ERDC/EL TR-02-11

Environmental Laboratory

US Army Corps
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Aquatic Plant Control Research Program

Review of USACE-Generated Efficacy and Dissipation Data for the Aquatic Herbicide Formulations Aquathol® and Hydrothol®

Susan L. Sprecher, Kurt D. Getsinger, and Jan Sharp

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Final report

Prepared for U.S. Army Corps of Engineers
Washington, DC 20314-1000
and Aquatic Ecosystem Restoration Foundation
Lansing, MI 48917-4048

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Preface

The work reported herein was conducted as part of the Aquatic Plant Control Research Program (APCRP), Work Unit 74001, and a special project through the Aquatic Ecosystem Restoration Foundation (AERF). The APCRP is sponsored by Headquarters, U.S. Army Corps of Engineers (HQUSACE), and is assigned to the U.S. Army Engineer Research and Development Center (ERDC) under the purview of the Environmental Laboratory (EL), Vicksburg, MS. Funding was provided under Department of Army Appropriation No. 96X3122, Construction General. Support was also provided by the AERF. The APCRP is managed under the Center for Aquatic Plant Research and Technology (CAPRT), Dr. John Barko, Director. Mr. Robert C. Gunkel, Jr., was Assistant Director, CAPRT. Program monitor during this work was Mr. Timothy R. Toplisek, HQUSACE.

The Principal Investigator of this work was Dr. Kurt D. Getsinger, Environmental Processes Branch (EPB), Environmental Processes and Engineering Division (EPED), EL, ERDC. This work was conducted and report prepared by Dr. Getsinger, Dr. Susan L. Sprecher, EPB, and Dr. Jan Sharp, Cerexagri, Inc. Technical reviews of this report were provided by Mr. Christopher Davis, Cerexagri, Inc., and Ms. Toni Pennington, Portland State University.

This work was performed under general supervision of Dr. Edwin A. Theriot, Director, EL; Dr. Richard E. Price, Chief, EPED; and Dr. Terrence Sobecki, Chief, EPB.

At the time of publication of this report, Director of ERDC was Dr. James R. Houston; Commander and Executive Director was COL John W. Morris III, EN.

This report should be cited as follows:

> Sprecher, S. L., Getsinger, K. D., and Sharp, J. (2002). "Review of USACE-generated efficacy and dissipation data for the aquatic herbicide formulations Aquathol® and Hydrothol®," ERDC/EL TR-02-11, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

1 Introduction

Herbicidal Properties

The herbicidal properties of endothall (7-oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid[1]; $C_8H_{10}O_5$; Figure 1) and its action as a defoliant and desiccant on terrestrial plants were first described in 1950 (Keckemet 1969). Endothall is a contact-type membrane-active herbicide that rapidly produces symptoms of defoliation and desiccation in terrestrial plant parts with which it comes in contact by disrupting solute transport processes in plant cells (Maestri 1967; Weed Science Society of America (WSSA) 1994). Endothall penetrates plant cuticles rapidly and is absorbed by roots; however, translocation is limited to the symplast (intra-cellular) and the compound is not phloem-mobile (MacDonald, Shilling, and Bewick 1993;WSSA 1994). Aquatic plants have similar symptoms to terrestrial plants, of defoliation and necrotic tissue, with death or peak injury usually occurring within 4 to 6 weeks of initial treatment. MacDonald, Shilling, and Bewick (1993) showed that endothall primarily acts to inhibit respiration, but the compound also has various physiological effects on different plant species, inhibiting lipid and protein synthesis, or causing increased ion leakage symptomatic of membrane disruption.

Endothall's ability to affect aquatic algae and macrophytic plants was discovered in 1953, and it was registered in the United States (U.S.) as an aquatic herbicide with the U.S. Department of Agriculture in 1960 (Keckemet 1969).

Aquatic Formulations

For use as an aquatic herbicide in the United States, the free organic diacid endothall is formulated as two of its salts (Figure 1) and provided as water-based concentrates and dry granular materials or granules. The currently available aquatic endothall formulations are registered for application to water by the U.S. Environmental Protection Agency (USEPA) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of 1974. The inorganic dipotassium salt is the active ingredient of the commercial Aquathol® K herbicides, used predominantly for lake and static water treatments to control aquatic macrophytes. They are available as Aquathol® K Aquatic Herbicide (soluble

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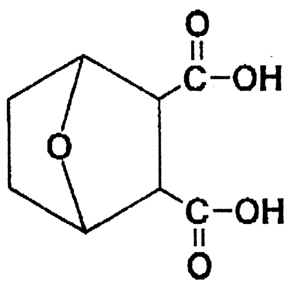
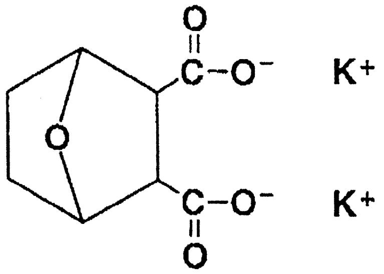
[1] Also known as endothal. The term 3,6-endoxohexahydrophthalic acid has been applied to endothall but is not regarded as the proper nomenclature (Keckemet 1969).

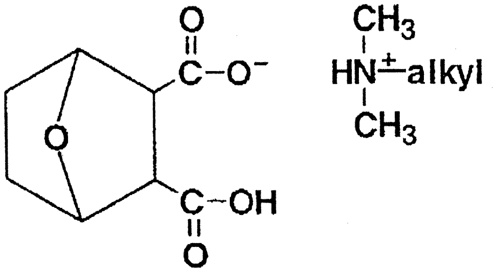
concentrate; USEPA Reg. No. 4581-204), Aquathol® K Granular Aquatic Herbicide (USEPA Reg. No. 4581-201), and, since 1998, as the Aquathol® Super K Granular Aquatic Herbicide (USEPA Reg. No. 4581-388), a concentrated granule formulated in the Culigel® super absorbent polymer (Elf Atochem 1996a, 1998b,c). The mono(*N,N*-dimethylalkylamine) endothall salt is registered as the liquid Hydrothol® 191 Aquatic Algicide and Herbicide (USEPA Reg. No. 4581-174) and as Hydrothol® 191 Granular Aquatic Algicide and Herbicide (USEPA Reg. No. 4581-172; Elf Atochem 1996b, 1999). 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.



Endothall diacid



Endothall dipotassium salt



Endothall mono(N,N-dimethylalkylamine) salt

Figure 1. Chemical structure of endothall and its salts
Endothall is a relatively simple structure and consists only of carbon, hydrogen, and oxygen.
Common name: Endothall acid
CAS Registry No.: 145-73-3
Chemical name: 7-oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid
Empirical formula: $C_8H_{10}O_5$
Molecular weight: 186

There are significant differences between the two types of endothall herbicide in their activity on plants and other aquatic organisms. The dimethylalkylamine salts (Hydrothol® 191) are generally two to three times more active on aquatic algae and macrophytes than the inorganic dipotassium salts. However, this effectiveness on aquatic macrophytes is accompanied by relatively greater toxicity to nontarget aquatic organisms, and this amine is 200 to 400 times more toxic to fish than the inorganic dipotassium salt (Aquathol® K), which has very low toxicity to aquatic vertebrates (Keckemet 1969; WSSA 1994). Keckemet notes that the amine salts are used with few detrimental effects on fish because: (a) part of the dimethylalkylamine is quickly adsorbed and decomposed by plants and soil; (b) fish detect the compound and will move into those portions of the waterbody left untreated as recommended in the label application directions; and (c) in flowing water systems such as canals, concentrations decrease rapidly.

Particulars associated with the current USEPA registration of these herbicides, recommended rates for a range of target species, and descriptions of application procedures are available on their labels (Elf Atochem 1996a,b, 1998b,c,f, 1999). Details of physical and chemical properties pertaining to safe handling are shown on the Material Safety Data Sheets (MSDS) of each product (Elf Atochem 1997, 1998a,d,e,f). Adjuvants, such as organic solvents or emulsifiers are not required for application of these endothall herbicides. However, adjuvants have been investigated and recommended by the Corps in certain situations (Steward 1979; Getsinger and Westerdahl 1988).

Endothall aquatic herbicides have been manufactured in the United States by the Pennsalt Corporation (Montgomery, AL), the Pennwalt Corporation (Philadelphia, PA), and Elf Atochem North America, Inc. (Philadelphia, PA). Commercial formulations are currently the products of Cerexagri, Inc. (Philadelphia, PA), which handles Aquathol® and Hydrothol® 191 through its Agrichemicals Group. Formulations of endothall have been commercially available or evaluated for aquatic use in the past include the disodium salt (Aquathol®) and the mono(*N,N*-dimethylalkylamine) granule Hydout®, which was available in the 1970s and 80s and registered under FIFRA Section 24(c), with a Special Local Needs label (Westerdahl 1983a,b). These compounds are summarized in Table 1.

Table 1
Endothall Aquatic Herbicide Formulations

Trade Name and Type	Endothall Active Ingredient	Concentration of Active Ingredient	Concentration of Acid Equivalent (ae)
AQUATHOL® K Aquatic Herbicide (soluble concentrate)	Dipotassium salt	40.3% 507 g L^{-1} (4.23 lb gal^{-1})	28.6% 360 g ae L^{-1} (3.0 lb ae gal^{-1})
AQUATHOL® Granular Aquatic Herbicide (granule)	Dipotassium salt	10.1%	7.2%
AQUATHOL® SUPER K Granular Aquatic Herbicide (granule)	Dipotassium salt	63.0%	44.7%
HYDOUT (slow-release pellet)	Mono(*N,N*-dimethylalkyl-amine) salt		10%
HYDROTHOL 47 (granule)	Di(*N,N*-dimethyl-alkylamine) salt	47%	
HYDROTHOL® 191 Aquatic Algicide and Herbicide (soluble concentrate)	Mono(*N,N*-dimethylalkylamine) salt	53.0%	23.36% 240 g ae L^{-1} (2 lb ae gal^{-1})
HYDROTHOL® 191 Granular Aquatic Algicide and Herbicide (granule)	Mono(*N,N*-dimethylalkylamine) salt	11.2%	5%

Objectives

Since the 1970s, the U.S. Army Corps of Engineers (CE) Aquatic Plant Control Research Program (APCRP), headquartered at the U.S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory, Vicksburg, MS, has carried out research on the efficacy, performance, and dissipation of various formulations of endothall against target and nontarget aquatic plant species. This body of research, often undertaken in cooperation with other Federal and state agencies, universities, and industry, has provided valuable information on the ability of this herbicide to control and manage nuisance aquatic vegetation under static and flowing water conditions and on the fate of endothall in the aquatic environment. Data generated in some of these studies have been used by industry to fulfill requirements for U.S. and state registration or reregistration of specific herbicide formulations.

The objective of this report is to provide a review and summary of studies directed and conducted by the Corps of Engineers on the aquatic uses of endothall over the past 3 decades. This summary will include a discussion on the efficacy of endothall against invasive weed species, as well as selected nontarget plants, and how efficacy is based upon application rates and techniques, water-exchange characteristics, and herbicide exposure time mechanisms. Information from growth chamber, mesocosm, and field studies will be provided to link effective plant control to endothall concentration/exposure time relationships. In addition, this summary will focus on the degradation and dissipation of endothall under field conditions and how those processes relate to selective plant control and potential impacts to the aquatic environment.

2 Evaluations of Endothall Efficacy

The CE has funded and carried out studies on aquatic efficacy of endothall since the early 1970s. These studies originally focused on suitable concentrations for controlling target plant species (Blackburn, Boyer, and Timmer 1971, Steward 1979, Westerdahl 1983a,b). More recent work has addressed minimizing application rates by identifying threshold concentration and exposure time combinations for aquatic plant control in static and flowing water conditions (Van and Conant 1988; Green 1989; Netherland 1990; Netherland 1991a; Netherland, Green, and Getsinger 1991a,b; Getsinger and Netherland 1997), and efficient delivery systems and application methods for flowing water (Dunn et al. 1988; Fox and Haller 1990; Getsinger 1991; Fox and Haller 1992; Fox, Haller, and Getsinger 1988, 1989, 1991a,b, 1993; Turner et al. 1993; Turner, Getsinger, and Burns 1996; Netherland and Sisneros 1994; Netherland et al. 1994; Netherland and Turner 1995; Getsinger and Netherland 1997). Current research is involved in evaluating the ability of endothall used at selective rates to control target weeds without removing desirable plant species from aquatic ecosystems (Skogerboe and Getsinger 1998, 1999), and in investigating effects of water temperature on endothall activity (Netherland et al. 2000).

Comparison of concentration among herbicide formulations is often based on amount of active ingredient (ai) of compound, regardless of carriers, inert materials, etc. With endothall, acid equivalency (ae) units are also used to allow comparisons of concentration among different salts of the parent acid, since the dipotassium and dimethylalkylamine salts are converted to endothall acid upon entering water. Aquathol® K, for example, produces an acid equivalency concentration of 70 percent of a given concentration of the dipotassium salt active ingredient (Elf Atochem 1998b). Usage rate recommendations for Hydrothol® 191 are given as concentrations of endothall acid, or acid equivalents (Elf Atochem 1998e). Either ai or ae units are used to describe endothall application rates in technical and scientific evaluations, usually depending on whether commercial formulations or technical grade compounds were used. These are reported, where known, herein.

