiveness of Control and Registration Status for Listed Species**

Species Controlled	Labeled Use and/or Effectiveness of Control	
	Aquathol®	Hydrothol®
<i>Najas spp.</i> Bushy pondweed, Water nymphs or Naiads	Labeled Use Excellent Control <sup>2</sup>	Labeled Use Excellent Control <sup>2</sup>
<i>Potamogeton crispus</i> Curly-leaf pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. natans</i> Floating-leaf pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>Zannichellia spp.</i> Horned pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. pectinatus</i> Sago pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. diversifolius</i>	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. pusillus</i> Thin-leaf pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>Ceratophyllum spp.</i> Coontail	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. zosteriformis</i> Flat-Stem pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. amplifolius</i> Bass weed or Big-leaf pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>Hydrilla verticillata</i> Hydrilla	Labeled Use Good Control <sup>4</sup> Excellent Control <sup>1</sup>	Labeled Use Good Control <sup>4</sup> Excellent Control <sup>1</sup>
<i>Myriophyllum spicatum</i> Eurasian \watermilfoil	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>Myriophyllum spp.</i> Milfoil	Labeled Use Good Control <sup>3</sup> Excellent Control <sup>2</sup>	Labeled Use Good Control <sup>3</sup> Excellent Control <sup>2</sup>
<i>P. americanus</i>	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. filiformis</i>	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>P. nodosus</i> Floating-leaf pondweed	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>Heteranthera spp.</i> Water stargrass	Labeled Use	No Efficacy Claimed <sup>5</sup>
<i>Sparganium spp.</i> Bur reed	Labeled Use	No Efficacy Claimed

**Table 2: Species Controlled, Effectiveness of Control and Registration Status for Listed Species (Continued)**

Species Controlled	Labeled Use and/or Effectiveness of Control	
	Aquathol®	Hydrothol®
<i>Hygrophila polysperma</i> Hygrophila	Labeled Use	Labeled Use
<i>Lythrum salicaria</i> Purple loosestrife	No Efficacy Claimed	No Efficacy Claimed
<i>Egeria densa</i> Brazilian Elodea	No Efficacy Claimed	Good Control <sup>6</sup> No Efficacy Claimed
<i>Myriophyllum aquaticum</i> Parrotsfeather	Labeled Use Excellent Control <sup>1,2</sup>	Labeled Use Excellent Control <sup>1,2</sup>
<i>Vallisneria spp.</i> Water celery	No Efficacy Claimed	Labeled Use
<i>Elodea spp.</i> American waterweed.	No Efficacy Claimed	Labeled Use Good Control <sup>4</sup>
<i>Cabomba caroliniana</i> Fanwort	No Efficacy Claimed	No Efficacy Claimed
<i>Tamarix ramosissima</i> Saltcedar	No Efficacy Claimed	No Efficacy Claimed
<i>Amorpha fruticosa</i> Indigobush	No Efficacy Claimed	No Efficacy Claimed
<i>Polygonum sachalinense</i> Giant knotweed	No Efficacy Claimed	No Efficacy Claimed
<i>Polygonum cuspidatum</i> Japanese knotweed	No Efficacy Claimed	No Efficacy Claimed
<i>Lysimachia vulgaris</i> Garden loosestrife	No Efficacy Claimed	No Efficacy Claimed
<i>Phalaris arundinacea</i> Reed canarygrass	No Efficacy Claimed	No Efficacy Claimed
<i>Elodea canadensis</i> American Waterweed	Tolerant <sup>7</sup> No Efficacy Claimed	Labeled Use
<i>Nuphar spp.</i> White water lilies	Tolerant <sup>8</sup> No Efficacy Claimed	No Efficacy Claimed
<i>Nymphaea spp.</i> Splatterdock	Tolerant <sup>8</sup> No Efficacy Claimed	No Efficacy Claimed
<i>Typha spp.</i> Cattails	Tolerant <sup>8</sup> No Efficacy Claimed	No Efficacy Claimed
<i>Hydrilla venticillata</i>	No Efficacy Claimed	No Efficacy Claimed
<i>Spartina, S. alterniflora</i> Smooth cordgrass	No Efficacy Claimed	No Efficacy Claimed
<i>Phragmites australis</i> Common reed	No Efficacy Claimed	No Efficacy Claimed
<i>Trapa natans</i> Water chestnut	No Efficacy Claimed	No Efficacy Claimed

**Table 2: Species Controlled, Effectiveness of Control and Registration Status for Listed Species  
(Continued)**

Species Controlled	Labeled Use and/or Effectiveness of Control	
	Aquathol®	Hydrothol®
Algae species		
<i>Cladophora spp.</i>	No Efficacy Claimed	Labeled Use
<i>Pithophora spp.</i>	No Efficacy Claimed	Labeled Use
<i>Spirogyra spp.</i>	No Efficacy Claimed	Labeled Use
<i>Chara spp.</i> (muskgrass)	Tolerant <sup>9</sup> No Efficacy Claimed	Labeled Use

<sup>1</sup> (Robinette, 1998-1999)

<sup>2</sup> (Westerdahl et al., 1988)

<sup>3</sup> (Robinette, 1998-1999)

<sup>4</sup> (Westerdahl et al., 1988)

<sup>5</sup> Indicated formulation has not been shown to control this species.

<sup>6</sup> Not listed as a controlled species on the Label.

<sup>7</sup> (Getsinger, 1999 ,PC)

<sup>8</sup> (Corp, 1982 in Ecology, 1989)

<sup>9</sup> (Sikka, 1977)

<sup>10</sup> Serns, 1977

## LIST OF APPENDICES

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## **APPENDIX 1: Current Labels**

Elf Atochem

# AQUATHOL®

## GRANULAR AQUATIC HERBICIDE

## ACTIVE INGREDIENT:

Dipotassium salt of endothall\* ..... 10.1%

OTHER INGREDIENTS: ..... 89.9%

TOTAL ..... 100.0%

\*7-oxabicyclo [2.2.1]heptane-2,3-dicarboxylic acid equivalent 7.2%

EPA Registration No. 4581-201

EPA Establishment No. 4581-MI-1

**KEEP OUT OF REACH OF CHILDREN****DANGER****FIRST AID:****IF IN EYES:** Hold eyelids open and flush with a steady, gentle stream of water for 15 minutes. Call a physician.**IF SWALLOWED:** Drink promptly a large quantity of milk, egg whites, gelatin solution or if these are not available, drink large quantities of water. Avoid alcohol. Call a physician immediately.**IF ON SKIN:** Immediately flush with plenty of water for at least 15 minutes. Remove and wash contaminated clothing before reuse.**NOTE TO PHYSICIAN:** Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression and convulsion may be needed.**PRECAUTIONARY STATEMENTS****HAZARDS TO HUMANS (AND DOMESTIC ANIMALS)****DANGER**

CORROSIVE. CAUSES IRREVERSIBLE EYE DAMAGE. HARMFUL IF SWALLOWED, ABSORBED THROUGH SKIN OR INHALED. AVOID CONTACT WITH SKIN OR CLOTHING. DO NOT GET IN EYES. WEAR GOGGLES OR FACE SHIELD WHEN HANDLING. Avoid breathing dust. Wash thoroughly with soap and water after handling. Remove contaminated clothing and wash before reuse.

**ENVIRONMENTAL HAZARDS**

Avoid contact with or drift to other crops or plants as injury may result. Do not use water from treated areas for irrigation or for agricultural sprays on food crops or for domestic purposes within 7 days of treatment. Do not use fish from treated area for food or feed within 3 days of treatment.

**GENERAL INFORMATION**

AQUATHOL GRANULAR is a granular aquatic herbicide for use in ponds and lakes which, under field test conditions has shown to be effective against a broad range of aquatic plants with a margin of safety to fish. Dosage rates indicated for the applications of AQUATHOL GRANULAR are measured in "Parts Per Million" (ppm). 1 ppm as a dosage rate means that there would be 1 part of AQUATHOL GRANULAR'S active ingredient in 1,000,000 parts of water. Only 1/2 to 5 ppm are generally required for aquatic weed control, whereas some fish species are tolerant to approximately 100 ppm or over. For best results treat areas of one acre or more and/or margins of at least 100 feet in large bodies of water. Thoroughly clean application equipment immediately after use.

**DIRECTIONS FOR USE**

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

**HOW TO APPLY:**

AQUATHOL GRANULAR is a contact killer, consequently, do not apply before weeds are present. Application as early as possible after weeds are present is recommended to permit use of lower application rates. However, for best results water temperature should be at a minimum of 65°F. If an entire pond is treated at one time, or if the dissolved oxygen level is low at the time of application, decay of weeds may remove enough oxygen from the water causing fish to suffocate. Water containing very heavy vegetation should be treated in sections to prevent suffocation of fish. Sections should be treated 5-7 days apart. Carefully measure size and depth of area to be treated and determine proper amount of AQUATHOL GRANULAR to apply from chart. For best results apply on a calm day where there is little wave action.

Scatter AQUATHOL GRANULAR as evenly as possible over treated areas. A cyclone seeder is useful for this purpose.

In instances where the nuisance to be controlled is an exposed surface problem (i.e., some of the broadleaved pond weeds) it is important to get good contact coverage of the problem.

Necessary approval and/or permits should be obtained in states where required.

**HOW TO DETERMINE DOSAGE RATE****(Active Ingredient)**

AQUATHOL GRANULAR is recommended for the control of the following aquatic weeds at the rates indicated. Since AQUATHOL GRANULAR'S active ingredient is water soluble and tends to diffuse from the area treated, select the

dosage rate applicable to the area to be treated. Use the lower rate in each range of rates when the growth is young and growing and/or where the weed stand is not heavy. Marginal treatments of large bodies of water require highest rates as indicated.

**WEEDS CONTROLLED AND AQUATHOL GRANULAR DOSAGE RATE CHART**

COMMON NAME	LATIN NAME	ENTIRE POND OR LARGE AREA TREATMENT	SPOT OR LAKE MARGIN TREATMENT
Bass Weed	Potamogeton amplifolius	2.0-3.0 ppm	3.0-4.0 ppm
Bur Reed	Sparganium spp.	3.0-4.0 ppm	4.0-5.0 ppm
Coontail	Ceratophyllum spp.	1.0-2.0 ppm	2.0-3.0 ppm
Hydrilla	Hydrilla verticillata	2.0-3.0 ppm	3.0-4.0 ppm
Hygrophila	Hygrophila polysperma	4.0-5.0 ppm	5.0 ppm
Milfoil	Myriophyllum spp.	2.0-3.0 ppm	3.0-4.0 ppm
Pondweed			
Bushy	Najas spp.	0.5-1.5 ppm	2.0-3.0 ppm
Curly-Leaf	Potamogeton crispus	0.5-1.5 ppm	2.0-3.0 ppm
Flat-Stem	Potamogeton zosteriformis	2.0-3.0 ppm	3.0-4.0 ppm
Floating-Leaf	Potamogeton natans	1.0-2.0 ppm	2.0-3.0 ppm
Horned	Zannichellia spp.	1.0-2.0 ppm	2.0-3.0 ppm
Sago	Potamogeton pectinatus	1.0-2.0 ppm	2.0-3.0 ppm
	Potamogeton nodosus	2.0-3.0 ppm	3.0-4.0 ppm
	Potamogeton diversifolius	1.0-2.0 ppm	2.0-3.0 ppm
	Potamogeton filiformis	2.0-3.0 ppm	3.0-4.0 ppm
	Potamogeton pusillus	1.0-2.0 ppm	2.0-3.0 ppm
Water Star Grass	Heteranthera spp.	2.0-3.0 ppm	3.0-4.0 ppm

**HOW TO DETERMINE QUANTITY TO BE APPLIED**

The following charts indicate the total quantity of material to be applied for certain size areas.

**APPROXIMATE POUNDS OF AQUATHOL GRANULAR FOR ONE ACRE\* TREATMENT DOSAGE IN POUNDS FOR VARIOUS CONCENTRATIONS IN PPM**

DEPTH	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm
1 Ft. Deep	13 lbs.	27 lbs.	40 lbs.	54 lbs.
2 Ft. Deep	27 lbs.	54 lbs.	81 lbs.	108 lbs.
3 Ft. Deep	40 lbs.	81 lbs.	121 lbs.	161 lbs.
4 Ft. Deep	54 lbs.	108 lbs.	161 lbs.	215 lbs.
5 Ft. Deep	67 lbs.	135 lbs.	202 lbs.	269 lbs.
6 Ft. Deep	81 lbs.	161 lbs.	242 lbs.	323 lbs.

DEPTH	2.5 ppm	3.0 ppm	4.0 ppm	5.0 ppm
1 Ft. Deep	67 lbs.	81 lbs.	108 lbs.	135 lbs.
2 Ft. Deep	134 lbs.	161 lbs.	215 lbs.	269 lbs.
3 Ft. Deep	202 lbs.	242 lbs.	323 lbs.	403 lbs.
4 Ft. Deep	269 lbs.	323 lbs.	430 lbs.	538 lbs.
5 Ft. Deep	336 lbs.	403 lbs.	538 lbs.	673 lbs.
6 Ft. Deep	403 lbs.	484 lbs.	646 lbs.	807 lbs.

**FOR 1000 SQUARE FEET TREATMENT DOSAGE IN POUNDS FOR VARIOUS CONCENTRATIONS IN PPM**

DEPTH	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm
1 Ft. Deep	0.3 lbs.	0.6 lbs.	0.9 lbs.	1.2 lbs.
2 Ft. Deep	0.6 lbs.	1.2 lbs.	1.9 lbs.	2.5 lbs.
3 Ft. Deep	0.9 lbs.	1.9 lbs.	2.8 lbs.	3.7 lbs.
4 Ft. Deep	1.2 lbs.	2.5 lbs.	3.7 lbs.	4.9 lbs.
5 Ft. Deep	1.5 lbs.	3.1 lbs.	4.6 lbs.	6.2 lbs.
6 Ft. Deep	1.9 lbs.	3.7 lbs.	5.6 lbs.	7.4 lbs.

DEPTH	2.5 ppm	3.0 ppm	4.0 ppm	5.0 ppm
1 Ft. Deep	1.5 lbs.	1.9 lbs.	2.5 lbs.	3.1 lbs.
2 Ft. Deep	3.1 lbs.	3.7 lbs.	4.9 lbs.	6.2 lbs.
3 Ft. Deep	4.6 lbs.	5.6 lbs.	7.4 lbs.	9.3 lbs.
4 Ft. Deep	6.2 lbs.	7.4 lbs.	9.9 lbs.	12.4 lbs.
5 Ft. Deep	7.7 lbs.	9.3 lbs.	12.4 lbs.	15.4 lbs.
6 Ft. Deep	9.3 lbs.	11.1 lbs.	14.8 lbs.	18.5 lbs.

\*One acre equals approximately 208' x 208'

Where the area to be treated is greater than those listed in the charts proceed as follows:

- Compute the approximate surface acreage
- Compute the average depth
- Multiply a. by b. to determine the total number of acre/feet
- Multiply the pounds required at the 1 foot depth under the rate to be used by the number of acre/feet to determine total quantity to be used.

**STORAGE AND DISPOSAL**

Do not contaminate water, food, or feed by storage or disposal.

**Storage Instructions:** Store in the original container, preferably in a locked storage area. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. If spilled during storage or handling sweep up spillage and dispose of in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

**EMERGENCY TELEPHONE NUMBERS:**

**CHEMTREC:** (800) 424-9300

**MEDICAL:** (303) 623-5716

Rocky Mountain Poison Control Center

**WARRANTY AND DISCLAIMER**

Elf Atochem North America warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. ELF ATOCHEM MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL ELF ATOCHEM OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COST; OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Elf Atochem and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Elf Atochem.

5-K103S-03 CI (9/98)

## Elf Atochem

# AQUATHOL® K

## AQUATIC HERBICIDE

## ACTIVE INGREDIENT:

Dipotassium salt of endothall\* ..... 40.3%

INERT INGREDIENTS: ..... 59.7%

TOTAL ..... 100.0%

\*7-oxabicyclo [2.2.1]heptane-2,3-dicarboxylic acid equivalent 28.6%

Contains per gallon 4.23 lbs. dipotassium endothall

(equivalent to 3.0 lbs. endothall acid)

EPA Registration No. 4581-204

EPA Establishment No. 4581-MI-1

**KEEP OUT OF REACH OF CHILDREN****DANGER****STATEMENT OF PRACTICAL TREATMENT****IF IN EYES:** Hold eyelids open and flush with a steady, gentle stream of water for 15 minutes. Get medical attention.**IF SWALLOWED:** Call a physician or Poison Control Center. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger. If person is unconscious, do not give anything by mouth and do not induce vomiting.**IF INHALED:** Remove victim to fresh air. If not breathing, give artificial respiration, preferably mouth-to-mouth. Get medical attention.**IF ON SKIN:** Wash with plenty of soap and water. Get medical attention.**NOTE TO PHYSICIAN:** Measures against circulatory shock, respiratory depression and convulsion may be needed.**GENERAL INFORMATION**

AQUATHOL K is a liquid concentrate soluble in water which is effective against a broad range of aquatic plants with a margin of safety to fish.

Dosage rates indicated for the application of AQUATHOL K are measured in "Parts Per Million" (ppm) of dipotassium endothall. Only 0.5 to 5.0 ppm are generally required for aquatic weed control, whereas some fish species are tolerant to approximately 100 ppm or over.

**DIRECTIONS FOR USE**

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

**AQUATIC WEEDS CONTROLLED AND DOSAGE RATE CHARTS**

AQUATHOL K is recommended for the control of the following aquatic weeds in irrigation and drainage canals, ponds and lakes at the rates indicated. Since the active ingredient is water soluble and tends to diffuse from the area treated, select the dosage rate applicable to the area to be treated. Use the lower rate in each range of rates where the growth is young and growing and/or where the weed stand is not heavy. Marginal treatments of large bodies of water require higher rates as indicated.

**HOW TO APPLY:**

AQUATHOL K is a contact killer; consequently, do not apply before weeds are present. Application as early as possible after weeds are present is recommended to permit use of lower application rates. However, for best results water temperature should be at least 65°F or above. If an entire pond is treated at one time, or if the dissolved oxygen level is low at time of application, decay of weeds may remove enough oxygen from the water, causing fish to suffocate. Water containing very heavy vegetation should be treated in sections to prevent suffocation of fish. Sections should be treated 5-7 days apart. Carefully measure size and depth of area to be treated and determine amount of AQUATHOL K to apply from chart. For best results apply on a calm day where there is little wave action.

AQUATHOL K should be sprayed on the water or injected below the water surface and should be distributed as evenly as possible. It may be applied as it comes from the container or diluted with water depending on the equipment. Some dilution will give better distribution.

In instances where the nuisance to be controlled is an exposed surface problem (i.e., some of the broad-leaved pond weeds) it is important to get good contact coverage utilizing the highest concentration (least water dilution) compatible with the type of equipment used so that even distribution is achieved.

Necessary approval and/or permits should be obtained in states where required.

COMMON NAME	LATIN NAME	ENTIRE POND OR LARGE AREA TREATMENT	SPOT OR LAKE MARGIN TREATMENT
Bass Weed	Potamogeton amplifolius	2.0-3.0 ppm	3.0-4.0 ppm
Bur Reed	Spartanium spp.	3.0-4.0 ppm	4.0-5.0 ppm
Coontail	Ceratophyllum spp.	1.0-2.0 ppm	2.0-3.0 ppm
Hydrilla	Hydrilla verticillata	2.0-3.0 ppm	3.0-4.0 ppm
Hygrophila	Hygrophila polysperma	4.0-5.0 ppm	5.0 ppm
Milfoil	Myriophyllum spp.	2.0-3.0 ppm	3.0-4.0 ppm
Pondweed			
Bushy	Najas spp.	0.5-1.5 ppm	2.0-3.0 ppm
Curly-Leaf	Potamogeton crispus	0.5-1.5 ppm	2.0-3.0 ppm
Flat-Stem	Potamogeton zosteriformis	2.0-3.0 ppm	3.0-4.0 ppm
Floating-Leaf	Potamogeton natans	1.0-2.0 ppm	2.0-3.0 ppm
Horned	Zannichellia spp.	1.0-2.0 ppm	2.0-3.0 ppm
Sago	Potamogeton pectinatus	1.0-2.0 ppm	2.0-3.0 ppm
	Potamogeton americanus	2.0-3.0 ppm	3.0-4.0 ppm
	Potamogeton diversifolius	1.0-2.0 ppm	2.0-3.0 ppm
	Potamogeton filiformis	2.0-3.0 ppm	3.0-4.0 ppm
	Potamogeton pusillus	1.0-2.0 ppm	2.0-3.0 ppm
Water Star	Heteranthera spp.	2.0-3.0 ppm	3.0-4.0 ppm
Grass			

**RATE OF APPLICATION—LAKES AND PONDS**

The following chart indicates the total quantity of material to be applied.

**APPROXIMATE GALLONS OF AQUATHOL K FOR ONE ACRE (208' × 208') TREATMENT**

DEPTH	DOSAGE IN GALLONS FOR VARIOUS CONCENTRATIONS IN PPM						
	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm	3.0 ppm	4.0 ppm	5.0 ppm
1 ft. ....	0.3	0.6	1.0	1.3	1.9	2.6	3.2
2 ft. ....	0.6	1.3	1.9	2.6	3.8	5.1	6.4
4 ft. ....	1.3	2.6	3.8	5.1	7.7	10.2	12.8
6 ft. ....	1.9	3.8	5.8	7.6	11.5	15.3	19.2

**RATE OF APPLICATION—IRRIGATION AND DRAINAGE CANALS\*\***

The following indicates the total quantity of material to be applied.

**GALLONS OF AQUATHOL K REQUIRED TO TREAT 1 MILE BY 1 FOOT DEEP\***

PPM	WIDTH OF CANAL IN FEET			
	5	10	15	20
1.0 ppm	0.4	0.75	1.2	1.5
2.0 ppm	0.75	1.5	2.3	3.0
3.0 ppm	1.2	2.3	3.5	4.5
4.0 ppm	1.5	3.0	4.5	6.0
5.0 ppm	2.0	3.8	5.7	7.5

The minimum contact time with weeds for optimum results should be 2 hours.

\*For deeper water, adjust rate accordingly.

\*\*Not for this use in California.

**PRECAUTIONARY STATEMENTS****HAZARDS TO HUMANS (AND DOMESTIC ANIMALS)****DANGER****CORROSIVE. CAUSES IRREVERSIBLE EYE DAMAGE. MAY BE FATAL IF SWALLOWED OR INHALED. HARMFUL IF ABSORBED THROUGH SKIN. DO NOT GET IN EYES, ON SKIN, OR ON CLOTHING. DO NOT BREATHE SPRAY VAPORS.**

Applicators and other handlers must wear:

- Long-sleeved shirt and long pants
- Waterproof gloves
- Shoes plus socks
- Protective eyewear

**USER SAFETY RECOMMENDATIONS:**

Users should:

- Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet.
- Remove clothing immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing.
- Remove protective clothing and equipment immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing.

**ENVIRONMENTAL HAZARDS**

Avoid contact with or drift to other crops or plants as injury may result. Wash out spray equipment with water after each operation.

Do not use fish from treated areas for food or feed within 3 days of treatment. Do not use water from treated areas for watering livestock, for preparing agricultural

sprays for food crops, for irrigation or for domestic purposes within the following periods:

Up to 0.5 ppm dipotassium salt  
(0.35 ppm acid equivalent)—7 days after application

Up to 4.25 ppm dipotassium salt  
(3.0 ppm acid equivalent)—14 days after application

Up to 5.0 ppm dipotassium salt  
(3.5 ppm acid equivalent)—25 days after application

Treated water can be used for sprinkling bent grass immediately.

#### STORAGE AND DISPOSAL

Do not contaminate water, food, or feed by storage or disposal.

**Storage Instructions:** Store in the original container. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. Storage at temperatures below 32°F may result in the product freezing or crystallizing. Should this occur the product must be warmed to 50°F or higher and thoroughly agitated. In the event of a spillage during handling or storage, absorb with sand or other inert material and dispose of absorbent in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

#### WARRANTY AND DISCLAIMER

Elf Atochem North America warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. ELF ATOCHEM MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL ELF ATOCHEM OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COST; OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Elf Atochem and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Elf Atochem.

5-C102S-03 15 (1/98)

**elf atochem**



# AQUATHOL<sup>®</sup> SUPER K

## GRANULAR AQUATIC HERBICIDE

ACTIVE INGREDIENT:  
Dipotassium salt of endothall\* 63.0%  
INERT INGREDIENTS: 37.0%  
TOTAL 100.0%

\*7-oxabicyclo [2.2.1]heptane-2,3-dicarboxylic acid equivalent 44.7%  
EPA Registration No. 4581-388 EPA Establishment No. 39578-TX-1

### KEEP OUT OF REACH OF CHILDREN

### DANGER

#### STATEMENT OF PRACTICAL TREATMENT

**IF IN EYES:** Hold eyelids open and flush with a steady, gentle stream of water for 15 minutes. Get medical attention.

**IF SWALLOWED:** Call a physician or Poison Control Center. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger. If person is un-conscious, do not give anything by mouth or do not induce vomiting.

**IF ON SKIN:** Wash with plenty of soap and water. Get medical attention if irritation persists.

**NOTE TO PHYSICIAN:** Probable mucosal damage may contraindicate the use of gastric lavage.

#### PRECAUTIONARY STATEMENTS

##### HAZARDS TO HUMANS (AND DOMESTIC ANIMALS)

### DANGER

**CORROSIVE. CAUSES IRREVERSIBLE EYE DAMAGE. MAY BE FATAL IF SWALLOWED. HARMFUL IF ABSORBED THROUGH THE SKIN.** Do not get in eyes, on skin or on clothing. Wear protective eyewear (goggles or face shield). Wash thoroughly with soap and water after handling and before eating, drinking or using tobacco. Remove contaminated clothing and wash clothing before reuse.

#### ENVIRONMENTAL HAZARDS

Avoid contact with or drift to other crops or plants as injury may result.

Do not use water from treated areas for irrigation or for agricultural sprays on food crops or for domestic purposes within 7 days of treatment.

Do not use fish from treated areas for food or feed within 3 days of treatment.

#### GENERAL INFORMATION

AQUATHOL SUPER K is a granular aquatic herbicide for use in ponds and lakes which, under field test conditions has shown to be effective against a broad range of aquatic plants with a margin of safety to fish. Dosage rates indicated for the applications of AQUATHOL SUPER K are measured in "Parts Per Million" (ppm). 1 ppm as a dosage rate means that there would be 1 part of AQUATHOL SUPER K's active ingredient in 1,000,000 parts of water. Only 0.5 to 5 ppm are generally required for aquatic weed control, whereas some fish species are tolerant to approximately 100 ppm or over. For best results treat areas of one acre or more and/or margins of at least 100 feet in large bodies of water.

Thoroughly clean application equipment immediately after use.

#### DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

#### HOW TO APPLY

AQUATHOL SUPER K is a contact herbicide, consequently, do not apply before weeds are present. Treat as early as possible after weeds are present and are actively growing. If an entire pond is treated at one time, or if the dissolved oxygen level is low at the time of application, decay of weeds may remove enough oxygen from the water causing fish to suffocate. Water containing very heavy vegetation should be treated in sections to prevent suffocation of fish. Sections should be treated 5-7 days apart. Carefully measure size and depth of area to be treated and determine proper amount of AQUATHOL SUPER K to apply. For best results apply on a calm day where there is little wave action.

Scatter AQUATHOL SUPER K as evenly as possible over treated areas. A cyclone seeder is useful for this purpose. In instances where the nuisance to be controlled is an exposed surface problem (i.e., some of the broadleaved pond weeds) it is important to get good contact coverage of the problem.

Necessary approval and/or permits should be obtained in states where required.

#### HOW TO DETERMINE DOSAGE RATE (Active Ingredient)

AQUATHOL SUPER K is recommended for the control of the following aquatic weeds at the rates indicated. Since AQUATHOL SUPER K's active ingredient is water soluble and tends to diffuse from the area treated, select the dosage rate applicable to the area to be treated. Use the lower rate in each range of rates when the growth is young and growing and/or where the weed stand is not heavy. Marginal treatments of large bodies of water require highest rates as indicated.

**WEEDS CONTROLLED AND AQUATHOL GRANULAR DOSAGE RATE CHART**

Common Name	Latin Name	Entire Pond Or Large Area Treatment	Spot Or Lake Margin Treatment
Bass Weed .....	Potamogeton amplifolius .....	2.0-3.0 ppm .....	3.0-4.0 ppm
Bur Reed .....	Sparganium spp. ....	3.0-4.0 ppm .....	4.0-5.0 ppm
Coontail .....	Ceratophyllum spp.....	1.0-2.0 ppm .....	2.0-3.0 ppm
Hydrilla.....	Hydrilla verticillata.....	2.0-3.0 ppm .....	3.0-4.0 ppm
Hygrophila .....	Hygrophila polysperma.....	4.0-5.0 ppm .....	5.0 ppm
Milfoil .....	Myriophyllum spp. ....	2.0-3.0 ppm .....	3.0-4.0 ppm
Pondweed.....			
Bushy.....	Najas spp. ....	0.5-1.5 ppm .....	2.0-3.0 ppm
Curly-Leaf.....	Potamogeton crispus.....	0.5-1.5 ppm .....	2.0-3.0 ppm
Flat-Stem.....	Potamogeton zosteriformis.....	2.0-3.0 ppm .....	3.0-4.0 ppm
Floating-Leaf.....	Potamogeton natans .....	1.0-2.0 ppm .....	2.0-3.0 ppm
Horned.....	Zannichellia spp. ....	1.0-2.0 ppm .....	2.0-3.0 ppm
Sago .....	Potamogeton pectinatus.....	1.0-2.0 ppm .....	2.0-3.0 ppm
.....	Potamogeton nodosus.....	2.0-3.0 ppm .....	3.0-4.0 ppm
.....	Potamogeton diversifolius .....	1.0-2.0 ppm .....	2.0-3.0 ppm
.....	Potamogeton filiformis.....	2.0-3.0 ppm .....	3.0-4.0 ppm
.....	Potamogeton pusillus .....	1.0-2.0 ppm .....	2.0-3.0 ppm
Water Star Grass.....	Heteranthera spp.....	2.0-3.0 ppm.....	3.0-4.0 ppm

**APPROXIMATE POUNDS OF AQUATHOL SUPER K FOR ONE ACRE\*  
TREATMENT DOSAGE IN POUNDS FOR VARIOUS CONCENTRATIONS IN PPM**

DEPTH	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm	3.0 ppm	4.0 ppm	5.0 ppm
1 Ft. Deep	2.2 lbs.	4.4 lbs.	6.6 lbs.	8.8 lbs.	13.2 lbs.	17.6 lbs.	22 lbs.
2 Ft. Deep	4.4 lbs.	8.8 lbs.	13.2 lbs.	17.6 lbs.	26.4 lbs.	35.2 lbs.	44 lbs.
3 Ft. Deep	6.6 lbs.	13.2 lbs.	19.8 lbs.	26.4 lbs.	39.6 lbs.	52.8 lbs.	66 lbs.
4 Ft. Deep	8.8 lbs.	17.6 lbs.	26.4 lbs.	35.2 lbs.	52.8 lbs.	70.4 lbs.	88 lbs.
5 Ft. Deep	11 lbs.	22 lbs.	33 lbs.	44 lbs.	66 lbs.	88 lbs.	110 lbs.

\*One acre equals approximately 208' x 208'

Where the area being treated is greater than those listed in the charts, proceed as follows:

- Compute the approximate surface acreage
- Compute the average depth
- Multiply a. by b. to determine total number of acre/feet
- Multiply the pounds required at the 1 foot depth under the rate to be used by the number of acre/feet to determine the total quantity to be used.

**EMERGENCY TELEPHONE NUMBERS:**

**CHEMTREC: (800) 424-9300**

**MEDICAL: (303) 623-5716**

Rocky Mountain Poison Control Center

**WARRANTY AND DISCLAIMER**

Elf Atochem North America warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. ELF ATOCHEM MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL ELF ATOCHEM OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COST, OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Elf Atochem and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Elf Atochem.

5-A104S-01-B7 (9/98)

Made and Printed in U.S.A.

**STORAGE AND DISPOSAL**

Do not contaminate water, food, or feed by storage or disposal.

**Storage Instructions:** Store in the original container, preferably in a locked storage area. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. If spilled during storage or handling sweep up spillage and dispose of in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

# AQUATHOL SUPERK

## GRANULAR AQUATIC HERBICIDE

**ACTIVE INGREDIENT:**

Dipotassium salt of endosulf\*

63.0%

**OTHER INGREDIENTS:**

37.0%

TOTAL

100.0%

\*7-oxabicyclo [2.2.1]heptane-2,3-dicarboxylic acid equivalent 44.7%

**KEEP OUT OF REACH OF CHILDREN**

**DANGER**

**FIRST AID:**

**IF IN EYES:** Hold eyelids open and flush with a steady, gentle stream of water for 15 minutes. Get medical attention.

**IF SWALLOWED:** Call a physician or Poison Control Center. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger. If person is unconscious, do not give any- thing by mouth or do not induce vomiting.

**IF ON SKIN:** Wash with plenty of soap and water. Get medical attention.

**NOTE TO PHYSICIAN:** Probable mucosal damage may contraindicate the use of gastric lavage.

See back panel for additional Precautionary Statements.

EPA Registration No. 4581-388

EPA Establishment No. 62171-MS-001

**Net Weight** \_\_\_\_\_

**Cerexagri, Inc.**

2000 Market Street, Philadelphia, PA 19103

1 800-438-6071 • [www.cerexagri.com](http://www.cerexagri.com)



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## PRECAUTIONARY STATEMENTS

### HAZARDS TO HUMANS (AND DOMESTIC ANIMALS)

#### DANGER

CORROSIVE. CAUSES IRREVERSIBLE EYE DAMAGE. MAY BE FATAL IF SWALLOWED. HARMFUL IF ABSORBED THROUGH THE SKIN. Do not get in eyes, on skin or on clothing. Wear protective eyewear (goggles or face shield). Wash thoroughly with soap and water after handling and before eating, drinking or using tobacco. Remove contaminated clothing and wash before reuse.

### ENVIRONMENTAL HAZARDS

Avoid contact with or drift to other crops or plants as injury may result.

Do not use water from treated areas for irrigation, for agricultural sprays on food crops or for domestic purposes within 7 days of treatment.

Do not use fish from treated areas for food or feed within 3 days of treatment.

### GENERAL INFORMATION

AQUATHOL SUPER K is a granular aquatic herbicide for use in ponds and lakes which, under field test conditions has shown to be effective against a broad range of aquatic plants with a margin of safety to fish. Dosage rates indicated for the applications of AQUATHOL SUPER K are measured in "Parts Per Million" (ppm). 1 ppm as a dosage rate means that there would be 1 part of AQUATHOL SUPER K's active ingredient in 1,000,000 parts of water. Only 0.5 to 5 ppm are generally required for aquatic weed control, whereas some fish species are tolerant to approxi-mately 100 ppm or over. For best results treat areas of one acre or more and/or margins of at least 100 feet in large bodies of water. Thoroughly clean application equipment immediately after use.

### DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

## HOW TO APPLY

AQUATHOL SUPER K is a herbicide, consequently, do not apply before weeds are present. Treat as early as possible after weeds are present and are actively growing. If an entire pond is treated at one time, or if the dissolved oxygen level is low at the time of application, decay weeds may remove enough oxygen from the water causing fish to suffocate. Water containing very heavy vegetation should be treated in sections to prevent suffocation of fish. Sections should be treated 5-7 days apart.

Carefully measure size and depth of area to be treated and determine proper amount of AQUATHOL SUPER K to apply. For best results apply when water is quiescent and/or flows are minimal.

Apply AQUATHOL SUPER K as evenly as possible over treated areas. A cyclone spreader is useful for this purpose. In instances where the nuisance weed(s) to be controlled is an exposed surface problem (i.e., some of the broad-leaved pond weeds) coverage is important. Necessary approval and/or permits should be obtained in states where required.

### WEEDS CONTROLLED AND AQUATHOL SUPER K DOSAGE RATE CHART

Aquatic Weed	Entire Pond/Lake or Large Area Treatment		Spot or Lake Margin Treatment	
	Lbs. per Acre Ft.	Lbs. per Acre Ft.	Lbs. per Acre Ft.	Lbs. per Acre Ft.
Bur Reed, Sparganium spp.	3.0-4.0 ppm	13.2-17.6 lbs.	4.0-5.0 ppm	17.6-22.0 lbs.
Coontail, Ceratophyllum spp.	1.0-2.0 ppm	4.4-8.8 lbs.	2.0-3.0 ppm	8.8-13.2 lbs.
Horned Pondweed, Zannichellia palustris	1.0-2.0 ppm	4.4-8.8 lbs.	2.0-3.0 ppm	8.8-13.2 lbs.
Hydrilla, Hydrilla verticillata	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.
Hydrophila, Hydrophila polysperma	4.0-5.0 ppm	17.6-22.0 lbs.	5.0 ppm	22.0 lbs.
Milfoil, Myriophyllum spp.	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.
Naiad, Naias spp.	1.0-3.0 ppm	4.4-13.2 lbs.	2.0-4.0 ppm	8.8-17.6 lbs.
Pondweed, Pontamogeton spp.	0.5-3.0 ppm	2.2-13.2 lbs.	1.5-4.0 ppm	6.6-17.6 lbs.
Including:				
American, P. nodosus	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.
Largeleaf (Bass Weed), P. Amplifolius	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.
Curlleaf, P. crispus	0.5-1.5 ppm	2.2-6.6 lbs.	1.5-3.0 ppm	6.6-13.2 lbs.
Flatstem, P. zosteriformis	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.
Floating-leaf, P. natans	1.0-2.0 ppm	4.4-8.8 lbs.	2.0-3.0 ppm	8.8-13.2 lbs.
Illinois, P. Illinoensis	1.5-2.5 ppm	6.6-11.0 lbs.	2.5-3.5 ppm	11.0-15.4 lbs.
Narrowleaf, P. pusillus	4.4-8.8 lbs.	19.8-39.6 lbs.	8.8-13.2 lbs.	39.6-52.8 lbs.
Slender, P. filiformis	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.
Sagp, P. pectinatus	4.4-8.8 lbs.	19.8-39.6 lbs.	8.8-13.2 lbs.	39.6-52.8 lbs.
Variable Leaf, P. diversifolius	1.0-2.0 ppm	4.4-8.8 lbs.	2.0-3.0 ppm	8.8-13.2 lbs.
Parrot Feather, Myriophyllum aquaticum	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.
Water Stargrass, Heteranthera spp.	2.0-3.0 ppm	8.8-13.2 lbs.	3.0-4.0 ppm	13.2-17.6 lbs.

### APPROXIMATE POUNDS OF AQUATHOL SUPER K FOR ONE ACRE\*

DEPTH	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm	3.0 ppm	4.0 ppm	5.0 ppm
1 Ft. Deep	2.2 lbs.	4.4 lbs.	6.6 lbs.	8.8 lbs.	13.2 lbs.	17.6 lbs.	22 lbs.
2 Ft. Deep	4.4 lbs.	8.8 lbs.	13.2 lbs.	26.4 lbs.	39.6 lbs.	52.8 lbs.	66 lbs.
3 Ft. Deep	6.6 lbs.	13.2 lbs.	19.8 lbs.	26.4 lbs.	39.6 lbs.	52.8 lbs.	66 lbs.
4 Ft. Deep	8.8 lbs.	17.6 lbs.	26.4 lbs.	35.2 lbs.	52.8 lbs.	70.4 lbs.	88 lbs.
5 Ft. Deep	11 lbs.	22 lbs.	33 lbs.	44 lbs.	66 lbs.	88 lbs.	110 lbs.

\*One acre equals approximately 208' x 208'

Where the area being treated is greater than those listed in the charts, proceed as follows:

- Compute the approximate surface acreage
- Multiply a. by b. to determine total number of acre/feet
- Determine the average depth
- Multiply the pounds required at the 1 foot depth under the rate to be used by the number of acre/feet to determine the total quantity to be used.

### APPROXIMATE POUNDS OF AQUATHOL SUPER K FOR 1000 SQUARE FEET

DEPTH	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm	3.0 ppm	4.0 ppm	5.0 ppm
1 Ft. Deep	0.06 lbs.	0.1 lbs.	0.15 lbs.	0.2 lbs.	0.3 lbs.	0.4 lbs.	0.5 lbs.
2 Ft. Deep	0.1 lbs.	0.2 lbs.	0.3 lbs.	0.6 lbs.	0.9 lbs.	1.2 lbs.	1.5 lbs.
3 Ft. Deep	0.15 lbs.	0.3 lbs.	0.45 lbs.	0.6 lbs.	0.9 lbs.	1.2 lbs.	1.5 lbs.
4 Ft. Deep	0.2 lbs.	0.4 lbs.	0.6 lbs.	0.8 lbs.	1.2 lbs.	1.6 lbs.	2.0 lbs.
5 Ft. Deep	0.25 lbs.	0.5 lbs.	0.75 lbs.	1.0 lbs.	1.5 lbs.	2.0 lbs.	2.5 lbs.

Where the depth is greater than 5 feet, multiply the depth by the approximate rate for 1 ft. depth to determine the amount of product required per 1000 square feet.

## HOW TO DETERMINE DOSAGE RATE (Active Ingredient)

AQUATHOL SUPER K is recommended for the control of the following aquatic weeds at the rates indicated. Since AQUATHOL SUPER K's active ingredient is water soluble and tends to diffuse from the treated area, select the dosage rate applicable to the area to be treated. Use the lower rate in each range when the growth is young and growing and/or where the weed stand is not heavy. Marginal treatments of large bodies of water require higher rates as indicated.

### STORAGE AND DISPOSAL

Do not contaminate water, food or feed by storage or disposal.

**Storage Instructions:** Store in the original container, preferably in a locked storage area. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. If spilled during storage or handling sweep up spillage and dispose of in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

### WARRANTY AND DISCLAIMER

Cerexagri, Inc. warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. CEREXAGRI MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL CEREXAGRI OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COST, OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Cerexagri and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Cerexagri.

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## AQUATHOL SUPER K

–Material Safety Data Sheet–  
Elf Atochem North America, Inc.

### 1 PRODUCT AND COMPANY IDENTIFICATION

#### Agrichemicals Group

Elf Atochem North America, Inc.  
2000 Market St.  
Philadelphia, PA 19103-3222

#### EMERGENCY PHONE NUMBERS:

Chemtrec: (800) 424-9300 (24hrs) or (703) 527-3887  
Medical: Rocky Mountain Poison Control Center  
(303) 623-5716 (24Hrs)

Information Telephone Numbers	Phone Number	Available Hrs
R&D Technical Service	610-878-6100	8:00am to 5:00pm EST
Customer Service	1-800-438-6071	8:00am - 5:00 pm EST
Product Name	AQUATHOL SUPER K	
Product Synonym(s)		
Chemical Family	Dicarboxylic acid	
Chemical Formula	C8H8O5K2	
Chemical Name	Dipotassium endothall	
EPA Reg Num	4581-388	
Product Use	Aquatic herbicide	

### 2 COMPOSITION / INFORMATION ON INGREDIENTS

Ingredient Name	CAS Registry Number	Typical Wt. %	OSHA
Endothal-potassium	2164-07-0	63.0%	Y
2-Propenamide, polymer with potassium	31212-13-2	27.5%	Y

The substance(s) marked with a "Y" in the OSHA column, are identified as hazardous chemicals according to the criteria of the OSHA Communication Standard (29 CFR 1910.1200)

### 3 HAZARDS IDENTIFICATION

#### Emergency Overview

Beige granular material, odorless.  
KEEP OUT OF REACH OF CHILDREN.  
DANGER!  
Causes irreversible eye damage  
MAY BE FATAL IF SWALLOWED.  
HARMFUL IF ABSORBED THROUGH SKIN.

Do not get in eyes, on skin or on clothing.  
Avoid breathing dust.

#### Potential Health Effects

Inhalation and skin contact are expected to be the primary routes of occupational exposure to this material. Based on single exposure animal tests, it is considered to be moderately toxic if swallowed, no more than slightly toxic if absorbed through skin, severely irritating to eyes and slightly irritating to skin.

# AQUATHOL SUPER K

–Material Safety Data Sheet–  
Elf Atochem North America, Inc.

## 4 FIRST AID MEASURES

IF IN EYES, Hold eyelids open and flush with a steady, gentle stream of water for 15 minutes. Get medical attention.

IF ON SKIN, Wash with plenty of soap and water. Get medical attention if irritation persists.

IF SWALLOWED, Call a physician or Poison Control Center. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger. If person is unconscious, do not give anything by mouth and do not induce vomiting.

IF INHALED, Remove victim to fresh air. If not breathing, give artificial respiration, preferably mouth to mouth. Get medical attention.

## 5 FIRE FIGHTING MEASURES

### Fire and Explosive Properties

Auto-ignition Temperature	NE	
Flash Point	NE	Flash Point Method
Flammable Limits - Upper	NE	
Lower	NE	

### Extinguishing Media

Use water spray, carbon dioxide, foam or dry chemical.

### Fire Fighting Instructions

Fire fighters and others who may be exposed to products of combustion should wear full fire fighting turn out gear (full Bunker Gear) and self-contained breathing apparatus (pressure demand NIOSH approved or equivalent). Fire fighting equipment should be thoroughly decontaminated after use.

### Fire and Explosion Hazards

None known.

## 6 ACCIDENTAL RELEASE MEASURES

### In Case of Spill or Leak

Contain spill. Sweep or scoop up and remove to suitable container. Flush with water. Prevent spilled product from entering sewers or natural water. Consult a regulatory specialist to determine appropriate state or local reporting requirements, for assistance in waste characterization and/or hazardous waste disposal and other requirements listed in pertinent environmental permits.

## 7 HANDLING AND STORAGE

# AQUATHOL SUPER K

–Material Safety Data Sheet–  
Elf Atochem North America, Inc.

## 7 HANDLING AND STORAGE

### Handling

Do not breathe dust. Avoid contact with eyes, skin and clothing.  
Wash thoroughly after handling. Keep container closed.  
Empty container may contain hazardous residues.  
KEEP OUT OF REACH OF CHILDREN.

### Storage

Do not store in a manner where cross-contamination with pesticides, fertilizers, food or feed could occur.

## 8 EXPOSURE CONTROLS / PERSONAL PROTECTION

### Engineering Controls

Investigate engineering techniques to reduce exposures. Provide ventilation if necessary to minimize exposure. Dilution ventilation is acceptable, but local mechanical exhaust ventilation preferred, if practical, at sources of air contamination such as open process equipment. Consult ACGIH ventilation manual or NFPA Standard 91 for design of exhaust systems.

### Eye / Face Protection

Where there is potential for eye contact, wear chemical goggles and have eye flushing equipment immediately available.

### Skin Protection

Minimize skin contamination by following good industrial hygiene practice. Wearing rubber gloves is recommended. Wash hands and contaminated skin thoroughly after handling.

### Respiratory Protection

Where airborne exposure is likely, use NIOSH approved respiratory protection equipment appropriate to the material and/or its components. If exposures cannot be kept at a minimum with engineering controls, consult respirator manufacturer to determine appropriate type equipment for a given application. Observe respirator use limitations specified by NIOSH or the manufacturer. For emergency and other conditions where there may be a potential for significant exposure, use an approved full face positive-pressure, self-contained breathing apparatus or positive-pressure airline with auxiliary self-contained air supply. Respiratory protection programs must comply with 29 CFR § 1910.134.

### Airborne Exposure Guidelines for Ingredients

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The components of this product have no established Airborne Exposure Guidelines

- Only those components with exposure limits are printed in this section.
- Skin contact limits designated with a "Y" above have skin contact effect. Air sampling alone is insufficient to accurately quantitate exposure. Measures to prevent significant cutaneous absorption may be required.
- ACGIH Sensitizer designator with a value of "Y" above means that exposure to this material may cause allergic reactions.

# AQUATHOL SUPER K

–Material Safety Data Sheet–  
Elf Atochem North America, Inc.

## 9 PHYSICAL AND CHEMICAL PROPERTIES

Appearance/Odor	Beige granular material, odorless.
pH	6.9 (1% aqueous soln)
Specific Gravity	0.607 g/cm <sup>3</sup>
Vapor Pressure	Negligible
Vapor Density	N/A
Melting Point	N/A
Freezing Point	N/A
Boiling Point	N/A
Solubility In Water	>65 g/100ml
Evaporation Rate	N/A
Percent Volatile	N/A

## 10 STABILITY AND REACTIVITY

### Stability

This material is chemically stable under normal and anticipated storage and handling conditions.

### Hazardous Polymerization

Does not occur.

### Incompatibility

None known.

### Hazardous Decomposition Products

Elevated temperatures convert endothal to anhydride, a strong vesicant, causing blisters of eyes, mucous membranes, and skin.

## 11 TOXICOLOGICAL INFORMATION

### Toxicological Information

Data on this material and/or its components are summarized below.

Single exposure (acute) studies indicate:

Oral - Moderately Toxic to Rats (LD<sub>50</sub> 98 mg/kg)

Dermal - No More than Slightly Toxic to Rabbits (LD<sub>50</sub> >2,000 mg/kg)

Eye Irritation - Severely Irritating to Rabbits

Skin Irritation - Slightly Irritating to Rabbits

No skin allergy was observed in guinea pigs following repeated exposure.

Endothal-potassium (technical active ingredient)

Although no allergic skin reactions were observed in guinea pigs following exposure to this material in water, allergic skin reactions were observed following exposure to this material in ethanol. Repeated application to the skin of rats produced severe skin irritation, liver and kidney effects considered to be secondary to irritation, and increased mortality. Long-term dietary administration produced no adverse effects in rats.

# AQUATHOL SUPER K

–Material Safety Data Sheet–  
Elf Atochem North America, Inc.

## 12 ECOLOGICAL INFORMATION

### Ecotoxicological Information

Data on this material and/or its components are summarized below.

Endothal-potassium (technical active ingredient)

This material is practically non-toxic to bluegill sunfish (LC50 316-501.2 mg/l), rainbow trout (LC50 107-528.7 mg/l), eastern oysters (LC50 117 mg/l), largemouth bass (LC50 130 mg/l), fiddler crab (LC50 752.4 mg/l) and sheepshead minnow (LC50 340 mg/l), and slightly toxic to mysid shrimp (LC50 79 mg/l), walleye (LC50 16-54 mg/l) and smallmouth bass (LC50 47 mg/l). It is practically non-toxic to slightly toxic to *Daphnia magna* (EC50 72-319.5 mg/l) and no more than moderately toxic to freshwater blue-green algae (LC50 >4.8 mg/l), freshwater diatoms (LC50 >3.6 mg/l), freshwater green algae (LC50 >4.8 mg/l) and marine diatoms (LC50 >9.0 mg/l).

The 8-day LC50 for bobwhite quail and mallard ducklings is >5,000 ppm, the 21-day LD50 for mallard ducks is 344 mg/kg, the 14-day EC50 for duckweed is 0.84 mg/l and the 14-day LC50 for juvenile chinook salmon is 62.5 ppm.

7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid

Endothall is slightly toxic to bluegill sunfish (96-hr LC50 77 mg/l), rainbow trout (96-hr LC50 49 mg/l), *Daphnia magna* (48-hr LC50 92 mg/l), eastern oysters (96-hr LC50 54 mg/l), mysid shrimp (96-hr LC50 39 mg/l) and fiddler crab (96-hr LC50 85.1 mg/l). It is practically non-toxic to sheepshead minnow (96-hr LC50 110 mg/l) and common mummichog (96-hr LC50 213.9 mg/l).

Endothall has an 8-day LC50 of >5,000 ppm (bobwhite quail and mallard ducklings), a 21-day LD50 of 111 mg/kg (mallard ducks), a 30-day MATC of 19 mg/l (fathead minnows) and a 21-day MATC of 6.7 mg/l (*Daphnia magna*). No adverse effects were observed in mallard ducks and bobwhite quail following repeated (20-weeks) administration in the diet.

### Chemical Fate Information

Data on this material and/or its components are summarized below.

Endothal-potassium (technical active ingredient)

This material is rapidly degraded in aqueous systems by the indigenous microbial population to CO<sub>2</sub> and other non-toxic natural products.

## 13 DISPOSAL CONSIDERATIONS

### Waste Disposal

Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

## 14 TRANSPORT INFORMATION

DOT Name	Pesticides, solid, toxic, n.o.s.
DOT Technical Name	Endothall
DOT Hazard Class	6.1
UN Number	2588
DOT Packing Group	PG III
RQ	1,000 POUNDS

**AQUATHOL SUPER K**  
–Material Safety Data Sheet–  
*Elf Atochem North America, Inc.*

**15 REGULATORY INFORMATION**

**Hazard Categories Under Criteria of SARA Title III Rules (40 CFR Part 370)**

Immediate (Acute) Health	Y	Fire	N
Delayed (Chronic) Health	N	Reactive	N
		Sudden Release of Pressure	N

**Ingredient Related Regulatory Information:**

<b>SARA Reportable Quantities</b>	<u>CERCLA RQ</u>	<u>SARA TPQ</u>
Endothal-potassium	NE	
2-Propenamide, polymer with potassium	NE	

**SARA Title III, Section 313**

This product does contain chemical(s) which are defined as toxic chemicals under and subject to the reporting requirements of Section 313 of Title III of the Superfund Ammendments and Reauthorization Act of 986 and 40 CFR Part 372. See Section 2

Endothal-potassium

**16 OTHER INFORMATION**

**Revision Information**

Revision Date	12 SEP 2000	Revision Number	2
Supercedes Revision Dated	19 JUN-2000		

**Revision Summary**

Updated to incorporate product specific tox data and add information to physical properties and hazardous decomposition sections

**Key**

NE = Not Established                      NA= Not Applicable                      (R) = Registered Trademark

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## Elf Atochem

# HYDROTHOL® 191

GRANULAR AQUATIC ALGICIDE AND HERBICIDE

ACTIVE INGREDIENT:  
Mono(N,N-dimethylalkylamine\*) salt of endothall\*\* ..... 11.2%  
OTHER INGREDIENTS: ..... 88.8%

TOTAL ..... 100.0%

\*Alkyl groups as derived from Coconut Oil

\*\*7-oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid equivalent 5%

EPA Registration No. 4581-172

EPA Establishment No. 4581-MI-1

## KEEP OUT OF REACH OF CHILDREN

### DANGER

#### FIRST AID:

**IF IN EYES:** Hold eyelids open and flush with a steady, gentle stream of water for 15 minutes. Call a physician.

**IF SWALLOWED:** Drink promptly a large quantity of milk, egg whites, gelatin solution or if these are not available, drink large quantities of water. Avoid alcohol. Call a physician immediately.

**IF ON SKIN:** Immediately flush with plenty of water for at least 15 minutes. Remove and wash contaminated clothing before reuse.

**NOTE TO PHYSICIAN:** Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression and convulsion may be needed.

### PRECAUTIONARY STATEMENTS

#### HAZARDS TO HUMANS (AND DOMESTIC ANIMALS)

##### DANGER

**CORROSIVE. CAUSES IRREVERSIBLE EYE DAMAGE. HARMFUL IF SWALLOWED, ABSORBED THROUGH SKIN OR INHALED. AVOID CONTACT WITH SKIN OR CLOTHING. DO NOT GET IN EYES. WEAR GOGGLES OR FACE SHIELD WHEN HANDLING. Avoid breathing dust. Wash thoroughly with soap and water after handling. Remove contaminated clothing and wash before reuse.**

#### ENVIRONMENTAL HAZARDS

Avoid contact with or drift to other crops or plants as injury may result.

Fish may be killed by dosages in excess of 0.3 ppm. Do not use fish from treated areas for food or feed within three days after treatment.

Do not use water from treated areas for watering livestock, for preparing agricultural sprays for food crops, for irrigation or for domestic purposes within the following periods:

Up to 0.3 ppm—7 days after application  
Up to 3.0 ppm—14 days after application  
Up to 5.0 ppm—25 days after application

#### GENERAL INFORMATION

HYDROTHOL 191 Granular is a highly effective algicide and aquatic weed killer for use in irrigation and drainage canals, lakes and ponds to control the following weeds and algae: Hydrilla, Najas, Elodea, Coontail, Potamogeton, Milfoil sp., Zannichellia, Vallisneria, Cladophora, Spirogyra, Pithophora and Chara, when weeds are actively growing. Dosage rates indicated are measured in "Parts per Million" (ppm). 1 ppm as a dosage rate means that there would be 1 part endothall (acid) in 1,000,000 parts of water. Thoroughly clean application equipment immediately after use.

Necessary approval and/or permits should be obtained in states where required. Consult state water or conservation authorities before applying to public waters or to ponds, canals or streams which flow into public waters.

#### DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

#### IRRIGATION AND DRAINAGE CANALS

**HEAVY INFESTATIONS**—Evenly spread 160 to 270 lbs. HYDROTHOL 191 Granular per acre foot of water (3.0 to 5.0 ppm) with suitable aerial or ground equipment.

**MODERATE OR LIGHT INFESTATIONS**—Use 55 to 110 lbs. per acre foot HYDROTHOL 191 Granular (1.0 to 2.0 ppm) applied evenly.

#### IRRIGATION AND DRAINAGE CANAL APPLICATION

Pounds of HYDROTHOL 191 Granular required per mile of canal or swath, 1 ft. deep.					
ppm	Width of Canal, Ditch or Swath				
	10	15	20	30	40
0.5	33	49	65	95	130

Pounds of HYDROTHOL 191 Granular required per mile of canal or swath, 1 ft. deep.					
ppm	Width of Canal, Ditch or Swath				
	10	15	20	30	40
1.0	65	98	130	190	260
2.0	130	195	260	380	520
3.0	195	294	390	570	780
4.0	260	392	520	760	1040
5.0	325	490	650	950	1300

Note: 5.5 lbs. per acre foot equals 0.1 ppm of Endothall (acid).

#### LAKES AND PONDS

**ALGAE CONTROL**—Cladophora, Pithophora, Spirogyra, and Chara can be controlled by even applications of 3 lbs. to 11 lbs. HYDROTHOL 191 Granular per acre foot (0.05 to 0.2 ppm) applied by suitable air or water equipment. HYDROTHOL 191 Granular is especially effective on bottom growth control. Pithophora may require 0.2 ppm or higher. Dosages may be increased to 27-82 lbs. of HYDROTHOL 191 Granular (0.5 to 1.5 ppm) where greater longevity of control is desired and for marginal treatments. For floating mats HYDROTHOL 191 Granular should be scattered as evenly as possible over the mat. Repeat treatments when algal growth reappears.

**SUBMERGED AQUATICS**—Due to the toxicity to fish, the use of HYDROTHOL 191 Granular for submerged aquatics is suggested only by commercial applicators on a marginal or sectional treatment basis. Use 27 to 136 lbs. HYDROTHOL 191 Granular per acre foot (0.5 to 2.5 ppm) scattered evenly as possible. Use dosages over 1.0 ppm on narrow margins or in areas where some fish kill is not objectionable.

Do not treat more than 1/10 of the lake or pond at one time with doses in excess of 1.0 ppm. Approximate pounds of HYDROTHOL 191 Granular for one acre\* treatment at various depths and ppm concentrations.

#### LAKES AND PONDS APPLICATIONS

Depth	PPM Concentrations					
	0.05 ppm	0.1 ppm	0.2 ppm	0.5 ppm	1.0 ppm	5.0 ppm
1 ft.	3	5	11	27	54	250
2 ft.	5	11	22	54	109	550
4 ft.	11	22	44	109	217	1100
6 ft.	16	33	65	163	326	1650

\*One acre equals approximately 208' x 208'.

#### STORAGE AND DISPOSAL

Do not contaminate water, food, or feed by storage or disposal.

**Storage Instructions:** Store in the original container, preferably in a locked storage area. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. If spilled during storage or handling sweep up spillage and dispose of in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

#### EMERGENCY TELEPHONE NUMBERS:

**CHEMTREC:** (800) 424-9300

**MEDICAL:** (303) 623-5716

**Rocky Mountain Poison Control Center**

#### WARRANTY AND DISCLAIMER

Elf Atochem North America warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. ELF ATOCHEM MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL ELF ATOCHEM OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COSTS; OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Elf Atochem and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Elf Atochem. 5-K111S-03 J6 (12/96)

Elf Atochem

# HYDROTHOL<sup>®</sup> 191

## AQUATIC ALGICIDE AND HERBICIDE

ACTIVE INGREDIENT:  
Mono(N,N-dimethylalkylamine\*\*) salt of endothall\* ..... 53.0%  
INERT INGREDIENTS: ..... 47.0%  
TOTAL ..... 100.0%

Contains 2 lb. endothall\* per gallon

\*7-oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid equivalent 23.36%

\*\*Alkyl groups as derived from Coconut Oil

EPA Registration No. 4581-174

EPA Establishment No. 4581-MI-1

**KEEP OUT OF REACH OF CHILDREN**

### DANGER

#### FIRST AID:

**IF IN EYES:** Hold eyelids open and flush with a steady, gentle stream of water for 15 minutes. Get medical attention.

**IF ON SKIN:** Wash with plenty of soap and water. Get medical attention.

**IF SWALLOWED:** Call a physician or Poison Control Center. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger. If person is unconscious, do not give anything by mouth and do not induce vomiting.

**IF INHALED:** Remove victim to fresh air. If not breathing, give artificial respiration, preferably mouth-to-mouth. Get medical attention.

**NOTE TO PHYSICIAN:** Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression and convulsion may be needed.

### PRECAUTIONARY STATEMENTS

#### HAZARDS TO HUMANS (AND DOMESTIC ANIMALS)

##### DANGER

FATAL IF ABSORBED THROUGH SKIN. MAY BE FATAL IF SWALLOWED. CORROSIVE, CAUSES IRREVERSIBLE EYE DAMAGE AND SKIN BURNS. MAY BE FATAL IF INHALED. DO NOT GET IN EYES, ON SKIN OR ON CLOTHING. WEAR PROTECTIVE CLOTHING, RUBBER GLOVES AND GOGGLES OR FACE SHIELD WHEN HANDLING. Wash thoroughly with soap and water after handling and before eating or smoking. Remove contaminated clothing and wash before reuse. Do not breathe vapor or spray mist.

#### ENVIRONMENTAL HAZARDS

Fish may be killed by dosages in excess of 0.3 ppm.

Avoid contact with or drift to desirable plants or crops as injury may result.

Clean out application equipment after each operation.

Do not use fish from treated areas for food or feed within three days after treatment.

Do not use water from treated areas for watering livestock, for preparing agricultural sprays for food crops, for irrigation or for domestic purposes within the following periods:

Up to 0.3 ppm—7 days after application

Up to 3.0 ppm—14 days after application

Up to 5.0 ppm—25 days after application

#### GENERAL INFORMATION

HYDROTHOL 191 is a liquid concentrate soluble in water and is a highly effective aquatic herbicide and algicide for use in irrigation and drainage canals, lakes and ponds to control the following weeds and algae: Hydrilla, Najas, Elodea, Coontail, Potamogeton, Milfoil sp., Zannichellia, Vallisneria, Cladophora, Pithophora, Spirogyra, and Chara, when weeds are actively growing. Dosage rates indicated are measured in "Parts per Million" (ppm). 1.0 ppm as a dosage rate means that there would be 1 part endothall (acid) in 1,000,000 parts of water.

Necessary approval and/or permits should be obtained in States where required. Consult state water or conservation authorities before applying to public waters or to ponds, canals or streams which flow into public waters.

#### DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

#### IRRIGATION AND DRAINAGE CANALS

Apply HYDROTHOL 191 as a surface spray with uniform coverage or inject under the surface of the water. The minimum contact time with weeds for optimum results should be two hours.

**HEAVY INFESTATION**—Apply at rate of 4.0 to 6.75 gal. per acre foot (equivalent to 3.0-5.0 ppm). See table below.

**MODERATE OR LIGHT INFESTATIONS**—Apply at rate of 1.4 to 2.7 gal. per acre foot (equivalent to 1.0-2.0 ppm). See table below.

#### GALLONS OF HYDROTHOL 191 REQUIRED TO TREAT 1 MILE OF DITCH, 1 FOOT DEEP

ppm	WIDTH OF DITCH OR CANAL IN FEET									
	4	6	8	10	12	14	16	18	20	22
1.0	0.7	1.0	1.3	1.7	1.9	2.3	2.6	2.9	3.3	3.6
2.0	1.3	2.0	2.6	3.3	3.9	4.6	5.2	5.9	6.5	7.2
3.0	2.0	2.8	3.9	4.9	5.9	6.8	7.8	8.8	9.8	10.8
4.0	2.6	3.9	5.2	6.6	7.8	9.1	10.4	11.8	13.1	14.4
5.0	3.2	4.9	6.5	8.2	9.7	11.5	13.1	14.7	16.4	18.0

Note: 1.1 pt. HYDROTHOL 191 per acre foot equals 0.1 ppm of endothall (acid).

#### LAKES AND PONDS

**ALGAE CONTROL:** Cladophora, Pithophora, Spirogyra, and Chara can be controlled with applications of 0.6 to 2.2 pints per acre foot (0.05 to 0.2 ppm) applied as a uniform surface spray or injected under water surface. Pithophora may require 0.2 ppm or higher. Dosages may be increased to 0.4 to 1.1 gals (0.3 to 0.8 ppm) where greater longevity of control is desired and for marginal treatments. Repeat treatments when algal growth reappears.

**SUBMERGED AQUATICS:** Due to the toxicity to fish, the use of HYDROTHOL 191 for submerged aquatic weeds is suggested only by commercial applicators on a marginal or sectional rather than overall type treatment. Use 0.7 to 3.4 gals. per acre foot (0.5 to 2.5 ppm) on a marginal treatment either sprayed on or injected below the surface. Use dosages over 1.0 ppm on very narrow margins or in areas where some fish kill is not objectional.

Do not treat more than 1/10 of the lake or pond at one time with doses in excess of 1.0 ppm.

#### APPROXIMATE QUANTITY OF HYDROTHOL 191 FOR ONE ACRE\* TREATMENT

DEPTH	DOSAGES FOR VARIOUS CONCENTRATIONS IN PPM								
	0.05	0.1	0.2	0.3	0.5	0.8	1.0	2.0	5.0
1 ft.	0.6	1.1	2.2	.4	.7	1.1	1.4	2.7	6.8
	pts	pts	pts	gal	gal	gal	gal	gal	gal
2 ft.	1.1	2.2	4.3	.8	1.4	2.2	2.8	5.4	13.6
	pts	pts	pts	gal	gal	gal	gal	gal	gal
4 ft.	2.2	4.3	8.6	1.6	2.7	4.4	5.4	10.9	27.2
	pts	pts	pts	gal	gal	gal	gal	gal	gal
6 ft.	3.3	6.5	12.9	2.5	4.1	6.5	8.2	16.3	40.8
	pts	pts	pts	gal	gal	gal	gal	gal	gal

\*One acre equals approximately 208' × 208'

#### STORAGE AND DISPOSAL

Do not contaminate water, food, or feed by storage or disposal.

**Storage Instructions:** Store in the original container. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. In the event of spillage during handling or storage, absorb with sand or other inert material and dispose of absorbent in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

#### EMERGENCY TELEPHONE NUMBERS:

CHEMTREC: (800) 424-9300

MEDICAL: (303) 623-5716

Rocky Mountain Poison Control Center

#### WARRANTY AND DISCLAIMER

Elf Atochem North America warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. ELF ATOCHEM MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL ELF ATOCHEM OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT

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NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COST; OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Elf Atochem and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Elf Atochem.  
5-C110S-03 C6 (1/97)

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## **APPENDIX 2: Historic Labels**

March 1990 (Draft)

# AQUATHOL<sup>®</sup> K

## AQUATIC HERBICIDE

<b>ACTIVE INGREDIENT</b>		
Dipotassium salt of endothall* .....	40.3%	
<b>INERT INGREDIENTS</b> .....	59.7%	
	<b>TOTAL</b> .....	<b>100.0%</b>

\*7-oxabicyclo [2.2.1]heptane-2,3-dicarboxylic acid equivalent 28.6%  
 Contains per gallon 4.23 lbs. dipotassium endothall  
 (equivalent to 3.0 lbs. endothal acid)

### KEEP OUT OF REACH OF CHILDREN

#### STATEMENT OF PRACTICAL TREATMENT

**IF SWALLOWED**, drink promptly a large quantity of milk, egg whites, gelatin solution or if these are not available, drink large quantities of water. Avoid alcohol. Call a physician immediately.

**IF ON SKIN**, immediately flush with plenty of water for at least 15 minutes. Remove and wash contaminated clothing before reuse.

**IF IN EYES**, immediately flush with plenty of water for at least 15 minutes. Call a physician.

**NOTE TO PHYSICIAN:** Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression and convulsion may be needed.

See Side Panel for Additional Precautionary Statements

**NOTE:** For **GENERAL INFORMATION** and **DIRECTIONS FOR USE** refer to accompanying brochure.



EPA Registration No. 4581-204  
 EPA Establishment No. 4581-TX-1

Net Contents \_\_\_\_\_ Gallons/\_\_\_\_\_ Liters

**AGCHEM DIVISION—ATO CHEM NORTH AMERICA**

Philadelphia, PA 19102

**PRECAUTIONARY STATEMENTS  
HAZARDS TO HUMANS  
(AND DOMESTIC ANIMALS)**

**DANGER**

FATAL IF ABSORBED THROUGH SKIN. MAY BE FATAL IF SWALLOWED. HARMFUL IF INHALED. CORROSIVE, CAUSES IRREVERSIBLE EYE DAMAGE. DO NOT GET IN EYES, ON SKIN OR ON CLOTHING. WEAR PROTECTIVE CLOTHING, RUBBER GLOVES, AND GOGGLES OR FACE SHIELD WHEN HANDLING. Wash thoroughly with soap and water after handling and before eating or smoking. Remove contaminated clothing and wash before reuse. Avoid breathing spray mist.

**ENVIRONMENTAL HAZARDS**

Avoid contact with or drift to other crops or plants as injury may result. Wash out spray equipment with water after each operation.

Do not use fish from treated water for food or feed within 3 days of treatment. Do not use treated water for watering livestock, for preparing agricultural sprays for food crops, for irrigation, or for domestic purposes within the following periods:

Up to 0.5 ppm dipotassium salt  
(0.35 ppm acid equivalent)— 7 days after application

Up to 4.25 ppm dipotassium salt  
(3.0 ppm acid equivalent)—14 days after application

Up to 5.0 ppm dipotassium salt  
(3.5 ppm acid equivalent)—25 days after application

NOTE: Areas treated with AQUATHOL K may be used for swimming twenty-four hours after treatment.

Treated water can be used for sprinkling bent grass immediately.

**STORAGE AND DISPOSAL**

Do not contaminate water, food, or feed by storage or disposal.

**Storage Instructions:** Store in the original container. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. Storage at temperatures below 32°F may result in the product freezing or crystallizing. Should this occur the product must be warmed to 50°F or higher and thoroughly agitated. In the event of a spillage during handling or storage, absorb with sand or other inert material and dispose of absorbant in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

5-C102S-01 H6 (3/90)

Made and Printed in U.S.A.

### GENERAL INFORMATION

AQUATHOL K is a liquid concentrate soluble in water which is effective against a broad range of aquatic plants with a margin of safety to fish.

Dosage rates indicated for the application of AQUATHOL K are measured in "Parts Per Million" (ppm) of dipotassium endothall. Only 0.5 to 5.0 ppm are generally required for aquatic weed control, whereas some fish species are tolerant to approximately 100 ppm or over.

### DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

### AQUATIC WEEDS CONTROLLED AND DOSAGE RATE CHARTS

AQUATHOL K is recommended for the control of the following aquatic weeds in irrigation and drainage canals, ponds and lakes at the rates indicated. Since the active ingredient is water soluble and tends to diffuse from the area treated, select the dosage rate applicable to the area to be treated. Use the lower rate in each range of rates where the growth is young and growing and/or where the weed stand is not heavy. Marginal treatments of large bodies of water require higher rates as indicated.

#### HOW TO APPLY:

AQUATHOL K is a contact killer; consequently, do not apply before weeds are present. Application as early as possible after weeds are present is recommended to permit use of lower application rates. However, for best results water temperature should be at 65°F or above. If an entire pond is treated at one time, or if the dissolved oxygen level is low at time of application, decay of weeds may remove enough oxygen from the water, causing fish to suffocate. Water containing very heavy vegetation should be treated in sections to prevent suffocation of fish. Sections should be treated 5-7 days apart. Carefully measure size and depth of area to be treated and determine amount of AQUATHOL K to apply from chart. For best results apply on a calm day where there is little wave action.

AQUATHOL K should be sprayed on the water or injected below the water surface and should be distributed as evenly as possible. It may be applied as it comes from the container or diluted with water depending on the equipment. Some dilution will give better distribution.

In instances where the nuisance to be controlled is an exposed surface problem (i.e., some of the broad-leaved pond weeds) it is important to get good contact coverage utilizing the highest concentration (least water dilution) compatible with the type of equipment used so that even distribution is achieved.

Necessary approval and/or permits should be obtained in states where required.

Common Name	Latin Name	Entire Pond Or Large Area Treatment	Spot Or Lake Margin Treatment
Bass Weed	Potamogeton amplifolius	2.0-3.0 ppm	3.0-4.0 ppm
Bur Reed	Sparganium spp.	3.0-4.0 ppm	4.0-5.0 ppm
Coontail	Ceratophyllum spp.	1.0-2.0 ppm	2.0-3.0 ppm
Hydrilla	Hydrilla verticillata	2.0-3.0 ppm	3.0-4.0 ppm
Milfoil	Myriophyllum spp.	2.0-3.0 ppm	3.0-4.0 ppm
Pondweed			
Bushy	Najas spp.	0.5-1.5 ppm	2.0-3.0 ppm
Curly-Leaf	Potamogeton crispus	0.5-1.5 ppm	2.0-3.0 ppm
Flat-Stem	Potamogeton zosteriformis	2.0-3.0 ppm	3.0-4.0 ppm
Floating-Leaf	Potamogeton natans	1.0-2.0 ppm	2.0-3.0 ppm
Horned	Zannichellia spp.	1.0-2.0 ppm	2.0-3.0 ppm
Sago	Potamogeton pectinatus	1.0-2.0 ppm	2.0-3.0 ppm
	Potamogeton americanus	2.0-3.0 ppm	3.0-4.0 ppm
	Potamogeton diversifolius	1.0-2.0 ppm	2.0-3.0 ppm
	Potamogeton filiformis	2.0-3.0 ppm	3.0-4.0 ppm
	Potamogeton pusillus	1.0-2.0 ppm	2.0-3.0 ppm
Water Star Grass	Heteranthera spp.	2.0-3.0 ppm	3.0-4.0 ppm

**RATE OF APPLICATION—LAKES AND PONDS**

The following chart indicates the total quantity of material to be applied.

**APPROXIMATE GALLONS OF AQUATHOL K FOR ONE ACRE (208' x 208') TREATMENT**

**DOSAGE IN GALLONS FOR VARIOUS CONCENTRATIONS IN PPM**

DEPTH	DOSAGE IN GALLONS FOR VARIOUS CONCENTRATIONS IN PPM						
	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm	3.0 ppm	4.0 ppm	5.0 ppm
1 ft.	0.3	0.6	1.0	1.3	1.9	2.6	3.2
2 ft.	0.6	1.3	1.9	2.6	3.8	5.1	6.4
4 ft.	1.3	2.6	3.8	5.1	7.7	10.2	12.8
6 ft.	1.9	3.8	5.8	7.6	11.5	15.3	19.2

**RATE OF APPLICATION—IRRIGATION AND DRAINAGE CANALS\*\***

The following indicates the total quantity of material to be applied.

