DISSIPATION OF THE HERBICIDES ENDOTHALL, DIQUAT, AND A 1:1 MIXTURE IN WATER, SEDIMENT, AND *EGERIA DENSA*.

by

Scott Lee Van Horn

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APPROVED:

Carl B. Schreck, Chairman

Roderick W. Young

Robert T. Lackey

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INTRODUCTION

Herbicides, such as diquat[6,7 dihydrodipyrido-(1,2-a:2', 1-c) pyrazidiinium salt] and endothall [7-oxabicyclo (2.2.1) heptane-2,3-dicarboxylic acid] are commonly used to control nuisance aquatic vegetation. A 1:1 mixture of diquat and endothall has often been employed to control aquatic macrophytes (Corning and Prosser 1969, Blackburn and Weldon 1969, MacKenzie et al. 1971, Daniel 1972), but few studies have evaluated the phytotoxicity and persistence of the herbicide combination in aquatic systems.

An understanding of herbicide environmental persistence is necessary for judicious use of toxicants for aquatic weed control. While little data are available on the 1:1 mixture of diquat and endothall, the persistence of both components individually in aquatic systems has been investigated under widely differing treatment conditions. Coates et al. (1964) found diquat concentrations at up to 0.5 mg/l undetectable in water from artificial pools; 1 mg/l to 2 mg/l treatments were undetectable in pond water in 8 days. Hiltibran et al. (1972) found diquat treatments from 0.5 mg/l to 2 mg/l of water in ponds undetectable in 1 to 6 days. Blackburn and Weldon (1963) reported that diquat was undetectable in water 8 to 11 days after treating two ponds at 2.5 mg/l diquat. Frank and Comes (1967) treated a pond at a concentration of 0.62 mg/l of water diquat and were unable to recover the herbicide after 4 days. Grzenda et al. (1965) treated a pond at 2.5 mg/l diquat which was undetectable in less than 1 month. Gilderhus (1967) treated fish pools with diquat at 1 mg/1 and 3 mg/1 of water which was unrecoverable in 3 wk and 6 wk, respectively. Yeo (1967) found diquat undetectable within 12 days of treating reservoirs at 0.125 mg/1 to 1.0 mg/1. Beasly (1965) found 1.7 µg/g diquat present in hydrosoils (sediments) 4 years following a 3.36 kg/ha (0.3 lb/A) treatment. Frank and Comes (1967) found diquat was still present in hydrosoils 160 days following a 0.62 mg/1 treatment. MacKenzie et al. (1971) reported diquat persisting in Egeria densa at 25 µg/g following treatment concentrations in water of 1.0 mg/1.

Lindaberry (1961) found an endothall concentration of 5 mg/1 of water in a reservoir undetectable within 4 days. Walker (1963) determined that endothall was undetectable 25 days following 1 mg/1 to 3 mg/1 of water treatments. Frank and Comes (1967) treated a pond at 1 mg/1 of water with endothall and failed to recover the herbicide 24 days after treatment. Hiltibran (1962) found field applications of endothall from 0.3 mg/1 to 10 mg/1 of water were undetectable in an average of 2.5 days with the maximum being 4 days. Yeo (1970) treated 14 ponds at concentrations from 0.3 mg/1 to 1.4 mg/1 of water with endothall. The herbicide in four ponds was undetectable in 8 to 20 days. The remaining 10 ponds declined an average of 71% of the initial herbicide concentration, the range being 23% to 160%, over a 20 day period. Sikka and Rice (1973) found endothall undetectable in water from aquaria containing hydrosoils after 7 days from initial concentrations of 2 mg/1 and 4 mg/1. The herbicide persisted for 35 days in hydrosoils from the aquaria treated at 4.0 mg/1 of water with endothall.

The wide range of persistence reported for both diquat and endothall can be attributed to different experimental environments and often to different herbicide assay methodologies. Water hardness is an environmental component common to every aquatic herbicide application. Some controversy exists concerning the effects of water hardness on herbicide phytotoxicity. Yeo (1964) delayed the treatment symptoms of several aquatic weeds to endothall by increasing water hardness. Parker (1966) illustrated the capacity of increased water hardness to suppress the phytotoxicity of paraquat, suggesting a similar effect may exist with diquat. However, MacKenzie and Hall (1967) working with diquat in Florida waterways, concluded water quality did not appear to affect herbicide efficacy. Yeo (1967) stated that "different levels of hardness did not influence the rate of dissipation" in studies using diquat in artificial pools. The latter studies, rather than refuting the importance of hardness on herbicide phytotoxicity, indicated that, for the ranges of hardness studied and under the variabilities inherent to the experimental designs, hardness had no measurable effect.

In connection with a study[1] on the use of a 1:1 mixture of diquat and endothall to control Egeria densa in Chickahominy Reservoir (Walker's Dam Impoundment), New Kent County, Virginia (Schreck et al.

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[1] Post treatment data on the persistence of diquat and endothall in water, plants, and hydrosoils collected from Chickahominy reservoir are presented in Appendix I.