In most of the work reviewed here, efficacy or control is measured as percent reduction in viable biomass compared to plant material in untreated (reference or control) experimental units.

The principal species for which the Corps of Engineers has produced endothall efficacy data have been hydrilla (*Hydrilla verticillata* (L.f.) Royle; Hydrocharitaceae) and Eurasian watermilfoil (*Myriophyllum spicatum* L.; Haloragaceae). Hydrilla, a native of the Old World, is one of the most competitive species of submersed aquatic vegetation. It is found as far north as Connecticut in North America and is a noxious weed particularly along the U.S. Gulf Coast. Eurasian watermilfoil is also an invasive exotic with nuisance status in the central and northern states of the United States and in parts of Canada. To date, the Corps of Engineers has directed its endothall efficacy research only to aquatic macrophytes and has not investigated the algicidal properties of these herbicides.

Early Efficacy Studies

Blackburn, Boyer, and Timmer (1971) showed that the dimethylalkylamine salt of endothall was more effective on hydrilla than the dipotassium salt and that speed of herbicidal activity and length of control varied with formulation. The authors compared liquid, technical, granule, and experimental controlled release pellet formulations of Hydrothol® with liquid dipotassium endothall (Aquathol® K) in laboratory, mesocosm, and field experiments for control of hydrilla, measured as percent reduction in plant biomass compared to untreated material. In laboratory evaluations, Hydrothol® liquid was initially two- to four-fold more phytotoxic to hydrilla than dipotassium endothall and acted more rapidly than the other dimethylalkylamine formulations. In mesocosm (4.4-m^3 volume) populations, technical Hydrothol® and the commercial liquid at 2.0 parts per million by weight (mg ai L^{-1}) removed 100 percent of hydrilla, as well as *Naias guadalupensis* (Spreng.) Magnus.(southern naiad), by 4 weeks posttreatment, and maintained 95 to 100 percent control through 12 weeks. However, mortality of stocked bluegill sunfish (*Lepomis macrochirus*) was 100 percent. Granular Hydrothol® at the same treatment rate achieved a maximum of 85 percent control at 12 weeks, with fish mortality of 65 percent. The controlled release pellet applied at this rate gave optimum performance by removing 98 percent of plants by 8 weeks and maintaining 100 percent control through 20 weeks, with no mortality of fish. This was attributed to slow release of herbicide and a subsequent slow plant kill that did not deplete oxygen levels in water. Applications in the field also demonstrated that granules and pellets maintained effective concentrations over longer periods of time than did liquids and that Hydrothol® was significantly more effective on hydrilla than dipotassium endothall. Controlled release pellets at 2.0 mg ai L^{-1} maintained ≥ 92-percent control for 4 months, while 4.5 mg ai L^{-1} dipotassium endothall never exceeded the 68-percent control level reached at 1-month posttreatment.

Steward (1979) evaluated lower rates of dipotassium endothall for hydrilla control in laboratory studies. Concentrations of 0.1, 0.25, and 0.5 mg ai L^{-1} did not produce significant control of hydrilla, but 1.0 mg ai L^{-1} controlled 89 percent of hydrilla by 8 weeks and maintained ≥ 95-percent control from 10 through 14 weeks. Addition of the adjuvant SA-77 (D-limonene and emulsifiers: JLB International Chemicals, Inc., Hialeah, FL) provided complete and significantly more rapid control at all these endothall concentrations.

The phytotoxicity determined in these laboratory and mesocosm exposures was in response to static exposures; contact times were not varied or curtailed by removing or dissipating herbicide following treatment. Field exposures allow studies to address the process pertaining in most operational situations where maximum application concentrations are expected to be present for only a limited time as herbicide dissipates continuously with normal water exchange and degradation processes through the treated area.

The Lake Gatun Study

In 1979, the Pennwalt Corporation, the Panama Canal Commission, and the Corps of Engineers cooperated on a field study evaluating endothall for control of hydrilla in Gatun Lake, Panama (Westerdahl 1983a,b). Objectives of the study were to (a) evaluate efficacy for hydrilla control of two endothall formulations, the soluble concentrate Aquathol® K and the slow-release pellet Hydout®, which consisted of dimethylalkylamine endothall salt-impregnated clay (Table 1); (b) determine their effects on water quality and nontarget planktonic organisms; (c) evaluate herbicide dispersion; and (d) determine persistence of herbicide residues in water, hydrilla plant tissue, and sediment within the test areas. At that time, Hydout® was registered under a Section 24(c) permit of the 1974 FIFRA for use in Alabama, Florida, Georgia, and Texas, and an application for U. S.-wide registration (Section 3 Label) had been submitted to the USEPA.

The Lake Gatun study comprised eight experimental plots in the Frijoles Bay area, from 1.2 to 1.8 ha in area and 4 to 8 m in depth, each with an estimated cover of 90-percent hydrilla. Water was considered soft, with low alkalinity, and rapid phytotoxicity was expected under these conditions. Treatment rates of 27, 34, and 50 kg ae ha^{-1} surface area were projected to give aqueous concentrations of approximately 1.0, 1.5, and 2.0 mg ae L^{-1}, based on a mean water depth of 3.5 m in all plots, and on endothall acid equivalency of 29 percent by weight for the liquid dipotassium Aquathol® K, and 10 percent by weight for Hydout® (Table 1). Rates were expected to bracket the actual concentration required to achieve hydrilla control. Three plots received one treatment level each of Aquathol® K via trailing weighted hoses, three received Hydout® from a blower-type spreader, and two plots remained untreated as references. Treatments were not replicated. Estimates of treatment concentrations actually achieved ranged from 0.63 to 1.10 mg ae L^{-1} (Table 2). The applied concentrations of granular Hydout® were not immediately available in the water column as a result of the slower release of material from the pellet.

Table 2
Concentrations of Endothall Treatments on Hydrilla in Gatun Lake, Panama (Westerdahl 1983a,b)

Formulation/ Compound	Amount Applied	Application Rate kg ae ha^{-1}	Concentration Achieved, mg ae L^{-1}
Untreated Reference	Plot 8 0	0	0.0
	Plot 2 0	0	0.0
Aquathol® K liquid Dipotassium salt	Plot 1 75 L ha^{-1}	27	0.67
	Plot 6 93 L ha^{-1}	34	0.65
	Plot 5 140 L ha^{-1}	50	1.10
Hydout Granular Dimethyl-alkylamine salt	Plot 3 269 kg ha^{-1}	27	0.63
	Plot 7 336 kg ha^{-1}	34	0.86
	Plot 2 504 kg ha^{-1}	50	1.06

Pretreatment hydrilla biomass ranged from 720- to 1,080-g fresh weight m^{-3} water volume. Plants treated with dipotassium endothall liquid exhibited pronounced herbicide effects within 48- to 72-hr posttreatment, with browning (necrosis) of leaf tissue, loss of chlorophyll, and loss of stem integrity. The plant canopy dropped below the water surface during this time, receding nearly 2 m by 7 days after treatment (DAT), when extensive tissue degradation was evident. By 14 DAT, hydrilla biomass had settled to the bottom of the lake, and although some tissue remained green, it was flaccid and had little firmness or integrity. By 21 DAT, maximum reduction in biomass volume was observed and no tissue was available in the water column for sampling (Figure 2). At this time, some new growth was observed from rootcrowns and from stems lying on the sediment. At 49 DAT, regrowth was still sparse. By 90 DAT, dense regrowth was present along treated shorelines and in shallow water, and biomass was between 300 ± (standard error) 37.4 to 557 ± 172 g m^{-3}, an approximate 50-percent recovery. By 4 months posttreatment, hydrilla in these plots had recovered to near pretreatment levels.

The granular dimethylalkyamine was also effective against hydrilla, but control was slower and herbicide effect developed in a significantly different way (Figure 3). No obvious deterioration of the plant tissue was observed before 14 DAT, and only leaves and stems near the apical meristems were brown and translucent (Westerdahl 1983b). The mat of plants remained buoyant until 14 DAT, when it began to settle to 1 to 2 m below the surface. On the basis of unchanged levels of dissolved oxygen in water, it was thought that little or no damage to hydrilla had occurred through 11 DAT. Standing crop remained similar to untreated areas at 21 DAT. Defoliation continued through 49 DAT, when one plot was clear of weeds except along its shoreline. At 90 DAT, plants were still declining rather than recovering, with biomass reduced to 113 ± 33.1 to 291 ± 89.2 g m^{-3}. At this time, divers observed nearly complete degradation of hydrilla, and evidence of regrowth was not apparent in any of the plots. At 5 months posttreatment, hydrilla had returned to all plots, but plants remained below the water surface at decreased nuisance levels in two out of three of these areas.

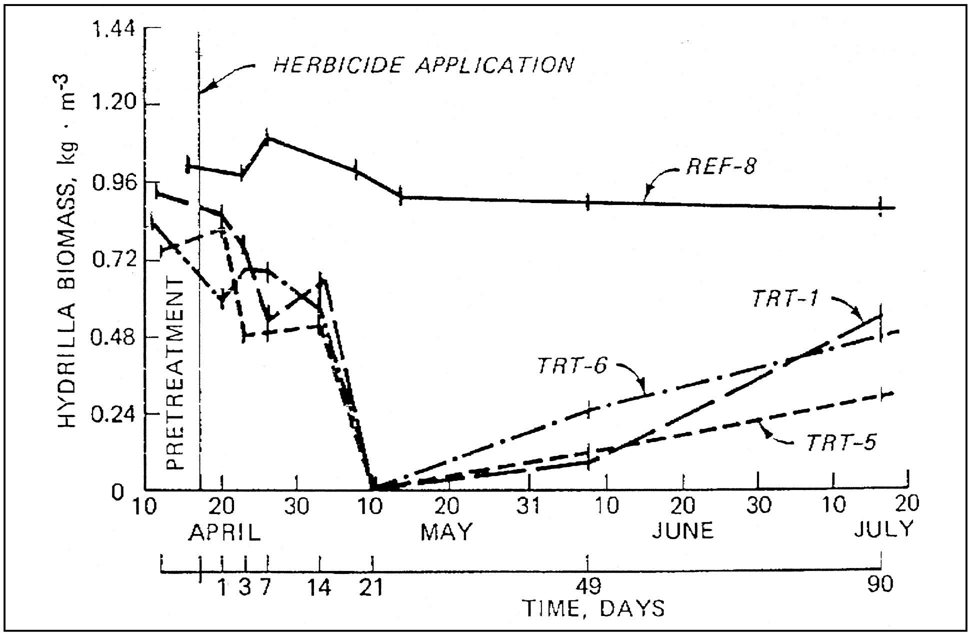


Figure 2. Effects of dipotassium endothall treatments on hydrilla biomass. Endothall application rates were 0.7, 1.1, 0.6, and 0.0 mg ae L^{-1} to TRT-1, -5, -6, and REF-8, respectively. Each point is the mean of approximately 15 replicate samples, i.e., 12 samples per hectare (Westerdahl 1983a). TRT = treatment plot; REF = untreated reference plot

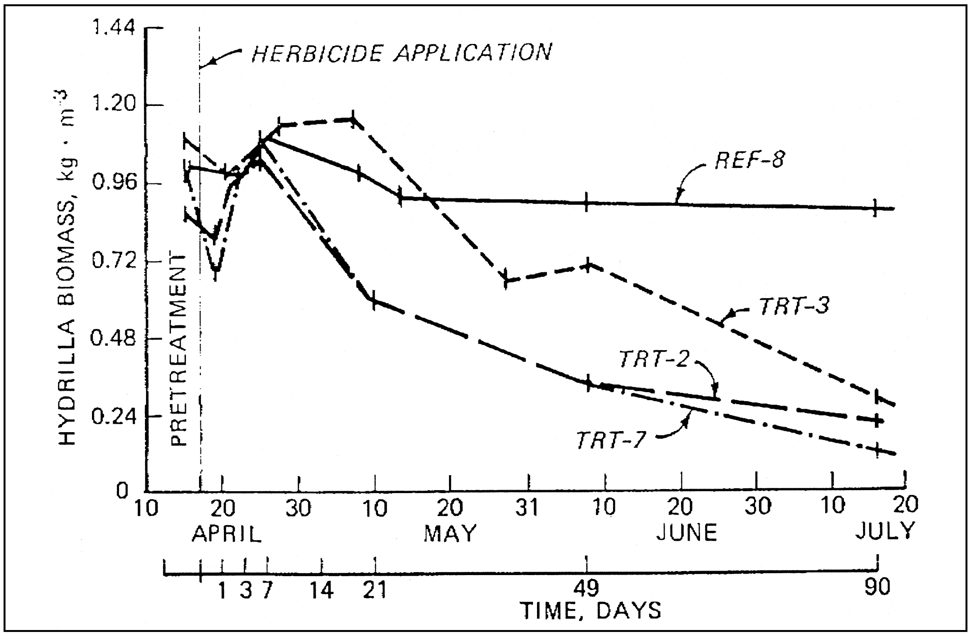


Figure 3. Effects of dimethylalkylamine endothall treatments on hydrilla biomass. Endothall application rates were: 1.1, 0.6, 0.9, and 0.0 mg ae L^{-1} to TRT-2, -3, -7, and REF-8, respectively. Each point is the mean of approximately 15 replicate samples, i.e., 12 samples per hectare (Westerdahl 1983a)

During the 49-day water quality sampling period, no adverse impacts were seen on parameters of dissolved oxygen, pH, water temperature, total Kjeldahl nitrogen, ammonia nitrogen, and total phosphorous. Shifts in the plankton community composition and in their vertical distribution were only transitory. Average water temperatures of 28.0 to 31.0 °C were expected to accelerate endothall degradation.