**GALLONS OF AQUATHOL K REQUIRED TO TREAT 1 MILE OF CANAL 1 FOOT DEEP\***

PPM	WIDTH OF CANAL IN FEET			
	5	10	15	20
1.0 ppm	0.4	0.75	1.2	1.5
2.0 ppm	0.75	1.5	2.3	3.0
3.0 ppm	1.2	2.3	3.5	4.5
4.0 ppm	1.5	3.0	4.5	6.0
5.0 ppm	2.0	3.8	5.7	7.5

The minimum contact time with weeds for optimum results should be 2 hours.

\*For deeper water, adjust rate accordingly.

\*\*Not for this use in California.

**WARRANTY AND DISCLAIMER**

Atochem North America warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. ATOCHEM MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL ATOCHEM OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COST; OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Atochem and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Atochem.

# HYDROTHOL 191

## AQUATIC ALGICIDE AND HERBICIDE

<b>ACTIVE INGREDIENT</b>		
Mono(N,N-dimethylalkylamine**) salt of endothall*	.....	53.0%
<b>INERT INGREDIENTS</b>	.....	47.0%
<b>TOTAL</b>	.....	100.0%

Contains 2 lb. endothall\* per gallon

\*7-oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid equivalent 23.36%  
\*\*Alkyl groups as derived from Coconut Oil

### KEEP OUT OF REACH OF CHILDREN

#### STATEMENT OF PRACTICAL TREATMENT

**IF SWALLOWED**, drink promptly a large quantity of milk, egg whites, gelatin solution or if these are not available, drink large quantities of water. Avoid alcohol. Call a physician immediately.

**IF ON SKIN**, immediately flush with plenty of water for at least 15 minutes. Remove and wash contaminated clothing before reuse.

**IF IN EYES**, immediately flush with plenty of water for at least 15 minutes. Call a physician.

**NOTE TO PHYSICIAN:** Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression and convulsion may be needed.

See Side Panel for Additional Precautionary Statements



EPA Registration No. 4581-174  
EPA Establishment No. 4581-TX-1

Net Contents \_\_\_\_\_ Gallons/\_\_\_\_\_ Liters

**AGCHEM DIVISION-PENWALT CORPORATION**  
Philadelphia, PA 19102

## PRECAUTIONARY STATEMENTS

### HAZARDS TO HUMANS (AND DOMESTIC ANIMALS)

#### DANGER

FATAL IF ABSORBED THROUGH SKIN. MAY BE FATAL IF SWALLOWED. CORROSIVE, CAUSES IRREVERSIBLE EYE DAMAGE AND SKIN BURNS. HARMFUL IF INHALED. DO NOT GET IN EYES, ON SKIN OR ON CLOTHING. WEAR PROTECTIVE CLOTHING, RUBBER GLOVES, AND GOGGLES OR FACE SHIELD WHEN HANDLING. Wash thoroughly with soap and water after handling and before eating or smoking. Remove contaminated clothing and wash before reuse. Avoid breathing spray mist.

#### ENVIRONMENTAL HAZARDS

Fish will be killed by dosages in excess of 0.3 ppm. Do not use where fish are important resources.

Avoid contact with or drift to desirable plants or crops as injury may result.

Clean out application equipment after each operation.

Do not use fish from treated water for food or feed within three days after treatment.

Do not use treated water for watering livestock, for preparing agricultural sprays for food crops, for irrigation or for domestic purposes within the following periods:

Up to 0.3 ppm— 7 days after application

Up to 3.0 ppm—14 days after application

Up to 5.0 ppm—25 days after application

## STORAGE AND DISPOSAL

Do not contaminate water, food, or feed by storage or disposal.

**Storage Instructions:** Store in the original container. Do not store in a manner where cross-contamination with other pesticides, fertilizers, food or feed could occur. In the event of spillage during handling or storage, absorb with sand or other inert material and dispose of absorbant in accordance with the Pesticide Disposal Instructions listed below.

**Pesticide Disposal Instructions:** Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

**Container Disposal Instructions:** Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

Made and Printed in U.S.A.

5-C110S-01 H8 (7/88)

### GENERAL INFORMATION

HYDROTHOL 191 is a liquid concentrate soluble in water and is a highly effective aquatic herbicide and algicide for use in irrigation and drainage canals, lakes and ponds to control the following weeds and algae: Najas, Elodea, Coontail, Potamogeton, Milfoil sp., Zannichellia, Vallisneria, Cladophora, Pithophora, Spirogyra, and Chara, when weeds are actively growing. Dosage rates indicated are measured in "Parts per Million" (ppm). 1.0 ppm as a dosage rate means that there would be 1 part endothall (acid) in 1,000,000 parts of water.

Necessary approval and/or permits should be obtained in States where required. Consult state water or conservation authorities before applying to public waters or to ponds, canals or streams which flow into public waters.

### DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

### IRRIGATION AND DRAINAGE CANALS

Apply HYDROTHOL 191 as a surface spray with uniform coverage or inject under the surface of the water. The minimum contact time with weeds for optimum results should be two hours.

HEAVY INFESTATION—Apply at rate of 4.0 to 6.75 gal. per acre foot (equivalent to 3.0-5.0 ppm). See table below.

MODERATE OR LIGHT INFESTATIONS—Apply at rate of 1.4 to 2.7 gal. per acre foot (equivalent to 1.0-2.0 ppm). See table below.

GALLONS OF HYDROTHOL 191 REQUIRED TO TREAT 1 MILE OF DITCH, 1 FOOT DEEP

ppm	Width of Ditch or Canal in Feet									
	4	6	8	10	12	14	16	18	20	22
1.0 ppm	0.7	1.0	1.3	1.7	1.9	2.3	2.6	2.9	3.3	3.6
2.0 ppm	1.3	2.0	2.6	3.3	3.9	4.6	5.2	5.9	6.5	7.2
3.0 ppm	2.0	2.8	3.9	4.9	5.9	6.8	7.8	8.8	9.8	10.8
4.0 ppm	2.6	3.9	5.2	6.6	7.8	9.1	10.4	11.8	13.1	14.4
5.0 ppm	3.2	4.9	6.5	8.2	9.7	11.5	13.1	14.7	16.4	18.0

Note: 1.1 pt.:HYDROTHOL 191 per acre foot equals 0.1 ppm of endothall (acid).

## LAKES AND PONDS

**ALGAE CONTROL:** Cladophora, Pithophora, Spirogyra, and Chara can be controlled with applications of 0.6 to 2.2 pints per acre foot (0.05 to 0.2 ppm) applied as a uniform surface spray or injected under water surface. Pithophora may require 0.2 ppm or higher. Dosages may be increased to 0.4 to 1.1 gals (0.3 to 0.8 ppm) where greater longevity of control is desired and for marginal treatments. Repeat treatments when algal growth reappears.

**SUBMERGED AQUATICS:** Due to the toxicity to fish, the use of HYDROTHOL 191 for submerged aquatic weeds is suggested only by commercial applicators on a marginal or sectional rather than overall type treatment. Use 0.7 to 3.4 gals. per acre foot (0.5 to 2.5 ppm) on a marginal treatment either sprayed on or injected below the surface. Use dosages over 1.0 ppm on very narrow margins or in areas where some fish kill is not objectionable. Do not treat more than 1/10 of the lake or pond at one time with doses in excess of 1.0 ppm.

APPROXIMATE QUANTITY OF HYDROTHOL 191 FOR ONE ACRE\* TREATMENT

Depth	Dosages for Various Concentrations in ppm								
	0.05	0.1	0.2	0.3	0.5	0.8	1.0	2.0	2.5
1 ft.	0.6 pts	1.1 pts	2.2 pts	.4 gal	.7 gal	1.1 gal	1.4 gal	2.7 gal	3.4 gal
2 ft.	1.1 pts	2.2 pts	4.3 pts	.8 gal	1.4 gal	2.2 gal	2.8 gal	5.4 gal	6.8 gal
4 ft.	2.2 pts	4.3 pts	8.6 pts	1.6 gal	2.7 gal	4.4 gal	5.4 gal	10.9 gal	13.6 gal
6 ft.	3.3 pts	6.5 pts	12.9 pts	2.5 gal	4.1 gal	6.5 gal	8.2 gal	16.3 gal	20.4 gal

\*One acre equals approximately 208' x 208'

### WARRANTY AND DISCLAIMER

Pennwalt Corporation warrants that this material conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the Directions for Use, subject to the risks referred to therein. PENNWALT MAKES NO OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY. IN NO CASE SHALL PENNWALT OR SELLER BE LIABLE FOR CONSEQUENTIAL, SPECIAL OR INDIRECT DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT INCLUDING, BUT NOT LIMITED TO, LOSS OF PROFITS, BUSINESS REPUTATION, OR CUSTOMERS; LABOR COST; OR OTHER EXPENSES INCURRED IN PLANTING OR HARVESTING.

Pennwalt and seller offer this product and the buyer and user accept it subject to the foregoing conditions of sale and warranty which may be varied only by agreement in writing signed by a duly authorized representative of Pennwalt.



# Endothall

## Volume 2, Section 2

### CHEMICAL CHARACTERISTICS

**14 PAGES**

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## 2.0 CHEMICAL CHARACTERISTICS

The physical/chemical data in the following sections are those required by USEPA when a product is registered for use in the US as a pesticide. These characteristics assist in the basic understanding of the molecule and are later used in predicting environmental behavior or are considered when higher tiered studies are designed or requested. Pure active ingredient or technical grade active ingredient refers to the active compound(s), which cause the desired biological effect when applied to a target system. The technical grade active ingredient is typically formulated into end-use products, also known as formulated products. The end-use products consist of a known percentage active ingredient plus a solvent or solid carrier and may include surface active components to aid in dissolution, emulsification, suspension, *etc.*, of the active ingredient. Technical products such as endothall and 2,4-D exist as the acid, which is rarely the desired form in the end-use product. One method used to produce a useful end-use product is to combine the acid with the ion of an alkali metal such as potassium to form the salt. The salts are typically soluble in water and allow the preparation of an aqueous based product. Other salt forms include amines of varying complexity and chain length and other metals. A second commonly used formulation technique is the formation of an ester of the acid. In this instance, alcohols of varying chain length are reacted with the acid portion of the molecule to form an ester linkage. These esters are usually slightly more volatile than the acid itself, but by carefully choosing the ester, volatility can be minimized. In the case of both the salt and the ester, once the product is applied to the desired site, the active ingredient is freed either by ionization of the salt or breaking of the ester linkage to produce its desired effect.

### 2.1 ENDOTHALL

Endothall (7-oxabicyclo [2,2,1] heptane-2,3-dicarboxylic acid) is the active component in aquatic herbicides and algicides used in static and flowing water to control aquatic weeds and algae. Endothall is a contact herbicide that disrupts solute transport processes in plant cells. The mode of action of endothall is not fully understood, however, there are several hypotheses to explain endothall's activity. All of the hypotheses indicate that endothall disrupts biochemical processes at the cellular level, such as interfering with protein synthesis by affecting dipeptidase and proteinase enzymes (Mann, 1965 and Mann, 1968). These enzymes are needed to support the production of proteins used by the plant for growth. There is also indication that endothall interferes with lipid synthesis and metabolism in the cells (Mann, 1968). Lipids are incorporated, along with proteins, as structural components in the plant cells. Additionally, it has been suggested that endothall may interfere with the transport of nutrients and cellular materials across the cell membranes (Maestri, 1966). This would suggest a weakening or disruption of the cell wall and is likely related to the structural components discussed above.

Endothall is formulated in two active ingredient forms, the dipotassium salt and the dimethylalkylamine salt. These salts forms are found in five different formulated products used for control of aquatic weed species. The potassium salt is formulated as Aquathol® K Aquatic Herbicide (EPA Reg. No. 4581-204), Aquathol® Granular Aquatic Herbicide (EPA Reg. No. 4581-201), and Aquathol® Super K Granular Aquatic Herbicide (EPA Reg. No. 4581-388). The Aquathol® products are used predominantly for lake and static water treatments to control aquatic macrophytes. The amine salt is formulated as Hydrothol® 191 Aquatic Algicide and Herbicide (EPA Reg. No.

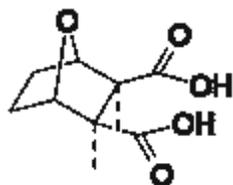
4581-174) and Hydrothol® 191 Granular Aquatic Algicide and Herbicide (EPA Reg. No. 4581-172). The Hydrothol products are used predominantly for canal treatments to control algae and submerged macrophytes. Both Aquathol and Hydrothol products are sometimes combined in lake treatments to control algae and submerged macrophytes.

### 2.1.1 Composition

Endothall is a relatively simple molecule containing only carbon, hydrogen and oxygen. There is no nitrogen, sulfur, halide, metal or other element that could contribute to persistent or exotic degradates/metabolites.

- **Active Ingredient**

Common name: Endothall acid  
CAS Registry No.: 145-73-3  
Chemical name: 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid  
Empirical formula: C<sub>8</sub>H<sub>10</sub>O<sub>5</sub>  
Molecular weight: 186  
Structure: (dotted lines indicate stereo chemistry of Hydrogen groups)



- **Impurities**

There are no known impurities identified by the manufacturers or the US EPA which are known to be of toxicological or environmental concern. The US EPA has established guidelines that require that impurities of concern, such as N-nitrosoamines and chlorinated dioxins and furans must be disclosed. No such compounds are present in the endothall products.

Intentionally added inert or “other” ingredients in endothall formulations include potassium hydroxide used to produce the K or potassium salt in some formulations and dimethylalkylamine to produce the amine salt in others. Other formulation ingredients included in the end-use products have been reviewed by the USEPA and approved when used for their intended purpose, however, these are not reported, as they are confidential manufacturing information.

The USEPA has established a category listing system for the “other” (inert) compounds used in pesticide formulations. The lists are designated 1, 2, 3, 4a and 4b. Compounds are assigned to the various lists according to their toxicological concern and to the extent their safety has been reviewed by the Agency. In the case of each list, if USEPA determines that a compound is no longer used in any pesticide formulation, it will be removed from the list.

List 1 contains eight compounds, which, due to their toxicological profile, require special labeling if used in a pesticide formulation. These compounds are generally not used in pesticidal formulations any longer. There are no List 1 compounds in the endothall formulations used in the State of Washington.

List 2 compounds are those for which USEPA has not yet determined a full profile but is reviewing existing information. At the completion of their evaluation, it is expected that the compounds still in use in pesticide formulations will be moved to List 1 or to List 4. There are no List 2 compounds in the endothall formulations used in the State of Washington.

List 3 contains those compounds which have not been fully evaluated, but which have profiles of lesser concern in the USEPA evaluation scheme. It is expected that most of these compounds will be moved to List 4 once their evaluation by the Agency is complete. There are some List 3 inert compounds in the endothall products.

List 4 is divided into two categories. List 4A contains compounds generally regarded as safe for use in pesticide formulations and includes such compounds as corn cobs and attapulgite clay. List 4B contains those compounds that have sufficient data on file at EPA to substantiate that they can be used safely in pesticide products.

There are compounds from Inerts List 4 in the endothall formulations. The levels of these compounds are relatively low in the granular formulations as the clay carrier makes up the bulk of the formulation and the active ingredient accounts for 10 to 63% of the weight and the majority of the balance of the formulation.

In addition to the above-mentioned review by the USEPA, all registered pesticidal end-use products (the products actually applied to the environment to control weeds or pests) must undergo a series of toxicological tests to establish their safety. Because these tests are performed on the actual end-use formulation, the effects of the “other” ingredients are effectively tested simultaneously. This toxicological screen of the “other” compounds affords an additional opportunity to examine comparative data on the active ingredient versus the end-use product to determine if there is a need to test each of them in a complete testing battery.

- **Intentionally added inert ingredients**

Intentionally added inert or “other” ingredients in endothall formulations include: potassium ion in the Aquathol® K liquid and granular formulations, N,N-dimethylalkylamine in the Hydrothol® 191 liquid and granular formulations and water, which serves as the primary diluent/solvent in the liquid products. The granular products also contain clay, which is impregnated with the active ingredient, either dipotassium endothall (Aquathol® K) or mono-N,N-dimethylalkylamine salt (Hydrothol® 191).

### 2.1.2 Color

Color is an end-point observation of the product used to assist in identification.

	<b>Color</b>	<b>Citation</b>
Endothall Acid	White to off White	(Merck, 1989)
Aquathol® K Aquatic Herbicide	Amber	(Wojcieck, 1993a)
Aquathol® Granular Aquatic Herbicide	Tan	(Wojcieck, 1993b)
Aquathol® Super K Granular Aquatic Herbicide	Tan	(Gibson, 1997)
Hydrothol® 191 Aquatic Algicide and Herbicide	Amber/Brown	(Wojcieck, 1993d)
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	Grey/Brown	(Wojcieck, 1993c)

### 2.1.3 Physical State

Physical state is an end-point observation of the product, solid, liquid or gaseous used to assist in identification.

	<b>Physical State</b>	<b>Citation</b>
Endothall Acid	Solid	(Merck, 1989)
Aquathol® K Aquatic Herbicide	Liquid	(Wojcieck, 1993a)
Aquathol® Granular Aquatic Herbicide	Solid	(Wojcieck, 1993b)
Aquathol® Super K Granular Aquatic Herbicide	Solid	(Gibson, 1997)
Hydrothol® 191 Aquatic Algicide and Herbicide	Liquid	(Wojcieck, 1993d)
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	Solid	(Wojcieck, 1993c)

### 2.1.4 Odor

Odor is an end-point observation of the product used to assist in identification. Odor may also serve as a warning in cases where odorants are added as a safety factor.

	<b>Odor</b>	<b>Citation</b>
Endothall Acid	Slight to none	(Merck, 1989)
Aquathol® K Aquatic Herbicide	Faint Chlorine	(Wojcieck, 1993a)
Aquathol® Granular Aquatic Herbicide	Sharp Musk	(Wojcieck, 1993b)
Aquathol® Super K Granular Aquatic Herbicide	Slight to none	(Gibson, 1997)
Hydrothol® 191 Aquatic Algicide and Herbicide	Slightly sweet	(Wojcieck, 1993d)
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	Damp Musk	(Wojcieck, 1993c)

### 2.1.5 Melting Point

The melting point is a physical end point observation used for identification of pure compounds and may provide some indication of thermal stability. For the pure acid active ingredient (endothall acid) the melting point is not defined as there is a loss of water and conversion to the anhydride at approximately 90°C. Melting point is not applicable to the formulations because they are either liquids or impregnated clay granules (Merck, 1989).

### 2.1.6 Boiling Point

The boiling point is a physical end point observation for identification of pure compounds. The boiling point for the pure acid active ingredient is undefined (A solid at room temperature). The boiling points for the liquid formulations are essentially the same as water, 100°C as they are aqueous based. The boiling points for the granular formulations are not applicable.

### 2.1.7 Density, Bulk Density or Specific Gravity

Bulk density is a measure of the weight per unit volume of the product and is useful for physical identification or differentiation of two similar products. The value may also be needed to calculate application rates in some instances. Density is typically reported as grams per cubic centimeter at 25°C.

	Density (g/cc)	Citation
Endothall Acid	0.481	(Davis, 2000)
Aquathol® K Aquatic Herbicide	1.285	(Wojcieck, 1993c)
Aquathol® Granular Aquatic Herbicide	0.729	(Wojcieck, 1993b)
Aquathol® Super K Granular Aquatic Herbicide	0.607	(Wojcieck, 1993e)
Hydrothol® 191 Aquatic Algicide and Herbicide	1.044	(Wojcieck, 1993d)
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	0.737	(Wojcieck, 1993c)

### 2.1.8 Solubility

Solubility is a physical end point useful for understanding potential environmental impact. High water solubility is frequently associated with mobility and affects distribution in water and soil. This endpoint is determined for the active ingredient in a product and is typically reported as grams per 100 ml water at 25°C.

	Solubility in Water @ 25°C (g/100 ml)	Citation
Endothall Acid	>11.0	Lorence, 1994a Hoffman, 1988b
Aquathol® K Aquatic Herbicide	>65	Lorence, 1994b
Aquathol® Granular Aquatic Herbicide	>65	Lorence, 1994b
Aquathol® Super K Granular Aquatic Herbicide	>65	Lorence, 1994b
Hydrothol® 191 Aquatic Algicide and Herbicide	>50	Lorence, 1994d
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	>50	Lorence, 1994d

### 2.1.9 Vapor Pressure

Vapor pressure is a physical end point useful for understanding the distribution of the active ingredient between water/soil and air. High volatility is an indication of potential impact in the air compartment. This endpoint is determined for the active ingredient in a product and is typically reported as mm mercury (Hg) at a specified temperature.

	<b>Vapor Pressure @ 24.3°C (mm Hg)</b>	<b>Citation</b>
Endothall Acid	$3.92 \times 10^{-5}$	Hoffman, 1988
Aquathol® K Aquatic Herbicide	$3.92 \times 10^{-5}$	Hoffman, 1988
Aquathol® Granular Aquatic Herbicide	$3.92 \times 10^{-5}$	Hoffman, 1988
Aquathol® Super K Granular Aquatic Herbicide	$3.92 \times 10^{-5}$	Hoffman, 1988
Hydrothol® 191 Aquatic Algicide and Herbicide	$2.09 \times 10^{-5}$	Lorence, 1994e
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	$2.09 \times 10^{-5}$	Lorence, 1994e

### 2.1.10 Disassociation Constant

Disassociation constant is a physical end point used to assess the distribution of the product in aqueous media. The reported pH values indicate the environmental pH at which the active ingredient molecule will dissociate to its ionic form. In the case of endothall, there are two dissociable functional groups resulting in two reportable values.

	<b>Dissociation Constant (pKa<sub>1</sub> &amp; pKa<sub>2</sub>)</b>	<b>Citation</b>
Endothall Acid	4.32, 6.22	Gallacher, 1993a
Aquathol® K Aquatic Herbicide	4.16, 6.14	Gallacher, 1993b
Aquathol® Granular Aquatic Herbicide	4.16, 6.14	Gallacher, 1993b
Aquathol® Super K Granular Aquatic Herbicide	4.16, 6.14	Gallacher, 1993b
Hydrothol® 191 Aquatic Algicide and Herbicide	4.24, 6.04	Gallacher, 1993c
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	4.24, 6.04	Gallacher, 1993c

### 2.1.11 Octanol/Water Partition Coefficient

Octanol/Water partition coefficient is a physical end point used to assess the potential of a compound to bioaccumulate in the environment. The value represents the ratio of product in octanol versus water at equilibrium at 25°C. Values less than 10 indicate little or no likelihood of bioaccumulation.

	<b>Octanol/Water Coefficient (Kow)</b>	<b>Citation</b>
Endothall Acid	0.0008	Loken, 1987
Aquathol® K Aquatic Herbicide	<1	Lorence, 1994c
Aquathol® Granular Aquatic Herbicide	<1	Lorence, 1994c
Aquathol® Super K Granular Aquatic Herbicide	<1	Lorence, 1994c
Hydrothol® 191 Aquatic Algicide and Herbicide	<1	Lorence, 1994e
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	<1	Lorence, 1994e

### 2.1.12 pH

pH is a physical end point used to identify the product and to assess the potential effect of the equilibrium in the environment. For endothall products, all are reported as 1% solutions in deionized water at 25°C.

	<b>pH</b>	<b>Citation</b>
Endothall Acid	2.7	
Aquathol® K Aquatic Herbicide	7.5	(Wojcieck, 1993c)
Aquathol® Granular Aquatic Herbicide	6.5	(Wojcieck, 1993b)
Aquathol® Super K Granular Aquatic Herbicide	6.9	(Gibson, 1997)
Hydrothol® 191 Aquatic Algicide and Herbicide	4.4	(Wojcieck, 1993d)
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	4.6	(Wojcieck, 1993c)

### 2.1.13 Stability

Stability is a chemical evaluation of the product to assess the potential effect of heat, light, metals and metal ions on the active ingredient. In the case of endothall acid and its two salts, there is no loss on exposure to 35°C for 30 days, exposure to light for 14 days or to the metals iron, tin and aluminum and heat (Malone, 1994a and Malone, 1994).

### 2.1.14 Oxidizing or Reducing Action

Oxidizing or reducing action is an assessment of the potential for a compound to react with common oxidizers or reducers. In the case of endothall and its formulated products, there is little likelihood of such reactions occurring.

### 2.1.15 Flammability

Determination of flammability is measurement of the temperature that will sustain a flame and is used to classify the product for hazard in storage and shipping.

Determination of flammability is not required for technical grade products. The formulated products are either aqueous or clay based and will not support combustion.

#### **2.1.16 Explodability**

Determination of explodability is measurement of the potential for a compound to explode when exposed to physical or thermal shock. Determination of explodability is not required for technical grade products. The formulated products are either aqueous or clay based and are not explosion hazards. Additionally, the endothall molecule contains no explodable functional groups.

#### **2.1.17 Storage Stability**

Storage stability is the physical determination of the stability of the active ingredient when stored in its commercial packaging over extended time periods, usually one to two years or more. Endothall products have been shown to be stable under normal storage conditions for periods of at least two years (Davis, 2000).

#### **2.1.18 Viscosity (Physical end point used to identify the product and to assess the ability of the product to be poured or pumped.)**

Viscosity is a physical end-point measurement used to identify the product and to assess the ability of the product to be poured or pumped. The measurement is not required on technical grade products or on solid products. The viscosity is reported in centipoise. For the endothall products, viscosity was measured with a Brookfield viscometer at spindle speeds of 12, and 30 rpm, thus there are two results.

	<b>Centipoise</b>	<b>Citation</b>
Endothall Acid	NA	
Aquathol® K Aquatic Herbicide	11, 16	(Wojcieck, 1993c)
Aquathol® Granular Aquatic Herbicide	NA	
Aquathol® Super K Granular Aquatic Herbicide	NA	
Hydrothol® 191 Aquatic Algicide and Herbicide	97, 99	(Wojcieck, 1993c)
Hydrothol® 191 Granular Aquatic Algicide and Herbicide	NA	

#### **2.1.19 Miscibility**

Miscibility is a physical assessment of the ability of a formulated product to mix with spray oils for use during application. Since the endothall aquatic products are not labeled for application in oil, this data requirement is not applicable.

#### **2.1.20 Corrosion Characteristics**

Corrosion characteristics requires the physical observation/measurement of the effects of the product on the commercial packaging. Measurements of the weight, deformation and strength of the packaging are reported. For the endothall formulations, no significant changes were noted in the packaging other than minor tensile strength and elongation properties (Sweetapple, 1993a, Sweetapple, 1993b, Sweetapple, 1993c, Sweetapple, 1993d).

### **2.1.21 Dielectric Breakdown Voltage**

Dielectric breakdown voltage is the physical measurement of the effect of an electric arc on the stability of the formulated product. This requirement applies only to formulations that are applied around electrical equipment or apparatus. As there is no likelihood of open electrical apparatus in the aquatic environment, this test is not applicable.

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# Endothall

## Volume 2, Section 3

### ENVIRONMENTAL FATE

**46 PAGES**

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### **3.0 ENVIRONMENTAL FATE**

The chemicals 2,4-D and endothall are aquatic herbicides that are included in the more general categories of "agricultural chemicals", "agrochemicals" or "pesticides". When speaking in general of environmental mechanisms in this section, the term "herbicides" will be used, with the understanding that the processes discussed also apply to other pesticides. The term environmental fate refers to the natural mechanisms of breakdown and removal from the environment of an applied herbicide and its breakdown products (degradates or metabolites). Processes involved include volatilization, chemical interaction with water (hydrolysis), the action of sunlight on the chemical (photolysis), and degradation by microflora (bacteria, fungi) in sediment and water systems or by chemical interaction with the sediments. In a wider sense, environmental fate also encompasses the adsorption of the parent agrochemical and/or its degradates to sediment, either on lake/river bottoms or as suspended particles in the water column, as well as the leaching of the parent and degradates downward through subsurface sediment and soil. Available data on the above processes are presented in this section for endothall formulations of Aquathol and Hydrothol 191. Uptake by aquatic vegetation and any subsequent degradation is addressed separately in Section 4 of this document.

The dividing line between a "pond" and a "lake" is sometimes subjective, particularly in the case of large ponds and small lakes. The distinction between the class names of water bodies also depends on local custom and perception. Most people have an intuitive personal perception of what constitutes a pond and what merits the term lake. Along with others, this reviewer's definitions are somewhat subjective. However, for purposes of discussion in this section, and in general accord with terms used in the studies reviewed here, a pond may be considered to be a small water body, less than 3 or 4 acres, comparatively shallow (perhaps 10 feet or less), with limited water inflow and outflow. Water bodies larger than this are considered lakes.

Because they are shallower and have less total volume per surface area than lakes, the hydrology and biota of ponds tend to be more sensitive to environmental variations such as wind, rainfall, nutrient input, and daily and seasonal changes in air temperature than lakes. Lakes and reservoirs have larger water masses, less sediment surface per water volume, and in general more environmental inertia or buffering that reduces or slows their responses to environmental perturbations. It is important to keep these general principles of sensitivity or response in mind when reading the reviews below. In many cases, seeming contradictions in results between two studies can be explained simply by the differences in the types of water bodies that were studied.

#### **3.1 ENDOTHALL**

Endothall has been used for aquatic macrophyte control for a number of years. Because of its relatively early introduction in the form of various products, most of the investigative environmental fate work for this compound was conducted in the late 1970's and 1980's. Because of an EPA reregistration data call-in for almost all registered agrochemicals, additional work was conducted in the 1990's by, or for, Elf Atochem, North America, the registrant for endothall formulations (formerly named Pennwalt Corporation). The 1990's work largely served to upgrade the EPA registration acceptability of earlier data. This was mostly a matter of reconducting earlier "registration" studies using specific EPA study procedures, and/or supplying data that

were not generated in the original registration studies by Pennwalt. Another major reason for conducting additional studies was that in many cases the studies had been conducted by independent researchers (published studies) and did not address specific data needs of the EPA. Although new studies had to be conducted in many circumstances, the scientific validity of earlier study data, both registration studies and independent published studies, is rarely in question.

There are little specific environmental fate data presented in the 1992 endothall EIS in the form of actual numbers, so the current document utilizes data from as far back as 1970 for completeness.

Endothall has a very low vapor pressure (Section 2), so volatilization is virtually zero and is not a significant mechanism in removal of endothall from the environment.

### **3.1.1 Hydrolysis**

*Summary: Only one hydrolysis study report was located. Endothall acid was extremely stable in water. There was no measurable breakdown in 30 days at pH 5 and pH 9. A half-life in pH 7 water was calculated to be 2,825 days. No degradation products were identified.*

Hydrolysis refers to the chemical interaction of the agrochemical with water as a mechanism of agrochemical breakdown. While aqueous or aquatic (the terms are synonymous) persistence studies are sometimes conducted in natural water bodies, true hydrolysis studies are conducted in laboratories using sterile distilled or deionized water so that the chemical effects of an aqueous environment can be isolated from biological, sunlight, or sediment interactions. Aquatic persistence in natural water are addressed in Section 3.1.4.

Laboratory hydrolysis studies for EPA submission are typically performed with radioactive <sup>14</sup>C endothall in sterile water buffered to each of three pH values (pH 5, pH 7, pH 9, corresponding to slightly acid, neutral, and mildly alkaline, respectively) for a period of 30 days at 25°C.. Sampling for breakdown products and the remaining concentration of parent material is done at frequent intervals.

#### **3.1.1.1 Half-life**

Because laboratory hydrolysis studies are normally only conducted to fulfill EPA registration requirements, only one such study by the sole registrant (Elf Atochem) was found. In this study (46), hydrolysis testing was conducted with endothall acid for 30 days at the 3 nominal pH values and 25°C in a water concentration of 10 parts per million endothall (ppm, mg/L). Endothall was stable under the test conditions, with an extremely limited amount of degradation at pH 7. Calculated half-lives were 2,825 days at pH 7, and "infinitely stable" at pH 5 and 9. In short, endothall was shown to be stable in pure sterile water at a wide range of pH values, and to undergo no degradation.

#### **3.1.1.2 Degradation Products**

No degradation products were observed in any of the studies.

### 3.1.2 Aqueous Photolysis

*Summary: Experiments showed that in water of pH 5, pH 7, and pH 9, endothall acid does not significantly degrade as a result of exposure to light. The acid also does not significantly degrade as a result of light exposure when applied to the surface of a soil.*

As with hydrolysis, photolysis testing is carried out in a laboratory. Vessels containing solutions of the herbicide in sterile distilled or deionized water are irradiated with either a mercury vapor lamp or with natural sunlight and periodic samples are taken. Identical vessels are kept in the dark for the duration of the study and sampled in order to compensate for the effects of any hydrolysis occurring. Testing is usually carried out at 25°C, at pH 5, 7 and 9, but this is not always the case, particularly with very early studies. Other photolysis testing, such as photolysis of a pesticide on the surface of a soil, is also required by the EPA for products that might be incidentally applied to soil, as is the case for endothall.

The purpose of photolysis experiments is to isolate the effect of sunlight, specifically the ultraviolet and near-ultraviolet part of the spectrum, on the degradation of an herbicide without biological or chemical interactions. Natural sunlight's visible spectrum covers wavelengths from about 800 nm (deep red) to about 300 nm (deep violet). Generally speaking, only light in the violet and ultraviolet end of the spectrum has enough energy to initiate or influence chemical reactions ("photochemical reactions"). Air, as well as ozone, strongly filters near-ultraviolet and ultraviolet radiation, and cuts off nearly all radiation below 290 nm wavelength. Water is transparent to radiation with wavelengths as short as approximately 180 nm (far ultraviolet), assuming that there are no suspended solids or dissolved colored material such as humic acids to impair passage of the light.

As with hydrolysis, laboratory photolysis testing is generally conducted only in response to specific EPA registration requirements. Two endothall aqueous photolysis and one soil photolysis "registration" studies were found.

#### 3.1.2.1 Half-life

Zwick *et al.* (1990) conducted aqueous photolysis testing at pH 5, 7, and 9, with irradiation at 12 hours of xenon light and 12 hours of darkness for the "irradiated" samples, and constant darkness for the "dark controls" for 30 days. They found endothall to be infinitely stable at pH 7 and pH 9, with no measurable degradation occurring in either the pH 5 dark control samples or in the pH 7 and 9 irradiated and dark control samples. However, endothall degraded very rapidly in the pH 5 irradiated samples, with only 5% of parent material (endothall acid) remaining after 24 hours. The test solution constitution continued to change up to Day 7 after study initiation, with no changes observed after that time.

Another aqueous photolysis study was performed by the same laboratory (Battelle) the following year (Saxena *et al.*, 1991) at pH 5 only to confirm the first results. The second study was conducted in the same manner as the previous study, but only for 15 days, rather than 30 days. The second study detected no measurable degradation of endothall at pH 5 in 15 days. Table 3.1.2 illustrates the results for the three studies discussed above.

In order for light to influence chemical reactions such as degradation, it is necessary for the molecule to absorb that light. Since endothall does not significantly absorb light at wavelengths shorter than 290 nm, it would not be expected to undergo photolysis. The reason for the breakdown of endothall in the pH 5 irradiated solution in Zwick's experiment is not known, but it may be due to contaminants in the water, unsterile water, or other undiscovered causes. This reviewer feels that the original half-life of less than 24 hours should be viewed with extreme suspicion, however, and that endothall in irradiated aqueous solutions is indefinitely stable at pH 5, 7, and 9.

Saxena *et al.*'s (1992) study of soil photolysis is of interest as the only other photolysis data found. Such photolysis could occur if a lake or pond's water level were lowered to expose the sediment to sunlight or in the case of accidental overspray or drift onto shorelines. Since the experiment, conducted on a sterile damp soil, resulted in degradation of endothall in both the lighted test samples and the dark control samples, the authors felt that the degradation resulting in a half life of about 49 days was a soil-mediated hydrolysis due to the presence of various soil minerals rather than being the result of photolysis. However, the biological degradation of endothall (discussed later in this Section) would be more influential in degrading endothall than such photolysis.

### 3.1.2.2 Degradation Products

In their three-pH study, Zwick *et al.* found that the main degradate at pH 5 was carbon dioxide (CO<sub>2</sub>), which formed 24% of the trapped volatile products at Day 30 of the experiment. No organic (carbon-containing) volatile compounds other than CO<sub>2</sub> were detected. When the radiolabeled degradates were separated by thin layer chromatography, each constituted less than 10% of the initially applied radioactivity, and therefore were not identified, in line with EPA guidelines.

In the soil study, 6.5% of the originally applied radioactivity was found to be CO<sub>2</sub> by Day 30. At least one radioactive degradate was found to total 14.3% of applied activity on Day 12 in the irradiated sample, and 16.4% in the dark control samples on Day 32. It was not identified, but is not likely to be a photolysis product.

**Table 3.1.2: Photolysis of Endothall**

Matrix	Initial Concentration	pH	Temp (°C)	Half life (DT <sub>50</sub> )	Reference
Water	10 ppm	5, 7, 9	25	pH 5 = < 24 h pH 7 = ∞ <sup>1</sup> pH 9 = ∞	(51) Zwick <i>et al.</i> , 1990
Water	9.9 ppm	5.0	25	∞	(32) Saxena <i>et al.</i> , 1991
Soil	24.7 µg/g soil	not specified	25	ca <sup>2</sup> 49 days	(33) Saxena <i>et al.</i> , 1992

1 ∞ = infinite

2 ca = approximately

### 3.1.3 Degradation and Persistence - Soil

*Summary: Information on endothall persistence in soil can be useful in predicting its environmental fate when accidentally oversprayed on shorelines or when water levels drop in treated lakes and ponds, exposing sediment to the air. Endothall half-lives in aerobic soils with viable microbial populations ranged from less than one week to approximately 30 days. In two field tests, residues were non detectable after 21 days. In soils suspected of not having sufficient microbial populations, or populations of microorganisms able to degrade endothall, two studies found a half-life of 166 days, and persistence of residues over 0.05 ppm of more than one year.*

Although only the aquatic uses of endothall are considered in this document, the chemical is registered as an herbicide for terrestrial uses. Data regarding endothall's persistence in soil are therefore required to be submitted to the EPA. This information has a relevance to accidental terrestrial overspray on lake or stream shorelines, and peripherally as an indication of possible fate on near-shore lake bottoms exposed by drought or drawdown following an endothall application.

Only three field and greenhouse soil studies were considered useful for inclusion in this review. All three were "registration" studies. Two (48, 49) were field dissipation studies. Four separate trials were conducted in California and Pennsylvania on typical agricultural soils wherein endothall was applied to field soil, and its disappearance and any movement through the soil were monitored by periodic analysis of soil cores. The third study (31) involved a greenhouse study where endothall was applied to containers of agricultural soil and residues were monitored over 1 year's time. Three "registration" laboratory studies were also reviewed.

#### 3.1.3.1 Half-life

In the year-long laboratory "registration" aerobic metabolism studies (1, 26, 47), endothall degraded with a half-life of 10 days, 14.5 days, and approximately 166 days, respectively. The last of these was conducted at a moisture content of 75% FMC (field moisture content - a measure of the maximum amount of water that a soil can hold). Since endothall does not undergo hydrolytic or photolytic breakdown, the very long 166 day half-life (26) probably resulted from the absence of a viable microbial population, or at least of a population able to degrade endothall, and should not be considered as typical of endothall persistence in a natural environment.

Endothall dissipation under field conditions was rapid at low to medium application rates. In the field dissipation studies (48, 49), half-life ranged from less than 1 week to 19 days. The time required for reduction of the residues to less than the detection limit (approximately 0.05 ppm) was 21 days or less.

Under greenhouse conditions (31), the half-life in soil was approximately 30 days, but the time for disappearance of residues was more than a year. The very long persistence in the latter study is at extreme variance with the field studies and in the opinion of this reviewer, is not an accurate depiction of endothall dissipation in "real world" field conditions. The year-long persistence in the greenhouse study combined with the 30 day half-life indicates problems in maintaining an initially viable microbial culture in the soil.

Microorganism populations were obviously adequate to degrade endothall moderately rapidly in the first month, but the subsequent extended persistence shows that the population declined or died off after that time. The most likely cause was a change in cultural conditions in the greenhouse that severely impacted the microorganism viability.

### 3.1.3.2 Degradation Products

Only the Atkins and Reynolds <sup>14</sup>C endothall radiolabeled laboratory studies (1, 26) and Sanger's greenhouse study (31) attempted to determine the degradation products of endothall. Williams *et al.*, 1999 does not give metabolism information in their review. In both the Atkins and Reynolds studies, CO<sub>2</sub> was the major degradate. Reynolds found that 43% of the original radioactivity applied in that study was released as CO<sub>2</sub> after one year. Atkins reported 72% of the original radioactivity as CO<sub>2</sub> by Day 209 of the study. Reynolds found two late-forming polar degradates that each constituted less than 2% of the original radioactivity. Both of the laboratory studies also measured radioactivity that could not be extracted from the soil, which is not unusual with this type of study. That activity was associated with fulvic acid, humic acid, and humin, all typical soil constituents. In the Sanger study, CO<sub>2</sub> release was significant. Several polar, unidentified products were found, but no identification was attempted. As will be discussed later, as radiolabeled endothall is broken down by soil microorganisms, the carbon atoms are liberated to be utilized by the microorganisms, and also to be incorporated into harmless soil minerals.

To avoid confusion, it is important to remember that the <sup>14</sup>C endothall radioactivity discussed above is only prepared and used in laboratory studies to track endothall's fate, and will not occur in the environment as a result of using endothall formulations.

**Table 3.1.3: Endothall persistence in soil**

State	Application rate	Half life (DT <sub>50</sub> )	Time to residues < 0.05 ppm	Reference
Lab aerobic soil mesocosm	3.3 ppm dipotassium salt	14.5 D	n.r. <sup>2</sup>	(1) Atkins <i>et al.</i> , 1999
Lab aerobic soil mesocosm	ca. <sup>1</sup> 10 ppm dipotassium salt	ca. 166 D	n.r.	(26) Reynolds, 1993b
Lab aerobic soil mesocosm	n.r.	10 D	n.r.	(47) Williams <i>et al.</i> , 1999
CA	Dipotassium salt. Rate not given	< 1 Wk	14 D	(48) Wright 1993a
CA	Monoethyl-amine salt 1.04 lb a.e. <sup>3</sup> /acre	12.6 D	14 D	(49) Wright 1993b

State	Application rate	Half life (DT <sub>50</sub> )	Time to residues < 0.05 ppm	Reference
PA	Dipotassium salt. Rate not given	9 D	14 D	(48) Wright 1993a
PA	Monoethylamine salt 1.04 lb a.e./acre	19.2 D	21 D	(49) Wright 1993b
Greenhouse	Compound not specified. 2.5 lb a.i. <sup>4</sup> /acre	approx. 30 D	> 1 Yr	(31) Sanger 1994

1 ca. = approximately

2 n.r. = not reported

3 a.e. = endothall acid equivalent

4 a.i. = active ingredient (in the formulation)

### 3.1.4 Degradation and Persistence - Aquatic Systems

*Summary:* Endothall can be absorbed or adsorbed by aquatic plants and algae, but may be released back into the water when they die. Section 4 discusses the fate of endothall with regard to aquatic vegetation. Endothall is rarely persistent in natural waters. It does not undergo hydrolysis or photolysis, but rather is broken down by the action of microorganisms that utilize it as a carbon/energy source. The half-life of endothall in water is generally ranges from less than one day to about 8 days. Total persistence time in water normally varies from a day or two to about 35 days, although persistence to more than 62 days has been reported. Endothall persistence in sediment has not been investigated as thoroughly as in water, but half-lives of 8 to 32 days were reported, with disappearance taking 22 to 36 days. Many reviewed studies did not address water and sediment persistence separately, but reported disappearance in the "system" as taking 1 to 26 days. Sediment persistence can be expected to be longer when granular formulations are used as opposed to liquid formulations, since granules resting on the sediment continue to release endothall over a period of days.

The major product of the degradation of endothall is CO<sub>2</sub>, the end product of microbial metabolism of endothall's carbon atoms. Small amounts of humic acid, fulvic acid, and humin have been identified. Their presence reflects the incorporation of endothall carbon into naturally-occurring soil components.

The disappearance of endothall from a lake or other natural water body is influenced by a number of environmental factors, which makes it difficult to precisely calculate the degree of persistence for a specific water body. Higher water and sediment temperatures will facilitate the metabolism of endothall, while cooler temperatures, such as those found at the bottom of stratified lakes, will retard it. Water pH has little effect on endothall persistence, unless it is so extremely acidic or basic as to affect the microbial community. The amount of oxygen dissolved in a water body has a direct effect on the speed of endothall metabolism since the microorganisms that break down endothall are aerobes that must have oxygen to thrive. Warmer water, aerobic decay of organic materials on/in the sediment, oxygen depletion resulting from decay of a large aquatic vegetation kill are examples of situations that can deplete dissolved oxygen. In many

*cases, eutrophic and even mesotrophic lakes are more likely to support large populations of microorganisms that can metabolize endothall than lakes with lower nutrient levels. On the other hand, if carbon sources are not abundant, competition for the carbon in endothall can favor the growth of the microbiota that can utilize endothall exclusively. There is disagreement among researchers as to whether adsorption of endothall to sediment increases the availability to microorganisms by concentrating it on the surfaces, or decreases the availability for metabolism due to strong binding. The variable strength of the binding, depending on the nature of the sediment, is probably responsible for conflicting findings.*

*Probably the most important physical process affecting endothall persistence in larger water bodies is transport of treated water away from the treated area and replacement with untreated water through lateral circulation or vertical movement of water. In this regard, the larger the lake, the more wind blowing across the lake surface, and the more water exchange through inlet and outlet streams or rivers, the more likely it is that endothall residues will be rapidly dispersed and diluted to below detection limits. In small lakes, detectable concentrations of endothall may be carried a significant distance down an outlet stream if the flow is sufficient and endothall degradation is slow. Vertical dispersion is the dominant mechanism of dilution in whole-treated lakes, while a combination of vertical and horizontal water movement contribute to dispersion and dilution in lakes treated over only a part of their surface.*

*Liquid formulations can be expected to result in higher initial water concentrations than granular formulations, since all of the endothall is applied directly to the water. Granular formulations generally yield higher endothall sediment concentrations and longer persistence in or on sediments due to a prolonged release of endothall from the granules. Granular formulations can therefore result in lower water concentrations that may persist somewhat longer than if liquid formulations are used.*

#### **3.1.4.1 Half-life and Disappearance Time**

Endothall is adsorbed or absorbed by various aquatic vegetation and algae. This process removes endothall from the water and can result in significant reduction of residues in the water. However, some vegetation and algae then release endothall back into the water when they die. This process is discussed in Section 4 of this document.

Table 3.1.4.A summarizes the half-lives of endothall reported in research papers, as well as the time to non-detection or very low levels as specified in the table. Depending on the intent of the reference, either one or the other parameter may not be reported. A half-life is the time required for an herbicide to reach half of its initial concentration following application. Depending on the type of study and the data collected, a half-life may be mathematically calculated using several analyses over time, or may be interpolated from tabular data or figures given in a cited paper, as was frequently necessary in this review.

Time to disappearance is the time necessary for an herbicide concentration to drop below the lower limit of analytical detection. This value is usually 0.05 ppm endothall for sediment and 0.02 ppm for water. Because of the variety of available analytical techniques used over time (chemical analysis, bioassay), the Limit of Detection (LOD), the lowest herbicide concentration that can be reliably quantified, has varied over time. Unless otherwise noted, the values of 0.02 ppm endothall for water and 0.05 ppm

endothall for sediment are used in this section. These values are a good average over the span of time of the work reviewed. Also, virtually all of the relevant data found for laboratory work, ponds and lakes are for the disodium and dipotassium salts of endothall. Unless otherwise noted, results in this discussion refer to Aquathol® treatments.

Half-life values are important for calculations, but can be misleading if the herbicide remains in the environment at significant concentrations after the half-life time. Times to disappearance are useful tools for predicting impacts on biota and wildlife, particularly when used with calculated or estimated half-lives. The persistence of endothall varies widely depending on the conditions of the system being tested, as will be discussed later. Therefore it is not surprising that a wide range of half-life and disappearance times has been reported in the literature.

Two laboratory anaerobic aquatic studies were reported (25, 47). This type of study, performed in small flasks containing sediment and water, is designed to generate half-life data and to examine any degradates that are formed. Calculated half-lives for the water/sediment system were 8.5 days and 10 days. A similar study conducted under aerobic conditions (24) reported "rapid" decline of endothall.

Other laboratory aquarium/mesocosm experiments using water and sediment from natural water bodies (21, 22, 37, 39) yielded water half-lives from 5 to 8.5 days and disappearance times of 7 to 62 days. Sediment half-lives ranged from 8 to 16 days, with disappearance times from 22 to more than 62 days. For comparison, the Syracuse farm pond from which sediment and water were taken for laboratory studies (37), yielded water and sediment times a little longer than seen in the aquaria experiments in the same study. This was possibly due to the slightly lower temperature in the pond, and an expected nightly temperature decline.

Endothall persistence times in sediment, measured from the application dates, are frequently longer than that in water, since the maximum concentration in or on sediment is generally not reached immediately when liquid formulations are used. It may take several days for the herbicide to reach the sediment through the water column, build up, and then begin to decline. However, once the decline begins, the time to disappearance is usually fairly rapid, since the sediment concentration is rarely as high at its highest point as the concentration in water.

One of the mesocosm studies (39) displayed a two phase decline. The first half-life, based on the early decline pattern, was about 30 days. This was followed by a rapid decline and a half-life estimate of about 5 days from that point on. This pattern resulted from the inhibition of aerobic endothall-utilizing microflora growth caused by the depletion of dissolved oxygen in the water as the aquatic plants died and decayed. The microflora reproduced rapidly after natural reestablishment of oxygenated conditions, using the newly-available carbon, and began feeding on the endothall. This initial lag may be expected in natural water bodies with a large macrophyte population if a significant portion of the lake is treated, resulting in a heavy macrophyte kill, and there is little water circulation to quickly restore dissolved oxygen.

Reported persistence in a number of unidentified ponds (11, 13, 14, 15, 47, 50) is similar to those in laboratory mesocosms. Water and system half-lives ranged from 0.5 days to more than 20 days. While not shown in the table, the half-lives of more than 20 days

were only found in a few farm ponds; the next shortest times in the data were somewhat more than 12 days. Water and system disappearance times from 6 hours to 26 days, where reported.

Half-lives in treated areas of lakes tended to be shorter than in ponds, primarily because of the availability of a greater volume of water, as well as water currents, that result in dilution and dispersion of the treated water (3, 8, 9, 10, 14, 17, 19, 27, 28, 30, 35). Half-lives ranged from less than 6 hours to 8.5 days for water, including two lakes treated with the amine salt. In Lake Parker, Florida, Ritter and Williams (1996) reported a 0.4 day half-life in the open lake and two-phased initial half-lives of 5.4 and 8.5 days for the first two to three days after application, followed by rapid 0.12 day and 0.4 day half-lives thereafter in 6-foot enclosures in the same lake. This is evidence of the effects of endothall dispersion by water movement through the treated areas in open water.

Sediment half-lives were 0 (no residues found immediately after treatment) to 4 days, while a single system half-life in Pay Mayse Lake, Texas, was 1.1 to 1.2 days (17). The zero-time half-life was probably due to sampling errors. Disappearance times were less than 24 hours to less than 30 days for water, and 2 days to less than 30 days for sediment. In Gatan Lake in the Panama Canal, system persistence was less than 3 days for the dipotassium salt and more than 21 days for the amine salt. There did not appear to be more than a minor correlation between application rate and half-lives, though persistence times were somewhat longer at higher application rates.

Detailed data were only found for three Washington State lakes where experiments were conducted (8, 35). Lake Sylvia in Mason County, treated with Hydrothol® 191, the amine salt at 0.3 ppm endothall, yielded a half-life of 5.9 days in the treated waters, with persistence of somewhat more than 7 days. Endothall was found in water from an outlet stream 0.4 miles from the lake at a concentration of 0.03 ppm at seven days after application (the last sampling date).

Lakeland Village Lake in Mason County and Gravelly Lake in Pierce County were treated with Aquathol® K at approximately 1.3 and 3.5 ppm, respectively. Lakeland Village Lake is a 40 acre moderately eutrophic shallow lake that was extensively treated, while Gravelly Lake is a 160 acre closed basin lake with a mean depth of 38 feet that received treatment in a very small stretch of shoreline. Unfortunately, there was such extensive contamination and loss of samples that it is difficult to draw definite conclusions regarding endothall degradation patterns in either lake from the study report. Persistence was 8 to 16 days for Lakeland Village Lake and less than 8 days for Gravelly Lake in the treated areas.

### **3.1.4.2 Degradation Products**

Few of the available studies were intended to produce data regarding the identity of specific endothall degradates. The two Reynolds papers (24, 25) summarized immediately below were EPA guideline studies specifically designed to address that question. A few other researchers confined themselves to measuring evolved CO<sub>2</sub>, since that degradate can be identified without involved laboratory procedures.

Reynolds (1992) conducted a one-year anaerobic water/sediment study of the persistence of dipotassium endothall and the degradates formed. The major degradate was CO<sub>2</sub>, with

64% of applied endothall released as CO<sub>2</sub> by Day 270 of the study. Two unidentified polar metabolites first appeared at Day 14 and totaled approximately 10% of the applied radioactivity by Day 30. Reynolds believed these to have been fulvic acids associated with sediment organic constituents. Residues bound to the sediment totaled 53% of the applied radioactivity by Day 30, then declined to 24% by Day 365. These were tentatively identified as fulvic acid (20% of applied activity), humic acid (19%), and humin (14%). These are all typical sediment /soil organic compounds.

The same author (Reynolds, 1993a) conducted a 30-day laboratory aerobic water/sediment study. The primary metabolite was <sup>14</sup>CO<sub>2</sub>, with 36% of the applied radioactivity released as CO<sub>2</sub> by Day 30. Two unidentified polar degradates first appeared on Day 7, and by Day 30 totaled 6% of the applied radioactivity. Since the chromatographic characteristics are the same as those for the two polar compounds formed in the anaerobic study, they are probably the same. Sediment-bound degradates were associated with low levels of fulvic acid and humic acids, and 27% humin by Day 30.

Simsman and Chesters (1975) reported significant release of CO<sub>2</sub> from laboratory sediment/water aquaria and flask tests. Reinert *et al.* (1986) reported results from a sediment/water laboratory test showing 86% to 100% of the radioactive carbon applied to the flasks as endothall was evolved as CO<sub>2</sub> by Day 17 of the test.

The conclusion evident from these papers is that endothall is degraded to yield CO<sub>2</sub> as the major degradate. Other degradates are primarily the products of microbial breakdown of the endothall molecule (discussed below), and incorporation of the liberated carbon into organic soil/sediment acids and humins that are strongly bound to the sediment.

#### **3.1.4.3 Physical and Chemical Factors**

This section discusses the potential impact of individual physical and chemical factors on endothall persistence. It is difficult to separate the effects of the numerous water and sediment chemical and physical parameters on endothall persistence. Temperature obviously will have an effect, as will pH. The aerobicity (presence or lack of dissolved oxygen) of a system, the trophic state and consequent microbial population present, adsorption to suspended and bottom sediment, sediment characteristics, transport/dilution, and the type of formulation used can also influence endothall breakdown. While most references do not address factors in isolated experiments, conclusions can be drawn from inference when the data are viewed as a whole.

- **Temperature**

Temperature has a pronounced effect on the rate of chemical reactions and metabolic processes. In the case of endothall, where degradation is a biological process, temperatures outside the optimum range for endothall-degrading microflora will increase endothall persistence. Water temperatures high enough to inhibit endothall metabolism in bacteria and fungi are unlikely to occur in Washington lakes. In this moderate climate, the most likely effect is that caused by cooler temperatures at night and at greater lake depths. Because of the high specific heat of water, it is a good thermal insulator, so the temperature of average size lakes does not vary much from night to day at the surface and even less at greater depths. Water temperatures of

perhaps 50°F to 70°F may be expected in medium size lakes during the times when aquatic weed control is a concern. Smaller or shallow lakes may be expected to be warmer than larger lakes.

In deeper lakes a thermocline can form during summer months wherein there is a sharp boundary between the warmer surface water and cold deeper water. Thermoclines can increase endothall persistence in two ways. 1) As there is little exchange of water across the thermocline, there is less water volume to dilute the herbicide, particularly in lakes treated over a large percentage of their surface. 2) Any endothall that penetrates the thermocline encounters a colder environment where degradation by microbes is slowed.

Laboratory studies, typically conducted at 20°C to 25°C (68°F to 77°F) may yield endothall half-lives that are somewhat shorter than studies in ponds or lakes. In addition, the latitude of the lake, with varying temperature regimes, make comparisons difficult. Overall, though, studies summarized in Table 3.1.4.A show little effect of temperature on endothall persistence, due in part to the absence of very low or very high temperatures.

- **pH**

Few data are available on the effect of pH on endothall persistence. Since endothall does not undergo chemical breakdown in water, any pH effects would be expected from action on the biological processes of microflora in the water or on sediment surfaces. Water/sediment pH values below the second dissociation constant ( $pK_{a2}$ ) of 6.1 to 6.2 may contribute to greater adsorption to more positively charged sediment with a high CEC (cation exchange capacity), which would concentrate endothall and make it more available to the microflora if it is not too tightly bound. Since there are a number of other factors involved in endothall persistence, and since sediment concentrations of endothall are generally low in natural water bodies, any pH effect on sediment adsorption is likely to be minimal.

- **Aerobic state**

The amount of gaseous oxygen dissolved in the water has a distinct effect on endothall persistence since endothall degradation is the result of the action of microflora, most of which are aerobes, requiring oxygen to live. Dissolved oxygen (DO) levels are typically 6 ppm to 10 ppm in well-mixed natural water bodies, although levels outside of that range may occur. The colder a water body, the higher the saturation value, or maximum amount of DO that it can hold.

Some people have a misconception regarding DO. "Dissolved oxygen" does not refer to the oxygen atom in the water molecule ( $H_2O$ ), which is not available for use by aquatic organisms, but to oxygen gas ( $O_2$ ) physically dissolved in the water.

DO enters the water primarily from the atmosphere and from the photosynthesis of algae and submerged plants. Dissolved oxygen is consumed by fish, by microflora in the water column and on the sediments, and by zooplankton and bottom-dwelling organisms such as aquatic insects. Aquatic plants also consume limited amounts of oxygen in the "dark cycle" of their metabolism at night. Decay of vegetation and

other organic materials, primarily on the lake bottom, also consumes significant oxygen. In lakes where surface and deeper waters do not mix well, a thermocline can form that prevents upper and lower depth waters from mixing. In this case, water circulation is impaired and the water below the thermocline will become anaerobic if all of the dissolved oxygen is consumed.

Simsiman and Chesters (1975) documented the effect of oxygen depletion in 17 gallon aquaria containing Lake Mendota, Wisconsin, water and sediment and a large population of aquatic plants to which 3 ppm of endothall acid were added. The macrophytes were killed very rapidly and decomposed in the aquaria. The decomposition consumed most of the DO in the tanks, and there was little for endothall-consuming microorganisms to use. Little endothall decomposition occurred until about 30 days after treatment, when the DO in the tanks had recovered and aerobic microorganisms could increase their numbers, after which endothall decomposition was very rapid. These aquaria probably regained their oxygen through diffusion from the atmosphere. In water/sediment flasks without macrophytes, they found little difference in aerobic vs. anaerobic residence times in flasks that appeared to have a low population of endothall-utilizing microflora.

Two Washington State studies illustrate that oxygen depletion should not always be anticipated. In Lake Sylvia, Mason County, Washington, endothall disappeared in less than 7 days, despite a large macrophyte infestation and treatment of half of the lake surface. The lack of a delay in endothall breakdown from the suppressing effects of low DO following macrophyte kill was most probably due to the "considerable" water movement through the lake following treatment, from an inlet stream past an outlet dam. In Lakeland Village Lake, Mason County, endothall persisted for 8 to 16 days. Despite extensive shoreline treatment, there was only a low to moderate macrophyte concentration, and hence oxygen depletion from macrophyte decay was less likely. The authors, in fact, reported little or no dissolved oxygen changes during the 16 days of monitoring and little through-lake flow.

The speed of restoration of oxygen in a natural lake is dependent on water temperature, mixing throughout the water column, introduction of oxygenated water from elsewhere in the lake, and the contributions of algal and surviving macrophyte photosynthesis. In the case of a poorly mixed lake or of a treated shoreline area having a heavy macrophyte kill, reoxygenation might be delayed and endothall persistence extended. The effect would be more pronounced in lakes with heavy macrophyte growth given a whole-lake treatment.

- **Trophic state**

The trophic state of a natural water body exerts an indirect influence on endothall persistence. Because eutrophic and high-end mesotrophic lakes are likely to have a larger macrophyte population, they are more likely to be included in an aquatic weed control program. In eutrophic lakes (high levels of nutrients), microflora populations can be expected to be larger than in mesotrophic or oligotrophic lakes (medium to low nutrient concentrations). Therefore a larger population of microflora, many of which can degrade endothall, can be expected to be present and endothall persistence can be expected to be shorter. Conversely, when a large pool of carbon is available from decaying plant and animal matter, endothall may not be utilized by

microorganisms as readily as in lower-trophic state lakes. Mesotrophic and especially eutrophic water bodies usually have a higher population of algae that can substantially contribute to the restoration of DO following an aquatic plant kill from an endothall application as discussed above, and can thus help speed endothall degradation by aerobic microflora such as *Arthrobacter*.

One possible negative effect of a eutrophic state on endothall persistence should be mentioned. As stated above, the high nutrient levels usually give rise to a dense population of algae and various macrophytes as well as phytoplankton and benthic organisms. In any lake, there is a continuous process of decay of a large number of dead organisms occurring, particularly on the lake bottom. In a eutrophic lake a proportionately larger amount of decaying organisms can be expected. The first stages of this decay are generally aerobic, which uses dissolved oxygen. If conditions occur such as poor water circulation, the formation of a thermocline, or a population crash of a dense species population, the bottom of the lake (and possibly shallower depths) can become anaerobic. The inhibiting effects of low DO on endothall-degrading microorganisms then becomes a significant factor in the persistence of the compound.

- **Adsorption to sediment**

Adsorption and uptake of endothall by aquatic macrophytes and algae is addressed in Section 4 of this document. No unequivocal proof was found as to whether adsorption of endothall to sediment increases or decreases the availability of the chemical to microbial breakdown. Simsman and Chesters (1975) speculated that adsorption to the sediment surface concentrates the endothall on a substrate where degrading microflora may also be concentrated. They felt that some endothall may be loosely enough bound to permit microflora to metabolize the concentrated herbicide.

Biever (1996) found sediment concentrations of endothall of 0.56 ppm one day after application in a shallow four-foot deep treatment, with detectable concentrations down to 6 inches during the first three days. However since the sediment was sand with less than 1% organic matter, the endothall was probably in solution in the lake water that penetrated the sand interstices and little adsorption took place. Adsorption would be expected to be greater in a shallower lake or pond where the sediment surface:water ratio is higher and there are more potential active sites on the sediment surface that are exposed to the endothall in the water.

Sikka and Rice (1973) found the maximum concentration of endothall in aquarium sediment 3 days after treatment with the dipotassium salt. They reported that in a shallow farm pond, endothall sediment concentrations continued to increase slowly for the first 22 days after Aquathol® treatment, then slowly declined. The rate at which endothall migrates to the sediment will depend on the application rate, the depth of the water, and circulation in the water body, with shallower ponds and lakes expected to transfer the herbicide to the bottom faster than deeper or more static lakes. Once in contact with sediment, endothall may be adsorbed, but then be desorbed back into the water as the concentration in the overlying water decreases. This migration-adsorption-desorption pathway can lead to extended endothall persistence.

In a turbid water body with significant amounts of particulate sediment suspended in the water, there is a greater solid surface area for endotoxin adsorption and release to lower-concentration water than in an essentially two-dimensional lake bottom. Since endotoxin-degrading microflora can populate the suspended sediment as well as bottom hydrosol, adsorption to suspended sediment can make endotoxin more readily available for attack by those organisms (39). This can facilitate endotoxin degradation in medium to large lakes without a large microbial population in the water column.

- **Transport and dilution**

Probably the most important and obvious physical processes affecting endotoxin concentration in larger water bodies are dispersion or transport from the treated site by water currents and dilution by untreated water. With its high water solubility, endotoxin is easily transported within water currents in a lake. Obviously, the larger the area of a lake that is treated, the more water current will be needed to dilute and disperse the herbicide, with the extreme case occurring in whole-lake treatment. An elaborate model for predicting endotoxin dispersion and dilution was developed by Singh *et al.* (1999).

In lakes without significant inflow or outflow, most dilution of endotoxin-treated water will occur through vertical movement in the water column. Solar heating is not as important to water movement in these lakes as the effects of wind. While sunlight can heat the surface waters, the warmer water tends to stay at the surface and little vertical circulation occurs. Wind can induce mixing between water depths even at low velocities. Surface water driven against a shoreline is driven downward and mixes with lower depth water. This dilutes the endotoxin concentration of the surface water and possibly carries it into contact with sediment-dwelling microflora.

In lakes treated over only a part of their surface, dilution is a very significant mechanism for reducing endotoxin concentration in the treated areas. Dilution can occur from wind-driven water currents or water flow through the lake, both of which can give rise to vertical and horizontal mixing and dilution. Movement of water through the lake can result from inlet streams and rivers, storm runoff outlets, submerged springs, or diffuse surface runoff into the lake from the surrounding basin. Operation of dams or weirs or other controls on lake outlets will impact the magnitude of water movement in lakes or reservoirs and consequently the dispersal of treated water.

Endotoxin can be carried out of a lake and into outlet streams if a large portion of the lake is treated, if water movement is rapid, or if there are insufficient microflora to break the herbicide down quickly. In view of the potential impacts on river biota, including fish, far from the treated lake, water mass movement and the specific water budget for a particular lake must be taken into consideration when applying endotoxin. In western Washington, rainfall events, particularly in the months preceding July and after mid-September, can rapidly dilute endotoxin residues in a treated lake due to stream inflow and surface runoff, and can also move treated water into outflow streams more rapidly than anticipated before degradation is completed.

Biever (1996) Treated a 2.75 acre plot in Lake Parker, Florida. Lake Parker is a 2200 acre reservoir "infested" with *Hydrilla*. The plot extended 400 feet alongshore and 300 feet offshore. The mean depth of the treated littoral area was 3.7 feet. The plot was treated by injection 2 inches under the surface with 3.2 gallons of Aquathol K liquid per acre-foot for a nominal concentration of 4.2 ppm endothall acid (5 ppm dipotassium salt). During the first seven days of the study, water currents varied from 0 to 0.07 feet per second in the treated area and 0 to 0.08 feet at a testing location approximately 50 feet farther offshore than the outer edge of the treated area. Current direction varied widely from day to day during the study.

The initial mean water residue value for the eight treated sampling stations of was 2.9 ppm (endothall acid) on Day 0, immediately after application. The mean concentration dropped to 1.6 ppm by Day 1, 0.3 ppm by Day 3, and 0.45 ppm on Day 5. No endothall was detected on Day 7 or thereafter (residues less than 0.01 ppm). At the eight peripheral sampling stations 100 feet from the borders of the treated area, mean residues were 0.26 ppm acid on Day 0, 0.18 ppm on Day 1, 0.83 ppm on Day 3, and 0.015 ppm on Day 5. No residues were detected at Day 7. The peripheral concentrations were therefore roughly 10% to 30% of those in the treated plot until the end of the study when residues dropped very low. In order for the endothall to have persisted in the treated and peripheral areas, the *Hydrilla* must have been dense enough to impede endothall dispersion despite the water currents present. Unfortunately, the density of the *Hydrilla* infestation was not reported.

Endothall can be carried out of a lake and into outlet streams as part of the water mass movement if a large portion of the lake is treated, if water movement is rapid, or if there are insufficient microflora to break the herbicide down quickly enough. In 12-acre Sylvia Lake in Mason County, five acres of the lake were treated with 1.8 lb ppm Hydrothol® 191 with a target concentration of 0.3 ppm (8). The lake has an inlet stream and an impoundment weir (over which water was flowing) and an average depth of 4 feet. The application was made as a "whole lake" treatment to the area of the lake farthest from the weir. There was a 75% coverage of the treatment site with various aquatic weeds and algae such as *Chara*, *Nitella*, *Spirogyra*, Coontail, and elodea.

By 24 hours after treatment (Day 1), mean residues were 0.11 ppm endothall acid equivalent in the treated area, 0.09 ppm 200 feet away near the outlet weir, and 0.05 ppm at a site far down the outlet stream 2100 feet from the treated area where it empties into Mark Dickson Creek. Heavy rainfall then occurred in the area 36 hours after the application that raised the level of the outlet stream 12 inches by Day 7. On Day 3, mean residues were 0.10 ppm, 0.10 ppm, and 0.06 ppm at the three locations, respectively. By Day 7 after treatment, "considerable water" was moving out of the lake, and mean endothall residues were 0.07 ppm, 0.08 ppm, and 0.03 ppm.

The decline of endothall residues from a theoretical Day 0 value of 0.3 ppm to about 0.1 ppm in 24 hours, along with the appearance of endothall in the lake near the weir and in the outlet stream is suggestive of the herbicide being adsorbed by plants and algae, and also being carried out of the lake. Control of the macrophytes and algae was "good", so the plants probably inhibited transport of the herbicide by water currents until they had absorbed a significant amount. However, comparable residues in the treated area and 200 feet away indicate that transport certainly did occur,

particularly after the rain event increased flow through the lake. The low level of residues found 2100 feet away from the lake were mostly the result of dilution, although adsorption to the stream sediments and by vegetation and algae along the stream may have played a part. While streamflow was not measured, an estimate of the magnitude of endothall transport can be made. A residue level of 0.056 ppm endothall (the highest residue at that point, seen on Day 3), is equivalent to one pound of endothall flowing past the sampling station with every 120,000 gallons (16,000 cubic feet), less than one percent of the approximate two million cubic foot lake volume. Removal of endothall by the rapidly-flowing stream was therefore a likely major fate process in this study.

Gangstad (1986) reported that endothall dissipated within 72 hours from 93 acres of treated areas in 6000-acre Pat Mayse Lake following a 250 lb/acre (2.5 ppm) treatment with Aquathol® K granular. Endothall was not detected in Paris, TX, city water intakes 3000 feet from the treated area in Pat Mayse Lake.

In a review paper, Keckemet and Sharp (1999) surveyed five internal Elf Atochem pumping studies in reservoirs partially treated with 3.0 ppm Aquathol® K. The measured concentration in the treated area following application was 1.6 ppm endothall. At 48 hours after application, the maximum measured residue at 250 feet from the treated areas was 0.3 ppm; endothall was not detected at a greater distance.

The authors also briefly summarized endothall mobility in several studies, though data are sparse. Two tests in finger-shaped inlets of a California lake were treated with Aquathol® K at 0.3 ppm in a band across the inlet. The first test measured water on the shoreline side of the inlet. Water residues as high as 0.28 ppm were measured at a distance of 100 feet during the 18 hours after the application. No endothall was detected (LOD 0.02 ppm) 300 feet from the application band despite a quartering wind from the band toward the sampling stations.

In the second test, sampling was conducted only as far as 100 feet from the application. Water residues as high as 0.5 ppm were measured 100 feet away on the lake side of the application band in the first 18 hour, slightly upwind from the application. Measurements were not made farther from the application band.

In a Florida lake, estimated by this reviewer as being at least 2000 acres from a drawing in the report, Aquathol® K liquid was applied at 7.5 gallons per acre to 24 shoreline acres. The application was made near the outflow end of the lake, which had an inflow stream at the opposite end. Residues in the center of the treated plot ranged from 1.8 to 5.1 ppm in the first 6 hours (ignoring a 19.8 ppm "hot spot" residue), then dropped to 0.7 ppm on Day 1, 0.3 ppm by Day 7, and to less than 0.2 ppm (the LOD) by Day 10. No endothall was detected 1000 feet away from the treated site (toward the inflow stream) at a potable water intake at any time.

Ritter and Williams (1998) describe a study wherein Aquathol®-K liquid was applied by helicopter to about 44 acres of 10 to 20 foot deep water in Pinopolis Cove in Lake Moultrie, a very large reservoir in South Carolina. Sampling was concentrated in an approximately 14 acre plot at the end of the 44 acre treated area closest to a water treatment plant 4400 feet northeast of the plot edge. An outlet dam was located about 2 miles northeast of the sampling plot, beyond the water treatment plant.

Initial water concentrations in the plot averaged 3.5 ppm after application. Nine hours after application, endothall residues of 0.37 ppm were detected 500 feet northeastward along the shore. At 24 hours after treatment, residues of 0.02 ppm were measured at the water treatment plant intake, at a time when surface residues in the treated area were 0.09 to 0.16 ppm. Residues of 0.01 to 0.03 ppm persisted at the water treatment intake (surface and 10 feet depth) but were below 0.01 ppm (the LOD) in the Day 7 and Day 10 samples. Endothall residues were less than 0.01 ppm in all areas by Day 7. The authors conclude that endothall residues migrated at an average velocity of 0.05 feet per second due to prevailing lake current and wind-induced currents, however recorded currents were very erratic in direction during the 10 days of sampling, and did not flow from the treated area toward the intake until Day 3. No water was released from the dam for in the first two days of the study.

Guntersville Reservoir on the Tennessee River is a 68,000 acre water body. Keckemet and Sharp (1999) briefly summarized a study that found when Guntersville Reservoir was treated at a rate of 1.8 ppm with Aquathol® K, no endothall was detected (LOD - Limit of Detection - 0.005 ppm) 1/2 mile away 24 hours after treatment.

In another study in Guntersville Reservoir (30), Aquathol® K liquid was injected into a 30 acre area in Brown's Creek in a narrow bay at the southern (outlet) end of the reservoir at 5 gal/acre (1.5 ppm) and water was sampled for 7 days. The only endothall residue detected at any sampling station (0.01 LOD) was 0.034 ppm in the treatment area at 6 hours after treatment. The nearest sampling station outside the treated area was 3.8 miles away at the mouth of the bay. The authors attribute the failure to detect endothall to water flow in the lake and subsequent dilution.

In Lakeland Village Lake, Mason County (35), extensive shoreline was treated with Aquathol® K, including areas near the outlet stream. Results are difficult to interpret due to sample contamination, but indications are that endothall migrated at least 500 feet into the untreated lake center by the second day after application, where it persisted at about 0.05 ppm until at least Day 8. Residues in a treated area were measured as 0.05 ppm on that date. Water flow through the lake also carried the herbicide to the outlet stream by Day 8 and possibly earlier.

An example of endothall dispersion in a closed lake system, Gravelly Lake in Pierce County, Washington, is given in the same reference. Endothall applied as Aquathol® K at 3 to 4 ppm to a small shoreline area was found in the middle of the lake about 2500 feet away by Day 8 (0.04 ppm), and possibly by Day 3 (0.03 ppm), though the Day 3 apparent residues may be due to sample contamination. Residues in the treated area had declined 0.02 ppm by Day 8. It is likely that wind-induced water currents were responsible for dispersing the herbicide.

In summary, endothall is frequently dispersed away from the treated areas of a lake and consequently diluted by water currents. Such currents can be caused by wind action or inlet and outlet streams or rivers. Vertical dispersion is the mechanism of dilution in whole-treated lakes. In partially-treated lakes, vertical dispersion occurs, but horizontal movement is usually the dominant mechanism for movement. Dispersion and dilution are more likely to occur in larger lakes and thus become a more significant factor in the disappearance of endothall from treated areas.