1973), this study was conducted to meet a number of objectives. The decline of endothall and diquat in water was compared to the decline of the herbicides from water in the presence of plants and hydrosoils to determine the effects of the presence of plants and hydrosoils on decline rates in water. The decline of the 1:1 mixture of the herbicides in water, plants, and hydrosoils from lotic water was compared to that from a lentic pool to investigate the effects of water movement on herbicide decline. The persistence of the mixture in a lentic pool containing water, plants, and sediments was compared to the persistence of each herbicide individually under identical experimental conditions to determine if using the mixture altered the persistence of its components. The phytotoxicity of the mixture and of diquat and endothall alone under varying hardness regimes was investigated to determine if water hardness affects herbicide toxicity and if differences between the phytotoxicity of the mixture and its components exist at the same water hardness level. Decline data obtained for all herbicides in the phytotoxicity test were evaluated to determine if herbicide persistence was affected by varying water hardness and if differences exist in persistence between the mixture and its components at the same level of water hardness.

MATERIALS AND METHODS

Decline characteristics

Two 1.22 x 1.22 x 1.83 m pools were constructed of plywood and coated with non-leaded white enamel paint. One pool was modified using a submersed pump to force water through a system of perforated pipes at various depths creating a current around a centerboard in the box. Each pool was illuminated with two Westinghouse^R cool white and two Westinghouse Plant-Gro^R fluorescent lights on a 15 hr photoperiod. The bulbs generated 41.28 lux (340 ft candles) and 13.34 lux (145 ft candles) of light, respectively, as measured on the water's surface below each light.

Approximately 2,000 l of dechlorinated water was used in each pool. Temperature was maintained at 21° C ± 2°C in both pools. Water hardness, alkalinity, and dissolved oxygen were monitored during each trial according to APHA (1971) methodology; pH was determined *in situ* with a Corning model 610A pH meter.

Three trials were conducted in the pools using field grade Aquathol^R (endothall) and diquat in the pools. A box containing only water was treated with a 1:1 mixture of the two herbicides at a rate corresponding to the treatment rate recommended for use at Chickahominy Reservoir (Corning and Prosser 1969, and Schreck et al. 1973). The treatment rate yielded initial concentrations in water of 0.17 mg/l diquat and 0.25 mg/l endothall. Two pools, one static and the other flowing at rate less than 15 cm/sec, containing water, 13.61 kg (30 lbs) of *Egeria densa*, and hydrosoils to a depth of approximately 7.62 cm, also received the mixture. In another trial the boxes, both static and containing _E. densa_ and hydrosoil, were treated separately, one receiving endothall and the other receiving diquat at the same treatment rate as the previous trials.

Egeria was obtained from Chickahominy Reservoir, Virginia. Plants were drained 20 min before being added to the pools. Hydrosoil was obtained from Pandapas Ponds, Montgomery County, Virginia, and the physical composition and cation exchange capacity determined for the hydrosoils used in each trial. Artificial pools were permitted to equilibrate for 1 wk before herbicide application. Treatment was accomplished by diluting the necessary herbicide(s) with 400 ml of water and pouring the mixture over the surface of each box, simulating surface spray methods used in the field.

Water samples were collected by lowering a glass tube into the pool and withdrawing the entire column of water. Samples were collected in 100 ml and 250 ml aliquots for diquat and endothall determinations, respectively. Samples were taken 1 hr before treatment, immediately afterwards, and at 4 hr, 12 hr, 1, 2, 4, 8, 12, 20, and 28 days following treatment. Diquat samples were acidified with H_2SO_4 to a pH of 1 and both samples of both herbicides were stored in glass at -15°C.

Hydrosoils were collected in containers 9 cm in diameter and 7.5 cm deep placed in each pool before treatment. Samples were collected 1 hr before treatment and 3, 6, 12, 18, and 28 days following treatment and stored at -15°C. Egeria was collected 1 hr before treatment and 1, 4, 8, 18, and 28 days following treatment. Samples were stored in glass jars at -15°C.

Phytotoxicity - hardness

Eight 0.61 x 0.61 x 0.41 m boxes were constructed and painted with a non-toxic white enamel. Sylvania Gro-Lux^R fluorescent lights were positioned immediately above each box and set on a 15 hr photoperiod. Light intensity at the water's surface directly below the light source was determined to be 16.56 lux (180 ft candles).

Dechlorinated tap water was used to fill the boxes to approximately 113 l. Water hardness was adjusted to 30, 150, or 450 mg/l as $CaCO_3$ by dilution with distilled water or the addition of $NaHCO_3$, $CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, and KCl in a ratio of 24:15:30:1. Water temperature was maintained at 20°C ± 2°C. Dissolved oxygen, water hardness, pH, and alkalinity were monitored during each trial.

Egeria was drained for 20 min and 454 g added to each box. Visual observations of plant conditions were made and the weight of drained plants was determined at the conclusion of a trial.

The phytotoxicity of endothall and diquat at concentrations in water of 1.5 mg/l and 1.0 mg/l, respectively, was tested for each herbicide individually on plants established in water at 32 mg/l and 450 mg/l hardness (as $CaCO_3$). A 1:1 mixture of the herbicides, calculated to yield initial treatment concentrations of 1.5 mg/l endothall and 1.0 mg/l diquat, was tested for phytotoxic response of egeria at 32 mg/l, 150 mg/l, and 450 mg/l water hardness. The herbicide mixture was also applied to water containing no plants at the three hardness levels. The boxes containing water or water and plants were permitted to stand 1 wk before treatment.