A comparison of outcomes from the two formulations revealed differences in time-course of efficacy pertinent to long-term vegetation management practices. Low levels of liquid dipotassium endothall, 0.65 to 1.10 mg ae L^{-1}, provided rapid control of a full standing crop of hydrilla within 3 days, but biomass recovered to pretreatment levels by 4 months. The dimethylalkylamine granule at a total application concentration of 0.63 to 1.06 mg ae L^{-1} provided slower control, by 21 DAT, and recovery was delayed to 6 months. Thus, fewer applications would be required to maintain control under similar conditions in low-flow environments with this formulation. It was suggested that an initial application of Aquathol® K be used, followed about 1 month later by treatment with the 10-percent dimethylalkylamine granule to provide control exceeding 6 months duration (Westerdahl 1983a). Other options suggested for reducing the quantity of herbicide required and the cost of repeated treatments were to apply endothall to hydrilla at slightly higher rates of 1.5 to 2.0 mg ae L^{-1} in Lake Gatun and similar environments to provide longer knock-down and to use an adjuvant or polymeric thickener to maintain liquid dipotassium endothall in contact with plant tissue for a longer period, especially in areas of high water exchange (Westerdahl 1983b).

3 Determining Concentration/Exposure-Time Relationships for Endothall Efficacy

After these early examinations of effect, the Corps of Engineers' work on endothall efficacy has followed the multi-tier research approach it has used for other aquatic herbicides. Evaluations using replicated designs in controlled-environment laboratory and mesocosm systems have supported and complemented field research efforts. There has been an emphasis on identifying precise concentration and exposure time relationships in smaller-scale facilities and then validating these findings in the field, so that it has been possible to predict control when methods are used in operational work. These efforts are based on the knowledge that while many factors can affect performance of aquatic herbicides (temperature, water quality, plant density, application rate, etc.), it is the too-rapid dispersion of herbicide residues that can be the primary cause of failure to control submersed plants in the field (Netherland et al. 1998). With this principle in mind, CE research has evaluated a range of methods to ensure an adequate exposure of plants to herbicide and an accumulation of lethal tissue burden levels of herbicide.

Uptake and Dosage Rate Determinations

As part of a Corps of Engineers investigation of the potential for chemical control of the newly discovered monoecious hydrilla biotype that had invaded the flowing water environment of the tidal Potomac River, Maryland, Van and Conant (1988) evaluated concentration/exposure-time relationships and uptake characteristics for dipotassium and alkylamine endothall. Initial evaluations of rooted plants under static exposures in 4-L aquaria demonstrated that both the Aquathol® K and Hydrothol® 191 liquid formulations controlled the new Potomac (monoecious) plant type at about the same threshold rate of 0.5 to 1.0 mg ae L^{-1} that was efficacious on the more robust-looking Florida (dioecious) biotype.

These researchers investigated minimum contact time required for control to determine what concentrations would be successful under the short exposure periods allowed by the tidal nature of the Potomac River. At the time there was limited information on endothall contact time for hydrilla or on uptake and accumulation of a lethal concentration (burden) of this herbicide in plant tissue. The then-current endothall label recommendation for hydrilla in flowing water (canals) in Florida specified 2 hr at 3 to 5 mg ae L^{-1} (Van and Conant 1988).

These authors demonstrated the dynamic relationship between endothall concentration and exposure time for hydrilla control. They first identified minimum contact times required for control by exposing rooted plants and shoots emerging from sprouting tubers to 1.0, 2.0, 3.0, and 5.0 mg ae L^{-1} dipotassium endothall (Aquathol® K) for 3, 6, 12, 24, 48, 96, or 168 hr in 4-L aquaria. Dosage rates required to achieve an approximately 80-percent reduction of plant biomass in rooted plants ranged from 12-hr contact time with 5.0 mg ae L^{-1} endothall to 48- to 96-hr exposure to 1.0 mg ae L^{-1}.Young hydrilla plants emerging from sprouting tubers were equally susceptible to endothall as excised apical tissue, and it was confirmed that there was no significant difference between monoecious and dioecious hydrilla in response to this herbicide.

These authors determined that endothall could provide control of hydrilla in the Potomac River with a minimum of 6-hr contact to 5.0 mg ae L^{-1} endothall and suggested that this exposure could be provided by the tidal window 3 hr before and after flood tide. Treatment would have more chance of success if carried out early in the growing season prior to plant growth reaching the water surface. Since their results indicated that higher rates of regrowth occurred when hydrilla was treated with high concentrations and short contact times, Van and Conant (1988) predicted that at least two or more annual applications would be required for effective control in the Potomac River.

Van and Conant (1988) then examined the time-course of endothall uptake by hydrilla, using radiolabeled compound. They determined lethal tissue burden thresholds by monitoring incorporation of radioactivity into 4-cm excised apices following static exposure to 1.0-, 2.0-, 3.0-, and 5.0-mg ^{14}C-radiolabeled endothall L^{-1} for 3 to 168 hr. Phytotoxic response to these rates of herbicide was monitored in a duplicate set of apices that were planted into 4-L aquaria after exposure to dipotassium endothall (Aquathol® K), also after exposure to 1.0, 2.0, 3.0, and 5.0 mg ae L^{-1} for 3 to 168 hr. Maximum ^{14}C was found in hydrilla exposed to labeled endothall for 4 days, at which time tissue levels of herbicide ranged from about 75 to 350 μg endothall g^{-1} dry weight (Figure 4). Tissue burden increased in proportion to ambient concentrations in water, and the time course of uptake at all test concentrations was best described by second-order polynomial equations (Van and Conant 1988). The nonzero intercepts for the associated regression curves (Figure 4) were attributed to an initial adsorption phase of passive diffusion of endothall into intercellular free space of the plants; this increased with increasing ambient concentrations.

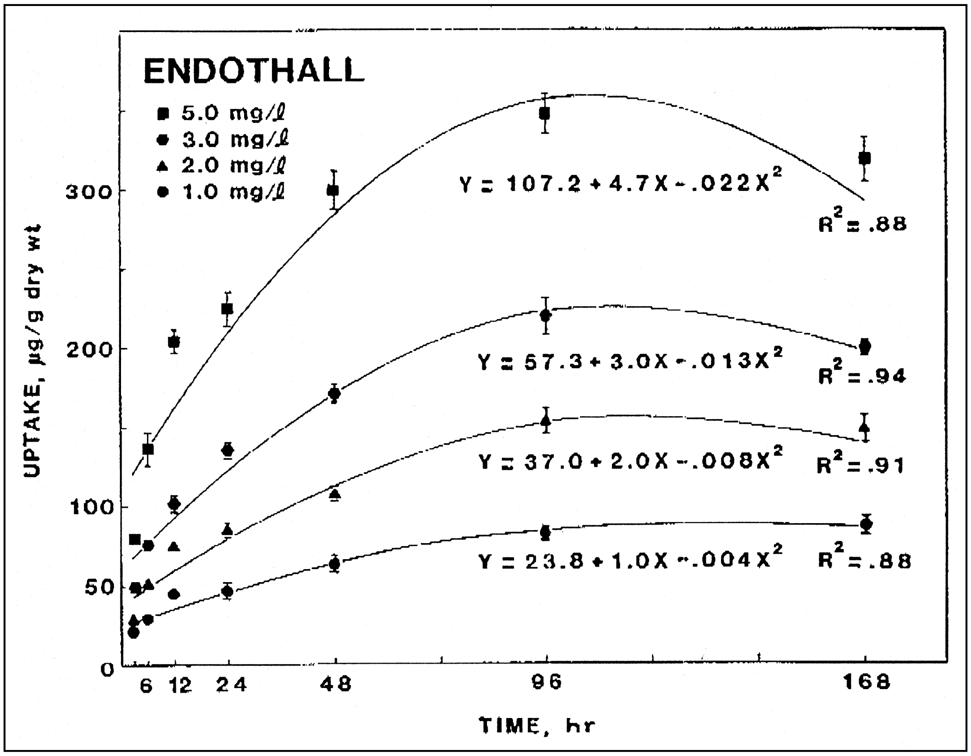


Figure 4. Time-course of ^{14}C uptake by excised hydrilla tissue from various combinations of ^{14}C-endothall concentrations and exposure periods (Van and Conant 1988)

For shoots planted following treatment at these same rates, ≥ 80 percent control was produced by 72 hr exposure to 1.0 mg ae L^{-1} and by 6 to 12 hr at 5.0 mg ae L^{-1} (Figure 5). These results clearly show the inverse relation between exposure time and concentration, within certain limits, for efficacy. Comparison of these results to uptake curves (Figure 4) and calculation show that at the lower rate a tissue burden of 75.1 µg g^{-1} was sufficient to produce this level of control. At the higher treatment level, an uptake of 135 to 160 µg g^{-1} occurred during the shorter exposure period that produced the same level of control. These differences in tissue concentrations with varying efficacious doses may be partially explained by the elevation in initial passive adsorption with increasing levels of ambient endothall (Van and Conant 1988).

The bioconcentration factor (BCF), calculated here as the ratio of herbicide concentration in plant tissue divided by the concentration in water, can indicate relative efficiency in uptake of aquatic herbicides. These factors were the same for the various treatment levels over the same endothall exposure periods, increasing to a maximum of 77 after 4 days of contact time and then declining (Figure 6). Van and Conant (1988) compared these results to bioconcentration of ^{14}C-diquat (an aquatic herbicide) in hydrilla, which they showed in similar experiments as increasing linearly to a BCF of 550. They suggested that this greater accumulation may explain why diquat is effective in hydrilla control at lower rates than is endothall.

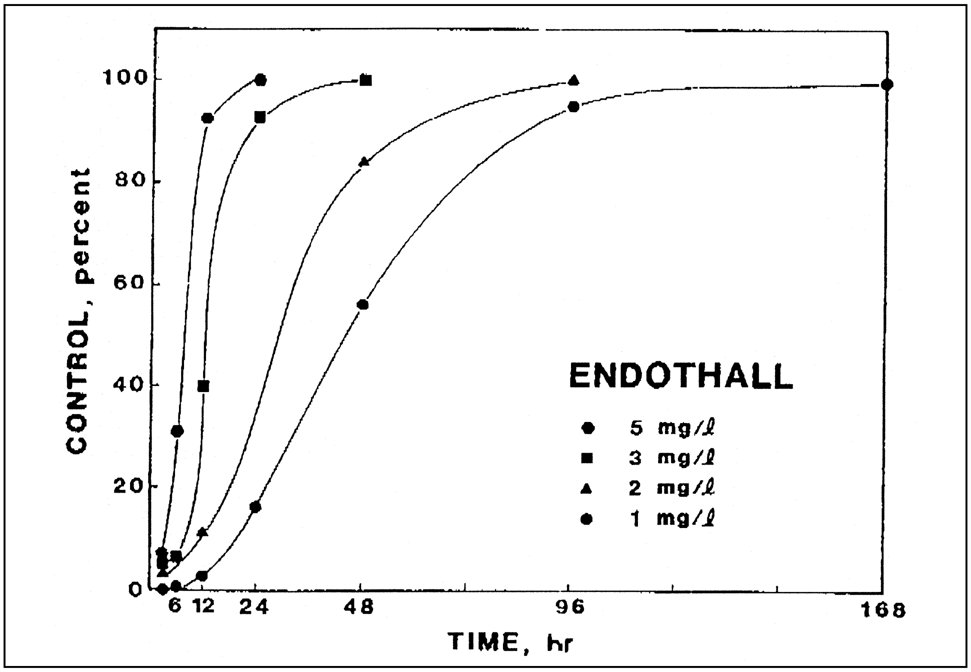


Figure 5. Phytotoxic response of excised hydrilla tissue to various ^{14}C-endothall concentrations and exposure periods (Van and Conant 1988)