Table 3.1.4.B from Williams *et al.* (1999) summarizes maximum movement of endotoxin in partially treated reservoirs and lakes, using data from a number of studies.

In an interesting effort, Singh *et al.* (1999) constructed a computer model of endotoxin dissipation and movement in lakes and moving water such as canals, based on data from field studies. Tables 3.1.4.C and 3.1.4.D are taken from their report. The first of these presents modeled predictions of endotoxin dissipation in lakes and reservoirs given various application rates and intra-lake current velocities. The second table presents predictions of maximum distances traveled by endotoxin before dissipation. The emphasis in these two tables is on a level of 0.2 ppm, the current endotoxin tolerance for potable water or potential potable water. While the tables represent idealized model situations, they are useful for providing baseline scenarios to which natural condition modifiers may be added.

- **Type of formulation**

The use of liquid formulations usually results in higher initial water residues than with granular formulations since the entire application is present immediately in the water column. Sediment concentrations can be expected to be lower with liquid formulations since the chemical is injected in the upper water column, relatively far from the sediment surface, and must be carried to the sediment by water currents or dispersion.

In contrast, use of a granular formulation can be expected to give higher initial sediment concentrations and lower water concentrations. As endotoxin (or most other pesticides) is released from the granules over time, sediment concentrations will likely persist, albeit at low levels, for a longer period than with a liquid formulation and water concentrations are likely to be very low or non-detectable. Since the bottom waters in deeper lakes and shoreline areas are frequently colder than surface and mid-water depths, the higher sediment concentrations that granulars may produce are more likely to persist for a longer period in the colder water due to inhibition or slowing of microbial metabolism of the chemical.

Reinert *et al.* (1985b) put Aquathol granules in 2 liter flasks, added lake water, and shook the flasks gently for several hours at 22°C. They found that half of the endotoxin was released in 5.1 hours. Conditions in a lake sediment would not include such agitation, and the release rate would be impaired if the granules penetrated softer sediments. Also, the water temperature could be expected to be less than 22°C in most larger lakes, but their results serve to give a rough idea of how quickly granules can release endotoxin.

Except in very shallow littoral areas, endotoxin in liquid formulations can be expected to have less direct impact on deep-water or sediment-dwelling organisms than comparable granular formulations applied at equal rates of active ingredient because of generally lower sediment concentrations and shorter persistence resulting from use of the liquid form.

**Table 3.1.4.A: Endothall Persistence in Aquatic Systems**

<b>System</b>	<b>Formulation</b>	<b>Initial application rate</b>	<b>Half-life (DT<sub>50</sub>)</b>	<b>Time to disappearance<sup>1</sup></b>	<b>Comments</b>	<b>Reference</b>
Lab aerobic aquatic microcosm*	dipotassium salt	ca. 10 ppm	"rapid"	n.r.	Silt loam sediment. 24°C. 36% of applied endothall converted to CO <sub>2</sub> by Day 30.	(24) Reynolds, 1992
Lab anaerobic aquatic microcosm*	dipotassium salt	ca. 10 ppm	9 D (system)	n.r.	25°C. 64% of applied endothall converted to CO <sub>2</sub> by Day 270	(25) Reynolds 1993a
Lab anaerobic aquatic microcosm	n.r. Probably dipotassium salt	n.r.	8.5 D (system)	n.r.	Review paper. Details not given.	(47) Williams <i>et al.</i> , 1999
Laboratory aquarium, Syracuse NY silt loam pond sediment & water	dipotassium salt	2 ppm endothall	water: ca. 5 D sed: ca. 8-10 D	water: 7 D sed: 22 D	10 gal aquarium with pond water and hydrosoil. 25°C. pH 8.7. Sediment residue maximum at 3 days for both treatments.	(37) Sikka and Rice, 1973
Laboratory aquarium, Syracuse NY silt loam pond sediment & water	dipotassium salt	4 ppm endothall	water: ca. 6 D sed: ca. 16 D	water: 7 D sed: 35 D	10 gal aquarium with pond water and hydrosoil. 25°C. pH 8.7. Sediment residue maximum at 3 days for both treatments.	(37) Sikka and Rice, 1973
Farm pond, Syracuse, NY	Aquathol® K	2 ppm endothall	water: ca. 8 D sed: ca. 32 D	water: ca. 44 D sed: ca. 36 D	Pond 0.1 acre, 4 ft depth. No outlet. Sediment residue maximum at 22 days. Water pH 7.8. Surface temperature 21-24°C.	(37) Sikka and Rice, 1973
Laboratory flasks. Pat Mayse Lake, TX water.	endothall acid	0.5, 2.0, and 4.0 ppm	water: 8.45 D	n.r.	Water only, no soil. Water pH 6.5 to 7.5. No significant difference in half-life at the 3 concentrations.	(22) Reinert <i>et al.</i> , 1986
Laboratory mesocosm. Lake Mendota, WI water and sediment	endothall acid	3 ppm	water: first DT <sub>50</sub> ca. 30 D. Second DT <sub>50</sub> ca. 5 D	water: > 62 D	In 17 gal tanks in laboratory. Several macrophytes planted and allowed to establish. Little degradation for about 30 days, due to effect on microflora of DO depletion from decay of killed macrophytes. Rapid degradation of endothall when DO was restored naturally thereafter	(39) Simsiman and Chesters, 1975

**Table 3.1.4.A: Endothall Persistence in Aquatic Systems (continued)**

<b>System</b>	<b>Formulation</b>	<b>Initial application rate</b>	<b>Half-life (DT<sub>50</sub>)</b>	<b>Time to disappearance<sup>1</sup></b>	<b>Comments</b>	<b>Reference</b>
Three plastic greenhouse pools	Aquathol® K (dipotassium salt)	0.03, 1.6, and 4.5 ppm acid equivalent	4.1 D (system)	n.r.	133 L pools containing water, sediment and Eurasian milfoil. 30 day study.	(21) Reinert <i>et al.</i> , 1985a in (47)
Partial pond treatment	n.r.	n.r.	1.2 to 7.3 D (system)	6 H to 36 D (system)	Conditions and pond data not reported	(14) Keckemet and Sharp, 1999
Whole pond treatments	n.r.	5 ppm	4.1 D (system)	n.r.	Conditions and pond data not reported	(14) Keckemet and Sharp, 1999
"Over 100 recorded applications for 30+ years"	n.r.	n.r.	0.5 D to 2 D (system)	1 D to 15 D, with average of 5 D (system)	Review paper. Details not given.	(14) Keckemet and Sharp, 1999
W1 pond	Aquathol® K	5.0 ppm endothall acid	4.1 D (system)	ca. 18 D to decline to 0.1 ppm (system)	milfoil and chara. An abrupt decrease in concentration was reported at about 13 days.	(11) Holmberg and Lee, 1976, in (47)
7 shallow farm reservoirs, Davis, CA	dipotassium and disodium salts	0.3 ppm to 3.0 ppm	water: < 4 D to 8 D	water: 8 D to ca. 20 D	Areas 0.5 to 6 acres; 2 ft to 8 ft depth; pH 7.4 to 8.2. 12-inch depth water temperatures at application 17°C to 28°C.	(50) Yeo, 1970
7 shallow farm reservoirs, Davis, CA	dipotassium and disodium salts	0.3 ppm to 1.9 ppm	water: 8 D to >20 D	water: 8 D to >20 D	Areas 0.25 to 2.5 acres; 3 ft to 8 ft depth; pH 7.2 to 9.1. 12-inch depth water temperatures at application 21°C to 25°C.	(50) Yeo, 1970
Several pond sediments	n.r.	n.r.	< 1 D to 7 D	n.r.	Keckemet is a review paper. Details not supplied.	(13) Keckemet, 1980 in (20)
Two NC ponds	Aquathol® K	2.1 ppm	water: ca. 13 D	water: 26 D	No data given about the ponds. Report states data pooled for the two ponds. Half-life and disappearance calculated from author's linear regression, R squared = 0.68. Measured residues at 21 days: ca. 4 ppm.	(15) Langeland and Warner, 1986. Also summarized in (20)
Unidentified ponds	n.r.	n.r.	0.8 D to 7 D (presumably system - water or sediment not specified)	n.r.	(review article) Half-lives are for whole-pond treatments wherein no dilution occurs)	(47) Williams <i>et al.</i> , 1999

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**Table 3.1.4.A: Endothall Persistence in Aquatic Systems (continued)**

<b>System</b>	<b>Formulation</b>	<b>Initial application rate</b>	<b>Half-life (DT<sub>50</sub>)</b>	<b>Time to disappearance<sup>1</sup></b>	<b>Comments</b>	<b>Reference</b>
Several lake studies	Aquathol®-K (dipotassium salt) and Hydrothol® 191 (amine salt)	3 ppm	n.r.	sed: ca. 2-4 days	Review paper. Details not given.	(14) Keckemet and Sharp, 1999
Lake Sylvia, Mason County, WA	Hydrothol® 191	ca. 0.3 ppm	water: 5.9 D	water: > 7 D	11-12 acres, treated 5 acres; average 4 ft depth; heavy macrophyte growth. Water pH 7.6, 20°C.	(8) Elf Atochem, 1998
Lakeland Village Lake, Mason Co., WA.	Aquathol® K	Target 1 to 2.5 ppm. 1.28 ppm immediately after treatment	n.r.	water: 8 - 16 D	Lake 40 acres, somewhat eutrophic, mean depth 8 ft. Extensive Aquathol® shoreline treatment., but only low to moderate macrophyte infestation. Many contaminated samples - conclusions difficult.	(35) Serdar and Johnson, 1993
Gravelly Lake, Pierce Co., WA	Aquathol® K	3-4 ppm	n.r.	water: < 8 D	Lake 160 acres, closed basin, mean depth 38. Anoxic below 40 feet in summer, autumn. Few macrophytes. 21-25°C. Small area treated at one end of lake. Many contaminated samples - conclusions difficult.	(35) Serdar and Johnson, 1993
Lake Jane, Pierce Co., WA	Aquathol® K liquid	Target 5 ppm	water: ca. 5 D	water: 10-15 D	20 acre lake, average 6 ft depth. Treated 1/4 acre of NE shoreline, ca. 3 ft depth. 100% macrophyte density in treated area.	(14) Keckemet and Sharp, 1999
Lake Josephine, WA	Aquathol® K liquid	Target 3 ppm	n.r.	water: <7 D	88 acre lake, average depth ca. 15 feet. Treated 1/2 acre shoreline. 0.12 ppm 1 day after application.	(14) Keckemet and Sharp, 1999
Pat Mayse Lake near Paris, TX	Aquathol® K granular	250 lb/acre (2.5 ppm)	n.r.	water: < 30 D sed: < 30 D	6000 acre lake, treated 93 acres. watermilfoil. "Endothall rapidly dissipated within 72 hours from treatment area."	(10) Gangstad, 1986
Pat Mayse Lake, TX	Aquathol® K	2 ppm salt	n.r.	water: 72 H	Treated 100 of 6000 acres	(17) Reinert <i>et al.</i> , 1988 in (47)
Pat Mayse Lake, TX	Aquathol® K	n.r.	1.1 D to 1.2 D (system)	n.r.	Lake margin partial treatment	(19) Reinert and Rodgers, 1986 in (20)

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**Table 3.1.4. A: Endothall Persistence in Aquatic Systems (continued)**

<b>System</b>	<b>Formulation</b>	<b>Initial application rate</b>	<b>Half-life (DT<sub>50</sub>)</b>	<b>Time to disappearance<sup>1</sup></b>	<b>Comments</b>	<b>Reference</b>
Lake Parker, FL. Two 6-ft diameter enclosures	Aquathol® K	ca. 5.0 ppm endothall	water: (1) 5.4 D then 0.12 D for days 2 to 3 (2) 8.5 D then 0.4 D (days 3 to 6)	n.r.	Biphasic water breakdown: slow initial half-life for first two to three days, then more rapid breakdown. Increased breakdown probably due to microflora growth.	(27) Ritter and Williams, 1996
Lake Parker, FL	Aquathol® K	ca. 5.0 ppm endothall	water: 0.4 D sed: ca. 2-4 D	ca. 6 D (below 0.07 ppm) (system)		(27) Ritter and Williams, 1996
Lake Parker, FL	Aquathol® K (dipotassium salt)	5 ppm dipotassium salt	water: 19 H sed: < 3 D	water: 7 D sed: 15 D	Results here are for treated area, and for sediment surface. Sediment was sand. Lake is 2200 acres; 2.75 acres treated. Treated plot 4 feet deep. Temp 23-30°C. Hydrilla infestation. Surface pH 7.3 on day 1, 9.0 on day 2, 7.4 thereafter; pH 6.5 at 4 feet. Surface DO <sup>5</sup> 11.2 ppm on day 1, 2.5 ppm on day 2, and 6.4-9.8 ppm thereafter; bottom DO variable 1.7 to 7.6.	(3) Biever, 1996
Guntersville Reservoir, TN, on Tennessee River	Aquathol® K	5 gal/acre (1.5 ppm)	water: 0.034 ppm at 6H - estimate DT50 < 6H. sed: no residues found	water: estimate < 24 H	Lake 68,000 acres; 30 acres in bay treated. Water depth < 3 ft. Endothall decline probably due to flow dispersion.	(30) Rodgers <i>et al.</i> , 1992
Lake Moultrie, SC	Aquathol® K	3 ppm acid equivalent	n.r.	water: ≤ 7 D	Lake (reservoir) size not specified, but large. Helicopter application to 44 acres of lake near shoreline. Mean water depth 7.5 ft where treated. Disappearance mainly due to dispersion and along-shore flow.	(28) Ritter and Williams, 1998

**Table 3.1.4.A: Endothall Persistence in Aquatic Systems (continued)**

<b>System</b>	<b>Formulation</b>	<b>Initial application rate</b>	<b>Half-life (DT<sub>50</sub>)</b>	<b>Time to disappearance<sup>1</sup></b>	<b>Comments</b>	<b>Reference</b>
Gatan Lake, Panama Canal	Amine salt (Hydrothol® formulation)	2 ppm endothall	n.r.	> 21 days (system)		(9) Gangstad, 1983 in (20)
Gatan Lake, Panama Canal	Aquathol® K	2 ppm endothall	n.r.	< 3 days (system)		(9) Gangstad, 1983 in (20)

1 Detection limit in water = 0.01-0.02 ppm, sediment = 0.05 ppm

2 System = soil and sediment not distinguished in the reference

3 n.r. = not reported

4 ca. = approximately

5 DO = dissolved oxygen

\* = EPA guideline registration study

**Table 3.1.4.B: Summary of Maximum Movement of Endothall - Partially Treated Reservoirs/Lakes From Williams *et al.*, 1999**

Study Location	Target Conc. Aquathol K	Maximum Concentration	Maximum Distance from Treated Area with Detectable Residues
Riverside, CA (Keckemet, 1999)	3 ppm (acid equivalent)	0.34 ppm at hr 6 - 50 ft	100 ft - 0.09 ppm at 18 hrs
Riverside, CA (Keckemet, 1999)	3 ppm (acid equivalent)	0.53 ppm at hr 3 - 50 ft	100 ft - 0.43 ppm at hr 3
Fresno, CA (Keckemet, 1999)	3 ppm (acid equivalent)	0.69 ppm at hr 6 - treated area	150 ft - 0.51 ppm at hr 6
Ft. Collins, CO (Keckemet, 1999)	3 ppm (acid equivalent)	0.19 ppm at hr 3 - 250 ft	250 ft - 0.19 ppm at hr 3
Indian Springs, CA (Keckemet, 1999)	3 ppm (acid equivalent)	1.6 ppm at hr 3 - treated area	300 ft - 0.3 ppm at hr 48
Back River Reservoir, SC (DeKozlowski, 1992)	3 ppm	0.82 ppm at day 1 - treated area	0. ' 25 miles - 0.18 ppm at day 2, ND at city water intakes (1.5 miles)
Lake Moultrie, SC (Ritter and Williams, 1998)	3 ppm (acid equivalent)	4.42 ppm at hr 1 - treated area	4,400 ft - 0.03 ppm at day 2 (intake), 500 ft - 0.37 ppm at hr 9
Lake Parker, FL (Ritter and Williams, 1996)	5 ppm as dipotassium salt of endothall	4.82 ppm of potassium salt of endothall 1 (3.42 ae) at hr 0 - treated area	100 ft - 1.38 ppm as dipotassium salt of endothall I at hr 6
Lake Washington, FL (Keckemet, 1999)	7.5 gal/ac (9.7 ha) (acid equivalent)	19.6 ppm at hr 6 - treated area	10 m - 0.4 ppm at day 7, ND* at potable water intake 0 000 ft)
Pat Mayse Lake, TX (Reinert <i>et al.</i> , 1988)	2 ppm (41 ha) (dipotassium salt)	0.41 ppm at Lamar Point and 1.64 ppm (ae) at Pat Mayse Park-East	914 m (city water intakes)- ND**
Guntersville Reservoir, AL Keckemet, 1999)	1.8 ppm (2 plots of 0.5 acres) (acid equivalent)	1.0 ppm at hr 3 – treated area	0.5 miles - ND at all sample times
Chickahomiy Res. Newport News, VA (Schreck, 1974)	0. 17 ppm (SWQ) 0. 12 ppm (FWQ) (acid equivalent)	0. 18 ppm (SWQ) (0.02 ppm (FWQ)	samples taken in/near treatment area
Lakeland Village, WA (Serder and Johnson, 1993)	1 - 2.5 ppm (dipotassium salt)	1.3 ppm at day 1 - treated area	Approximately 500 ft - 0.03 ppm
Gravelly Lake, WA (Serder and Johnson, 1993)	3 - 4 ppm (dipotassium salt)	1.0 ppm at day 1 - treated area	Approximately 2, 100 ft - 0.04 ppm

ND - not detectable (< 0.0 1 ppm), \*ND < 0. 2 ppm, \*\*ND < 0.002 ppm

SWQ - still water quality

FWQ - flowing water quality

Reviewer's note: Williams *et al.*'s "Keckemet, 1999" is the same as this document's Keckemet and Sharp, 1999.

**Table 3.1.4.C: Required Time in Hours for Endothall Residues to Dissipate Below 0.2 ppm  
Lake/Reservoir Scenarios  
From Singh *et al.*, 1999**

Application Area	Dose	Current Velocity		
		0.001 m/s	0.01 m/s	0.1 m/s
Shoreline	0.35 ppm	15	7	3
	1.0 ppm	36	29	4
	3.0 ppm	61	37	7
	5.0 ppm	73	42	7
Mid-lake	0.35 ppm	12	3	3
	1.0 ppm	30	22	3
	3.0 ppm	53	36	5
	5.0 ppm	64	41	5

Scenarios represented above based on a dispersion rate of 0.1 m<sup>2</sup>/hr.

**Table 3.1.4.D: Maximum Distance Traveled by Endothall Residues at Concentrations ≥0.2 ppm and Total Time Required for Endothall Concentrations to Drop Below 0.2 ppm  
From Singh *et al.*, 1999**

Scenario	Target Concentration (ppm)	Maximum Distance (ft)	Time (hr)
13 (shore-line)	0.35	400	7
	1.0	2250*	29
	3.0	2900*	37
31 (mid-lake)	0.35	200	3
	1.0	1800	22
	3.0	2900*	36

\*Transport distance was beyond the modeled grid and estimated by linear extrapolation of end segments.

### 3.1.5 Microbial Degradation

*Summary: The primary (and probably only) mode of endothall breakdown is the action of microflora - bacteria and fungi that are found in soil, water, and sediment. The microorganisms break the molecule apart into carbon, hydrogen and oxygen atoms. Conditions that are favorable to such microorganisms can be expected to decrease endothall persistence. Thus, initial lag times in endothall degradation may occur as a result of oxygen depletion following a large-scale macrophyte or algal kill. Initial lag times are also usually seen when there are low initial microflora populations, or at least low populations of microorganisms that can degrade endothall.*

Some microflora can utilize endothall as their sole source of carbon, while others can metabolize endothall, but still require other carbon sources. Genera identified as endothall utilizers include *Arthrobacter*, *Bacillus*, *Pseudomonas*, *Rhizopus*, and *Aspergillus*, though other as yet unidentified genera undoubtedly can also utilize endothall as a carbon source (7, 11, 12, 14, 22, 38, 39, 40).

Most endothall-degrading microflora are aerobes. That is, they require oxygen and so cannot function in anaerobic oxygen-starved water or sediments. This explains the "lag" phenomena discussed in the next subsection. One type of lag occurs when a large macrophyte (aquatic plant) kill depletes the oxygen in a treated area as it decays. The aerobic microflora cannot flourish until the oxygen is restored by photosynthesis, or diffusion from the atmosphere, or until oxygenated water enters the treated area from elsewhere in the lake. Until that time endothall decline will be very limited. Upon re-oxygenation, the microorganism population is restored and the lag phase ends. This phenomenon was well-documented by Simsiman and Chesters (1975), and others.

Another type of lag is seen as a result of endothall treatment of a lake with a low population of endothall-utilizing microorganisms. In that situation, endothall breakdown is initially slow while the microorganism population increases to take advantage of the increased "food". As the population grows, endothall degradation increases in step. In cases where the organic content of water or soil is low, the microflora capable of utilizing only endothall as a carbon source will have a competitive advantage and can quickly become the dominant species and reach large numbers, facilitating endothall degradation (36, 37).

Endothall is metabolized by microorganisms through breaking of the oxygen bridge (see Section 2) and disruption of the carbon ring. The carbon atoms then enter what is termed the carbon pool, ceasing to be endothall *per se* and becoming a source of carbon for numerous biological processes, the same as carbon from any other organic source such as decaying plant and animal matter (14, 44).

### 3.1.6 Mobility

*Summary: Endothall exhibits variable adsorption to soil and sediment. For most soils, adsorption is moderate to low, but the adsorbed material tends to stay bound to the soil particles once adsorbed. Studies reviewed indicate that higher organic matter content of soils and sediments results in higher adsorption of endothall. Soil clay content, cation exchange capacity, and pH have not been shown to affect the degree of adsorption*

*except in one sediment study that concluded that lower pH and amorphous mineral contents, as well as high organic content, were responsible for stronger adsorption.*

*Overall, evidence indicates that endothall does not bind strongly to most soils or sediments. This would normally raise concerns of potential groundwater contamination. However, rapid degradation in soils and aquatic systems means that endothall will be destroyed before it has a chance to move very far through the soil and therefore does not pose a significant threat to groundwater.*

When a chemical is applied to soil, a potential exists for the chemical to be carried down into the soil with water movement from rain and irrigation. Pesticides exhibit a wide range of leaching potential, from those that adsorb strongly to soil particles and are not released before they break down, to those that do not adsorb significantly (or adsorb, then desorb) and will travel considerable distances down through the soil, sometimes as far as the ground water table. The sorption of various chemicals to soil is affected in a number of ways by soil parameters such as organic matter, clay content and type, and pH.

Washington State (1992) states "Due to its water solubility, endothall tends to follow water movement in the environment." Evaluation of mobility based solely on water solubility can be misleading. Mobility is affected by a number of factors including soil composition, soil characteristics, the presence of organic matter, and degradation rate.

Soil mobility data points out expected behavior of endothall oversprayed on shoreline vegetation and to some extent indicates what may happen if a lake level drops, exposing shoreline sediment to drying, soon after treatment. The data also give at least an indication of endothall's adsorption potential on sediment. Sediment will usually have a higher organic material content than typical soils except for muck soils and therefore soil tests may underestimate the potential for endothall adsorption to high-organic matter sediments.

Controlled laboratory "batch equilibrium" studies are designed to measure the adsorptive properties of endothall to four representative soils. There are currently no comparable test guidelines specifically for sediment. The results for two of these soil tests conducted for Elf Atochem (6, 45) are presented in Table 3.1.6. The soil partition coefficients  $K_{d_{ads}}$  and  $K_{d_{des}}$  are measures of the potential for adsorption to soil and for desorption from that soil, respectively, and are calculated as the endothall concentration in soil divided by the concentration in water at equilibrium in a soil/water system with a single endothall starting concentration in the water. The Freundlich  $K_{ads}$  and  $K_{des}$  are another way of calculating leaching potentials, but use the results of a series of tests with different starting concentrations. The parameters are particular to the specific soil being tested, and soils are chosen to represent typical agricultural soil types. To calculate  $K_{d_{ads}}$  (and Freundlich  $K_{ads}$ ), soil plus sterile water containing radiolabeled endothall are put in a sealed vial and shaken slowly for several hours until an adsorption equilibrium is reached (no more endothall can be adsorbed by the soil). The amount of endothall in the water and soil is determined by measuring the radioactivity in each. The water is then removed, replaced with fresh water, and the vial shaken again to allow the endothall to desorb from the soil back into the water. From measurements then taken, the  $K_{d_{des}}$  is calculated in the same manner as  $K_{d_{ads}}$ . Taken together, the adsorption and desorption parameters indicate how well endothall is adsorbed to and released from that typical soil and hence will give a measure of leaching potential.

Although there is some disagreement as to exact classification values, generally  $K_{d_{ads}}$  and Freundlich  $K_{ads}$  values greater than 5 are characteristic of compounds that are not appreciably mobile, values from about 1 to 5 indicate a potential for greater mobility, while values less than 1 denote considerable mobility potential. In a similar manner, high  $K_{d_{des}}$  and Freundlich  $K_{des}$  values indicate that a compound will remain bound to soil and resist being carried downward.

$K_d$  and Freundlich  $K$  values are composite values measuring adsorption caused by any of several soil characteristics such as clays, aluminum content, cation exchange capacity (CEC), and organic carbon.  $K_{oc}$  values represent an attempt to separate out the role of organic carbon in soil adsorption from the other factors. Because organic carbon plays a significant role in the soil adsorption of many pesticides,  $K_{oc}$  values are often used to predict pesticide mobility. But since  $K_{oc}$  depends on two variables ( $K_d$  and carbon content), it must be used with caution.

$K_{oc}$  values are calculated by dividing  $K_d$  and  $K$  values by the decimal percent of organic carbon in a soil (e.g. for a silt loam soil (Vigon, 1989),  $K_{oc_{ads}}$  is calculated as  $7.12/0.02 = 356$ ).  $K_{oc}$  values give an idea of the role of organic carbon in soil/sediment in adsorbing a chemical.  $K_{oc}$  values generally are numerically higher than  $K_d$  or  $K$  values. A higher value indicates organic carbon is more influential in trapping a pesticide.

It is emphasized that all of the "K" parameters discussed above are specific to a particular soil or sediment, and to the initial concentration of a chemical applied to the soil or in water over a sediment. A Freundlich  $K$  for a particular soil is a single value calculated using the adsorption or desorption results from all of the initial concentrations used in an experiment, but a  $K_d$  is calculated from the result of each initial concentration separately. Unless specified otherwise,  $K_d$  and Freundlich  $K$  parameters reported in published literature are for adsorption; measurement of desorption values is rare. Where  $K$  values are given without the soil type and chemical concentration being specified, care should be exercised in using those values for evaluation of leaching potential.

As indicated in Section 3.1.3, endothall is metabolized primarily into  $CO_2$  and humic acid, humin, and fulvic acid, all strongly-bound soil minerals that are no longer of environmental concern.

### 3.1.6.1 Soil

Results in Table 3.1.6 show that endothall responds in different ways to various soils. There was no pronounced effect on adsorption from pH, nor from clay content or cation exchange capacity in these studies (6, 45). There is a tendency for endothall to bind more strongly to soils with high organic matter content, as indicated by high  $K_{oc_{ads}}$  and  $K_{oc_{des}}$  values for several of the soils. It is probable that if these studies had been conducted with lake sediments, even higher  $K_{oc}$  values would have been seen.

In four 3-month soil dissipation studies, no endothall was found below 8 inches in soil cores taken to 18 inches depth (48, 49), indicative of a combination of rapid degradation and/or strong binding to the soils.

Lovato *et al.* (1999) measured limited movement of endothall from a treated Michigan pond sideways through a fine sand soil to a shallow sampling well 5 feet away from the pond. However a pumping well only 12 feet from the pond was pulling pond water through the soil past the sampling well at the time. Both wells were in a fine sand soil over a clay layer 10 feet down in the soil. The movement of the water through the soil was considerably faster that would be experienced under natural conditions, and there was little chance for the endothall to be degraded or to adsorb to soil particles before being pulled past the sampling well. Graphically-presented data in the report indicate that on any given day, the endothall concentration in the pumping well (12 feet from the pond) was about one-half of that in the sampling well. Endothall was detected in pond water, the pumping well, and the sampling well for about a month.

It is unlikely that wells in a real-world situation would draw water directly from a water body so rapidly that any endothall present in the lake would not have a chance to be diluted, broken down, or adsorbed to soil unless the wells were drilled immediately adjacent to the lake- or pond shore.

### 3.1.6.2 Sediment

In a sediment batch equilibrium study, Reinert and Rodgers (1984) measured adsorption by sediment from Pat Mayse Lake and Roseland Cemetery Pond, both in Texas. They reported  $K_d$  values for five initial concentrations of Aquathol® K from 2.0 to 6.3 ppm acid equivalent. Values ranged from 0.43 to 1.35 ppm, with a mean of 0.94 ppm for Pat Mayse Lake. The  $K_d$ 's for Roseland Cemetery Pond were 1.0 to 2.1 ppm with a mean of 1.4 ppm. The authors found that differences between the two means were not statistically significant. They concluded that "Due to the relatively low  $K$  exhibited for endothall sorption in this study, sorption is not a significant process affecting the fate of endothall in the aquatic environments studied in this research". The same conclusion was reached by Reinert and Rodgers (1987).

Simsiman and Chesters (1975) found that endothall adsorbed much more strongly to one sediment than to another type, attributing the effect to the higher organic matter (15% vs. 8%), amorphous mineral contents, and lower pH (5.6 vs. 7.1) in the stronger-binding soil. In their review of that report, Reinert and Rodgers (1984) calculated a  $K_d$  range of 0.41 to 0.90 for one of the sediments. Biever (1996) found endothall residues in sediment for less than 15 days, as did several other researches cited in Section 3.1.3. There was no attempt in any of these papers to ascertain whether those residues were simply loosely associated with the sediment surface or firmly bound to the sediment. Biever found low residue concentrations down to 6 inches depth in the sediment, but as discussed earlier, this may have been due to water movement within the sand sediment.

Reinert and Rodgers (1987) calculated a  $K_d$  of about 0.4 using Sikka and Rice (1973) data from a Syracuse New York farm pond treated with endothall dipotassium salt. They also reported  $K_{oc}$  values of 110 for a small eutrophic pond and 138 from an oligotrophic (low nutrient level) reservoir from their earlier research (18). They felt that the low octanol water coefficient ( $K_{ow}$ ) of 1.9 for the acid and 1.4 for the potassium salt indicates that endothall would not significantly partition to sediments.

Many lake bottoms have fluffy, light (flocculent) sediments rather than a solid surface, particularly in more eutrophic lakes with a large amount of decaying organic material on

the bottom. The much larger amount of particle surface in these flocculent sediments greatly increases the likelihood of endothall adsorption compared with firm-surfaced sediment, particularly in view of their typically higher organic content.

### **3.1.6.3 Groundwater**

*From the above data, it is clear that endothall does not pose a significant threat to groundwater. This is the same conclusion reached in the 1992 SEIS (43). Though endothall is mobile in most soils and sediments, it is readily adsorbed to high organic content sediments. Because endothall is so readily degraded, with half-lives typically less than 30 days, it is gone from lake sediments before it can seep into surrounding soil. Overspray onto lake shores, or exposure of treated shallow lake sediments is expected to be negligible. Even if those situations occur, endothall is not mobile enough in less-than-saturated soil situations to move beyond the immediate subsurface layers.*

**Table 3.1.6: Endothall Acid Adsorption/Desorption Constants**

Soil/sediment type	% organic matter	pH	$Kd_{ads}^1$	$Kd_{des}^2$	$Koc_{ads}$	$Koc_{des}$	Freundlich $K_{ads}$	Freundlich $K_{des}$	Freundlich $Koc_{ads}$	$Koc_{des}$	Reference
Clay loam soil	1.4%	8.0	1.02	1.81	72.9	129	1.12	1.88	80.0	134	(6) Dykeman, 1985
Clay loam soil	1.3%	6.7	0.49	3.94	37.7	303	0.56	2.57	43.1	198	(45) Vigon, 1989
Silt loam soil	1.4%	6.2	22.0	33.9	1571	2421	17.6	22.8	1257	1629	(6) Dykeman, 1985
Silt loam soil	2.0%	5.2	7.12	37.1	356	1854	7.94	37.3	397	1865	(45) Vigon, 1989
Fine sandy loam soil	1.9%	5.7	3.9	10.2	205	537	4.21	9.15	222	483	(6) Dykeman, 1985
Sandy loam soil	1.5%	6.8	0.68	6.04	45.3	4.3	0.80	4.30	53.3	287	(45) Vigon, 1989
Loamy sand soil	0.2%	6.6	0.13	-1.32 <sup>3</sup>	650	0 <sup>3</sup>	0.15	0	7.50	0	(45) Vigon, 1989
Sand	0.4%	4.9	4.0	7.5	1000	1875	0.44	6.81	11.0	275	(6) Dykeman, 1985

1 ads: adsorption

2 des: desorption

3 Difficulties in measuring very small amounts of radioactivity can lead to slightly negative values. In this test situation, -1.32 is essentially zero, since negative values mean that there is more radioactivity at the end of the experiment than at the beginning.

### 3.1.7 Canal and Flowing Water Use

*Summary: Hydrothol 191 is used in many areas for control of algae and aquatic vegetation in canals, irrigation ditches, and riparian situations. Treatment is by injection for a specific amount of time. This results in a slug of treated water that moves down the canal (or similar flowing water body). As the slug moves, the residue profile shifts from an abrupt increase in residues followed by a sustained level and sharp drop-off, to a more extended picture, with slower onset and a distinct tailing off of residues as the slug passes. Water residues are typically non-detectable before and after the passage of the slug. Endothall residues have been found in sediments during slug passage, but decline and disappear shortly afterward, probably as a function of the water flow over the bottom.*

*Depending on the nature of the canal and the water flow speed, endothall peak residues may decline slowly or may persist for many miles. This is largely due to the relatively short duration of the slug's residence of a few days in canals of typical length as compared to the several days half-life found in lakes and ponds. Another factor in endothall canal persistence is the relative scarceness in canals of large microbial populations adapted to degrade endothall and the short exposure time to microbes in any given mass of sediment to the passing slug.*

*The flow of water through a canal depends on many factors such as geometry, wall and bottom character, and the presence of large amounts of vegetation. Therefore a slug of treated water past a specific point in the canal may not occur when calculated. Dye injected during endothall application can be used to track the size and passage time of the treated water and therefore can be used to determine when to close potable water and branch canal intakes to avoid drawing off treated water. Alternately, for a canal for which multiple treatments are anticipated, preliminary dye tests can characterize the movement time for a slug of water past given points for varying flow rates, and that information can be used when the actual endothall applications are made without using dye.*

Hydrothol 191 is used in many areas for control of algae and aquatic vegetation in canals, irrigation ditches, and riparian situations. The primary purpose of determining the concentrations of endothall in canal water and the time that the treated water passes various downstream points is to allow branch canals and potable water intakes to be closed during the passage of the treated water. A secondary purpose is to gauge the extent of exposure of aquatic organisms and of humans and animals using the water.

The same environmental fate processes work on the endothall in canals as in lakes, ponds, and other static water bodies, but some are of less importance. When a canal is treated (this term will be used here for all such flowing water situations including rivers), endothall is typically applied for a given number of hours at a single location by metering or pumping through a hose, by a controlled stream from a container, or by similar means. This results in a "slug" of treated water that travels through the canal as a more or less coherent mass, leaving little or no residue in the water and sediments behind it (2). The duration of application and the water velocity and cross-section of the canal (and hence the moving water volume) determine the time required for the slug to reach a given downstream location and the time required for the slug to pass that location. Those

factors plus the rate of application all contribute to the maximum residue levels seen during a treatment. Due to the wide variation found in flow rates, geometry, hydrology, and vegetation content of canals, ditches, rivers, and similar systems, it is more difficult to predict herbicide behavior and fate than is the case with static water bodies. Because of the relatively rapid movement of the water in a canal, there is less opportunity for adsorption to sediments at a particular location. On the other hand, the relatively large sediment surface to water volume ratio, and the constant exposure the endothall slug to "fresh" sediment may offset the short contact time.

One very important fact is apparent from the studies described and reviewed below (2, 14, 47). Regardless of how far downstream from the application samples were taken (up to 23 miles), endothall was always detected when the slug passed the sampling station. Since the passage occurred within a few days at most, the time at which endothall in the slug dropped to non-detectable levels was never determined. Therefore, downstream receiving waters could be impacted by varying amounts of endothall depending on the length of the canal. Perhaps the most important reason for endothall persistence is the relative scarceness in canals and other rapidly moving waters of large microbial populations adapted to degrade endothall and the short exposure time to microbes in any given mass of sediment to the passing slug.

Few original experimental reports were found dealing specifically with residues resulting from canal treatment. Biever (1998) conducted such a study in North Delta Canal near Delta, Colorado. The canal is a sinuous 22 mile long water body about 10 feet wide and has a depth of 2 to 4.5 feet. The canal was treated with Hydrothol 191 by controlled pour-out from a container for 3 hours at a rate calculated to yield a water concentration of 5 ppm endothall acid equivalent (a.e.). Samples were taken at five locations downstream from the application point. T1 was immediately below the application point. T2, T3, T4 and T5 were 3.6 miles, 10 miles, 13 miles, and 15 miles downstream, respectively. "Treatable aquatic plant" populations were found between T1 and T2 and between T3 and T5. Water flow on the day of treatment (Day 0) was 2.9 ft/second (24 ft<sup>3</sup>/second) at the shallow T1 station. Flow at T2 to T4 was 0.85 to 0.98 ft/second (17-23 ft<sup>3</sup>/second), and 1.6 ft/second (7 ft<sup>3</sup>/second) at T5. The drop in volume at T5 is due to diversion of about 50% of the water to an overflow ditch and about 25% to an irrigation canal between T4 and T5.

Results in the report clearly indicate that the chemical traveled in a fairly compact slug down the canal. Duration of detectable residues in the water (LOD=0.023 ppm) was fairly consistent from T2 through T4. The total detectable residue duration rose from 4.5 to 5.75 hours from T2 to T4, indicative of some lengthening of the treated slug, but the highest residues were always found during the central two hours of detection (sampling was terminated during high residue values at T5). Peak residue values occurred at about 0.5, 10, 19-20, 22, and 29 hours at T1 through T5. The concentrations peaked at 7.7 ppm, 5.4 ppm, 4.6 ppm, 4.0 ppm, and 3.4 ppm at T2 - T5, indicating that endothall was being removed from the water by various processes as it moved down the canal. No residues were detected in the water at any station 24 hours after the plume passage.

Residues in the sediments (LOD=0.14 ppm) were found during the passage of the plume. Samples were taken to 4-6 inches at times when the plume was expected (based on dye studies) and therefore residues coincided with high water residues (except for the T1 sampling that occurred at 2.0 hours after application). Maximum 0-4 inch depth residues

ranged from 0.3 ppm at T1 through 0.85 ppm for T2-T4. No residues were detected at T5. No sediment residues were detected at any stations when next sampled about 24 hours later (excepting a probable contaminated or mislabeled T1 sample). On the basis of endothall residue decline from T1 to T4, the author calculated an endothall half-life of 49.4 hours.

Keckemet and Sharp (1999) reviewed several historical endothall studies in canals and flowing water, most of them Atochem internal studies. In one of these (Carlson, 1986), the Tempe-Western Canal in Tempe, Arizona was treated in August, 1986, with Hydrothol 191 at a rate to give 0.18 ppm in the water. A total of 405 gallons was pumped into the canal over a period of 4 days and 3 hours. Water samples were taken one mile below the application point, at a water treatment plant 10 miles downstream, and at points 10.5 and 18.2 miles downstream. Sediment samples were taken 1.8 miles and 13.0 miles from the application point.

The Tempe-Western Canal is concrete-lined with a length of 22 miles, an average width of 30 feet, and an average water depth of 4 feet. Water flow during the test varied from 195 to 225 ft<sup>3</sup>/second. Water temperature was 27°C, and pH was 8.0-8.2. Aquatic plants present were sago pond weed (15% density), waterstar grass (10%), *Spirogyra* spp (10%), and *Cladophora* spp. (10%).

Endothall (acid equivalent) water residues near the application point were 0.04 to 0.09 ppm during the application, and were non-detectable (LOD=0.01 ppm) within 4.5 hours of completion of the application. At the water treatment plant and the 10.5 mile station, residues were 0.01 to 0.04 ppm from 9 hours after the start of application to 5 hours before the completion, and were absent 19 hours after completion. Residues in the water 18.2 miles downstream were 0.01 to 0.04 ppm from 24 hours after application start to 20 hours after completion, and were non-detectable 24 hours later. No sediment residues were detected (LOD=0.05 ppm) 1.8 miles below the application point at any time, while at the 13.0 mile sampling point, residues of 0.07 to 0.09 ppm were found from 24 hours after application start to 21 hours after completion.

The following Hydrothol studies, believed to all be Atochem internal studies, were also briefly summarized, or graphically presented, by Keckemet and Sharp (1999). A dye was injected with the treatments, but the arrival time of the dye is not given relative to treatment times. Plume durations are timed from the arrival of the dye at a given sampling station.

The Y Canal in Jerome, Idaho was treated at 3 ppm acid equivalent for 3 hours, with a 98 ft<sup>3</sup>/second flow. Samples were taken every 5 miles. The plume (first detection to last detection) increased from 3 hours at the head of the canal (immediately below the application mixing area) to 11 hours 15 and 20 miles downstream. Maximum residues (4 ppm at the head) were uniformly about 1.5 ppm at all sampling stations.

The same canal, with a flow of 90 ft<sup>3</sup>/second was treated at 2.2 ppm a.e. for 4 hours. The plume duration increased from 5 hours at 0.5 miles downstream to 8 hours at 10 miles and 16 hours at 20 miles downstream. Maximum endothall residues were about 2 ppm for all sampling stations.

For a third application to the same canal at 2.5-3 ppm a.e. for 3.5 hours, when the water flow was 110 ft<sup>3</sup>/second, plume duration was 3.5 hours at 0.5 miles downstream, about 7.5 hours at 13 miles, and 14 hours at 25 miles downstream. The latter plume reached a peak about 3 hours after dye arrival, but tailed off very slowly. Peak endothall concentration was about 2.0 ppm for all stations.

The Highline Canal in Phoenix, Arizona, was treated at 3 ppm a.e. for 5 hours, with a water flow of 7.5 ft<sup>3</sup>/second. Slug duration was 5.5 hours at 0.5 miles, 10 hours at 4 miles, and 12 hours at 9 miles downstream. The same early peak and subsequent trailing as in the Jerome canal was observed. Maximum endothall concentrations were about 2.5 ppm at 0.5 and 4 miles, and about 1.8 ppm at 9 miles.

At Winters, California, Brynes Canal, flowing at 32 ft<sup>3</sup>/second, was treated at 0.5 ppm a.e. for 12 hours. Plume width was 12.5 hours at the head, 13 hours at 2 miles, 18 hours at 4 miles, and 21 hours with tailing at 6 miles. Maximum endothall residues were about 0.7 ppm at all stations.

Corning Canal in Proberta, California, was treated at 3 ppm a.e. for 3 hours, at a canal flow of 45 ft<sup>3</sup>/second. Plume durations were 4 hours at 0.1 and 2 miles, 7 hours at 4 miles, 10 hours at 6 miles, 15.5 hours at 11 miles, and more than 20 hours at 16 miles downstream. There was no tailing in this case. Maximum residues were 2.5-3 ppm in the first 6 miles, and 1.5 to 2 ppm at the 11 and 16 mile stations.

Graphical presentations of the above data by Keckemet and Sharp allow two generalizations to be made. 1) The rise and fall of residues was abrupt, with a nearly constant level over the plume duration time for the first 10 miles or so, though the plume duration slowly widened and began to show tailing with distance down the canal. After this, residue profiles showed a slower buildup of residues to an early peak, then increased tailing as the distance increased. 2) Maximum endothall residues decreased as tailing increased, but the total exposure time to the plume was of course longer. In some canals the plume may destabilize earlier, as illustrated in the Brynes Canal, where tailing was observed at 6 miles downstream.

The three Jerome Y Canal studies were conducted at similar water flow volumes, and no significant differences attributable to small differences in water flow volume are apparent. In the absence of more studies in the same canal at significantly different flow rates, it is not possible to state the effect of water flow volume or speed on plume dispersion. It is probable that the most important factors in plume stability are the morphology of the canal, the roughness of the sides and bottom, and the density of aquatic macrophytes, all of which will affect the movement of water.

Williams *et al.* (1999) summarized data from Sisneros and Turner (1996) wherein Aquathol K was applied to the S-19 Canal in Twin Falls, Idaho at a rate of 0.4 ppm dipotassium salt for 24 hours. The canal was 14 feet wide, 3 miles long, and 2 feet deep. Flow varied from 12 to 22 ft<sup>3</sup>/second. Endothall residues peaked at about 0.45 ppm approximately 36 hours after treatment. The concentration was consistent at or above 0.1 ppm for about 80 hours over the 2 miles sampled.

Table 3.1.7.A is taken from Williams *et al.* (1999) and summarizes a number of canal studies, many of them Atochem internal studies. Many of the studies are taken from

Keckemet and Sharp (1999). The table focuses on the interim tolerance for endothall in potable or potential potable water (0.20 ppm) rather than half-lives or disappearance, but provides a good overall picture of typical endothall behavior in canals.

As mentioned earlier, Singh *et al.* (1999) constructed a computer model of endothall aquatic fate processes for Elf Atochem. Table 3.1.7.B, taken from their report, presents predicted times for endothall concentrations greater than 0.2 ppm (the potable water tolerance) at various points in treated canals. The 10-day assumed half-life is not unrealistic, and the predictions would be useful in canals with relatively uncomplicated geometries, fairly smooth walls and bottoms, a lack of heavy vegetation, and the absence of other factors that would significantly alter the hydrology from an ideal flow.

As a practical matter, dye injected during endothall application can be used directly to track the size and passage time of the treated water slug and therefore can be used to determine when to close potable water and branch canal intakes to avoid drawing off treated water. Alternately, for a canal for which multiple treatments are anticipated, preliminary dye tests can characterize the movement time for a slug of water past given points for varying flow rates, and that information can be used when the actual endothall applications are made.

**Table 3.1.7.A: Summary of Canal Monitoring Studies  
From Williams *et al.* (1999)**

Study Location	Target Concentration	Time	Distance from Treated Area
Jerome, ID 1964 (Keckemet, 1999)	3 ppm (a.e.) for 3 hrs (Hydrothol® 191)	> IT for 11 hrs after residue arrival at last sampling point (20 mi)	> IT for all sampling points (1, 5, 10, 15, and 20 miles)
Highline Canal Phoenix, AZ 1964 (Keckemet, 1999)	3 ppm (a.e.) for 5 hrs (Hydrothol® 191)	> IT for 12 hrs after residue arrival at last sampling point (9 mi)	> IT for all sampling points (0.5, 4, and 9 miles)
Y Canal, Jerome, ID 1965 (Keckemet, 1999)	2.2 ppm (a.e.) for 4.05 hrs (Hydrothol® 191)	> IT for 15 hrs after residue arrival at last sampling point (20 mi)	> IT for all sampling points (0.5, 10, and 20 miles)
Brynes Canal, Winters, CA 1965 (Keckemet, 1999)	0.5 ppm (a.e.) for 12 hrs (Hydrothol® 191)	> IT for 16 hrs after residue arrival at last sampling point (6 mi)	> IT for all sampling points (2, 4, and 6 miles)
Y Canal, Jerome, ID 1966 (Keckemet, 1999)	2.5 - 3 ppm (a.e.) for 3.5 hrs (Hydrothol® 191)	> IT for 13 hrs after residue arrival at last sampling point (20 mi)	> IT for all sampling points (0.5, 13, and 20 miles)
Coming Canal, Proberta, CA 1966 (Keckemet, 1999)	3 ppm (a.e.) for 3 hrs (Hydrothol® 191)	> IT for 24 hrs after residue arrival at last sampling point (16 mi)	> IT for all sampling points (0.1, 2, 4, 6, 11, and 16 miles)
Foxglove Canal, AZ 1979 (Keckemet, 1999)	0.18 ppm for 5 days	> IT for 4 days at last sampling point (7 mi)	>IT at all sampling points (0.5 and 7.0 mi) and < IT at 4.5 miles
Eastern Canal, Chandlers, AZ 1979 (Keckemet, 1999)	0.2 ppm for 5 days	< IT at all sampling times (24 days AT)	<IT at all sampling points (1.5, 14.5 mi)
Maricopa, AZ 1979 (Keckemet, 1999)	0.2 ppm for 4 days	< IT at 1-3 days AT for all sampling points. > IT at 4 days for last sampling point (23 mi).	<IT at all sampling points (2.5, 8, 23 mi) up to 3 days AT and <IT for all except last sampling site (23 mi) at 4 day AT.
Red Willow Canal, NE 1980 (Keckemet, 1999)	0.2 ppm for 5 days	<IT at all sampling times for all sampling sites	< IT at all sampling points (2.3, 5.1, and 10.5 mi)
Meeke Canal, NE 1980 (Keckemet, 1999)	0.2 ppm for 3 days	< IT at all sampling times (day 1-2 AT) except for first sampling point (4.1 mi) on day 1	> IT at 4.1 mi for 1 day AT and <IT for 8.2 mi and 12.4 mi
Cherry Creek, WY 1981 (Keckemet, 1999)	0.2 ppm for 3 days	< IT at all sampling times (1 -3 days AT)	< IT for all sampling points (3.7, 7.3, 12.6, and 16 mi)
Tempe Canal, AZ 1986 (Carlson 1986)	0.18 ppm for 5 days	< IT at all sample times (1-6 days AT)	<IT at all sample sites (1, 10, 10.5, and 18 mi) -

IT - Interim Tolerance (0.20 ppm), AT - After Treatment, ND - Not Detectable (< 0.01 ppm) a.e. -acid equivalent

**Table 3.1.7.A: Summary of Canal Monitoring Studies (Continued)  
From Williams *et al.* (1999)**

Study Location	Target Concentration	Time	Distance from Treated Area
Tempe Canal, AZ 1982 (Keckemet, 1999)	0.2 ppm for 4 days	<IT at all sample times (1-6 days AT) each of 7 trials	< IT at all sample sites (1, 10, 18 mi) each of 7 trials
Chandlers, AZ, 1994 Trial 1 (Keckemet, 1999)	0.18 ppm for 5 days	< IT at all sample times (1-5 days AT)	< IT at all sample points 1, 3, and 6.5 miles (water treatment plant)
Chandlers, AZ, 1994 Trial 2 (Keckemet, 1999)	0.18 ppm for 5 days	< IT at all sample times (1-5 days AT)	< IT at all sample points 1, 3, and 6.5 miles (water treatment plant)
Chandlers, AZ, 1994 Trial 3 (Keckemet, 1999)	0.18 ppm for 5 days	> IT at 1 mile on days 2 and 3 AT	> IT 1 mile and < IT 6.5 miles (water treatment plant)
Chandlers, AZ, 1994 Trial 4 (Keckemet, 1999)	0.18 ppm for 5 days	< IT at all sample times (1-5 days AT)	< IT at all sample points 1, 3, and 6.5 miles (water treatment plant)
Chandlers, AZ, 1994 Trial 5 (Keckemet, 1999)	0.18 ppm for 5 days	> IT at 1 mile on sample day 2 AT	> IT 1 mile and < IT 6.5 miles (water treatment plant)
Chandlers, AZ, 1994 Trial 6 (Keckemet, 1999)	0.18 ppm for 5 days	< IT at all sample times (1 -5 days AT)	< IT at all sample points 1, 3, and 6.5 miles (water treatment plant)
Delta, CO 1997 (Biever, 1998)	5 ppm dipotassium salt for 3 hours (Aquathol® K)	> IT for at least 5 hrs after residue arrival at last sampling point (15.2 mi). No samples taken at last sample point between 28.75 (3.7 ppm) and 47.75 hrs (<0.025 ppm).	> IT at all sample points (0, 3.6, 9.96, 12.8, and 15.2 miles)
S-1 9 Canal, Twin Falls, ID 1994 (Sisneros and Turner, 1996)	0.4 ppm dipotassium salt for 96 hours (Aquathol® K)	> IT 0-12 hrs after treatment (depending on location) until approximately 80 hours (all locations)	> IT at all sample points (0.25 to 2.0 miles) except within holding pond below 2-mi sample location

IT - Interim Tolerance (0.20 ppm), AT - After Treatment, ND - Not Detectable (< 0.01 ppm) a.e. -acid equivalent

Reviewer's note: Williams *et al.*'s "Keckemet, 1999" is the same as this document's Keckemet and Sharp, 1999.

**Table 3.1.7.B: Residue Predictions - Canal Scenarios with 10-Day Half-Life  
From Singh *et al.* 1999**

Dose	Velocity M/s	Flow Rate cfs	Miles from Point of Application							
			0	1.5	6	12	18	30	42	54
120 hours @ 0.2 ppm	0.05	12.4	0-120	n/a <sup>2</sup>	n/a	n/a	n/a	n/a	n/a	n/a
	0.18	44.1	0-120	8-121	n/a	n/a	n/a	n/a	n/a	n/a
	0.30	73.7	0-120	5-120	18-123	n/a	n/a	n/a	n/a	n/a
24 hours @ 1.0 PPM	0.05	12.4	0-24	8-40	43-83	95-137	150-186	n/a	n/a	n/a
	0.18	44.1	0-24	3-28	12-41	26-56	40-72	69-102	99-132	128-162
	0.30	73.7	0-24	2-26	8-34	16-43	24-53	41-71	59-89	76-107
6 hours @ 2.0 ppm	0.05	12.4	0-6	6-24	41-66	99-113	n/a	n/a	n/a	n/a
	0.18	44.1	0-6	2-11	11-24	24-40	38-56	67-87	96-116	126-146
	0.30	73.7	0-6	1-9	7-17	15-27	23-36	40-55	57-73	74-92
3 hours @ 3.0 ppm	0.05	12.4	0-3	6-21	42-60	n/a	n/a	n/a	n/a	n/a
	0.18	44.1	0-3	2-8	11-22	24-38	38-53	67-83	97-112	128-141
	0.30	73.7	0-3	1-6	7-14	14-24	22-34	39-52	56-71	74-89
3 hours @ 5.0 ppm	0.05	12.4	0-3	4-26	34-73	83-128	136-181	254- 273	n/a	n/a
	0.18	44.1	0-3	2-10	9-24	22-41	35-58	62-89	90-120	119-151
	0.30	73.7	0-3	1-7	6-16	13-26	21-36	37-55	53-74	70-93

1 Time period in hours (from t1 to t2) during which endothall concentrations are predicted to be equal to or above 0.2 ppm.

2. n/a - not applicable (residues exceeding 0.2 ppm were not predicted to occur)

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# Endothall

## Volume 2, Section 4

### ENVIRONMENTAL EFFECTS

**140 PAGES**

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#### 4.0 ENVIRONMENTAL EFFECTS ASSESSMENT

*Executive Summary: Information was compiled from reports submitted by the sponsor, collected from EPA computer web-sites and the open literature on the toxicity of Aquathol® K (dipotassium endothall salt), disodium endothall salt, endothall acid and Hydrothol® 191 [mono(dimethylalkylamine) endothall salt]. Acute toxicity data was collected for the standard test species of algae, plants, fish, free-swimming invertebrates and benthic (sediment) invertebrates. Chronic toxicity data was also collected for fish and free-swimming invertebrates. No chronic toxicity data was collected for algae, plants or sediment organisms. Since chronic data was in short supply an estimate of the chronic no observed effects level was made based on the acute/chronic toxicity ratio for animals on which we had received both acute and chronic data. Additional data were collected on species other than the standard test species to further supplement the data. A risk assessment was conducted based on the procedures outlined in Urban and Cook (1986). Urban and Cook state that if acute risk quotients are less than 0.1 and chronic risk quotients are less than 1.0, the biota should be safe from the toxic effects of the tested pesticide with assurance that 95% of the tested biota will be protected. These values are termed the acute and level of concern and the chronic level of concern, respectively.*

*Acute risk quotients are defined as the four day geometric mean of the Expected Environmental Effects Concentration (EEC) divided by the concentration of the herbicide that will cause mortality in 50% of the test species exposed in a standardized acute toxicity test (LC50). These values were calculated from the initial concentration of Aquathol® 3.5 mg a.e./L or Hydrothol® (5.0 mg a.e./L) and their most representative half-life (0.8-days). The EECs for acute exposure with Aquathol® K and Hydrothol® 191 were determined to be 1.0 ppm mg a.e./L and 1.4 mg a.e./L, respectively. These values are identical to those provided by Ecology in their 1991/1992 Environmental Impact Statement. Chronic Risk Quotients are defined as the 28-day geometric mean for the expected environmental effects concentration (EEC) divided by the no observed effect concentration (NOEC) for the test species after exposure in a standardized chronic toxicity test that can last up to several months. These values were calculated from the initial concentration of Aquathol® (3.5 mg a.e./L) or Hydrothol® (0.3 to 0.5 mg a.e./L) and their most representative half-life (0.8-days). The EECs for Aquathol® K and Hydrothol® 191 were determined to be 0.14 mg a.e./L and 0.01 mg a.e./L, respectively. These values are similar to those provided by Ecology in their 1991/1992 Environmental impact statement, which were 0.06 mg a.e./L for Aquathol® and 0.02 mg a.e./L for Hydrothol® 191. The reason for the differences is not entirely understood but may be due to slight differences in the estimated initial concentration and typical use concentrations based on formulation concentration or active ingredient concentration rather than acid equivalence concentration.*

*Each subclass of animals within the biota was evaluated separately by the risk assessment methods of Urban and Cook (1986). These separate classes included fish, free-swimming invertebrates and benthic (sediment) invertebrates. Endangered species were evaluated under a separate acute risk assessment since the acute level of concern for endangered species is 0.05 rather the 0.1 value used for less sensitive members of the biota.*

- **Aquathol®**

*Aquathol® K (dipotassium endothall salt), disodium endothall salt and endothall acid were analyzed together for risk since EPA believes that the toxicity for these herbicides should be similar. Hydrothol® 191 [mono(dimethylalkylamine) salt of endothall] was analyzed for risk separately from the endothall acid and its inorganic salts since its toxicity is much higher due to the presence of the mono(dimethylalkylamine) constituent. Summaries of the toxicity study results are presented in Table 2. For the herbicides specified above, each subclass of plants and animals within the biota was evaluated separately by the risk assessment methods of Urban and Cook (1986). These separate classes included algae and macrophytes, fish, free swimming invertebrates and benthic (sediment) invertebrates. The risk analysis was conducted in this manner because the different classes of organisms had the potential to exhibit greatly differing toxic effects. Endangered species were evaluated under a separate acute risk assessment since the acute level of concern for endangered species is 0.05 rather the 0.1 value typically used for less sensitive members of the biota.*

- **Aquathol® (disodium endothall salt)**

*Aquathol® K is toxic to aquatic macrophytes. The representative species in the laboratory is Lemna gibba and the toxicity (EC50) of Aquathol® K to Lemna gibba is 0.35 mg a.e./L (0.5 mg a.i./L). Since typical use rates may be as high as 3.5 mg a.e./L (5.0 mg a.i./L), this macrophyte would typically be controlled under field situations. Results from field studies indicate that pondweeds (Potamogeton) milfoil (Myriophyllum), coontail (Ceratophyllum), American waterweed (Elodea canadensis) and Zannichelia paustris should be controlled by Aquathol® K concentrations in the range of 2.0 to 3.5 mg a.e./L (2.8 to 5.0 mg a.i./L). For a list of species with which efficacy has been demonstrated please see Table 2 and Appendix 1 of Section 1.*

*Aquathol® K, and endothall acid have a very low toxicity to algal species. The EC50 is greater than 2.6 mg a.e./L for freshwater diatoms and from 25 to 3000 mg a.e./L for a marine haptophyte (Isochrysis galbana). At typical use rates up to 3.5 mg a.e./L (5.0 mg a.i./L) control would be expected, and in field studies Chara spp. (anchored macrophytic algae) has been shown to not be controlled and to dominate a pond for up to two years after application of this control measure.*

*Aquathol® K, disodium endothall salt and endothall acid have a low acute toxicity to fish. The toxicity ranges from an LC50 of 11 mg a.e./L for seven to eight day old (early life-stage) walleye to ~560 mg a.e./L for fathead minnow. For other species of concern that were tested, the toxicity of Aquathol® K ranged from an LC50 of 23 mg a.e./L to >71 mg a.e./L for Chinook and Coho salmon, respectively. Since the maximum use rate of Aquathol® K is 3.5 mg a.e./L even the most sensitive species of fish within the biota should not suffer adverse impact from the effects of Aquathol® K. Maximum field rates of Aquathol® have been shown to not adversely impact survival, growth, reproduction or nesting behavior in bluegill sunfish, and largemouth bass over a two-year period. Exposure of anadromous fish to sublethal concentrations of Aquathol® K may interfere with the parr to smolt metamorphosis and result in significant mortality when smolts are subsequently exposed to seawater. Both laboratory and field tests indicate that fish do not bioaccumulate Aquathol® by up-take from the water or by an oral exposure route. Several fish species may avoid*

*Aquathol® K at concentrations typically encountered in the field particularly when it is mixed with dalapon. Despite this “trend” evidence for avoidance behavior, the best-run laboratory studies indicate that behavior is not significantly different between treated and controls.*

*Aquathol® K, disodium endothall salt and endothall acid have a low acute toxicity to free-swimming invertebrates. LC50 ranges from 39 to 92 mg a.e./L. The only species tested was Daphnia magna. At the projected maximum use rate of 3.5 mg a.e./L, Aquathol® K and its surrogate test substances will not acutely impact members of this segment of the biota. However, testing of more species of free swimming biota would lend greater confidence to the risk assessment dealing with this segment of the biota. Since the maximum use rate of Aquathol® K is 3.5 mg a.e./L even the most sensitive species of invertebrate within the biota should not suffer adverse impact from the effects of Aquathol®. The use of maximum field rates of Aquathol® has not been shown to adversely impact the numbers or generic density (species diversity) of Cladocerans (daphnids), Copepoda, Cyclopsida and Calanoida when these species were monitored over a growing season which lasted from May through October. Neither the direct impact of Aquathol® nor secondary effects such as decreased oxygen content or decreased surface cover by resident plants had any observable adverse impact on the free-swimming invertebrate population. The only species of aquatic invertebrate that has exhibited mortality in the field is due to the indirect effect of Aquathol® K is the Hydrillia fly. At concentrations of Aquathol® K that controlled Hydrilla, 74% of Hydrillia flies died. However, this mortality was probably due to a reduction in habitat as the number of Hydrilla leaflets decreased and not due to the direct effects of endothall.*

*Aquathol® K, disodium endothall salt and endothall acid have low acute toxicity to benthic (sediment dwelling) invertebrates. For environmentally relevant species, the toxicity ranges from an LC50 of ~200 to ~354 mg a.e./L for Gammarus spp.; some marine and estuarine species exhibit similar toxicity to Aquathol® K from 39 mg a.e./L for the mysid shrimp to as high as 750 mg a.e./L for the fiddler crab. At the projected maximum use rate of 3.5 mg a.e./L, Aquathol® K and its surrogate test substances will not acutely impact members of this segment of the biota. For example, the risk quotient is below the acute level of concern (0.1 for typical species) for all species tested.  $RQ = 1.0 \text{ ppm a.e.} / 39 \text{ ppm a.e.} = 0.03$  for the most sensitive species (mysid shrimp). Field studies have not been conducted with these sediment species. However, typical sediment concentrations (~ 0.5 mg a.e./L) are lower than the typical acute EEC in water. Therefore, exposure to sediment containing these concentrations is not likely to produce significant mortality or other adverse impact.*

*The chronic toxicity of Aquathol® K, disodium endothall salt and endothall acid ranges from an NOEC of 5 mg a.e./L for rainbow trout to over 80 mg a.e./L for bluegill sunfish. At the projected maximum use rate of 3.5 mg a.e./L, Aquathol® K and its surrogate test substances will not chronically impact members of this segment of the biota. For example, the risk quotient is below the chronic level of concern (1.0 for typical species) for all species tested.  $RQ = 0.06 \text{ ppm a.e.} / 5 \text{ ppm a.e.} = 0.012$ . Predictions of a chronic NOEC are as low as 1.7 mg a.e./L for early life-stage walleye and 3.6 mg a.e./L in Chinook salmon based on acute toxicity divided by the acute to chronic toxicity ratio of 6.4. Using these predicted chronic NOECs produces a risk quotient that does not exceed the chronic level of concern (1.0) for protection of the biota; e.g.,  $RQ = 0.06 \text{ ppm a.e.} / 3.6 \text{ ppm a.e.} = 0.016$ . True chronic*

exposure probably does not exist in the field since treatment with Aquathol® generally does not occur more than once per year, or once every other year, in a typical water body.

Only one species of free-swimming invertebrate has been tested with Aquathol® for chronic toxicity. The chronic toxicity (NOEC) to *Daphnia magna* is 5.0 mg a.e./L to endothall acid. At a projected maximum use rate of 3.5 mg a.e./L, Aquathol® and its surrogate test substance will not chronically impact *Daphnia magna* (free-swimming invertebrate). The risk quotient is below the chronic level of concern (1.0 for typical species) for all species tested.  $RQ = 0.06 \text{ ppm a.e.} / 5 \text{ ppm a.e.} = 0.012$ . Predictions of a chronic NOEC are not necessary, since the empirical chronic NOEC for the most sensitive species is somewhat lower (5.0 mg a.e./L) than the estimated chronic NOEC value (6.1 mg a.e./L).

Since no laboratory studies were conducted for the benthic (sediment) invertebrates, predicted chronic NOECs for Aquathol® K and its surrogates are used to predict risk. The predicted chronic NOEC for the most sensitive environmental relevant species would be 34 mg a.e./L which gives a risk quotient that is well below the chronic level of concern of 1.0 ( $RQ = 0.06 \text{ ppm a.e.} / 34 \text{ ppm a.e.} = 0.017$ ). Therefore, use of Aquathol® at the maximum projected rate will not chronically impact the benthic biota. Even if the highest short-term concentration of endothall in the sediment (0.25 to 2.0 mg a.e./L) were substituted for the chronic water EECs, the risk quotient would still be below the chronic level of concern for protection of this segment of the biota.

**Conclusion: Aquathol® K (dipotassium endothall salt), disodium endothall salt and endothall acid will not effect the biota acutely or chronically when applied at concentrations (3.5 mg a.e./L = 5.0 mg dipotassium endothall salt/L) recommended on the label. The concentrations listed on the label will control the aquatic macrophytes listed on the label including milfoil (*Myriophyllum spp.*), pondweed (*Potamogeton spp.*, *Najas spp.*), coontail (*Ceratophyllum spp.*), hydrilla (*Hydrilla verticillata*) *hygrophila* (*Hygrophila polysperma*) and *Sparganium spp.* Aquathol® K should not be used to control species of weeds that are not specified on the label. Some species are known to be tolerant to Aquathol® including *Chara spp.* (muskgrass) American waterweed (*Elodea canadensis*), cattails (*Typha spp.*), spatterdock (*Nuphar spp.*) and fragrant water lilies (*Nymphaea spp.*) and may become dominant after other more susceptible species have been controlled. Aquathol® K is not an algaecide and is generally ineffective in controlling algal species. Algal species may bloom after treatment with Aquathol® if proper water quality conditions occur and released nutrients reach levels that can sustain algal growth.**

- **Hydrothol®**

*Hydrothol® 191* is toxic to aquatic macrophytes. The representative species in the laboratory is *Lemna gibba* and the toxicity (EC50) of *Hydrothol®* to *Lemna gibba* is 0.83 mg a.e./L (3.5 mg product/L). Typical use rates may be as high as 5.0 mg a.e./L (5.0 mg product/L), therefore, this macrophyte would normally be controlled under field situations. Results from controlled field studies are not available. However, the 1999 label for *Hydrothol® 191* indicates that pondweeds (*Potamogeton*) milfoil (*Myriophyllum*), coontail (*Ceratophyllum*), American waterweed (*Elodea canadensis*), Brazilian elodea (*Egeria densa*) and *Zannichelia spp.* will be controlled with

*Hydrothol® concentrations in the range of 0.5 to 2.5 mg a.e./L (2.1 to 11 mg product./L). For a list of species with which efficacy has been demonstrated please see Table 2 and Appendix 1 of Section 1).*

*Hydrothol® has a very high toxicity to many algal species. The EC50 ranges from 0.0023 mg a.e./L for the green algae (Selenastrum capricornutum) to >0.27 mg a.e./L for the marine diatom (Snydra sp.) and the green algae (Chlorella vulgaris). There are a number of species that are not significantly affected by concentrations higher than the typical maximum use rate of 0.2 mg a.e./L. For these species, higher use rates (up to 0.8 mg a.e./L) may be necessary for control. Experimental algae control in Lake Steilacoom was not entirely effective at concentrations up to 0.2 mg a.e./L Hydrothol® although this may be the maximum concentration that risk assessments or field evaluations indicate is safe to the biota in acute or chronic exposure.*

*Hydrothol® 191 has a high acute toxicity to fish. The toxicity ranges from an LC50 of 0.079 mg a.e./L for cutthroat trout to 0.82 mg a.e./L for sheepshead minnow. It is noteworthy that the cutthroat trout is a threatened species in addition to being the most sensitive species tested. Since the maximum use rate of Hydrothol® is 5.0 mg a.e./L this most sensitive species of fish within the biota will suffer adverse impact from the effects of Hydrothol® 191. For example, the risk quotient is substantially above the acute level of concern (0.1 for typical species and 0.05 for endangered species) for all species tested.  $RQ = 1.4 \text{ ppm a.e.} / 0.079 \text{ ppm a.e.} = \sim 18$ . Therefore, the use of Hydrothol® 191 at the maximum use rate will not be safe to sensitive species within the biota. The field use rates of Hydrothol® 191 that are considerably below the maximum rate have been shown to impact resident fish populations including channel catfish, threadfin shad, red shiner and mosquito fish adversely when used at concentrations as low as 0.20-0.5 mg a.e./L in irrigation canals for periods as short as 120-hours. Modeling indicates that these effects can be decreased to less than 10% of the resident species if concentrations of Hydrothol® 191 are kept at or below 0.2 mg a.e. for 120 hours or less and some additional mitigation measures are used. Additional mitigation could be obtained by treating canals with high suspended organic carbon and low hardness (~20 mg calcium carbonate/L). Exposure of anadromous fish to sublethal concentrations (0.2 mg a.e./L) of Hydrothol® 191, that might typically be encountered in the environment, may interfere with the parr to smolt metamorphosis and result in significant mortality when smolts are subsequently exposed to seawater. The manufacturer and some local applicators claim that fish are able to avoid exposure to Hydrothol® 191 and its toxic dimethylalkylamine constituent. They claim that fish may be driven away from the herbicide treatment plume if the herbicide is applied from the shore outline outward with skill and understanding of fish avoidance behavior. However, these observations are not supported by credible studies using proper controls.*

*Hydrothol® 191 has a high acute toxicity to free-swimming invertebrates. The LC50s range from 0.080 mg a.e./L for Daphnia magna to 0.37 mg a.e./L for the rotifer. At the projected maximum use rate of 5.0 mg a.e./L, Hydrothol® 191 is likely to acutely impact members of this segment of the biota. However, testing of more species of free swimming biota would lend greater confidence to risk assessment dealing with this segment of the biota. Since the maximum use rate of Hydrothol® 191 is 5.0 mg a.e./L even the least sensitive species of invertebrate within the biota will suffer adverse acute impact from the effects of Hydrothol®. For example, the risk quotient is significantly above the acute level of concern (0.1 for typical species) for all*

species tested.  $RQ = 1.4 \text{ ppm a.e.} / 0.080 \text{ ppm a.e.} = \sim 18$ . Field studies have not been conducted with free-swimming invertebrates exposed to Hydrothol® 191. Nevertheless, modeling studies indicate that treatment of canals with concentrations of Hydrothol® 191 as low as 0.2 mg a.e./L for 120 hours to control algae results in 20% of the resident invertebrate species being affected for 10 to 50 miles down stream. Significant mitigation can be achieved if the steps taken in the previous paragraph are followed.

Hydrothol® 191 has a high acute toxicity to benthic (sediment dwelling) invertebrates. For environmentally relevant species, the toxicity ranges from an LC50 of 0.12 mg a.e./L for the mayfly (*Hexagenia* sp.) to 1.6 mg a.e./L the northern crayfish (*Orconectes virilis*); some marine and estuarine species exhibit similar LC50s from 0.022 mg a.e./L for the grass shrimp to as high as 6.2 mg a.e./L for the fiddler crab. At a projected maximum use rate of 5.0 mg a.e./L, Hydrothol® 191 will acutely impact members of this segment of the biota. Field studies have not been conducted with these sediment species. However, since typical endofall sediment concentrations are 0.25 to 2 mg/L for a short period of time after application, the acute risk quotient may still exceed the level of concern (0.1) from this sediment exposure source. Therefore, exposure to sediment, or water (overlying, associated or pore) containing these concentrations of Hydrothol® 191 is likely to produce significant mortality or other adverse impact on this segment of the biota.

The chronic toxicity of Hydrothol® 191 ranges from a chronic NOEC of 0.022 to 0.056 mg a.e./L for fathead minnow chronic exposure tests that lasted from 7 to 35 days. There was no obvious correlation with exposure time and NOEC. Since only one species was tested, an estimate of the chronic NOEC was made from the acute LC50 for cutthroat trout and the acute to chronic toxicity ratio. At the projected maximum use rate of 0.3 to 0.5 mg a.e./L, Hydrothol® 191 will chronically impact members of this segment of the biota. Due to the degree of uncertainty in the EEC value, the level of concern cannot be considered to be less than one in this case. True chronic exposure probably does not exist in the field since treatment with Hydrothol® 191 does not generally occur more often than once per year or once every other year in a typical water body. In irrigation canals, chronic exposure does not occur because once the herbicide plume has passed, the EEC is essentially zero. Chronic field studies have not been conducted with Hydrothol® 191. However, the 1999 label indicates, that treatment rates of 1.0 mg a.e./L should not significantly impact the biota. And this recommendation is supported by the experimental use of Hydrothol® 191 at 0.2 mg a.e./L during the 1999 season. However, since Hydrothol® has the potential to be chronically adverse at concentrations in the 0.3 to 0.5 mg a.e./L range, use of Hydrothol® 191 at concentrations that exceed 0.2 mg a.e./L cannot be recommended.

Only two species of free-swimming invertebrate have been tested with Hydrothol® 191 for chronic toxicity. The experimental chronic toxicity (NOEC) is 0.016 mg a.e./L for *Daphnia magna* and <0.005 mg a.e./L for *Ceriodaphnia dubia*. At a projected maximum use rate of 0.3 to 0.5 mg a.e./L, Hydrothol® 191 will probably not chronically impact these Daphnid species (free-swimming invertebrate). Predictions of a chronic NOEC are not necessary, since a predicted chronic NOEC can not be more accurate than a value empirically obtained. True chronic exposure probably does not exist in the field when treatment with Hydrothol® 191 does not occur more often than once per year, or once every other year, in a typical water

body. No field studies were conducted that verify or deny the low chronic risk associated with Hydrothol® 191 against this segment of the biota.