Water samples for herbicide analysis were collected in glass jars or Nalgene^R bottles 1 day before treatment and 1, 2, 4, 9, 15, 20, and 30 days following treatment and treated as mentioned previously.

A secondary study was conducted to determine if the lighting systems or construction material of the artificial pools influenced the decline of endothall. Two of the 0.61 x 0.61 x 0.41 m painted wood boxes were filled with tap water and treated at 0.50 mg/l herbicide. One box was covered to prevent light penetration while the other was exposed to the same lighting arrangement used in the hardness study. An 18.9 l glass jar was also treated at the same amount to determine if persistence varied with container material.

Analytic procedures

A modification of the analysis described by Chevron Corporation (1970) was used to recover diquat. A 25 ml buret was packed with 8 ml of AG 50W-X8; 100-200 mesh Hydrogen form cation exchange resin (Bio Rad Laboratories^R). The column was prepared by passing 25 ml of saturated NH_4Cl followed by 50 ml of distilled water through the resin at 5 ml/min. The acidified sample was then passed through the column. Twenty-five ml of distilled water, 25 ml of 1 N HCl, 25 ml of distilled water, and 75 ml of 0.1 saturated NH_4Cl were passed through the column consecutively at 5 ml/min. Finally, 25 ml of saturated NH_4Cl were passed through the resin and collected. The diquat containing eluate was reacted with a dithionite indicator to produce a brilliant green color which was compared to a known concentration standard on a Bausch and Lomb Spectronic^R 700 or Beckman D. U.^{R} at 378 nm.

Acidified water samples were passed directly through the column while plant and sediment samples were extracted by refluxing in 18 N H_2SO_4 for 30 min and 5 hr, respectively, and filtered. The pH of plant filtrate was adjusted to 9.0 using 10 M NaOH at which point it was placed on the column. Sediment filtrate was diluted with water to reduce the solution to 1 N H_2SO_4 before being passed through the column.

By analyzing known concentration standards, it was determined that the recovery of diquat from water averaged 80% with a limit of detection of approximately 0.01 mg/1. Recovery of diquat from plants was 55% with a limit of detection between 0.05 μg/g and 0.10 μg/g, and recovery from sediment was 66% with 0.10 μg/g the limit of detection. All diquat data presented in this study have been corrected for recovery.

Sikka and Rice (1973) and Pennwalt (1974) described the procedures which were modified slightly in this study to recover endothall from water, plants, and sediments. Two hundred ml water samples with a low hardness level were boiled with acetic acid until the water was entirely replaced by acid. The remaining acid was evaporated to approximately 10 ml. Any endothall in the sample was converted to the endothall-N-imide form by the addition of 0.1 g of Beta-chloroethylamine HCl, 0.1 g of anhydrous sodium acetate, and heating for 1 hr at just below the boiling point. The sample was then transferred with water to a separatory funnel and extracted with 70 ml of chloroform. One half g of activated charcoal and Attaclay^R each were added to the sample and swirled for one minute to absorb impurities, then removed by filtration. The chloroform was evaporated to dryness and the residue transferred with 0.2-0.5 ml absolute methanol to a 2 ml vial.

Because the high mineral content of hard water samples can interfere in the endothall extraction, an alternate procedure was employed. Activated charcoal (5 g) was added to a 200 ml water sample and stirred for 1 hr to absorb any herbicide. The water was filtered off and the charcoal extracted with acetic acid and boiled until the sample temperature was 118°C. The charcoal was filtered off, and the remaining acetic acid solution was concentrated, carried through the imide derivation, extracted with chloroform, taken to dryness, and transferred to a vial with methanol.

Endothall was extracted from Egeria densa with acetone and water adjusted to a pH less than 3 with HCl in a blender. The mixture was filtered to remove plant debris and stirred for 30 min with 10 g of activated charcoal. The charcoal was filtered off and the filtrate boiled, removing the acetone, until 100 ml of water remained. The solution was washed with 75 ml of ether in three portions and 50 ml of chloroform in two portions. The water layer was saved and boiled to remove the chloroform. Five g of charcoal was added to the sample and stirred at a moderate rate for 1 hr to absorb any endothall. After filtration, the charcoal was transferred to a beaker and boiled in acetic acid until the temperature reached 118°C, keeping the final volume above 100 ml. Filtering again, the charcoal was discarded and the acetic acid sample carried through the imide formation as it was with the water samples. The endothall-N-imide solution was transferred to a separatory funnel with water and extracted with 70 ml of chloroform. The chloroform extracted was washed with two 30 ml portions of water, two 30 ml .1 N NaOH washes, and a final 30 ml of water. Attaclay^R and charcoal were used in 0.5 g amounts to remove impurities, filtered off, the remaining chloroform dryed and the residue picked up in absolute methanol.

The herbicide was extracted from soil by shaking a 15 to 25 g sample with 100 ml of methanol-HCl (10:1). After filtering, 5 g of activated charcoal was added to the filtrate and stirred for 30 min. After filtering and discarding the charcoal, 400 ml of water was added to the filtrate and boiled to remove the methanol. Five g of charcoal was added and the sample stirred for 1 hr to absorb any endothall. Filtering once more, the charcoal was transferred to a beaker and boiled in acetic acid until the temperature reached 118°C. The sample was filtered and the filtrate carried through the imide formation to the vial as described in the plant procedure.