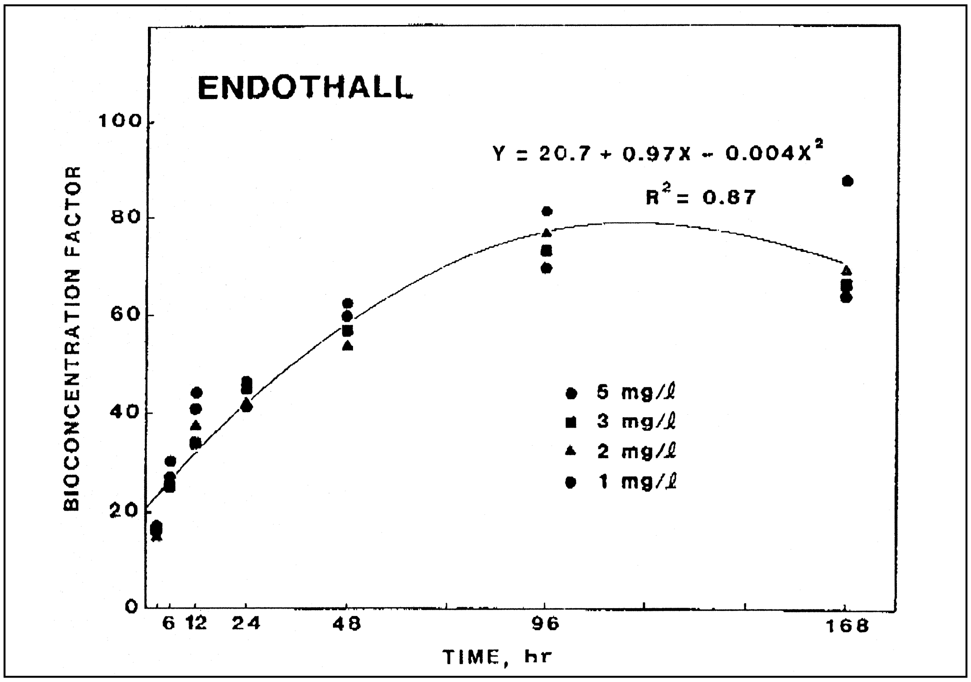


Figure 6. Bioconcentration factors of ^{14}C-endothall uptake by excised hydrilla tissue treated with various herbicide concentrations and exposure periods (Van and Conant 1988)

Threshold Dosage Rates for Efficacy

In the early 1990's, the Corps of Engineers addressed concerns expressed earlier (Haller and Sutton 1973; Reinert and Rodgers 1986; Van and Conant 1988) that relatively slow initial uptake of endothall by submersed plants and inappropriately low application concentrations were presenting problems in controlling weeds in flowing water. Under normal hydrodynamic conditions of operational weed control applications, aquatic plants are exposed to diminishing concentrations of herbicide over time, resulting from water-exchange characteristics, thermal stratification (which can prevent herbicide mixing), dispersion, plant uptake, adsorption to suspended particulates, and microbial degradation. In order to develop improved formulations and application techniques for endothall in hydrodynamic systems, information was needed on the threshold dosage rates required for control and on the range of concentration and exposure times that were effective on various target species. Netherland (1991a) and Netherland, Green, and Getsinger (1991a,b) expanded the work of Van and Conant (1988) to establish functional relationships among concentration, exposure time, and control for Eurasian watermilfoil and dioecious hydrilla.

Evaluations were carried out on rooted plants grown in 50-L aquaria in controlled environment growth chambers and treated under static exposures to 0.5- to 5.0-mg ae L^{-1} liquid dipotassium endothall for 2 to 72 hr (Netherland 1991a; Netherland, Green, and Getsinger 1991a,b). In Eurasian watermilfoil, severe (> 90 percent) shoot biomass reduction, compared to untreated reference material, occurred with exposure to 0.5-mg ae L^{-1} ae endothall for 48 hr, 1.0-mg ae L^{-1} for 36 hr, 3.0-mg ae L^{-1} for 18 hr, and 5.0-mg ae L^{-1} for 12 hr. At these rates, initial collapse of plants occurred within 1 week posttreatment, and subsequent regrowth through 4 weeks posttreatment consisted of few, short, viable shoots. Higher exposure times at these concentrations produced > 98-percent reduction in biomass with almost no shoot tissue regeneration during the 4 week-posttreatment. Lower exposure periods produced similar initial collapse of plants but allowed subsequent production of large numbers of viable shoots, and evidence of the potential for complete regrowth.

Hydrilla required higher concentrations and longer exposure times than Eurasian watermilfoil to achieve desirable levels of control (Netherland 1991a; Netherland, Green, and Getsinger 1991a,b). Biomass reduction of > 85 percent occurred with exposure to 2.0 mg ae L^{-1} for 48 hr and with contact to 3.0, 4.0, and 5.0 mg ae L^{-1} for 24 hr or more. A lack of regrowth from rootcrowns and destruction of existing root tissue characterized these treatments. Results were consistent with those seen by Van and Conant (1988) throughout the dosage rates examined.

The authors used these data to develop graphs that predicted control at minimal and increasing endothall concentration/exposure-time combinations. As shown in Figures 7 and 8, combinations of endothall concentrations and exposures that fall within Zone A were expected to provide < 70 percent plant control; within Zone B, from 70 to 85 percent control; and within Zone C, from 85 to 100 percent control. These ranges of control are applicable to operational use, with the proviso that they be adapted to account for dissipating concentrations over time and for more robust field-grown plants. This information also suggests that 0.3- to 0.4-mg ae L^{-1} endothall may represent a threshold of concentration required for submersed plant control, and this was supported by later evaluations of low-dose liquid dipotassium applied via metering pumps in the field (Netherland and Turner 1995)

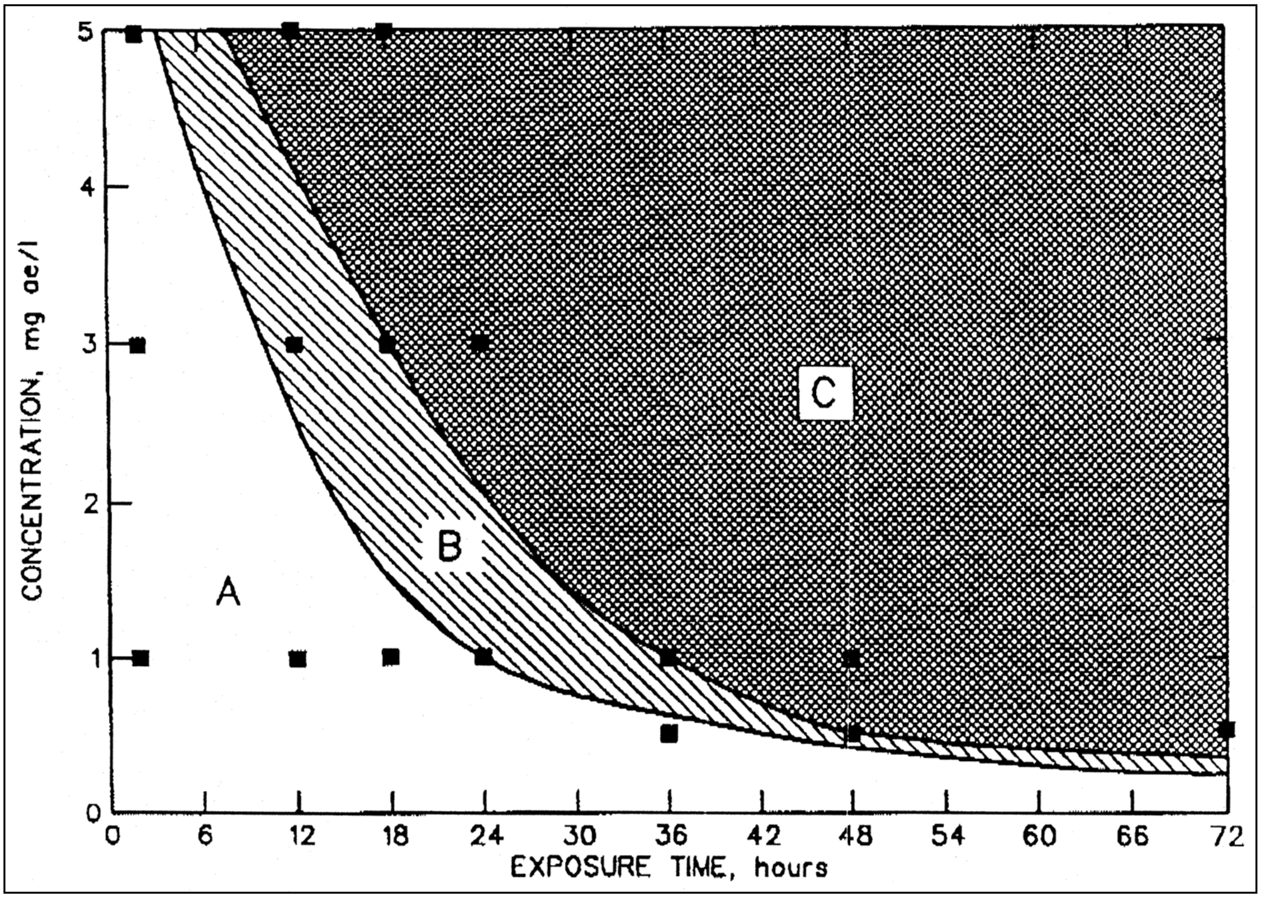


Figure 7. Endothall concentration and exposure-time relationships for control of Eurasian watermilfoil. Solid squares represent actual endothall concentration/exposure-time (CET) test coordinates. Zones A, B, and C were estimated using these test coordinates. Zone A represents CET combinations that should provide < 70 percent milfoil control along with a high probability of rapid regrowth within 1 week posttreatment; Zone B represents CET combinations that should provide between 70 and 85 percent milfoil control with regrowth beginning approximately 3 to 4 weeks posttreatment; and Zone C represents CET combinations that should provide 85 to 100 percent milfoil control with very limited regrowth up to 4 weeks posttreatment

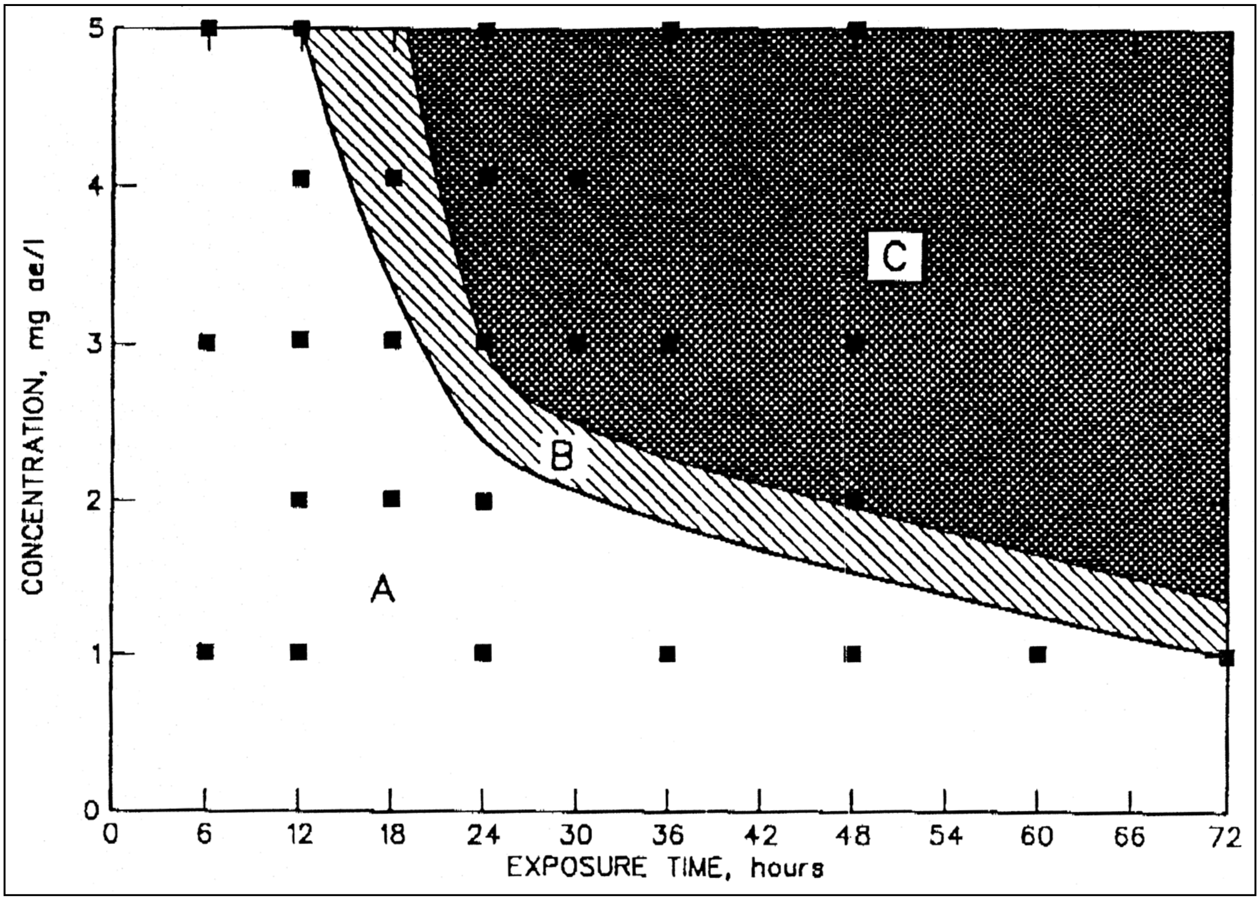


Figure 8. Endothall concentration and exposure-time relationships for control of hydrilla. Solid squares represent actual endothall concentration/exposure-time (CET) test coordinates. Zones A, B, and C were estimated using these test coordinates. Zone A represents these CET combinations that should provide < 70 percent hydrilla control and a high probability of rapid regrowth within 1 to 2 weeks; Zone B represents CET combinations that should provide between 70 and 85 percent hydrilla control with regrowth beginning approximately 4 to 6 weeks posttreatment; and Zone C represents CET combinations that should provide 85 to 100 percent hydrilla control with very limited or no regrowth up to 6 weeks posttreatment

4 Enhancing Endothall Efficacy in Flowing Water

In view of the contact-type mode of action and relatively rapid herbicidal activity of endothall, it has always been regarded as particularly suitable for application to flowing water systems where exposure time is limited. The pressing need for aquatic weed control in high water exchange environments such as canal systems, as well as in the active hydrodynamics of open waterbodies, has motivated research into a variety of methods for improving efficacy of endothall in flowing water. Netherland (1991a,b) pointed out that, since aquatic vegetation takes up only a fraction of endothall in water and at slow rates (Haller and Sutton 1973; Reinert and Rodgers 1986; Van and Conant 1988), extending contact time was a key to improving efficacy of this herbicide in hydrodynamic systems.