Predicted chronic NOECs for Hydrothol® are used for benthic (sediment) invertebrates to predict risk since no laboratory studies were conducted. The predicted chronic NOEC for the most sensitive environmentally relevant species (mayfly) would be 0.019 mg a.e./L which leads to a risk quotient below the chronic level of concern of 1.0 ( $RQ = 0.02 \text{ ppm a.e.} / 0.019 \text{ ppm a.e.} = 1.05$  or  $0.01 \text{ ppm a.e.} / 0.019 \text{ ppm a.e.}$  or with a geometric mean of 0.53 ). Therefore, use of Hydrothol® 191 at the maximum projected rate will not chronically impact the benthic biota. However, if concentrations that may be found for 28 days in the sediment are considered (0.25 mg a.e./Kg) as representative of the EEC, the chronic level of concern would be exceeded and the sediment biota would be at risk. True chronic exposure probably does not exist in the field when treatment with Hydrothol® does not occur more often than once per year or once every other year in a typical water body. Although no field studies were conducted to verify the accuracy of this risk assessment, there is no reason to assume that predicted values for Hydrothol® for the chronic NOEC should follow a different acute to chronic toxicity ratio rules than for Aqauthol® K, disodium endothall salt or endothall acid.

**Conclusion: Hydrothol® 191 [mono(dimethylalkylamine) salt of endothall will have an acute or chronic impact on the biota when applied at concentrations (5.0 mg a.e./L = 21 mg product/L) recommended on the label. Furthermore, the concentrations listed on the label will control the aquatic macrophytes listed including milfoil (Myriophyllum spp), pondweed (Potamogeton spp., naid (Najas spp.), coontail (Ceratophyllum spp.), hydrilla (Hydrilla verticillata) hygrophila (Hygrophila polysperma) and Sparganium spp. Hydrothol® 191 should not be used to control species of weeds that are not specified in the label. Further more, Hydrothol®191 may also be used at lower concentrations (0.05 to 0.8 mg a.e./L) to control various species of algae including Vallisneria, Cladophora, Pithophora, Spirogyra and Chara. Hydrothol® 191 has been recommended by some for the control of toxic blue-green algae at concentrations that may not harm green algae. Insufficient field data has been collected to know with certainty, what concentrations Hydrothol® can be maximally used and not harm the resident biota. However, enough data has been collected to show that Hydrothol® at concentrations higher than 0.2 to 0.5 mg a.e./L can harm fish and possibly free-swimming and benthic biota. To mitigate the effects of the use of Hydrothol® 191, the lowest concentration that will achieve the desired control of aquatic macrophytes and algae should be used. Currently, a safe treatment rate of higher than 0.2 mg a.e./L cannot be recommended without potential for acute and chronic adverse impact. The exposure period should be as low as possible (high flow-rates in canals), the minimum area possible should be treated; treatments of water bodies that contain hard water should be avoided; and treatments should occur from the shoreline outward to allow for the possible avoidance of Hydrothol® by free-swimming fish.**

#### **4.0.1 OBJECTIVE**

The purpose of this section is to update the environmental toxicity data and to use this data to assess the potential risks to wildlife and the environment from using endothall products including Aquathol®, Aquathol® K, Hydrothol® 191 and Hydrothol® 191 Granular. For the purpose of this section, wildlife refers to aquatic plants and animals, terrestrial plants and animals and microorganisms including algae, bacteria and fungi.

#### **4.0.2 APPROACH**

##### **4.0.2.1 Information Compilation**

In order to collect appropriate wildlife toxicological information, several sources of information were used. A primary source of data are reports submitted to the EPA Environmental Effects Branch by the registrant (Elf Atochem) to support the registration and re-registration of endothall products. These submittals are considered to be the best sources for wildlife toxicology data for endothall because the tests are standardized. The organisms used are considered to be good representatives or good surrogates of plants and animals that are highly sensitive environmental indicators. Other sources of acute and chronic toxicity data include public literature searches with the DialogOnline Database for peer reviewed journals, articles, and compilations of data in the form of literature reviews (Shearer and Halter, 1980; Ecology, 1982, 1989 and 1993). Similar compilations of EPA data were also searched such as EPA's Brian Database (1999) and EPA's ECOTOX Database. These are online databases for retrieval of data submitted to support registration (Brian, 1999) and data from peer reviewed journals used as supplemental material to be used for risk assessment and evaluation (Ecology, 1999).

The US EPA and the Washington State Department of the Ecology (Ecology) use these data for the following evaluations:

- To establish the acute toxicity of active ingredients to test organisms.
- To compare toxicity information with measured or estimated pesticide residues in the environment to assess potential impacts to fish and wildlife.
- To provide data which determines the need for precautionary label statements and permit requirements in order to minimize potential adverse effects to wildlife and aquatic organisms.
- To indicate the needs for further laboratory and field studies to support regulatory decisions.

If an unreasonable adverse impact is noted in the basic studies, additional tests are conducted and evaluated to determine the effects of the product on sensitive species and sensitive stages of those species. These studies typically take the form of long term chronic, early life stage, reproductive effects and life-cycle effects. These tests take into account the toxicity of the product and compare that toxicity with expected environmental concentrations. If an adverse impact is noted at levels consistent with environmental concentrations, further "field" or laboratory work is necessary to evaluate the acute and chronic effects on captive sentinel organisms and wildlife populations

#### 4.0.2.2 Risk Assessment Methodology

Risk assessment is conducted in a manner similar to that described in EPA, (1982), Brooks (1973 in Ebasco (1993), Ecology, 1992 and in Urban and Cook (1985) and Giddings (1999). For assessment of acute risk, the LC50 value is determined for a variety of organisms within a class (fish, aquatic invertebrates, algae, other aquatic and terrestrial plants, birds and mammals). The relative toxicity is determined in two ways. 1) The EPA has certain specific descriptive classifications for inter-chemical comparisons only. These classifications do not reflect actual environmental concentrations or hazards to the test species. (For an example of these classifications please see Table 1.) The Acute LC50 or LD50 is compared with the Expected Environmental Concentration or Expected Environmental Dose (EEC or EED). The Acute Risk Quotient (ARQ) is determined by dividing the EEC or EED by the laboratory measured acute toxicity (LC50, LD50). The ARQ is based on the most sensitive environmentally relevant species i.e. algae, other microbes, macrophytes, fish, free-swimming marine aquatic invertebrates, or benthic organisms. If the ARQ is <0.1, the evaluated pesticide is generally considered to be safe to that segment of the biota for exposures of short duration. A short duration is generally defined as 4 or 5 days. A low ARQ indicates that most exposed species (probably around 95%) will not be at risk.

For an assessment of aquatic chronic risk, calculations similar to those outlined above are used. However, chronic risk is based on an exposure period of seven or more days. Seven days exposure is considered to be a short-term chronic risk and typically 21 to 90 days exposure is considered to be long-term chronic risk. For fish, short-term chronic risk involves the exposure of sac-fry or fry to the toxic substance and long term chronic risk involves the exposure fish from the newly deposited egg stage through the free swimming and actively growing fry stage. For invertebrates, the chronic life cycle test usually involves exposure of newly deposited young from days 21 through 28 or some other appropriate life cycle interval.

The Chronic Risk Quotient (CRQ) is determined by dividing the EEC by No Observed Effect Concentration (NOEC). The CRQ is based on the most sensitive environmentally relevant species. If the CRQ is <1.0, the pesticide is generally considered to be safe to that segment of the biota for exposures of chronic duration.

To determine how well acute toxicity can predict chronic toxicity, an acute (LC50)/chronic (NOEC) was evaluated for species where both values were available.

#### 4.1 ENDOTHALL ENVIRONMENTAL TOXICITY REVIEW: EFFECTS ON THE PHYSICAL AND CHEMICAL ENVIRONMENT THAT MAY AFFECT HABITAT

*Summary: Sites that have never been exposed to endothall products may degrade Aquathol® and Hydrothol® more slowly than sites that have had a previous exposure history. This is because it normally takes several weeks for bacteria capable of using endothall as their sole carbons source to develop out of their lag-phase and rapidly degrade applied Aquathol® or Hydrothol® 191 if they have not been previously exposed. Rapid degradation leads to a very short half-life in non-flowing water, which is usually less than 10 days. However, if experienced degradation, sorption, and dilution factors*

*are interacting, the field half-life in water can be less than one-day. Therefore, long-term persistence of Aquathol at concentrations that will cause environmental damage is not likely. However, due to the extremely high toxicity of the dimethylalkylamine constituent of Hydrothol® 191, concentrations of Hydrothol® 191 although similar to those of Aquathol® may be high enough to cause observable damage to the biota.*

*Bioconcentration in plants and animals is not likely for Aquathol® or Hydrothol® 191. Most species of fish and aquatic invertebrates do not bioaccumulate dipotassium endothall. Some plants appear to bioaccumulate 14C labeled endothall at concentrations that are ~4-fold higher than environmental concentrations, but tissue analysis indicates that these residues are incorporated into natural plant constituents in the leaves and stems.*

In the United States there are currently five registered formulations for endothall. Four of these products are currently registered for use in the State of Washington. This review addresses only those formulations registered for aquatic use by Ecology and the Washington Department of Agriculture as of 1999. The toxicity of the disodium endothall formulation and technical endothall acid is reviewed for historic purposes and a better understanding of the aquatic toxicity of the endothall products. When endothall was registered originally for aquatic use, the EPA agreed that disodium endothall and endothall acid could be used as surrogate test substances for Aquathol® K, since all inorganic salt forms were likely to have similar toxicity to endothall acid and were easier to work with than Aquathol® K (Atochem, Chris Davis, 2000, personal communications). Inspection of the data contained in this report indicates that the conclusions surrounding similar toxicity for endothall acid, disodium endothall and dipotassium endothall (Aquathol® K) are probably correct. The products currently registered in Washington State are as follows:

Aquathol® K Aquatic Herbicide – A liquid formulation containing 40.3% dipotassium endothall (28.6% endothall acid equivalents).

Aquathol® Granular Aquatic Herbicide – A solid (granular) formulation containing 10.1% dipotassium endothall (7.2% endothall acid equivalents).

Hydrothol® 191 Aquatic Algicide & Herbicide – A liquid formulation containing 53.0% mono(dimethylalkylamine) salt of endothall (23.36% endothall acid equivalents).

Hydrothol® 191 Granular Aquatic Algicide and Herbicide – A solid (granular) formulation containing 11.2% mono(dimethylalkylamine) salt of endothall (5.0% endothall acid equivalents).

Chemical structures and formulae for endothall acid are provided in the Section 2.0 (Chemical Characteristics portion of this review).

The most commonly used forms of endothall are the Aquathol® products. They are proven to be safe to most aquatic animals and have a wide spectrum of activity against submerged aquatic weeds. In Washington State, the Hydrothol® products are currently used only on an experimental basis, primarily for the control of algae and for spot and margin control of weeds where fish kill is not a serious issue. Fish-kill is generally considered an important issue if indigenous fish species are present in public waterways.

#### 4.1.1 EVALUATED ORGANISMS AND SENSITIVE STAGES

In order to develop the most sensitive risk assessment possible, appropriate species and appropriate life stages must be chosen for each class of organisms. The classes of organisms of interest are microorganisms (bacteria, fungi and algae), macrophytes, fish, aquatic invertebrates, sediment organisms, terrestrial plants, birds, mammals and terrestrial invertebrates. The life stages that are usually tested are selected for high sensitivity and ease of manipulation. Each class of organisms is broken down into appropriate test species as indicated in Table 2.

#### 4.1.2 EVALUATED AQUATIC ORGANISMS AND SENSITIVE STAGES (EPA, 1982)

- Bacteria -- Ideally these one-celled creatures should be tested when their numbers are increasing rapidly. However, the results of this work indicate that the organisms selected for the study (EPA, 1982) were in the slow phase of their growth (Sikka and Saxena, 1973).
- Algae -- Four standard species of algae are typically evaluated in algal toxicity tests. They are *Anabaena flos-aquae* (freshwater blue-green algae), *Selenastrum capricornutum* (fresh water green algae), *Naviculla pelliculosa* (fresh water diatom) and *Skeletonema costatum* (marine diatom). These have been selected as the standard species since there is an extensive database on the effects of many pesticides on their growth rate. Other species may be selected as surrogates when data does not exist for the standard species. For example *Dunaliella tertiolecta* (green algae), *Chlorococcum spp.* (green algae) *Isochrysis galbana* (marine haptophyte) and *Phaeodactylum tricornerutum* (freshwater diatom) were selected to compare toxicity of endothall acid with the toxicity of Aquathol® K in acid equivalence. The endpoint of interest in algal studies is a 50% reduction in log-phase growth usually after five days of exposure to a static solution. Field studies generally measure the amount of chlorophyll a or cell counts at the test site as an indicator of population size.
- Aquatic Macrophytes -- For macrophytes, *Lemna gibba* (duckweed) is typically used in the laboratory. It is a species with an extensive database regarding the effects of pesticides on its growth rate. This was the only species of macrophyte tested for acute toxicity in the laboratory of endothall-containing products by the registrant. The endpoint of interest in duckweed studies is a 50% reduction in growth after 14 days of exposure to static renewal conditions solution. Field studies utilized whatever species were available in whatever growth stage they were in at the time of the study and measured the percent reduction in lake coverage as an endpoint. See Table 2 for a species listing.
- **Fish Toxicity**
  - **Acute toxicity:** For fish, the standard species tested in the laboratory include rainbow trout (*Onchorhynchus mykiss*), bluegill sunfish (*Lepomis macrochirus*), fathead minnow (*Pimephales promelas*), sheepshead minnow (*Cyprinodon variegatus*) and channel catfish (*Ictalurus punctatus*). These were the only species tested with Aquathol®K, Hydrothol®191, and endothall acid. The standard acute LC50 test is run with juvenile fish of a uniform age-class or size. The test is typically run for 96 hours although some of the LC50s may be based

on 1, 2 or 4-day mortality data. The measured end point is mortality. The species selected are representative of a broad sensitivity range and are ecologically and economically relevant. Other species were also tested. Those of particular interest based on ecological relevance or sensitivity are cutthroat trout (*Salmo clarki*) with Hydrothol®, and Coho and Chinook salmon (*Oncorhynchus kisutch* and *Oncorhynchus tshawytscha*) with Aquathol®K. Although other species were also tested (Table 2), they are not generally considered to be standards or special needs organisms.

- **Chronic fish toxicity:** The standard fish species tested for chronic toxicity are fathead minnows, rainbow trout and sheepshead minnow. These species represent a warm freshwater species, a cold freshwater species and warm estuarine species, respectively. These tests can be run on fish in the sac-fry stage for 7 days but the standard period of time is 35 to 90 days. In addition to mortality, the endpoints monitored are growth and sub-lethal behavioral effects. A better study design is the early life-stage test where the endpoints are percent hatch, time to first and last hatch (95%), swim-up or first-feed, growth, and sub-lethal behavioral effects. The effective concentration is the lowest NOEC obtained for any endpoint. In some reporting formats, the effective concentration may be termed the Lowest Observed Effect Concentration (LOEC) or the Maximum Allowable Toxic Concentration (MATC). This is a very sensitive test and it may yield an unacceptably high CRQ when the ARQ indicates a high degree of safety for the more sensitive species in the biota.
- **Aquatic Invertebrates**
  - **Acute aquatic invertebrate toxicity:** The standard aquatic invertebrate species tested for acute toxicity include daphnia (*Daphnia magna* and *Ceriodaphnia dubia*), mysid shrimp (*Mysidopsis bahia*), and eastern oyster (*Crassostrea virginica*), which represent two warm freshwater species and two warm estuarine species. The endpoints monitored for these tests are immobility for the three arthropod species and shell growth for the eastern oyster. The endpoint is expressed as the 96 hour EC50 or LC50 for the three arthropods, and EC50 (dosage causing 50% decrease in shell growth). A number of other non-standard species were tested with endothall products and are listed in Table 2. The standard species were tested on all of the endothall products including (Aquathol® K, endothall acid and Hydrothol® 191).
  - **Life-cycle invertebrate toxicity:** Life-cycle invertebrate toxicity studies are typically conducted with daphnia (*Daphnia magna* and *Ceriodaphnia dubia*), and mysid shrimp (*Mysidopsis bahia*). Life-cycle studies are usually conducted on the standard invertebrate species instead of classic chronic studies. The life-cycle of the standard species is less than one cycle of chronic exposure (28 days). However, only a very limited database is available for endothall products and their effects on invertebrates. For example, Hydrothol® has been tested with *Daphnia magna* and *Ceriodaphnia dubia*, and endothall acid has been tested as a surrogate for Aquathol® K with *Daphnia magna*. Aquathol® K and disodium endothall have not been tested in life-cycle tests with invertebrates. These tests are routinely run for 21 days with *Daphnia magna*, 7 days with *Ceriodaphnia dubia* and 28 days with mysid shrimp. The parent generation is selected from a group of animals less than 24 hours old. The endpoints are immobility, reduction

in number of live young produced per female, and growth of the parent daphnids during the test.

- **Sediment organisms**
  - **Sediment organism acute toxicity:** There are major disagreements among researchers about how sediment organism studies should be conducted. The main problem with sediment organism studies is that sediment organisms require sediment with a specific particle size in order to function properly. In acute tests the sediment is often eliminated from the study because it adsorbs the toxicant and interferes with analytical chemistry. Most short-term (acute)  $\leq 96$ -hour sediment organism studies are conducted without sediment present. There is a need for these tests since there is no reason to assume that sediment organisms will respond in a manner similar to other aquatic invertebrates. These acute sediment organism toxicity studies are conducted in a similar manner to acute tests with other invertebrates except that the age at initial exposure and the exposure period is specific for each species. These specific characteristics are listed in Table 2.
  - **Sediment organism chronic toxicity:** Currently there is an on-going discussion in the scientific community concerning the manner in which chronic sediment organism studies should be conducted. However, agreement on how these studies should be conducted has not been reached. There are serious disagreements primarily over which species should be tested as representative of the biota. Disagreements persist because the indigenous species in North America, Europe, Japan and Australia differ significantly. It cannot be assumed cogenetic species will respond in a similar manner. Therefore, serious discussion is still occurring on the best guidelines and which species to use for these studies.

#### **4.1.3 ENDOTHALL POTENTIAL IMPACTS TO TERRESTRIAL WILDLIFE AND PLANTS**

The goal of this portion of the document is to discuss the effects of single applications/exposures and chronic applications/exposures to terrestrial wildlife (birds and mammals) and terrestrial plants exposed to aquatic herbicides containing endothall (Aquathol® and Hydrothol®). In addition possible effects on the food chain and threatened and endangered species will be discussed as well as ways to mitigate exposure of these organisms to the aquatic uses of endothall. The information presented summarizes toxicological studies to determine the effects of endothall containing products (Aquathol® and Hydrothol®) on plant and animal species.

##### **4.1.3.1 Effects on Terrestrial Animals (Birds, Mammals and Insects)**

Studies have been conducted to assess the toxicity of technical grade endothall and the endothall containing products Hydrothol® 191 and Aquathol® on various animal groups. Acute oral (LD50), acute dietary (LC50) and chronic dietary studies are presented.

#### 4.1.3.1.1 Acute effects on birds

Acute oral data for technical endothall, Hydrothol® 191 and Aquathol® are available for both bobwhite quail (*Colinus virginianus*) and mallard ducks (*Canas platyrhynchos*). The acute oral LD50 for bobwhite quail ranges from 494 mg/kg to 736 mg/kg (Hydrothol® and endothall technical) (Table 3). The acute oral LD50 for mallard duck ranges from 111 mg/kg to 389 mg/kg (Table 4). This data indicates that endothall is moderately to slightly toxic (Table 1) to birds when orally dosed.

Acute dietary (LC50) data for bobwhite quail and mallard ducks are also available. The LC50 for bobwhite quail ranges from > 1000 ppm to > 10000 ppm (Table 1). The acute dietary LC50 for mallard ducks ranges from > 1000 ppm to > 10000 ppm. These data indicate that technical grade endothall and the endothall containing products Hydrothol® 191 and Aquathol® are slightly to practically non-toxic when consumed in the diet by bobwhite quail and mallard ducks.

#### 4.1.3.1.2 Chronic effects on birds

Twenty-week dietary studies were performed on both bobwhite and mallard ducks using the technical product. The lowest observable effect level (LOEL) for endothall in bobwhite quail was > 250 ppm. The no observable effect level (NOEL) for endothall in mallard ducks was 50 ppm a.i. (adverse effect on early embryonic development at 250 ppm).

#### 4.1.3.1.3 Acute effects on mammals

Acute oral rat data is available for endothall technical (LD50 45.4 mg/kg), Aquathol® K (LD50 186.8 mg/kg and 99.5 mg/kg) and Hydrothol® 191 (LD50 209.8 mg/kg) (Table 5). This data indicates that the formulations (Hydrothol® 191 and Aquathol®) are moderately toxic (Table 1).

#### 4.1.3.1.4 Subchronic and Chronic effects on mammals.

A two-generation rat reproduction (dietary) study (Trutter, 1993) was undertaken using disodium salt of endothall (Aquathol®). The no observable adverse effect level (NOAEL) was determined to be 150 ppm based on differences in body weights of parents and offspring at the next highest dose.

### 4.1.4 MITIGATION OF EFFECTS ON BIRDS AND MAMMALS

- **Mitigation measures specific to endothall products**

There are two common routes of exposure of livestock and terrestrial wildlife to aquatic applications of endothall products. The two routes are exposure through drinking water treated with products containing endothall or eating aquatic plants, fish or other aquatic organisms from the treatment site. Based on the acute and chronic studies listed above, endothall and its products used as aquatic herbicides do not pose a significant acute or chronic risk to wild birds or terrestrial mammals. However, in order to mitigate possible problems with the watering of livestock the labels for these products do not allow watering of livestock with treated water for

from 7-25 days after application depending on the rate applied to the water body. Many studies have been run on these products to ensure their safety to wildlife and the label directions and warnings reflect the results of these studies. *Therefore, if the chemicals are applied according to the label the effect on terrestrial wildlife should be minimal.*

- **General mitigation measures**

Although endothall products used as aquatic herbicides do not pose a significant risk to terrestrial wildlife, the following measures should be considered prior to all aquatic herbicide applications. One possible mitigation measure would be not allowing applications if large populations of birds use shorelines or islands in the water body to be treated for nesting until after nesting is complete. Another mitigation measure would be to time applications to avoid migratory waterfowl and other bird species that use certain water bodies during migration. Efforts to avoid effects on migratory and nesting birds would best be coordinated between the permit writer and The Washington State Department of Fish and Wildlife (WDFW) prior to granting the permit.

#### **4.1.5 POSSIBLE EFFECTS ON THE FOOD CHAIN**

The potential of endothall to bioaccumulate in birds and mammals has not been well studied. However, it is unlikely that bioaccumulation will occur due to endothall's low Kow and its rapid degradation in the environment. Adverse effects on the food chain are also unlikely because of the relatively high LC50 and LD50 values reported and the low observable effect levels seen in chronic studies with birds and mammals.

#### **4.1.6 EFFECTS ON ENDANGERED TERRESTRIAL PLANTS, BIRDS AND MAMMALS**

A list of endangered terrestrial plants, birds and mammals is located in Table 6. Minimal effects to these organisms are expected from application of aquatic herbicides containing endothall. It should also be noted that Aquathol® and Hydrothol® appear to be of similar toxicity to terrestrial organisms. Mitigation of possible effects on listed endangered species is best accomplished by following the mitigation sections for terrestrial plants, birds and animals. As stated previously, the best way to mitigate possible effects on all terrestrial species is to follow the directions listed on the label.

Other mitigation measures involve the contact of WDFW by the issuer of the permit to ascertain if any endangered species may be affected by the application of the chemical to the water body in question. Questions asked by the permit writer would ascertain if any resident endangered bird or animal species are known to use the water body in question or its shorelines or islands as breeding or forage areas, or if the application coincides with the migration of any endangered species. If endangered species are present, mitigation measures may involve postponing application until after the breeding season or postponement of application until after migration of the species in question. Use of an alternate means of control (i.e. mechanical) if the risk is determined to be too great to the species in question may also be an option.

#### **4.1.7 EFFECTS ON TERRESTRIAL PLANTS**

#### **4.1.7.1 Acute Effects of Endothall on Terrestrial Plants**

A study was conducted to assess seed germination, seedling emergence and vegetative vigor of plants exposed to dipotassium salt of endothall (Hoberg, 1992). Ten representative and economically important terrestrial plant species were evaluated following EPA guidelines. Each species was incubated and treated with the test material at or below the maximum application rate for this material (9.3 lb. A.I./A, via water (germination), silica sand (emergence) and foliar (vegetative vigor) routes of administration. Tests were conducted with cabbage, corn, cucumber, lettuce, oats, onions, radish, ryegrass, soybean and tomato. The lowest no observable effects concentrations (NOEC) for the three endpoints tested were as follows: Cabbage, 0.29 lb A.I./A; corn, 0.58 lb A.I./A; cucumber, < 0.15 lb A.I./A; lettuce, 0.018 lb A.I./A; oat, 0.073 lb A.I./A; onion, 0.15 lb A.I./A; radish, < 0.60 lb A.I./A; ryegrass, 0.0093 lb A.I./A; soybean, 0.019 lb A.I./A, and tomato, <0.037 lb A.I./A. These numbers are based on the most sensitive growth stage for the test species. The minimum effective concentration to inhibit growth in 25% of the tested species (EC25) value determined during this study was 0.0063 lb A.I./A for ryegrass (during the vegetative vigor phase).

A study was conducted to assess seedling emergence and vegetative vigor of plants (Hoberg, 1995) exposed to Hydrothol® 191. The lowest NOEC data for the endpoints tested is as follows: cabbage, 0.11 lb A.I./A; corn, 0.11 lb A.I./A; cucumber, 0.11 lb A.I./A; lettuce, 0.0064 lb A.I./A; oat, 0.034 lb A.I./A; onion, 0.030 lb A.I./A; turnip, 0.053 lb A.I./A; ryegrass, 0.015 lb A.I./A; soybean, 0.028 lb A.I./A; tomato, 0.079 lb A.I./A.

A determination of effects of Hydrothol® 191 on the seed germination of ten plant species was conducted (Hoberg, 1993). The effective concentration to inhibit growth in 50% of the plants (EC50) for cabbage, corn, oat, tomato and turnip was > 0.17 to < 1.7 lb A.I./A with the most sensitive parameter being radicle length. The soybean EC50 was > 0.17 < 1.7 lb A.I./A with the most sensitive parameter being percent germination. The EC50 for cucumber and onion was > 1.7 lb A.I./A with the most sensitive parameters being percent germination and radicle length. The EC50 for lettuce and ryegrass was > 0.017 to < 0.17 lb A.I./A.

These studies indicate that endothall can effect the growth rate of terrestrial plants at fairly low levels of application.

#### **4.1.7.2 Chronic Effects of Endothall on Terrestrial Plants**

No chronic studies have been found which assess the effects of endothall on terrestrial plants. However, due to the use pattern for endothall products in Washington State (one application per water body per year) chronic effects on terrestrial plants are not expected.

#### **4.1.7.3 Mitigation of the effects on Terrestrial Plants**

While endothall products are labeled for use on potatoes, hops, seed alfalfa and cotton, many terrestrial plants are highly susceptible to the effects of endothall (See seed germination, seedling emergence and vegetative vigor studies above). The main routes of exposure for terrestrial plants from aquatic herbicides are over spray/drift and the use of treated water as irrigation. In order to mitigate problems with agriculture, all labels for aquatic herbicides containing endothall have wording prohibiting the use of endothall

treated water for irrigation for from 7 – 25 days depending on the products and the application rate. In addition, all labels specifically state that contact or drift (over spray) to other plants or crops should be avoided as injury to the plants may occur. If these label directions are followed, adverse effects to terrestrial plants following application of endothall containing aquatic herbicides will be minimal.

#### **4.1.8 EXPOSURE ROUTES**

Regardless of the organism, aquatic exposure to endothall can take several routes. Those include absorption from the water column, the consumption of treated water or organisms while eating, contact with plants or sediments that have been treated with the test substance, or eating granules of the product in the case of Aquathol® Granular or Hydrothol® 191 Granular. More detail on exposure routes is given below:

- Aquatic algae: Exposure is through adsorption from the water column.
- Fish and aquatic invertebrates can be exposed to endothall by:
  - Absorption through the “skin” or cuticle.
  - Absorption through the gills, booklungs or lungs.
  - Absorption through the gut from the consumption of other animals or plant and algal material containing endothall.
  - Absorption through the gut after eating the formulated pesticide granules found at the bottom of the water body.
- Detritivores can be exposed through eating detritus found in the sediment or catching the detritus as it floats past.
- Although avoidance has been claimed for Hydrothol® 191 and the mono(dimethylalkylamine) component of this formulation by the manufacturer, we found no scientific evidence for this claim. However, applicators claim that skill and knowledgeable application of Hydrothol® from shore outline outward will drive fish from the application area. There is some evidence that salmonids and goldfish will avoid Aquathol® alone and will particularly avoid a combination treatment with dalapon at rates that approach field application rates [Dodson and Mayfield, 1979, Lorz et al, 1979, and Liguori et al, 1983 in (Berry, 1984) and Berry, 1984].

#### **4.1.9 ENVIRONMENTAL TOXICITY REVIEW: EFFECTS ON THE PHYSICAL AND CHEMICAL ENVIRONMENT THAT MAY AFFECT HABITAT**

*Summary: Sites that have never been exposed to endothall products may degrade Aquathol® and Hydrothol® more slowly than sites that have had a previous exposure history. This is because it normally takes several weeks for bacteria capable of using endothall as their sole carbons source to develop out of their lag-phase and rapidly degrade applied Aquathol® or Hydrothol® 191 if they have not been previously exposed. Rapid degradation leads to a very short half-life in non-flowing water, which is usually less than 10 days. However, if experienced degradation, sorption, and dilution factors are interacting, the field half-life in water can be less than one-day. Therefore, long-term persistence of Aquathol at concentrations that will cause environmental damage is not likely. However, due to the extremely high toxicity of the dimethylalkylamine constituent*

*of Hydrothol® 191, concentrations of Hydrothol® 191 although similar to those of Aquathol® may be high enough to cause observable damage to the biota.*

*Bioconcentration in plants and animals is not likely for Aquathol® or Hydrothol® 191. Most species of fish and aquatic invertebrates do not bioaccumulate dipotassium endothall. Some plants appear to bioaccumulate 14C labeled endothall at concentrations that are ~4-fold higher than environmental concentrations, but tissue analysis indicates that these residues are incorporated into natural plant constituents in the leaves and stems.*

#### **4.1.9.1 Potential Soil and Sediment Interactions**

##### **4.1.9.1.1 Impact of Various Soils (Sediment/Substrate) Composition**

*Summary: Due to their high water solubility and low soil/water distribution coefficient, Aquathol® (dipotassium endothall salt) and Hydrothol® 191 [mono(dimethylalkylamine) salt of endothall] do not adsorb well to most soils. Therefore the concentration of endothall in hydrosol is rarely higher than 0.5 mg a.e./L.*

Endothall will not adsorb well to most soils. For example, the adsorption coefficients (K<sub>d</sub>s) for endothall will typically vary from approximately 0.426 to 2.12 (Rheinert and Rogers, 1984). These low K<sub>d</sub> values indicate that sorption is not a significant factor affecting the fate of endothall in aquatic environments. This limited soil adsorption capability combined with high solubility (110,000mg/L to 650,000 mg/L) (Section 2.1.8 9 Solubility) suggest that the active ingredient in Aquathol® and Hydrothol® formulations will not be transported in soil and sediment.

However, Sikka and Rice (1973) have found that endothall disappeared from water in three phases: 1) Initial rapid disappearance attributed to adsorption to the hydrosol; 2) Further disappearance of endothall attributed to the proliferation of microorganisms with the ability to degrade endothall; 3) Longer persistence of endothall in sediment than in water attributed to decreased availability of bound endothall to the metabolic processes of these microorganisms.

##### **4.1.9.1.2 Potential for Increased Erosion and Re-suspension of Soils and Sediments from Plant Removal**

Since endothall products are applied directly to water and not the terrestrial environment, classic erosion, does not occur. Removal of plants from lentic water systems may allow for the re-suspension of sediment from the bottom of a lake or pond due to wind mixing of the water, interactions with benthic organisms, and direct effects of human beings with the hydrosol. However, the one published study in this area indicates that the water remained clear throughout the portion of an experiment that measured water clarity (June through August of 1973) (Serns, 1975).

The only possibility of classical erosion occurring during aquatic applications is if treated ponds evaporate or are drawn down. Under such conditions the previously submerged banks and bottom of the lake may become (temporarily) terrestrial environment subject to classical wind and water erosion. Erosion in these areas would initially be high due to lack of plant cover. However, dead aquatic vegetation would function like a mulch to help reduce erosion until the area is re-vegetated with terrestrial plants or re-flooded with

water. A worst case scenario could occur if the area does not re-vegetate before the dead vegetation completely decomposes and exposes the underlying soil/sediment to the erosion effects of wind and rain (water).

Without plant species providing soil stability, physical characteristics of the soil/sediment are the primary factors affecting soil erosion. The two most important soil characteristics affecting water-influence are infiltration capacity and structural stability. Soil texture, organic content and clay content also influence infiltration capacity (Brady 1974 in Ebasco, 1993), structural stability depends on the ability of soil/sediment aggregates to withstand breakup. This depends on many factors, including organic/inorganic component interaction that provides bridging between organic matter and soil clays (Brady, 1974 in Ebasco, 1993).

The Soil Conservation Service (USDA, 1978a in Ebasco, 1993) has developed simplified erodibility factors (K) based on soil texture of different topsoil and subsoil regimes. These K factors can be used as approximate erosion estimates. The K values listed in Ebasco (1993) are used in predicting rainfall erosion losses with the universal soil loss equation (USDA, 1978b in Ebasco, 1993) and may be used as relative indicators of erosion across different soil texture classifications.

In the case of canals treated with Aquathol® K, Hydrothol® 191 Granular or Hydrothol® 191, erosion is unlikely to be a problem. The major aquatic weed problems in irrigation canals are emergent weeds and fully aquatic species including Sago pondweed, aquatic moss and milfoil; and hydrilla has been a problem in California. However, there are times during the season when algae, submerged weeds or floating weeds may become a problem. Algae may effect the quality of the water used for irrigation purposes and submerged or floating weeds may effect the flow of the canal. These herbicides are used to control both algae and aquatic macrophytes within the flowing water of the ditchbank or canal. Canals typically are constructed with 3:1 bank slopes and are designed to convey peak demand flows without eroding. The main objective in canal design is to minimize water loss from the canal and maximize flow. Therefore irrigation districts actively remove nuisance plant growth. Irrigation canals are typically designed to operate at capacity under unvegetated conditions, therefore removal of submergent and floating weeds is unlikely to result in destabilization of irrigation canals. However, depending on site specific conditions, erosive processes and the amount of sediment trapped by submerged plants, removal of these plants may contribute to limited sediment erosion and transport.

#### **4.1.9.1.3 Effects on Pristine Sites**

If the treatment site has not experienced endothall treatments before, it can take several weeks before the resident bacteria become active and start degrading endothall at their maximum potential. Presumably, the slow initial period represents the time during which the microorganisms capable of degrading endothall develop (Sikka and Rice, 1973). Prior to this development, physical processes such as sorption may remove endothall from the water body. (See Section 4.1.9.1.1 for an explanation of the process of physical removal of endothall). Due to the combined effects of the biodegradation and the adsorption process, the concentration of endothall in the aqueous phase decreases during the first couple of days while the concentration in the hydrosol increases. Under aerobic conditions, *Arthrobacter* and other bacterial species degrade endothall to natural products

including citric acid, amino acids, nucleic acids and eventually CO<sub>2</sub> that will be incorporated into the soil/sediment complex.

#### 4.1.9.1.4 Habitat Effects of Removing Endothall from Previously Unexposed Sites

Although the site can no longer be considered pristine in a strict sense, the action of resident microbes should allow for the rapid elimination of endothall as a “pollutant” from the habitat and return the water body to a condition suitable for the resident biota. New plants should root rapidly and provide organisms with new surface to colonize and free-swimming organisms refuge sites to hide from predators and build nests in. In addition, this new growth will provide habitat and food for waterfowl (Frank, 1979). Since the levels of endothall can potentially build up in the hydrosol during the lag phase of bacterial growth, the habitat of bottom dwelling organisms may be effected. It is known that species like *Gammarus fasciatus*, that use sediment as their preferred habitat, are not significantly impacted by Aquathol® K products (LC<sub>50</sub> = 222 mg a.e./L). This should provide a sufficient safety factor with an Risk Quotient (RQ) of ~0.002 since one would not expect to find endothall in sediment at concentrations higher than 0.5 mg a.e./L in waters treated with 2 mg a.e./L (Sikka and Rice, 1973).

Using similar calculations for Hydrothol® 191 does not present a safe acute risk picture for sediment organisms. The sediment organism LC<sub>50</sub>s for Hydrothol® range from 0.22 to 0.72 mg a.e./L. This results in a RQ for the most sensitive test species of 2.3 (0.5 ppm/0.22 ppm) which is considerably above the acute level of concern of 0.1 (Urban and Cook, 1985 in Giddings, 1999).

#### 4.1.9.1.5 Effects on Contaminated Sites

If the site has experienced endothall treatment previously, the bacteria present will start rapidly degrading endothall almost immediately (Sikka and Rice, 1977). However, if oxygen-free conditions exist *Arthrobacter* species are not capable of metabolizing endothall to the previously mentioned natural products. This is a consideration when treating heavily weed-infested ponds or lakes completely with endothall where stripping of the dissolved oxygen content is likely to occur. (Sikka & Rice, 1973, Sikka and Saxena, 1973, Simsiman et al, 1976, Simsiman & Chesters, 1973, Reinert and Rogers, 1984 and Reinert et al., 1986). In this situation, endothall will remain in the water and soil/sediment environment for longer periods of time and has potential to effect benthic organisms. There is very little data on chronic or life cycle effects of endothall on invertebrate organisms, but the data that is available indicates that endothall acid will probably be safe to free-swimming marine invertebrates chronically exposed to endothall (Aquathol® K) chronic (EC<sub>50</sub> = 24 mg a.e./L; chronic NOEC = 5 mg a.e./L). This chronic toxicity evaluation is based on one evaluation with *Daphnia magna* and therefore, the uncertainty of these results is quite significant.

#### 4.1.9.2 Environmental Persistence

*Summary: Endothall® degrades more slowly at newly treated sites than sites that have had a previous exposure history. It may take several weeks for bacteria capable of using endothall as their sole carbon source to develop out of their lag-phase and rapidly degrade applied Aquathol® or Hydrothol®. Such rapid degradation leads to a very short half-life in non-flowing water, which is usually less than 10 days. However, if degradation, sorption and dilution factors interact, the field half-life in water can be less*

*than one-day. Therefore, long-term persistence of Aquathol® at concentrations that will cause environmental damage is not likely. However, due to the extremely high toxicity of the dimethylalkylamine constituent of Hydrothol® 191 similar to those of Aquathol® may be high enough to cause observable damage to the biota.*

*Bioconcentration in plants and animals is not likely for Aquathol® or Hydrothol® 191. Although the mosquito fish has been observed to bioaccumulate endothall at tissue levels that are 10-fold higher than environmental, most species of fish and aquatic invertebrate do not bioaccumulate dipotassium endothall. Some plants appear to bioaccumulate 14C labeled endothall at concentrations that are ~4-fold higher than environmental concentrations, but tissue analysis indicates that these residues are incorporated into the natural plant constituents in the leaves and stems.*

In most non-flowing water (i.e. lakes) cases the environmental persistence of endothall products in the field is short; the half-life in water is usually less than 10-days in water (Atochem, 1998, State of Wisconsin, 1990 in Ecology, 1993, Keckemet & Sharp, 1999), Reinert & Rogers, 1987, Rogers, et al, 1992, Yeo, 1979 in Dynamac, 1990). The rate of dissipation in the field is controlled by a number of factors including presence of *Arthrobacter spp.* associated with appropriate sediment (Simsiman & Chesters, 1975), adsorption of endothall by aquatic weeds, amount of dissolved oxygen in the water depth of the water column (Simsiman and Chesters, 1975) and prior experience of the sediment associated bacteria in degrading endothall (Sikka & Rice, 1973). If degradation, sorption and dilution factors are considered, the field dissipation half-life in water can be considered to be less than one day. See Section 4.1.10.2.5.

Due to their low adsorption coefficient (Reinert & Rogers, 1984), endothall products usually do not accumulate on sediment. However, when endothall products do adsorb onto sediment at up to 2 mg/L they are eliminated rapidly, usually within 2 to 4 days (Kechemet & Sharp, 1999).

#### **4.1.9.2.3 Persistence in Water**

A detailed review of the persistence of endothall in water can be found in Section 3.1.4. The half-life for endothall ranges from 1 to 10 days depending on the conditions found in the water at the time of treatment. However, the most representative half-life is 4.1 days (Reinert & Rogers, 1987). Endothall products have been noted to persist in water at low levels for up to 36 days and could be found as high as 0.02 mg a.e./L at 29 days when the initial treatment concentration was 2 mg a.e./L (Sikka and Rice, 1973). Using such basic information Ecology (1991) estimated the typical weighted expected environmental concentration to be 1.0 mg a.e./L at four days for Aquathol® K and 1.43 mg a.e./L at four days for Hydrothol® 191. For a 28 day period, Ecology estimated the weighted expected environmental concentration to be 0.06 mg a.e./L for Aquathol® K and 0.02 mg a.e./L for Hydrothol® 191.

#### **4.1.9.2.4 Persistence in Sediment**

A detailed review of the persistence of endothall in sediment can be found in Section 3.1.4. The half-life for endothall in sediment is usually not relevant as endothall does not adsorb readily to sediment. Exposure of sediment organisms is generally believed to be influenced by pore-water which will have concentrations similar to the over lying

water in cases where adsorption of the herbicide to sediment plays a minimal role in environmental dissipation. Concentration in sediment can briefly be as high as one or two mg/L but usually dissipates within 2 to 4 days to <0.1 mg/L. (Keckemet & Sharp, 1999). However, in at least one case the concentration of endothall has been known to be present in sediment at concentrations of 0.25 mg/L for up to 28 days and can persist at detectable levels for up to 44 days (Sikka and Rice, 1973). An actual sediment half-life is difficult to predict since the concentration in the hydrosol may continue to increase for several weeks after treatment due to interaction with endothall that remains in the aqueous phase.

#### **4.1.9.2.5 Persistence in Soil**

The presence of endothall (Aquathol® or Hydrothol® 191) in soil is not expected from aqueous treatment unless flooding occurs or the water is used for irrigation prior to the end of the water use restriction imposed by the labels. Details on the persistence of endothall products in soils can be found in Section 3.1.3. The effects of flooding or irrigation are presented in Table 3 where various crops were treated at various rates from 3 to 100 mg a.e./L. Hydrothol® was phytotoxic to spinach and lettuce at concentrations of 3 and 10 mg a.e./L, respectively. Since Hydrothol® is not phytotoxic to agricultural crops when taken from irrigation ditches, it is unlikely that Aquathol® would be toxic under the same circumstances.

On field soils, residues in the top 0 to 4 inches of soil had a half-life ranging from 7 to 19.2 days in California and Pennsylvania when the soils were treated with 1.04 lbs. a.e./acre (1.17 Kg/ha) (Wright, 1993). The level of Hydrothol® that the crop would be exposed to if irrigated or flooded with 3 to 10 mg a.e./L would be 8 to 30 pounds/acre (9.0 and 27 Kg/ha), respectively.

#### **4.1.9.2.6 Potential for Bioaccumulation or Bioconcentration in Fish, Aquatic Invertebrates, Phytoplankton, Zooplankton, Birds, Mammals and Insects**

The potential for bioaccumulation (BAF) and bioconcentration (BCF) is extremely low. The bioconcentration factor can be predicted throughout most of its range from the following equation:  $BCF = K_{ow} \times 0.05$ . The BCF is predicted to be less than unity for all endothall products [0.0004 for endothall acid, <0.05 for dipotassium endothall (Aquathol®) and <0.05 for the monodimethylalkylamine salt of endothall (Hydrothol®)]. Since the octanol/water partition coefficient ( $K_{ow}$ ) is very low for all endothall products [0.0081 for endothall acid, <1.0 for dipotassium endothall (Aquathol®) and <1.0 for monodimethylalkylamine salt of endothall (Hydrothol®)], little bioconcentration or bioaccumulation is likely to occur. Exact values are difficult to predict when the  $K_{ow}$  is significantly less than unity. Also the solubility of endothall products is very high in water. Therefore, it would not be expected that this extremely hydrophilic compound would either bioconcentrate or bioaccumulate.

- **Bioaccumulation and bioconcentration**

Endothall is rapidly adsorbed by most aquatic plants (Thomas, 1996 in Davis 1999 and Formella, 1998 in Davis, 1999). However, after exposure of Coontail, *Potamogeton nodosus*, or *Elodea canadensis* to radiolabeled endothall at ~5 ppm, the plants accumulated the radioactivity at concentrations of about 4-times the concentration applied to the water. This conflicts with the BCF predicted by Lockhart

et al. (1973) in EPA (1988). Lockhart et al predicted that *Lemna* would not bioconcentrate endothall (Aquathol® K) based on the extremely low Kow (Kow = << 1.0). However, extensive break down and incorporation of the radiolabeled material into leaf tissue and other plant constituents appears to occur (Thomas, 1966 and Freed & Gauditz, 1961 in Davis, 1999). These researchers believe that plants do not metabolize endothall directly. Any metabolism of endothall that appears to occur in plant tissue is probably due to the metabolic action of *Arthrobacter spp.* which metabolize endothall into various components including citric acid, glutamic acid, aspartic acid, alanine, other amino acids, proteins, nucleic acids and lipids. These products are ultimately incorporated into the plants cellular products and/or eventually released as carbon dioxide (CO<sub>2</sub>).

After field exposure of sediment, fish, mollusks and plants to nominal concentrations of Aquathol® K of 1.5 mg/L in water for seven days, no endothall (<0.2 mg/L) could be detected. This is not surprising in light of a half-life of 1.1 to 1.2 days for Aquathol® in the Guntersville, Alabama reservoir water where the study was conducted. This level of Aquathol® K treatment, effectively controls aquatic macrophytes and has a low toxicity to non-target organism (Rogers et al., 1992).

Serns (1977) found that fish in a Wisconsin pond treated with 5.0 mg a.i./L Aquathol® did not bioaccumulate endothall. The BCF values obtained from bluegill sunfish in this study ranged from 0.003 to 0.008. Elimination of endothall occurred rapidly from these fish with less than <0.01 mg a.e./L detected in the fish tissue after three days despite concentration in the water column remaining high (6.2 to 3.4 mg a.e./L) for the first 10 days (Table 7).

Endothall does not bioconcentrate or bioaccumulate in most aquatic fauna. In bluegill sunfish, the bioconcentration factor was less than unity (<1.0) for edible (BCF = 0.05), inedible (BCF = 0.3) and whole fish tissues (BCF = 0.2). A steady state was reached in all bluegill tissues in less than 7 days using carbon-14 radiolabeled endothall. The elimination half-life for the resident 14C was less than one day for the whole body and for inedible tissues. After residues reached steady state in tissues, fish were moved to clean water to allow release of tissue residue. After 14-days there was less than 50% release from edible tissue. 88.4% of the accumulated radioactivity, was bound and unextractable from edible tissue. Of the remainder, 3.4% was non-polar, and 13.6% was polar (possibly endothall) (Dionne, 1992, and Sikka et al, 1975).

When bluegills ingested endothall at 10 mg endothall/Kg tissue, 73% of the administered dosage was eliminated in 48 hours. Fish exposed for 48 hours to water containing 2 ppm endothall did not degrade endothall; it was extracted unchanged from the tissue (Sikka, et al., 1975). This work supports data from Dionne (1992) that had a much longer exposure period (28 days).

Studies to characterize the radioactivity in fish tissue demonstrated that dipotassium endothall was extensively degraded and incorporated into endogenous natural products including fatty acids, cholesterol, glycerol, amino acids and carbohydrates (succinic acid and other Krebs' Cycle Intermediates Dionne, 1994). It is likely that this degradation was accomplished by *Arthrobacter* or other microorganisms that are known to metabolize endothall.

Similar metabolic pathways were noted in channel catfish, bluegills, freshwater clams and northern crayfish after exposure to potassium endothall at 5.0 mg a.i./L (3.5 mg a.e./L) for up to 7-days in a static aquatic system containing water and soil/substrate. None of these organisms accumulated endothall. The highest levels of endothall acid found in aquatic animal tissue was non-detectable in catfish, 0.035 mg a.e./Kg in bluegill, 0.23 mg a.e./Kg in northern crayfish and 1.1 mg a.e./Kg in freshwater clams. Results of these studies showed no bioaccumulation of endothall in any of the species tested (Dionne et al., 1999). The bioconcentration factor (BCF) in these aquatic organisms were therefore <1.0 in all cases.

However, previous work has shown that bioconcentration can vary slightly between different classes of organisms. Insensee, 1976 (Reinert and Rogers, 1987) demonstrated a BCF of 10 in mosquito fish while Insensee, 1976 and Walker, 1963 in Reinert and Rogers, 1987 and EPA, 1988) demonstrated a BCF considerably less than one in several fish species for Aquathol® K and Hydrothol® 191. These values are in line with the predicted values of Neely et al. (1974) and Chiou et al (1977) in Reinert and Roger (1987) and in EPA (1988) who predicted from Kow/BCF regressions that Aquathol® K and Hydrothol® 191 would have BCFs of 0.65 and 1.05 respectively.

Some organisms will temporarily bioconcentrate endothall residues to levels that exceed two orders of magnitude. For example, the water flea, green algae (*Oedogonium*) and the snail (*Physa*) bioconcentrated endothall to levels of 150, 63 and 36, respectively (EPA, 1988 and Reinert and Rogers, 1987). However, endothall concentrations within the organisms were rapidly eliminated and were not passed (bioaccumulated) up the food chain.

- **Persistence within the organism**

Most organisms do not bioconcentrate endothall and those that do, do not pass the concentrated endothall along the food chain (Reinert and Rogers, 1987). Fish that have adsorbed endothall from the water eliminate the majority (more than 50%) of endothall from their tissues within one, two, or three days (Dionne, 1992, Serns, 1977 and Sikka, 1975). Seventy-three percent of the orally administered endothall was eliminated by bluegill sunfish within 48 hours of administration. In the field, caged bluegill sunfish grown in ponds treated with 5.0 mg/L endothall have eliminated all of the endothall in their tissues within three days of treatment; less than 0.01 mg a.e./Kg can be detected in fish tissue three days (Table 7).

- **Potential impacts on the food chain**

The fact that there is little tendency of endothall to bioconcentrate in sediment, plants, or animals combined with rapid elimination of endothall administered orally to fish makes it unlikely that endothall is bioaccumulated as it is transported up the food chain. This observation is also supported by observations that 90% of orally dosed endothall is eliminated from experimental fish, rats, cow and chickens in the feces and or urine. Residues in meat milk and eggs are negligible and are not detected after two days (Davis to Morrissey, 1997 in a letter from Elf Atochem to EPA's Office of Toxic Substances).

#### **4.1.9.3 Potential Impacts of Water Quality on Survival of Aquatic Organisms**

#### 4.1.9.3.1 Effects of Physiological Sustaining Water Chemistry

*Summary: Exposure of living plant tissue to endothall products or other herbicides usually results in secondary effects that may impact the biota. When plants start to die, there is often a drop in the dissolved oxygen content associated with the decay of the dead and dying plant material. Reduction in dissolved oxygen concentration may result in aquatic animal mortality or a shift in the dominant form or diversity of biota. There may also be changes in the levels plant nutrients due to release of phosphate from the decaying plant tissue and anoxic hypolimnion. Also ammonia may be produced from the decay of dead and dying plant tissue and may reach levels that may be toxic to the resident biota. Ammonia may be further oxidized to nitrite, which is also toxic to fish. The presence of these nutrients may cause an algal bloom to occur. However, if significant living plant biomass persists after treatment, the released nutrients may be removed before an algal bloom can occur. Hardness and pH will not have an impact on the toxicity of disodium endothall salts when they are used at concentrations typically found in the field. However, Hydrothol® 191 may exhibit significantly higher fish-kill in hard water than in soft at application rates that are typically found in the field since the acute predicted environmental concentrations are approximately equal to the LC50 (1.18 to 1.6 mg/L) in soft water and as much 2 to 5-fold higher than the LC50 (0.32 to 0.96 mg/L) in hard water.*

- **Potential impacts of dissolved oxygen**

The key factor to survival and maintenance of the aquatic environment is adequate dissolved oxygen. Ideally the oxygen content of the water should be as close to saturation as possible. For warm water environments (15 to 25°C) oxygen saturation is 10 mg/L at 15 degrees and 8.2 mg/L at 25°C. For cold water environments (5 to 15°C), oxygen saturation is 12.2 mg/L at 5°C and 8.2 mg/L at 15 degrees centigrade. Cold and warm water are somewhat arbitrary designations. Table 8 shows the sea level saturation concentration for oxygen at temperatures from 5 to 25°C.

In general, warm water fish like sunfish, bass, catfish, carp and shiners can survive and reproduce at oxygen concentrations of about 5 mg/L (Littler, 1983, personal communications). Cold water fish, need much high dissolved oxygen concentrations for long term survival. It is unlikely that cold water species could go through a life cycle at dissolved oxygen concentration below approximately 9.0 mg/L (Welch, 1992 in Shearer et al, 1996).

Treatment with endothall products usually does not produce adverse changes in pH, and nutrient levels. However, treatments may cause an oxygen slump from saturation (10 mg/L) to about 6.0 mg/L and last for several days to several weeks (Serns, 1977). Daniels (1972) and Simsiman et al (1972 in Serns, 1977) reported that endothall treatments caused a pronounced oxygen sag 16 to 27 days and 21 to 23 days after treatment, respectively. Although warm water fish can live and breed in water with a dissolved oxygen content of 6.0 mg/L oxygen slumps of this magnitude would prevent most salmonids from breeding successfully.

- **Potential impacts of ammonia, nitrite and nitrate production**

It is rare that nitrogen is the limiting factor for production within a freshwater body. The ability of several species of blue-green algae to fix nitrogen makes any additions of nitrogen to water bodies a minor issue. However the toxicity of ammonia and nitrites to aquatic organisms can be an issue. Experimental endothall treatments have failed to produce significant increases in ammonia, nitrate and nitrite. Shearer and Halter (1980) interpreted the work of Simsiman et al (1972 in Serns, 1975) and Daniel (1972 in Serns, 1975) to show that an increase in the availability of nitrogen and phosphorus after treatment with endothall may have contributed to algal blooms in model ecosystems.

However, Serns (1975), interpreting his own work and that of previous investigators found that while there was a slow release of nitrogen and phosphorus, it was rapidly adsorbed by unaffected plants. Although there was a moderate growth of filamentous algae (*Cladophora* spp.) in both the control and treatment ponds, it was not considered to be of nuisance proportions. Although slowly released nitrogen and phosphorous may have contributed to plant growth in the treated ponds, it certainly did not contribute to an algal bloom.

In Washington waters, even a small release of ammonia can be a serious issue. The whole lake levels of ammonia-nitrogen in Lake Steilacoom during the 1995 season exceeded the criterion of 0.100 mg/L during the months of May and October. These levels of ammonia are toxic to fish and near-shore runoff containing fertilizers may have contributed to the October ammonia peak (Shearer et al., 1996). These levels of ammonia are higher than the maximum recommended levels for the culture of aquatic organisms and are higher than the EPA criteria (0.091 mg/L) for 4-day exposure of salmonids.

The toxicity of ammonia increases with both temperature and pH. As temperature and pH increase, the amount of unionized ammonia increases (Table 7). The unionized forms of ammonia ( $\text{NH}_4\text{OH} + \text{NH}_3$ ) that are toxic to aquatic animals. The ionized form of ammonia ( $\text{NH}_4^+$ ) is almost harmless (Goldman and Horne, 1983).

Adsorption of nitrogen containing nutrients by aquatic macrophytes and algae can influence the seasonal dynamics of nitrite and nitrate concentrations. The levels of nitrite/nitrate are often higher at the surface of a lentic water body than at the bottom because under anoxic conditions, some bacteria utilize nitrate as a terminal electron (Hydrogen) acceptor when oxygen is not available.

Nitrite although fairly toxic, is rarely a problem in well aerated waters because it is rapidly converted to nitrate and under anoxic conditions it is rapidly converted to ammonia. Nitrate is usually not toxic in the quantities found in lakes and rivers (up to 1 mg/L) with the drinking water standard being set at about 10 mg/L. Polluted streams can contain up to 2 mg/L of nitrite and small areas near the thermocline may contain relatively large quantities of nitrite. Pollution can theoretically be caused by sewage, agricultural waste or other decaying matter including aquatic plants killed by herbicides.

If nitrogen is the limiting nutrient, nitrate can participate in the next algal bloom. Nitrate and nitrite are formed from the oxidation of ammonia and may persist long

after the ammonia has been utilized by algae and plants in their biological processes. However, from the time ammonia becomes in short supply, it may take several days for the next bloom to occur because nitrate uptake is slow relative to ammonia uptake and induction of nitrate reductase in algae is also fairly slow. Nitrate must be reduced to ammonia in algae prior to the initiation of an algal bloom; algae cannot use nitrate directly and it must be converted to ammonia before it is utilized in their biological processes (Goldman and Horne, 1983).

- **Potential impacts of nutrient cycling and the release of phosphates and other plant nutrients**

Phosphate is usually the limiting nutrient in freshwater aquatic systems because it is tied up in growing plant and animal tissue as well as the sediment. Typically the sediment retains phosphorus under aerobic conditions and releases it under anaerobic conditions. This released phosphate may result in growth of phytoplankton in the hypolimnion provided that the depth is not so great that photosynthesis is precluded. When plants are treated with endothall or other herbicides they die, and degradation of the plant tissue by microbes can cause phosphate and other nutrients to be released. Phosphorous in its organic form, cannot be utilized and must first be converted to phosphate (PO<sub>4</sub>) by excretion and decay. Normally, phosphates will be at very low levels in the epilimnion even in eutrophic lakes and rarely exceed 0.020 mg/L in the summer or 0.030 mg/L in the winter. Nitrate and ammonia levels on the other hand are often many times higher than the phosphate levels and plants typically require a 7:1 Nitrogen/Phosphate ratio by weight for a maximum growth rate. Therefore, phosphorous depletion is likely in many freshwaters. Therefore the treatment of a water body with endothall has the potential to cause an algal bloom.

Shearer and Halter (1980) interpreted the work of Simsiman et al (1972 in Serns, 1975) and Daniel (1972 in Serns, 1975) and concluded that an increase in the availability of nitrogen and phosphorus after treatment with endothall may have contributed to algal blooms in model ecosystems. However, Serns (1975) interpreting his own work and that of previous investigators found that while there was a slow release of nitrogen and phosphorus, it was rapidly adsorbed by unaffected plants. Although there was a moderate growth of filamentous algae (*Cladophora spp.*) in both the control and treatment ponds, it was not considered to be of nuisance proportions. Slowly released nitrogen and phosphorous may have contributed to plant growth in the treated ponds, but did not contribute to an algal bloom.

The only other nutrient, which frequently is in short supply, is iron. Ferric iron may either react with or be adsorbed with phosphate into the sediments under typical oxic conditions and become biologically unavailable. Under anaerobic conditions, ferrous iron is formed from ferric iron/phosphate complexes and is released into the hypolimnion (bottom layer of a lake containing much colder water) where plants may utilize it for growth provided that the light is sufficient for photosynthesis to occur. E<sub>h</sub>, (Redox potential) pH and DOC govern this reaction. Unfortunately, the different nature of water/sediment phase reactions prevents easy extrapolation of laboratory results to real lake sediment systems. Iron availability may limit the growth of algae in lakes and streams especially when the production of ammonia due nitrogen fixations is the limiting factor in algal growth (Goldman & Horne, 1983, Reid, 1961).

Typical nutrient cycling starts with the bloom of algae, which comes to an end when one of the nutrients or other factors become in short supply. At that point the algae die and release phosphates, iron and ammonia through the degradative process. When enough of the nutrient in shortest supply becomes sufficient to sustain growth, algae will start growing quickly again and will result in an algal bloom if conditions of light, temperature, pH, N: P ratio, and iron concentration are adequate to sustain a log phase growth.

- **Potential impacts of pH and water hardness changes**

The pH of most natural waters falls between 4 and 9. A pH of 7 is neutral, neither acid nor basic. One important way in which pH is controlled is by removing carbon-dioxide from the water. A pH of greater than 8 in a lake or pond is probably due largely to a high rate of photosynthesis, which increases pH by removing carbon dioxide from the water. If the pH of a lake or pond is low (<6), it probably is due to leaching of organic acids from peat, anthropogenic sources such as acid rain or leachate from mines. Bottom waters are typically lower in pH than surface waters because bacterial respiration and decomposition of organic matter produces carbon-dioxide and organic acids which lower pH (Shearer, 1996).

After aquatic macrophytes die off, the pH may drop. If an algal bloom occurs after the release of nutrients, the pH may rise due to the removal of carbon-dioxide from the water column by photosynthesis. A pH that is either too high or too low may be directly lethal to fish. A pH greater than 9 can be directly lethal to fish. Toxicity for high pH arises from the inhibition of ammonia secretion by gills and respiratory alkalosis (Heath, 1995 in Shearer, 1996). Sub-lethal alkaline or acidic conditions can indirectly harm fish and other aquatic animals by increasing their susceptibility to other stresses such as pollutants (like endothall), ammonia, high temperatures and low dissolved oxygen.

Although not directly connected to pH, hardness can have an effect on the toxicity of herbicides. Hard waters, due to the presence of bicarbonate, have a tendency to be alkaline (basic) while soft water, due to the presence of low bicarbonate levels has a tendency to be acidic. (Hard water is defined as water containing >275 mg calcium carbonate/L, and soft water is defined as water containing <27 mg calcium carbonate/L). Hardness often effects the toxicity of herbicides. This appears to be true for disodium endothall salt although the difference in toxicity of disodium endothall salt in soft and hard water appears minimal. The trend is a slight decrease in the toxicity of sodium endothall salt in hard water, that is to raise the LC50 slightly. For example, Surber and Pickering (1962 in Serdar, 1993) found that bluegill sunfish had a tolerance (LC50) for disodium endothall salt of 160 mg/L in soft water and 180 mg/L in hard water. Fathead minnows had a similar tolerance for the same herbicide, 320 mg/L in soft water and 610 mg/L in hard water. However, this slight increase in toxicity due to the effects of hard water is unlikely to have significant impact in the field where the maximum use rate would be 5.0 mg/L.

However, Finlayson (1980) found an effect strongly reversed to this trend with the Hydrothol® 191 products; golden shiner had a tolerance of 1.6 mg/L for soft water and 0.32 mg/L for hard water. In variety of species, there were trends for differences in the toxicity of endothall products due to hardness (Table 10). But in general,

Hydrothol® products appear to be significantly more toxic in hard water than in soft water.

Finlayson (1980) indicates that in the field, Hydrothol® 191 is probably more toxic in hard water than in soft water. The toxicity is such that field testing showed high mortality in fish when irrigation channels of the Imperial Valley were treated with 0.2 to 0.5 mg Hydrothol® 191/L for 120 hours. The susceptible species included channel catfish (*Ictalurus punctatus*), threadfin shad (*Dorosoma petenense*), red shiner (*Notropis lutrensis*) and mosquito fish (*Gambusia affinis*). However, green sunfish and carp showed no mortality in irrigation ditches treated at 0.5 mg Hydrothol® 191/L, “some” mortality in areas treated with 1.0 mg/L and high mortality in areas treated with 3.0 mg/L. The conclusion reached was that since hydrilla cannot be controlled at Hydrothol® treatment rates of 0.5 mg/L, effective control of hydrilla can only be achieved with a great loss of fish. This seems to be a reasonable conclusion based on typical label use rates for hydrilla control of at least 1.0 mg a.e./L. Therefore hydrilla control with Aquathol® products is a more reasonable control measure because the fish acute LC50 in hard water is greater than 120 mg a.i./L (>85 mg a.e./L). Fish should be safe if the labeled rate for hydrilla control with Aquathol® products is used.

#### 4.1.9.4 Effects of Endothall in Water

*Summary: In the State of Washington, pesticides that exceed the Federal drinking water standard (MCL) have not been found in public drinking water in any counties east of the Cascade Mountains. In some situations throughout the country, dipotassium endothall has been seen in ground water where recharge areas have been treated with Aquathol® K. These recharge areas usually had porous bottoms (sand or gravel) with clay layers located below the bottom of the well shaft. Usually, water treatment plants that are located a mile or more down stream from the treatment site will not experience concentrations of endothall higher than the Federal drinking water standard due to extensive dilution and lateral mixing. Endothall is not likely to be found in the water of sewage outfalls since waste water treatment plants only process water from household waste and water runoff from street level. Therefore, endothall from treatment of public water bodies will not be found in waste water outfalls. Due to the short half-life of endothall in water bodies, additional procedures for removing endothall from sewage outfalls or potable water systems is not necessary; however, natural bacteria have the potential to remove excessive endothall from any water system in which they are found.*

According to Scott Fink (2000, personal communications) of the Spokane Department of Health: Drinking Water Division, for all counties east of the Cascades, herbicides have never been detected above the Federal Drinking Water Standard in the surface water system. In public well water there has never been a herbicide detection that exceeds the EPA’s Drinking Water Criterion. The current MCL for drinking water is less than 0.100 mg/L for endothall products. However, there have been a few cases where herbicides were found in well water at concentrations that exceed Washington States Detection limits.

- **Potential impacts on recharge areas**

In light of the above findings, it is unlikely that endothall will have an adverse impact on sensitive well recharge areas. There has been one recent case of well

contamination with endothall due to the pumping of water upland from a treated lake that could have been considered a recharge area. 32.5 gallons of endothall were applied over a 2.7 acre periphery of an 11.7 acre Michigan Lake. This works out to a calculated rate of about 5.4 mg a.i./L (3.85 mg a.e./L) for the periphery of the lake assuming an average depth of one foot or 1.33 mg a.i./L (0.95 mg a.e./L) for the entire 11.7 acre lake. A pumping well was installed 12 feet from the edge of the lake and water was pumped from this well at a rate of 2.5 gal/min. Thirty samples were collected over 43 days from wells located 5 feet out in the lake (LW), 5 feet from the lake edge (OW2) and from the pumping well.

After 6-days, the lake well (LW) exhibited a high of 0.080 mg/L. At 11-days OW2 exhibited a high endothall concentration of 0.130 mg/L and the pumping well exhibited a high endothall concentration of 0.020 mg/L on day-12. After 40 days the concentration in all three wells fell to below the detection limit (0.010 mg/L). This is of concern since the high concentration in the lake edge well is higher than the current U.S. EPA MCL level of 0.100 mg/L although it remained below the current 10 day health advisory level (HAL). Previous work at a the same site indicated that when endothall was applied at 2-times the typical field rate, endothall occurred in groundwater at 0.280 mg/L after 2 to 4 weeks. This concentration is higher than the 0.200 mg/L drinking water criterion that was in effect in 1988 when this study was conducted.

At first examination this data is alarming. However, some factors that made the observations unrealistic were that the wells were very shallow (not more than 12 feet deep) and the soil (soil/sediment) was very porous consisting of tailings from a gravel mining operation. Also the location of the wells was closer to the water (-5 feet, 5 feet and 12-feet from the water's edge) and the most upland well maintained a pumping rate of 2.5 gallons/min throughout the duration of this study.

Each year numerous permits are issued by other states specifying a required "isolation distance" be maintained between the area of application and drinking water wells. The isolation distances are based upon several factors including herbicide mobility, environmental half-life, and toxicity. Endothall is very mobile, has a short half-life ( $t_{1/2} = \sim 4.1$  days) and fairly low toxicity. Clearly, none of these procedures given in the above case are standard practice but it does indicate the problems that can occur if state guidelines are not followed. The Michigan state guidelines were not specified in this report (Lovato et al., 1999 and Ragalbuto and Payne, 1988 (in Lovato et al, 1999)).

- **Impact of pesticide application on down stream water treatment plants**

Due to rapid degradation and dilution with untreated water, the effects of endothall on down stream water treatment plants is expected to be minimal.

After a treatment of 3.0 mg endothall/L at a site in Pinopolis Cove, only 0.02 to 0.03 mg/L of endothall was detected in raw untreated water at the Santee Cooper (South Carolina) water treatment plant 2 to 4 days after treatment. Seven-days after treatment <0.01 mg endothall/L were found at the water treatment plant (Ritter & Williams, 1991). The water treatment plant is located about one mile from the treatment site. These concentrations are below the current maximum allowable drinking water level of 0.100 mg/L for endothall.

Work by Serdar & Johnson, 1993 indicates that when one end of Gravelly Lake near Tacoma, WA was treated at a 3-4 mg/L endothall, the concentration of endothall at the center of the lake was 0.04 mg/L after eight days. Through 16 days of the experiment, no endothall was detected at the bottom of the water column in the center of the lake.

“The available data indicate that under similar scenarios in western Washington, endothall does not persist in the water column of treated lakes, nor does it significantly affect water quality. Results of this survey also suggest that significant downstream transport is not likely to occur (Serdar & Johnson, 1993)”.

- **Presence of pesticide in the outfalls**

Because the concentrations of endothall are low at water intake pipes only three or four days post treatment, the amount of endothall in the outfall of drinking water or waste water treatment plants is likely to be negligible. In Eastern Washington, there has never been any herbicide detected in surface water systems (Scott Fink, Spokane Department of Health: Drinking Water Division, 2000, personal communications). Since wastewater treatment plants only process water from household waste and water runoff from street level, endothall from treatment of lakes, ponds, streams and irrigation canals will not be present in the outfall (Jim Milton, Ecology Manager of Sewage Treatment Plant Permits, 2000).

It has been proposed that Hydrothol® 191 be used in wastewater treatment plants to lower the total dissolved solids due to the growth of blue-green algae in the water of the plant. In an experiment using Hydrothol®, three days after treatment with 3 mg a.e./L the levels of endothall detected in the microcosm water was <0.015 mg a.e./L. Similar experiments in whole ponds using 1.5 mg a.e./L gave algal control that was similar to the microcosm studies but endothall persisted for a longer time due to lower temperatures. However, the authors believed that Hydrothol® 191 could be useful in controlling total suspended solids in wastewater stabilization ponds (Axler et al, 1994). Certainly, if Hydrothol® 191 is added to the wastewater to control algae, it is unlikely to be a wildlife toxicity problem due to the low concentrations at which it will occur prior to release from the outfall. 0.015 mg a.e./L is below the criterion level specified by Ecology (1992) of 1.43 and 0.02 mg a.e./L specified for acute toxicity and chronic toxicity, respectively.

- **Need for additional procedures to remove pesticide from the out fall**

Due to the short half-life, high levels of dilution, and low toxicity to aquatic wildlife, additional procedures to remove endothall from the out fall or potable water systems are not likely to be necessary. However, *Arthrobacter* and other species of bacteria have the potential to remove excessive endothall from any water system since they are capable of using endothall as their sole carbon source and converting it into natural “cellular” products connected with the Krebb’s cycle (Sikka and Rice 1973, Sikka and Saxena, 1973, Simsiman et al., 1976, Reinert and Rogers 1984 and Reinert et al 1986).

#### 4.1.9.5 Mixtures with Other Pesticides and Incidental Presence of Other Pesticides

*Summary: Tank mixes (with other pesticides) are not permitted in Washington State. However, when liquid endothall products (Aquathol® or Hydrothol® 191) are used to control floating aquatic weeds, low levels of surfactants can improve the efficacy of liquid endothall products. If surfactants are used, care should be taken to use surfactants that are registered for aquatic use that have low toxicity to fish. Thickening agents like Polysar® or Nalquatic® may be used to control drift with liquid endothall products that are applied to floating weeds and may also allow subsurface applications to sink more deeply into the water column where they can be most effective.*

*There are no substantiated claims for antagonistic or additive effects with endothall products in the presence of other pesticides. Also, endothall products do not appear to cause cumulative effects due to multiple exposures. However, Aquathol® K and Hydrothol® 191 are occasionally used together, outside of Washington State, where both macrophytes and algae species are being controlled. The combined effect is better than either herbicide alone. Aquathol® K and chelated copper compounds are also occasionally used in impounded water situations to control aquatic macrophytes and algae. Applicators claim that the mixture is more effective than either herbicide alone.*

In general, tank mixes are not permitted in the state of Washington for the control of aquatic weeds in public waterways. Occasionally, endothall will be mixed with copper sulfate for the control of algae in impounded golf course ponds. It is believed by some that this combination has better algae controlling properties than either of the compounds alone.

Not all formulations of endothall have a similar toxicity on an acid equivalent basis. We know that Hydrothol® is considerably more toxic to fish and aquatic invertebrates than Aquathol® K, disodium endothall or endothall acid. The “inert materials” may interact with the pesticide to give antagonistic, additive, cumulative or synergistic effects against target (aquatic weeds and algae) and non-target fish and aquatic invertebrates. For example: endothall acid containing 17.5% a.i. was considerably more toxic to rainbow trout, and bluegill sunfish than endothall acid containing 77.9% a.i. possibly due to a synergistic effect with “inert” formulation ingredients. This indicates that all formulation ingredients may not be “inert”. The LC50s ranged from 1.8 to 4.3 mg a.i./L and from 49 to 77 mg a.i./L for the products containing 17.5% a.i. and 77.9% a.i. endothall acid, respectively (FWS, 1986 in Brian, 1999 and Bettencourt, 1992, 1992 and 1993) (Table 11).

- **Adjuvant effects**

It is not necessary to use adjuvants with subsurface injections of endothall (Aquathol® K or Hydrothol® 191) or when using granular products of endothall (Aquathol® or Hydrothol® 191 granular). However, a thickener is often used with liquid formulations to allow the treatment to sink more deeply into the water column where it can be most effective.

When liquid endothall products (Aquathol® K) are used to control floating weeds by direct contact with a spray, the use of a surfactant and a thickening agent have been suggested by applicators (Dorling and McNabb, 1999 personal communication) and a well respected researcher (Getsinger, 1999 personal communication). The surfactant

should be used to allow for better wetting of the floating weeds and the thickening agent should be used to prevent drift. There are a number of adjuvants registered for aquatic use in Washington State. Most surfactants should be mixed at 0.25 to 0.5% by weight of application solution when endothall is being applied to floating (surface) aquatic macrophytes. None of these aquatic adjuvants should be toxic to fish or aquatic invertebrates when applied at labeled rates. However, it has been noted by Watkins et al (1985) that some aquatic adjuvants have a potential to be toxic to aquatic organisms when applied to shallow water. For example: 1) If Spray-Mate is applied at the labeled use rate to water with a depth of less than 1.5 meters, it can be toxic to bluegill sunfish. 2) If Cide-Kick, X-77, Formula 403, or IVOD are applied at the labeled use rate to water with a depth of less than 0.1 meters, they may be toxic to fish. Details of the toxicity and depth considerations for a number of aquatically applied adjuvants can be found in Table 13. Although adjuvants are typically considered to be “nearly inert”, they are not entirely inert. Adjuvants can either enhance, diminish, or have no effect on the activity of herbicides.

- **Antagonist effects**

There are no credible report of antagonism when endothall products are mixed with other products. However, some products like 2,4-D appear to stimulate growth of blue-green algae at concentrations below 10 mg a.i./L (Wang et al. 1991, Kobraei and White, 1996, Das and Singh, 1977, Wong and Chang, 1988, Mishra and Padney, 1998). Therefore mixing 2,4-D with endothall (Hydrothol® 191) has the potential to antagonize the action of endothall (Hydrothol® 191). This has not been an issue when 2,4-D is present with endothall at low concentrations due to drift and/or run off from home lawn treatments.