Endothall determinations were made by injecting 1 to 6 μl of sample on a Tracor^R M.T. 220 gas-liquid-chromatograph using a Coulson^R nitrogen detector, and sample peak areas were compared with standard injection peak areas. It was equipped with a 1.06 m, 0.64 cm (3 1/2 ft, 1/4 in) glass column packed with Chronosorb WHP in a 80/100 mesh with a liquid phase of SE-30, 3% by weight. Helium gas was used as a carrier at 80 ml/min. Injection port temperature was 225°C, column temperatures used were between 180°C and 200°C. The Coulson detector inlet was 260°C and the pyrolysis furnace 820°C.

Endothall recovery in water of low mineral content or hardness was 90% with a limit of detection at 0.01 mg/l. Determinations were variable; ± 50% at levels as low as 0.10 mg/l. Herbicide recovery from hard water was approximately 55%, and the limit of detection was 0.05 mg/l. Endothall recovery in plants was 53% with a detection limit of 0.05 μg/g. Due to the extreme variability of sediment recovery values, no extraction efficiency is reported. However, it is sufficient to know that the limit of detection was 0.20 μg/g because no endothall was recovered from any hydrosoil samples in the study. All endothall data presented in this study has been corrected for recovery.

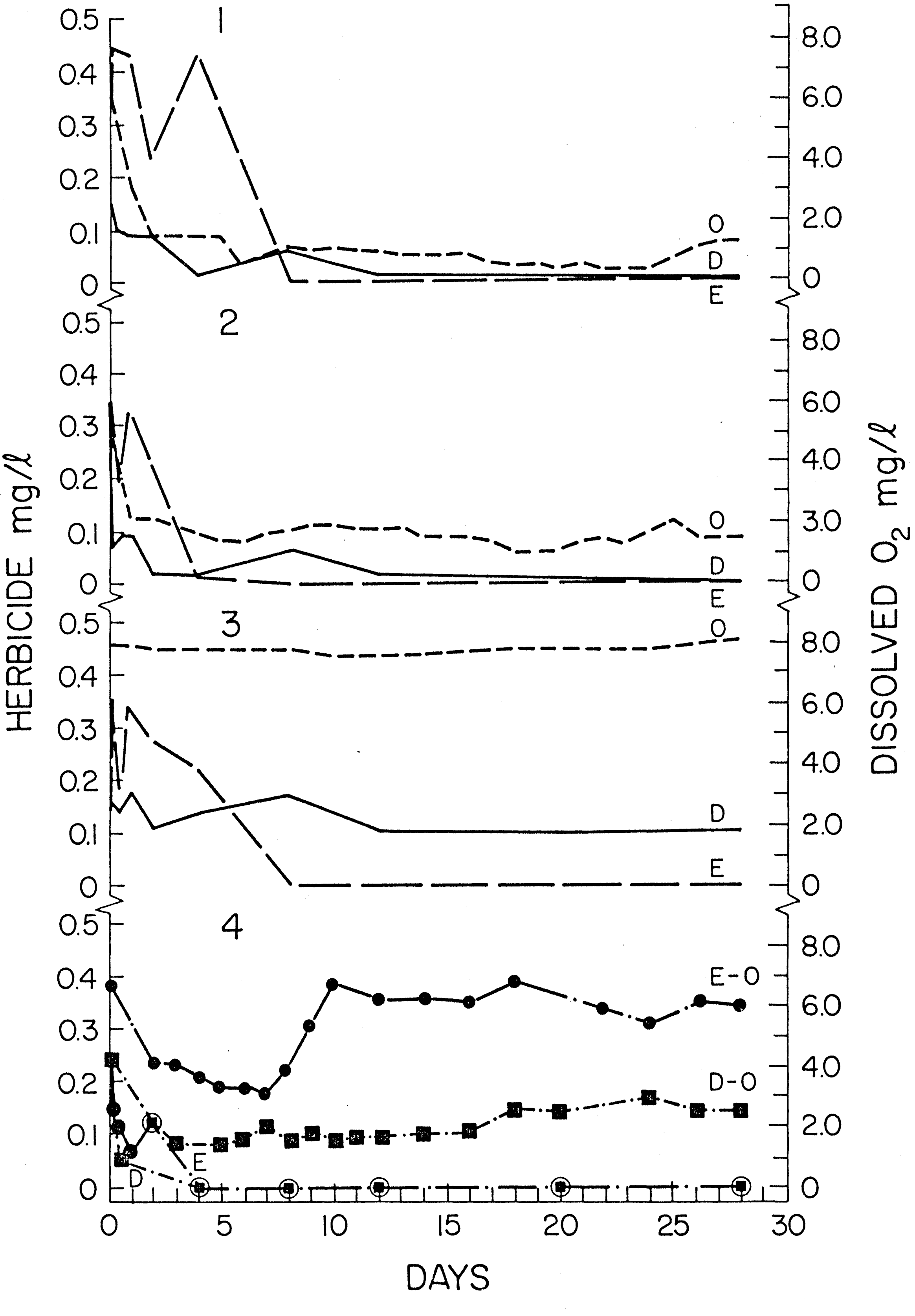
RESULTS

Decline characteristics

In the pool containing only water and treated with the herbicide mixture, the maximum endothall level measured in water, 0.33 mg/1, was determined 4 hr after treatment and was sustained for an additional 20 hr. The herbicide level then declined until no longer detectable 8 days following treatment (Fig. 1). The maximum amount of diquat recovered from water was 0.18 mg/1 and occurred 1 day following treatment. This level of concentration had changed little by 8 days following treatment and had declined to 0.11 mg/1 by the 28th day (Fig. 1). The water hardness of 45 mg/1 did not change during the study. Alkalinity, 35 mg/1, did not change in the first 21 days but had risen to 40 mg/1 by the 28th day. The pH also remained steady at 7.0 through the first 3 wk but had risen to 8.1 by the 28th day. Dissolved oxygen levels remained close to 7.8 mg/1 until the 26th day, then increased to 8.2 mg/1 by the 28th day (Fig. 1). Green algae had begun to appear in the box on the 22nd day and had increased its numbers by the 28th day, a possible explanation for the upward trend of the alkalinity, pH, and dissolved oxygen.

In the still water pool stocked with egeria and sediment and treated with the herbicide mixture, endothall was measured at its highest concentration in water, 0.45 mg/1, 4 hr after treatment and sustained approximately that level at the end of 4 days (Fig. 1). The herbicide was undetectable 8 days after treatment. Diquat reached