The Corps of Engineers addressed research efforts to endothall application in flowing water from the mid 1980s onward. The primary objectives of this effort were to (a) characterize flow velocities and water-exchange patterns in submersed plant stands under a variety of simulated and field conditions; (b) evaluate endothall application techniques that maximized herbicide contact time in flowing-water environments; and (c) provide guidance to operational personnel for improving the control of nuisance submersed vegetation in high water-exchange environments (Getsinger, Fox, and Haller 1996). By acquiring techniques to monitor and predict contact time in treatment systems, it has been possible to extend exposure periods sufficiently to allow submersed macrophytes to absorb a lethal tissue burden of herbicide (Ashton and Crafts 1981; Van and Conant 1988; Netherland 1991b). This research on contact time and delivery systems in flowing water was primarily conducted at the mesocosm level and in canal and lake systems.

Delivery Systems for Endothall in Flowing Water

Information on the effectiveness of low concentrations of endothall when longer exposure periods are possible (Netherland 1991b; Netherland, Green, and Getsinger 1991a,b) was the basis for developing and evaluating application and delivery systems that would maximize herbicide contact time against submersed macrophytes within a treatment area (Netherland et al. 1994; Getsinger, Fox, and Haller 1996). Preliminary evaluations were made of several passive delivery system matrices for endothall formulations, including a controlled-release (CR) clay pellet (Dunn et al. 1988), a 27.5-percent ai conventional-release clay pellet (Getsinger 1991; Turner et al. 1993; Turner, Getsinger, and Burns 1996), and a gypsum-based slow release matrix device (Netherland and Sisneros 1994; Netherland et al. 1994). Hydraulic flume evaluations of a 14-percent ae gypsum/endothall matrix targeted to achieve 5.0 mg ae L^{-1} for a 4-day exposure period showed that release rates in flowing water were consistent, and the dosage was highly effective at controlling Eurasian watermilfoil and *Najas* spp. at 96-hr exposure (Netherland et al. 1994).

Although these prototype passive controlled-release devices and formulations remained in the experimental evaluation stage, the Corps of Engineers also carried out laboratory and mesocosm-scale tests of a superabsorbent polymer formulation (SPF) of dipotassium endothall that was in the process of development as a commercial product (Netherland et al. 1994; Netherland and Turner 1995; Turner et al. 1995; Netherland et al. 1998). Release characteristics and efficacy on a population of mixed submersed species dominated by Eurasian watermilfoil were similar to those of the Aquathol® K clay granule (Netherland and Turner 1995; Netherland et al. 1998). Field testing of the 63-percent ai SPF carried out in Lake Weohyakapka, Florida, confirmed its efficacy on hydrilla and its ease of handling (Fox and Haller 1996; Netherland et al. 1998). This information was used to support the aquatic registration of the Aquathol® Super K granular formulation (Table 1) by the USEPA.

Active delivery of low endothall concentrations via metered pumping devices was first evaluated in outdoor hydraulic flume studies. Metered application of 0.4 mg ae L^{-1} of Aquathol® K for 48 to 72 hr resulted in good control of Eurasian watermilfoil and southern naiad and showed that continuous exposure to low herbicide concentrations in high-flow environments can be as or more efficacious than one-time application at higher rates (Netherland and Turner 1995; Turner et al. 1995).

These results supported the potential for use of low-dose rates to reduce concerns for discharge of herbicide-treated waters into potable water supplies. Operational evaluations were carried out in variable-flow irrigation canals in the Western U.S. (Sisneros and Turner 1995, 1996; Netherland et al. 1998). Dipotassium endothall was delivered via metering pumps that released low rates, 0.3 to 0.5 mg ae L^{-1}, over 72 to 96 hr. Treatments significantly reduced the target weed *Potamogeton pectinatus* L. (sago pondweed; Potamogetonaceae) biomass by 17 to 28 DAT, and water flow was significantly increased as early as 7 DAT as plants receded from the surface and upper layers of the water column. The acceptable residue level in drinking water (ARLDW) of 0.2 mg ai L^{-1} endothall[1] was not exceeded in discharge water (Sisneros and Turner 1995, 1996; Netherland et al. 1998). The development of a automatic metering pump has greatly improved the feasibility of conducting treatments in remote settings where flow rates often vary greatly within a 24-hr period (Netherland et al. 1998; Sisneros, Lichtwardt, and Greene 1998).

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[1] Current Maximum Contaminant Level (MCL) for endothall in water is 0.1 mg L^{-1}.

Dosage Rates for Endothall in Flowing Water

Previously, the effectiveness of the amine salt of endothall (Hydrothol® 191) for weed control in the flowing water environment of irrigation canals had been demonstrated by Price (1969) and Corbus (1982). Price (1969) reported that 3 to 4 ppm by weight (mg ae L^{-1}) of the endothall amine salt (Hydrothol® 191, defined as the dimethylcocoamine) for a contact period of 3 hr provided acceptable control of the submersed weed species *Potamogeton pectinatus*, *P. nodosus* Poir (American pondweed), *P. foliosus* Raf. (leafy pondweed), *Zannichellia palustris* L. (horned pondweed), and *Alisma* species (water plantain). Control was achieved for a distance of over 32 km in canals in western states of the United States where water velocity was 1.6 km per hour. Irrigation water containing 10 mg ae L^{-1} amine salt did not injure crops such as sugar beets, lettuce, beans, alfalfa, and cotton, or reduce yields. Where water was hard (alkaline), an increase in concentration and exposure time to 4-mg ae L^{-1} for 5 hr was required for equally satisfactory weed control. However, only variable plant control was reported in several situations where herbicide concentration dissipated to low levels soon after application (Price 1969; Bowmer et al. 1979; Bowmer and Smith 1984). Once concentration and exposure time relationships for endothall were well-defined (Netherland, Green, and Getsinger 1991a,b), further research could address specific application and residue goals in hydrodynamic systems.

Getsinger and Westerdahl (1988) used outdoor linear mesocosms (hydraulic flumes), 70 cm deep with flow velocities of 1.5 or 3 cm s^{-1} and planted with Eurasian watermilfoil, to evaluate release profiles in flowing water of liquid dipotassium endothall in combination with four adjuvants. Efficacy was not monitored in this study. Endothall was applied as Aquathol® K at 5 mg ai L^{-1}. Adjuvants were an invert emulsifier (Asgrow 403), a D-Limonene inverting oil (I'vod), and polymers (Nalquatic, Poly Control), compatible with endothall and commonly used for aquatic plant control.[1] All of the endothall/adjuvant combinations released herbicide for longer periods than did the endothall formulation alone at the 1.5-cm s^{-1} flow velocity. Polymer formulations released endothall for longer periods (72- to 84-min posttreatment) than the invert formulations (36- to 48-min posttreatment). At a flow rate of 3 cm s^{-1}, endothall residues were below detection (0.01 mg ai L^{-1}) at 12-min posttreatment with all combinations. The authors concluded that release profiles of the polymeric adjuvants Nalquatic and Poly Control showed the greatest potential for use in flowing water systems where velocities within Eurasian watermilfoil plant stands were < 3 cm s^{-1}.

A major research area in the CE investigations of herbicide application techniques for flowing water has been the use of tracer dye to monitor water movement and to estimate contact times available for endothall uptake under hydrodynamic conditions (Fox, Haller and Getsinger 1988, 1989, 1991a,b; Fox, Haller, and Getsinger 1993; Getsinger, Fox, and Haller 1996). Liquid and pellet

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[1] Asgrow 403: Asgrow Seed Co., LLC; I'vod and Poly Control: Brewer International, Inc., Vero Beach, Florida; Nalquatic: Nalco Chemical Co., Naperville, Illinois.

formulations of the inert dye rhodamine WT[1] have demonstrated the high level of variability in dispersion rates that exist once a chemical is applied to water, and the rapid movement and dilution of residues from a treatment site, even in waters that seem to be quiescent (Fox, Haller and Getsinger 1988; Netherland et al. 1998). Dye studies have allowed more precise quantification of water movement and exchange and improved herbicide efficacy by identifying optimal application timing and methods. Consequently, management practices for use of endothall to control hydrilla in flowing water systems such as canals have become more predictable, reliable, and economical (Fox and Haller 1992; Fox, Haller, and Getsinger 1993).

Two components of herbicide movement related to efficacy can be modeled from dye tracings: location and dilution. Variation in vertical distribution of dye in the water column indicates incomplete mixing, usually the result of thermal stratification or vegetation density. Dilution and dispersion of dye from a treatment site is closely correlated to herbicide dilution and follows the pattern of an exponential decay curve. This sequence can be transformed to a linear regression from which a half-life of dissipation is derived (Fox, Haller and Getsinger 1988, 1991a, 1993). These dye half-lives indicate rates of water exchange and potential contact time of herbicides. They have been used to estimate persistence of both liquid and granular dipotassium endothall and to identify conditions where dilution rates were slowest, to predict optimal application times and to provide maximum herbicide exposure to plants (Fox, Haller, and Getsinger 1993). Seasonal differences in vertical distribution of dye based on water temperature have also been identified. For example, where reduced flow and temperatures in late autumn had extended half-life of dye to 120 hr (5 da) in tidal canals of the Crystal River, Florida, 3 mg ae L^{-1} endothall applied as liquid Aquathol® K reduced density of hydrilla vegetation from 97 to 18 percent by 13 DAT, and biomass remained at 15 percent through 57 DAT (Fox and Haller 1992; Fox, Haller, and Getsinger 1993). These data indicated that herbicide use in similar systems in the Southeast United States should be restricted to autumn and springtime, when water flow was low and /or when water temperature was isothermal.

In the U.S. Pacific Northwest, evaluations of dye behavior in exposed riverine locations and protected cove sites of the Pend Oreille and Columbia River systems revealed that water exchange half-lives ranged from 6.3 to 16.8 hr (Getsinger, Sisneros, and Turner 1993). Based on the potential exposure periods provided by this dispersion rate, endothall was suggested as a suitable candidate for controlling Eurasian watermilfoil in these sites.

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[1] Approved by the USEPA and U.S. Geological Survey for use in potable water at concentrations up to 10 $\mu g\ L^{-1}$.

5 Selective Efficacy of Endothall

Although endothall is used selectively in some terrestrial crops (MacDonald, Shilling, and Bewick 1993), it has generally been considered to provide only broad-spectrum contact-type activity for aquatic plants. Without physiological effects related to its mode of action that would allow it to target any specific group of aquatic plant species, it has not been considered as a candidate for selective use in the past. However, recent CE research has shown that plants can vary in their sensitivity to contact herbicides on the basis of application rates, seasonal or phenological timing of application, and area of treatment (Skogerboe and Getsinger 1998, 1999; Netherland et al. 2000). Manipulation of these factors can allow endothall to control submersed target weeds selectively, while reducing or preventing long-term damage to various desirable nontarget plant species in the ecosystem.