- **Additive effects**

There are no credible reports of additive effects of endothall products with other herbicides or non-herbicidal products. However, Ecology (1982, 1992) considers the use of endothall and fluridone to have potential additive effects due to a similar mode of action. Therefore, the use of these compounds at the same time or during times when their effectiveness would overlap is prohibited.

- **Cumulative effects**

There are no credible reports of cumulative effects of endothall. Due to the short half-life, direct cumulative effects from the use of endothall products are not likely.

- **Synergistic effects**

There are no credible reports of additive effects of endothall products with other herbicides or non-herbicidal products. However, it has been reported by McNabb (1999 personal communications) and Getsinger (1999 Personal communications) that Aquathol® K and Hydrothol® 191 are occasionally used together outside of Washington State for treating lakes, ponds and irrigation ditches where both algae and aquatic macrophytes are a present nuisance. Aquathol® K does an adequate job controlling the macrophytes while Hydrothol® does an excellent job of controlling

the algal species including *Chara spp* at concentrations listed in the label. The combined effect is better than either herbicide alone. Whether this can be interpreted as an additive, cumulative or synergistic effect is not known.

#### 4.1.9.6 Potential Impacts on Agriculture

*Summary: At typical use rate concentrations, irrigation or flooding of crops with water that has been treated with Hydrothol® 191 should not cause significant damage. Aquathol® (dipotassium endothall salt) will not bioaccumulate in wheat, spinach and table beets. Endothall is unlikely to bioaccumulate in livestock or fish. Since the mode of application of Aquathol® and Hydrothol® is typically by subsurface injection or sinking granules, drift is likely to be minimal. When used at concentrations below 3.5 mg a.e./L (5.0 mg a.i./L) Aquathol® should not have acute effects on aquaculture; but effects on more sensitive species cannot be ruled out.*

If water use restrictions are followed as described in Section One and the Federal Use labels, there should be no impact on agriculture. There are very strong indications that endothall treatments will not persist in the environment beyond about eight days if it is applied at the labeled rates (Sikka and Rice, 1973, Serdar and Johnson, 1993, Ritter and Williams, 1998, Keckemet and Sharp, 1999).

- **Potential impacts of water on irrigation**

When the treatment rates are 3 to 4 mg/L, the levels of endothall in the treated water should be low (<0.01 mg/L) within 8 to 16 days (Ritter and Williams, 1991, Serdar and Johnson, 1993). At lower treatment rates, you would not expect to see concentrations any higher than 0.01 mg/L. According to Scott Fink (Public Health Department: Drinking Water Division, 2000 personal communication), the levels of herbicides in public drinking water are always below the current allowable limit. In surface waters used for drinking water purposes, herbicides have never been detected east of the Cascades at levels above the Federal Drinking Water Standard.

It is unlikely that endothall (dipotassium endothall salt) will be bioconcentrated in crops that are irrigated with treated water. Crop rotation studies indicate that there is no tendency to bioaccumulate endothall 14C-labeled residues from the soil. Most of the water extractable residues from crop rotation studies remaining in the soil contained endothall. However, the percent of water extractable residues in the soil decreased with time from ~90% at time zero to 13.5% in soil aged 120 to 365 days. Residues that were extracted from plant material into either an aqueous phase, acetonitrile, or acid hydrolysis consisted of several unidentified polar metabolites. Endothall was not present in the studied plants (wheat, swisschard and table beets). This indicates that if flooding occurs, crops will not be effected adversely. Their growth should be adequate and no residues that should interfere with marketability will be present at detectable levels (Keckemet, 1991, Gangstad, 1986 and undated abstract from Elf Atochem Numbered HWI 6120-148).

- **Potential impacts of water used to water livestock**

Three days after treatment, the level of endothall in water at intakes of a typical water treatment plant were not higher than 0.03 mg/L (Ritter and Williams, 1991). This

concentration is considerably below the allowable level of 0.100 mg/L. (U.S. EPA, 1993). Therefore, it is unlikely that livestock will be affected by drinking water that has aged for at least 7-days. Seven days is the minimal time for the water use restriction prior to watering livestock with Aquathol® treated water. The other products (Hydrothol® 191, Hydrothol 191 Granular and Aquathol®K) require a 7, 14 or 25 day of water restriction before watering livestock with water at varying concentrations specified in the label.

Endothall is unlikely to bioaccumulate in livestock. When <sup>14</sup>C-labeled endothall was given to rats in the diet, 90% was eliminated in two to three days. No endothall was found in fat or milk. When goats were exposed to endothall in a similar manner, no endothall was found in the milk. However, a small amount the <sup>14</sup>C-label derived from endothall was found in goat's milk. This <sup>14</sup>C-label was in the form of natural products including <sup>14</sup>C-lactose (Shearer and Halter, 1980). In reports submitted to support endothall registration, goats and chicken eliminated 75% to 88% of the administered endothall dose in their excreta or feces and urine, respectively. Low levels of residue (0.002 to 0.088 mg/Kg) were detected in muscle tissue, organ tissue, fat, and milk for goats, or eggs for chickens. Almost all of the residue found in excreta or feces and urine were in the form of endothall and its mono and dimethyl esters. Most residue found in tissues (>45% - 54%) was unchanged endothall with the remainder being mono or dimethyl (ester of endothall). This is not surprising since endothall is extremely water soluble, metabolism is not necessary for the transformation of the herbicide to a less toxic chemical (HWI 6120 – 158 and HWI 6120 – 160).

- **Potential impacts on fishing and the consumption of fish**

It has been shown that endothall does not bioaccumulate or bioconcentrate in fish. The concentration of endothall in most treated aerobic systems is likely to be very low after 3-4 days. Typically, if water criterion or level of concern methods are used, the time weighted average levels of Aquathol® or Hydrothol® typically would not exceed 1.0 in water where fish are present. Since the BCF for edible tissues is typically about 0.05, concentrations higher than 0.05 mg/Kg would not be expected in fish flesh.

In a typical field situation, the concentration of endothall in edible bluegill sunfish flesh was even lower. Concentrations in the fish flesh were <0.01 mg/Kg after three days of exposure to concentrations ranging from 6.2 mg/Kg to 4.9 mg/Kg in a typical Wisconsin pond (Serns, 1977). The levels of endothall found in water and edible fish flesh after treatment with endothall at 5.0 mg/L are given in Table 7.

- **Potential impact of air quality on crop plants and livestock**

The label warns the user to avoid contact with or drift to other crops or plants as injury may result (Aquathol® K label, 1998). The main methods of using these products, largely preclude the effects of drift. For the granules, a cyclone seeder is used to spread the granules which sink upon contact with water. The liquid products are normally injected by subsurface methods (which preclude drift), or applied as large droplets at low pressure (which mitigates the effects of drift). It is also recommended that a thickening agent be used when applying to the surface to control drift. However, even small amounts of drift can be an issue.

Due to the low vapor pressure of the commercial products of endothall  $3.92 \times 10^{-5}$  mm Hg for the active ingredient of Aquathol® K and  $2.09 \times 10^{-5}$  mm Hg for the active ingredient of Hydrothol® 191), endothall products should have very little effect on air quality or cause crop damage. The mode of application is usually subsurface injection for liquid formulations, and the weight of the granular formulations makes drift unlikely. For those cases where a liquid formulation is applied by boom sprayer, as much as 1% of this application may drift out of the treatment area. In cases where aerial application might be necessary due to remoteness or inaccessibility of the treatment site, as much as 17% of the treatment would not strike the target area (Forsythe et al, 1996). In aerial application drift out of the treatment area could impinge on non-target organisms at a very great distance from the site or application. Depending on how much endothall was deposited per unit area outside the site, there could be a significant impact on non-target wild plants or crops.

Odor is unlikely to be noticed except for short periods of time following application of endothall. Posting and communications requirements specified in the aquatic weed control permit should make the public aware of any potential odor problems. Since there is rarely more than one application of endothall for aquatic weed control per water body per year in the state of Washington, any adverse impact due to odor from endothall applications should be weighed carefully with the impact on quality of life due the effects of poor navigability, and effects on the recreational and fisheries use of the water body.

- **Potential impact of flooding or irrigation on agriculture**

Flooding of agricultural land with endothall treated water should be rare. When flooding occurs, the dilution effects should mitigate the effects of the concentration of endothall. Data from irrigated crop studies indicate that “flooding” (furrow, overhead or drip irrigation) will not adversely impact most crops if the “flood” water contains less than 10 mg a.e./L Hydrothol® 191. For crops treated at 10 mg/L, 3 mg/L and 1 mg/L, there were slight effects on lettuce, spinach and soybeans, respectively (Keckemet, 1991 and Gangstadt, 1986). Crop rotation studies indicate there was no tendency to bioaccumulate endothall equivalence of the <sup>14</sup>C-labeled residues in the soil. Most of the water extractable residues remaining in the soil were endothall. However, the percent of water extractable residues in the soil decreased with time from ~90% at time zero to 13.5% in soil aged 120 to 365 days. Residues that were extracted from plant material into either an aqueous phase or by acid hydrolysis consisted of several unidentified polar metabolites. Since the use of overhead irrigation, also having little or no effect on crop plants, the use of treated irrigation water to make up agricultural sprays will probably not be a serious issue.

- **Potential impacts on aquaculture**

Under most conditions, Aquathol® should not have acute effects on aquaculture when the concentration is below 3.5 mg a.e./L. However, more sensitive species have the potential to be adversely impacted. The concentration that acutely effects the sensitive species is relatively high, ranging from 11 mg a.e./L for walleye to 92 mg a.e./L for largemouth bass, but predicting chronic effects would be difficult since a reliable acute/chronic is not attainable. Acute to chronic ratios vary depending on species from 1.7 with bluegill sunfish tested with disodium endothall to ~33 with

rainbow trout tested with Aquathol® acutely and disodium endothall chronically. The geometric mean for acute/chronic ratio was determined to be 6.4, which is comparable to the value of 5.2 given by Ecology (1991) (Table 19). The higher value is due to additional acute/chronic pairs collected since the 1991 SEIS. The data from the previous SEIS was noted and utilized in generating the acute/chronic toxicity ratio.

#### **4.1.10 ENVIRONMENTAL TOXICITY REVIEW -- TOXICITY TO THE AQUATIC BIOTA AND RISK ASSESSMENT**

Except for their direct contact effect on plant foliage and algae, endothall products are not chronically toxic to aquatic life (Leonard 1982 in Ecology, 1992). The activity of endothall products can be improved on emergent or floating weeds by adding surfactants and accelerators so that endothall is more readily adsorbed. Addition of a thickening agent may improve the effect of endothall products by allowing the herbicide to drop lower in the water column where the submerged plants are located. Endothall products are primarily applied from boats using a spray boom or subsurface injection (liquids), or use of an electrical hopper spreader (granular). Endothall liquid products may be occasionally applied from a shore vehicle using a spray boom. It is very unusual for endothall to be applied by aircraft except for application to remote sites. Aerial application is usually avoided due to public perception that drift problems may have an adverse impact on the human and wildlife habitat (Getsinger, 1999, personal communications).

The acute effects of Aquathol® disodium endothall salt and their free acid (endothall acid) are not a major concern. Possible problems could occur with the food chain issues, disruption of habitat (Haag and Buckingham, 1991), potential disruption of nesting (breeding behavior) in fish (Bettoli and Clark, 1992), disruption of smoltification in salmon (Liguori et al. 1983, Bouk and Johnson, 1979) and changes in numbers and diversity of aquatic macrophytes (Corps 1984 in Ecology, 1989).

Due to the mode of action, endothall is expected to cause more rapid die-back, and result in earlier re-growth than herbicides that translocate to the roots and cause death of the total plant (Killgore, 1984 in Ecology, 1989). At the subcellular level, endothall inhibits the incorporation of malonic acid into lipids thus inhibiting the formation of fats, and waxes (Simsiman et al., 1976).

Biochemical degradation of endothall is extensive. Bacteria metabolizes endothall rapidly, converting it initially into citric acid which is ultimately metabolized to carbon dioxide. Citric acid is used to form a variety of cellular products. These include glutamic acid, aspartic acid, alanine, other amino acids, proteins, nucleic acids and lipids which are incorporated into cellular products and soil bound natural products (Sikka and Saxena 1973, Simsiman et al., 1976, Reinert and Rogers 1984 and Reinert et al 1986).

Fish (Dionne, 1994) and plants (Freed & Gauditz, 1961 in Davis, 1999, and Thomas, 1966) appear to extensively metabolize endothall to basically the same end products as *Arthrobacter* does.

#### 4.1.10.1 Effects and Selectivity on Aquatic Plants

*Summary: Aquathol® (dipotassium endothall) and endothall acid are toxic to aquatic macrophytes (EC50 = 0.60 mg a.e./L) but do not appear to be toxic to algal species (EC50 >2.6 to 3000 mg a.e./L) at labeled rates. These results are verified by field studies at concentrations from 2.0 to 5.0 mg a.e./L that control the species listed in the label but permit Chara spp., American waterweed (Elodea canadensis), cattails (Typha spp.) and spatterdock (Nuphar spp.) and fragrant water lilies (Nymphaea spp.) to continue growing and become dominant within the biota. Field studies indicate that removal of the milfoil species and a community shift to other plant species does not adversely impact invertebrate, bluegill or largemouth bass populations. Risk analysis is not typically done with a herbicide on aquatic plant species since it is assumed that herbicides will harm plants.*

*Hydrothol® [mono(dimethylalkylamine) salt of endothall] is toxic to macrophytes (EC50 = 0.85 mg a.e./L) and all species of green algae tested (EC50 = 0.0071 mg a.e./L for Selenastrum capricornutum to 0.19 mg a.e./L for Scenedesmus acuminatus). Blue-green algae are typically more susceptible to the effects of Hydrothol® than either diatoms or green algae. This could lead to reduction in numbers and a shift in the dominant species of algae where Hydrothol® 191 is used.*

Endothall is not extremely selective. However, it is known for its excellent control of *Potamogeton amplifolius* (bass weed), *P. crispus* (curly-leaf pondweed), *P. zosteriformis* (flat-stem pondweed), *P. natans* (floating pondweed), *P. pectinatus* (sago pondweed), *P. americanus*, *P. diversifolius*, *P. filiformis*, *P. pusillus*, *Najas spp.* (naiads), horned pondweed, bur reed, coontail, water stargrass, hydrilla and milfoil (Aquathol®, 1998 and Aquathol® K labels, 1998, 1990, Robbinette, 1998-1999, and Westerdahl et al, 1988). It is not effective against water lilies and cattails (Shearer and Halter, 1980), and of reduced effectiveness to *Elodea canadensis* (Thomas, 1966 in Frank, 1997) and *Chara spp.* (muskgrasses) (Serns, 1977). See Section 1.1 for a list of weeds and algae and how well they are controlled by treatment with endothall products at the labeled use rates. The aquatic macrophytes currently of greatest concern in the northern tier of states (including Washington) are *Myriophyllum spicatum* (Eurasian watermilfoil), curly-leaf pondweed, Brazilian elodea, monoesius hydrilla, smooth cordgrass, and purple loosestrife; of these only Eurasian watermilfoil, curlyleaf pondweed and monesius hyrdilla are effectively controlled with Aquathol® and Hydrothol® products (Robinette 1998-1999 and Westerdahl et al. 1988). Hydrothol® may also control Brazilian elodea.

##### 4.1.10.1.1 Acute Effects on Aquatic Plants

The indicator species for aquatic toxicity in aquatic plants and algae are *Lemna gibba* (duckweed, aquatic macrophyte), *Anabaena flos-aquae* (blue-green algae), *Selenastrum capricornutum* (green algae), *Navicula pelliculosa* (fresh water diatom) and *Skeletonema costatum* (marine diatom). However, in the case of endothall acid, surrogate species were tested including *Chlorococum spp.* (green algae), *Dunaliella tertiolecta* (green algae), *Phaeodactylum tricornerum* (marine diatom) and *Isochrysis galbana* (marine haptophyte). These surrogate species were tested with Aquathol® K in addition to the standard species. In the cases of endothall acid and Aquathol® K, the typical LC50s (>3.4 mg a.e./L for *Anabaena flos-aquae* to 3000 mg a.e./L for *Isochrysis galbana*) were higher than the usual field rates (2.0 to 3.0 mg a.e./L) for the control of aquatic plants (Table

11). This is not unexpected since the Aquathol® K product is not registered for the control of algae. Aquathol® K effects the aquatic macrophyte (*Lemna gibba*). The LC50 and NOEC for Aquathol® K for this species is 0.6 and 0.35 mg a.e./L, respectively. This also is not unexpected since Aquathol® K is registered for control of aquatic macrophytes with typical field-use rates of 2.0 to 3.0 mg a.e./L. However, in the case of Hydrothol® 191, typical algal LC50s (0.0076 to 0.12 mg a.e./L) are considerably less than the typical field application rates = (0.05 to 0.2 mg a.e./L). The duckweed LC50 for Hydrothol® (0.83 mg a.e./L) is considerably less than the typical field application rate (0.5 to 2.5 ppm a.e.) for the control of aquatic macrophytes (Table 2, Table 14, Appendix 1). However, because plants are the intended targets of aquatic herbicides containing endothall, effects on plants are not considered in the risk assessment.

#### 4.1.10.1.2 Chronic Effects on Aquatic Plants

Laboratory work to determine the chronic effects of herbicides on aquatic algae and plants is currently not conducted for the purposes of registration.

#### 4.1.10.1.3 Potential Impacts of Single Versus Multiple Applications

In a field study at Lake Washington, applications of Aquathol® products/L (2.0 mg a.e./L) for the control of milfoil reduced the biomass of native aquatic macrophytes like *Potamogeton richarsonii*, *P. crispus*, *Zannichelia palustris* and *Ceratophyllum sp.* and *Charophytes sp.* Removal of a large portion of the biomass allowed *Elodea canadensis*, which was not adversely affected by this endothall treatment rate, to become the dominant species at the treatment site (Corp, 1984 in Ecology, 1989). Endothall did not affect *Elodea canadensis* adversely at these treatment rates since neither *Elodea* nor its associated bacteria metabolized endothall to nontoxic metabolites (Thomas, 1966 in Frank, 1971).

Aggressive treatment may create more open water for fish habitat. However, aggressive treatment may eliminate areas containing milfoil that are used by juvenile fish (Killgore et al 1987 in Ecology, 1980, 1989). Invertebrates are more abundant on macrophytes other than milfoil, so a community shift to other plant species may result in greater abundance of invertebrates, which would provide more food for the grazing planktivorous fish. In most cases where an adverse effect has occurred on fish food organisms, it has been as a result of anaerobiosis rather than loss of habitat. (Frank, 1971).

- **Potential impact on numbers**

A field study was conducted in Wisconsin in May, 1973 (Serns, 1977). Treatment of the entire pond at maximum field rates of 5 mg a.i./L (3.5 mg a.e./L) with Aquathol® K completely eliminated *Myriophyllum sibiricum*, *Ceratophyllum demersum*, *Potamogeton crispus*, *Elodea canadensis*, *P. zosteriformis*, and *P. pectinatus* within 3 weeks of application. All species except *E. canadensis* and *Chara spp.* were eliminated within two weeks of application. *E. canadensis* was eliminated within three weeks after application and *Chara spp.* appeared to be unaffected.

All species showed signs of recovery within one year of treatment. However, *Chara spp.* spread over the entire pond and became the dominant anchored macrophytic green algae by the end of the 1973 growing season.

- **Potential impact on diversity**

As previously discussed (Corp, 1984 in Ecology, 1989), treatment of Lake Washington with 2 mg a.i. Aquathol®/L led to *Elodea canadensis* becoming the dominant plant. The target species (milfoil) was largely eliminated. Other species of plants are also tolerant to the effects of endothall. e.g., *Nuphar spp* (spatterdock), *Nymphaea spp.* (fragrant water lilies) and *Typha spp.* (cattails) are not susceptible to endothall at normal application rates and therefore would not be expected to be killed as a result of endothall treatments (Shearer and Halter, 1980, Pennwalt Corporation, 1979 in Ecology, 1992). Any species that is not susceptible to the effects of a control agent has the potential to become a dominant species within any habitat if other measures are not taken for control.

In a Wisconsin lake, the distribution and diversity of rooted plants changed greatly from the time of treatment (May, 1973) until the times of intermediate and final evaluation in October, 1973 and 1974, respectively (Serns, 1977). For example, prior to treatment, the pond contained 80% *Myriophyllum sibiricum* and the other 20% consisted of *Ceratophyllum demersum*, *Chara spp.* with small amounts of *Potamogeton zosteriformis*, *P. crispus* and *P. pectinatus*. Within two weeks of treatment, all plants had died except *Elodea canadensis* and *Chara spp.* Within three weeks of treatment, all plants had died except *Chara spp.* By October of 1973, the *Chara spp.* had spread over the entire pond and 90%-95% of the vegetation consisted of *Chara spp.* and approximately 5% consisted of the native pondweed, *P. pectinatus*.

At the end of the 1974 season (October, 1974) the dominant species still remained as *Chara spp.* (75-80%). Approximately 10-15% consisted of *E. canadensis*, 5% or *Najas flexilis*, which was not observed before treatment, and 5% as pondweeds, *P. pectinatus* and *P. crispus*.

By the end of October, 1975 the diversity of the aquatic weeds was returning to pretreatment levels. Fifty percent of the rooted vegetation consisted of *M. sibiricum*, and the remaining 50% of the surface cover consisted of *Chara spp.*, *E. canadensis*, *P. crispus*, *P. pectinatus* and *N. flexilis*.

Potential impact to numbers and diversity also occurs with algae. Preliminary studies to investigate the utility of Hydrothol® for the control of blue-green algae (Cyanobacteria) in wastewater stabilization ponds indicate that Hydrothol® 191 is very effective at controlling cyanobacteria with a 50% reduction occurring at 0.04 to 0.1 mg a.i. /L (0.02 to 0.04 mg a.e./L) while it typically takes 0.4 to >0.6 mg a.i./L to reduce growth of green algae by 50% and 0.2 to >0.6 mg a.i./L (0.1 to 0.3 mg a.e./L) to reduce growth of freshwater diatoms by 50% (Tables 2 & 14, Appendix 1). This could potentially cause a shift in the dominant algal species in a water body or settling pond if treatment occurs at the minimum Hydrothol® 191 rates suggested for the control of algae (0.05 to 0.2 mg a.e./L). Even if higher than recommended rates are used (0.3 to 0.8 mg a.e./L), the Cyanobacteria will be reduced to a much greater degree than the Chlorophyta or diatoms (Ruzycki et al., 1998). However, further research in this area is necessary to confirm this hypothesis. In practical situations, this may cause a shift in the dominant species of algae in wastewater stabilization ponds (Axler et al. 1994a and Owen et al. 1994). However, there is not enough field

data collected from either wastewater stabilization ponds or other ponds, lakes, reservoirs and canals to determine if this is a conclusion.

- **Potential impacts on habitat for growth and reproduction of aquatic plants**

No literature was found that directly addressed the impact of endothall on the habitat for growth and reproduction of aquatic plants. Typical half-lives for endothall range from 8 to 11 days; and after about one month, no measurable levels of endothall will be present in water or the top one inch of hydrosol in a pond treated with 2 mg/L of endothall (Sikka and Rice, 1973). By that time, the water quality will have recovered sufficiently to sustain growth and reproduction of rooted aquatic plants. By the end of the treatment season, good growth and reproduction for non-exotic species should have been established in the treated pond or lake. However, return to pretreatment conditions may take several years due to effects of differential growth rate on diversity and numbers of the native species. If the maintenance of fish populations is not a priority item, treatment of lakes, ponds, and canals at 0.2 mg a.e./L with Hydrothol® 191 will eliminate *Chara Spp.* (Hydrothol® 191 Label) and possibly allow other less competitive native plants to return more readily to the treatment area.

- **Naturally occurring re-growth of reproduction of non-noxious or non-invasive plants**

Most noxious plants (i.e. Eurasian watermilfoil) are eliminated upon treatment with endothall. Nevertheless, it is clear that while desirable native species do recover, some of the more invasive native species like *Elodea canadensis* or *Chara spp.*, water lilies and cattails may dominate the biomass after treatment (Corps, 1983 in Ecology, 1989, Sedar, 1977 and Shearer and Halter, 1980).

- **Post treatment plantings of non-noxious or non-invasive species**

In a general review article, Frank (1972) recommended the planting of non-noxious, and non-invasive native plants after the elimination of exotic noxious and invasive plants. He indicated that such plantings will be competitive, once the faster growing exotics have been eliminated. These native species can serve as both food and habitat for waterfowl, fish food organisms, and fish. For further discussion of the effects of endothall on numbers and diversity of aquatic animals, please see Section 4.1.10.2.3.

Fish food organisms do not appear to be adversely impacted by the presence of less milfoil, so a community shift to other species may result in a greater abundance of invertebrates (Ecology, 1989). Serns (1975) found that most zooplankton, including *Cladocera* (*Daphnia spp.*, *Ceriodaphnia spp.* and *Chydorus spp.*), *Copepoda*, *Cyclopsida* and *Calanoida*, were not adversely affected by treatment with Aquathol® K at 5 mg a.i./L. Numbers of these species were either unaffected by the treatment with endothall or appeared to increase in the treatment ponds.

A negative impact would be the elimination of refuge habitat for juvenile fish prior to the growth of any introduced plantings. However, Radomski et al. (1998) found that whole lake applications of endothall as a fisheries management tool to eliminate submerged vegetation had no effect on size structure and growth

of bluegills and largemouth bass in the two years following treatment. Similar lack of general effect on bluegill sunfish was observed for a pond treated with endothall (Serns, 1977). However, while survival and reproduction were not affected, growth rate of fish in the treated pond was lower than in the untreated pond. Furthermore, removal of submergent vegetation appeared to increase the number of young of the year and their size range without effect on adult abundance (Radomski, 1995).

#### **4.1.10.1.4 Effects on Endangered Aquatic Plant Species.**

To protect endangered aquatic plants, some knowledge must be gained on the toxicity of endothall to these plants, or endothall must not be applied in areas that will adversely impact the habitat or population of these plants. In the case of threatened aquatic plants, the endangered species act does not allow for the control of noxious weeds to take precedence over the protection of these species. The permit for treatment of water bodies to control noxious or invasive plants may be denied or amended if Ecology believes that populations of threatened or endangered plants may be adversely impacted by treatments to control these weeds (McNabb, 1999 and Dorling, 1999 personal communications).

Endangered aquatic plant species in the State of Washington are water Howella and marsh sandwort.

#### **4.1.10.1.5 Risk Analysis for Aquatic Species of Plants**

It is not standard procedure to conduct a Risk Assessment with a herbicide for aquatic plants. The assumption is that herbicides will harm plants.

#### **4.1.10.2 Effects of Endothall on Aquatic Animals**

*Summary: Aquathol® K (dipotassium endothall salt), disodium endothall salt and endothall acid are not significantly toxic to fish, free-swimming invertebrates or benthic invertebrates. The LC50 of these materials range from 23 to 166 mg a.e./L for salmonids, 77 to 560 mg a.e./L for warm water fish (sunfish, bass minnows and others), 39 to 92 for Daphnids (free-swimming invertebrates) and 39 to 354 mg a.e./L for benthic invertebrates. Chronic toxicity (NOEC) is also low with the NOEC ranging from 5.0 mg a.e./L for early life stage rainbow trout to ~80 mg a.e./L for chronically exposed bluegill sunfish. Daphnids (free-swimming invertebrates) are tolerant to endothall acid in a 21-day life cycle study with a NOEC of 5 mg a.e./L. Since the acute toxicity to this herbicide is low, concentrations of Aquathol® K encountered in the environment ( maximum use rate = 3.5 mg a.e./L = 5.0 mg a.i./L) are unlikely to cause mortality or adverse impacts in fish. Since the chronic NOEC values are higher than the maximum use rate for these herbicides, Aquathol® K is unlikely to cause adverse chronic impact to any segment of the biota.*

*Field studies using Aquathol® K at the maximum use rate eliminated milfoil and most other macrophytes for up to two growing seasons, and allowed tolerant anchored macrophytic algal species, like Chara spp. to dominate the water body. In spite of the effects on the aquatic plant biota, bluegills and largemouth bass appeared to be mostly unaffected by Aquathol® treatment; there did not appear to be significant compound related effects on survival, growth, reproduction or nesting behavior. Although some*

*species of fish appear to be able to avoid Aquathol® K in the laboratory, no observations of avoidance behavior were seen in the field.*

*Laboratory exposure of Coho and Chinook salmon at field rates (1.5 to 3.5 mg a.e./L) of Aquathol® K appears to interfere with the parr to smolt metamorphosis. After exposure to Aquathol® K in freshwater, salmon smolts may not survive a 96-hour seawater challenge.*

*Field studies indicate that removal of milfoil and other sensitive plants do not appear to adversely impact the single season numbers or diversity of free-swimming aquatic invertebrates such as Cladocera, Copepoda, Cyclopsida and Calanoida. Some species appear to increase in numbers to a greater degree in the absence of milfoil.*

*Only one species of invertebrate appeared to be adversely impacted by the use of Aquathol® K to control Hydrilla. While the Hydrellia fly was not acutely affected by Aquathol® treatments that controlled Hydrilla, they exhibited up to 74% mortality within a relatively short time after the host plant started to die. This effect was probably due to a loss of habitat rather than acute or chronic toxicity effects of Aquathol® on the insect.*

*Hydrothol® 191 [mono(dimethylalkylamine) salt of endothall] is toxic to fish, free-swimming invertebrates and benthic invertebrates. The LC50 of this material ranges from 0.079 mg a.e./L for cutthroat trout to 0.82 mg a.e./L for sheepshead minnow (fish), ~0.080 mg a.e./L for daphnia to 0.37 mg a.e./L for the rotifer (free-swimming invertebrates) and 0.022 mg a.e./L for grass shrimp to 6.2 mg a.e./L for fiddler crab (benthic invertebrates). Chronic toxicity is also high with the NOEC ranging from 0.022 to 0.056 mg a.e./L for early life stage fathead minnow (fish). Daphnids (free-swimming invertebrates) are also very susceptible to Hydrothol® 191. A 21-day life cycle study demonstrated an NOEC of <0.005 mg a.e./L for Ceriodaphnia dubia and 0.016 mg a.e./L for Daphnia magna. Since fish and invertebrates are acutely and chronically sensitive to Hydrothol® 191, a formal risk assessment is necessary to determine if the use of Hydrothol® 191 to control aquatic plants and algae will put fish, free-swimming invertebrate and benthic invertebrate biota at risk.*

*A field study in hard water indicates that Hydrothol® 191 is extremely toxic to a variety of fish in irrigation canals treated for 120 hours at 0.5 mg/L Hydrothol® 191. Further acute and chronic field studies have not been performed with Hydrothol® 191 on aquatic animals. However, a 1999 treatment of Lake Steilacoom at 0.2 mg a.e./L for control of algae did not produce any obvious fish-kill. Fish avoidance has been claimed for Hydrothol® 191 by both the manufacturer and skilled applicators. However, the lack of valid controls for these field observations makes interpretation of these observations difficult.*

*Laboratory exposure of Chinook salmon at field rates of (0.2 mg a.e./L) indicates that Hydrothol® 191 interferes with the parr to smolt metamorphosis. It has been shown that after exposure to Hydrothol® 191 in freshwater, salmon smolts may not survive a seawater challenge.*

*Sensitive, endangered or threatened species of aquatic animals that may need protection through mediation include several salmon and trout species, thriteen rockfish species,*

*two species of dace, two species of herring, and seven species of amphibian. Other species may also be sensitive, endangered, or threatened.*

Application of endothall to fully aquatic (lentic and lotic), palustrine and margins of aquatic systems may affect aquatic animals. Except in a few cases, aquatic animals are not adversely impacted by Aquathol® (dipotassium endothall salt) concentrations typically used for submerged weed control (low ppm levels). The dimethylalkylamine salt of endothall (Hydrothol®) has been shown to affect aquatic animals at concentrations in the sub-ppm range (0.24 to 1.4 mg/L) therefore, Hydrothol® is likely to be acutely toxic to aquatic animals. However, in Washington State, Hydrothol® is not usually applied for control of submerged aquatic macrophytes and is only occasionally applied under a Washington State Experimental Use Permit (EUP) for the control of toxic blue-green algae. Refer to the Section 4.1.10.2.3 for more detailed discussion of the effects of endothall on aquatic animals.

Endothall and its formulations are not likely to bioaccumulate. Since the Octanol/Water Partition Coefficient is less than unity (<1.0), the standard estimate indicates that the bioconcentration factor will be less than one ( $BCF = 0.05 \times Kow = 0.05 \times <1.0 = <0.05$ ). This estimate is born out in biological tests. Bluegill sunfish do not accumulate endothall (Dionne, 1992), nor do catfish, crayfish or clams (Formella 1998). Invertebrates adsorb significant amounts of endothall, but these organisms (or their comensal bacteria) rapidly degrade endothall to natural products, which are rapidly eliminated or utilized in the animal's essential metabolic processes. This keeps the endothall concentration in the tissue below the exposure concentration. Therefore, bioconcentration of endothall in tissues of aquatic organisms is not expected to be significant. See Section 4.1.10.2.4 for a more detailed discussion.

Tank mixes of endothall and other pesticides are not permitted for use in public waterways in the state of Washington. However, Aquathol® is sometimes combined with chelated copper compounds for the control of algae and aquatic macrophytes in impounded golf course lakes. (Terry McNabb, 1999 personal communications). Endothall products may be combined with various surfactants (Accelerators) at 0.25 to 0.5% by weight and thickening agents. Accelerators are chemicals which increase the herbicidal effects probably by increasing transluminal penetration. These materials should not be used with herbicides injected below the surface of a water body, but some applicators and scientists believe that surfactants like CideKick® and X-77® improves the effectiveness and should be used with endothall products when surface (floating) weed control is necessary (Getsinger, 2000 personal communications). A thickener like Nalquatic® or Polysar® may allow the subsurface injected pesticides to sink down into the water column where they will be most effective against aquatic macrophytes. If the herbicide is sprayed on, thickeners also control potential drift. Although all adjuvants registered for use with aquatic herbicides should be safe to fish and other aquatic animals when used according to the label, they are not without risk to aquatic life (Watkins et al, 1985). Their 96-hour toxicity (LC50) ranges from 0.96 mg/L to >1000 mg/L. In lakes and ponds with reasonable depth, dilution should prevent toxic effects from these additives; this is particularly so if the application is a spot or margin treatment. A more detailed discussion of the effects of adjuvants can be found in Section 4.1.9.5 and in Table 13.

#### 4.1.10.2.1 Acute Effects on Aquatic Animals

Toxicity information indicates that Aquathol® K, disodium endothall and endothall acid are not significantly toxic to most species of fish; that is they have an LC50 of greater than >100 mg/L (Table 2, Table 15 and Appendix 2). Aquathol® K has 96-hour LC50 ranges from 11 mg acid equivalent (a.e./L) for early life stage walleye to an average of >100 mg a.e./L (range 57 to 319 mg a.e./L) in rainbow trout, bluegill and channel catfish. Endothall acid has a similar mean range of 96-hour LC50s: 77 to 220 mg a.e./L for bluegill sunfish to 120 mg a.e./L for largemouth bass, ~180 mg a.e./L for bullhead catfish and carp. Most of the minnows and shiners seem to be somewhat more sensitive with LC50s ranging from 95 to 120 mg a.e./L. Disodium endothall also falls in this range: Mean 96-hour LC50 = 60 to 135 mg a.e./L for sunfish, 125 mg a.e./L for largemouth bass and ~140 mg a.e./L for bullhead catfish and carp. Again the minnows and shiners appear to be somewhat more sensitive with LC50s ranging from 76 to 186 mg a.e./L.

These toxicity values fall into EPA's general ecological risk categories ranging from slightly toxic (>10 to 100 mg/L) to practically non-toxic (>100 mg/L). The application rate for Aquathol® typically ranges between 2.0 and 3.0 mg a.i./L (1.42 to 2.13 mg a.e./L) with the highest labeled use rate being 5.0 mg a.i./L (3.5 mg a.e./L). Therefore, concentrations of Aquathol® K encountered in the environment are unlikely to cause mortality in fish.

Aquathol® K, and endothall acid are not significantly toxic to most species of aquatic invertebrates; that is the LC50 is typically >100 mg/L (Table 16, Appendix 3). Aquathol® K has an LC50 that ranges from 71 to 91 mg a.e./L for daphnia to 750 mg a.e./L for the fiddler crab. Endothall acid has a similar range of LC50s: 39 mg a.e./L for mysid shrimp to 130 mg a.e./L for the fiddler crab. There is no data available for disodium endothall's effects on aquatic invertebrates.

These values fall into EPA's general ecological risk categories ranging from slightly toxic (>10 to 100 mg/L) to practically non-toxic (>100 mg/L). Even when using the highest labeled use rate of 5.0 mg a.i./L (3.5 mg a.e./L), Aquathol® K is unlikely to cause acute mortality or adverse impact (Table 2, Table 16 and Appendix 3).

Hydrothol® 191 does present some ecological risk to both fish and aquatic invertebrates. The acute fish toxicity (96-hour LC50s) of Hydrothol® 191 ranges from 0.079 mg a.e./L for cutthroat trout to 0.82 mg a.e./L for sheepshead minnow; and the acute invertebrate toxicity ranges from 0.022 mg a.e./L for grass shrimp to 6.2 mg a.e./L for the fiddler crab. Hydrothol® 191, therefore, is two to three orders of magnitude more acutely toxic than Aquathol® K. Based on the toxicity of the dimethylalkylamine moiety (LC50s = 0.11 to 1.1 mg/L), Giddings (1999) concluded that the toxicity of Hydrothol® 191 is primarily a function of the dimethylalkylamine concentration rather than the endothall acid concentration. These toxicity values fall into EPA's general ecological risk categories of very highly toxic (<0.1 mg/L) to moderately toxic (>1 to <10 mg/L).

#### 4.1.10.2.2 Chronic Effects of Endothall on Aquatic Animals

To date, minimal data has been generated on the chronic or early life-stage effects of endothall on aquatic animals (fish). There are studies that deal with the early life stage (egg to fry) toxicity of endothall in the stoneroller and fathead minnow. In addition, there

are several studies that deal with the toxicity of endothall to sac fry on a variety of fish that were exposed from 7 to 14 days. For Aquathol® K and disodium endothall, the NOEC for early life stage studies ranged from 5.0 mg a.e./L for rainbow trout fry exposed for 21-days to 80 mg a.e./L for bluegill fry exposed for 21 days (Table 2, Table 17 and Appendix 4).

Not all of these studies are of good enough design to pass current EPA guidelines as early life-stage studies. The most sensitive and well designed studies that we have are an egg-fry rainbow trout study with disodium endothall by Pennwalt (1986 in Ecology 1989), and an egg-fry fathead minnow study with endothall acid (Bettencourt, 1994). In these studies the NOECs ranged from 5 to 13 mg a.e./L. Since the NOECs are higher than the maximum use rate, this segment of the biota should not be chronically affected. (See Section 4.1.10.2.5).

The amount of data that has been generated on life-cycle effects of endothall against aquatic invertebrates is also minimal (Table 2, Table 15 and Appendix 5). Life-cycle tests have been conducted with endothall acid. The NOEC for the *Daphnia magna* life-cycle test is 5 mg a.e./L. This is well above the maximum exposure rate of 3.5 mg a.e./L expected after the initial application of Aquathol®. Since the NOECs are higher than the maximum use rate, this segment of the biota should not be chronically affected. (See Section 4.1.10.2.5).

With Hydrothol® 191, the amount of chronic data that has been generated is extremely limited. Only a few studies with fathead minnow and daphnia have been conducted. The lowest NOEC for fish was 0.022 to 0.056 mg a.e./L with an end point of reduced growth. It is not possible to determine risk without a formal risk analysis because fish and invertebrates are chronically sensitive to Hydrothol® 191. For a risk analysis based on predicted NOEC or empiracle NOEC, please see Section 4.1.10.2.

#### **4.1.10.2.3 Potential Impacts of Single Versus Multiple Applications**

*Summary: Risk analysis indicates that Aquathol® K should be safe to aquatic biota when used at all concentrations specified on the label. However, acute Hydrothol® exposure would probably adversely impact the entire biota causing high fish-kill when used at the maximum concentrations specified on the label. Hydrothol® 191 may chronically affect the biota when used at concentrations as low as 0.3- 0.5 mg a.e./L; but if the treatment concentration is lowered to 0.2 mg/L, risk analysis indicates that acute or chronic exposure may not adversely impact the biota. Fish species appear to be more sensitive than free-swimming invertebrates and benthic invertebrates to Hydrothol® 191.*

It is an extremely rare event for lakes in the state of Washington to be treated with endothall products more than once in a season. Therefore, very little practical field knowledge is available on this subject. Some laboratory work on the effects of multiple exposures of endothall to the goldfish have been conducted. Berry (1984) found that one-time exposure of goldfish for 96 hours to concentrations of endothall at concentrations between 32 to 200 mg a.i./L produced no pathological signs such as lesions on the gills, cephalic lateral line, nares or taste buds. However, if prior experience with endothall exposure had occurred at levels higher than standard field treatment rates (1 to 5 mg a.i./L), gill hypertrophy was observed upon second exposure to endothall at concentrations greater than or equal to 80 mg a.i./L. This exposure level is

unreasonable based on the theoretical field exposure. However, more reasonable exposure rates of 10 mg a.i./L for 96 hours with Aquathol® K produced gill lesions in Chinook salmon (Liquori et al., 1983) but not in Coho salmon, or bluegills (Lorz et al, 1979 and Berry, 1975 in Berry, 1984). Aquathol® K field rate exposures for ten days did not produce pathological effects on gills, liver or kidney in a number of species (Walker, 1963 and Geilderhaus, 1967 in Berry, 1977).

- **Potential impacts on numbers**

There is not a large literature base concerning negative or positive impacts of endothall treatment on numbers of fish and invertebrates in natural ecosystems. There is data on the effect of failure to remove weeds when they become so dense they interfere with the movement of fish. However, this data is rather ambiguous. Klusmann et al. (1988 in Bain and Boltz, 1992) found that catch rates for largemouth bass were greatest when the plant densities were highest. Colle et al. (1987 in Bain and Boltz, 1992) found that largemouth bass catches were unaffected by a reduction in plant density. Plant cover of about 36% appears optimal for production of largemouth bass (Ware and Gasaway, 1978 in Bain & Boltz, 1992) and complete removal of aquatic plants can cause a major decline in forage fish and large-mouth bass abundance (Moxley and Langford, 1985 in Bain & Boltz, 1992). There can also be a decrease in the numbers of certain size classes (intermediate size largemouth bass) and not others (large largemouth bass) if foliage is entirely removed (Klusman et al., 1988 in Bain & Boltz, 1992).

When Aquathol® K was applied at the maximum use rate of 5.00 mg a.i./L to ponds in Wisconsin, there did not appear to be any significant effects on the bluegill population in terms of numbers (534,000/ha for control pond and 581,000/ha for the treatment pond) for the young of the year, or adult survivorship (39% for the control pond and 56.4% for the treatment pond) (Serns, 1977). However, growth rate was markedly decreased in the treatment pond (0.16 g mean weight and 24.7 mm mean length) when compared with the control pond (0.67 g mean weight and 37 mm mean length). For the first generation produced in this ecosystem, survivorship was reduced in the treatment pond (23%) versus the control pond (34%) while the growth rate was higher in the treatment pond (49 mm mean length) than in the control pond (40 mm mean length). The higher growth rate in the treatment pond can be attributed to lower fish densities. A trend towards equality in survivorship and growth could be seen in the first generation during the following year with survival at 61% and 67% in the treatment and control ponds respectively, and a growth rate of 75 mm and 92 mm in the treatment and control ponds respectively. The number of young of the year produced by the first generation was higher in the treatment pond (95,500/ha) than in the control pond (33,000/ha) while the growth weight of fish in the treatment pond was significantly lower (0.20 g mean weight and 24 mm mean length) than in the control pond (1.51 g mean weight and 48 mm mean length) Serns, 1977.

In a similar experiment, a single application of endothall eliminated all submergent vegetation in Little Horseshoe Lake, Minnesota. There were no apparent changes in size structure and abundance of bluegill and Northern pike during the next two years. However, removal of submergent vegetation appeared to increase the number of young of the year and their size range without affecting adult abundance in largemouth bass. Temperature appeared to have a greater effect on the growth of bluegill and largemouth bass than the abundance of submerged vegetation. Improving

bluegill populations by increased predation through submerged vegetation reduction shows little promise as a fisheries management tool (Radomski et al., 1998).

It is not known whether the observed effects on bluegill populations was due to the chronic toxicity of endothall, changes in the treatment ponds aquatic weed density, redistribution of plant species, or to some other more subtle parameter. There were marked effects on weed density and diversity of species during the course of this experiment. For details please see Sections 4.1.10.1.3. It was demonstrated that these differences were not due to an adverse impact of endothall on zooplankton. Zooplankton numbers were either similar in the treatment and control ponds (Copepods) or considerably higher in the treatment ponds versus the controls.

A possible effect of endothall is the marked increase in Ostracod numbers in the treatment ponds in August (~100/L) versus the control ponds (~20/L) although seasonal numbers for the treatment and control do not appear to be significantly different between July and October. These differences could be due to improved growth of *Chara spp.* which are colonized by Ostracods or a sampling error due to the association of Ostracods with growing *Chara spp.* (Serns 1975).

Endothall has been shown to have an impact on insects associated with hydrilla in some cases (Haag & Buckingham, 1991). The hydrilla weevil (*Bagous affinis*) did not experience significant mortality (<5%) when exposed to 2 to 4 mg a.i /L Aquathol® K. There is some evidence for other herbicides that exposure of plants to these herbicides may improve the biological control effectiveness of *Bagous affinis* against *Hydrilla* (Hagg and Habeck, 1991).

However, the Hydrellia fly (*Hydrellia pakistanae*) exhibited significant mortality (74%) when exposed to endothall while *in situ* on hydrilla. This effect was believed to be due to the loss of habitat after the destruction of hydrilla leaflets and not to the direct effect of the herbicide itself. If endothall is applied in an integrated pest management program to control hydrilla, it is important to avoid treatment when fly larvae or pupae are present (Hagg & Buckingham, 1991). Although the data presented here shows us significant impact on aquatic animal numbers, the design of these studies is flawed. Since these data are based on individual treatments rather than replicated treatments, a complete statistical evaluation of the results is not possible.

- **Impacts on diversity**

The detailed study on the numbers and diversity of fish conducted by Olaley et al. (1993) concluded that areas infested heavily with water hyacinth contained a very low number (8) per unit area of the anabantid, *Ctenopoma kinglayae*, and no other species. However, if no water hyacinth or other weeds were present, the numbers of this Anabantid went up to 30 individuals per unit area and eight other families of fish were present at low levels. Since this work was conducted in Nigeria, it may not be directly applicable to the State of Washington. Significant work with native U.S. Northern tier states fish has not been done with endothall to show whether it has an impact on fish diversity. However, due to its short half-life and use patterns in Washington makes any long term impacts on fish populations unlikely.

An increase in the numbers of zooplankton was noted when a water body was treated at the maximum usage rate for endothall (5.0 mg a.i./L = 3.5 mg a.e./L) but the zooplankton species composition and generic density (diversity) were unaffected by the use of Aquathol® K despite marked change in the numbers and diversity of aquatic weeds (Serns, 1975 & 1977). The treatment of these weeds produced an oxygen slump, but did not cause an increase in nitrogen levels (NH<sub>3</sub>, NO<sub>2</sub>, NO<sub>3</sub> or organic nitrogen), dissolved phosphorous and total phosphorous. A decrease in dissolved oxygen from 20 to 10 ppm appeared to have no effect on fish numbers, survival, or reproduction. The fact that there was no apparent release of organic nutrients may have been due to the presence of rapidly growing *Chara* species which adsorbed these nutrients before they had a chance to increase. The lack of an increase in nutrient levels was somewhat surprising because an increase in nutrient levels is often seen as a result of the decay of aquatic vegetation due to herbicide treatment of a water body (Frank, 1973, Shearer and Halter, 1980)

- **Potential impacts on habitat use for spawning, rearing and growth**

- **Effects on freshwater trout**

Aquathol® K has been shown to have low toxicity to early life stage fresh-water trout, but this is not an absolute proof that endothall is safe to fresh water trout during spawning and breeding times (Folmar, 1977 in Ecology, 1992). However, the long term Risk Quotient indicates a very low risk to trout. Without further data, risk (albeit low risk) can not be ruled out. A standard Early Life-Stage study compliant with EPA current guidelines would improve the likelihood that the risk is low but without a life-cycle study risk cannot be ruled out. Life-cycle studies require considerable manpower and financial resources and the results are not easy to interpret because control values can vary considerably from study to study. Since the Level of Concern concentrations for chronic studies are low for both Aquathol® and Hydrothol® ( $\leq 1/L$ ), and the NOEC is high, these studies are probably not warranted.

- **Effects on salmon smoltification**

Effects on salmon smoltification is of potential concern. Bouck and Johnson (1979 in Shearer and Halter, 1980) found that Coho salmon smolts exposed to 5 mg a.i./L endothall for one hour and then immediately challenged with sea water produced 100% mortality in one trial and 0% mortality in the second trial. Exposure of the controls to fresh water for four additional days produced no significant mortality.

Chinook salmon exposed to 1.5 to 3 mg a.e./L for four days, showed similar results (Ligouri et al, 1984). Fish challenged with seawater after exposure to 3 mg a.e./L did not survive more than three days. However, fish exposed to either zero or 1.5 mg a.e./L survived for a full 10 days without any significant mortality. Fish exposed to higher concentrations of endothall (16 to 55 mg a.e./L) showed  $\geq 80\%$  mortality when exposed to sea water for 4 days. A possible explanation of this effect is that fish exposed to higher than 10 mg a.e./L exhibited gill hypertrophy but those that were exposed to less than 10 mg a.e./L did not. Irritation and pathological effects of endothall at levels of  $< 10$  mg a.e./L were not apparent during histological examination. However, the pathological

condition may have been present at levels high enough to interfere with the parr to smolt metamorphosis. Similar gill hypertrophy has been seen in goldfish exposed to endothall (Berry, 1977).

Serdar and Johnson (1996) exposed Coho salmon smolts to 5.0 mg a.e./L for 96 hours, then challenged them with seawater for 24 hours, and measured the plasma sodium concentrations in both exposed and control fish. The concentration in the exposed and control fish plasma was 170.7 and 170.9 meq/L, respectively.

The differences in results may be due to different effects on different species, parr not completely smolted, or effects of inert ingredients that caused gill damage and prevented the fish from osmoregulating properly. Introduction of fish directly into seawater in the first two experiments but not the plasma sodium level experiments may have unduly stressed the animals and contributed to the lethal response to the seawater challenge.

More recent work has been done on the effects of Hydrothol® 191 on the smoltification process in Chinook salmon. Exposure to Hydrothol® 191 at 0.200 mg a.e./L caused no direct mortality of Chinook smolts. However, 45% of these smolts died when challenged with seawater. Mortality was not due to a change in ATPase activity or in the ability of the exposed smolts to osmoregulate. At lower concentrations (0.50 or 0.100 mg a.e./L), smolts exposed to Hydrothol® 191 survived a seawater challenge. The reasons for mortality in the seawater challenge are unclear but may be due to respiratory distress due to gill hypertrophy (Serdar et al, 1995).

Although avoidance has been claimed for Hydrothol® and its mono(dimethylalkylamine) by the manufacturer, we found no scientific evidence for this claim. However, applicators claim that skill and knowledgeable application of Hydrothol® from shore outline outward will drive fish from the application area. There is some evidence that salmonids and goldfish will avoid Aquathol® alone and will particularly avoid a combination treatment with dalapon at rates that approach field application rates [Dodson and Mayfield, 1979, Lorz et al, 1979, and Liguori et al, 1983 in (Berry, 1984) and Berry, 1984].

In light of the discrepancies found in this research, continued research on the species tested and other species of salmon may be warranted. To find out if the failure to make the parr to smolt metamorphosis is due to peculiarities in the formulation, it would be of value to test the inert ingredients in Aquathol® K and Hydrothol® 191. To discover whether there may be a problem with potassium in the endothall acid, it could be important to test for failure to smolt properly with endothall acid, dipotassium endothall and disodium endothall in the absence of inert ingredients.

Although effects on salmon smoltification is of legitimate concern, the threat to salmon and trout, parr-smolts will probably be low. Application of endothall would generally occur several months after salmon and trout smoltification has been completed.

- **Effects on searun cutthroat trout**

No work was found on the effect of endothall on searun cutthroat trout other than acute toxicity data (LC50 = 0.18 mg a.i./L = 0.079 mg a.e./L for Hydrothol® 191). This toxicity is above the EEC of about 1.43 mg a.e./L for Hydrothol® 191 and yields an unacceptable Risk Quotient of 19.25 = (1.43 ppm/0.08 ppm). However, additional information on the acute and chronic toxicity of Hydrothol® 191 would be useful to aid in risk assessment with either this species or a related species.

The potential difficulty with searun cutthroat trout is similar to the parr to smolt metamorphosis except that searun cutthroat trout may go through this process several times in their lifetime including each time the adults migrate to the sea. Experiments, both with adults preparing to enter seawater and smolts preparing to enter seawater, where exposure to endothall at field rates is the first step and the second step is a seawater challenge may be of value. With the adults, the reverse experiment could also be conducted where fish leaving ocean water are challenged with fresh water containing field notes of endothall to understand if the adults can survive this process.

- **Effects on other species (sunfish, minnow and catfish)**

The acute toxicity for these three groups is very low for Aquathol® K ( LC50 = 11 to 312 mg a.e./L and very high for Hydrothol® 191 (0.079 to 0.82 mg a.e./L). This led Finlayson (1980) to conclude that Hydrothol® should not be used unless fish mortality is acceptable at typical treatment rates of 0.2 to 0.5 mg/L.

According to Ecology (1992), Hydrothol ® 191 and Aquathol® K do not represent a significant risk for chronic exposure (0.02 – 0.06) mg a.e./L if fathead minnow is used as the most sensitive indicator species. However, the fathead minnow is not the most sensitive indicator species. To determine risk, a formal risk assessment is necessary for Hydrothol®, because the acute and chronic toxicities are fairly high to most aquatic species. A formal risk assessment for both Aquathol® K and Hydrothol® 191 are performed in Section 4.1.10.2.5.

In a field test conducted by Bettoli and Clark (1992), no significant difference in nesting behavior was seen in bluegills where the nesting area was treated with Aquathol® K and control ponds. Since the sample size was very small (6 controls and 8 Aquathol® K treatments), this conclusion needs further investigation. This is particularly so since 88% of the Aquathol® treated cohorts abandoned their nests and only 50% of the water treated cohorts abandoned their nests. This is important since abandoned nests are frequently attacked by cogener predators (86% for the Aquathol® treated cohorts and 33% for the water treated cohorts). Such a dramatic impact could have a marked influence on the number of young of the year surviving to the free-swimming stage.

It should be noted that field treatments at Lake Steilacoom with 0.2 mg/L Hydrothol® 191 to control algae did not produce any obvious fish-kill (Resource

Management, 1999). While this is encouraging, lack of valid scientific controls makes interpretation of this observation difficult.

#### 4.1.10.2.4 Effects on Endangered Species

A number of fish species have been listed as sensitive, threatened or endangered (Appendix 6). The most important species groups for Washington State are salmon and searun trout (cutthroat and steelhead). There are also a number of species that are listed by the Washington Department of Fish and Wildlife, but not by the federal government. These include thirteen species of rockfish, two species of dace, two species of herring and several other species. Also included are four species of salmonids and two toad species. Although some toxicity data is available on Aquathol® for salmon or searun trout species, there are no data available for most species of sensitive, threatened, and endangered fish.

#### 4.1.10.2.5 Risk Analysis for Aquatic Species

A great deal of the risk analysis was discussed in Sections 4.1.10.2.2. Tying the toxicological effects with the Risk Analysis may improve the understandability of the analysis.

Certain mitigating behavioral and toxicity factors can improve the Risk Analysis picture. Ecology (1992) states that “trout will avoid Aquathol® at concentrations above 10 mg/L”. Berry (1984) noted that goldfish avoided endothall concentrations when they exceeded 17.1 mg a.i./L however, this is clearly above levels that fish would normally be exposed to in the field. Berry cited cases indicating that endothall tested near the field rate was avoided by salmonids (Dodson & Mayfield, 1979 in Berry, Lorz et al. 1979 in Berry and Liquouri et al, 1983 in Berry). Folmar (1976) tested Aquathol® K against rainbow trout and found no statistical basis that rainbow trout avoided Aquathol® K concentrations up to 10 mg a.e./L. The data indicate a trend of increasing avoidance of Aquathol® at concentrations of 0.1, 1.0 and 10.0 mg a.e./L. 42, 55 and 64%, respectively, but these values do not differ significantly from the expected 50% value if no avoidance is occurring.

Aquathol® has a very short residence time in lakes and ponds and is not acutely toxic, therefore fish are unlikely to be influenced in their distribution patterns by the presence of Aquathol® at normal treatment levels of 3.5 mg a.e./L.

To generate an EEC similar to the EEC presented in the 1992 SEIS certain assumptions must be made:

- 1) If treatment was at the maximum use rate (3.5 mg a.e./L) for Aquathol® K, a half-life of 0.8 days must be assumed. This will give a 4-day weighted EEC of 1.0 mg a.e./L. Ecology (1992) gives an acute EEC of 1.0 mg a.e./L
- 2) If a similar assumption is made for Hydrothol®. The maximum use rate will be 5.0 mg a.e./L with a half-life of only 0-8 days. This will give a 4-day weighted EEC of 1.40 mg a.e./L. Ecology, 1992 gives an acute EEC of 1.43 mg a.e./L

While the values obtained here are similar to those generated by Ecology (1992), the concept of the most representative half-life has a very strong element of opinion

connected to it. While half-lives found in the literature vary from hours to over a week, the values used for any particular situation should be based on past experience with the water body to be treated.

For Chronic Risk Assessment similar assumptions should be made:

- 1) If treatment was at the maximum use rate (3.5 mg a.e./L) for Aquathol® K, and again a half-life of 0.8 days is assumed, the 28-day geometrically weighted EEC will be 0.14 mg a.e./L. This value is approximately twice the Ecology (1992) EEC estimate of 0.06 mg a.e./L for Aquathol® K.
- 2) The EEC estimate for Hydrothol® 191 has the additional component of flow rate if the herbicide is used to control weeds and algae within a canal. There may be no chronic effect issues if the flow rate is rapid, and almost all of the herbicide is removed from the treatment area shortly after exposure ceases. The amount typically remaining in the sediment after the treatment plume of 0.2 mg a.e./L passes is typically less than 0.1 mg a.e./Kg sediment. The residue in the sediment rapidly disappears after treatment (Keckemet & Sharp, 1999). Under these conditions where the chronic EEC in water approaches zero, chronic toxicity is not an issue.
- 3) However, if Hydrothol® is used to control algae in a lake or pond at 0.3 mg a.e./L and the 0.8 day half-life is estimated, the 28-day weighted EEC will be ~0.01 mg a.e./L which is about half the value estimated by Ecology (1992). However, this may be very close to the Ecology value if you factor in the fact that the EEC value determined by Ecology appears to be uncorrected for endothall acid equivalence and is expressed as formulation concentration of Hydrothol® 191. If a somewhat lower treatment rate (0.02 mg a.e./L) is used the 28-day weighted EEC will be ~0.008.

There is uncertainty in the estimates of chronic EEC based on acute to chronic toxicity ratios (Table 16). These ratios were generated by dividing the acute LC50 by the chronic NOEC value for the species and endothall products indicated. The data from Keller (1988) for both fish and invertebrates were eliminated as being outliers and therefore unreliable. The data for Chinook salmon generated by Pennwalt (1986 in Ecology, 1991) and Ligouri et al. had chronic toxicity values based on LC50s and not NOEC. The ratio of 6.4 is close to the ratio of 10 that is often used as an initial screening value when chronic studies are run for the first time. However, if the values are used for this risk assessment, the following results will be obtained (Table 19 & 20).

- 1) The most sensitive species and stage (early-life stage walleye) to Aquathol® has an LC50 of 11 mg a.e./L, the Acute Risk Quotient is 0.090 ( $RQ = 1 \text{ ppm}/11 \text{ ppm} = 0.090$ ). Since the criteria value of 0.10 is not exceeded, it should be possible to use this herbicide without significant risk to 95% or more of the aquatic animal species.

Conducting acute tests on early life stages is not standard practice and may result in numbers which are not a true reflection of a chemical's toxicity in the field. Therefore, if one uses the same sensitive species used by Ecology (1991, 1992), one gets an acute Risk Quotient of 0.04 (1.0 ppm/23 ppm) for Chinook salmon at the expected environmental concentration for endothall salt (Aquathol® K, disodium endothall in endothall acid). This risk quotient is well below the level of concern for sensitive, threatened, or endangered fish species that Ecology and the general public desires to protect (Table 15). It has been recommended in Urban and Cook (1986)

that the acute risk quotient level of concern be reduced to 0.05 for the protection of threatened and endangered species. And at least for Chinook salmon, this acute level of concern has been obtained.

The acute effects of Aquathol® K and endothall acid on free-swimming invertebrates and sediment organisms (LC50 = 39 to 750 mg a.e./L, RQ = 0.06) are less than those for fish. Therefore, it should be possible to use Aquathol® at maximum labelled use rates without significant impact to invertebrate segments of the biota.

- 2) The most sensitive species to Hydrothol® 191 is cutthroat trout (*salmo clarki*) has an LC50 of 0.079 mg a.e./L, the acute risk quotient is ~12 (RQ = 1.40 ppm/0.079 ppm = ~18). Since the criteria value of 0.10 is exceeded greatly, it is not possible to use Hydrothol® 191 without significant risk to aquatic animals.

The acute effects of Hydrothol® [mono(dimethylalkylamine) salt of endothall] on free-swimming invertebrates (LC50 = 0.080 to 0.37 mg a.e./L) and environmentally relevant benthic organisms (LC50 = 0.12 to 1.0 mg a.e./L) are similar to those found for fish. Hydrothol® cannot be used at maximum label rates without significant acute impact on these invertebrate segments of the biota (RQ = ~18 to ~12). However, if the acute treatment levels with Hydrothol® 191 are lowered from 5.0 mg a.e./L to ≤ 0.2 mg a.e./L with exposure periods of less than 120 hours, it may be possible to use Hydrothol® 191 for the control of aquatic algae in irrigation canals and whole lakes without significant impact on the aquatic biota. This view is supported by the modeling work of Giddings (1999) and observations by Finlayson (1980) on work done in the field by several other authors. Furthermore, work done at Lake Steilacoom indicates that Hydrothol® can be used at concentrations as high as 0.2 mg/L without obvious fish-kill due to the rapid dissipation of the active ingredient (Resource Management, 1999). However, classical risk assessment procedures of Urban and Cook (1986) would indicate that safety to the biota cannot be provided unless the treatment rate drops below the lowest concentration (0.05 mg a.e./L) recommended on the label. In this case the acute Risk Quotient would still be higher than the acute level of concern of 0.10 (RQ = 0.014 ppm a.e./0.079 ppm a.e. = 0.17 in cutthroat trout).

Even at a reduced canal treatment (120 hours at 0.2 mg a.e./L) for the control of more sensitive algal species like *Cladophora*, *Pithophora*, *Spirogyra* and *Chara*, Giddings (1992) estimated that 30% of the non-target species would be affected at the point of application; and 20% would be affected 10 to 50 miles downstream depending on flow rate. At higher treatment rates, nearly all species would be affected at the point of discharge. Furthermore, the adverse downstream impact would be greater after 24 hours of treatment at 1 mg a.e./L than after 3 hours of treatment at 3 mg a.e./L. At medium and high flow rates, more than 50% of the species would be affected for 30 or more miles downstream after 3 hours at 3 mg a.e./L or 24 hours at 1 mg a.e./L. It is estimated that with a 24 hour exposure period to 1 mg a.e./L 80% of the species within the canal would be affected for 30 or more miles downstream.

In US EPA evaluation of pesticides under FIFRA, an Acute Risk Quotient higher than 0.1 is interpreted as exceeding the Level of Concern, and leads to the conclusion that the risk may be unacceptable unless further analysis shows otherwise (Urban and Cook, 1985 and Giddings, 1999).

Even though the Acute Risk Quotient is  $<0.1$  we cannot conclude that Aquathol® K does not represent an acute risk to all aquatic organisms. It is not possible to conjecture that no risk exists. Herbicide concentrations identified here as not causing significant adverse impact may still adversely impact more sensitive aquatic species. However, the economically important and endangered/threatened species are expected to be protected at the forecasted herbicide application rates and estimated exposure conditions (Giddings, 1999, Ecology, 1992).

- 3) For chronic studies, the most sensitive species tested with Aquathol® K, disodium endothall or endothall acid were *Daphnia magna* and rainbow trout. The chronic NOEC for these species was 5.0 mg a.e./L. If an estimate of NOEC for Aquathol® is made based on the LC50 (23 mg a.e./L) of Chinook salmon (the most sensitive species), one would divide the LC50 by the acute to chronic toxicity ratio (6.4, Table 19) and get a predicted chronic NOEC of 3.6 mg a.e./L; the value of 3.6 mg a.e./L does not differ significantly from the value of 5 mg a.e./L obtained empirically for rainbow trout and *Daphnia magna*. The chronic EEC based on the above parameters was between 0.06 mg a.e./L (Ecology, 1991) and 0.14 mg a.e./L for the current assessment. Using either value gives a Chronic Risk Quotient of  $<0.1$  ( $RQ = 0.06 \text{ ppm}/5.0 \text{ ppm} = 0.012$  or  $0.14 \text{ ppm}/5.0 \text{ ppm} = 0.028$ ); These values may be slightly higher ( $RQ = 0.4$ ) than those presented here, if the estimated chronic NOEC is utilized for the Risk Quotient calculations. The values generated in the Chronic Risk Quotient for the indicated products are well below the level of concern (1.0). Therefore, it should be possible to use the endothall salts and the endothall acid without significant chronic risk to aquatic species. Since the most sensitive environmentally relevant benthic invertebrate species has an acute toxicity (LC50 = 222 mg a.e./L) that is higher than *Daphnia magna*, it (lined scud) and members of this segment of the biota should not be impacted by chronic exposure to Aquathol® K (predicted NOEC = 34 mg a.e./L;  $RQ = 0.017$ ).

One cannot say that no credible risk exists for chronic exposure of invertebrates to Aquathol® K. Further research to expand the database on the chronic toxicity of endothall acid and particularly Aquathol® to aquatic invertebrates needs to be conducted to give the life-cycle NOECs greater credibility. Typical tests that would be conducted are life-cycle tests with *Daphnia magna*, *Ceriodaphnia dubia* and the mysid shrimp. These species are easy to rear in the laboratory and the procedures for conducting life-cycle studies are well accepted by state and federal regulatory agencies.

- 4) The Chronic Risk for Hydrothol® 191 is more difficult to predict. There are a number of vertebrate and invertebrate species that would give Chronic Risk Quotients that exceed the criterion values if the predicted chronic NOECs are used for the denominator (Tables 19 & 20). For example, if the most sensitive predicted environmentally relevant NOEC is used, the value for cutthroat trout would be selected. This predicted chronic NOEC value was 0.012 mg a.e./L for Hydrothol®. Using this value gives a Chronic Risk Quotient generally  $>1.0$  ( $RQ = 0.02 \text{ ppm}/0.012 \text{ ppm} = 1.67$  or  $0.01 \text{ ppm}/0.012 \text{ ppm} = 0.833$  with a geometric mean of 1.17) based on either of the chronic EEC values generated above in Ecology (1991) or the current assessment. However, other species that are chronically sensitive to Hydrothol® 191 include *Ictalurus punctatus* (channel catfish), *Hexagenia spp.* (mayfly), *Hyallela azteca* (amphipod) and *Gammarus fasciatus* (lined scud). Since the benthic species

should be considered in this Chronic Risk Assessment, the Chronic Risk Quotient is approximately 1.0 for the more sensitive species ( $RQ = 0.02 \text{ ppm}/0.019 \text{ ppm} = 1.05$  or  $0.01 \text{ ppm}/0.019 \text{ ppm} = 0.53$  with a geometric mean of 0.74). However, whether or not safety to the benthic biota can be assessed depends on the expected environmental concentration that is believed to be most accurate. Effects of the concentration of Hydrothol® 191 that has partitioned into the sediment were ignored as adsorption is believed to play a minimal role in environmental dissipation. Since the Chronic Risk Assessment is so close to being acceptable for the benthic biota, this would be an ideal situation for mitigation. If these sediment-associated organisms are eliminated from the Chronic Risk Assessment, the Chronic Risk Quotient becomes less than unity ( $RQ = 0.02 \text{ ppm}/0.16 \text{ ppm} = 1.25$  or  $0.01 \text{ ppm}/0.016 \text{ ppm} = 0.63$  with a geometric mean of 0.89) using the *Daphnia magna* as the indicator species. Marine and estuarine species were eliminated as being not environmentally relevant for the purposes of this risk assessment since dilution in estuarine and marine environments will decrease Hydrothol® 191 levels to below detectable limits. The value generated in this Chronic Risk Quotient for Hydrothol® 191 is below the level of concern of 1.0 for invertebrates, but above the level of concern for fish. Therefore, it should be possible to use the Hydrothol® 191 without significant chronic risk to free-swimming fresh water invertebrates. However, due to the extreme sensitivity of cutthroat trout, sensitive fish species may not be protected. If the treatment concentration dropped to 0.2 mg a.e./L the chronic Risk Quotient will drop below the level of concern for protection of the entire animal biota. E.g for most sensitive species (cutthroat trout), the chronic Risk Quotient becomes 0.67 (0.008 ppm a.e./0.012 ppm). This treatment rate should protect the most sensitive species of fish, free-swimming invertebrates and benthic invertebrates.

#### **4.1.11 ADDITIONAL POTENTIAL DIRECT AND INDIRECT IMPACTS OF HERBICIDE USE ON WET LAND ENVIRONMENTS**

Because of the manner in which endothall products are applied, significant impact to other wetland environments is not probable. There may be some drift or flow into other wet land environments or a flow of water into estuarine, palustrine, riparian, lentic or lotic environments. However, it not anticipated that the impact would be measurable due to dilution effects. Treated ponds, lakes, and canals flow into streams and rivers and ultimately into estuaries.

##### **4.1.11.1 Estuarine (Intertidal) Environments**

Water from a stream or river containing endothall may flow into an estuary. However, the water already present in the estuary and tides should dilute endothall to levels where it is not significant in the water column. Some estuaries have sediment that is anaerobic, and there is potential for a build up of endothall in this anaerobic sediment. It has been demonstrated that endothall in anaerobic conditions (Simsiman and Chesters, 1975) does not degrade readily.

Marine (estuarine) organisms tested have LC50s similar to those that were seen for freshwater organisms. For Hydrothol® 191, the marine organisms had LC50s that ranged from 0.022 to 1.13 mg a.e./L. Freshwater organisms had Hydrothol® LC50s that ranged from 0.075 to 1.89 mg a.e./L. Therefore, the effects on the biota are likely to be

similar in the estuarine and freshwater environment. The most sensitive species in both environments have the potential to be adversely affected.

Even with extensive dilution, the more sensitive species in an estuarine environment may be adversely affected.

#### **4.1.11.2 Palustrine (Marshy) Environments**

Extensive growth of rooted aquatic macrophytes may effectively dam a marsh and increase depth by several fold. In this way the aquatic macrophytes assist in spreading waters onto the surrounding land to increase its fertility and provide additional areas for fish and amphibians to feed and spawn (Goldman & Horne, 1983). Even without flooding, these plants may have an effect on habitat suitability for wild birds, mammals and other terrestrial organisms.

The dominant plants found in palustrine environments are emersed. Most emersed plants are not likely to be adversely impacted at the concentrations of endothall used to control fully aquatic weeds. However, floating and rooted submersed plants, that are typically found in a palustrine environment may be impacted by water that enters these areas from lakes and ponds. If these rooted macrophytes are destroyed, there will be less tendency for the marsh to flood and therefore potential habitat will be lost to fish and amphibians. Also, if these plants are lost, and flooding does not occur, loss of suitable habitat for wild birds and mammals may occur.

#### **4.1.11.3 Riparian (Margin and Bank) Environments**

Endothall products are used to treat the submerged margins of lakes and ponds to eliminate weeds and algae that interfere with the recreational use of the lake or pond. Any non-target aquatic plants and animals have a potential to be impacted by endothall products as described in Sections 4.1.10.1 (Effects and Selectivity on Aquatic Plants) and 4.1.10.2 (Effects on Aquatic Animals).

#### **4.1.11.4 Other Wetland Environments**

Pasture which is routinely flooded may be impacted by endothall treated waters. Although, endothall does not typically impact most grasses adversely, some of the more sensitive species may be impacted. No efficacy claim has been made by the manufacturer for the control of plants that typically grow in pastures. This makes it difficult to determine if treated water from a lake or pond will impact a flooded pasture site adversely.

#### **4.1.11.5 Lentic Environment**

Potential impacts on lentic and lotic environments as to the chemical ecology were discussed extensively in Sections 4.1.9.3. Effects on the biota in these environments were discussed extensively in Section 4.1.10.

#### 4.1.11.6 Lotic Environment

The lotic environment can be influenced by the presence of endothall in water from a lake or pond outlet. If endothall is present at levels that controls weeds and the outlet gate is closed, a type of habitat favorable to sunfish and amphibians will develop. If the outlet gate is open, a type of habitat more favorable to salmonids may develop.

- **Closed outlet gate or absence of endothall**

If the outlet gate from a pond or lake to a river or stream remains closed, dense growths of rooted aquatic macrophytes may effectively dam rivers and streams and increase the depth of the lotic system by several fold. In this way the aquatic macrophytes assist in spreading waters onto the surrounding land to increase its fertility and provide additional areas for fish and amphibians to feed and spawn (Goldman & Horne, 1983). Similar effects may occur if the lake or pond is not treated with endothall.

- **Open outlet gate in presence of endothall**

If water that contains endothall at effective concentrations passes, through the outlet gate of a lake or pond into a river or stream, the rooted aquatic macrophytes may be destroyed. This can have a substantial impact during the next flood event. Normal spring floods in absence of rooted aquatic macrophytes can dig up and kill large numbers of benthic organisms while summer floods can completely denude streams of benthic biota.

Most biota avoid high water either by migrating to calm back waters or by having life cycles which are terrestrial or aerial at these times. However, when floods occur at unusual times the fauna may be severely depleted and require several years to recover (Goldman & Horne 1983).

Larger organisms, like salmonids, choose to ascend rivers or streams during high water or floods because there are fewer shallow water barriers. Severe floods are detrimental to smaller biota if they leave only inhospitable rocks and gravel. However, these floods may improve fish migration by removing major obstacles. Smaller floods can improve the environment for salmonid mating and egg survival by removing excessive silt. These benefits cannot occur if the lotic system has been dammed by aquatic weeds.