Fig. 1. Dissolved oxygen (O), diquat (D), and endothall (E) in water from (1) a lentic pool containing egeria and hydrosoil; (2) a lotic pool containing egeria and hydrosoil; (3) a pool containing only water; and (4) dissolved oxygen (D-O) and diquat (D) from one lentic pool containing egeria and hydrosoil, and dissolved oxygen (E-O) and endothall (E) from a second lentic pool containing egeria and hydrosoils.


1
2
3
4
HERBICIDE mg/ℓ
DISSOLVED O2 mg/ℓ
DAYS
0.5
0.4
0.3
0.2
0.1
0
8.0
6.0
4.0
2.0
O
D
E
E-O
D-O
0
5
10
15
20
25
30

a maximum 0.14 mg/l 4 hr after treatment, was 0.06 mg/l on the 8th day, 0.01 mg/l on the 12th day and undectable by the 28th day (Fig. 1). No endothall was recovered from any plant samples while diquat was found in plants at 3.36 μg/g, 1 day after treatment and increased to 5.63 μg/g by the 18th day (Fig. 2). Concomitant with the herbicide decline in water and the increase in plants, the healthy green mat of egeria occupying the entire water column rapidly exhibited loss of color and turgor. The plants eventually lost all color, settled to the bottom of the water column and disintegrated, preventing obtaining plants for analysis on the 28th day. Duck weed (Lemna sp.) was eliminated in 30 days. The water quality of the pool was altered by the dying macrophytes producing an increase in alkalinity from 45 mg/l to 95 mg/l on the 28th day. The pH dropped from 7.05 to 6.1 on the 21st day but had returned to 6.6 by the 28th day following treatment. Dissolved oxygen decreased from 6.8 mg/l to 0.4 mg/l on the 24th day (Fig. 1) reflecting either the lack of autotrophic production of oxygen or a biological oxygen demand exerted by microbial metabolism of plant material or both. Once the plants had disintegrated the dissolved oxygen began to increase again to 1.3 mg/l recorded on the 28th day, although no algal increase was apparent. Water hardness increased from 50 mg/l to 60 mg/l. Diquat was undetectable in hydrosoils on the 3rd day after treatment but had increased to 2.24 μg/g on the 28th day (Fig. 3). No endothall was recovered in any sediment samples (Fig. 3). The hydrosoils were 9.48% sand, 48.19% silt, and 42.31% clay with a cation exchange capacity of 25.4 meg/100 mg.

Fig. 2. Diquat (D) and endothall (E) in _Egeria densa_ from (1) a lentic pool containing egeria and hydrosoil; (2) a lotic pool containing egeria and hydrosoil; and (3) a lentic pool containing egeria and hydrosoil treated with diquat (D), and a second lentic pool containing egeria and hydrosoil treated with endothall (E).