Selectivity Studies

Endothall selectivity studies have been carried out in 7,000-L mesocosm facilities at the Corps of Engineers' Lewisville Aquatic Ecosystem Research Facility (LAERF), TX. The purpose of these studies was to evaluate the sensitivity of 16 species of submersed and emergent or floating-leaved native plants, representative of northern and southern U.S. aquatic communities, to liquid dipotassium endothall at rates that could be used to control three exotic species, hydrilla, Eurasian watermilfoil, and curlyleaf pondweed (*Potamogeton crispus* L.; Skogerboe and Getsinger 1998, 1999). These exotics and various southern ecosystem plants (Table 3) were exposed to concentrations of 1.0, 2.0, and 5.0 mg ae L^{-1} in static exposures (Skogerboe and Getsinger 1998). The northern community was treated along with the target plants Eurasian watermilfoil and curlyleaf pondweed at initial concentrations of 0.5, 1.0, 2.0, and 4.0 mg ae L^{-1}, which were dissipated with a 24-hr half-life to simulate treatment in flowing water (Skogerboe and Getsinger 1999). Evaluations at 8 weeks after treatment showed that at 0.5 and 1.0 mg ae L^{-1}, endothall (10 to 20 percent of the maximum labeled rate) controlled the milfoil and curlyleaf pondweed and had only slight injury or no effect at all on 11 of the native species. Six native species were significantly injured by the herbicide but grew back to an extent that showed they would not be removed by treatment at this level (Table 3).

Treatment at 2 to 5 mg ae L^{-1} also controlled hydrilla and the native species *Ceratophyllum demersum* L. (coontail); *P. illinoensis* (Illinois pondweed), sago pondweed, and *Vallisneria americana* Michx.(wild celery) regrew from injury; and 12 species experienced only slight injury or no effect (Table 3).

Table 3
Differential Response of Native and Nonnative Aquatic Plants to Increasing Levels of Dipotassium Liquid Endothall Dissipated with a 24-hr Half-life (Skogerboe and Getsinger 1998, 1999)

Aquatic Plant Type	**Species**	**Response to 0.5 to 1.0 mg ae L^{-1} endothall**	**Response to 2.0 to 5.0 mg ae L^{-1} endothall**
Exotic Target Species	*Hydrilla verticillata* Hydrilla	Injury/regrowth	Control
	Myriophyllum spicatum Eurasian watermilfoil	Control	Control
	Potamogeton crispus curlyleaf pondweed	Control	Control
Native Species	*Brasenia schreberi* watershield	Slight injury/no effect	Slight injury/no effect
	Ceratophyllum demersum coontail	Slight injury/no effect	Contol/injury/regrowth
	Elodea canadensis elodea	Slight injury/no effect	Slight injury/no effect
	Heteranthera dubia waterstargrass	Slight injury/no effect	Slight injury/no effect
	Najas guadalupensis Southern naiad	Injury/regrowth	Slight injury/no effect
	Nuphar advena spatterdock	Slight injury/no effect	Slight injury/no effect
	Nymphaea odorata fragrant waterlily	Slight injury/no effect	Slight injury/no effect
	Polygonum hydropiperoides smartweed	Slight injury/no effect	Slight injury/no effect
	Pontederia cordata pickerelweed	Slight injury/no effect	Slight injury/no effect
	Potamogeton illinoensis Illinois pondweed	Injury/regrowth	Injury/regrowth
	Potamogeton nodosus American pondweed	Injury/regrowth	Slight injury/no effect
	Potamogeton pectinatus sago pondweed	Injury/regrowth	Injury/regrowth
	Sagittaria latifolia arrowhead	Slight injury/no effect	Slight injury/no effect
	Scirpus validus bulrush	Slight injury/no effect	Slight injury/no effect
	Typha latifolia cattail	Slight injury/no effect	Slight injury/no effect
	Vallisneria americana wild celery	Injury/regrowth	Injury/regrowth

Figures 9 and 10 summarize, respectively, the gradation in response to various concentration and exposure time combinations of endothall in three native plant species which occur in northern and southern aquatic communities (Skogerboe and Getsinger 1998, 1999). In comparison with Eurasian watermilfoil and hydrilla, the natives require more concentrated or longer herbicide applications to achieve control, and this indicates that endothall can be used at rates that allow selective control of target weeds without doing equally severe harm to desirable plants.

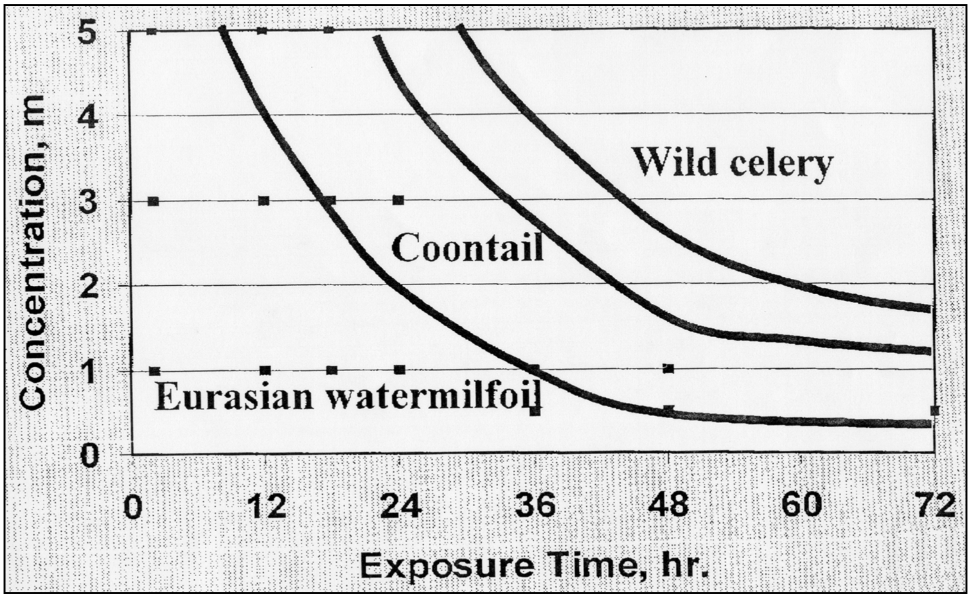

Figure 9. Endothall concentration and exposure-time combinations that produce > 85 percent control of Eurasian watermilfoil, *Ceratophyllum demersum* (coontail), and *Vallisneria americana* (wild celery). Increasing concentration and/or exposure times are required for control of the latter nontarget species

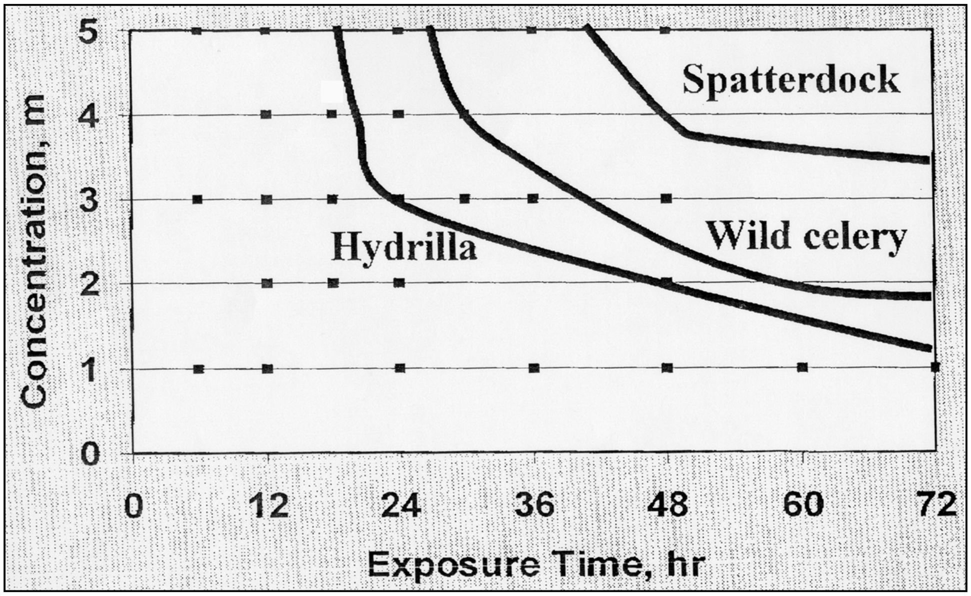

Figure 10. Endothall concentration and exposure-time combinations that produce > 85 percent control of hydrilla, *Vallisneria americana* (wild celery), and *Nuphar advena* (spatterdock). Increasing concentration and/or exposure times are required for control of the latter nontarget species

Physiological Response

Physiological, as well as physical, differences in response to endothall have been demonstrated in the related species hydrilla and *Egeria densa* Planch. (egeria; Hydrocharitaceae), suggesting a mechanism for selective activity of this herbicide (Sprecher, Stewart, and Brazil 1993). Egeria exposed to liquid dipotassium Aquathol® K in controlled-environment growth chambers at the ERDC exhibited no change in the stress-induced enzyme peroxidase through 28 DAT following exposure to 2 mg ae L^{-1} for 2, 16, and 36 hr. Treated hydrilla exhibited significant increase in peroxidase above reference levels after 8 DAT. Biomass harvested at 77 DAT showed that egeria was unaffected by treatment, while ≥ 16-hr exposure had reduced hydrilla by 70 percent or more . The two salts of endothall also evoke different physiological responses in these species (Sprecher, unpublished data). Under the concentration and exposure times used above, dimethylalkylamine endothall lowered levels of phytoene and carotene (pigments involved in chlorophyll maintenance) in both species, compared to untreated and to dipotassium salt-treated material.

6 Temperature Selective Efficacy

Endothall uptake in hydrilla is enhanced by high temperatures and low light levels (Haller and Sutton 1973), and efficacy is generally considered to be negatively affected by cool water temperature, probably the result of low metabolic activity (e.g., respiration) in target plants (Westerdahl and Getsinger 1988; MacDonald, Shilling and Bewick 1993). Aquathol® K is recommended for use at or above 18 °C (Elf Atochem 1998b). However, adequate efficacy at lower temperatures on species with early-season growth would allow it to provide another mode of selectivity.

Curlyleaf pondweed is a target species that initiates growth at temperatures below those considered as the threshold for adequate endothall activity. Netherland et al. (2000) evaluated temperature effects on endothall efficacy against curlyleaf pondweed in greenhouse and pond studies at the LAERF. They showed that a long-term management strategy of reducing production of vegetative propagules can be successful with this species at lower water temperatures than usually considered ideal for endothall use. While the liquid dipotassium salt was less efficient in reducing biomass at lower temperatures, the late March applications to 18-°C water reduced curlyleaf turion densities by 86 percent, whereas mid-May application to 25-°C water reduced production of these propagules by only 40 percent. This suggests that this early-season treatment strategy used over several growing seasons could eliminate the turion banks that are the main form of reproduction of this species. This use of endothall is also an example of selective control, where phenological timing could eliminate this weed while maintaining later-emerging native species.

Early-season endothall treatment of curlyleaf pondweed had also been suggested by James (1984), following application of a coupled granular/liquid treatment to an Ohio lake at the beginning of May, significantly prior to local turion formation and senescence in late June. James (1984) suggested that low doses of endothall herbicide at intervals in the early stages of the curlyleaf pondweed growing season might protect water quality and maintain adequate dissolved oxygen levels by allowing plants to die back and decompose slowly.

7 Evaluating Endothall Dissipation

Dissipation and degradation of herbicidal chemicals are of importance in aquatic systems because of their relation to contact time, efficacy, water use following treatment, and fate and persistence of these xenobiotics in the environment. Fate of aquatic herbicides is a function of inherent physiochemical characteristics that influence breakdown and degradation as well as of external conditions of dilution and dispersion via water flow. Water solubility and adsorption are some of the most important characteristics influencing the environmental fate and persistence of aquatic herbicides. These traits affect their partitioning to water, sediment, or biota through dilution, bioaccumulation, biodegradation, and metabolic depuration. Water exchange-related dissipation is also affected by the chemical and biological properties of the water body, the hydrodynamics, volume, and configuration of the treated area, the thermal stratification and mixing of herbicide through the water column, and plant density, plant uptake, sediment type, and adsorption.

Fate Characteristics of Endothall

Endothall has consistently been considered to be a highly biodegradable compound (Keckemet 1969), and numerous studies show that it is neither bioaccumulated nor persistent in the environment (Isensee and Davis 1962; Johnson 1973; Simsiman, Chesters, and Daniel 1972). Endothall ($C_8H_{10}O_5$) is uncommon among pesticide compounds in that it contains only carbon, hydrogen, and oxygen, along with potassium ions in the inorganic salt, or nitrogen in the diamine (Figure 1). This composition allows it to be readily and completely broken down by bacteria and fungi in water, soil, and sediment for use as a source of carbon, and biotransformation and biodegradation are the dominant fate processes. Endothall undergoes very little chemical degradation; volatilization, photodegradation, hydrolysis, or oxidation are not significant characteristics affecting its persistence in aquatic environments. Radiolabel studies indicate that degradation is complete, resulting in mineralization and release of endothall carbon from microorganisms and plants in the form of carbon dioxide without formation of toxic intermediate compounds (Freed and Gauditz 1961; Thomas 1966; Keckemet 1969; Sikka and Saxena 1973; Haller and Sutton 1973). Since many species of microorganisms normally present in soils and water degrade endothall, it breaks down rapidly in aquatic environments at rates directly dependent on water temperature and microbial activity (WSSA 1994). Other hydrosoil and/or water factors such as temperature, texture, pH, and organic matter content may influence the rate of endothall degradation indirectly through changes in bioavailability of endothall to microorganisms.