#### 4.1.12 UNCERTAINTY ANALYSIS

*Summary: The uncertainty analysis indicates that field studies often reflect the risk analysis that has been used to generate the label. Models that have been used since 1975 indicate that an acute risk quotient of  $<0.1$  or a chronic risk quotient of  $<1$ , reflects safety of the product to exposed aquatic animals under field situations. An acute risk quotient is generated by dividing the acute predicted environmental concentration (acute EEC) by the LC50 of the most sensitive species of concern within the ecosystem. Providing a 10-fold safety factor will insure that less than 5% of the animals with similar sensitivity will be adversely affected. A chronic risk quotient is generated by dividing the chronic EEC by the chronic NOEC or chronic predicted NOEC for the most sensitive*

*species. A safety factor is not necessary in chronic risk assessment since all animals with a similar sensitivity will also not be affected by exposure to chronic EECs for the compound being evaluated. For both Aquathol® and Hydrothol®, field studies indicated that risk quotients can predict the safety or lack of safety of a herbicide to the biota. Aquathol® has an acute risk quotient of 0.043, and field studies indicate that exposure in the field to typical use rates will not effect the survivorship of bluegills or largemouth bass (Serns, 1977 and Radomski, 1995). Conversely, Hydrothol® 191 has an acute risk quotient of ~18 and field studies indicate that a variety of fish will be affected adversely by exposure to concentrations of Hydrothol® 191 that are significantly less than typical field rates. The predictive value of a chronic risk quotient much less than unity for Aquathol® K ( $RQ = 0.12$ ) has been shown by field studies that indicate mortality, growth and reproduction are unaffected by concentrations Aquathol® that may be encountered in the field (Serns, 1977, and Radomski, 1995). However, insufficient field data exist to show that fish may be adversely affected when the chronic RQ is greater than unity ( $RQ = 1.17$ ) in the case of Hydrothol® 191.*

The assumptions of risk analysis contain specific safety factors that are discussed by Urban and Cook (1986). The model discussed by Urban and Cook has been used since 1975 and was designed to provide a safety factor that would allow for differential variability and sensitivity among fish and wildlife species.

It was assumed that the slope of the dose response curve for the effects of a pesticide on most fish and wildlife species would be unknown. Since it is impossible to test every non-target-species that might be exposed, the following factors influence whether a correct risk management decision will be made:

- 1) Does the model predict risk so that the biota will be protected? Statistical analysis of the effects of slope on the estimating the acute LC50 indicates that an expected environmental concentration (EEC) value that is actually 10-times less than the acute LC50 would lead to 1 to 4% mortality.
- 2) Terrestrial organisms are believed to be less susceptible to environmental assault than aquatic species. Therefore, the less stringent acceptable EEC is used to designate unacceptable risk in these species. The less stringent acceptable EEC of 5-times less than the acute LC50 or LD50, which would lead to a field mortality of approximately 10%, is used as a level of unacceptable risk in birds and mammals. The higher safety factors listed in item 1) for aquatic organisms is believed to be necessary since aquatic organisms are less likely to be able to limit their exposure through behavioral modifications such as moving out of the treated area or switching to an alternative food source.
- 3) Larger safety factors are warranted for the protection of threatened and endangered species where a factor of 10-fold is insufficient to protect that segment of the biota. E.g. In cases where no mortality is acceptable an EEC of 20 times less than the acute LC50 should be sufficient to ensure protection of species in which even a single death is of special concern.
- 4) For chronic effects, an EEC equal to the no observed effect concentration (NOEC) or no observed effect level (NOEL) is believed to be sufficient to reduce risk to a minimum level, since statistical analysis indicates that if the EEC is less than the

NOEC there is a 95% probability that no adverse impact to long term survival, growth or reproduction will occur.

- 5) The above precautions will adequately protect any species that is acutely exposed to residues 10-fold lower than the EEC. However, to protect the biota or a segment of the biota, the acute EEC must be 10-fold lower than the LC50 for the most sensitive species that you wish to protect and the chronic EEC must be less than the chronic NOEC of the most sensitive species that you wish to protect.

The above criteria are considered rough estimates of potential risk to non-target organisms. The model used for ecological risk assessment does not provide a mechanism for estimating absolute uncertainty or an unchallengeable probability of safety to the biota.

If the tested species are representative of the biota and are sufficient in number, uncertainty can be reduced to a minimum. For Aquathol® K (dipotassium endothall salt), disodium endothall salt and endothall acid, which the EPA considers to be functionally equivalent, three species of cold water fish, at least 10 species of warm water fish and 4-species of benthic fish have been tested for acute toxicity in the laboratory. One species of free-swimming invertebrate and five species of benthic invertebrates have been tested in the laboratory. Many of these invertebrates are not considered relevant to this assessment since they are estuarine or marine species. However, with the possible exception of sheepshead minnow, all of the test species were selected for testing because they are believed to be acutely sensitive to the effects of pesticides. The marine and the freshwater species respond similarly to the exposure from endothall salts and endothall acid. For example, the LC50s for freshwater species ranged from 11 mg a.e./L for early life-stage walleye to 354 mg a.e./L for fathead minnow and bright scud (*Gammarus lacustris*) while the LC50s for saltwater species ranged from 39 mg a.e./L for mysid shrimp to 750 mg a.e./L for fiddler crab.

The Expected Environmental Concentration (EEC), as presented in Section 4.1.10.2.5 (Risk Analysis in Aquatic Species), are believed to be fairly accurate based on many years of successful risk management. However, field data for individual water bodies, indicating both the acute and chronic average concentrations, could improve the ability to assess and manage risk particularly for sensitive species.

The acute and chronic risk quotient values for Aquathol® K (dipotassium endothall salt) are very low for all species tested including fish and free-swimming and benthic invertebrates. These acute risk quotient (0.09) and chronic risk quotient (0.06) values for the most sensitive species in the entire biota are significantly lower than the level of concern (0.1 for acute RQ and 1.0 for chronic risk quotient) for protection of the biota. Such low RQ values indicate that the biota is unlikely to be at risk from exposure to Aquathol®. This data has been confirmed for fish (bluegills and largemouth bass) and free-swimming aquatic invertebrates (*cladocera*, *copepoda*, *cyclopsida* and *calanoida*) in field studies that indicate they are not affected in their survival, growth, nesting behavior and reproduction (Serns, 1977, Serns, 1977 and Radomski et al, 1995). Therefore, there is a high degree of confidence that Aquathol® is safe when it is used according the product label.

EEC values have been generated for Hydrothol®. The acute risk quotient for the most sensitive species of fish, free-swimming and benthic invertebrates is much greater than

the level of concern (0.10) for the most (RQ = ~18 for cutthroat trout) and least sensitive (RQ = 0.88 for northern crayfish) species. According to Barnhouse et al (1982 in Urban and Cook, 1986), probable adverse effects will be demonstrated if the risk quotient is higher than 10 and possible adverse effects will be demonstrated if the risk quotient is greater than 0.1 but less than 10. This gives good confidence that field mortality will occur if the maximum-labeled use rate of Hydrothol® is used for control of aquatic weeds. Faith in this confidence is provided by field data (Moore and Armor, 1979 in Finlayson, 1980) that indicates that exposure of various species of fish to 0.5 mg/L Hydrothol® for 120 hours will result in significant fish-kill.

The chronic risk assessment indicates less significant problems with Hydrothol® 191. If the EEC (0.02 mg/L) provided by Ecology (1992) is utilized, all test species produce a chronic risk quotient that is greater than the chronic level of concern (1.0). Typical risk quotients were 1.05, 1.25 and 1.67 for the most sensitive species of free-swimming invertebrate, fish and benthic invertebrate respectively. Lowering the EEC to 0.01 mg a.e./L causes the chronic risk quotient values to drop below the chronic level of concern (1.0) with typical risk quotients of 0.53, 0.63 and 0.83, respectively. However, confidence that application rates of 0.5 mg/L will cause adverse chronic impact and 0.3 mg a.e./L will not cause adverse impact is tenuous since the risk quotient values are ~1.0 when the number of significant digits for the EEC value are taken into account. The only field data available indicates that application to Lake Steilacoom of 0.2 mg a.e./L Hydrothol® to control algae did not produce obvious fish-kills (Resource Management, 1999).

The number of species and the fact that many are either found in Washington or similar to species found in Washington makes prediction of risk fairly accurate. Comparison of risk is fairly concrete when compounds that induce such widely varying risk, like Aquathol® and Hydrothol®, are evaluated.

To ensure that the maximum value is obtained from a risk assessment treatments must be conducted with a pesticide formulation that is fundamentally the same as the test substance used to evaluate toxicity of the active ingredient. It has been shown in section 4.1.9.5 that endothall acid formulations containing different percentages of the a.i. and hence different percentages of inert ingredients may show great differences in toxicity to tested animals, and hence may also behave very differently from each other when applied in the field.

EPA has assumed that the toxicity data for endothall acid and disodium endothall salt is functionally equivalent to the toxicity of Aquathol® (dipotassium endothall salt. Since on an acid equivalence basis, these materials are similar in toxicity, the assumption appears to be valid (Davis, Personal communications, 1999). However, to confirm this, testing each compound with each organism of interest would be needed. These studies would have to eliminate effects of season, time of day and even physical position within the laboratory in order to be valid.

## 4.1.13 ADDITIONAL INFORMATION NEEDS

### 4.1.13.1 Soil and Sediment

Concentration of endothall in sediment due to the use of granular Aquathol® needs to be further investigated. The effects of partitioning ( $K_d$ ) between soils and water with different soils also needs further investigating. Without well-determined values for how much endothall a given soil type removes and how rapidly, the assumption that the persistence of endothall in the water column is not strongly affected by partitioning between the water phase and the soil phase, may lead to an estimated water column half-life that is too long. Without knowledge of the partitioning and persistence of endothall in sediment, an underestimate of the EEC for sediment dwelling organisms is also likely. A knowledge of the concentration of endothall in the sediment is necessary, so that an adequate Risk Quotient and evaluation can be made for sediment organisms. This additional need is based on sediment quality and its effect on aquatic organisms are currently becoming important topics among representatives from industry and the regulatory community.

### 4.1.13.2 Water

The effects of water quality on the toxicity of endothall products have not been thoroughly investigated. It is generally believed that dissolved oxygen content, ammonia, nitrite and nitrate, phosphate, iron, pH, hardness and alkalinity effect the toxicity and secondary effects of endothall but the database is far from complete. The areas of debate among scientists are whether or not the increase of nitrogen and phosphate on the death of treated aquatic weeds cause an algal bloom. In most cases the majority of “added” nitrogen and phosphate are removed from the water column by unaffected aquatic macrophytes. Model ecosystems indicate that decaying aquatic plants causes an oxygen slump and an increase in nitrogen and phosphorous potentially leading to an algal bloom (Shearer and Halter, 1980 and Daniels, 1972). There is not strong evidence that this actually occurs under natural conditions. These model ecosystems also indicate endothall treatment of aquatic plants may alter iron and trace element cycling in sediments, but there is no credible field data to support this contention.

### 4.1.13.3 Plants

Serns (1977), Daniel (1972) and Simsiman et al 1972 in Serns (1975) postulate that dead and dying plants release nitrogen and phosphorous which is rapidly, taken up by unaffected plants. However, it is not as clear from the data that this is the case. Better information exists on these effects with other herbicides than with endothall. In the case of endothall, field data indicates that the levels of nitrogen and phosphate do not change significantly after treatment with endothall.

The planting of desirable vegetation after treatment with endothall has yet to receive serious investigation. It has been noted that *Elodea canadensis* (Corp, 1987 in Ecology, 1989) *Chara spp.* (Serns, 1977), water Lilies (*Nuphar spp* and *Nymphaea spp*). and cattails (*Typha spp.*) (Shearer and Halter, 1980) are not affected by typical use rates of endothall. Those plants may become dominant after the biomass of the more susceptible plants has been reduced. Post-treatment plantings of native and non-invasive plants could increase diversity and decrease the numbers of these less desirable endothall resistant plants

through competition. This would improve habitat since a more diverse plant community would attract a more diverse animal community. The practicality and utility of post-treatment plantings of native plants should be investigated further.

#### **4.1.13.4 Chronic Toxicity Studies for Plants and Animals**

There are few well designed chronic toxicity studies that have been conducted with Aquathol® and Hydrothol®. For an ideal understanding of chronic effects, early life stage studies need to be conducted on all end use products or their technical equivalence with rainbow trout, fathead minnow and sheepshead minnow. Since Coho salmon and Chinook salmon are so important in the Northwest, Early Life Stage (ELS) studies and further smoltification studies should also be conducted with these species. There are a variety of surrogate species that EPA will accept in ELS studies.

#### **4.1.14 MITIGATION MEASURES**

*Summary: Concentrations of endothall requiring mitigation will not occur under normal conditions. However, levels of Hydrothol® 191 and Aquathol® K that would be found in the environment due to typical treatment practices may interfere with the salmon smoltification process resulting in death when smolts migrate from freshwater to saltwater. Extra caution should be taken when dealing with endangered species allowing for a level of concern of <0.05 rather than the more typical value of <0.1 for non endangered species. Restrictions on season of application are warranted to protect sensitive salmon smolts from the effects of endothall products; similar restrictions may be applied to protect fish and fisheries and prevent water use restrictions during the height of the recreational and commercial fishing seasons. When Hydrothol® is used, mitigation steps that should be taken include low treatment rate, small treatment areas and minimal exposure time; and treatment with Hydrothol® 191 in hardwater situations should be avoided. Treatment with Hydrothol® 191 in the presence of suspended particle concentration should be encouraged.*

The use of endothall may itself be considered a mitigation measure when floating and submersed aquatic macrophytes are out of control. Treatment with appropriate concentrations of Aquathol®, Aquathol® K, Hydrothol® 191 and Hydrothol® 191 Granular may improve habitat for fish, pelagic aquatic invertebrates (zooplankton) and benthic organisms (catfish and sediment dwelling organisms).

Treatment with endothall can produce unfortunate side effects, which need to be mitigated. The release of too much phosphate from decaying plants and anoxic sediment located in the hypolimnion and cause an algal bloom. In order for these releases from the hypolimnion to be useful to photosynthetic organisms, the water must be shallow and transparent enough for photosynthesis to occur. Removal of excess phosphate may be achieved by the addition of ferric iron, metals in fly ash, or salts of aluminum or zirconium. This method is occasionally used to clean up the phosphate from eutrophic lakes and may be approved as a remedial measure when high phosphate levels are noticed due to the decay of herbicide treated aquatic plants. However, by the time high phosphate levels are noticed, it may already be too late to prevent an algal bloom

Levels of endothall that need remediation are unlikely to occur except in cases where there has been an accident. For example, if a treatment boat sinks, concentrations near

the boat will be high enough to cause extensive fish kill. However, there is some evidence that salmonids and carp may avoid areas where the concentration of endothall is higher than 10 and 17 mg/L, respectively.

Since the effect of endothall products on smolting salmonids is still unclear, Ecology, in consultation with Washington Department of Fish & Wildlife, should determine when and where treatment with endothall products should be avoided. Endothall products may interfere with the parr to smolt morphogenesis and therefore, care should be taken to avoid weed control measures using endothall products during the salmon breeding season and when salmon parr or smolts are present. Similar precautions should be taken with other anadromous fish species.

It has been recommended in Urban and Cook (1986), that the level of concentration for acute risk quotients for endangered species be two-fold less than that for the general biota. That is, an RQ of 0.05 is at the level of concentration for endangered and threatened species. However, the most sensitive endangered/threatened species tested (Chinook salmon) has an LD50 23 mg a.e./L. This value is high enough to yield an acute risk quotient that is below the level of concentration protection of endangered threatened biota (AR Q = 1 ppm a.e./23 ppm a.e. = 0.043). The calculations for Chronic Risk Quotient are the same as for the general biota which has been previously shown to be less than the critical value (1.0) for protection of the biota and hence, should also protect the endangered/threatened biota.

However, since salmon are of such importance to fishing and fisheries, care should still be taken to avoid using Aquathol® products during the salmon breeding season or when parr or smolts are present.

If impact on fishing or fisheries is an issue, Ecology, in consultation with Washington Department of Fish & Wildlife, should determine applicable restrictions. The current Federal label specifies that fish will not be used for food or feed for at least 3 days.

When Hydrothol® 191 is being used for algal control, the lowest effective concentration, the smallest treatment area and the shortest feasible exposure time should be used. Treatment with Hydrothol® in hard water situations, should be avoided. Toxicity of Hydrothol® should be reduced in the presence of high-suspended particle concentrations, especially if those particles contain a high percentage of oxygen matter. These measures should be taken to avoid the effects of acute toxicity on the indigenous biota.

#### **4.1.15 COMPARISON OF THE TOXICITY OF HYDROTHOL® 191 AND COPPER CONTAINING ALGAECIDES AND HERBICIDES**

There are currently nine products containing copper which may be used for control of algae and aquatic weeds in Washington State. They are copper sulfate distributed by Phelps Dodge algaecide), Captain® (elemental copper – liquid formulation) manufactured by Sepro (algaecide), Nautique® manufactured by Sepro (Herbicide and Algaecide), Cutrine® Plus manufactured by Applied Biochemists (Algaecide), Cutrine® Granular manufactured by Applied Biochemists (algaecide), K-Tea® manufactured by Griffen (algaecide) and Komeen® manufactured by Griffen (herbicide), Cleargate® manufactured by Applied Biochemists (algaecide) and Earthtec® (algaecide). Unlike Hydrothol® 191 which is significantly more toxic to fish in hard (alkaline) than in soft

water (acidic), products containing chelated copper are usually more toxic in soft water (acidic) than hard water (alkaline).

Many of these products contain more than one active ingredient containing copper. For example, Komeen® contains ethylenediamine and copper sulfate pentahydrate with an elemental copper concentration of 8% by weight and K-Tea® contains copper triethanolamine and copper hydroxide with an elemental copper concentration of 8% copper by weight. Copper sulfate pentahydrate usually contains 99% active ingredient. Other copper sulfate containing products used for algal control contain anhydrous copper sulfate at ~98% active ingredient.

For this Risk Assessment, only limited data is available on the toxicity of copper containing algaecides and herbicides. Products containing copper, often have more than one active ingredient of which the percentages are not specified. These active ingredients are typically basic copper sulfate, anhydrous copper sulfate, pentahydrate copper sulfate, copper triethanolamine or copper ethylenediamine.

Many of these products have a maximum application rate of 1 mg copper equivalence/L of water. The toxicity of these copper containing algaecides and herbicides to fish varies considerably with both formulation and fish or invertebrate species tested.

Some of these products have an acute toxicity that is very similar to Hydrothol® 191 on an acid equivalent (a.e.) basis. For example, Hydrothol® 191 has an acute LC50 ranging from 0.18 to 1.6 mg a.e./L on fish, an LC50 of 0.075 to 0.085 mg a.e./L to *Daphnia magna* and 0.22 mg a.e./L to the bright scud (*Gammarus lacustris*). The two algaecidal copper products (anhydrous copper sulfate and copper sulfate pentahydrate) have acute LC50 values which are similar to that of Hydrothol® 191; the LC50 for anhydrous copper sulfate ranges from 0.135 to 3.4 mg copper/L on fish; and the LC50 for copper sulfate pentahydrate ranges from 0.13 to 2.95 mg copper/L on fish and 0.18 mg copper/L on *Daphnia magna*. The effects of copper sulfate products on fish are significantly higher for salmonids (LC50 = ~0.13 mg copper/L) than warm water species (LC50 = 0.88 to 3.4 mg copper/L for sunfish and 0.8 mg copper/L for fathead minnow (Table 22).

The typical maximum use rate for Hydrothol® 191 used to control algae is 0.2 mg a.e./L. This leads to an estimated 4-day acute EEC of 0.06 mg a.e./L. This EEC will allow for more than 50% survival of rainbow trout and warm water species like sunfish, minnows and shiners. However, more sensitive, threatened and endangered species may be heavily affected. Nevertheless, data from modeling, some field data and observations of applicators indicate that large portions of the biota may be unaffected at these treatment rates (Resource Management, 1999, Giddings, 1999, Finlayson, 1980). For example, if irrigation canals are treated at concentrations of 0.2 mg a.e./L with an exposure time of less than 120-hours, the affected species may be as low as 10% or as high as 30%. Factors that tend to lower acute toxicity include soft water, reduced exposure time, high levels of suspended particles and a high flow-rate. Finlayson (1980) discussed similar observations for work done in the field by other researchers. In 1999, treatments of Lake Steilacoom at 0.2 mg a.e./L did not produce any obvious fish-kill. The lack of obvious fish-kill was probably due to a rapid dissipation that exceeds the typical dissipation half-life of 0.8-day (Resource Management, 1999).

Treatments with preparations containing copper sulfate at levels as high as 1.0 mg copper/L have the potential to cause extreme adverse impact on many species of fish and

invertebrates. Copper levels will remain high in the aquatic ecosystem for a long time since elemental copper does not degrade readily. Furthermore, copper residues normally remain in the water column for up to 24 hours. Copper concentrations from copper sulfate treatments as high as 1 mg copper/L will kill more than half of the rainbow trout present and may kill more than half of the sunfish and minnows as well. **Therefore, Hydrothol® 191 may be the compound of choice if salmonids are present and algae control is necessary with either copper sulfate or Hydrothol® 191.**

However, if salmonids are not present, products like Komeen® for the control of aquatic weeds or K-Tea® for the control of algae may be preferred over Hydrothol®. Komeen® should have low acute impact on sunfish and shiners when used at the maximum use rate (1 mg copper/L) concentrations since the LC50 for Komeen® on non-salmonids is 67 to 630 mg copper/L for golden shiner and 480 mg copper/L for bluegill sunfish. The safety of Komeen® is supported by field data that indicates that combined treatments with Komeen® and diquat at 0.3 mg/L each had no impact on abundance, size, structure, condition or movement of largemouth bass in the Guntersville Reservoir, Alabama. Even salmonids like rainbow trout may not be adversely affected since the acute LC50 (4 mg copper/L) is considerably above typical treatment rates of 0.5 to 1 mg copper/L for Komeen®. However, the risk assessment indicates that use of Komeen® may not be safe to more sensitive members of the biota since the risk quotient is above the acute level of concern of 0.1 ( $RQ = 0.5 \text{ ppm}/4 \text{ ppm} = 0.13$  for rainbow trout). Therefore, if acute toxicity is the main issue in a treatment situation, Komeen® would be preferred over Hydrothol® 191 for the control of aquatic weeds. Nevertheless, Hydrothol® and Komeen® may not present significant differences in risk on rainbow trout. ( $RQ$  for Hydrothol =  $0.25 = 0.06 \text{ ppm}/0.24 \text{ ppm}$ ) and  $RQ$  for Komeen® =  $0.25 = 1 \text{ ppm}/4 \text{ ppm}$ ).

Similar toxicity data for the active ingredient of K-Tea® have been found. One active ingredient, copper triethanolamine, has a low toxicity to bluegill sunfish and *Daphnia magna* ( $LC50 = \sim 50 \text{ mg copper/L}$ ) while the toxicity to rainbow trout is high ( $LC50 = 0.84 \text{ mg copper/L}$ ). The other active ingredient, copper hydroxide, will probably have low toxicity to bluegill sunfish since the related compound, copper chloride hydroxide, has a low toxicity ( $LC50 = 180 \text{ mg copper/L}$ ). However, copper chloride hydroxide is highly toxic to rainbow trout ( $LC50 = 0.55 \text{ to } 2.42 \text{ mg copper/L}$ ). Although this data is favorable for copper triethanolamine at 54% a.i., other formulations are considerably more toxic; e.g., Copper triethanolamine at 7.1% a.i. is 30 to 139-fold more toxic than the 54% a.i. material to sunfish ( $LC50 = 1.3 \text{ mg copper/L}$  for sunfish and  $0.026 \text{ mg copper}$  for rainbow trout). K-Tea® may have low impact on sunfish when used at the typical maximum use rates of 1.0 mg copper/L. Even salmonids, like rainbow trout, may be unharmed when algae are controlled by K-Tea® and may not have their total populations adversely impacted since the acute LC50 ( $0.84 \text{ mg copper/L}$ ) is above the typical control rate for most blue-green algae ( $0.5 \text{ mg copper/L}$ ). However, risk assessment indicates that the use of K-Tea® may not be safe to more sensitive members of the biota since the risk quotient is above the acute level of concern of 0.10 ( $RQ = 0.5 \text{ ppm}/0.84 \text{ ppm} = 0.60$ ). Therefore, if acute toxicity were the main issue in a treatment situation, K-Tea® would be preferred over Hydrothol® 191 for control of aquatic algae. Nevertheless, Hydrothol® and triethanolamine or copper chloride hydroxide may not present significant differences in risk in their effects on rainbow trout ( $RQ$  for Hydrothol® 191 =  $0.25$ ;  $RQ$  for triethanolamine =  $0.60 = 0.5 \text{ ppm}/0.84 \text{ ppm}$ ;  $RQ$  for copper chloride hydroxide =  $>0.43 = 0.5 \text{ ppm}/1.15 \text{ ppm}$ ).

If chronic toxicity is the major concern, Hydrothol® should probably be used as the treatment of choice since its rate of degradation within the aquatic system is very high and treatment at 0.2 mg a.e./L will result in a 28-day EEC that is below 0.008 mg a.e./L which will probably permit survival of the most sensitive non-endangered species since the risk quotient does not exceed the chronic level of concern of 1.0 (0.008 ppm a.e./0.11 ppm a.e. = 0.073 for catfish). However, the level of concern of 0.05 for endangered species is exceeded slightly (0.008 ppm/0.079 ppm = 1.01) so more sensitive, threatened and endangered species may be at chronic risk from use Hydrothol® 191 at the most typical use rate for control of algae.

Copper compounds do not degrade readily in the aquatic system and accumulate in the sediment (up to 384 mg/kg in Lake Steilacoom) over long periods (Hugget et al, 1999). When a fall overturn occurs in a lake, the concentration in the water column may become high enough to be toxic to the resident fish biota. Furthermore, the build up of copper in these situations may induce the resident biota to become tolerant to copper and while the resident biota may not be affected at fairly high concentrations of copper due to this tolerance, inexperienced animals entering the system from areas where copper has not been used may suffer acute toxicity from exposure to high levels of copper.

If seasonal overturns do not typically occur in a treated water body, concentrations of copper may become very high in the sediment, thus adversely impacting sediment organisms. On the other hand, Hydrothol® 191 is rapidly eliminated from the sediment and rarely accumulates at concentrations higher than 1 – 2 mg/kg in the sediment (Kechemet and Sharp, 1999). Therefore, the impact of Hydrothol® 191 on sediment organisms should be minimal relative to the impact of copper.

These observations are rough comparisons of the potential effects of Hydrothol® versus copper and do not take into account all contingencies. The species that need to be controlled, the species that need to be protected, what the water body is used for, the direct costs, and other financial impacts must be considered before deciding on a treatment regimen. Therefore, the decision of which herbicide to use must be made on a case-by-case basis.

#### 4.1.16 SUMMARY AND CONCLUSIONS

*Summary for Aquathol® K: Aquathol® (dipotassium endothall salt), disodium endothall salt and endothall acid, do not adversely affect the tested fish, free-swimming invertebrates or benthic organisms. Acute toxicity for these compounds is low with the LC50 for all species tested >23 mg a.e./L. Since the acute EEC is very low (1 mg a.e./L), the acute risk quotient is below the level of concern of 0.1 for all species tested (RQ = 0.043). The chronic toxicity determined by prediction from the acute to chronic ratio or empirically is also very low (chronic NOEC = 3.6 to 5.0 mg a.e./L, respectively). Therefore, the predicted chronic risk quotient is below the level of concern of 1.0 for all species tested (RQ = 0.025) since the geometric mean of the chronic EEC = 0.091 mg a.e./L. Because the acute and chronic risk quotients do not exceed the level of concern, Aquathol® can be used for control of aquatic weeds without significant impact to fish, free-swimming invertebrates and benthic organisms. The field data that has been collected to date confirms this observation.*

*Summary for Hydrothol® 191: Hydrothol® 191 [mono(dimethylalkylamine) salt of endothall], adversely affects test fish, free-swimming invertebrates and benthic organisms. Acute toxicity for this compound is very high with the LC50 for the most sensitive environmentally relevant species (cutthroat trout) being 0.079 mg a.e./L. The LC50 for all environmentally relevant species ranged between 0.079 mg a.e./L for cutthroat trout and 1.6 mg a.e./L for northern crayfish. Although the acute EEC is low (1.4 mg a.e./L), the toxicity is great enough that the acute level of concern (0.10) is exceeded for most species (19 of 21) tested. Field data cited by Finlayson (1980) indicates that Hydrothol® 191 cannot be used to control weeds at concentrations higher than 0.5 mg a.e./L without significant fish-kill. [The chronic toxicity determined empirically or by prediction, from the acute to chronic ratio is also very high for the most sensitive environmentally relevant fish species (chronic NOEC = 0.012 to 0.016 mg a.e./L, respectively)]. Therefore, the predicted chronic risk quotient is above the level of concern of 1.0 for the species tested ( $RQ = 1.17$ ) since the geometric mean of the chronic EEC = 0.014 mg a.e./L. Hydrothol® cannot be used for control of aquatic weeds without significant impact to fish because the acute and chronic risk quotients exceed the level of concern. The chronic toxicity of Hydrothol® for the most sensitive free-swimming and benthic invertebrates is 0.016 to 0.019 mg a.e./L. Therefore, the Chronic Risk Quotient is less than 0.74 ( $RQ = 0.014 \text{ ppm a.e.}/0.019 \text{ ppm a.e.}$ ). Since the Chronic Risk Quotient is less than the Chronic Level of Concern (1.0) for free-swimming and benthic invertebrates, Hydrothol® used to control nuisance weeds and algae at concentrations of 0.30 mg a.e./L would not chronically impact these species. No well conducted chronic studies have been conducted in the field. However, mitigation procedures that may reduce chronic impact include the use of the lowest practical treatment rate, low exposure time, treatment under hard water conditions and treating from the shoreline outward.*

***In conclusion, Aquathol® (dipotassium entothall salt) is safe to use for control of nuisance aquatic vegetation at labeled use rates and provides a large safety factor for protection of the biota from acute and chronic effects.***

***Although risk assessments exhibit a high potential for acute risk with a Risk Quotient that greatly exceeds the level of concern (0.1), the label indicates that Hydrothol® 191 [mono(dimethylalkylamine) endothall salt can be used without significant fish-kill at concentrations that do not exceed 1.0 mg a.e./L.***

***Hydrothol® does not appear to be safe to the more sensitive species of fish at treatment concentrations of 0.3 to 0.5 mg a.e./L since the chronic level of concern is exceeded. However, application at these concentrations should not be harmful to free-swimming invertebrates and benthic invertebrates. Also, both standard risk assessments and observations from treatment of Lake Steilacoom (Resource Management, 1999) indicates the 0.2 mg a.e./L Hydrothol® 191 should not harm the biota significantly, although such treatments may not be entirely effective in controlling nuisance algae.***

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**Table 1: U.S. EPA Ectoxicological Categories<sup>1</sup> for Mammals Birds and Aquatic Organisms**

Acute Oral Toxicity in Mammals (mg/Kg body wt)	Toxicity in Birds		Acute Toxicity in Fish mg/L test solution	Toxicity Ranking
	Acute Oral (mg/Kg body weight)	Dietary mg/Kg feed		
<10	<10	<50	<0.1	Very Highly Toxic
10-50	10-50	50-500	0.1-1.0	Highly Toxic
>50-100	>50-500	>50-1000	>1-10	Moderately Toxic
>500-2000	>500-2000	>1000-5000	>10-100	Slightly Toxic
>2000	>2000	>5000	>100	Practically Non-Toxic

<sup>1</sup> EPA, (1982) Pesticide Assessment Guidelines, Section E: Ecological Effects, Brooks, 1973 in Ebasco, 1993.

Table 2: Acute and Chronic Aquatic Toxicity Data

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals			
						Hydrothol®191	Aquathol®K	Disodium Endothall	Endothall Acid
Algae	<i>Anabeana flos-aquae</i>	Blue-green algae	Static Acute	Log growth phase	5-days	0.042 <sup>1</sup> (0.024) <sup>2</sup>	>3.4 (3.4)		
Algae	<i>Microcystis aeruginosa</i>	Blue-green algae	Static Acute	Log growth phase	4-days	0.042			
Algae	<i>Phoridium inundatum</i>	Blue-green algae	Static Acute	Log growth phase	4-days	0.042			
Algae	<i>Chlamydomonas noctingama</i>	Blue-green algae	Static Acute	Log growth phase	4-days	0.12			
Algae	<i>Selenastrum capricornutum</i>	Green algae	Static Acute	Log growth phase	5-days	0.0023 (0.00071)	>3.4 (3.4)		
Algae	<i>Chlorococcum spp.</i>	Green algae	Static Acute	Log growth phase	10-days		1500		50
Algae	<i>Scenedesmus acuminatus</i>	Green algae	Static Acute	Log growth phase	4-days	0.19			
Algae	<i>Chlorella vulgaris</i>	Green algae	Static Acute	Log growth phase	4-days	>0.27			

Table 2: Acute and Chronic Aquatic Toxicity Data (Continued)

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Hydrothol®191	EC50 or LC50 and (NOEC) in (mg a.e./L)	Aquathol® K	Disodium Endothall	Endothall Acid
Algae	<i>Dunaliella tertiolecta</i>	Green algae	Static Acute	Log growth phase	10-days		1500			50
Algae	<i>Navicula pelliculosa</i>	Freshwater diatom	Static Acute	Log growth phase	5-days	0.0076 (0.0054)	>2.6 (2.6)			
Algae	<i>Cyclotella meneghiana</i>	Marine diatom	Static Acute	Log growth phase	4-days	0.103				
Algae	<i>Syndra sp.</i>	Marine diatom	Static Acute	Log growth phase	5-days	>0.27				
Algae	<i>Skeletonema capricornutum</i>	Marine diatom	Static Acute	Log growth phase	5-days	0.018 (0.012)	>6.4 (<6.4)			
Algae	<i>Phaeodactylum tricornutum</i>	Marine diatom	Static Acute	Log growth phase	10-days		500			15
Algae	<i>Isochrysis galbana</i>	Marine haptophyte	Static Acute	Log growth phase	5-days		3000			25
Plant	<i>Lemna gibba</i>	Duckweed	Static Acute	3-4 leaf stage	14 days	0.83 (<0.35)	0.60 (0.35)			
Fish	<i>Oncorhynchus mykiss</i>	Rainbow trout	Static Acute	Juvenile	4-days	0.31 <sup>3</sup>	166 <sup>3</sup> (51)			

**Table 2: Acute and Chronic Aquatic Toxicity Data (Continued)**

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals		
						Hydrothol® 191	EC50 or LC50 and (NOEC) in (mg a.e./L)	Disodium Endothall
Fish	<i>Oncorhynchus mykiss</i>	Rainbow trout	Flow Acute	Juvenile	4-days	0.24 (0.038)	109 (41)	49 (13)
Fish	<i>Oncorhynchus mykiss</i>	Rainbow trout	Flow ELS <sup>4</sup>	Egg-fry	NS <sup>5</sup>		(<7.2)	
Fish	<i>Oncorhynchus mykiss</i>	Rainbow trout	NS <sup>2</sup> ELS	Egg-fry	NS <sup>5</sup>			(5)
Fish	<i>Salmo clarki</i>	Cutthroat trout	Static Acute	Juvenile	4-days	0.079		
Fish	<i>Oncorhynchus kisutch</i>	Coho salmon	Static Acute	Juvenile	4-days		>71	
Fish	<i>Oncorhynchus tshawytscha</i>	Chinook salmon	Static Acute	Juvenile	4-day		23	
Fish	<i>Oncorhynchus tshawytscha</i>	Chinook salmon	NS <sup>2</sup> Chronic	Fry-smolt	14-day		62	
Fish	<i>Lepomis macrochirus</i>	Bluegill sunfish	Static Acute	Juvenile	4-days	0.34 <sup>3</sup> (<0.23)	132 <sup>3</sup> (51)	220
Fish	<i>Lepomis macrochirus</i>	Bluegill sunfish	Flow Acute	Juvenile	4-days	0.40 (0.082)	218 (50)	77 (18)
Fish	<i>Lepomis macrochirus</i>	Bluegill sunfish	NS <sup>6</sup> Chronic	Sac-fry	8-days			>20 (>20)
Fish	<i>Lepomis macrochirus</i>	Bluegill Sunfish	NS <sup>6</sup> Chronic	Sac-fry	12-days			>80 (>80)
Fish	<i>Lepomis macrochirus</i>	Bluegill sunfish	NS <sup>7</sup> Chronic	Sac-fry	21-days			(80)
Fish	<i>Lepomis cyanellus</i>	Green sunfish	NS <sup>6</sup> ELS	NS <sup>8</sup>	NS			20

Table 2: Acute and Chronic Aquatic Toxicity Data (Continued)

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals			
						Hydrothol® 191	Aquathol® K	Disodium Endothall Acid	
Fish	<i>Lepomis cyanellus</i>	Green sunfish	NS <sup>6</sup> Chronic	Sac-fry	8-days			>20 (>20)	
Fish	<i>Lepomis microlophus</i>	Redear sunfish	NS <sup>1</sup> Acute	NS <sup>8</sup>	4-days			100	125
Fish	<i>Fundulus heteroclitus</i>	Mumichog	Static Acute	Juvenile	4-days				213 (56)
Fish	<i>Micropterus salmoides</i>	Largemouth bass	NS <sup>6</sup> Acute	Juvenile	4-days			125 <sup>3</sup>	120
Fish	<i>Micropterus salmoides</i>	Largemouth bass	Static Acute ELS	9-13 days post-hatch	4-days		92 (35)		
Fish	<i>Micropterus salmoides</i>	Largemouth bass	NS <sup>7</sup> Chronic	NS <sup>9</sup>	21-days			(8)	
Fish	<i>Stizostedion vitreum</i>	Walleye	Static Acute ELS	8-10 days post-hatch	4-days		11 (4.0)		
Fish	<i>Stizostedion vitreum</i>	Walleye	Static Acute ELS	41-43 days post-hatch	4-days		38 (16)		
Fish SW <sup>10</sup>	<i>Morone saxatilis</i>	Striped bass	Static Acute	Fingerlings	4-days			135	
Fish	<i>Micropertus dolomieu</i>	Smallmouth bass	Static Acute ELS	1-day post-hatch	4-days		33 (16)		
Fish	<i>Pimephales promelas</i>	Fathead minnow	Static Acute	Juvenile	4-days		0.18 <sup>3</sup> (<0.23) <sup>3</sup>	186 <sup>3</sup>	560
Fish	<i>Pimephales promelas</i>	Fathead minnow	Renewal Acute	NS <sup>8</sup>	4-days		0.189		
Fish	<i>Pimephales promelas</i>	Fathead minnow	NS <sup>1</sup> Chronic	Sac-fry	7-days 25°C		0.134 (0.022)		

**Table 2: Acute and Chronic Aquatic Toxicity Data (Continued)**

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals			
						Hydrothol® 191	EC50 or LC50 and (NOEC) in (mg a.e./L)	Disodium Endothall	Endothall Acid
Fish	<i>Pimephales promelas</i>	Fathead minnow	Flow ELS	Egg-fry	35-days	(0.028)			(13)
Fish	<i>Pimephales notatus</i>	Bluntnose minnow	NS <sup>7</sup> Chronic	NS <sup>9</sup>	21-days			(32)	
Fish	<i>Cyprinodon variegatus</i>	Sheepshead minnow	Flow Acute	Juvenile	4-days	0.82 (0.16)	100 (35)		110 (44)
Fish	<i>Notropis umbratilis</i>	Redfin shiner	NS <sup>6</sup> Acute	NS <sup>8</sup>	4-days			76	95
Fish	<i>Notropis umbratilis</i>	Redfin shiner	NS <sup>6</sup> Chronic	NS <sup>9</sup>	21-days			(32)	
Fish	<i>Notropis lutrensis</i>	Red shiner (Redsided shiner)	NS <sup>6</sup> Acute	NS <sup>8</sup>	4-days			84	105
Fish	<i>Notropis umbratilis</i>	Redfin shiner	NS <sup>6</sup> Chronic	NS <sup>8</sup>	21-days			(32)	
Fish	<i>Erimyzon suceta</i>	Lake chubsucker	NS <sup>7</sup> Chronic	Sac-fry	8-days			>20 (>20)	
Fish	<i>Notomogonus chrysolucas</i>	Golden shiner	Flow Acute	FW	5-days	0.72			
Fish		Harlequin fish	NS <sup>6</sup> Acute	NS <sup>8</sup>	1-day				565
	<i>Compostoma anomalum</i>	Stoneroller	NR <sup>7</sup> Chronic	Egg-fry	8-days			(>40)	
Fish	<i>Ciprinus carpio</i>	Carp or Goldfish	NS <sup>6</sup> Acute	NS <sup>8</sup>	4-days		264	140	175

Table 2: Acute and Chronic Aquatic Toxicity Data (Continued)

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals		
						Hydrothol® 191	Aquathol® K	Disodium Endothall
Fish	<i>Cyprinodon variegatus</i>	Sheepshead minnow	NS <sup>6</sup> Acute	NS <sup>8</sup>	4-days		100 (35)	110
Fish Benthic	<i>Ictalurus punctatus</i>	Channel catfish	Static Acute	Juvenile	4-days	0.11	>106	
Fish Benthic	<i>Ictalurus melas</i>	Black bullhead catfish	NS <sup>6</sup> Acute	NS <sup>8</sup>	4-days			180
Fish Benthic	<i>Ictalurus nebulosus</i>	Brown bullhead catfish	NS <sup>6</sup> Acute	NS	4-days		138	
Fish Benthic	<i>Ictalurus natalis</i>	Yellow bullhead catfish	NS <sup>6</sup> Acute	NS <sup>8</sup>	4-days		138	175
Amphibian		Fowler's toad	NS <sup>6</sup> Acute	Tadpole	4-days	0.80		
Invertebrates	<i>Daphnia magna</i>	Daphnia	Static Acute	<24 hrs	2-days	0.085 (0.024)	91 (29)	39 (18)
Invertebrates	<i>Daphnia magna</i>	Daphnia	Flow Acute	<24 hrs	2-days	0.075 (0.018)	71 (41)	92 (24)
Invertebrates	<i>Daphnia magna</i>	Daphnia	Flow Chronic	<24 hrs	21-days	(0.016)		24 (5)
Invertebrates	<i>Ceriodaphnia dubia</i>	Daphnia	Static Acute	NS <sup>11</sup>	2-day	0.63		

**Table 2: Acute and Chronic Aquatic Toxicity Data (Continued)**

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals			
						Hydrothol®191	Aquathol® K	Disodium Endothall	Endothall Acid
Invertebrates	<i>Ceriodaphnia dubia</i>	Daphnia	Flow Chronic Life-Cycle	NS <sup>11</sup>	7-day	0.073 (<0.005)			
Invertebrates	<i>Brachionus calyciflorus</i>	Rotifer	Static Acute	Adult	1-day	0.37 (0.20)			
Invertebrates SW Benthic Sediment	<i>Crassostrea virginica</i>	Eastern oyster	Flow Acute Shell growth	Juvenile	4-days	0.20 (0.016)	97 (<44)		43 (16)
Invertebrates SW	<i>Mysidopsis bahia</i>	Mysid shrimp	Flow Acute	<24 hrs	4-days	0.56 (0.18)	79 (15)		39 (47)
Invertebrates SW Estuarine	<i>Mytilus edulis</i>	Bay mussel	Static Acute EC50 attachment	embryo	2-days	2.15			49
Invertebrates Benthic Sediment	<i>Orconectes virilis</i>	Northern crayfish	Flow Acute	Adults	4-days	1.6 (0.46)			
Invertebrates Benthic Sediment	<i>Gammarus fasciatus</i>	Lined scud	Static Acute	Mature	4-days	0.14	222		
Invertebrates Benthic Sediment	<i>Gammarus lacustris</i>	Bright scud	Static Acute	Mature	4-days	0.22	354		

Table 2: Acute and Chronic Aquatic Toxicity Data (Continued)

Taxa	Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals		
						Hydrothol®191	Aquathol® K	Disodium Endothall Acid
Invertebrates Benthic Sediment	<i>Chironomus tentans</i>	Midge	Flow Acute	Larvae	4-days	0.51 (0.30)		
Invertebrates Benthic	<i>Hexagenia spp.</i>	Mayfly	Flow Acute	Larvae	4-days	0.12		
Invertebrates Benthic Sediment	<i>Hyalella azteca</i>	Amphipod	Flow Acute	NS <sup>12</sup>	4-days	0.17 (0.027)		
Invertebrates Benthic	<i>Pteronarcys californica</i>	Stonefly	Static Acute	Larvae	2-days	1.4		
Invertebrates Benthic Sediment	<i>Lumbriculus variegatus</i>	Variegated oligochaete	Flow	NS <sup>12</sup>	4-days	0.42 (0.17)		
Invertebrate SW	<i>Panaeus azteca</i>	Brown shrimp	Flow	Juvenile	2-days			>1.0
Invertebrate SW	<i>Palaemonetes pugio</i>	Grass shrimp	Static Acute	Mature	4-days	0.022		85
Invertebrate SW	<i>Uca pugilator</i>	Fiddler crab	Static Acute	Adult	4-days	6.2	750	130
Invertebrate Benthic	<i>Libellulidae</i>	Dragonfly	Static	Larvae	4-days		>100	
Invertebrate Benthic	<i>Coenagrionidae</i>	Damselfly	Static Acute	Larvae	4-days		>100	

<sup>1</sup> L50 or EC50

<sup>2</sup> NS = NOEC

- 3 Geometric Mean
- 4 ELS = Early Life Stage
- 5 NS = Not specified but presume to be about 90-days
- 6 NS = Not Specified and presumed to be Static
- 7 NS = Not Specified and presumed to be Flow-through
- 8 NS = Not specified but presumed to be Juveniles
- 9 NS = Not specified and presumed to be <24 hour old
- 10 SW = Salt Water
- 11 NS = Not specified and presumed to be adults.
- 12 NS = Not specified but presumed to be fry or sac-fry

**Table 3: Endothall Bobwhite Quail Toxicity Data**

Test Type	Formulation Used	Test Results	Toxicity Ranking	Reference/Study Date
8-day acute dietary LC50	Aquathol® K	LC50 > 5000 ppm	Practically nontoxic	Pedersen, 1994b
8-day acute dietary LC50	Hydrothol® 191	LC50 > 5000 ppm	Practically nontoxic	Pedersen & Thompson, 1994b
8-day acute dietary LC50	Endothall Technical	LC50 > 5000 ppm	Practically nontoxic	Pedersen & Solatycki, 1994b
8-day acute dietary LC50	Endothall, dimethylalkylamine	LC50 > 1000 ppm	Slightly toxic	Brian Database, 1999/1977 <sup>1</sup>
8-day acute dietary LC50	Endothall Technical	LC50 > 10000 ppm	Practically nontoxic	Brian Database, 1999/1975 <sup>1</sup>
8-day acute dietary LC50	Endothall, dipotassium salt	LC50 > 10000 ppm	Practically nontoxic	Brian Database, 1999/1977 <sup>1</sup>
14 day acute oral	Endothall Technical	LD50 494 mg/kg	Moderately toxic	Brian Database, 1999/1979 <sup>1</sup>
14 day acute oral	Endothall, dimethylalkylamine	LD50 736 mg/kg	Slightly toxic	Brian Database, 1999/1977 <sup>1</sup>
20 wk dietary study	Endothall Technical	LOEL > 250 ppm	N/A	Pedersen, Fletcher & Lesar, 1992b

1. Indicates year the actual study was conducted.

**Table 4: Endothall Mallard Duck Toxicity Data**

Test Type	Formulation Used	Test Results	Toxicity Ranking	Reference/Study Date
8-day acute dietary LC50	Endothall Technical	LC50 > 10000 ppm	Practically nontoxic	Brian Database/1977 <sup>1</sup>
8-day acute dietary LC50	Endothall Technical	LC50 > 5000 ppm	Practically nontoxic	Pedersen & Solatycki, 1994a
8-day acute dietary LC50	Endothall, dipotassium salt	LC50 > 10000 ppm	Practically nontoxic	Brian Database/1977 <sup>1</sup>
8-day acute dietary LC50	Endothall Technical	LC50 > 5000 ppm	Practically nontoxic	Brian Database/1994
8-day acute dietary LC50	Endothall, dimethylalkylamine	LC50 > 1000 ppm	Slightly toxic	Brian Database/1977 <sup>1</sup>
8-day acute dietary LC50	Aquathol® K	LC50 > 5000 ppm	Practically nontoxic	Pedersen, 1994a
8-day acute dietary LC50	Hydrothol® 191	LC50 > 5000 ppm	Practically nontoxic	Pedersen & Thompson, 1994a
14 day acute oral LD50	Endothall Technical	LD50 229 mg/kg	Moderately toxic	Brian Database/1984 <sup>1</sup>
21-day acute oral	Endothall Technical	LD50 111 mg/kg	Moderately toxic	Brian Database/1992
21-day acute oral	Aquathol® K	LD50 344 mg/kg	Moderately toxic	Pedersen & Helsten, 1992c
21-day acute dietary	Endothall, dipotassium salt	LD50 328 mg/kg	Moderately toxic	Brian Database/1992 <sup>1</sup>
21-day acute dietary	Endothall Technical	LD50 111 mg/kg	Moderately toxic	Pedersen & Helsten, 1992a
21-day acute oral	Hydrothol® 191	LD50 389 mg/kg	Moderately toxic	Pedersen & Helsten, 1992b
20 wk. Toxicity and reproduction test	Endothall Technical	NOEL 50 PPM a.i.	N/A	Pedersen, Fletcher & Lesar, 1992a

1. Indicates year the actual study was conducted.

**Table 5: Endothall Laboratory Mammal Toxicity Data**

Test Type	Test Species	Formulation Used	Test Results (LD50)	Toxicity Ranking	Reference
Acute Oral	Rat	Aquathol® K (pelletized)	186.8 mg/kg	Moderately Toxic	Mallory, 1991a
Acute Oral	Rat	Aquathol®K	99.5 mg/kg	Moderately Toxic	Mallory, 1991b
Acute Oral	Rat	Hydrothol® 191	209.8 mg/kg	Moderately Toxic	Mallory, 1993
Acute Oral	Rat	Endothall Technical	45.4 mg/kg	Highly Toxic	Mallory, 1991c

**Table 6: Federally Endangered Terrestrial Plant, Bird, Mammal, and Fish Species Found in the State of Washington**

Terrestrial Plants	Common Name	Scientific Name
	Ute Ladies' - Tresses	<i>Spiranthes diluvialis</i>
	Golden Paintbrush	<i>Castilleja levisecta</i>
	Nelson's Checker-Mallow	<i>Sidalcea nelsoniana</i>
Birds		
	Aleutian Canada Goose	<i>Branta Canadensis</i> <i>Leucopareia</i>
	American Peregrine Falcon	<i>Falco peregrinus anatum</i>
	Bald Eagle	<i>Haliaeetus leucocephalus</i>
	Brown Pelican	<i>Pelecanus occidentalis</i>
	Marbled Murrelet	<i>Brachyramphus marmoratus</i>
	Northern Spotted Owl	<i>Strix occidentalis caurina</i>
	Western Snowy Plover	<i>Charadrius alexandinus nivosus</i>
Mammals		
	Gray Wolf	<i>Canis lupis</i>
	Grizzly Bear	<i>Ursus arctos horribilis</i>
	Woodland Caribou	<i>Rangifer tarandus caribou</i>
	Columbian White-Tailed Deer	<i>Odocoileus virginianus leucurus</i>

**Table 7: Concentration of Endothall in Water and Fish Tissue in a Wisconsin Pond<sup>1</sup>**

Sampling Time (Days)	Endothall Residues (mg/L)	
	In Water	In Edible Bluegill Tissue
0	<0.01	<0.1
0.083	6.2	0.02
1	4.9	0.04
3	4.9	<0.01
6	4.4	<0.01
10	3.4	<0.01
15	0.8	<0.01
25	0.1	<0.01

<sup>1</sup> Serns, 1977

**Table 8: Dissolved Oxygen Concentration (mg/L) at Different Temperatures**

Temperature in Degrees Centigrade	Dissolved Oxygen Concentration in mg/L
0	14.2
1	13.9
2	13.5
3	13.1
4	12.7
5	12.4
6	12.1
7	11.7
8	11.5
9	11.2
10	10.9
11	10.7
12	10.5
13	10.2
14	10.0
15	9.8
16	9.6
17	9.4
18	9.1
19	9.0
20	8.9
21	8.6
22	8.5
23	8.4
24	8.3
25	8.2

**Table 9: Relationship of pH and Temperature to the Percentage of Unionized Ammonia [NH<sub>4</sub>OH + NH<sub>3</sub> (dissolved)] in Freshwater**

pH	Temperature (°C)				
	5	10	15	20	25
6.5	0.04	0.06	0.09	0.13	0.18
7.0	0.12	0.19	0.27	0.40	0.55
7.5	0.39	0.59	0.85	1.24	1.73
8.0	1.22	1.83	2.65	3.83	5.28
8.5	3.77	5.55	7.98	11.2	15.0
9.0	11.0	15.7	21.4	28.5	35.8

**Table 10: Toxicity of Endothall (Aquathol® and Hydrothol®) to a Variety of Fish in Hard and Soft Water**

Endothall Product	Species	Soft Water LC50 (mg/L) <sup>1</sup>	Hard Water LC50 (mg/L) <sup>1</sup>	Reference
Hydrothol® 191	Golden shiner	1.6 <sup>2</sup>	0.32 <sup>2</sup>	Finlayson, 1980; S. Giddings, 1999
Hydrothol® 191	Bluegill sunfish	1.18 <sup>3</sup>	0.96 <sup>3</sup>	Ecology, 1992
Sodium Endothall Salt	Bluegill sunfish	160 <sup>3</sup>	180 <sup>3</sup>	Surber & Pickering, 1962
Sodium Endothall Salt	Fathead minnow	320 <sup>3</sup>	610 <sup>3</sup>	Surber & Pickering, 1962

<sup>1</sup> LC50 is in units reported in the original text.

<sup>2</sup> mg a.e./L

<sup>3</sup> mg a.i./L

**Table 11: Effects of Two Formulations of Endothall Acid on Various Fish Species**

Endothall Acid Formulation	Species	LC50 (mg a.e./L)	LOEC (mg a.e./L)	Reference
17.5% a.i	Rainbow trout	1.8	NR	FWS, 1986
77.9% a.i	Rainbow trout	49	13	Bettencourt, 1992
17.5% a.i.	Bluegill sunfish	4.3	NR	FWS, 1986
77.9 a.i.	Bluegill sunfish	47	18	Bettencourt, 1992
17.5% a.i.	Channel catfish	2.1	NR	FWS, 1986
77.9% a.i	Sheepshead minnow	110	44	Bettencourt, 1993

**Table 12: Species of Fish that are Particularly Sensitive to Aquathol® K**

Species	Common Name	Age	Toxicity (mg a.e./L) <sup>1</sup> Aquathol® K	
			LC50	NOEC
<i>Oncorhynchus tshawytscha</i> <sup>2</sup>	Chinook salmon	N.S. <sup>3</sup>	23	NS <sup>4</sup>
<i>Stizostedion vitreum</i> <sup>5</sup>	Walleye	8-10 days	11	4.0
<i>Stizostedion vitreum</i> <sup>5</sup>	Walleye	41-43 days	38	16
<i>Micropterus dolomieu</i> <sup>5</sup>	Smallmouth bass	1 day	33	6
<i>Micropterus salmoides</i> <sup>5</sup>	Largemouth bass	9-13days	92	35
<i>Oncorhynchus tshawytscha</i>	Chinook salmon	1.4 g	23	NS

- <sup>1</sup> All values expressed as mg a.e./L. Original values were expressed as mg formulation/L or mg a.i./L.  $\text{mg a.e./L} = \text{mg formulation/L} \times \% \text{ a.e./100} = \text{mg a.i./L} \times (\% \text{ a.e./}\% \text{ a.i.})$
- <sup>2</sup> Pennwalt, 1986 in Ecology, 1992
- <sup>3</sup> NS = Not specified; Probably juvenile.
- <sup>4</sup> NS = Not specified.
- <sup>5</sup> Paul et al., 1994

**Table 13: Toxicity of Adjuvants Registered for Aquatic Use to Aquatic Animals**

Adjuvant	Use	Use Rate L/ha	Depth for LC50 to be Achieved (meters)	96 hr LC50 (mg/L)		
				Bluegill	Rainbow Trout	Daphnia magna
Spray-Mate®	Surfactant	140	1.5	0.96		
R-11®	Surfactant			4.2-5.5	3.8	19
X77®	Surfactant	4.7	0.1	4.3	4.2	2.0
Cide-Kick II®	Surfactant	7.0	0.1	4.3-5.2		
Widespread®	Surfactant			7.0	6.6	16
Induce®	Surfactant/ Accelerant			7.3	8.3	18
Super Spread 200®	Surfactant			9.3		
Liqua Wet®	Surfactant			11.0	13	7.2
Spreader Sticker	Surfactant/ Sticker			35	36	48
Formula 403		18.7	0.1	37		
IVOD®		18.7	0.1	37		
Passage®				52	75	17
Big Sur®		4.7	<0.1	112		
Nalqautic®	Thickener	9.3	<0.1	200		
LI-700®				210	130	170
Agri Dex®	Surfactant/ Accelerant			>1000	>1000	>1000
Polysar®	Thickener	4.7	<0.1	3600		
Herbex®		2.3	<0.1	8000		
Foamer®	Anti-Foam					
No Foam A®	Anti-Foam					
Dyne Amic®	Surfactant					
Penetrator®	Surfactant/ Accelerant					

**Table 14: Acute Toxicity of Endothall to Algae and Aquatic Plants**

Test Substance	Species	Test Type	Growth Stage	Time (Hours)	LC50 (mg a.e./L) <sup>1</sup> (ppm)	NOEC (mg a.e./L) <sup>1</sup>	Reference
Hydrothol® 191	<i>Microcystis aeruginosa</i>	Static	Log	96	0.041 <sup>2</sup>	NS <sup>3</sup>	Ruzycki, 1997
Hydrothol® 191	<i>Phoridium inundatum</i>	Static	Log	96	0.042	NS	Ruzycki, 1997
Hydrothol® 191	<i>Anabaena flos-aquae</i>	Static	Log	120	0.042	0.024	Drottar et al., 1999
Hydrothol® 191	<i>Anabaena flos-aquae</i>	Static	Log	120	~0.012		Hoberg, 1994
Hydrothol® 191	<i>Chlamydomonas noctingama</i>	Static	Log	96	0.12	NS	Ruzycki, 1997
Hydrothol® 191	<i>Chlorella vulgaris</i>	Static	Log	96	>0.27	NS	Ruzycki, 1997
Hydrothol® 191	<i>Selenastrum capricornutum</i>	Static	Log	120	0.0023	0.00071	Drottar et al., 1999
Hydrothol® 191	<i>Selenastrum capricornutum</i>	Static	Log	120	~0.0037		Hoberg, 1994
Hydrothol® 191	<i>Scenedesmus acuminatus</i>	Static	Log	96	0.19	NS	Ruzycki, 1997
Hydrothol® 191	<i>Neviculla pelliculosa</i>	Static	Log	120	0.0076	0.0054	Drottar et al., 1999
Hydrothol® 191	<i>Synedra sp.</i>	Static	Log	96	>0.27	NS	Ruzycki, 1997
Hydrothol® 191	<i>Cyclotella meneghiana</i>	Static	Log	96	0.103	NS	Ruzycki, 1997
Hydrothol® 191	<i>Neviculla pelliculosa</i>	Static	Log	120	~0.16	NS	Hoberg, 1994
Hydrothol® 191	<i>Skeltonema costatum</i>	Static	Log	120	0.018	0.012	Drottar et al. 1999
Hydrothol® 191	<i>Skeltonema costatum</i>	Static	Log	120	~0.016	NS	Hoberg, 1994
Hydrothol® 191	<i>Lemna gibba</i>	Static renewal	Log	168	0.83	<0.35	Drottar et al. 1999
Hydrothol® 191	<i>Lemna gibba</i>	Static renewal	Log	336	~0.16		Hoberg, 1994
Endothall Acid	<i>Chlorococcum spp.</i>	Static	Log	240	50	NS	Walsh, 1972 in Gidding, 1999
Endothall Acid	<i>Dunaliella tertiolecta</i>	Static	Log	240	50	NS	Walsh, 1972 in Gidding, 1999
Endothall Acid	<i>Isochrysis galbana</i>	Static	Log	240	25	NS	Walsh, 1972 in Gidding, 1999

**Table 14: Acute Toxicity of Endothall to Algae and Aquatic Plants (Continued)**

Test Substance	Species	Type	Age	Time (Hours)	LC50 (mg a.e./L) <sup>1</sup> (ppm)	NOEC (mg a.e./L) <sup>1</sup>	Reference
Endothall Acid	<i>Phaeodactylum tricornutum</i>	Static	Log	240	15	NS	Walsh, 1972
Aquathol® K	<i>Anabaena flos-aquae</i>	Static	Log	120	>3.4	3.4	Hoberg, 1992
Aquathol® K	<i>Selenastrum capricornutum</i>	Static	Log	120	>3.4	3.4	Hoberg, 1992
Aquathol® K	<i>Chlorococcum spp.</i>	Static	Log	240	1500	NS	Brian Database, 1999
Aquathol® K	<i>Dunaliella tertiolecta</i>	Static	Log	240	1500	NS	Brian Database, 1999
Aquathol® K	<i>Neviculla peliculosa</i>	Static	Log	120	>2.6	2.6	Hoberg, 1992
Aquathol® K	<i>Skeltonema costatum</i>	Static	Log	120	>6.4	<6.4	Hoberg, 1992
Aquathol® K	<i>Isochrysis galbana</i>	Static	Log	240	3000	NS	Brian Database, 1999
Aquathol® K	<i>Phaeodactylum tricornutum</i>	Static	Log	240	500	NS	Brian Database, 1999
Aquathol(R) K	<i>Lemna gibba</i>	Static renewal		336	0.60	0.35	Hoberg, 1992

<sup>1</sup> All LC50 and NOEC values were converted to endothall acid equivalence (mg a.e./L). Original values were expressed in mg a.i./L mg formulation/L or mg a.e./L mg a.e./L = mg formulation/L x % a.e./100 = mg a.i./L x (%a.e./% a.i.)

<sup>2</sup> Geometric mean of a range of specified toxicities

<sup>3</sup> Not Specified

**Table 15: Acute Toxicity of Endothall to Fish**

Test Substance	Species	Test Type	Size Class Tested	Time (hours)	LC50 (mg a.e./L) <sup>1</sup>	NOEC (mg a.e./L) <sup>1</sup>	Reference
Hydrothol® 191	Rainbow trout	Static	0.6+g	96	0.24-0.51 (0.35) <sup>9</sup>	NR	2
Hydrothol® 191	Rainbow trout	Flow thru	0.75g	96	0.24	0.038	Bettencourt, 1994
Hydrothol® 191	Cutthroat trout	Static	1.0g	96	0.079	NR <sup>3</sup>	Johnson & Finley, 1980
Hydrothol® 191	Bluegill sunfish	Flow thru	0.59g	96	0.40	0.082	Bettencourt, 1994
Hydrothol® 191	Bluegill sunfish	Static	0.12-0.5g	96	0.28-0.41 (0.34) <sup>4</sup>	0.23 (0.18) <sup>4</sup>	5
Hydrothol® 191	Fathead minnow	Flow thru	NR	96	0.19	0.14	Dionne, 1996
Hydrothol® 191	Fathead minnow	Renewal	NR	96	0.189	NR	Keller et al, 1988 <sup>E</sup>
Hydrothol® 191	Fathead minnow	Static	NR	96	0.18	0.23	UCE, 1979 Brian, 1999
Hydrothol® 191	Sheepshead minnow	Flow thru	0.24g	96	0.82	0.16	Bettencourt, 1994
Hydrothol® 191	Channel catfish	Static	0.30g	96	0.11	NR	Johnson & Finley, 1980
Hydrothol® 191	Fowlers toad	NR	Tadpole	96	0.53-1.2 (0.80) <sup>4</sup>	NR	6
Endothall Acid	Rainbow trout	Flow thru	1.3g	96	49	13	Bettencourt, 1992
Endothall Acid	Bluegill sunfish	Static	NR	96	220	NR	Pennwalt, 1986
Endothall Acid	Bluegill sunfish	Flow thru	1.2g	96	77	18	Bettencourt, 1992
Endothall Acid	Redear sunfish	NR	NR	96	125	NR	Walker, 1963
Endothall Acid	Spot	Flow thru	Juvenile	48	>1.0	NR	
Endothall Acid	Largemouth bass	NR	NR	96	120	NR	Walker, 1963
Endothall Acid	Black bullhead	NR	NR	96	180	NR	Walker, 1963

**Table 15: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	Species	Test Type	Size Class Tested	Time (hours)	LC50 (mg a.e./L) <sup>1</sup>	NOEC (mg a.e./L) <sup>1</sup>	Reference
Endothall Acid	Yellow bullhead	NR	NR	96	175	NR	Walker, 1963
Endothall Acid	Carp	NR	NR	96	175	NR	Walker, 1963
Endothall Acid	Redfin shiners	NR	NR	96	95	NR	Walker, 1963
Endothall Acid	Redsided shiner	NR	NR	96	105	NR	Walker, 1963
Endothall Acid	Bluntnose minnow	NR	NR	96	120	NR	Walker, 1963
Endothall Acid	Mumichog	Static	0.8+g	96	213	56	UCE, 1980 <sup>B</sup>
Endothall Acid	Sheepshead minnow	Flow thru	25mm	96	110	44	Bettencourt, 1993
Aquathol® K	Rainbow trout	Flow thru	0.64g	96	109	41	Bettencourt, 1993
Aquathol® K	Rainbow trout	Static	0.4-1.2g	96	151-319 (166) <sup>4</sup>	51	7
Aquathol® K	Coho salmon	Static	1.4g	96	>71	NR	Johnson & Finley, 1980
Aquathol® K	Chinook salmon	Static	NR	96	23	NR	Pennwalt 1986
Aquathol® K	Bluegill sunfish	Static	0.3-1.5g	96	57-312 (132) <sup>4</sup>	51	8
Aquathol® K	Bluegill sunfish	Flow thru	1.5g	96	218	50	Bettencourt, 1993
Aquathol® K	Walleye	Static	8-10 days	96	11	4.0	Paul et al, 1994
Aquathol® K	Walleye	Static	41-43 days	96	38	16	Paul et al, 1994
Aquathol® K	Largemouth bass	Static	9-13 days	96	92	35	Paul et al, 1994
Aquathol® K	Smallmouth bass	Static	1 day	96	33	16	Paul et al, 1994
Aquathol® K	Emerald shiner	Static	Adult	96	80	2.5	WRC, 1963
Aquathol® K	Goldfish	NR	NR	96	264	NR	Berry, 1984
Aquathol® K	Sheepshead minnow	Flow thru	0.31g	96	100	35	Bettencourt, 1993
Aquathol® K	Channel catfish	Static	1.2g	96	>150 (>106) <sup>4</sup>	NR	Johnson & Finley, 1980,
Disodium Endothall	Bluegill sunfish	Static	NR	96	60-224 (135) <sup>4</sup>	NR	9
Disodium Endothall	Redear sunfish	NR	NR	96	100	NR	Walker, 1963 & 1964 <sup>w80</sup>
Disodium Endothall	Largemouth bass	NR	NR	96	98-160 (125)	NR	10

**Table 15: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	Species	Test Type	Size Class Tested	Time (hours)	LC50 (mg a.e./L) <sup>1</sup>	NOEC (mg a.e./L) <sup>1</sup>	Reference
Disodium Endothall	Striped bass	NR	Fingerling	96	135	NR	Wellborn, 1971
Disodium Endothall	Fathead minnow	NR	NR	96	98-354 (186)	NR	11
Disodium Endothall	Carp or Goldfish	NR	NR	96	140	NR	Walker, 1963
Disodium Endothall	Bluntnose minnow	NR	NR	96	92	NR	Walker, 1963
Disodium Endothall	Red shiner	NR	NR	96	84	NR	Walker, 1963
Disodium Endothall	Redfin shiner	NR	NR	96	76	NR	Walker, 1963
Disodium Endothall	Black bullhead	NR	NR	96	146	NR	Walker, 1963
Disodium Endothall	Brown bullhead	NR	NR	96	138	NR	Walker, 1963
Disodium Endothall	Yellow bullhead	NR	NR	96	138	NR	Walker, 1963

<sup>1</sup>All LC50s and NOECs were converted to mg a.e./L. Original values may have been expressed in mg formulation/L or mg a.i./L.  $\text{mg a.e./L} = \text{mg formulation/L} \times \% \text{a.e./100} = \text{mg a.i./L} \times (\% \text{a.e./}\% \text{a.i.})$

<sup>2</sup>UCE, 1979<sup>b</sup>, FWPCA, 1968<sup>w80</sup>, Johnson & Finley, 1980 & Mudge et al., 1986<sup>E</sup>

<sup>3</sup>NR = Not reported

<sup>4</sup>Geometric mean of all acceptable LC50s.

<sup>5</sup>UCE, 1979<sup>b</sup> & Johnson & Finley, 1980

<sup>6</sup>Johnson & Finley, 1986<sup>11</sup> & Sanders, 1970<sup>10</sup>

<sup>7</sup>UCE, 1979<sup>b</sup>, Johnson & Finley 1980, FWS, 1987<sup>B</sup> & Pennwalt, ND<sup>A93</sup>

<sup>8</sup>UCE, 1979<sup>b</sup>, Johnson & Finley 1980, Bettencourt, 1993 & Pennwalt, 1986<sup>w91</sup>

<sup>9</sup>Surber & Pickering, 1962<sup>3,6</sup>, Inglis & Davis, 1973<sup>3,6</sup>, Walker, 1963 & 1964<sup>3,6</sup>, Pennwalt, 1986<sup>w91</sup>

<sup>10</sup>Walker, 1963 & 1964, Surber & Pickering, 1962, Folmar, 1977<sup>w91</sup>, Bond, 1966<sup>w80</sup>

<sup>11</sup>Suber & Pickering, 1962 & Pennwalt, 1986<sup>w91</sup>

W80 = as reported in Ecology, 1981

W91 = as reported in Ecology, 1991.

A93 = as reported in Atochem, 1993.

B = Brian Database

E = Ecotox, 1999

<sup>7</sup>Ecology, 1980

**Table 16: Acute Toxicity of Endothall to Invertebrates**

Test Substance	Species	Test Type	Age	Time (hrs)	EC50 (mg a.e./L) <sup>1</sup>	NOEC (mg a.e./L) <sup>1</sup>	Reference
Hydrothol®191	Daphnid	Flow thru	<24 hrs	48	0.075	0.018	Putt, 1994
Hydrothol® 191	Daphnid	Static	<24 hrs	48	0.085	0.024	UCE, 1997 Brian, 1999
Hydrothol® 191	Daphnid	Static	NR <sup>2</sup>	48	0.63	NR	Keller, 1988
Hydrothol®191	Mysid shrimp	Flow thru	<24 hrs	96	0.56	0.18	Putt, 1994
Hydrothol®191	Eastern oyster	Flow thru	Juvenile	96	0.20	0.016	Dionne, 1995
Hydrothol®191	Bay mussel	Static	NR	48	2.15	NR	Keller, 1993
Hydrothol®191	Rotifer	Static	NR	24	0.37	0.20	Putt, 1996
Hydrothol®191	Tentans midge	Flow thru	NR	96	0.51	0.30	Putt, 1996
Hydrothol®191	Lined scud	NR	Mature	96	0.11-0.22 (0.14) <sup>2</sup>	NR	Johnson & Finley, 1980 Sanders, 1969
Hydrothol®191	Bright scud	Static	Mature	96	0.22	NR	Johnson & Finley, 1980
Hydrothol®191	Mayfly	Flow thru	NR	96	0.12	NR	Putt, 1996
Hydrothol®191	Amphipod	Flow thru	NR	96	0.17	0.027	Putt, 1996
Hydrothol®191	Variiegated oligochaete	Flow thru	NR	96	0.42	0.17	Putt, 1996
Hydrothol®191	Northern crayfish	Flow thru	NR	96	1.6	0.46	Dionne, 1996
Hydrothol®191	Grass shrimp	Static	Mature	96	0.022	NR	Johnson & Finley, 1980
Hydrothol®191	California stonefly	Static	Year Class 2	48	1.4	NR	Johnson & Finley, 1980
Hydrothol®191	Fiddler crab	NR	NR	96	6.2	NR	Giddings, 1999
Endothall Acid	Daphnid	Flow thru	<24 hrs	48	92	24	McNamara, 1992
Endothall Acid	Daphnid	Static	<24 hrs	48	33-46 (39) <sup>2</sup>	18	UCE, 1979, ATR, 1966 Brian, 1999

**Table 16: Acute Toxicity of Endothall to Invertebrates (Continued)**

Test Substance	Species	Test Type	Age	Time (hrs)	EC50 (mg a.e./L) <sup>1</sup>	NOEC (mg a.e./L) <sup>1</sup>	Reference
Endothall Acid	Mysid shrimp	Flow thru	<24 hrs	96	39	4.7	Bettencourt, 1993
Endothall Acid	Eastern oyster	Flow thru	Juvenile	96	43	16	Dionne, 1993
Endothall Acid	Bay mussel	Static	Embryo	48	49	<12.5	SRI, 1980 Brian, 1999
Endothall Acid	Brown shrimp	Flow thru	Juvenile	48	>1.0	NR	EPA, 1986 Brian, 1999
Endothall Acid	Grass shrimp	Static	0.1g	96	85	NR	UCE, 1980 Brian, 1999
Endothall Acid	Fiddler crab	Static	2.3+g	96	130	NR	UCE, 1980 Brian, 1999
Aquathol®K	Daphnid	Flow thru	<24 hrs	48	71	41	Putt, 1993
Aquathol®K	Daphnid	Static	<24 hrs	48	91	29	UCE, 1979 Brian, 1999
Aquathol®K	Mysid shrimp	Flow thru	<24 hrs	96	79	15	Bettencourt, 1993
Aquathol®K	Eastern oyster	Flow thru	Juvenile	96	97	<44	Dionne, 1993
Aquathol®K	Coegagrionid damselfly	Static	Nymph	96	>100	NR	OSU, 1965 Brian, 1999
Aquathol®K	Lined scud	Static	Mature	96	222	NR	Johnson & Finley, 1980
Aquathol® K	Bright scud	Static	Adult	96	354	NR	FWS, 1969 Brian, 1999
Aquathol®K	Libellulid dragonfly	Static	Nymph	96	>100	NR	OSU, 1967 Brian 1999
Aquathol®K	Fiddler crab	Static	Adult	96	750	320	UCE, 1977 Brian, 1999

<sup>1</sup>All LC50 values were converted to endothall acid equivalent (mg a.e./L). The original values were expressed as mg a.i./L, mg formulation/L or mg a.e./L. mg a.e./L = mg formulation/L x % a.e./100 = mg a.i./L x (% a.e./% a.i.)