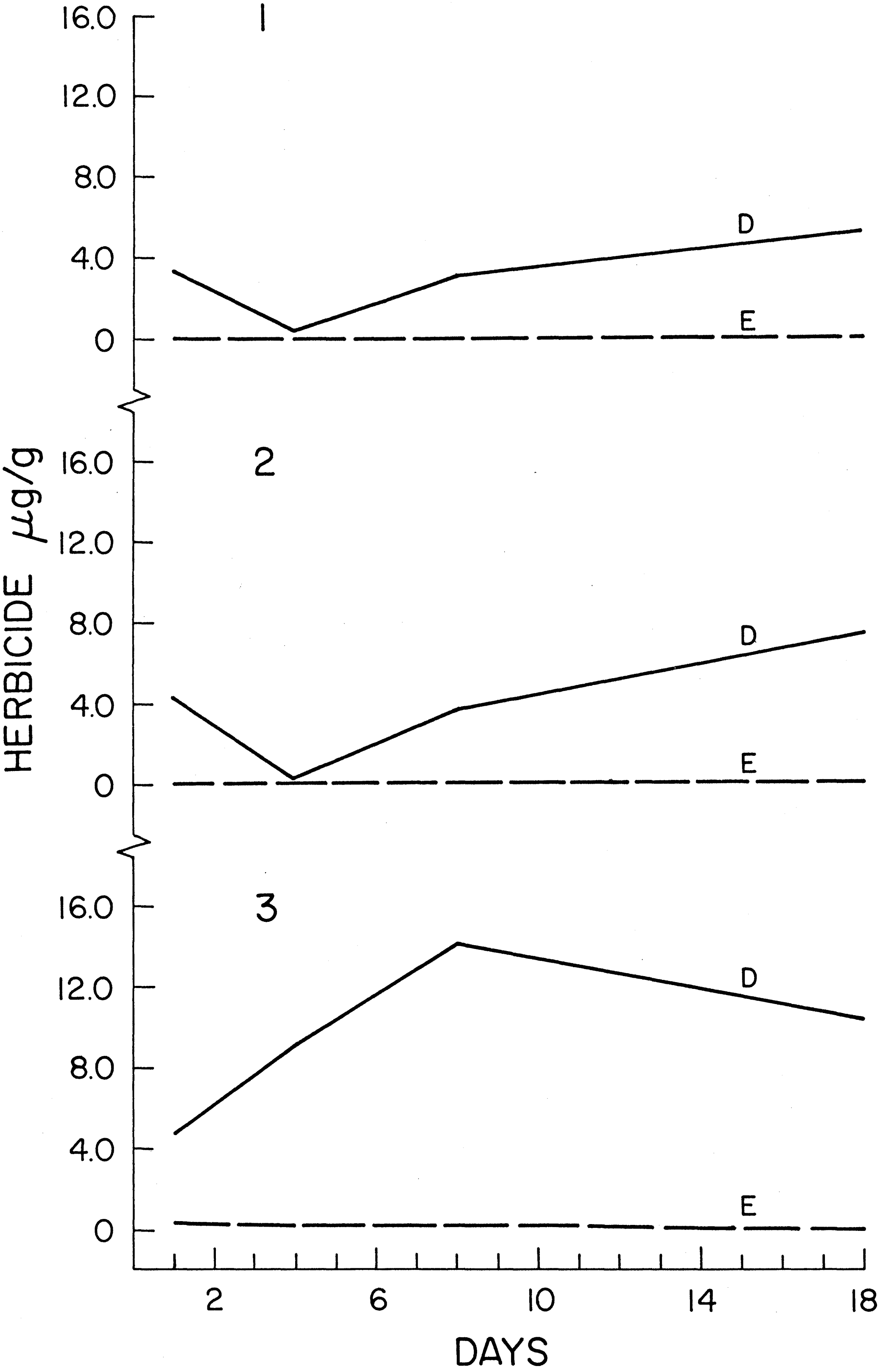
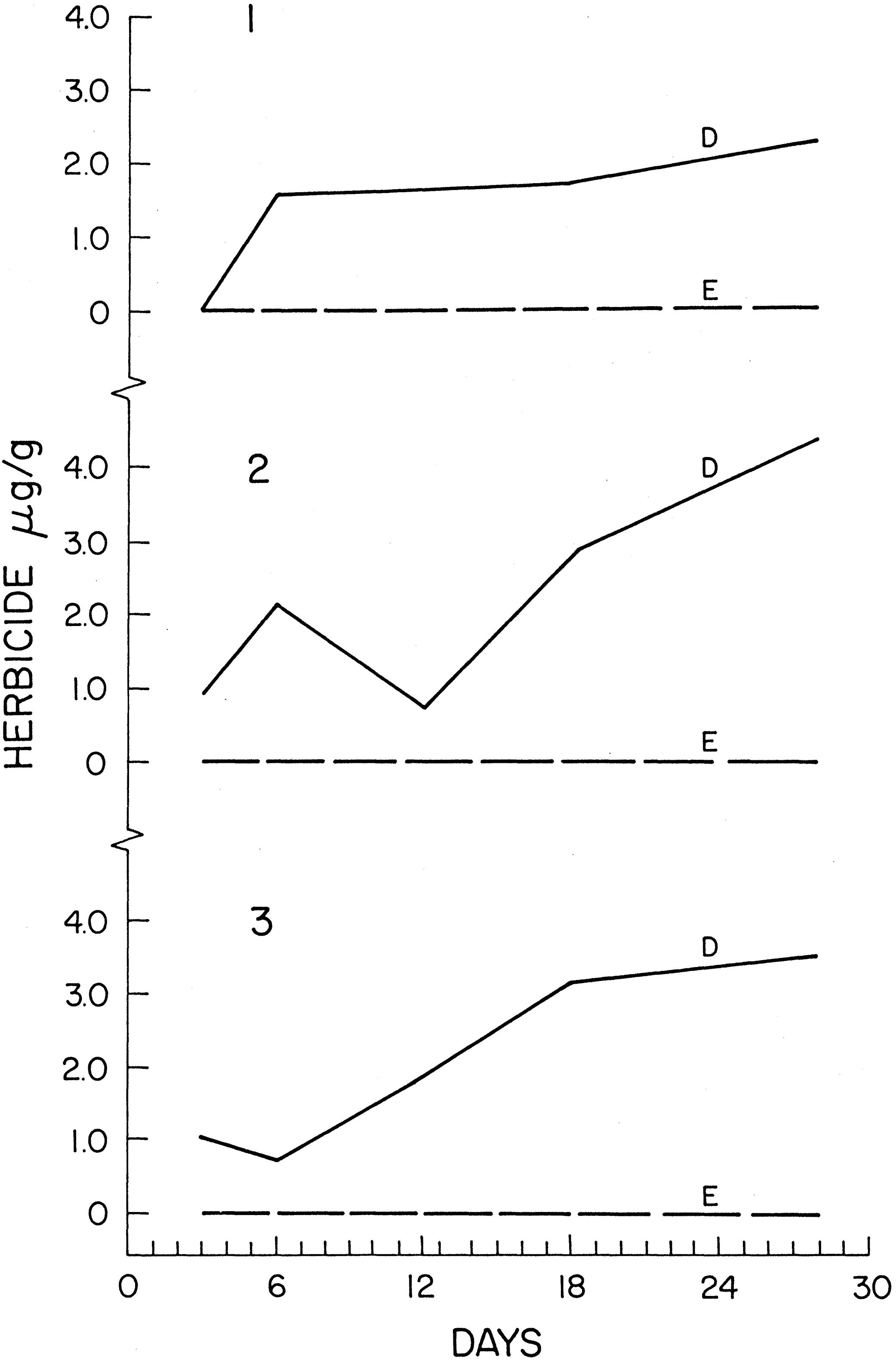