In general, recent laboratory studies indicate that endothall quickly degrades under aerobic and anaerobic aquatic conditions, with half-lives of approximately 10 and 8.5 days, respectively (Reynolds 1992, 1993). These environmental fate characteristics result from physical and chemical characteristics outlined in Table 4. Endothall is a highly water soluble, polar molecule with concommitant physical characteristics that allow rapid biodegradability. At pH's of 5, 7, and 9 at 25 °C, the acid has an average solubility of 12.8 g per 100 mL^{-1} in water (Lorence 1994a); dipotassium salt has a solubility of $>$ 65 g per 100 mL^{-1} (Lorence 1994b); and amine salt has a solubility of $>$ 50 g per 100 mL^{-1} (Lorence 1994c). At a 5-mg ai L^{-1} application rate, equivalent to 0.0005 g per 100 mL^{-1}, endothall remains entirely in solution in the field.

Table 4
Environmental Fate Data for Endothall[1]

Characteristic	Value/Data
Water Solubility	Endothall acid and salts (g/L): >128 g/L, @ pH 5,7,9
Vapor Pressure	Amine salt: 2.09 X 10^{-5} mm Hg at 24.3 C, or 0.00278 Pascal
Hydrolysis	stable at pH 5, 7, and 9
Photolysis	stable at pH 5, 7, and 9
K_{ow}	Dipotassium salt <0.02 @ 9 mM
K_{oc}	Dipotassium salt: 110 to 138
K_{ads}	Dipotassium salt: 0.13 to 22 (adsorption) Dipotassium salt: -1.32 to 39.9 (desorption)
Aerobic Aquatic Metabolism of Dipotassium salt	Decay Rate: -0.0686 % day^{-1} Half-life:10.1 days
Anaerobic Aquatic Metabolism of Dipotassium salt	Decay Rate: -0.0813 % day^{-1} Half-life: 8.5 days
Field Dissipation Half-life	Dipotassium salt: 1 to 7 days Amine salt: 1 to 7 days

[1] Most of these data provided for this review come from studies submitted to EPA by Elf Atochem. However, some of the reports are incomplete regarding materials and methods used in the studies to determine the coefficients reported. Because of this, it is not possible to determine if these data are valid; that is, developed according to USEPA's Subdivision N Guidelines. For some parameters, the chemical form of endothall under study is not known and cannot be determined because of a lack of background information, such as pH. This is important in considering whether or not to use the K_{ow} value, for example.

Endothall shows characteristics typical for a highly polar acidic molecule. It has dissociation values for pK_{a1} between 4.16 and 4.32 and pK_{a2} values between 6.07 and 6.22 at 20 °C, depending upon salt form (Gallacher 1993a,b,c). Endothall will therefore be essentially fully dissociated in aquatic environments with a pH above 6.22. The monoprotonated form will occur predominantly in an aquatic environment with a pH between 4.16 to 6.22, and the fully protonated form will predominate below pH 4.16.

The ratio of octanol to water solubility, the octanol-water partition coefficient (K_{ow}), predicts partitioning to sediment or to nonaqueous liquids, such as lipids, present in aquatic organisms. The octanol-water partition coefficient of endothall can vary according to the salt form, is very low in all cases, and this indicates that accumulation in lipids is insignificant. The K_{ow} for the dipotassium salt was measured at < 0.02 and < 0.3 at concentrations of 9 and 0.9 mM, essentially showing no measurable partitioning into octanol (Lorence 1994c). The K_{ow} of the amine salt was measured at 2.1 and 0.25 at the same concentrations, and this is still very low (Lorence 1994e). Since these experiments were conducted in highly purified water, they do not represent the real world in which metal cations in solution would exchange quickly with the amine cation. The K_{ow} of endothall in the environment would therefore resemble the dipotassium salt K_{ow} no matter what the original salt form.

Endothall is not volatile, and this is another reason that it does not undergo standard chemical degradation. For instance, the amine salt of endothall has a vapor pressure of 2.09×10^{-5} mm Hg (0.00278 pascal) at 25 °C (Lorence 1994d). The low vapor pressure and high solubility of this compound combine to make its volatilization insignificant. Endothall does not degrade when exposed to artificial sunlight at pH 5, 7, and 9 or in soil (Zwick, Kazee, and Marsh 1992; Saxena, Zwick, and Marsh 1992). It does not degrade from hydrolysis (Wang 1991) or oxidation.

Endothall displays characteristics typical of a di-carboxylic acid in its physical behavior in soils. Depending upon soil type, soil pH, and percent organic carbon, the adsorption K_{ds} for endothall can vary significantly, from approximately 0.13 to 1.0 in soils with pHs just above the pK_{a2} (Vigon 1989; Dykeman 1985). However, soils with a pH at or below the pK_{a2} show considerably higher adsorption K_d's between 3.5 and 22. Soil pH does not correlate with the desorption K_d, which can range from -1.32 to 39.9. Thus, endothall will not adsorb well to many soils, but when it does, it tends to stay adsorbed. While such behavior can complicate K_{oc} calculations to correct sorption for organic content of sediment to give the adsorption coefficient, the endothall K_{oc} has been calculated as 110 to 138 in two aquatic sediments (Reinert and Rodgers 1987).

These characteristics ensure that the primary environmental fate of endothall is biotransformation and biodegradation, primarily via microorganisms and also by plants, which convert it primarily to carbon dioxide and soil bound natural products. Under aerobic aquatic conditions in the laboratory, endothall has recently exhibited a half-life of 10 days (Reynolds 1992), while it has a half-life of 8.5 days under otherwise similar anaerobic conditions (Reynolds 1993). Earlier studies are consistent with these laboratory observations. Static shake flask studies with lake water yielded an aqueous half-life of 8.45 days (Reinert et al., 1986). Radiolabeled studies isolated *Arthrobacter sp.* which transformed endothall initially into citric, aspartic, and glutamic acids as well as $^{14}CO_2$. Conversion was via the tricarboxylic acid cycle and an alternate, unidentified pathway (Sikka and Saxena 1973). Additional work demonstrated microbial degradation of endothall in pond water, and in aquaria in the laboratory using water and hydrosoil from the same pond (Sikka and Rice 1973). A half-life of approximately 6 days is calculable from the pond data, while aquaria showed much faster degradation, with an average half-life of 0.9 day for aquaria treated with 2 and 4 ppm endothall.

Metabolism by aquatic plants has been an additional and significant degradation pathway for endothall. Freed and Gauditz (1961) reported that extensive breakdown of ^{14}C-endothall occurred in an aquatic weed species (*Elodea* spp.) with radioactivity incorporated in various plant constituents. Key among the studies reporting absorption of endothall by aquatic plants is the dissertation by Thomas (1966), who found that leaf tissue of two species, American pondweed and *Elodea canadensis* Rich. in Michx. (elodea), extensively metabolized ^{14}C-endothall. No significant difference in uptake or metabolic products was seen between them, although elodea was resistant to endothall and a delay was observed in the first 6 hr of release of radiolabeled carbon from elodea compared to American pondweed (Thomas 1966). In aquatic plants, uptake of endothall has produced bioconcentrations reaching 77-fold (Van and Conant 1988), but subsequent disintegration of plant tissue did not increase posttreatment residues in water, suggesting plant metabolism and microbial degradation of the compound. Extrapolations can be made from field studies on the impact of aquatic plants on uptake and metabolism of endothall. A summary of several studies shows that the degradation half-life of endothall in aquaria and ponds was shortened from the laboratory-determined microbial rate of 9 to 10 days down to 4.1 to 7.3 days by the presence of aquatic plants (Reinert and Rodgers 1987). More recent work (Formella in preparation) showed a four-fold concentration of radiolabeled endothall in coontail after 5 days exposure to 5 mg ai L^{-1} dipotassium endothall. Therefore, heavy weed infestations at time of application could significantly increase rate of removal of endothall from treated water.

With environmental accumulation of endothall's being limited by its own characteristics, it has relatively short persistence. In the field, length of persistence can be related to differences in rate applied, physical and chemical formulation, hydrodynamics of the water body, presence of habituated microorganisms, and ratio of organic matter in water and sediment (Hiltibran 1962; Keckemet 1969; Westerdahl and Getsinger 1988; MacDonald, Shilling, and Bewick 1993). Field dissipation studies of endothall show rapid dissipation of residues. Williams et al. (1998) review in detail the historical record of dissipation of endothall in lake and canal systems. Overall, in lake treatments half-lives of 0.8 to 7 days were observed in a wide variety of systems. Endothall may persist where there is anoxia, resulting from rapid plant death, low density of weeds, low temperature, or low microbial activity. Degradation of endothall in water is usually not impacted by microbial degradation in faster moving waters of canal systems with relatively short exposure times of hours vs. days. Here, adsorption to plant, soil, and canal surfaces is the primary mode of dissipation. Observations in the field have shown detectable and efficacious levels of endothall up to distances of 10 to over 40 km (6 to over 25 miles), depending upon application rate. Following a recent surface application of Aquathol® K at 3.5 mg ai L^{-1} to an 18-ha (44-acre) reservoir shoreline site, residues were below the endothall maximum concentration level (MCL) of 0.1 mg L^{-1} for 4 days posttreatment within and outside the treatment area (Ritter and Williams 1996). At 7 days after this application, all sampled areas were below the detection limit of 0.01 mg ai L^{-1}, and residues had migrated at a rate of 15 cm s^{-1} (0.5 ft s^{-1}), with a dissipation half-life of 19 hr. Without dispersion, Ritter and Williams (1998) calculated the half-life to be 1.5 to 1.7 days from this author's data. Persistence in water is also affected by initial herbicide formulation, particularly whether liquid, granular, or sustained-release (Aquathol® Super K).

Endothall's solubility and hydrophilicity contribute to its low toxicity to mammals, since high solubility in water prevents accumulation in animal tissues. Endothall does not bioconcentrate in most aquatic fauna. Depending on species, bioconcentration factors of 0.003 to 1.05 have been seen or estimated; concentrations seen at much higher levels in *Daphnia* (150x), *Oedogonium* (green alga: 63x), and *Physa* (a snail: 36x) were transient and not passed to higher trophic levels (Westerdahl and Getsinger 1988). Residues in caged bluegill sunfish were consistently below detection limits of 0.1 $\mu g\ g^{-1}$ (Reinert and Rodgers 1986), and Dionne (1992) also showed that bluegill sunfish do not accumulate endothall. While crayfish to some extent and clams to a significant degree absorbed radiolabeled endothall, they rapidly metabolized it to natural products so that internal endothall concentrations remained below exposure levels (Formella in preparation). Bioconcentration in tissues of aquatic organisms is thus not expected to be significant for endothall.

Specific field dissipation scenarios seen in studies sponsored by the Corps of Engineers are summarized here.

Dissipation in the Lake Gatun Study

It was initially expected that the disappearance of endothall from the water column would vary with organic content of water, but posttreatment samples from Lake Gatun through 90 days after application, with detection limits of 0.01 mg ae L^{-1} endothall in water and 0.01 mg ae kg^{-1} in sediment and plants, indicated that differences in dissipation of the herbicide were primarily a function of the formulation applied (Westerdahl 1983a,b).

Endothall disappeared rapidly from water in all Aquathol®-treated plots. Within 24 hr following treatment, mean concentrations were approximately 30 to 60 percent of estimated initial concentrations, although the compound was not yet evenly distributed through the water column. By 3 DAT, endothall was very evenly distributed and had decreased to between 4 and 33 percent of treatment levels. By 7 DAT, less than 0.01 mg ae L^{-1} was present. Random checks of samples from subsequent dates confirmed that compound continued to remain below this concentration. Dispersion to the buffer areas (sampled 15 m out from the midpoint of each plot boundary) was detected within 3 DAT and occurred more readily from areas treated with Aquathol® K than with Hydout. Endothall residues in water did not persist in buffer areas longer than 3 DAT. Endothall from Aquathol® K was first detected in buffer areas at a midlevel depth of 2.0 m in water, and this was attributed to its specific gravity, slightly more than 1.0, causing it to sink in water before dispersing laterally, depending on water flow and density of vegetation (Westerdahl 1983a,b).

Endothall was released more slowly to water from the pelletized formulation than via the liquid. This was thought to result from pellets sinking into the organic silt layer at the bottom surface and then releasing endothall slowly to overlying water by diffusion through silt, with some absorption to particulate organic matter or to roots. Water residues showed that less than 30 percent of the endothall applied as pellets was available after 24 hr. Mean endothall concentrations in all three plots reached a maximum of 0.18 mg ae L^{-1} at 7 DAT, which was only 10 to 30 percent of estimated initial treatment concentrations. Levels were barely detectable at 0.05 mg ae L^{-1} by 14 DAT. The slower release of endothall also reduced the rate of herbicide dispersion out of the treated area. In contrast to the liquid, negligible endothall residues were found in the 15-m-wide buffer zone area around Hydout-treated plots throughout the posttreatment period. This indicated that endothall was being broken down in water as fast as it was being released by the 10-percent ae pellet.