<sup>2</sup>NR = Not reported

**Table 17: Chronic and Early Life Stage Toxicity of Endothall to Fish**

Test Substance	Species	Test Type	Water Type	Size Class Tested	Time (Days)	LC50 (mg a.e./L) <sup>1</sup>	NOEC (mg a.e./L) <sup>1</sup>	MATC (mg a.e./L)	LOEC (mg a.e./L)	Reference
Hydrothol® 191	Fathead minnow	Flow	FW	egg-fry	35	NR <sup>2</sup>	0.028	0.04	0.056	Bettencourt, 1994
Hydrothol® 191	Fathead minnow	NR	FW	<24 hrs	7	0.103	0.056	0.082	0.117	Keller, 1988
Hydrothol® 191	Fathead minnow	NR	FW	<24 hrs	7	0.134	0.088	0.101	0.116	Keller, 1988
Hydrothol® 191	Fathead minnow	NR	FW	<24 hrs	7	NR	0.022	0.035	0.058	Keller, 1988
Endothall Acid	Fathead minnow	Flow	FW	Egg-fry	35	NR	13	19	27	Bettencourt, 1994
Aquathol® K	Rainbow trout	Flow	FW	Egg-fry	NR	NR	<7.2	7.2	7.2	FWS, 1976 Brian, 1999
Aquathol® K	Chinook salmon	NR	FW	Fry	14	62	NR	NR	NR	Ligouri et al. 1984
Disodium Endothall	Rainbow trout	NR	FW	Egg-fry	NR	NR	5	NR	NR	Pennwalt, 1986
Disodium Endothall	Bluegill sunfish	Static	FW	NR	21	NR	80	NR	NR	Folmar, 1977
Disodium Endothall	Bluegill sunfish	NR	FW	Sac-Fry	12	>80	>80	NR	NR	Hiltbran, 1967
Disodium Endothall	Bluegill sunfish	NR	FW	Sac-Fry	8	>20	>20	NR	NR	Hiltbran, 1967
Disodium Endothall	Green sunfish	NR	FW	Egg-Fry	NR	NR	20	NR	NR	Pennwalt, 1986
Disodium Endothall	Green sunfish	NR	FW	Sac-Fry	8	>20	>20	NR	NR	Hiltbran, 1967

**Table 17: Chronic and Early Life Stage Toxicity of Endothall to Fish (Continued)**

Test Substance	Species	Test Type	Water Type	Size Class Tested	Time (Days)	LC50 (mg a.e./L) <sup>1</sup>	NOEC (mg a.e./L) <sup>1</sup>	MATC (mg a.e./L)	LOEC (mg a.e./L)	Reference
Disodium Endothall	Smallmouth bass	NR	FW	Sac-fry	8	>20	>20	NR	NR	Hiltbran, 1967
Disodium Endothall	Largemouth bass	Static	FW	NR	21	NR	8	NR	NR	Folmar, 1977
Disodium Endothall	Bluntnose minnow	Static	FW	NR	21	NR	32	NR	NR	Folmar, 1977
Disodium Endothall	Redfin shiner	Static	FW	NR	21	NR	32	NR	NR	Folmar, 1977
Disodium Endothall	Red shiner	Static	FW	NR	21	NR	32	NR	NR	Folmar, 1977
Disodium Endothall	Lake chubsucker	NR	FW	Fry	8	>20	>20	NR	NR	Hiltbran, 1967
Disodium Endothall	Lake chubsucker	NR	FW	Fry	8	>8	>8	NR	NR	Hiltbran, 1967
Disodium Endothall	Stoneroller	NR	FW	Egg-fry	8	NR	>40	NR	NR	Hiltbran, 1967

<sup>1</sup> All LC50s and NOECs were converted to mg a.e./L. Original values may have been expressed in mg formulation/L or mg a.i./L. mg a.e./L = mg formulation/L x %a.e./100 = mg a.i./L x (% a.e./%a.i.)

<sup>2</sup> NR = Not reported

**Table 18: Chronic Toxicity of Endothall to Invertebrates**

Test Substance	Species	Test Type	Age	Time (Days)	LC50 <sup>1</sup> (ppm)	NOEC <sup>1</sup> (ppm)	MATC (ppm)	LOEC (ppm)	Reference
Hydrothol®191	<i>Daphnia magna</i>	Flow	<24 hrs	21	NR	0.016	0.023	0.033	Putt, 1994c
Hydrothol®191	<i>Ceriodaphnia dubia</i>	Flow	<24 hrs	7	0.073	<0.005	<0.007	0.011	Keller, 1988
Endothall Acid	<i>Daphnia magna</i>	Flow	<24 hrs	21	24	5	6.7	8.9	Putt, 1993b

<sup>1</sup> All LC50s and NOECs were converted to mg a.e./L. Original values may have been expressed in mg formulation/L or mg a.i./L.

$$\text{mg a.e./L} = \text{mg formulation/L} \times \% \text{a.e./100} = \text{mg a.i./L} \times (\% \text{ a.e./}\% \text{a.i.})$$

**Table 19: Acute to Chronic Ratio for Endothall Salts and Acid for Several Species of Fish and Invertebrates**

Species	Acute LC50 (mg a.e./L) <sup>1</sup>	Chronic NOEC (mg a.e./L) <sup>1</sup>	Acute/Chronic Ratio
Bluegill sunfish	135 <sup>2</sup>	80 <sup>2</sup>	1.7
Red shiner	84 <sup>2</sup>	32 <sup>2</sup>	2.6
Redfin shiner	76 <sup>2</sup>	32 <sup>2</sup>	2.4
Fathead minnow	186 <sup>2</sup>	32 <sup>3</sup>	5.8
Rainbow trout	109 <sup>4</sup>	<7.2 <sup>4</sup>	>15.1
Largemouth bass	125 <sup>2</sup>	8 <sup>2</sup>	15.6
Rainbow trout	166 <sup>4</sup>	5 <sup>2</sup>	33.2
Fathead minnow	0.19 <sup>5</sup>	0.028 <sup>5</sup>	6.8
Daphnia magna	92 <sup>3</sup>	5 <sup>2</sup>	18.4
Daphnia magna	0.075 <sup>5</sup>	0.016 <sup>5</sup>	4.7
Geometric Mean for Fish = 5.8			
Geometric Mean for All species = 6.4			

<sup>1</sup> All values expressed as mg a.e./L. Original values were expressed as mg formulation/L or mg a.i./L. mg a.e./L = mg formulation/L x % a.e./100 = mg a.i./L x (% a.e./%a.i)

<sup>2</sup> Disodium endothall

<sup>3</sup> Endothall acid

<sup>4</sup> Aquathol® K

<sup>5</sup> Hydrothol® 191

**Table 20: Predicted Chronic NOEC for Hydrothol® In Fish**

Test Substance	Species	Acute LC50 (mg a.e./L) <sup>1</sup>	Predicted Chronic NOEC (mg a.e./L) <sup>1</sup>
Hydrothol® 191	Rainbow trout	0.24-0.51 (0.35) <sup>2</sup>	0.054
Hydrothol® 191	Rainbow trout	0.24	0.038
Hydrothol® 191	Cutthroat trout	0.079	0.012
Hydrothol® 191	Bluegill sunfish	0.40	0.063
Hydrothol® 191	Bluegill sunfish	0.28-0.41 (0.34) <sup>2</sup>	0.053
Hydrothol® 191	Fathead minnow	0.19	0.030
Hydrothol® 191	Fathead minnow	0.189	0.028
Hydrothol® 191	Fathead minnow	0.2	0.031
Hydrothol® 191	Sheepshead minnow	0.82	0.13
Hydrothol® 191	Channel catfish	0.11	0.017

<sup>1</sup> All values expressed as mg a.e./L. Original values were expressed as mg formulation/L or mg a.i./L.

mg a.e./L = mg formulation/L x % a.e./100 = mg a.i./L x (% a.e./%a.i)

<sup>2</sup> Geometric mean of collected data.

**Table 21: Predicted Chronic Toxicity for Endothall to Invertebrates**

Test Substance	Species	EC50 (mg a.e./L) <sup>1</sup>	Predicted Chronic NOEC (mg a.e./L) <sup>1</sup>
Hydrothol®191	Daphnid	0.075	0.012
Hydrothol®191	Daphnid	0.085	0.013
Hydrothol®191	Daphnid	0.63	0.098
Hydrothol®191	Mysid shrimp	0.56	0.088
Hydrothol®191	Eastern oyster shell growth	0.20	0.031
Hydrothol®191	Bay mussel (Attachment)	2.15	0.33
Hydrothol®191	Rotifer	0.37	0.057
Hydrothol®191	Tentans midge	0.51	0.050
Hydrothol®191	Lined scud	0.11-0.22 (0.14) <sup>2</sup>	0.022
Hydrothol®191	Bright scud	0.22	0.034
Hydrothol®191	Mayfly	0.12	0.019
Hydrothol®191	Amphipod	0.17	0.027
Hydrothol®191	Variegated oligochaete	0.42	0.066
Hydrothol®191	Northern crayfish	1.6	0.25
Hydrothol®191	Grass shrimp	0.022	0.0034
Hydrothol®191	California atonefly	1.4	0.22
Hydrothol®191	Fiddler crab	6.2	0.97

<sup>1</sup> All values expressed as mg a.e./L. Original values were expressed as mg formulation/L or mg a.i./L.

mg a.e./L = mg formulation/L x % a.e./100 = mg a.i./L x (% a.e./%a.i)

<sup>2</sup> Geometric mean of collected data.

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Appendix 1: Acute Toxicity of Endothall Algae and Aquatic Plants

Test Substance	%A.I.	Species	Test Type	Water	Size Class	Test Duration (Hour)	LC50 (mg/L)	NOEC	Status	Reference
Hydrothol® 191	53 <sup>a</sup> 23.6 <sup>b</sup>	<i>Microcystis aeruginosa</i>	Static	AAP	Log	96	0.065-0.14 <sup>c</sup> (0.042) <sup>e</sup>	NR <sup>d</sup>	NR	Ruzycki, 1997
Hydrothol® 191	53 23.6	<i>Phoridium inundatum</i>	Static	AAP	Log	96	0.094 <sup>c</sup> (0.042) <sup>e</sup>	NR	NR	Ruzycki, 1997
Hydrothol® 191	53 23.6	<i>Anabaena flos-aquae</i>	Static	AAP	Log	120	0.178 <sup>f</sup> 0.042 <sup>e</sup>	0.102 <sup>f</sup> (0.024) <sup>e</sup>	C <sup>g</sup>	Drottar et al., 1999
Hydrothol® 191	53 23.6	<i>Anabaena flos-aquae</i>	Static	AAP	Log	120	~0.05 <sup>f</sup> (~0.012) <sup>e</sup>		S <sup>h</sup>	Hoberg, 1994
Hydrothol® 191	53 23.6	<i>Chlamydomonas noctingama</i>	Static	AAP	Log	96	0.273 <sup>c</sup> (0.12) <sup>e</sup>	NR	NR	Ruzycki, 1997
Hydrothol® 191	53 23.6	<i>Chlorella vulgaris</i>	Static	AAP	Log	96	>0.60 <sup>c</sup> (>0.27) <sup>e</sup>	NR	NR	Ruzycki, 1997
Hydrothol® 191	53 23.6	<i>Selenastrum capricornutum</i>	Static	AAP	Log	120	0.0098 <sup>f</sup> (0.0023) <sup>e</sup>	0.0030 <sup>f</sup> (0.00071) <sup>e</sup>	C	Drottar et al., 1999
Hydrothol® 191	53 23.6	<i>Selenastrum capricornutum</i>	Static	AAP	Log	120	~0.016 <sup>f</sup> (~0.0037) <sup>e</sup>		S	Hoberg, 1994
Hydrothol® 191	53 23.6	<i>Scenedesmus acuminatus</i>	Static	AAP	Log	96	0.417 <sup>c</sup> (0.19) <sup>e</sup>	NR	NR	Ruzycki, 1997
Hydrothol® 191	53 23.6	<i>Neviculla pelliculosa</i>	Static	SiAAP	Log	120	0.032 <sup>f</sup> (0.0076) <sup>e</sup>	0.023 <sup>f</sup> (0.0054) <sup>e</sup>	C	Drottar et al., 1999
Hydrothol® 191	53 23.6	<i>Synedra sp.</i>	Static	SiAAP	Log	96	>0.60 <sup>c</sup> (>0.27)	NR	NR	Ruzycki, 1997
Hydrothol® 191	53 23.6	<i>Cyclotella meneghiana</i>	Static	SiAAP	Log	96	0.232 <sup>c</sup> (0.103) <sup>e</sup>	NR	NR	Ruzycki, 1997

Appendix 1: Acute Toxicity of Endothall Algae and Aquatic Plants (Continued)

Test Substance	%A.I.	Species	Test Type	Water	Age	Test Duration (Hour)	LC50 (mg/L)	NOEC	Status	Reference
Hydrothol® 191	53 23.6	<i>Neviculla pelliculosa</i>	Static	SiAAP	Log	120	~0.16 <sup>l</sup> (~0.16)	NR	S	Hoberg, 1994
Hydrothol® 191	53 23.6	<i>Skeltonema costatum</i>	Static	SiESW	Log	120	0.076 <sup>l</sup> (0.018) <sup>e</sup>	0.050 <sup>l</sup> (0.012) <sup>e</sup>	C	Drottar et al. 1999
Hydrothol® 191	53 23.6	<i>Skeltonema costatum</i>	Static	SiESW	Log	120	~0.016 <sup>l</sup> (0.016) <sup>i</sup>	NR	S	Hoberg, 1994
Hydrothol® 191	53 23.6	<i>Lemna gibba</i>	Static renewal	Hoagland's	Log	168	3.5 <sup>l</sup> (0.83) <sup>e</sup>	<1.5 <sup>l</sup> (<0.35) <sup>e</sup>	C	Drottar et al. 1999
Hydrothol® 191	53 23.6	<i>Lemna gibba</i>	Static renewal	Hoagland's	Log	336	~0.16 <sup>l</sup> (~0.16) <sup>e</sup>		S	Hoberg, 1994
Endothall Acid	91.21 <sup>l</sup>	<i>Chlorococcum spp.</i>	Static	ESW	Log	240	50 <sup>ca,e</sup> (50) <sup>e</sup>	NR	NR	Walsh, 1972 in Giddings, 1995
Endothall Acid	91.21	<i>Dunaliella tertiolecta</i>	Static	ESW	Log	240	50 (50)	NR	NR	Walsh, 1972 in Giddings, 1995
Endothall Acid	91.21	<i>Isochrysis galbana</i>	Static	ESW	Log	240	25 <sup>ca,e</sup> (25) <sup>e</sup>	NR	NR	Walsh, 1972 in Giddings, 1995
Endothall Acid	91.21	<i>Phaeodactylum tricornutum</i>	Static	SiESW	Log	240	15 <sup>ca,e</sup> (14) <sup>e</sup>	NR	NR	Walsh, 1972 in Giddings, 1995
Aquathol® K	40.3 <sup>k</sup> 28.6 <sup>l</sup>	<i>Anabaena flos-aquae</i>	Static	AAP	Log	120	>4.8 <sup>c</sup> (>3.4) <sup>e</sup>	4.8 (3.4)	S	Hoberg, 1992
Aquathol® K	40.3 28.6	<i>Selenastrum capricornutum</i>	Static	AAP	Log	120	>4.8 (>3.4)	4.8 (3.4)	S	Hoberg, 1992
Aquathol® K	40.3 28.6	<i>Chlorococcum spp.</i>	Static	ESW	Log	240	2113 <sup>c</sup> (1500) <sup>i</sup>	NR	S	Brian Database, 1999
Aquathol® K	40.3 28.6	<i>Dunaliella tertiolecta</i>	Static	ESW	Log	240	2113 (1500)	NR	S	Brian Database, 1999

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**Appendix 1: Acute Toxicity of Endothall Algae and Aquatic Plants (Continued)**

Test Substance	%A.I.	Species	Test Type	Water	Size Class	Test Duration (Hour)	LC50 (mg/L)	NOEC	Status	Reference
Aquathol® K	40.3 <sup>k</sup> 28.6 <sup>l</sup>	<i>Neviculla pelliculosa</i>	Static	SiAAP	Log	120	>3.6 <sup>c</sup> (>2.6) <sup>e</sup>	3.6 (2.6)	S	Hoberg, 1992
Aquathol® K	40.3 28.6	<i>Skeltonema costatum</i>	Static	SiESW	Log	120	>9.0 <sup>c</sup> (>6.4) <sup>e</sup>	<9.0 (<6.4)	C	Hoberg, 1992
Aquathol® K	40.3 28.6	<i>Isochrysis galbana</i>	Static	AAP	Log	240	4227 <sup>c</sup> 3000 <sup>i</sup>	NR	S	Brian Database, 1999
Aquathol® K	40.3 28.6	<i>Phaeodactylum tricornutum</i>	Static	SiAAP	Log	240	705 <sup>c</sup> (500) <sup>j</sup>	NR	S	Brian Database, 1999
Aquathol® K	40.3 28.6	<i>Lemna gibba</i>	Static renewal	Hoagland's		336	0.84 <sup>c</sup> (0.60) <sup>e</sup>	0.50 <sup>c</sup> (0.35) <sup>e</sup>	C	Hoberg, 1992

<sup>a</sup> 53% a.i.

<sup>b</sup> 23.36% a.e

<sup>c</sup> mg/L in terms of a.i.; a.e.=a.i.X/100 a.e./%a.i.=a.i.X/441 Hydrothol® and also a.e.=a.i.X.a.e.=a.i.X.0.7096 for Aquathol®K; a.e.=a.e.X0.802 for sodium endothall

<sup>d</sup> Not reported

<sup>e</sup> mg/L in terms of a.e.

<sup>f</sup> mg/L in terms of product; a.e.=product X 0.2336 for Hydrothol®; a.e.=product X0.286 for Aquathol®; a.e.=product X 0.802 for sodium endothall

<sup>g</sup> Study meets core requirements for risk assessment

<sup>h</sup> Study does not meet core requirement for risk assessment but provides useful information supplemental to the core studies

<sup>i</sup> mg/K in terms of a.e.; originally reported in terms of a.e.

<sup>j</sup> Technical endothall acid approx 100% a.e.

**Appendix 2: Acute Toxicity of Endothall to Fish**

Test Substance	%AI or Form	Species	Test Type	Water	Size Class	Test Duration (hours)	LC50 (mg/L)	NOEC (mg/L)	Status	Reference
Hydrothol® 191	NR <sup>a,b</sup>	Rainbow trout	Static	FW <sup>c</sup>	NR	96	1.7 <sup>d</sup> (0.40) <sup>e</sup>	NR <sup>a</sup>	NR <sup>a</sup>	Mudge et al. 1986 <sup>10</sup>
Hydrothol® 191	23.36 <sup>f</sup>	Rainbow trout	Static	FW	0.6+g	96	1.3 <sup>g</sup> (0.30) <sup>e</sup>	NR	C <sup>h</sup>	UCE, 1979 <sup>1,5,11</sup> Brian Database, 1999
Hydrothol® 191	53 <sup>i</sup>	Rainbow trout	NR	FW	NR	48	1.15 <sup>d</sup> (0.51)	NR	NR	FWPCA, 1968 <sup>3,8</sup>
Hydrothol® 191	23.5 <sup>f</sup>	Rainbow trout	Flow	FW	0.75g	96	1.0 <sup>g</sup> (0.24)	0.16 0.038	C	Bettencourt, 1994
Hydrothol® 191	53 <sup>i</sup>	Rainbow trout	Static	FW	1.2g	96 13°C	0.56 <sup>d</sup> (0.25)	NR	S <sup>j</sup>	Johnson & Finley, 1980
Hydrothol® 191	53 <sup>i</sup>	Cutthroat trout	Static	FW	1.0g	96	0.18 <sup>d</sup> (0.079)	NR	C	Johnson & Finley, 1980
Hydrothol® 191	23.36 <sup>f</sup>	Bluegill sunfish	Flow	FW	0.59g	96	1.7 <sup>g</sup> (0.40)	0.35 <sup>g</sup> (0.082)	C	Bettencourt, 1994
Hydrothol® 191	23.36 <sup>f</sup>	Bluegill sunfish	Static	FW	0.12g	96	1.2 <sup>g</sup> (0.28)	<1.0 (0.23)	C	UCE, 1979 <sup>1,5</sup> Brian Database, 1999
Hydrothol® 191	53 <sup>i</sup>	Bluegill sunfish	Static	FW	0.5g	96	0.94 <sup>d</sup> (0.41)	NR	S	Johnson & Finley, 1980
Hydrothol® 191	23.2 <sup>f</sup>	Fathead minnow	Flow	FW	0.74g	96	0.84 <sup>g</sup> (0.19)	0.62 <sup>g</sup> (0.14)	NR	Dionne, 1996
Hydrothol® 191	23.36 <sup>f</sup>	Fathead minnow	Static	FW	NR	96	0.75 <sup>g</sup> (0.18)	<1.0 <sup>g</sup> (0.23)	C	UCE, 1979 <sup>1,5</sup> Brian Database, 1999

**Appendix 2: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	%AI or Form	Species	Test Type	Water	Size Class	Test Duration (hours)	LC50 (mg/L)	NOEC (mg/L)	Status	Reference
Hydrothol® 191	53 <sup>i</sup>	Fathead minnow	R	FW	NR	96	0.39-0.47 <sup>d</sup> (0.189) <sup>e</sup>	NR	NR	Keller et al., 1988 <sup>10</sup>
Hydrothol® 191	53 <sup>i</sup>	Golden shiner	Flow	FW	NR	120	0.32-1.6 <sup>k</sup> (0.71) <sup>l,e</sup>	NR	NR	Finlayson, 1980 <sup>10</sup>
Hydrothol® 191	53 <sup>i</sup> 23.5 <sup>f</sup>	Sheepshead minnow	Flow	SW <sup>h</sup>	0.24g	96	3.5 <sup>g</sup> (0.82)	0.66 <sup>g</sup> (0.16)	C	Bettencourt, 1994
Hydrothol® 191	53 <sup>i</sup>	Channel catfish	Static	FW	0.30g	96	0.49 <sup>d</sup> (0.11)	NR	S	Johnson & Finley, 1980
Hydrothol® 191	53 <sup>i</sup>	Fowler's toad	NR	FW	Tadpole	96	1.2 <sup>d</sup> (0.53)	NR	S	Johnson & Finley 1980
Hydrothol® 191	23.36 <sup>f</sup>	Fowler's toad	NR	FW	Tadpole	24	3.2 <sup>k</sup> (3.2)	NR	NR	Sanders, 1970 <sup>10</sup>
Hydrothol® 191	23.36 <sup>f</sup>	Fowler's toad	NR	FW	Tadpole	48	1.8 <sup>k</sup> (1.8)	NR	NR	Sanders, 1970 <sup>10</sup>
Hydrothol® 191	23.36 <sup>f</sup>	Fowler's toad	NR	FW	Tadpole	96	1.2 <sup>k</sup> (1.2)	NR	NR	Sanders, 1970 <sup>10</sup>
Endothall Acid	77.9 <sup>m</sup>	Rainbow trout	Flow	FW	1.3g	96	49 <sup>d,k</sup> (49)	13 (13)	C	Bettencourt, 1992
Endothall Acid	NR <sup>a,n</sup>	Bluegill sunfish	NR	FW	NR	24	450 <sup>d,k</sup> (450)	NR	NR	Suber & Pickering, 1962 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Bluegill sunfish	NR	FW	NR	24	428 <sup>d,k</sup> (428)	NR	NR	Davies & Hughes, 1963 <sup>3,8</sup>

**Appendix 2: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	%AI or Form	Species	Test Type	Water	Size Class	Test Duration (hours)	LC50 (mg/L)	NOEC (mg/L)	Status	Reference
Endothall Acid	NR <sup>a,n</sup>	Bluegill sunfish	Static	FW	NR	96	220 <sup>g,d,k</sup> (220)	NR	Y	Pennwalt, 1986 <sup>1</sup>
Endothall Acid	77.9 <sup>m</sup>	Bluegill sunfish	Flow	FW	1.2g	96	77 <sup>d,k</sup> (77)	18 (18)	C	Bettencourt, 1992
Endothall Acid	NR <sup>a,n</sup>	Redear sunfish	NR	FW	NR	96	125 <sup>d,k</sup> (125)	NR	NR	Walker, 1963 <sup>3,8</sup>
Endothall Acid	Form	Spot	Flow	FW	Juv	48	>1.0 <sup>o</sup>	NR	S	EPA 1986 <sup>11</sup> Brian Database, 1999
Endothall Acid	NR <sup>a,n</sup>	Largemouth bass	NR	FW	NR	24	560 <sup>d,k</sup> (560)	NR	NR	Suber and Pickering, 1962 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Largemouth bass	NR	FW	NR	96	120 <sup>d,k</sup> (120)	NR	NR	Walker, 1963 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Black Bullhead	NR	FW	NR	96	180 <sup>d,k</sup> (180)	NR	NR	Walker, 1963 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Yellow bullhead	NR	FW	NR	96	175 <sup>d,k</sup> (175)	NR	NR	Walker, 1963 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Fathead minnow	NR	FW	NR	24	560 <sup>d,k</sup> (560)	NR	NR	Suber and Pickering, 1962 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Carp	96	FW	NR	96	175 <sup>d,k</sup> (175)	NR	NR	Walker, 1963 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Harlequin fish	NR	FW	NR	24	565 <sup>d,k</sup> (565)	NR	NR	Albaster, 1969 <sup>3</sup>
Endothall Acid	NR <sup>a,n</sup>	Redfin shiner	NR	FW	NR	96	95 <sup>d,k</sup> (95)	NR	NR	Walker, 1963 <sup>3,8</sup>
Endothall Acid	NR <sup>a,n</sup>	Redsided shiner	NR	FW	NR	96	105 <sup>d,k</sup> (105)	NR	NR	Walker, 1963 <sup>3,8</sup>

**Appendix 2: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	%AI or Form	Species	Test Type	Water	Size Class	Test Duration (hours)	LC50 (mg/L)	NOEC (mg/L)	Status	Reference
Endothall Acid	NR <sup>a,n</sup>	Bluntnose minnow	NR	FW	NR	96	120 <sup>d,k</sup> (120)	NR	NR	Walker, 1963 <sup>3,8</sup>
Endothall Acid	89.5 <sup>p</sup>	Mumichog	Static	FW	0.8+g	96	213 <sup>d,k</sup> (213)	56	C	UCE, 1980 <sup>11</sup>
Endothall Acid	77.9 <sup>q</sup>	Sheepshead minnow	Flow	SW	25mm	96	110 <sup>d,k</sup> (110)	44 (44)	C	Bettencourt, 1993
<hr/>										
Aquathol® K	29.5 <sup>t</sup>	Rainbow trout	Flow	FW	0.64	96	370 <sup>s</sup> (109)	140 (41)	C	Bettencourt, 1993
Aquathol® K	28.6 <sup>s</sup>	Rainbow trout	Static	FW	0.4-1+g	96	528.7 <sup>s</sup> (151)	180 (51)	S	UCE, 1979 <sup>1,5,11</sup> Brian Database, 1999
Aquathol® K	40.3 <sup>t</sup>	Rainbow trout	Static	FW	1.2g	96	450 <sup>d</sup> (319)	NR	C	Johnson & Finley 1980
Aquathol® K	40.3 <sup>t</sup>	Rainbow trout	Static	FW	1.2g	96	230 <sup>d</sup> (163)	NR	C	Johnson & Finley, 1980
Aquathol® K	Liquid <sup>u</sup>	Rainbow trout	NR	FW	NR	96	213 <sup>d</sup> (151)	NR	NR	Pennwalt, ND <sup>6</sup>
Aquathol® K	40.3 <sup>t</sup>	Coho salmon	Static	FW	1.4g	96	>100 <sup>d</sup> (>71)	NR	C	Johnson & Finley, 1980
Aquathol® K	28.6 <sup>u</sup>	Chinook salmon	Static	FW	NR	96	82 <sup>s</sup> (23)	NR	Y	Pennwalt, 1986
Aquathol®	28.6 <sup>a</sup>	Bluegill sunfish	Static	FW	0.3-0.4g	96	501.2 <sup>s</sup> (143)	180 (51)	S	UCE, 1979 <sup>1,5,11</sup> Brian Database, 1999
Aquathol® K	40.3 <sup>t</sup>	Bluegill sunfish	Static	FW	1.3g	96	440 <sup>d</sup> (312)	NR	C	Johnson & Finley 1980
Aquathol® K	40.3 <sup>t</sup>	Bluegill sunfish	Static	FW	1.3g	96	343 <sup>d</sup> (243)	NR	C	Johnson & Finley 1980

**Appendix 2: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	%AI or Form	Species	Test Type	Water	Size Class	Test Duration (hours)	LC50 (mg/L)	NOEC (mg/L)	Status	Reference
Aquathol® K	29.5 <sup>t</sup>	Bluegill sunfish	Flow	FW	1.5g	96	740 <sup>g</sup> (218)	170 (50)	C	Bettencourt, 1993
Aquathol® K	28.6 <sup>s</sup>	Bluegill sunfish	Static	FW	NR	96	230 <sup>g</sup> (66)	NR	Y	Pennwalt, 1986 <sup>1</sup>
Aquathol® K	Liquid <sup>u</sup>	Bluegill sunfish	NR	FW	NR	96	202 <sup>d</sup> (57)	NR	NR	Pennwalt, ND <sup>6</sup>
Aquathol® K	15.7 <sup>v</sup>	Emerald shiner	Static	FW	Adult	96	510 <sup>o</sup>	15.7	S	WRC, 1963 <sup>11</sup> Brian Database, 1999
Aquathol® K	NR	Goldfish	NR	FW	NR	96	372 <sup>d</sup> (264)	NR	S	Berry, 1984
Aquathol® K	29.5 <sup>u</sup>	Sheepshead minnow	Flow	SW	0.31g	96	340 <sup>g</sup> (100)	120 (35)	C	Bettencourt, 1993
Aquathol® K	40.3 <sup>1</sup>	Channel catfish	Static	FW	1.2G	96	>150 <sup>d</sup> (>106) <sup>e</sup>	NR	C	Johnson & Finley, 1980
Endothall Disodium Salt	Solid <sup>w</sup>	Chinook salmon	NR	FW	NR	48	136 <sup>d</sup> (109) <sup>e</sup>	NR	NR	Bond <i>et al.</i> , 1960 <sup>6</sup>
Endothall Disodium Salt	NR <sup>w</sup>	Bluegill sunfish	Static	FW	NR	96	280 <sup>g</sup> (224)	NR	Y	Folmar, 1977 <sup>1</sup>
Endothall Disodium Salt	Liquid <sup>x</sup>	Bluegill sunfish	NR	FW	NR	96	160-180 <sup>d</sup> (136) <sup>y</sup>	NR	NR	Suber & Pickering, 1962 <sup>6</sup>
Endothall Disodium Salt	Liquid	Bluegill sunfish	NR	FW	NR	96	102-140 <sup>d</sup> (96) <sup>y</sup>	NR	NR	Ingليس & Davis, 1973 <sup>6</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Bluegill sunfish	NR	FW	NR	96	170-175 <sup>d</sup> (138) <sup>y</sup>	NR	NR	Walker, 1963 & 164 <sup>3,6,8</sup>
Endothall Disodium Salt	NR <sup>w</sup>	Bluegill sunfish	Static	FW	NR	96	125-150 <sup>d</sup> (110) <sup>y</sup>	NR	Y	Walker, 1963 & 1964 <sup>3,8</sup>

**Appendix 2: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	%AI or Form	Species	Test Type	Water	Size Class	Test Duration (hours)	LC50 (mg/L)	NOEC (mg/L)	Status	Reference
Endothall Disodium Salt	NR <sup>w</sup>	Bluegill sunfish	Static	FW	NR	96	75 <sup>g</sup> (60)	NR	Y	Pennwalt, 1986 <sup>1</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Redear sunfish	NR	FW	NR	96	125 <sup>d</sup> (100)	NR	Y	Walker, 1963 & 1964 <sup>1,5</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Largemouth bass	NR	FW	NR	96	120-125 <sup>d</sup> (98) <sup>y</sup>	NR	Y	Walker, 1963 & 1964 <sup>1,6,8</sup> & Folmar, 1977
Endothall Disodium Salt	Liquid <sup>x</sup>	Largemouth Bass	NR	FW	NR	96	200 <sup>d</sup> (160)	NR	Y	Suber and Pickering, 1962 & Folmar, 1977 <sup>1</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Largemouth bass	NR	FW	NR	48	200 <sup>d</sup> (160)	NR	NR	Bond <i>et al.</i> , 1960 <sup>6</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Largemouth bass	NR	FW	NR	96	>135 <sup>d</sup> (>108)	NR	Y	Bond <i>et al.</i> , 1960 <sup>1,6</sup>
Endothall Disodium Salt	Liquid	Striped bass	NR	SW	Finger-lings	96	710 <sup>g</sup> (135)	NR	NR	Wellborn, 1971
Endothall Disodium Salt	Liquid	Fathead minnow	NR	FW	NR	96	320-610 <sup>d</sup> (354)	NR	NR	Surber & Pickering, 1962 <sup>6</sup>
Endothall Disodium Salt	NR <sup>w</sup>	Fathead minnow	Static	FW	NR	96	120-125 <sup>g</sup> (98) <sup>y</sup>	NR	Y	Pennwalt, 1986 <sup>1</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Carp or Goldfish	NR	FW	NR	96	145-210 <sup>d</sup> (140)	NR	NR	Walker, 1963 <sup>3,6,8</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Bluntnose minnow	NR	FW	NR	96	110-120 <sup>d</sup> (92) <sup>y</sup>	NR	NR	Walker, 1963 <sup>6,3,8</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Red shiner	NR	FW	NR	96	105 <sup>d</sup> (84)	Y	NR	Walker, 1963 <sup>1,5,6,8</sup>

Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides:  
Volume 2 - Endothall, Section 4 – ENVIRONMENTAL EFFECTS

**Appendix 2: Acute Toxicity of Endothall to Fish (Continued)**

Test Substance	%AI or Form	Species	Test Type	Water	Size Class	Test Duration (hours)	LC50 (mg/L)	NOEC (mg/L)	Status	Reference
Endothall Disodium Salt	Solid <sup>w</sup>	Redfin shiner	NR	FW	NR	96	95 <sup>d</sup> (76)	NR	Y	Walker, 1963 <sup>1,5,6,8</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Black bullhead	NR	FW	NR	96	180-185 <sup>d</sup> (146) <sup>y</sup>	NR	Y	Walker, 1963 <sup>1,5,6,8</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Yellow bullhead	NR	FW	NR	96	170-175 <sup>n</sup> (138) <sup>y</sup>	NR	Y	Walker, 1963 <sup>1,5,6,8</sup>
Endothall Disodium Salt	Solid <sup>w</sup>	Brown bullhead	NR	FW	NR	96	170-175 <sup>n</sup> (138) <sup>y</sup>	NR	Y	Walker, 1963 <sup>1,5,6,8</sup>

<sup>a</sup> Not reported

<sup>b</sup> Assumed to be 53% a.i. and 23.36% a.e.

<sup>c</sup> FW = fresh water

<sup>d</sup> Mg/L in terms of a.i.; a.e. = a.i.X/% a.e./%a.i. = a.i.X0.441 Hydrothol® and also a.e.= a.i.X.a.e.= a.i.X.0.7096 for Aquathol®K

<sup>e</sup> a.e.= a.e.X0.802 for sodium endothall

<sup>f</sup> Mg/L in terms of a.e.

<sup>g</sup> 23.36% a.e.

<sup>h</sup> Mg/L in terms of product; a.e.= product X 0.2336 for Hydrothol®

<sup>i</sup> a.e. = product X0.286 for Aquathol®

<sup>j</sup> a.e. = product X 0.802 for sodium endothall

<sup>k</sup> Study meets core requirements for risk assessment

<sup>l</sup> 53% a.i

<sup>m</sup> Study does not meet core requirement for risk assessment but provides useful information supplemental to the core studies

<sup>n</sup> Mg/K in terms of a.e.; originally reported in terms of a.e.

<sup>o</sup> Geometric mean of range in milligrams per liter

<sup>p</sup> 77.9% a.e.

<sup>q</sup> Technical endothall acid approx 100% a.e.

<sup>r</sup> Concentration terms not specific but presumed to be in terms of product

<sup>s</sup> 88.5% a.e.

<sup>t</sup> 77.9% a.e.

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Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides:  
Volume 2 - Endothall, Section 4 – ENVIRONMENTAL EFFECTS

## Appendix 2: Acute Toxicity of Endothall to Fish (Continued)

- r 29.5% a.e. or 19.2% a.e.  
s 28.6% a.e./40.3% a.i.  
t 40.3% a.i./28.6% a.e.  
u assume to be 40.3% a.i./28.6% a.e.  
v 15.7% a.e. but not sure  
w Technical endothal Di-Na salt approx 100% a.i./80.2% a.e.  
x Unspecified liquid formulation  
y Geometric mean  $X = a.e.mw/a.i.mw$  where  $a.e.mw/a.i.mw = 0.802$
- 1 WDOE, 1992  
2 WDOE, 1989 Draft  
3 WDOE, 1980 Draft  
4 RA, 1994  
5 Pennwalt, 1986  
6 Atochem, 1993  
7 Pennwalt, No Date  
8 Corp, 1979; also see #3  
9 JMPR, 1997  
10 Ecotox Database, 1999  
11 Brian Database, 1999  
12 Atochem Risk assessment; Giddings, 1999  
13 Ebasco, 1993

**Appendix 3: Acute Toxicity of Endothal to Invertebrates**

Test Substance	%A.I. Or Form	Species	Test Type	Water	Age	Test Duration (hrs)	EC50 (ppm)	NOEC (ppm)	Status	Reference
Hydrothol® 191	23.5 <sup>a</sup>	<i>Daphnia magna</i>	Flow	FW	<24 hrs	48	0.32 <sup>b</sup> (0.075) <sup>c</sup>	0.077 <sup>b</sup> (0.018) <sup>c</sup>	C <sup>d</sup>	Putt, 1994
Hydrothol® 191	23.5 <sup>a</sup>	<i>Daphnia magna</i>	Static	FW	<24 hrs	48	0.36 <sup>b</sup> (0.085) <sup>c</sup>	0.10 <sup>b</sup> (0.024) <sup>c</sup>	C	UCE, 1977 Brian, 1999
Hydrothol® 191	NR	<i>Ceriodaphnia dubia</i>	NR	FW	NR	48	0.495 <sup>e</sup> (0.22) <sup>f</sup>	NR	NR	Keller, 1993
Hydrothol® 191	53 <sup>b</sup>	<i>Ceriodaphnia dubia</i>	Static	FW	NR	48	1.43 <sup>e</sup> (0.63) <sup>c</sup>	NR	NR	Keller, 1988
Hydrothol® 191	23.5 <sup>a</sup>	Mysid shrimp	Flow	SW	<24 hrs	96	2.4 <sup>b</sup> (0.56) <sup>c</sup>	0.74 <sup>b</sup> (0.18) <sup>c</sup>	C	Putt, 1994
Hydrothol® 191	23.5 <sup>a</sup>	Eastern oyster	Flow	SW	Juvenile	96	0.85 <sup>b</sup> (0.20)	0.066 <sup>b</sup> (0.016) <sup>c</sup> a.e.	C	Dionne, 1995
Hydrothol® 191	23.5 <sup>a</sup>	Bay mussel	Static	SW	NR	48	4.85 <sup>e</sup> (2.15) <sup>c</sup>	NR	NR <sup>h</sup>	Keller, 1993
Hydrothol® 191	23.2 <sup>a</sup>	Rotifer	Static	FW	NR	24	1.6 <sup>b</sup> (0.37) <sup>c</sup>	0.90 <sup>b</sup> (0.20) <sup>c</sup>	NR	Putt, 1996
Hydrothol® 191	23.2 <sup>a</sup>	Tentans midge	Flow	FW	NR	96	2.17 <sup>b</sup> (0.51) <sup>c</sup>	1.3 <sup>b</sup> (0.30) <sup>c</sup>	NR	Putt, 1996
Hydrothol® 191	23.2 <sup>a</sup>	<i>Gammarus fasciatus</i>	Flow	FW	NR	96	0.48 <sup>b</sup> (0.11) <sup>c</sup>	NR	Y <sup>i</sup>	Folmar, 1977 <sup>1</sup>
Hydrothol® 191	53 <sup>b</sup>	<i>Gammarus fasciatus</i>	NR	FW	Mature	96	0.51 <sup>e</sup> (0.22) <sup>c</sup>	NR	Y	Johnson & Finley, 1980

**Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish**

Test Substance	%A.I. Or Form	Species	Test Type	Water	Size Class	Test Duration (hrs)	EC50 (ppm)	NOEC (ppm)	Status	Reference
Hydrothol® 191	23.36 <sup>a</sup>	<i>Gammarus fasciatus</i>	Static	FW	NR	24	3.1 <sup>b</sup> (0.72) <sup>c</sup>	NR	NR	Sanders, 1969 <sup>10</sup>
Hydrothol® 191	23.36 <sup>a</sup>	<i>Gammarus fasciatus</i>	Static	FW	NR	48	2.1 <sup>b</sup> (0.49) <sup>c</sup>	NR	NR	Sanders, 1969 <sup>10</sup>
Hydrothol® 191	23.36 <sup>a</sup>	<i>Gammarus fasciatus</i>	Static	FW	NR	96	0.48 <sup>b</sup> (0.11) <sup>c</sup>	NR	NR	Sanders, 1969 <sup>10</sup>
Hydrothol® 191	23.36 <sup>a</sup>	<i>Gammarus fasciatus</i>	Static	FW	NR	24	2.0 <sup>b</sup> (0.47) <sup>c</sup>	NR	NR	Sanders, 1969 <sup>10</sup>
Hydrothol® 191	23.36 <sup>a</sup>	<i>Gammarus fasciatus</i>	Static	FW	NR	48	1.0 <sup>b</sup> (0.23) <sup>c</sup>	NR	NR	Sanders, 1969 <sup>10</sup>
Hydrothol® 191	23.36 <sup>a</sup>	<i>Gammarus fasciatus</i>	Static	FW	NR	96	0.50 <sup>b</sup> (0.12) <sup>c</sup>	NR	NR	Sanders, 1969 <sup>10</sup>
Hydrothol® 191	53 <sup>b</sup>	<i>Gammarus lacustris</i>	Static	FW	Mature	96	0.50 <sup>b</sup> (0.22) <sup>c</sup>	NR	C	Johnson & Finley, 1980
Hydrothol® 191	23.5 <sup>a</sup>	Mayfly	Flow	FW	NR	96	(0.12) <sup>f</sup>	NR	NR	Putt, 1996 in Giddings
Hydrothol® 191	23.2 <sup>a</sup>	<i>Hyaleta azteca</i>	Flow	FW	NR	96	0.75 <sup>b</sup> (0.17) <sup>c</sup>	0.12 <sup>b</sup> (0.027) <sup>c</sup>	NR	Putt, 1996
Hydrothol® 191	23.3	Variegated oligochaete	Flow	FW	NR	96	1.8 <sup>b</sup> (0.42) <sup>c</sup>	0.72 <sup>b</sup> (0.17) <sup>c</sup>	NR	Putt, 1996
Hydrothol® 191	23.2 <sup>a</sup>	Orconectes crayfish	Flow	FW	NR	96	6.7 <sup>b</sup> (1.6) <sup>c</sup>	2.0 <sup>b</sup> (0.46) <sup>c</sup>	NR	Dionne, 1996

Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish

Test Substance	%A.I. Or Form	Species	Test Type	Water	Age	Test Duration (hrs)	EC50 (ppm)	NOEC (ppm)	Status	Reference
Hydrothol®191	53 <sup>®</sup>	Grass shrimp	Static	SW	Mature	96	0.05 <sup>°</sup> (0.022) <sup>°</sup>	NR	C	Johnson & Finley, 1980
Hydrothol®191	53 <sup>®</sup>	Californian stonefly	Static	FW	YC2	48	3.25 <sup>b</sup> (1.4) <sup>°</sup>	NR	C	Johnson & Finley, 1980
Hydrothol®191	53 <sup>®</sup>	Fiddler crab	NR	SW	NR	96	14.1 <sup>°</sup> (6.2) <sup>f</sup>	NR	C	Giddings, 1999
Endothall Acid	91.21 a.e.mh.	<i>Daphnia magna</i>	Flow	FW	<24 hrs	48	92 <sup>f</sup> (92) <sup>f</sup>	24 <sup>f</sup> (24) <sup>f</sup>	C	McNamara, 1992
Endothall Acid	75-86 a.e.	<i>Daphnia magna</i>	Static	FW	<24 hrs	26	46 <sup>f</sup> (46) <sup>f</sup>	NR	C	ATR, 1966 Brian, 1999
Endothall Acid	77.9 a.e.	<i>Daphnia magna</i>	Flow	FW	1 <sup>st</sup> Instar	48	33 <sup>f</sup> (33) <sup>f</sup>	18 <sup>f</sup> (18) <sup>f</sup>	C	UCE, 1979 Brian, 1999
Endothall Acid	91.21 a.e.mh.	Mysid shrimp	Flow	SW	<24 hrs	26	39 <sup>f</sup> (39) <sup>f</sup>	4.7 <sup>f</sup> (4.7) <sup>f</sup>	C	Bettencourt, 1993
Endothall Acid	91.21 a.e.mh.	Eastern oyster	Flow	SW	Juvenile	96	43 <sup>f</sup> (43) <sup>f</sup>	16 <sup>f</sup> (16) <sup>f</sup>	C	Dionne, 1993
Endothall Acid	89.5a.i.	Bay mussel	Static	SW	Embryo	48	49 <sup>f</sup> (49) <sup>f</sup>	NR	S	EPA, 1986 Brian, 1999
Endothall Acid	FORM	Brown shrimp	Flow	SW	Juvenile	48	>1.0	NR	C	EPA, 1986 Brian, 1999
Endothall Acid	89.5a.i.	Grass shrimp	Static	SW	0.1g	96	85 <sup>f</sup> (85) <sup>f</sup>	32	C	UCE, 1980 Brian, 1999

Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish

Test Substance	%A.I. Or Form	Species	Type Test	Water	Age	Test Duration (hrs)	EC50 (ppm)	NOEC (ppm)	Status	Reference
Endothall Acid	89.5a.i.	Fiddler crab	Static	SW	2.3+g	96	130 <sup>f</sup> (130) <sup>f</sup>	NR	C	UCE, 1980 Brian, 1999
Aquathol®K	29.5 a.e	<i>Daphnia magna</i>	Flow	FW	<24 hrs	48	240 <sup>b</sup> (71) <sup>c</sup>	140 <sup>b</sup> (41) <sup>c</sup>	C	Putt, 1993
Aquathol®K	28.6 a.e	<i>Daphnia magna</i>	Static	FW	<24 hrs	48	319.5 <sup>b</sup> (91) <sup>c</sup>	100 <sup>b</sup> (29) <sup>c</sup>	S	UCE, 1979 Brian, 1999
Aquathol®K	29.5 a.e.	Mysid shrimp	Flow	SW	<24 hrs	96	260 <sup>b</sup> (79) <sup>c</sup>	49 <sup>b</sup> (15) <sup>c</sup>	C	Bettencourt, 1993
Aquathol®K	29.5 a.e.	Eastern oyster	Flow	SW	Juvenile	96	330 <sup>b</sup> (97) <sup>c</sup>	<150 <sup>b</sup> (<44) <sup>c</sup>	C	Dionne, 1993
Aquathol®K	19.2	Coegagrionid damselfly	Static	FW	Nymph	96	>100 <sup>f</sup> (>100) <sup>f</sup>	NR	NR	OSU, 1963 Brian, 1999
Aquathol®K	40.3	<i>Gammarus fasciatus</i>	Static	FW	Mature	96	313 <sup>e</sup> (222) <sup>c</sup>	NR	NR	Johnson & Finley, 1980
Aquathol® K	NR	<i>Gammarus lacustris</i>	Static	FW	Adult	96	500 <sup>e</sup> (354) <sup>c</sup>	NR	S	FWS, 1969 Brian, 1999
Aquathol®K	19.2	Libellulid dragonfly	Static	FW	Nymph	96	>100 <sup>f</sup> (>100) <sup>f</sup>	NR	NR	OSU, 1967 Brian, 1999
Aquathol®K	40.3	Fiddler crab	Static	FW	Adult	96	750 <sup>f</sup> (750) <sup>f</sup>	320 <sup>f</sup> (320) <sup>f</sup>	NR	UCE, 1977 Brian, 1999

a. 23.36% a.e.

b. mg/L in terms of product; a.e.= product X 0.2336 for Hydrothol®; a.e.= product X0.286 for Aquathol®; a.e.= product X 0.802 for sodium endothall

c. mg/L in terms of a.e.

d. Study meets core requirements for risk assessment

#### Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish

- e. mg/L in terms of a.i.; a.e =a.i.X/% a.e./%a.i.=a.i.X0.441 Hydrothol® and also a.e.=a.i.X.a.e.=a.i.X.0.7096 for Aquathol®K a.e.=a.e.X0.802 for sodium endothall
- f. mg/K in terms of a.e.; originally reported in terms of a.e.
- g. 77.9% a.e.
- h. Not reported
- i. Refers to whether these data are of sufficient quality to meet the requirements of the EPA guidelines for criteria derivation (Stephan, et al, 1985)

FW = Fresh water  
SW = Salt water

- 1 WDOE, 1992
- 2 WDOE, 1989 Draft
- 3 WDOE, 1980 Draft
- 4 RA, 1994
- 5 Pennwalt, 1986
- 6 Atochem, 1993
- 7 Pennwalt, No Date
- 8 Corp, 1979; also see #3
- 9 JMPR, 1997
- 10 Ecotox Database, 1999
- 11 Brian Database, 1999
- 12 Atochem Risk assessment; Giddings, 1999
- 13 Ebasco, 1993

**Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish**

Test Substance	%A.I. or Form	Species	Type	Water	Age	Time (Days)	LC50 (ppm)	NOEC (ppm)	MATC	LOEC	Status	Reference
Hydrothol® 191	23.5 <sup>a</sup>	Fathead minnow	Flow	FW	egg-fry	35	NR	0.120 <sup>c</sup> (0.028) <sup>d</sup>	0.170 <sup>c</sup> (0.040) <sup>d</sup>	0.240 <sup>c</sup> (0.056) <sup>d</sup>	C <sup>c</sup>	Bettencourt, 1994
Hydrothol® 191	53 <sup>f</sup>	Fathead minnow	NR Mort	FW	<24 hrs	7 15°C	0.233 <sup>g</sup> (0.103) <sup>d</sup>	0.132 <sup>g</sup> (0.056) <sup>d</sup>	0.186 <sup>g</sup> (0.082) <sup>d</sup>	265 (0.117) <sup>d</sup>	NR	Keller, 1988
Hydrothol® 191	53 <sup>f</sup>	Fathead minnow	NR Mort	FW	<24 hrs	7 25°C	0.304 <sup>g</sup> (0.134) <sup>d</sup>	0.200 <sup>g</sup> (0.088) <sup>d</sup>	0.230 <sup>g</sup> (0.101)	0.265 <sup>g</sup> (0.116)	NR	Keller, 1988
Hydrothol® 191	53 <sup>f</sup>	Fathead Minnow	NR Growth	FW	<24 hrs	7 25°C	NR	0.050 <sup>g</sup> (0.022) <sup>d</sup>	0.081 <sup>g</sup> (0.035) <sup>d</sup>	132 <sup>g</sup> (0.058) <sup>d</sup>	NR	Keller, 1988
Endothall Acid	91.21 <sup>h</sup>	Fathead minnow	Flow	FW	Egg-fry	35	NR	13 <sup>i</sup> (13) <sup>j</sup>	19 <sup>i</sup> (19) <sup>j</sup>	27 <sup>i</sup> (27)	C	Bettencourt, 1994
Aquathol® K	40.3 <sup>j</sup>	Rainbow trout	Flow	FW	Egg-fry	NR <sup>b</sup>	NR	<12.5 <sup>g</sup> (<7.2) <sup>d</sup>	12.5 <sup>g</sup> (7.2)	12.5 <sup>g</sup> (7.2)	S <sup>k</sup>	FWS, 1976 Brian, 1999
Aquathol® K	Liquid	Chinook salmon	NR	FW	Fry	14	88 <sup>g</sup> (62) <sup>d</sup>	NR	NR	NR	NR	Ligouri et al. 1984
Aquathol® K	40.3 <sup>j</sup>	Walleye	Static	FW	8-10-day	96	16 <sup>g</sup> (11) <sup>d</sup>	5.7 <sup>g</sup> (4.0) <sup>d</sup>	7.9 <sup>g</sup> (5.6) <sup>d</sup>	11 <sup>g</sup> (7.8) <sup>d</sup>	NR	Paul et al., 1994
Aquathol® K	40.3 <sup>j</sup>	Walleye	Static	FW	41-43 day	96	54 <sup>g</sup> (38) <sup>d</sup>	23 <sup>g</sup> (16) <sup>d</sup>	32 <sup>g</sup> (23)	45 <sup>g</sup> (32)	NR	Paul et al., 1994
Aquathol® K	40.3 <sup>j</sup>	Smallmouth bass	Static	FW	<1 day	96	47 <sup>g</sup> (33) <sup>d</sup>	23 <sup>g</sup> (16) <sup>d</sup>	32 <sup>g</sup> (22) <sup>d</sup>	45 <sup>g</sup> (32)	NR	Paul et al., 1994

**Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish**

Test Substance	%A.I. or Form	Species	Type	Water	Age	Time (Days)	LC50 (ppm)	NOEC (ppm)	MATC	LOEC	Status	Reference
Aquathol® K	40.3 <sup>j</sup>	Largemouth bass	Static	FW	9-13 days post-hatch	96	130 <sup>g</sup> (92) <sup>d</sup>	50 <sup>g</sup> (35) <sup>d</sup>	71 <sup>g</sup> (50)	100 <sup>g</sup> (71)	NR	Paul et al., 1994
Disodium Endothall	NR	Rainbow trout	NR	FW	egg-fry	NR	NR	6.2 <sup>g</sup> (5) <sup>d</sup>	NR	NR	NR	Pennwalt, 1986 <sup>1</sup>
Disodium Endothall	NR	Bluegill sunfish	Static	FW	NR	21	NR	100 <sup>g</sup> (80) <sup>d</sup>	NR	NR	NR	Folmar, 1977 <sup>1</sup>
Disodium Endothall	Liquid	Bluegill sunfish	Static	FW	Fry	12	>100 <sup>g</sup> (>80) <sup>d</sup>	>100 <sup>g</sup> (>80) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	granular	Bluegill sunfish	Static	FW	Fry	12	>50 <sup>g</sup> (>40) <sup>d</sup>	>50 <sup>g</sup> (>40) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	Liquid	Bluegill sunfish	Static	FW	Fry	8	>25 <sup>g</sup> (>20) <sup>d</sup>	>25 <sup>g</sup> (>20) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	granular	Bluegill sunfish	Static	FW	Fry	8	>10 <sup>g</sup> (>8) <sup>d</sup>	>10 <sup>g</sup> (>8) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	NR	Green sunfish	Static	FW	Fry	NR	NR	25 <sup>g</sup> (20) <sup>d</sup>	NR	NR	Y	Pennwalt, 1986 <sup>1</sup>
Disodium Endothall	Liquid	Green sunfish	Static	FW	Fry	8	>25 <sup>g</sup> (>20) <sup>d</sup>	>25 <sup>g</sup> (>20) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	granular	Green sunfish	Static	FW	Fry	8	>10 <sup>g</sup> (>8) <sup>d</sup>	>10 <sup>g</sup> (>8) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	Liquid	Smallmouth bass	Static	FW	Fry	8	>25 <sup>g</sup> (>20) <sup>d</sup>	>25 <sup>g</sup> (>20) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	Granular	Smallmouth bass	Static	FW	Fry	8	>10 <sup>g</sup> (>8) <sup>d</sup>	>10 <sup>g</sup> (>8) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967 <sup>6</sup>

**Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish**

Test Substance	%A.I. or Form	Species	Type	Water	Age	Time (Days)	LC50 (ppm)	NOEC (ppm)	MATC	LOEC	Status	Reference
Disodium Endothall	NR	Largemouth bass	Static	FW	NR	21	NR	10 <sup>g</sup> (8) <sup>d</sup>	NR	NR	Y	Folmar, 1977 <sup>1</sup>
Disodium Endothall	NR	Bluntnose minnow	Static	FW	NR	21	NR	40 <sup>g</sup> (32) <sup>d</sup>	NR	NR	Y	Folmar, 1977 <sup>1</sup>
Disodium Endothall	NR	Redfin shiner	Static	FW	NR	21	NR	40 <sup>g</sup> (32) <sup>d</sup>	NR	NR	Y	Folmar, 1977 <sup>1</sup>
Disodium Endothall	NR	Red shiner	Static	FW	NR	21	NR	40 <sup>g</sup> (32) <sup>d</sup>	NR	NR	Y	Folmar, 1977 <sup>1</sup>
Disodium Endothall	Liquid	Lake chubsucker	NR	FW	Fry	8	>25 <sup>g</sup> (>20) <sup>d</sup>	>25 <sup>g</sup> (>20) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	Granular	Lake chubsucker	NR	FW	Fry	8	>10 <sup>g</sup> (>8) <sup>d</sup>	>10 <sup>g</sup> (>8) <sup>d</sup>	NR	NR	NR	Hiltbran, 1967
Disodium Endothall	NR	Stoneroller	NR	FW	Egg-fry	8	NR	>50 <sup>g</sup> (>40) <sup>i</sup>	NR	NR	NR	Hiltbran, 1967
Endothall Acid	91.21 <sup>h</sup>	Fathead minnow	Flow	FW	Egg-fry	35	NR	13 <sup>i</sup> (13) <sup>i</sup>	19 <sup>i</sup> (19) <sup>i</sup>	27 <sup>i</sup> (27)	C	Bettencourt, 1994

<sup>a.</sup> 23.36% a.e.

<sup>b.</sup> Not reported

<sup>c.</sup> mg/L in terms of product; a.e.=product X 0.2336 for Hydrothol®; a.e.=product X0.286 for Aquathol®; a.e.=product X 0.802 for sodium endothall

<sup>d.</sup> mg/L in terms of a.e.

<sup>e.</sup> Study meets core requirements for risk assessment

<sup>f.</sup> 53% a.i.

<sup>g.</sup> mg/L in terms of a.i.; a.e.=a.i.X/% a.e./%a.i.=a.i.X0.441 Hydrothol® and also a.e.=a.i.X.0.7096 for Aquathol®K  
a.e.=a.e.X0.802 for sodium endothall

<sup>h.</sup> 88.5% a.e.

<sup>i.</sup> mg/K in terms of a.e.; originally reported in terms of a.e.

#### Appendix 4: Chronic and Early Life Stage Toxicity of Endothall to Fish

- j. 40.3% a.i./ 28.6% a.e.
- k. Supplemental
- l. Geometric mean of range in milligrams per liter

FW=Fresh water  
SW=Salt water

- 14 WDOE, 1992
- 15 WDOE, 1989 Draft
- 16 WDOE, 1980 Draft
- 17 RA, 1994
- 18 Pennwalt, 1986
- 19 Atochem, 1993
- 20 Pennwalt, No Date
- 21 Corp, 1979; also see #3
- 22 JMPR, 1997
- 23 Ecotox Database, 1999
- 24 Brian Database, 1999
- 25 Atochem Risk assessment; Giddings, 1999
- 26 Ebasco, 1993

**Appendix 5: Chronic Toxicity of Endothall to Invertebrates**

Test Substance	%A.I. or Form	Species	Test Type	Water	Age	Test Duration (Days)	LC50 (ppm)	NOEC (ppm)	MATC (ppm)	LOEC (ppm)	Status	Reference
Hydrothol®191	23.5 <sup>a</sup>	<i>Daphnia magna</i>	Flow	FW	<24 hrs	21	NR <sup>b</sup>	0.068 <sup>c</sup> (0.016) <sup>d</sup>	0.098 <sup>c</sup> (0.023) <sup>d</sup>	0.140 <sup>c</sup> (0.033) <sup>d</sup>	NR	Putt 1994c
Hydrothol®191	53 <sup>d</sup> 23.5 <sup>a</sup>	<i>Ceriodaphnia dubia</i>	Flow	FW	<24 hrs	7 25°C	0.14-0.19 <sup>f</sup> (0.073) <sup>d,g</sup>	<0.011 <sup>f</sup> (<0.005) <sup>d</sup>	<0.015 <sup>f</sup> (<0.007) <sup>d</sup>	0.025 <sup>f</sup> (0.011) <sup>d</sup>	NR	Keller, 1988
Endothall Acid	23.5 <sup>a</sup>	<i>Daphnia magna</i>	Flow	FW	<24 hrs	21	24 <sup>h</sup> (24) <sup>d</sup>	5 <sup>h</sup> (5) <sup>d</sup>	6.7 <sup>h</sup> (6.7) <sup>d</sup>	8.9 <sup>u</sup> (8.9) <sup>d</sup>	NR	Putt, 1993b

a. 23.36% a.e.

b. Not reported

c. mg/L in terms of product; a.e.=product X 0.2336 for Hydrothol®; a.e.=product X0.286 for Aquathol®; a.e.=product X 0.802 for sodium endothall

d. mg/L in terms of a.e.

e. 53% a.i.

f. mg/L in terms of a.i.; a.e =a.i.X/% a.e./%a.i.=a.i.X0.441 Hydrothol® and also a.e.=a.i.X.a.e.=a.i.X.0.7096 for Aquathol®K  
a.e.=a.e.X0.802 for sodium endothall

g. Geometric mean of range in milligrams per liter

h. mg/K in terms of a.e.; originally reported in terms of a.e.

FW=Fresh water

**Appendix 6: Sensitive, Threatened and Endangered Species found in Washington State**

<b>Status</b>	<b>Region</b>	<b>Affected Counties within Region</b>	<b>Common Name</b>	<b>Species</b>
Endangered	Upper Columbia River	All counties	Spring-run Chinook	<i>Oncorhynchus tshawytscha</i>
Endangered	Upper Columbia River	All counties	Steelhead trout	<i>Oncorhynchus mykiss</i>
Endangered	Snake River	All counties	Sockeye salmon	<i>Oncorhynchus nerka</i>
Threatened	Puget Sound	All Counties	Chinook salmon	<i>Oncorhynchus tshawytscha</i>
Threatened	Puget Sound	Clallam, Jefferson, Mason, Kitsap	Hood Canal Summer Chum salmon	<i>Oncorhynchus kisutch</i>
Threatened	Puget Sound	All , excluding Kitsap, San Juan, Island	Bull trout	<i>Oncorhynchus mykiss</i>
Threatened	Washington Coastal	Callam	Lake Ozette Sockeye salmon	<i>Oncorhynchus nerka</i>
Threatened	Washington Coastal	All, excluding Pacific	Bull trout	<i>Salvelinus confluentus</i>
Threatened	Lower Columbia River	All counties	Spring-run Chinook salmon	<i>Oncorhynchus tshawytscha</i>
Threatened	Lower Columbia River	All counties	Chum salmon	<i>Oncorhynchus keta</i>
Threatened	Lower Columbia River	All counties	Steelhead trout	<i>Oncorhynchus mykiss</i>
Threatened	Lower Columbia River	All counties	Bull trout	<i>Salvelinus confluentus</i>
Threatened	Upper Columbia River	All counties	Bull trout	<i>Salvelinus confluentus</i>
Threatened	Middle Columbia River	All counties	Bull trout	<i>Salvelinus confluentus</i>

**Appendix 6: Sensitive, Threatened and Endangered Species found in Washington State (Continued)**

<b>Status</b>	<b>Region</b>	<b>Affected Counties within Region</b>	<b>Common Name</b>	<b>Species</b>
Threatened	Middle Columbia River	All counties	Steelhead trout	<i>Oncorhynchus mykiss</i>
Threatened	Middle Columbia River	All counties	Bull trout	<i>Salvelinus confluentus</i>
Threatened	Snake River	All counties	Spring/Summer-run Chinook salmon	<i>Oncorhynchus tshawytscha</i>
Threatened	Snake River	All counties	Fall-run Chinook salmon	<i>Oncorhynchus tshawytscha</i>
Threatened	Snake River	All counties	Steelhead trout	<i>Oncorhynchus mykiss</i>
Threatened	Snake River	All counties	Bull trout	<i>Salvelinus confluentus</i>
Threatened	Northeast Washington	All counties	Bull trout	<i>Salvelinus confluentus</i>
Proposed Threatened	Washington Coastal	Grays Harbor, Pacific, Lewis	Coastal cutthroat trout	<i>Oncorhynchus clarki</i>
Proposed as Threatened	Lower Columbia River	All counties	Coastal cutthroat trout	<i>Oncorhynchus clarki</i>
Potentially Threatened	Upper Columbia River	Chelan, Okanogan	Westslope cutthroat trout	<i>Oncorhynchus clarki</i>
Potentially Threatened	Middle Columbia River	Kittitas, Yakima, Klickitat	Westslope cutthroat trout	<i>Oncorhynchus clarki</i>
Potentially Threatened	Northeast Washington	All counties	Westslope cutthroat trout	<i>Oncorhynchus clarki</i>
Candidate	Puget Sound	All counties	Coho salmon	<i>Oncorhynchus kisutch</i>
Candidate	Washington Coastal	Grays Harbor, Pacific, Lewis, Thurston	Southwest Washington Coho salmon	<i>Oncorhynchus kisutch</i>

**Appendix 6: Sensitive, Threatened and Endangered Species found in Washington State (Continued)**

<b>Status</b>	<b>Region</b>	<b>Affected Counties within Region</b>	<b>Common Name</b>	<b>Species</b>
Candidate	Lower Columbia River	All counties	Coho salmon	<i>Oncorhynchus kisutch</i>
Candidate	I <sup>1</sup>	All counties	Pacific Cod	<i>Gadua macrocephalus</i>
Candidate	I	All counties	Walleye Pollock	<i>Sebastes</i> sp.
Candidate	I	All counties	Pacific Hake	<i>Merluccius productus</i>
Candidate	I	All counties	Brown Rockfish	<i>Sebastes</i> sp.
Candidate	I	All counties	Copper Rockfish	<i>Sebastes</i> sp.
Candidate	I	All counties	Quillback Rockfish	<i>Sebastes</i> sp.
Concern	I	All counties	Cherry point herring	Family Clupeidae
Concern	I	All counties	Discovery Bay Herring	Family Clupeidae
Concern	State Wide	All counties	River Lamprey	
Concern	State Wide	All counties	Van Dyke's Salamander	<i>Plethodon vandykei</i>
Concern	State Wide	All counties	Columbia torrent Salamander	<i>Rhyacotition olympicus</i>
Concern	State Wide	All counties	Columbia spotted frog	<i>Rana lutiventris</i>
Concern	State Wide	All counties	Great Columbia River Spire Snail	
Concern	State Wide	All counties	Newcomb's Littorine Snail	
Concern	State Wide	All counties	California floater	<i>Adonata californiensis</i>
Concern	State Wide	All counties	Northern Abalone	<i>Haliotis</i> sp.
Concern	State Wide	All counties	Olympia Oyster	unknown
State Endangered	State Wide	All Counties	Oregon spotted frog	<i>Rana pretiosa</i>

**Appendix 6: Sensitive, Threatened and Endangered Species found in Washington State (Continued)**

<b>Status</b>	<b>Region</b>	<b>Affected Counties within Region</b>	<b>Common Name</b>	<b>Species</b>
State Sensitive	State Wide	All counties	Pygmy whitefish	<i>Prosopium coulteri</i>
State Sensitive	State Wide	All counties	Margined sculpin	<i>Cottus marginatus</i>
State Sensitive	State Wide	All counties	Larch Mountain Salamander	<i>Plethodon larselli</i>
State Candidate	State Wide	All counties	Olympic mudminnow	
State Candidate	State Wide	All counties	Mountain sucker	<i>Catostomus platyrhynchus</i>
State Candidate	State Wide	All counties	Lake chub	<i>Coesius plumbeus</i>
State Candidate	State Wide	All counties	Leopard dace	<i>Rhinichthys falcatus</i>
State Candidate	State Wide	All counties	Umatilla dace	<i>Rhinichthys umatilla</i>
State Candidate	State Wide	All counties	Eulachon (Columbia River Smelt)	<i>Thaleichthys pacificus</i>
State Candidate	I	All counties	Black rockfish	<i>Sebastes</i> sp.
State Candidate	I	All counties	Tiger Rockfish	<i>Sebastes</i> sp.
State Candidate	I	All counties	Bocaccio rockfish	<i>Sebastes paucispinis</i>
State Candidate	I	All counties	Canary rockfish	<i>Sebastes</i> sp.
State Candidate	I	All counties	Yellowtail rockfish	<i>Sebastes</i> sp.
State Candidate	I	All counties	Greenstriped rockfish	<i>Sebastes</i> sp.
State Candidate	I	All counties	Widow rockfish	<i>Sebastes</i> sp.
State Candidate	I	All counties	China rockfish	<i>Sebastes</i> sp.
State Candidate	State Wide	All counties	Dunn's Salamander	<i>Plethodon dunnii</i>
State Candidate	State Wide	All counties	Cascade torrent salamander	<i>Rhyacotriton cascadae</i>
State Candidate Under Review	State Wide	All counties	Northern Leopard Frog	<i>Rana pipiens</i>
State Candidate	State Wide	All counties	Giant Columbia River Limpet	

<sup>1</sup> Within Puget Sound, the San Juan Islands, and the Strait of Juan de Fuca east of the Seiku River

# Endothall

## Volume 2, Section 5

### HUMAN HEALTH EFFECTS

**47 Pages**

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## **5.0 HUMAN HEALTH EFFECTS**

### **5.1 OBJECTIVE**

The Washington State Department of Ecology (WDOE) contracted with Compliance Services International (CSI) to prepare a document concerning potential human health impacts from aquatic applications of the herbicide endothall. This herbicide is currently being used to control noxious aquatic plants in the State of Washington.

The purpose of this section is to provide the most recent health information to the WDOE concerning the toxicology of endothall and potential health risks to the public associated with endothall aquatic weed control. It is also the intent of this section to assist the agencies in making decisions regarding continued endothall uses and establishing various swimming alerts and waiting periods for water use following herbicide application to bodies of water.

The objectives of this section are to: 1) provide a review of the available endothall toxicology information, 2) determine the degree and types of potential exposures that may be encountered during various time periods following endothall aquatic application, and 3) present a series of risk assessments of the different types of exposures to aquatic applied endothall and determine any need or recommendations for mitigation of exposure to ensure public health.

### **5.2 APPROACH**

#### **5.2.1 Information Compilation**

Information concerning endothall toxicology and health effects were obtained from computerized searches of the scientific and medical literature, EPA office of Pesticide Programs, WDOE and the herbicide registrant Elf Atochem North America, Inc.

#### **5.2.2 Risk Assessment Procedure**

##### **5.2.2.1 Endothall Toxicology Information and Assessment**

Section 1 of this document discusses the registration and regulation of pesticides. Part of registering any pesticide with the US Environmental Protection Agency (US EPA) is for the potential registrant to conduct a series of toxicology studies outlined in the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). The series of toxicology studies include acute (one exposure), subchronic (multiple exposures, e.g. weeks or months) and chronic exposure to the chemical over the entire lifetime of the animal. These types of studies have been conducted on technical endothall.

In addition, once the technical chemical or active ingredient has been registered for specific uses with the EPA, various product formulations of the active ingredient are prepared, tested for efficacy and acute toxicology. The results of the acute toxicology studies, see Table 1 (oral, dermal, inhalation, skin and eye irritation and skin sensitization studies), are used to evaluate the health hazards that may be associated with overexposure to the applicator, bystanders and others that may contact treated areas following application of the pesticide. Once the hazards have been determined by the results of the tests, the specific product label

warnings are then determined by FIFRA guidelines and serve to alert the consumer as to the associated product health hazards and precautions to take to prevent overexposure.

The endothall product labels bear the Danger signal word and precautionary statements warning the user that, depending upon the degree and duration of overexposure to the concentrated product, severe or irreversible eye effects may result and that ingestion and dermal contact with the undiluted formulation may be fatal.

Very little human exposure or toxicology data and information exists concerning overexposure to endothall. There are no epidemiology or worker exposure studies. Therefore, the basis for determining potential human health effects is from reviewing the results of the animal toxicology studies and extrapolating the findings to estimated human exposure situations.

As described in Section 1 of this document, animal toxicology studies are typically designed to include low, mid and high dose test groups. The objective of having at least 3 dose groups is to determine the health effects observed and measured by the various degrees of exposure. The high dose group receives an amount of test material designed to overwhelm the body defense mechanisms, e.g. in suicide attempts, while the low dose is intended to not cause any observable or quantitated adverse health effects. The low dose or dose level that does not demonstrate toxicological effects is termed the no observable adverse effect (NOAEL or NOEL) dose or level. The NOAEL is used in risk assessment calculations and sometimes is adjusted with an uncertainty factor(s) (UF) to compensate for extrapolation of calculated "safe" dose levels to humans from various animals species and toxicology endpoints, e.g. fetal developmental effects, cancer, etc.

The endothall toxicology investigations are discussed in the following sections and the NOAELs and toxicology endpoints listed in Table 4.

#### **5.2.2.2 Exposure Assessment**

The exposure assessment involves determination of populations that may be exposed to endothall, estimating degrees of exposure and doses likely to result from the various uses of the herbicide products following aquatic weed control. The exposure parameters evaluated in this section are listed in Tables 3 and 5 and include governmental health advisories and exposure parameters.

Exposure assessment for herbicidal use of endothall in this section, assumed that the average (3 ppm) and highest (5 ppm) use-rates for aquatic weed control served as the water concentrations of the chemical. Based on the assumed use-rates, exposure calculations were conducted for swimmers and bystanders or non-swimmers as to their daily exposure to endothall. Swimmers were expected to spend anywhere from 0.5 to 3 hours swimming in endothall treated water each day. Their routes of exposure include incidental ingestion of treated water and sediments, dermal contact with water and sediments and inhalation exposure of any volatilized endothall. The swimmers were divided into three groups consisting of 6 (22 kilogram weight) and 10 (35 kg) year olds and adults (70 kg).

The non-swimmers exposure included groups drinking potable water containing the maximum contaminant level (MCL) of 100 ug endothall/liter and those drinking endothall treated surface water on a daily basis. Also, the exposure from eating fish taken from endothall treated water was calculated. Since endothall is not intended to be used on food

crops and does not bioconcentrate in living organisms, other potential dietary sources of endothall exposure were not conducted.

Tables 16 and 17 present the combined sources of endothall exposure that includes swimmers and non-swimmers. The main factor in the exposure to endothall following aquatic application for weed control, concerned the incidental ingestion of water by the swimmer and ingestion of daily drinking water from endothall treated surface water.

### 5.2.2.3 Risk Characterization

The potential risk of non-carcinogenic effects is usually evaluated by comparing an environmental dose to a reference or “safe” dose. In the risk assessments for various endothall aquatic exposure doses the margin of safety (MOS) and reference dose (RfD) approaches were used.

The MOS is used to evaluate acute exposures. In this approach the lowest NOAEL or NOEL from the animal toxicology studies for specific endpoints, e.g. systemic toxicity, reproduction or developmental, were compared to the calculated human endothall doses. This method allows an evaluation and determination of a “safe” dose specific to each human route of exposure. Thus, the MOS is a ratio of the lowest NOAEL dose to the calculated dose and is meant to be an indicator of potential risk. The standard MOS is 100, meaning that MOSs greater than 100 represent degrees of negligible risk, while values below 100 signal an increased risk of the toxic endpoint effects (Shipp, 1986). MOS findings are included in calculations in Tables 6-17.

The reference dose or RfD represents a lifetime “safe” dose for protection against threshold (non-carcinogenic) health effects. The RfD is considered an exposure level below which adverse health effects are unlikely to occur for even sensitive human populations. Under the RfD approach UFs may be applied to the lowest NOAEL dose reported in the animal toxicology studies. An UF of 10 is generally used to estimate a “safe” human exposure level from experimental studies when there is no indication of carcinogenicity and valid human studies are available. A more conservative UF of 100 is supplied when there are few or no valid human studies available but here are valid long-term animal studies. In the case of endothall since no human exposure studies have been conducted the 100 UF was applied.