1
2
3
16.0
12.0
8.0
4.0
0
D
E
HERBICIDE µg/g
2
6
10
14
18
DAYS

Fig. 3. Diquat (D) and endothall (E) in hydrosoils from (1) a lentic pool containing egeria and hydrosoil; (2) a lotic pool containing egeria and hydrosoil; and (3) a lentic pool containing egeria and hydrosoil treated with diquat (D), and a second lentic pool containing egeria and hydrosoil treated with endothall (E).


4.0
3.0
2.0
1.0
0
1
D
E
2
4.0
3.0
2.0
1.0
0
D
E
3
4.0
3.0
2.0
1.0
0
D
E
HERBICIDE μg/g
0
6
12
18
24
30
DAYS

The maximum endothall measured in water from the flowing water pool containing egeria and sediments was 0.40 mg/l in a sample collected 15 min after treatment (Fig. 1). The herbicide had declined an additional 50% by the 2nd day, was 0.01 mg/l on the 4th day and undetectable by the 8th day after treatment. The maximum recovered value for diquat in water was 0.27 mg/l occurring 15 min after treatment (Fig. 1). The herbicide persisted at 0.07 mg/l on the 8th day, reached 0.02 mg/l by the 12th day and was undetectable on the 28th day. Endothall was not recovered in any egeria samples while diquat increased from 4.15 μg/g 1 day after treatment to 7.34 μg/g 18 days following treatment (Fig. 2). Treatment effects on plants included chlorosis and loss of turgor within 3 days. Color loss was not complete until the 21st day when disintegration was becoming very apparent. The water was heavy with particulates by the 25th day and assumed a dark color with a detectable smell of H_2S which was not lost by the 28th day. Plant disintegration prevented collecting samples on the 28th day. Duck weed was controlled within 3 days. Concurrent with the decline of the macrophytes, alkalinity increased from 40 mg/l to 65 mg/l. The pH dropped from 7.15 to 6.2 on the 21st day and 6.7 on the 28th day. Dissolved oxygen decreased from 5.4 mg/l to 2.2 mg/l after 1 day, 1.1 mg/l on the 18th day, and was 1.5 mg/l on the 28th day after treatment (Fig. 1). Hardness increased from 50 mg/l to 60 mg/l. No endothall was recovered from the hydrosoils but diquat increased from 0.94 μg/g in sediments 3 days after treatment to 4.31 µg/g on the 28th day (Fig. 3). The hydrosoil physical composition and cation exchange capacity were identical to those in the still water box mentioned previously.