The bottom surface of experimental plots in Gatun Lake was composed primarily of organic silt, approximately 0.3 to 1.5 m thick. Bathymetric profiles characterized the slope of plots and their relationship to the river channel so that herbicide transport, dispersion, and contact time could be evaluated with consideration of these parameters. Endothall persisted in sediment of Aquathol® K-treated plots for less than 3 days; where Hydout was used, endothall persisted in sediment for more than 21 days after treatment (Westerdahl 1983a,b). No detectable endothall levels were observed in sediment sampled from the two reference plots. Based on sediment residues, it was supposed that the majority of the pelletized herbicide sank into the organic silt and released herbicide at a relatively constant rate, as these plots had significantly higher sediment residues that persisted at 1.0 to 3.0 mg ae L^{-1} throughout the 21-day sampling period.

Absorption of endothall by hydrilla treated with Aquathol® K reached maximum tissue levels of 0.59 $\mu g\ g^{-1}$ by 1 to 3 DAT and then declined through 21 DAT, when mean residues ranged from 0.04 to 0.18 $\mu g\ g^{-1}$. Tissue residues from the slow-release formula increased through 7 to 14 DAT, and remained at over 0.20 $\mu g\ g^{-1}$ at 21 DAT.

This tissue uptake under dissipating concentrations may be compared to later laboratory work (Van and Conant 1988) that showed that at static concentrations of 1.0 mg ae L^{-1} in water, endothall uptake and accumulation by hydrilla increased through 4 to 7 DAT and reached about 80 $\mu g\ g^{-1}$ dry weight, with a bioconcentration factor of 77 (Figures 4 and 5). Plant uptake of endothall depends on its concentration in surrounding water and also the continuing ability of plants to assimilate it into functioning tissue.

The warm water temperatures of the Gatun Lake environment had been expected to facilitate rapid endothall uptake by hydrilla, and subsequent rapid microbial decomposition of the herbicide (Westerdahl 1983a). However, the study concluded that released endothall was rapidly adsorbed to the organic detritus and absorbed by hydrilla with the consequence that uptake and breakdown were minimized by low availability of the herbicide. Residue loss from treatment area water was attributed to density (mass) flow, aided by the sinking of hydrilla below the surface, and to absorption by macrophytes and phytoplankton.

Following treatment with the liquid dipotassium salt, no endothall residues were found in water or sediment by 3 DAT. Decrease of endothall residues in plant tissue through 21 DAT following dipotassium salt treatment followed an exponential decay curve, with half-lives of 11.0 days in Plots 1 and 5 and 2.9 days in Plot 6. This suggested rapid adsorption and metabolism of endothall when it was available in the water column. Residues from granular dimethylalkylamine were much slower in dissipating from sediment and tissue. Endothall was not detectable in water from 48 to 72 hr onward; however, residues did not decrease in other compartments through 21 DAT, remaining at 0.14 to 0.26 $\mu g\ g^{-1}$ in plant tissue and at 1.24 to 2.80 $\mu g\ g^{-1}$ in sediment. These more constant levels, which did not allow calculation of half-lives, were thought to result from delayed secondary release of endothall from the organic silt layer above the substrate.

Dissipation in U.S. Lakes

Studies of reservoirs in the Southern United States have also indicated that dissipation of endothall from lake systems is rapid and that the compound does not accumulate in aquatic systems. Endothall residues in water, sediment, and fish from Pat Mayse Lake, a drinking water reservoir in Lamar County, TX, were monitored following application of the dipotassium Aquathol® K Granular to six areas infested with Eurasian watermilfoil (Rodgers, Reinert, and Hinman 1984). Almost complete removal of Eurasian watermilfoil was obtained in treated areas. Endothall dissipated rapidly, within 72 hr, from treated areas. Water column concentrations of endothall in treated areas were below detection when sampled at 7 and 30 DAT; no residues were detected in the vicinity of the lake's potable water intake and the drinking water standard for endothall (0.1 mg ae L^{-1}) was not exceeded in any of the samples. The authors estimated that the aqueous dissipation half-life ranged from 1.1 to 1.2 days. No endothall was detected in sediment or fish samples that were collected at 30 DAT. Water quality parameters of dissolved oxygen, pH, turbidity, and chlorophyll *a* were not significantly altered by herbicide use, and no impacts on nontarget organisms were detected. The authors expected that both dispersion (dilution) and biodegradation contributed to rapid endothall transfer and degradation in this system.

A joint agency program of Tennessee Valley Authority (TVA) and the Corps of Engineers evaluated a range of herbicides for hydrilla and Eurasian watermilfoil control and for dissipation characteristics in Guntersville Reservoir, a navigation, flood control, and power generation component of the TVA located in Alabama and Tennessee. (Rodgers, Dunn, and Robison 1992). Dipotassium Aquathol®K endothall was applied to 12 ha of depth $\leq$ 1 m in the Brown's Creek area at the rate of 47 L ha^{-1}, calculated to give an aqueous concentration of 1.5 mg ae L^{-1}. Samples were collected pretreatment and at 6, 23, and 44 hr and 7 days posttreatment. Complete control of the milfoil was achieved in 7 days. Endothall was nondetectable in all matrices (sediment, fish, mollusks, plants) at all sample times, except water. Trace levels of endothall were detected in 6-hr water samples, at 0.348 mg ae L^{-1} well below the concentration applied, presumably because of flow and rapid dilution. Endothall was nondetectable in local potable water treatment facilities during the month of treatment and during the 3 months following.

Results of these examinations of endothall movement and persistence are comparable to the reservoir study of Ritter and Williams (1998). Half-lives of 1 to 2 days allowed complete endothall dissipation within 7 days, and residues in water supplied by an intake 0.8 km (0.5 miles) from the treatment site showed concentrations well below the MCL, at 0.02 and 0.03 mg L^{-1}, through 4 DAT.

There is no evidence that removal via uptake by plant tissue contributes significantly to dissipation of endothall from aquatic systems. Netherland, Green, and Getsinger (1991a,b) monitored herbicide residues in water following exposure of hydrilla and Eurasian watermilfoil to 5.0 mg ae L^{-1} dipotassium salt for periods of up to 72 hr and noted that endothall loss during this time was negligible. Based on their hydrilla biomass of 11.1 g DW shoot tissue per 50-L aquarium and an estimated accumulation of 333 μg g^{-1} (Van and Conant 1988; Figure 4), plant tissue uptake per experimental unit would have been 3.70 mg of endothall, or only 1.48 percent of total available herbicide.

8 Summary and Conclusions

Numerous studies and evaluations over 2 decades have confirmed that endothall is a highly effective and environmentally safe tool for management of submersed aquatic vegetation. This herbicide has two particularly desirable characteristics for aquatic use: it is effective with relatively short contact times, and it is rapidly and completely decomposed in aqueous systems without accumulation or formation of toxic intermediate compounds. Manipulation of endothall dosage rates for effective control of hydrilla and Eurasian watermilfoil is well-understood. The Corps of Engineers has identified those minimal rates of the dipotassium salt, as low as 0.5 mg ae L^{-1} for 48 hr for Eurasian watermilfoil and 48 hr exposure to 2.0 mg ae L^{-1} for hydrilla, that can provide cost-effective and environmentally sound control. Minimal effective dosage rates are becoming better known for locally important weed species, such as sago pondweed and curlyleaf pondweed. Application techniques suited to the various herbicide formulations are available to provide control under a wide range of water exchange conditions, including canals, rivers, lakes, and reservoirs.

Recent findings on the ability of endothall to control target plants selectively, through manipulation of dosage rate or application timing, show that this herbicide also has a role in the restoration of aquatic ecosystems that have been degraded by invasions of nuisance weed species. The suitability of endothall as a tool for aquatic vegetation management is firmly established.

From the CE research summarized here, it may be concluded that:

a. Endothall is effective in controlling the major species of submersed aquatic weeds of North America in static and flowing water environments.

b. Minimal effective endothall dosage rates for hydrilla and Eurasian watermilfoil have been identified and validated in the field.

c. Inherent physical and chemical characteristics of endothall allow it to dissipate from water, usually within 1 to 4 days posttreatment for the dipotassium salt and within 21 days for the alkylamine, without significant accumulation in sediments or aquatic organisms.

d. Endothall, through manipulation of application timing and dosage rates, has the ability to manage aquatic vegetation in a species-selective way and to maintain and enhance desirable vegetation within the aquatic ecosystem.

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REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* June 2002	**2. REPORT TYPE** Final report	**3. DATES COVERED** *(From - To)*

4. TITLE AND SUBTITLE Review of USACE-Generated Efficacy and Dissipation Data for the Aquatic Herbicide Formulations Aquathol® and Hydrothol®	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Susan L. Sprecher, Kurt D. Getsinger, Jan Sharp	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER 74001
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center, Environmental Laboratory, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199; Cerexagri, Inc., 200 Market Street, Philadelphia, PA 19103-3222	**8. PERFORMING ORGANIZATION REPORT NUMBER** ERDC/EL TR-02-11
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Corps of Engineers Washington, DC 20314-1000	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The contact-type membrane-active herbicide endothall (7-oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid; $C_8H_{10}O_5$) has been widely used in aquatic sites for nearly 50 years. (The herbicide is also known as endothal. The term 3,6-endoxohexahydrophthalic acid has been applied to endothall but is not regarded as the proper nomenclature.) For use as an aquatic herbicide, the free organic diacid endothall is formulated as two of its salts and provided as water-based concentrates and dry granular materials or granules. The currently available aquatic endothall formulations are registered for application to water by the U.S. Environmental Protection Agency (USEPA). The inorganic dipotassium salt is the active ingredient of the Aquathol® K herbicides, used predominantly for lake and static water treatments to control aquatic macrophytes. They are available as Aquathol® K Aquatic Herbicide, Aquathol® K Granular Aquatic Herbicide, and, since 1998, as the Aquathol® Super K Granular Aquatic Herbicide, a concentrated granule formulated in the Culigel® super absorbent polymer. The mono (*N,N*-dimethylalkylamine) endothall salt is registered as the liquid Hydrothol® 191 Aquatic Algicide and Herbicide, and as Hydrothol® 191 Granular Aquatic Algicide and Herbicide. Hydrothol® products are used predominantly for canal treatments to control algae and submerged macrophytes.

Since the 1970s, the U.S. Army Corps of Engineers (CE) Aquatic Plant Control Research Program has carried out research on the efficacy, performance, and dissipation of endothall various aquatic plant species. (Continued)

15. SUBJECT TERMS

Aquatic plant management	Herbicide efficiency
Endothall	Invasive weed control

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT UNCLASSIFIED	**b. ABSTRACT** UNCLASSIFIED	**c. THIS PAGE** UNCLASSIFIED		50	**19b. TELEPHONE NUMBER** *(include area code)*

14. Abstract (continued)

This body of research, often undertaken in cooperation with other Federal and state agencies, universities, and industry, has provided valuable information on the ability of this herbicide to control and manage nuisance aquatic vegetation under static and flowing water conditions and on the fate of endothall in the aquatic environment. Data generated in some of these studies have been used by industry to fulfill requirements for U.S. and state registration or reregistration of specific herbicide formulations.

The objective of this report is to provide a review and summary of CE studies on the aquatic uses of endothall over the past three decades. This summary includes a discussion on the efficacy of endothall against invasive weeds, as well as selected nontarget plants, and how efficacy is based upon application rates and techniques, water-exchange characteristics, and herbicide exposure time mechanisms. Information from growth chamber, mesocosm, and field studies will be provided to link effective plant control to endothall concentration/exposure time relationships. In addition, the degradation and dissipation of endothall under field conditions and how those processes relate to selective plant control and potential impacts to the aquatic environment are reviewed.

Numerous studies and evaluations over two decades have confirmed that endothall is a highly effective and environmentally safe tool for management of submersed aquatic vegetation. Furthermore, it is effective with relatively short contact times, and it is rapidly and completely decomposed in aqueous systems without accumulation or formation of toxic intermediate compounds. Manipulation of endothall dosage rates for effective control of hydrilla and Eurasian watermilfoil is well understood. The CE has identified those minimal rates of the dipotassium salt as low as 0.5 mg ae L^{-1} for 48 hr for Eurasian watermilfoil and 48-hr exposure to 2.0 mg ae L^{-1} for hydrilla that can provide cost-effective and environmentally sound control. Minimal effective dosage rates are becoming better known for locally important weed species, such as sago pondweed and curlyleaf pondweed. Application techniques suited to the various herbicide formulations are available to provide control under a wide range of water exchange conditions, including canals, rivers, lakes, and reservoirs.

Recent findings on the ability of endothall to control target plants selectively, through manipulation of dosage rate or application timing, show that this herbicide also has a role in the restoration of aquatic ecosystems that have been degraded by invasions of nuisance weed species. The suitability of endothall as a tool for aquatic vegetation management is firmly established.