In the calculations in Tables 6-17 the percentage of the daily RfD is presented for the various types of exposure doses. Thus, percentages below 100% of the RfD are considered negligible health risks while those greater than 100% serve as indicators that a potential health risk may exist at the specific exposure dose. Tables 16 and 17 include combined types of exposures and total daily endothall doses with their accompanying MOS and RfD risk assessments

## 5.3 CHEMICAL FORMULATIONS

The endothall products, Aquathol® and Hydrothol® contain the dipotassium and mono(N,N-dimethylalkylamine) salt, respectively. The Aquathol® liquid formulations contain either 40.3 or 63% dipotassium salt or 28.6 or 44.7% endothall acid equivalent, respectively. The granular Aquathol® product contains 10.1% dipotassium salt or 7.2% endothall acid equivalent. Similarly, the Hydrothol® 191 granular and liquid formulations contain 11.2 and 53% amine salt or 5 and 23.56% endothall acid equivalents, respectively. The average and high use-rates for both types of endothall products are approximately 3.0 and 5.0 ppm. These

are the endothall water concentrations used to conduct the exposure calculations in Tables 6-17.

#### **5.4 EXPOSURE ASSESSMENT**

Exposure assessments were conducted on three populations that included children and adults. The children were ages 6 and 10 weighing 22 and 35 kg, respectively. The population groups were evaluated according to their time spent swimming in endothall treated water containing either 3.0 or 5.0 ppm. Routes and types of exposure included incidental ingestion of water, skin contact with water and sediment and inhalation of any endothall vapor. In addition, the population groups were also evaluated as to their endothall exposure received from drinking potable water and treated surface water and daily consumption of fish taken from treated water. The exposure assessments appear in Tables 6-17.

#### **5.5 EXPOSED POPULATION**

The exposed population in this section refers to the general public and does not include people who may be occupationally exposed during mixing, loading or applying endothall to bodies of water. The exposed populations used in the exposure assessment are described in subsection 5.4 above.

#### **5.6 POTENTIAL ROUTES OF EXPOSURE**

The potential routes of exposure to the exposed population groups included primarily ingestion of endothall treated water either during swimming or through daily use of potable or treated water as a drinking water source. Other potential routes of exposure included dermal contact and inhalation of treated water and sediments and eating fish taken from the treated water.

The calculated doses received by the exposed population groups are discussed in subsection 5.11 Exposure and Risk Assessments and presented in Tables 6-17.

#### **5.7 TOXICITY ASSESSMENT**

The animal toxicology information concerning endothall is discussed in the following subsections and consists of a review of the acute, subchronic and chronic testing. An overview of the toxicology information indicates that the chemical is not considered to be a carcinogen or to cause adverse reproductive effects or birth defects (teratology). Endothall is considered to be a moderate systemically toxic chemical based on the findings in the acute and subchronic toxicology studies. However, the main adverse health effect appears to be associated with endothall's irritation potential. Results of the concentrated endothall technical and product acute eye irritation studies place the chemical in FIFRA Toxicity Category I as causing severe irreversible eye damage. Irritation effects to the gastrointestinal tract were also noted in some animals in the mid and high dose test groups in the endothall subchronic and chronic oral dosing and feeding studies. Label directed use of the endothall products for aquatic weed control, and dilution and degradation of the chemical following application, reduces the potential for overexposure.

## **5.8 PHARMACOKINETICS**

### **5.8.1 Oral**

A review of the pharmacokinetics of endothall indicates that the chemical is poorly absorbed through the oral and dermal routes of exposure. Investigations by Soo et al, 1967, revealed that approximately 5-10% of a rat oral dose was eventually absorbed from the gut and rapidly excreted by the kidneys. The investigators found that the rate of excretion of 14-C labeled endothall was 95 and 99% complete by 48 and 72 hours, respectively. This finding demonstrates that endothall is not accumulated in the fat or other body tissues.

Hallifax, 1990, also determined that endothall was poorly absorbed from the gut of the rat. He found that approximately, 89-98% of the oral dose of endothall remained in the gut and was excreted in the feces unchanged. The absorbed endothall was distributed throughout the body and removed by the kidneys.

Soo et al, 1967, also found that nearly 82% of the absorbed oral dose of endothall in a rat study, entered the system within the first 72 hours. Detectable levels of the absorbed chemical were found 1 hour following dosing, most in the liver and kidneys, while lesser amounts were detected in the heart, lungs, spleen and brain. No endothall was detected in the fat. Essentially, absorbed endothall does not undergo metabolism and is excreted unchanged in the urine, while a small portion may be exhaled as CO<sub>2</sub> through the lung. Approximately 90% of the endothall dose remaining in the gut was excreted in the feces, primarily as the parent molecule.

Findings from the Halifax, 1990, rat pharmacokinetic study also revealed that both the absorbed and unabsorbed chemical were not metabolized, but excreted in the urine and feces regardless of whether 14-C endothall was administered orally in a single dose or given subchronically for up to 15 days. Bile was found to be a very minor excretory route for endothall.

The half-life of endothall was dependent upon the dose. Single oral doses of 0.9 and 4.5 mg/kg demonstrated peak blood concentrations after 0.5 and 1 hour, respectively. The endothall half-lives of 1.8 and 2.5 hours, approximately 14 hours following dosing, were observed for the low and high doses, respectively (Hallifax, 1990).

### **5.8.2 Dermal**

Johnson et al, 1990, determined that the penetration rate for 14C endothall, applied to the skin of rats, was approximately 7% over 24 hours. The investigators applied 0.15, 0.75 and 1.5% endothall concentrations to the skin and found that total absorption values were similar, regardless of the exposure period, for each of the treatment groups. At the end of the investigation it was determined that from 20-42% of the applied dermal dose could not be washed from the skin.

## **5.9 SYNERGISM WITH OTHER PESTICIDES**

A review of the scientific and medical literature indicates that there have been no investigations conducted to determine the potential of endothall technical or its products to interact synergistically with other chemicals.

## 5.10 ACUTE TOXICITY

Concentrated (undiluted) endothall technical and its various aquatic herbicide formulations are highly irritating to biological tissues. The irritation of the gastric and intestinal mucosa has been described in acute, subchronic and chronic oral toxicology investigations. Depending upon the concentration of endothall in the product formulation tested, results of the acute oral toxicology studies class them in EPA Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) oral Toxicity Category II [Category I is the most toxic or irritating; Category IV is the least toxic or irritating]. The results of the endothall technical and product acute toxicology studies and the FIFRA Toxicity Categories are listed on Table 1.

It is important to understand that the results of the acute toxicology studies reflect the health effects of the concentrate or undiluted chemical or product. Once an endothall-containing product is applied to a body of water according to its label directions for aquatic weed control, the massive dilution factor of the water significantly reduces the chemical's toxicity and irritation potential.

Human overexposure to concentrated or undiluted endothall products during application can result in accidental spilling or splashing the chemical on the skin, in the eyes and mouth. Regardless of the route of overexposure, i.e. oral, dermal, inhalation or eye, the first aid procedures outlined on the endothall product label should be followed immediately and where indicated the overexposed person should be examined by a physician.

Also, depending upon the spray equipment settings, the applicator may be overexposed to the endothall spray mist during application of the product over the surface of the water. Overexposure to the concentrated endothall spray mist can result in irritation of the upper respiratory tract and possible systemic toxicity. However, spray application of endothall by either boat or air plane, involves equipment that forms large spray droplets that can be easily directed to the targeted aquatic treatment area. It is counter productive to apply smaller size spray droplets that would minimize the amount of herbicide contacting the designated treatment area and may result in formation of spray drift and the potential for endothall overexposure to the applicator or area bystanders.

### 5.10.1 Oral Toxicity

A review of the rat acute oral toxicity investigations indicates that technical endothall or endothall acid is highly toxic as evidenced by a LD50 = ~45 mg/kg. The endothall acid containing products are Aqualthol® (contains 28.6% endothall acid equivalent (eae)) and Hydrothol® 191 (23.4% eae). The formulated products of Aquathol® and Hydrothol® 191 are somewhat less toxic as evidenced by rat acute LD50s of approximately 233 and 100 mg/kg, respectively.

The findings from the acute toxicology investigations indicate that endothall is a severe irritant of the stomach and intestinal tract. Reported signs of toxicity observed in the studies included decreased activity, diarrhea, abnormal gait and stance, dyspnea, piloerection, decreased muscle tone, prostration and death. Findings from gross pathological examination of the treated animals revealed distended fluid filled stomachs and intestines, mottled kidneys and lungs, pale lungs and dark livers. The LD50 for endothall technical was approximately 45 mg/kg, placing it in EPA FIFRA Toxicity Category I regarding acute oral toxicity (Mallory, 1991a,b,c; Mallory, 1993; Mallory, 1994).

### 5.10.2 Dermal Toxicity

Results of the rabbit acute dermal toxicity studies primarily demonstrated that 24-hour application of the test material to the skin produced severe irritation and necrosis in most cases. Signs of systemic involvement included decreased activity and muscle tone, diarrhea, decreased body weights and death. Deaths occurred in rabbits treated with Hydrothol® 191. Findings from a gross pathological examination of the Hydrothol® dosed animals revealed distended and discolored intestines, pale and/or mottled kidneys, lungs and liver. The acute dermal LD50 for endothall acid and Aquathol® K is >2,000 mg/kg. Hydrothol® 191 demonstrated a greater degree of acute dermal toxicity as evidenced by a LD50 of 480 mg/kg (Mallory, 1991a,b,c; Mallory, 1993).

### 5.10.3 Inhalation Toxicity

Results of two rat acute inhalation toxicity studies concerning 4-hour exposures to respirable endothall technical aerosol particles indicated that the animals displayed signs of respiratory tract irritation during the exposure and recovery periods. Signs of respiratory tract irritation during exposure included labored breathing, decreased respiratory rates and increased eye and nasal secretions. Immediately after exposures and during the first week of the 14-day observation periods, signs of labored breathing and decreased respiratory rates persisted along with rales, eye and nasal discharge and decreased activity. The investigation by Cracknell revealed that signs of respiratory tract irritation and deaths occurred primarily in the high and mid dose groups and one death in the 0.446 mg endothall technical/kg low dose animals. The investigation by Hoffman demonstrated deaths occurred in the high and mid dose animals, while no mortalities resulted in the low dose group exposed to 0.26 mg endothall technical/L of air. No gross pathological findings were found at necropsy associated with exposure to the test material in either of the two studies. The combined sexes LC50s for the two investigations were 1.51 and 0.68 mg endothall technical/kg, thus classing the chemical in EPA FIFRA Toxicity Category range of III for acute inhalation toxicity (Cracknell, 1990; Hoffman, 1992b). See).

Results of the acute inhalation toxicology studies concerning Aquathol® K, Aquathol® K Pelletized and Hydrothol® 191 revealed similar findings and all products were classed in FIFRA Toxicity Category III. See Table for the endothall acute toxicology results. (Hoffman, 1992a,c,d).

Based on the results of the endothall rat acute inhalation studies, the type of spray application of endothall products and the size of agricultural spray equipment particles, it is unlikely that applicator workers or bystanders will be overexposed to the spray mist particles during aquatic herbicidal spraying.

In the animal inhalation studies the particle sizes were nearly all respirable (less than or equal to 10 microns), while agricultural spray equipment delivers particles typically in the 200 micro size range. In the case of endothall application to bodies of water the particle sizes would be much greater, thus minimizing formation of respirable particles. Due to the design of the mammalian respiratory tract, particles less than 10 microns are required to reach the air sacs or alveoli of the lung. Larger particles of 200 microns and greater are deposited in the nasal passages and throat of the upper respiratory tract.

#### 5.10.4 Skin Irritation

A review of the rabbit dermal irritation studies concerning endothall technical and Aquathol® K indicate that the chemicals were not irritating. The primary skin irritation scores for the two formulations were 0.0/8.0. Conversely, findings from the Hydrothol® 191 skin irritation study demonstrated the product to have a severe degree of irritation. It is noted that signs of severe dermal edema and erythema and necrosis were observed at 30-60 minutes, 24, 48 and 72 hours following dermal application. The primary skin irritation score was 7.83/8.0, classing Hydrothol® 191 as an EPA FIFRA Toxicity Category I skin irritant (Mallory, 1992a,b; Mallory, 1993).

#### 5.10.5 Eye Irritation

Based on the results of rabbit eye irritation studies, concentrated (undiluted) endothall technical, Aquathol® K and Pelletized Aquathol® K are considered severe eye irritants and classed in EPA FIFRA Toxicity Category I. In addition to severe eye involvement, endothall technical and Aquathol® K concentrate also produced signs of systemic toxicity and histopathological changes in some animals. The clinical findings included decreased activity, abnormal gait and stance distended intestines, diarrhea, dyspnea, prostration and death. Due to the severe eye irritation demonstrated by the concentrated endothall formulations, no eye irritation study was conducted on Hydrothol® 191. Instead, the product was classed and labeled as a Toxicity Category I eye irritant.

EPA defined animal toxicology studies that are conducted in order to register a chemical as a pesticide according to the guidelines in the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), must follow strict protocols. The protocol for conducting rabbit eye irritation studies requires that one eye receive 0.1 ml of the undiluted test material while the other eye serves as the control or nonexposed eye. The test material is not washed from the eye and remains for the duration of the 21 day observation period. The eyes are observed by a trained technician and findings recorded at 1 hour, 1, 2, 3, 7, 14 and 21 days following application. Based upon the study results and findings the product is classed in FIFRA Toxicity Category I – IV (most irritating to least irritating) and labeled accordingly. In the case of the endothall products they are all Category I eye irritants and bear a DANGER signal word and precautionary statements that warn that the undiluted product is corrosive and severely irritating to eyes. The rabbit eye irritation study is an extreme exaggeration of eye exposure since it involves the concentrated chemical remaining in the eye for the entire study.

Conversely, when Aquathol® K was applied to the eyes of rabbits in dilutions containing 5, 25 and 50 parts per million (ppm) of the product, no corneal opacity or iritis was observed. Minimal conjunctivitis was noted at all dose levels, however these effects cleared by 48 hours. All eyes were considered normal by 48 hours. The 5 ppm group is representative of ocular exposure to the maximum endothall aquatic herbicidal use rate.

There was no dose response as to the degree of eye irritation between the 3 groups. The highest incidence of mild conjunctivitis was observed at the one hour reading in five of the six animals in the 5 and 100 ppm groups and four in the 50 ppm group. At the 24 hour observation two animals in the low and high test group and three in the mid group demonstrated mild conjunctivitis. All eyes were normal at 48 hours. . The total maximum mean score regarding the degree of adverse eye effects for all test groups ranged from 0.7 – 1.0 out of a maximum total score of 110. The investigators concluded that based on the

current EPA policy and Consumer Product Safety Commission's evaluation of the degree of eye irritation observed in animals at 24 hours, they believed the scoring observed in the study "represents a negative response and is considered inconsequential." (Wnorowski, 1997).

However, the results of the endothall dilution eye irritation studies do indicate that when the products are applied for aquatic weed control at the highest use rate of 5 parts per million (ppm), the potential for eye conjunctival irritation is possible. Although the concentration of endothall in treated water decreases rapidly over 1-8 days due to dilution and degradation, a swimmer may want to minimize potential minor eye irritation by wearing a swim mask or goggles 1-2 days following herbicide application.

Nevertheless, the label use of Aquathol® K and Hydrothol® products for aquatic weed control are not expected to cause any severe or significant adverse ocular effects or systemic toxicity.

#### **5.10.6 Skin Sensitization**

Results of delayed contact hypersensitivity studies in guinea pigs using various endothall formulations, indicated a mixed response. The results of the skin sensitization study with endothall technical revealed a positive response in 10 of the 20 test animals when challenged with a 0.5% concentration in acetone. Findings from the Aquathol® K guinea pig skin hypersensitization study demonstrated negative and positive findings in two groups challenged with test material in water and 2.0% ethanol, respectively. Similar studies conducted with Pelletized Aquathol® K and Hydrothol® 191 demonstrated that the two formulations did not cause delayed contact hypersensitivity in guinea pigs. Based on the results of the skin sensitization investigations, allergic skin reactions would not be expected from persons contacting endothall treated bodies of water because of the low product use rates, water dilution factor and degradation of the chemical in the aquatic environment.. (Armondi, 1991a,b,c; Armondi, 1993).

#### **5.11 SUBCHRONIC TOXICITY**

Repeated daily or weekly chemical exposures for short time frames typically occur during the application of a chemical or through dietary intake of a treated food crop or water. Most human chemical exposures are either acute (one time exposure) or subchronic (exposure to a chemical for a few days or weeks). The potential for subchronic exposure to endothall would also occur when the chemical is used for aquatic weed control. Such exposures for persons in contact with recently treated water would primarily involve dermal contact with the chemical through swimming, ingesting the water or sediment, or dermal contact with treated sediments and aquatic weeds.

Inhalation exposures to endothall in aquatic herbicidal use situations basically apply to the applicator where generation of a spray mist or dust may occur. However, aquatic application of endothall-containing products in compliance with label directions is not expected to result in adverse health effects following contact with treated water. Further, factors mitigating against any adverse health effects from applied endothall are the significant water dilution, poor dermal and gut absorption, rapid excretion of absorbed endothall and short half-life in water all support the conclusion that overexposure to the chemical is unlikely.

Subchronic toxicology studies are designed to determine the target organ(s) associated with exposure to a chemical for a few weeks or months. Subchronic toxicology studies usually

consist of four groups of animals, a control (non-exposed group) and low, mid and high dose test groups. The parameters of subchronic investigations are designed to define the toxic effects of a chemical and include specific target organ(s) affected, signs of toxicity, changes in body weight and food consumption, blood chemistry and urine analyses, hematology and gross and histopathological examination.

Based on the results, the target organ(s) associated with overexposure to the test compound can be identified and a no observable adverse effect level (NOAEL) dose can be determined for the chemical. The findings from the investigation can also be used for determining the degree of toxicity of the chemical, risk assessments, establishment of acceptable exposure levels, dietary and drinking water standards, label precautionary statements and other sources of health information.

### 5.11.1 Oral

Results of a mouse 4-week dietary range finding study with disodium endothall salt determined that treatment related effects were observed in the 63, 105 and 315 mg endothall acid equivalent (Eae)/kg/dy approximate dose groups. The endothall-associated effects were listed as decreased food consumption and body weights. The NOAEL was determined to be approximately 32 mg Eae/kg/dy (WIL Res. Lab, 1985).

Results of the one year interim report of the rat chronic endothall toxicity test (Hazleton, 1986), revealed no signs of toxicity at any of the dose levels. However, the mid and high dose groups, approximately 45 and 90 mg Eae/kg/dy, respectively, demonstrated stomach lesions, e.g. acanthosis and hyperkeratosis of the squamous epithelium. Blood chemistry findings included decreased glucose and total protein values in the mid and high dose groups. The one-year no observed adverse effect level (NOAEL) was 15 mg Eae/kg/dy.

Rats fed diets containing 30.9% amine salt of endothall for 13 weeks at approximate dose levels of 150, 600 or 1800 parts per million (ppm) [6.6, 26.4, and 79 mg Eae/kg/dy] did not demonstrate any signs of toxicity or deaths. No clinical evidence of treatment related effects were noted in clinical findings, ophthalmoscope examination, hematology and serum chemistry analyses, organ weight data or necropsy and histopathology. High dose group animals demonstrated body weight decreases. The study NOAEL was 26.4 mg Eae/kg/dy based on the decreased body weights, while the LOAEL was considered to be >79 mg Eae/kg/dy (Trutter, 1994).

Brieger (1953) conducted a dog study and determined that oral administration of the disodium endothall salt at doses of approximately 14 and 35 mg Eae/kg/dy/wk/6 wks, produced severe stomach and intestinal mucosal changes. All dogs in the high dose group died within 11 days of dosing. The dogs administered 14 mg Eae/kg/dy/wk/6 wk displayed signs of toxicity of vomiting, diarrhea, and congestion of the stomach and intestine as evidenced by gross histological findings of edema, erosion and hemorrhage.

Trutter (1994) conducted a dog study feeding 30.9% amine salt of endothall in the diet for 13-weeks at dose levels of approximately 0, 100, 400 or 1000 ppm [0, 1.1, 4.4 and 11 mg Eae/kg/dy]. The results revealed no deaths or signs of toxicity indicative of systemic toxicity. No evidence of compound related effects were observed in the ophthalmoscopic examinations, hematology, organ weight data and necropsy. Signs of transient red discoloration of the perioral region and slight salivation were attributed to the irritation

potential of the chemical. The investigators of the study determined that the no observable effect (NOEL) was >11 mg Eae/kg/dy.

### **5.11.2 Dermal**

A 21-day rat dermal study with Aquathol® K (29.5% endothall acid equivalent), at an approximate dose of 56 mg Eae/kg/dy/ produced severe skin irritation and bilaterally mottled kidneys and enlarged adrenal glands. Changes were also noted in the clinical chemistry and hematology analyses (Margitich and Ackerman, 1992).

Results of an amine salt of endothall rat 21-day dermal subchronic toxicity study revealed that dose levels of approximately 13.2, 44, or 132 mg Eae/kg/dy/3 weeks produced moderate to severe skin irritation at all dose levels. A systemic response to the severe degree of skin irritation was related to histomorphological changes in the kidneys and liver in high dose animals and concurrent secondary changes in the liver and kidneys and extramedullary hematopoiesis in the spleen in all treated groups. The investigators concluded that the NOAEL for systemic toxicity was 13.2 mg Eae/kg/dy (Margitich, 1994).

### **5.11.3 Neurotoxicity**

A review of the animal toxicology studies and scientific and medical literature does not indicate any specific endothall neurotoxicity investigations have been conducted. However, a review of the chronic feeding studies (Keller, 1965), (Plankton, 1990), (Schellenberger, 1990a, 1990b) and the multigenerational rat reproduction studies (Scientific Associates, 1965), (Trutter, 1993) do not reveal that the test animals demonstrated signs or findings of neurotoxicity nor were there any reports of histopathological nerve tissue changes reported in any of the studies. In addition, no findings of neurological adverse effects were described in the subchronic studies conducted by Brieger (1953b), WIL Res. Lab (1985), Hazelton (1986) and Trutter (1994a, 1994b). Therefore based on the findings in the endothall subchronic and chronic animal toxicology investigations, overexposure to the chemical does not appear to be associated with neurotoxicity, peripheral neuropathy or adverse behavioral effects.

### **5.11.4 Immunotoxicity**

A review of the animal toxicology studies and scientific and medical literature does not indicate that any specific endothall immunotoxicity investigations have been conducted. However, based on the negative findings from the subchronic, chronic, multigenerational reproduction and mutagenicity toxicology studies, it seems unlikely that endothall has significant immunotoxic potential.

### **5.11.5 Estrogen Disruption**

There is no evidence or results from any toxicology investigation that demonstrates either exposure or overexposure to endothall results in any findings or changes associated with adverse endocrine function or mimicking effects. The results of the endothall teratology and reproduction studies did not demonstrate any evidence that the chemical demonstrated any teratogenic potential or reproductive changes. Similarly, results of the subchronic and chronic investigations did not provide any findings of behavioral, clinical or histopathological changes considered to be associated with adverse endocrine effects.

## 5.12 CHRONIC TOXICITY

Keller (1965) conducted a rat chronic 2-year disodium endothall feeding study and demonstrated increased stomach and small intestine weights in the mid and high dose groups of 6 and 16 mg Eae/kg/dy/24 months. The NOAEL for the investigation was 2 mg Eae/kg/dy/24 months. At the mid dose of 6 mg Eae/kg/dy/24 months, an increase in stomach and small intestine weights were observed and considered to be related to the irritation potential of the chemical. No effects of body weight gain or food consumption were observed in any of the dose groups.

Plankton (1990) conducted a chronic rat study, where disodium endothall (12.6% endothall acid equivalent) was administered at dietary dose levels of approximately 0, 5.3, 10.5, 31.5 or 63 mg Eae/kg/dy for 24 months. Rats treated in the three high dose groups demonstrated dose-related decreases in body weights and body weight gains and decreased glucose levels. In addition, gross necropsy revealed increased incidence of thickening of both the glandular and non-glandular stomach in the three high dose groups. Histopathology of the gross stomach lesions revealed acanthosis and hyperkeratosis. The lowest effect level of histopathological findings of stomach lesions was 31.5 mg Eae/kg/dy. There was no evidence of a carcinogenic effect of any of the study dose groups. The investigators concluded that 10.5 mg Eae/kg/dy was the NOAEL.

A one-year dog study with disodium endothall (16.1% endothall acid equivalent) was administered in the diet at doses of approximately 0, 6, 18 or 36 mg Eae/kg/dy. The high dose group dogs were initially dosed at approximately 54 mg Eae/kg/dy for 6 weeks, however they soon began demonstrating a marked reduction in body weights and food consumption. The initial high dose had exceeded the maximum tolerated dose. Five of the animals in the high dose group were moribund and subsequently sacrificed and necropsied. The dose was reduced to approximately 36 mg/Eae/kg/dy and the food consumption and body weight gains increased. The sacrificed animals were not replaced so that statistical analyses were not performed on the high dose group because of the low number of survivors. Absolute and relative testicular weights of the high dose animals was decreased however the investigators stated that the data cannot be evaluated with certainty because of the emaciated condition of the animals (Schellenberger, 1990).

Other clinical signs of toxicity observed in the mid and high dose group animals included reduced activity, emaciation, distended abdomen, decreased red blood cell parameters, reduced total protein and glucose, elevated alanine and aminotransferase. Necropsy findings revealed treatment related pathological changes of hyperplasia and hepatocyte shrinkage of the liver, esophageal epithelial necrosis, gastric epithelial hyperplasia and atrophy of the testicular seminiferous tubules. Minimal to very mild gastric epithelial changes were noted in the low dose animals and was considered to be a low grade reaction the chronic epithelial irritation by the test compound. The study NOAEL was 6 mg Eae/kg/dy (Schellenberger, 1990).

A chronic 21-month mouse feeding study was conducted with disodium endothall administered in the diet in approximate doses of 0, 5.3, 10.5, or 31.5 mg Eae/kg/dy. Treatment related effects were observed only in the high dose group males and consisted of increased body weight and body weight gain and an increased incidence or renal mineralization. There also appeared to be a statistically insignificant ( $p=0.20$ ) increased incidence of hepatocellular adenomas in the high dose groups males. The NOAELs for male and female mice were 10.5 and 31.5 mg Eae/kg/dy, respectively (Schellenberger, 1990).

No chronic toxicology study was conducted on the endothall monoamine salt or the Hydrothol® 191 product. Since doses in the toxicology studies are calculated in terms of endothall acid equivalents (Eae) for both the dipotassium and monoamine salts, the results from the current chronic toxicology investigations serve to represent the chronic toxicity of the monoamine salt. The EPA has accepted the use of Eae unit for establishing doses in toxicity for the endothall salts.

## **5.13 DEVELOPMENTAL AND REPRODUCTIVE TOXICITY**

A review of the endothall reproduction and teratology toxicology investigations, did not reveal any evidence that endothall has been associated with any significant findings of reproduction dysfunction or teratological effects.

### **5.13.1 Teratology Studies**

Results of a rat developmental investigation demonstrated that there was no evidence of embryotoxicity or teratogenic effects even at maternally toxic doses of 24 mg Eae/kg/dy administered on days 6-19 of gestation. The NOAEL was 8 mg Eae/kg/dy based on maternal toxic effects (Science Applications, Inc., 1982).

No evidence of teratological effects was observed in pregnant rats dosed with disodium salt of endothall during days 6-15 of gestation. Results of the investigation indicated no developmental effects noted at the maternally toxic high dose of 20 mg Eae/kg/dy. There were no compound effects on maternal survival, clinical signs or necropsy findings in the test groups. The maternal toxic and developmental NOAELs were 10 and 20 mg Eae/kg/dy. No fetal external, visceral or skeletal variations were observed at any dose level. (Trutter, 1995).

### **5.13.2 Reproduction Studies**

A rat 3-generation reproduction study involving dietary dosing of male and female animals with endothall at approximately 0, 4, 12 or 100 mg Eae/kg/dy, revealed that the reproductive NOAEL was 4 mg Eae/kg/dy. The high-dose group systemic effects included reduced body weight gains in parents and excessive mortality in the offspring. Due to the high incidence of systemic toxicity and deaths, the high dose group was eliminated from the second and third generation part of the investigation. Therefore, the study consisted of only two dose groups. The parental animals receiving 12 mg Eae/kg/dy did not demonstrate any signs of toxicity however there were signs of reduced pup weight and deaths. No signs of toxicity or deaths were observed in the low dose group in either the parents or offspring. (Scientific Associates, 1965).

A more recent endothall guideline 2-generation reproduction study conducted with rats did not demonstrate any evidence of compound related effects on reproductive performance at approximate endothall disodium salt dose levels of 1.2, 6 or 36 mg Eae/kg/dy. The only significant adverse effects were decreased body weights in parents and offspring in the high dose group. There were no treatment-related effects with regard to pregnancy rates, fertility, reproductive performance or offspring viability and survival. There were no gross necropsy or microscopic lesions of the reproductive organs. Findings from the histological examination revealed a nonsignificant number of minimal to moderate proliferation of the gastric epithelium. Based on the results of the investigation there were no endothall-related changes

associated with adverse reproductive performance. The NOAEL for the study was 6 mg endothall ion/kg/dy (Trutter, 1993).

A review of the two reproduction studies reveals that although the 1965 3-generation endothall study cannot be considered a guideline investigation based on current standards and protocol, a comparison of the two studies does demonstrate similar NOAELs of 4 and 6 mg Eae/kg/dy and that endothall did not produce any adverse reproductive effects in the rat.

#### **5.14 MUTAGENIC EFFECTS**

Overall, endothall does not appear to be a potential mutagen. Negative results have been found in Salmonella assays with and without metabolic activation (Andersen et al, 1972; Microbiological Associates, 1980a; Plankenhorn, 1990). However an Ames/Salmonella assay on technical endothall amine salt solution demonstrated equivocal findings (Stankowski, 1993). Evidence from other mutagenicity investigations have reported negative results as demonstrated in a sister chromatid exchange study in human lymphocytes (Vigfusson, 1981), absence of DNA damage in strains of Escherichia coli (Bootman, 1988), failure to induce mutations in the AS52/XPRT mammalian cell forward gene mutation assay (Stankowski, 1993) and no evidence of clastogenic activity in cultured human lymphocytes (Bootman, 1989). Similarly, *in vivo* testing demonstrated no evidence of induced chromosomal damage leading to micronucleus formation in polychromatic erythrocytes in mice treated at the high dose of 50 mg endothall technical/kg at 24, 48 or 72 hours following oral dosing (Mackay, 1989).

#### **5.15 CARCINOGENICITY REVIEW**

Based on the toxicology database, findings of the 4 endothall chronic feeding studies and several mutagenicity investigations, there is no definitive evidence that endothall is carcinogenic. The primary histopathological findings are due to the high irritation potential of endothall to the gastrointestinal tract. Signs of gastric irritation evidenced in the mid and high dose groups of chronic studies included: increased stomach weights, hyperplasia of the gastric epithelium, thickening of the glandular and nonglandular stomach, esophageal necrosis and an insignificant increase in the high dose male group of benign hepatocellular adenomas (Keller, 1965; Plankton, 1990; Schellenberger, 1990a; Schellenberger, 1990b).

#### **5.16 EPIDEMIOLOGY REVIEW**

A review of the scientific and medical literature provided no citations that any epidemiological or occupational investigations concerning endothall have been conducted.

#### **5.17 HUMAN CASE REPORTS AND STUDIES**

Human overexposure to endothall resulting in systemic poisoning is an uncommon finding. Allender (1983) reported a suicide case where the patient allegedly ingested 7-8 gm of disodium endothall and experienced vomiting and death. Autopsy findings revealed focal pulmonary hemorrhages and edema and gross hemorrhage of the gastrointestinal tract.

Aside from cases involving accidental and suicidal ingestion of massive amounts of endothall containing products, there have been anecdotal reports to poison control centers and the Washington State Pesticide Incident Reporting and Tracking database concerning oral, dermal, inhalation and eye exposures to the chemical. Since endothall products and spray

mixes may be irritating, depending upon the concentration, reports of irritation to the eyes, skin, respiratory tract and digestive tract following overexposure would not be unexpected. Accidental swallowing or inhalation of a strong spray dilution may irritate the gastrointestinal tract to produce signs and symptoms of nausea, vomiting and diarrhea. Similarly, inhalation of a strong spray dilution may also cause upper respiratory tract irritation as evidenced by nasal discharge, coughing, difficulty in breathing and sore throat. All of these effects are expected to remit once exposure is discontinued.

### **5.17.1 Human Neurological Case Reports**

There are no reports in the scientific and medical literature listing any findings that either animal or human exposure to endothall has resulted in adverse affects to the central or peripheral nervous systems. Endothall is not considered to be a neurotoxin based on results from laboratory animal toxicology testing and human use experience.

### **5.17.2 Human Reproduction Case Reports**

A review of the animal toxicology studies failed to demonstrate any findings of adverse developmental and reproductive effects. Further, no reports were found in the scientific and medical literature associating exposure to endothall with any human teratology or reproductive dysfunction (Science Applications Inc., 1982; Trutter, 1993; Trutter, 1995).

## **5.18 EXPOSURE AND RISK ASSESSMENTS**

The exposure and risk assessments of endothall use as an aquatic herbicide are presented in the following Tables, concerning persons engaged in swimming, drinking both potable and treated surface water and eating fish from bodies of water where the chemical has been applied. The different types of daily exposures and risk assessments were calculated for both individual and combined scenarios. Based on the estimated endothall exposures, the risk assessments were determined by the margins of safety (MOS) and the % of the reference dose (RfD). The endothall calculations were conducted using maximum and average use-rates of 5 and 3 ppm, respectively; time spent swimming ranging from 0.5 to 3 hours and body weights of 6 and 10 year old children and the traditional 70 kg adult.

Table 2 lists the quantitative toxicology parameters and endothall product use-rates that were utilized in conducting the exposure and risk assessments. EPA has determined that the endothall RfD is 20 ug/kg/dy, based on the NOAEL of 2.0 mg/kg/dy finding in the rat 2-year chronic feeding study, see Table 4 (Keller,1965). The acute oral toxicology NOAEL of 8.0 mg/kg was used in the short-term risk assessment calculations (Mallory, 1991c). The endothall dermal parameters of an approximate skin absorption rate of 7%/24 hours, permeability coefficient and flux rates were used to calculate herbicide dermal exposures from contacting herbicide treated water and sediment (Johnson, 1990; USEPA, 1993; Lunchick, 1994).

There are a number of different use-rates for the various endothall-containing products depending upon the intended target vegetation to be eliminated. The Aquathol® products have use-rate ranges of 0.5 – 5.0 ppm or ug/ml, while the Hydrothol® formulations range from 0.05 to 5.0 ppm or ug/ml. Therefore, based on the use-rates, the exposure estimates and risk assessments were conducted for persons exposed to water containing 3 and 5 ppm endothall. These concentrations of the chemical are considered immediate levels in the water and hypothetically maintained at this concentration for chronic exposure and risk

calculations. In the real world the concentration of endothall following application to water would decrease on a daily basis. Therefore, the risk calculations presented in the tables represent extreme situations.

Since endothall is primarily dripped, or sprayed directly over the surface of water for aquatic weed control, it is highly unlikely that the spray or vapor will drift to expose either applicators or bystanders. Similarly, aerial application of Hydrothol® involves delivery of large droplets that do not drift compared to finer agricultural crop spray mist. The other major means of applying endothall is through underwater injection. For these reasons applicator or bystander endothall exposure or risk assessments were not conducted.

Exposure estimates and risk assessments to endothall resulting from aquatic weed control were determined for cases involving ingestion and dermal contact with treated water and sediment while swimming, inhalation of any endothall vapor during swimming, drinking potable water containing the maximum contaminant level (MCL) of 100 ug endothall/day, daily drinking of treated surface water and ingestion of fish from treated water. These various calculations are presented in the following Tables.

Table 3 lists the EPA health advisories for endothall in drinking water (EPA, 1988). The exposure and risk assessment for ingestion of potable water utilized the maximum contaminant level (MCL) of 100 ug/L for endothall daily exposure. The short-term or acute endothall water exposure estimates for both 10, 35 and 70 kg persons included the 1-day health advisory of 800 ug/L. Since the chemical is not registered or intended for food crop use and the amounts of endothall found and calculated from eating fish was negligible, other potential dietary sources of exposure were not included in the calculations.

One of the purposes of conducting a review and health risk assessment for use of endothall as an aquatic herbicide is to determine whether swimming or contacting water that has been treated according to product label directions, should be a health concern. This situation is discussed in this section and the exposure dose and risk assessment calculations presented in Tables 5-12.

However, before addressing the exposure to endothall treated water, it is important to understand the classification of the undiluted endothall products according to their acute toxicities. As indicated on Table 1, the results of the Aquathol® products acute oral and dermal animal toxicology studies demonstrate that the products are not considered highly toxic and classed in FIFRA toxicity categories II and III, respectively. The results of the Hydrothol® acute oral and dermal toxicology studies place both routes of exposure in FIFRA category II. A review of Table 1 reveals that the most significant finding of the acute toxicology studies is that the concentrated endothall products are FIFRA category I eye irritants. The results of the eye irritation studies indicated irreversible eye damage. It must be remembered that the eye test protocol requires that the test material not be rinsed from the eye and observations of the eye effects are recorded over a 21-day observation period.

Therefore, based on the endothall product acute toxicology study findings, severe eye irritation and damage are the most significant adverse health effects. FIFRA also determines the precautionary warnings and precautionary and first-aid statements on pesticide product labels based on the results of the acute studies. In the case of endothall products, the label signal word is “Danger” and the precautionary statements include “causes irreversible eye damage” and “fatal if absorbed through skin and may be fatal if swallowed.” Although the endothall products in their undiluted form are severe eye irritants, once the products have

been applied to water according to label directions, they become diluted by the huge water volume, bind to vegetation, begin degradation and incorporate into the sediment. The decrease in the amount of endothall in the treated water reduces the amount of chemical available for exposure, thus decreasing the potential for systemic toxicity and eye irritation. The following discussion reviews the endothall diluted label use-rate water concentrations of 5 and 3 ppm and the calculated exposure doses and associated health risk assessments to swimmers and others receiving various types of exposure to the herbicide.

The endothall products are applied at prescribed label use-rates in terms of gallons of product/acre of water in order to obtain the specific herbicidal concentration to eradicate the targeted aquatic weed. As mentioned previously, the use-rates vary depending upon the aquatic type of vegetation and the size of the area to be treated. A common endothall use rate is approximately 3.0 ppm or ug/ml while weeds e.g. hygrophilia, may require the highest use-rate of 5.0 ppm.

The exposure and risk assessment parameters regarding persons swimming in endothall treated water are presented on Table 5. Calculation of endothall exposures utilized the swimmer's weight (kg), the skin surface area available for exposure (cm<sup>2</sup>), the amount of time (hours) spent in the treated water containing either 5 or 3 ppm endothall, amount of water swallowed while swimming over specific time periods, skin permeability coefficient and the endothall vapor pressure.

Tables 6-8 list the estimated endothall oral, dermal and inhalation exposures and risk assessments for swimmers. The exposure conditions are defined in Table 5. Based on the calculations, it appears that the greatest endothall exposure occurs from incidental ingestion of water while swimming. It is estimated that a swimmer swallows approximately 50 ml (nearly 2 ounces) of water/hour. A review of Table 6, indicates that the worst case exposure situation involves the 6 and 10 year old children groups that spend 2 and 3; and 3 hours, respectively, swimming in water containing 5 ppm endothall. The risk assessments using the margin of safety (MOS) of 2,000 ug/kg/dy and the % of the RfD (20 ug/kg/dy) for the two groups indicate the 6 year old is below the 100 mark for the MOS and the exposures exceed the daily RfD by 113.5 and 170%, respectively. Similarly, the 10 year old water ingestion dose at 3 hours of swimming is below the 100 level MOS and exceeds the RfD by 107%.

However, the dose is significantly reduced when compared to the degree of exposure when the children swim in water treated with 3 ppm endothall. The only significant exposure appears to be the 6 year old child swimming for 3 hours where the risk assessments are marginally exceeded as evidenced by the MOS and RfD of 98 and 103%, respectively.

A review of Tables 7 and 8, reveal that the swimmers dermal and inhalation exposures are insignificant compared to the oral exposure and further supported by the MOSs in the thousands. Based on the large MOSs, no RfDs were calculated for these routes of exposure.

Swimmer exposure to endothall through ingestion and dermal contact with sediment was also calculated to be very low. Using the USEPA Regional 10 Guidance formula (1991), the oral dose calculates to  $9.8 \times 10^{-6}$  ug/kg/dy. The exposure calculation was based on ingestion of sediment from water treated with the maximum use-rate of 5.0 ppm and containing approximately 2.0 mg/kg sediment (Keckemet and Sharp, 1999). Dermal sediment endothall exposures are presented in Table 10. A combination of oral and dermal sediment estimated endothall exposure doses and risk assessments appear in Table 11. The MOS calculations for the sediment endothall exposures are in the hundreds of thousands.

Table 12 is a compilation of the various exposure types and total estimated endothall doses that a person may receive when swimming in treated water containing either 5.0 or 3.0 ppm of the chemical. The incidental ingestion of water while swimming is the most significant route of exposure. In all cases, approximately 95-97% of the total endothall exposure that occurs while swimming is through the oral route. The same situation as discussed above concerning the exposure and risk assessments for oral exposure to endothall while swimming, also applies in the case of the combined chemical exposure where the exposure doses (ug/kg/day) and the MOSs and RfDs of the 6 and 10 year old children are similarly affected at the 5.0 and 3.0 ppm endothall use-rates. Although a few of the risk assessment calculations are exceeded, the exposure dose does not exceed the animal systemic toxicity NOAEL of 2,000 ug/kg/day.

At this point it is important to evaluate any adverse health effects that could potentially be associated with exposure to endothall while swimming in treated water. The largest acute exposure (single day exposure) would be expected to occur on the day of the endothall product application. Once applied, the concentration of the chemical will decrease with time, thus reducing the daily dose. The findings in Table 5 indicate that endothall had a range of half-lives in pond water ranging from 4.3-7.1 days.

However, assuming the water contains 5.0 ppm endothall and the swimmer has extensive eye contact with the water, some chemical associated temporary minor eye irritation or conjunctivitis may result. Even eye contact with water not containing endothall will result in some minor eye irritation. Results of the animal toxicology eye irritation study conducted on dilutions of endothall, found that minor conjunctivitis was demonstrated in the some eyes treated with 5.0 ppm. Although minor eye irritation was observed in 2 of the 6 treated animals at the 24-hour reading, all eyes were normal at 48-hours (Wnorowski, 1997).

In summary, it appears that persons swimming in water treated with the highest use-rate of endothall at 5.0 ppm are not expected to experience significant adverse health effects. Based on the results of the toxicology studies and the product use-rates, systemic toxicity seems unlikely unless a large amount of water containing 5ppm endothall is ingested. Minor eye irritation may be associated with prolonged contact with the 5 ppm treated water, however any redness or irritation would be minor and expected to remit within 1-2 days. The wearing of swim goggles or other eye protection may be useful in avoiding potential minor eye irritation while swimming in water on the day that endothall has been applied at the 5 ppm use-rate.

Drinking water sources are significant factors in determining the overall exposure to endothall, particularly during the first few days following application. Table 13 demonstrates that potable drinking water containing the established endothall MCL of endothall does not pose a significant exposure or health risk. The calculations assume daily ingestion of 1-2 liters of water containing 100 ug of endothall. The MCL represents the endothall concentration in drinking water that is not expected to cause any adverse noncarcinogenic health effects.

Conversely, Table 14 demonstrates that ingestion of drinking water from treated endothall surface water significantly increases the estimated daily exposures and adversely affects the calculated risk assessments. Based on the calculations, ingestion of endothall treated water as a daily drinking water source can result in dose levels that exceed the MOSs and RfDs.

Therefore, a waiting period as indicated on the product label of 25 days for domestic use may

be advisable so that the endothall water concentrations decrease to levels where the daily doses are within the risk assessment boundaries.

Consumption of fish taken from endothall treated bodies of water, may also be a potential dietary source of the chemical. As discussed in other sections of this document, endothall does not bioconcentrate in edible tissue of fish (Dionne, 1992; Formella, 1998). However, a report by Serns, 1977, notes the detection of 40 ug/kg in the edible portion of bluegill taken from a Wisconsin pond one day after endothall treatment. Using Serns' analytical finding in calculating the exposure doses in Table 15, it does not appear that ingestion of fish from endothall treated water poses any significant health problem or risk.

The total daily calculated endothall exposures are presented in Tables 16 and 17. The difference in the two tables concerns the potable vs. the endothall treated surface water as sources of daily drinking water. Apparently, there are locations that receive residential drinking water directly from treated water sources, e.g. ponds, lakes, rivers. Since ingestion of water accounts for the greatest potential exposure to endothall, both sets of exposure estimates and risk assessments are presented. The total daily exposures listed are the summation of endothall daily dose levels received from swimming (Table 12), type of water source (Tables 13 and 14) and ingestion of fish (Table 15).

The findings in Table 16 concerning the total daily estimated endothall exposures and risk assessments that includes potable water, essentially mimics the calculations presented in Tables 6 and 12. Again, the significant exposures are to the 6 and 10 year old children swimming in 5 ppm endothall treated water for 2 and 3 hours and 3 hours, respectively. Also, the 6 year old child swimming for 3 hours in the 3 ppm endothall treated water exceeds the total MOS and RfD risk assessment parameters.

Examination of Table 17 reveals a different situation whereby all of the MOSs and RfDs are exceeded. The daily dose levels resulting from ingestion of endothall treated surface water at both the 5 and 3 ppm concentrations significantly increases the daily dose in all subjects and swimming exposure times. Although the calculations represent significantly elevated endothall exposures, the doses still remain below the lowest animal chronic toxicology study NOAEL dose of 2,000 ug/kg/dy. Nevertheless, as stated above, it is important to follow the label directions for domestic water use of endothall treated water and wait 25 days following application of the chemical before resumption of using the water source.

## 5.19 CONCLUSION

*Based on a review of the endothall toxicology studies, biotransformation, chemical and physical properties, use-rates, exposure estimates and risk assessments, it appears that the label directed use of the herbicide for aquatic weed control purposes is not expected to result in any significant adverse health effects. The exposure evaluation of persons swimming in water containing 5.0 ppm (highest label use-rate) and 3 ppm endothall does not indicate that significant systemic effects would occur based on the exposure and risk assessment parameters. However, the risk assessments are exceeded when a 6 year old child swims in water containing 5 ppm endothall for 2 and 3 hours/day and in water containing 3 ppm endothall for 3 hours/day. Also, the 10 year old child, swimming in treated water containing 5.0 ppm endothall for 3 hours/day exceeds the risk assessments. Even though the risk assessments may be exceeded in these cases, the potential endothall doses (ug/kg/day) are more than 50 times less than the systemic MOS based on the animal chronic toxicology NOAEL of 2,000 ug/kg/day.*

*Results of the toxicology eye irritation study involving the diluted endothall formulations, indicated that a 5.0 ppm dilution caused minor eye irritation in some animals however all eyes were normal at the 48-hour reading. Based on these findings, wearing of eye goggles or other eye protection may be preventative in developing potential minor eye irritation when swimming in treated water on the day the chemical was applied at the 5.0 ppm use-rate.*

*Risk assessments were significantly exceeded in situations where the source of drinking water was endothall surface treated water. Although the calculated endothall daily doses were elevated they remained 9-23 times below the systemic MOS based on the animal chronic toxicology NOAEL. Again, it is important to follow the endothall product label that directs a 25 day waiting period for domestic purposes before resuming use of treated water as a drinking water source.*

*Based on the label use directions and the results of the endothall toxicology studies, the aggregate or combined daily exposure to the chemical from aquatic herbicidal weed control does not pose a significant adverse health concern.*

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**Table 1: Endothall Acute Toxicology**

Study Type	Results (mg/kg)	Toxicity Category	Reference
<b>Endothall Technical</b>			
Acute Oral Rats	LD50= 45.4	I	Mallory, 1991c
	“ M= 50.2	I	
	“ F= 44.4	I	
Acute Dermal Rabbits	LD50= >2,000	III	Mallory, 1991d
Acute Inhalation Rats	LC50= 1.51 (dust)	III	Cracknell, 1988
	“ M= 1.27	III	
	“ F = 2.20	IV	
Acute Inhalation Rats	LC50= 0.68 (aerosol)	III	Hoffman, 1992
	“ M= 1.1	III	
Dermal Irritation Rabbits	Primary Irritation Index = 0	IV	Mallory, 1991g
Eye Irritation Rabbits	Severe/systemic toxicity	I	Mallory, 1991i
Skin Sensitization Guinea Pigs	0.5% caused contact hypersensitivity		Armondi, 1991a
<b>Aquathol® K</b>			
Acute Oral Rats	LD50= 99.5	II	Mallory, 1991b
	“ M= 84.9	II	
	“ F= 135.2	II	
Acute Dermal Rabbits	LD50= >2,000	III	Mallory, 1991f
Acute Inhalation Rats	LC50= 0.83 (aerosol)	III	Hoffman, 1992a
Dermal Irritation Rabbits	Primary Irritation Index = 0	IV	Mallory, 1991h
Eye Irritation Rabbits	Maximum use rate dil 5 ppm	III	Wnorowski, 1997
	5 times max use rate dil	III	
	10 times max use rate dil	III	
Eye Irritation Rabbits	Severe / Systemic toxicity	I	Mallory, 1991j
Skin Sensitization Guinea Pigs	2.0% caused contact hypersensitivity		Armondi, 1991b
<b>Aquathol® K Pelletized</b>			
Acute Oral Rats	LD50= 186.8	II	Mallory, 1991a
	“ M= 165	II	
	“ F= 215.5	II	
Acute Dermal Rabbits	LD50= >2,000	III	Mallory, 1991e
Acute Inhalation Rats	LC50= 1.4 (dust)	III	Hoffman, 1992c
Eye Irritation Rabbits	Severe	I	Mallory, 1991k
Skin Sensitization	No hypersensitization		Armondi, 1991c
<b>Hydrothol® 191</b>			
Acute Oral Rats	LD50= 233.4	II	Mallory, 1993a
	“ F= 209.8	II	
Acute Dermal Rabbits	LD50= 480.9	II	Mallory, 1993b
	“ M= 714.6	II	
	“ F= 383.2	II	
Acute Inhalation Rats	LC50= 0.70 (aerosol)	III	Hoffman, 1992d

**Table 1: Endothall Acute Toxicology (Continued)**

<b>Study Type</b>	<b>Results (mg/kg)</b>	<b>Toxicity Category</b>	<b>Reference</b>
<b>Hydrothol® 191</b>			
Eye Irritation Rabbits	Deferred	I	
Skin Irritation Rabbits	Primary Irritation Index = 7.8	II	Mallory, 1993c
Skin Sensitization Guinea pigs	No hypersensitization		Armondi, 1993

**Table 2: Endothall Toxicology Quantitative Parameters**

<b>Regulatory Guideline</b>	<b>Standard/ Dose (mg/kg/dy)</b>	<b>Classification Category</b>
<b>Toxicology</b>		
Acute NOEL	8.0 mg/kg (Mallory, 1991c)	
Subchronic NOEL	13.2 mg/kg/dy/21 dys (Margitch, 1994)	
Chronic NOEL	2.0 mg/kg/dy (Keller, 1965)	
Chronic RfD	0.02 mg/kg/dy	
Reproduction NOEL	4.0 mg/kg/dy (Science Associates, 1965)	
<b>Cancer Classification</b>		
EPA		Group D (inadequate evidence in humans and animals)
IARC		Not Evaluated
<b>Dermal</b>	Absorption = ~7%/ 24-hours (Johnson, et.al., 1990) Permeability Coefficient = $1 \times 10^{-4}$ cm/hr Flux Rate (5 ppm use-rate) = $5 \times 10^{-7}$ mg/cm <sup>2</sup> /hr (3 ppm use-rate) = $3 \times 10^{-7}$ mg/cm <sup>2</sup> /hr	
<b>Endothall Label Use-Rates</b>		
Aquathol® Products	Range: 0.5 to 5.0 mg dipotassium salt of endothall equivalents/Liter of water = 0.35 to 3.5 mg endothall acid equivalents/Liter of water = 0.35 to 3.5 parts per million (ppm) or (ug/ml)	
Hydrothol® Products	Range: 0.05 to 5.0 mg endothall acid equivalents/ Liter of water = 0.05 to 5.0 parts per million (ppm) or (ug/ml) 5.0 ppm Highest Endothall Use-Rate	

**Table 3: Endothall Health Advisories**

Drinking Water	
MCLG <sup>a</sup>	0.1 mg/L
MCL <sup>b</sup>	0.1 mg/L
DWEL <sup>c</sup>	0.7 mg/L (RfD x 70 kg/ 2 L water/day)
1 day HA <sup>d</sup>	0.8 mg/L (10 kg child)
10 day Ha <sup>e</sup>	0.8 mg/L (10 kg child)
Longer term HA <sup>f</sup>	0.2 mg/L (10 kg child)
Longer term HA <sup>f</sup>	0.2 mg/L (70 kg adult)
Lifetime HA <sup>g</sup>	0.1 mg/L
Dietary ADI	0.02 mg/kg/dy (Chronic NOAEL / 100 uncertainty factor)
Tolerance	
Potable water	0.2 mg/L
Cotton seed	0.1 ppm
Potatoes	0.1 ppm
Rice	0.05 ppm

- <sup>1</sup> Maximum Contamination Level Goal – A non-enforceable concentration of a drinking water contamination that is protective of adverse human health effects and allows an adequate MOS.
- <sup>2</sup> Maximum Contamination Level – Maximum permissible level of contamination in water, which is delivered to any user of public water system.
- <sup>3</sup> Drinking Water Equivalent Level – A lifetime exposure concentration protective of adverse, noncancer health effects, that assumes all of the exposure to a contaminant that is from a drinking water source.
- <sup>4</sup> One-day health advisory – concentration of a chemical in drinking water that is not expected to cause any adverse non carcinogenic effects for up to 5 consecutive days of exposure, with a MOS.
- <sup>5</sup> Ten-day health advisory – same as one day HA for up to 14 consecutive days of exposure, with MOS
- <sup>6</sup> Longer Term health advisory – same as one day HA for up to 7 years (10% of lifetime of exposure) consecutive exposure, with MOS.
- <sup>7</sup> Lifetime health advisory – same as one day health advisory for a lifetime of exposure, with MOS.

Reference: USEPA, 1988

**Table 4: Endothall Risk Assessment Noncarcinogenic Parameters**

(Doses represent endothall acid)

Effect	Study	NOEL	LEL	Reference
Systemic Toxicity	Chronic 2-Yr Rat Dietary Doses: 0, 2, 6 or 16 mg/kg/dy	2.0 mg/kg/dy	16.0 <sup>a</sup>	Keller, 1965
Reproduction Toxicology	Rat 3-Generation Dietary Doses: 0, 4, 12 or 100 mg/kg/dy	4.0 mg/kg/dy	12 <sup>b</sup>	Scientific Associates, 1965
Teratology	Rats dosed on days 6-15 gestation Doses: 0, 4.4, 8.8, 17.5 mg/kg/dy	Developmental effects 17.5 Maternal toxicity 8.8	>17.5 17.5 <sup>c</sup>	Trutter, 1995

<sup>a</sup>Increase in stomach and small intestine weights due to irritation produced by test material.

<sup>b</sup>Reduced pup survival

<sup>c</sup>Signs of maternal toxicity included decreases in body weight and food consumption

**Table 5: Swimming: Endothall Aquatic Exposure and Risk Assessment Parameters**

SUBJECTS			
Age	Weight (kg)	Pounds	Body Surface Area (cm <sup>2</sup> )
6 years	22	48	8,800
10 years	35	77	12,000
Adult	70	154	18,000
WATER EXPOSURE TIME (hours)			
0.5			
1.0			
2.0			
3.0			
AMOUNT OF WATER INGESTED DURING SWIMMING			
25 ml/0.5 hours			
50 ml/ 1 hour			
100 ml/ 2 hours			
150 ml/ 3 hours			
ENDOTHALL CONSTANTS			
Maximum use-rate = 5.0 ppm or 5 mg/liter of water or 5 mg/1000 cm <sup>3</sup>			
Typical use rate = 2-3 ppm			
Permeability Coefficient (skin) = $8 \times 10^{-4}$ cm/hr			
Octanol/Water Partition Coefficient = 0.008			
Vapor pressure = $3.92 \times 10^{-5}$ mmHg			
HALF-LIVES			
Laboratory Aerobic Aquatic = 10 days			
Laboratory Anaerobic Aquatic = 8 ½ days			
Pond water = 6 days			
Pond water with aquatic plants = 4.1 – 7.3 days			

**Table 6: Swimming: Endothall Oral Exposure And Risk Assessment\***

Age (yrs)	Wt (kg)	Exposure Time (hrs)	Water Ingested (mls)	Endothall Total Exposure (ugs)	Daily Oral Dose (ug/ml/kg)	Margin of Safety		
						Systemic 2000 ug/kg/dy	Repro 4000ug/kg/dy	%RfD (ug/kg/dy)
<b>5 ppm use-rate</b>								
6	22	0.5	25	125	5.7	351	702	28.5
		1.0	50	250	11.4	175	351	57.0
		2.0	100	500	22.7	88	176	113.5
		3.0	150	750	34.1	59	118	170.0
10	35	0.5	25	125	3.6	556	1112	18.0
		1.0	50	250	7.1	282	564	35.5
		2.0	100	500	14.3	140	280	71.5
		3.0	150	750	21.4	93	187	107
Adults	70	0.5	25	125	1.8	1176	2354	9.0
		1.0	50	250	3.6	556	1112	18
		2.0	100	500	7.1	282	564	35.5
		3.0	150	750	10.7	187	374	53.5
<b>3 ppm use-rate</b>								
6	22	0.5	25	75	3.4	588	1176	17
		1.0	50	150	6.8	294	596	34
		2.0	100	300	13.6	147	294	68
		3.0	150	450	20.5	98	196	103
10	35	0.5	25	75	2.1	952	1904	11
		1.0	50	150	4.3	465	930	22
		2.0	100	300	8.6	233	466	43
		3.0	150	450	13.0	154	308	65
Adult	70	0.5	25	75	1.1	1818	3636	6
		1.0	50	150	2.1	952	1904	11
		2.0	100	300	4.3	465	930	22
		3.0	150	450	6.4	313	626	32

**Table 6: Swimming: Endothall Oral Exposure And Risk Assessment\* (Continued)**

\*Oral Exposure (OE) = Exposure Time (hrs) x 50 ml (water ingested/hr) x Endothall water con. (ppm)  
= Endothall exposure (mg/day)  
Oral Dose (OD) = OE / Body Weight (kg)  
= Endothall Dose (mg/kg/dy or converted as above to ug/kg/dy)

**Table 7: Swimming: Endothall Dermal Exposure And Risk Assessment\***

Total Dermal Exposure (TDE mg/day) = Exposure time (hrs) x SA x Flux Rate							
Total Dermal Dose (TDD mg/kg/dy) = TDE / BW							
ET = Exposure Time (0.5, 1.0, 2.0 or 3.0 hours swimming/day)							
SA = Total Body Surface Area (cm <sup>2</sup> )							
Flux Rate = permeability coefficient x endothall water concentration (1 x 10 <sup>-4</sup> ) x 5.0 ppm or ug/ml = 5 x 10 <sup>-7</sup> mg/cm <sup>2</sup> /hr							
TDD = Total Daily Endothall Exposure / Body Weight (expressed below in ug/kg/day)							
BW = Body Weight (kg)							
Age (yrs)	Wt (kg)	Exposure time (hrs)	Body surface area (cm <sup>2</sup> )	Flux rate	Dose/day dermal (ug/kg/day)	Margin of safety	
						Systemic 2000 ug/kg/day	Repro Tox 4000 ug/kg/day
6	22	0.5	8,800	5 x 10 <sup>-7</sup>	0.1	20,000	40,000
		1.0			0.2	10,000	20,000
		2.0			0.4	5,000	10,000
		3.0			0.6	3,333	6,667
10	35	0.5	12,000	5 x 10 <sup>-7</sup>	0.09	22,222	44,444
		1.0			0.17	11,765	23,537
		2.0			0.34	5,882	11,768
		3.0			0.51	3,922	7,846
Adult	70	0.5	18,000	5 x 10 <sup>-7</sup>	0.06	33,333	66,687
		1.0			0.13	15,385	30,779
		2.0			0.26	7,692	15,389
		3.0			0.39	5,128	10,260

\*Due to the low amounts of the endothall dermal doses calculated for the 5 ppm use-rate, no calculations were conducted to determine doses at the 3 ppm use-rate.

**Table 8: Swimming: Endothall Inhalation Exposure And Risk Assessment\***

<p>Total Inhalation Exposure (TIE mg/dy) = Cvp x ET x IR x C</p> <p>Total Inhalation Dose (TID mg/kg/dy) = TIE / BW</p> <p>Cvp = Vapor concentration of Endothall in water          = Cw x Pvp x 273oK x 0.8 / (760 mmHg x Ta oK)</p> <p>Cw = Concentration of endothall in water</p> <p>Pvp = Endothall vapor pressure</p> <p>Ta = Actual temperature (303oK = 86oF)          = 5 mg/L x 3.92 x 10-5 mmHg x 273oK x 0.8 / 760 mmHg x 303oK          = 1.9 x 10-7 mmHg</p> <p>ET = Exposure time (hrs)</p> <p>IR = Inhalation rate [40 liters/min- 6 yr.; 50 liters/min- 10 yr.; 65 liters/min- adult]</p> <p>C = Unitless constant based on the concentration of endothall in water</p>							
Age (yrs)	Wt (kg)	Vp	Exposure Time (mins)	Inhale Rate	Dose/Day Inhalation (ug/kg/day)	Margin of Safety	
						Systemic 2000 ug/kg/day	Repro Tox 4000 ug/kg/day
6	22	1.9 x 10-7	30	40	0.05	40,000	100,000
			60		0.11	18,182	45,455
			120		0.22	9,091	22,727
			180		0.33	6,061	15,152
10	35	1.9 x 10-7	30	50	0.04	50,000	125,000
			60		0.09	22,222	55,556
			120		0.17	11,765	29,412
			180		0.26	7,692	19,231
Adult	70	1.9 x 10-7	30	65	0.03	66,667	166,667
			60		0.06	33,333	83,333
			120		0.11	18,182	45,455
			180		0.17	11,765	29,412

\*Due to the low amounts of the endothall inhalation doses calculated for the 5 ppm use-rate, no calculations were conducted to determine doses at the 3 ppm use-rate.

**Table 9: Swimming: Endothall Oral Sediment Exposure and Risk Assessment**

Chronic daily intake of incidental ingestion of sediment is estimated as follows (USEPA Region 10 Guidance, 1991):

$$\text{Intake (mg/kg/day)} = \text{CS} \times \text{CF1} \times \frac{\frac{\text{IRc} \times \text{EF} \times \text{Edc}}{\text{BWc}} + \frac{\text{IRa} \times \text{EF} \times \text{EDa}}{\text{BWa}}}{\text{ATc} \times \text{CF2}}$$

CS = contaminant concentration in sediment (mg/kg)

CF1 = conversion factor (0.000001 kg/mg)

CF2 = conversion factor (365 days/year)

IRc = intake rate, child (200 mg/day)

IRa = intake rate, adult (100 mg/day)

EF = exposure frequency (22 days/year)

EDc = exposure duration, child (6 years)

EDa = exposure duration, adult (24 years)

BWc = body weight, child (22 kg)

BWa = body weight, adult (70 kg)

AT = Averaging time (30 years x 365 days/year = 10,950 days)

Based on the above formula the calculated endothall exposure received from ingestion of sediment from swimming in a body of water treated at the maximum use rate of 5 ppm and containing 2.0 mg endothall/kg sediment (Keckemet and Sharp, 1999), would be approximately  $9.8 \times 10^{-6}$  ug/kg/day. Oral exposure to sediment contaminated with endothall from aquatic herbicidal treatment is insignificant in comparison with the herbicide doses received from other routes and types of exposure.

**Table 10: Swimming: Endothall Dermal Sediment Exposure and Risk Assessment**

The following calculations are derived from the EPA formula for determining acute dermal exposure to endothall from skin contact with sediments in water treated at the maximum use rate of 5 ppm. The assumed concentration of endothall in the sediment is 2.0 mg/kg, based on the analyses listed by Keckemet and Sharp (1999). Dermal absorption is estimated to be 7% of the applied dose being absorbed over 24 hours (Johnson, 1990).

$$\text{Dermal Dose (mg/kg)} = \frac{C_s \times C_F \times S_A \times A_F \times A_B S}{B_W}$$

- C<sub>s</sub> = concentration in sediment (2.0 mg/kg)
- C<sub>F</sub> = conversion factor (0.000001 kg/mg)
- S<sub>A</sub> = surface area exposed – feet and lower legs (1840 cm<sup>2</sup>)
- A<sub>F</sub> = adherence factor (0.95 mg/cm<sup>3</sup>)
- A<sub>B</sub>S = absorption factor (7.0%)
- B<sub>W</sub> = body weight (calculated for 22, 35 and 70 kg persons)

$$\begin{aligned} \text{Dermal Dose} &= \frac{2.0 \times 0.000001 \times 1840 \times 0.95 \times 0.07}{B_W} \\ &= 0.0002447 / B_W \end{aligned}$$

Age (yrs)	Wt(kg)	Endothall Dose (ug/kg/dy)	Margin of Safety	
			Systemic	Reproduction Tox
6	22	0.011	181,818	363,636
10	35	0.007	285,714	571,429
Adult	70	0.003	666,667	1,333,333

**Table 11: Swimming: Endothall Total Sediment Exposure and Risk Assessment**

Total Sediment Exposure = Oral Exposure + Dermal Exposure (mg/kg/dy)                      (mg/kg/dy)                      (mg/kg/dy)						
Age (yrs)	Wt (kg)	Oral Sediment Exp (ug/kg/dy)	Dermal Sediment Exp (ug/kg/dy)	Total Dose (ug/kg/dy)	Margin of Safety	
					Systemic 2000 ug/kg/dy	Repro Tox 4000 ug/kg/dy
6	22	0.00017	0.0095	0.0097	206,186	412,371
10	35	0.00017	0.0059	0.0061	327,869	655,738
Adult	70	0.00017	0.0029	0.0031	645,161	1,290,323

**Table 12: Swimming: Endothall Total Exposure and Assessment**

TOTAL ENDOTHALL EXPOSURE = Total Oral + Total Dermal + Total Inhalation + Total Sediments (ug/kg/dy)

Age	Wt	Exp Time	Oral (ug/kg/dy)	% tot exp	Dermal (ug/kg/dy)	Inhal (ug/kg/dy)	Sediment (ug/kg/dy)	Total (ug/kg/dy)	Margin of Safety		% of RfD
									2000 ug/kg/dy	4000 ug/kg/dy	
5.0 ppm use-rate											
6	22	0.5	5.7	97	0.1	0.05	0.0097	5.85	342	855	29
		1.0	11.4	97	0.2	0.11	0.0097	11.71	171	427	59
		2.0	22.7	97	0.4	0.22	0.0097	23.32	86	214	117
		3.0	34.1	97	0.6	0.33	0.0097	35.03	57	143	175
10	35	0.5	3.6	96.5	0.09	0.04	0.0061	3.73	536	1,340	19
		1.0	7.1	96.5	0.17	0.09	0.0061	7.36	272	679	37
		2.0	14.3	96.5	0.34	0.17	0.0061	14.81	135	270	74
		3.0	21.4	96.5	0.51	0.26	0.0061	22.17	90	180	111
Adult	70	0.5	1.7	95	0.06	0.03	0.0031	1.79	1,117	2,235	9
		1.0	3.6	95	0.13	0.06	0.0031	3.79	528	1,055	19
		2.0	7.1	95	0.26	0.11	0.0031	7.47	268	535	37
		3.0	10.7	95	0.39	0.17	0.0031	11.26	178	355	56
3.0 ppm use-rate											
6	22	0.5	3.4	97	*	*	*	3.5	571	1,142	18
		1.0	6.8	97				7.0	286	572	35
		2.0	13.6	97				14.0	144	289	70
		3.0	20.5	97				21.1	96	191	150
10	35	0.5	2.1	96.5	*	*	*	2.2	918	1,836	11
		1.0	4.3	96.5				4.5	449	898	23
		2.0	8.6	96.5				8.9	227	454	45
		3.0	13.5	96.5				13.5	150	299	68
Adult	70	0.5	1.1	95	*	*	*	1.2	1,683	3,367	6
		1.0	2.1	95				2.2	918	1,836	11
		2.0	4.5	95				4.5	449	898	23
		3.0	6.4	95				6.7	301	603	34

\*Total doses calculated by adding 3, 3.5 and 5% of oral doses to oral doses of 22, 35 and 70 kg groups, respectively.

**Table 13: Endothall Exposure and Risk Assessment Drinking Potable Water**

PARAMETERS:						
Maximum Contaminant Level (MCL) = 100 ug endothall/liter water						
Drinking Water Intake/Day						
6 year old = 1000 ml or 1.0 liters						
10 “ “ = 1000 ml or 1.0 liters						
Adult = 2000 ml or 2.0 liters						
Age	Wt	Endothall Exposure (ug)	Water Dose (ug/kg/dy)	Margin of Safety		
				Systemic 2000 ug/kg/dy	Repro Tox 4000 ug/kg/dy	% RfD
6	22	100	4.5	444	889	23
10	35	100	2.9	690	1,379	15
Adult	70	200	2.9	690	1,379	15

**Table 14: Endothall Exposure and Risk Assessment Drinking Treated Surface Water**

<p>ORAL EXPOSURE (OE) = IR x WC</p> <p>ORAL DOSE (OD) = OE / BW</p> <p>OE = Oral Exposure (ug/day)                  IR = Ingestion Rate (6 and 10 year olds 1 liter/day; adult 2 liters/day)                  WC = Water Concentration (5.0 and 3.0 ppm or ug/ml)                  OD = Oral Dose (ug/kg/dy)                  BW = Body Weight (kg)</p>							
Age (Yrs)	Wt (Kg)	IR (L/dy)	OE (ug/kg/dy)	OD (ug/kg/dy)	Margin of Safety		
					Systemic 2000 ug/kg/dy	Repro tox 4000 ug/kg/dy	% of RfD
5.0 ppm Use-Rate							
6	22	1	5,000	227	9	18	1,135
10	35	1	5,000	143	14	28	715
Adult	70	2	10,000	143	14	28	715
3.0 ppm Use-Rate							
6	22	1	3,000	136	15	30	680
10	35	1	3,000	86	23	46	430
Adult	70	2	6,000	86	23	46	430

**Table 15: Endothall Exposure and Risk Assessment Ingestion of Fish**

1. Endothall does not bioconcentrate in edible tissue of fish.
2. Typical analytical level detected in fish from recently treated water has been reported to contain 0.04 mg/kg or 40 ug/kg (Serns, 1977)
3. Human fish consumption (USEPA, 1989):
  - 70 kg person fish intake/meal = 0.4 kg
  - 35 “ “ “ “ = 0.2 kg
  - 10 “ “ “ “ = 0.06 kg

Age	Wt	Fish Meal Wt (kg)	Endothall Exposure (ug)	Dose (ug/kg/dy)	Margin of Safety		
					Systemic 2000 ug/kg/dy	Repro Tox 4000 ug/kg/dy	% of RfD
6	22	0.06	2.4	0.11	0.5	18,181	36,363
10	35	0.2	8.0	0.23	1.1	8,696	17,391
Adult	70	0.4	16.0	0.23	1.1	8,696	17,391

**Table 16: Total Calculated Daily Exposure and Risk Assessment - Drinking Potable Water**

Age	Wt	Exposure Time (hrs)	Swim Dose (ug/kg/dy)	Water Dose* (ug/kg/dy)	Fish Dose (ug/kg/dy)	Total Dose (ug/kg/dy)	Margin of Safety		
							Systemic 2000 ug/kg/dy	Repro Tox 4000 ug/kg/dy	% of RfD
<b>5.0 ppm Use-Rate</b>									
6	22	0.5	5.85	4.5	0.3	10.65	188	376	53
		1.0	11.71	“	“	16.51	121	242	83
		2.0	23.32	“	“	28.12	71	142	141
		3.0	35.03	“	“	39.83	50	100	199
10	35	0.5	3.73	2.9	0.3	6.93	287	577	35
		1.0	7.36	“	“	10.56	189	379	53
		2.0	14.81	“	“	18.05	111	222	90
		3.0	22.17	“	“	25.37	79	158	127
Adult	70	0.5	1.79	2.9	0.3	4.99	400	802	25
		1.0	3.79	“	“	6.99	286	572	35
		2.0	7.47	“	“	10.67	187	375	53
		3.0	11.26	“	“	14.46	138	277	72
<b>3.0 ppm Use-Rate</b>									
6	22	0.5	3.5	4.5	0.3	8.3	241	482	42
		1.0	7.0	“	“	11.8	169	339	59
		2.0	14.0	“	“	18.8	106	213	94
		3.0	21.1	“	“	25.9	77	154	130
10	35	0.5	2.2	2.9	0.3	5.4	370	740	27
		1.0	4.5	“	“	7.7	260	519	39
		2.0	8.9	“	“	9.1	220	440	46
		3.0	13.5	“	“	16.7	120	239	84
Adult	70	0.5	1.2	2.9	0.3	4.4	455	909	22
		1.0	2.2	“	“	5.4	370	741	27
		2.0	4.5	“	“	7.7	260	519	39
		3.0	6.7	“	“	9.9	202	404	50

\* = Represents endothall exposure from potable drinking water (MCL = 100 ug/L)

**Table 17: Total Calculated Daily Exposure and Risk Assessment - Drinking Treated Surface Water**

Age	Wt	Exposure time (hrs)	Swim Dose (ug/kg/dy)	Water Dose* (ug/kg/dy)	Fish Dose (ug/kg/dy)	Total Dose (ug/kg/dy)	Margin of Safety		
							Systemic 2000 ug/kg/dy	Repro Tox 4000 ug/kg/dy	% of RfD
<b>5.0 ppm Use-Rate</b>									
6	22	0.5	5.85	227	0.14	233	9	18	1,165
		1.0	11.71			239	8	16	1,194
		2.0	23.32			250	8	16	1,252
		3.0	35.03			262	7.6	15	1,311
10	35	0.5	3.73	143	0.3	147	14	28	735
		1.0	7.36			151	13	26	753
		2.0	14.81			158	12.6	25	754
		3.00	22.17			166	12	24	828
Adult	70	0.5	1.79	143	0.3	145	14	28	725
		1.0	3.79			147	13.6	27	735
		2.0	7.47			151	13	26	754
		3.0	11.26			158	12.6	25	789
<b>3.0 ppm Use-Rate</b>									
6	22	0.5	3.5	136	0.14	140	14	28	698
		1.0	7.0			143	14	28	715
		2.0	14.0			150	13	26	750
		3.0	21.1			157	13	26	785
10	35	0.5	2.2	86	0.3	89	23	46	443
		1.0	4.5			91	22	44	455
		2.0	8.9			95	21	42	476
		3.0	13.5			100	20	40	499
<b>3.0 ppm Use-Rate</b>									
Adult	70	0.5	1.2	86	0.3	88	23	46	440
		1.0	2.2			89	22.6	45	442
		2.0	4.5			91	22	44	454
		3.0	6.7			93	21.5	43	465

\* = Represents endothall exposure from drinking treated surface water