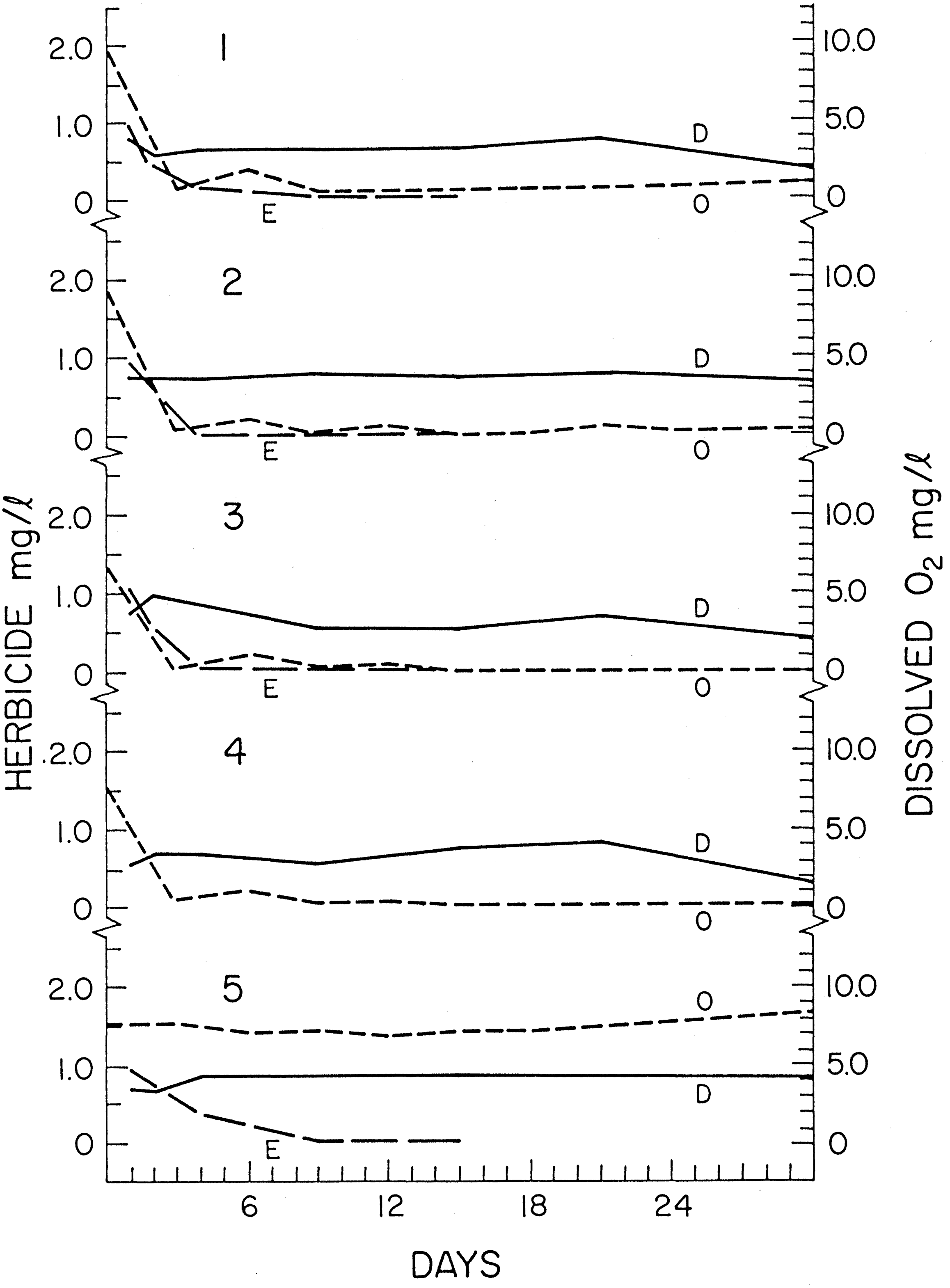
Endothall was measured at a high of 0.26 mg/l of water within 15 min after treating a pool stocked with plants and sediments with endothall alone (Fig. 1). The herbicide declined to 0.12 mg/l on the 2nd day and was undetectable on the 4th day following treatment. Endothall was present in egeria at 0.15 µg/g 1 day after treatment, 0.06 µg/g on the 4th day, and detectable traces existed on the 8th day (Fig. 2). No endothall was recovered from hydrosoils (Fig. 3). The sediment was 21.4% sand, 48.9% silt, and 29.6% clay with a cation exchange capacity of 28.7 meq/100 mg. Following treatment, the plants sank to within 45 cm of the bottom of the pool. No chlorosis or loss of turgor was apparent; rather, the macrophytes began to exhibit growth by the 6th day. By the 12th day, some new growth stems were as long as 10-13 cm. The appearance of the plants remained excellent throughout the remainder of the 28 day trial. The duck weed population increased until it covered the entire water surface. The poor treatment efficacy was reflected in the water quality stability. Alkalinity increased from 35 mg/l to 45 mg/l and hardness remained unchanged at 45 mg/l. The pH remained approximately 7.0. An oxygen sag developed immediately after treatment with the initial value of 6.8 mg/l decreasing to 3.2 mg/l 1 wk after treatment. Oxygen approached pretreatment levels again by the 10th day (Fig. 1).

Diquat declined from a measured high of 0.26 mg/l of water 1 day after treatment to 0.01 mg/l on the 8th day in water from the pool stocked with plants and hydrosoils and treated with diquat only (Fig. 1). The herbicide was undetectable on the 12th day. Analysis of egeria indicated diquat increased from 4.48 μg/g the 1st day to 14.26 μg/g on the 8th day (Fig. 2). Diquat levels in sediment increased from 1.06 μg/g on the 3rd day to 3.44 μg/g on the 28th day (Fig. 3). The hydrosoil was 10.52% sand, 53.9% silt, and 35.5% clay with a cation exchange capacity of 30.2 meq/100 mg. The response of plants to treatment was rapid with the macrophytes sinking to the bottom of the pool by the 3rd day after treatment; turgor decreased. Chlorosis and disintegration was noticeable by the 7th day and accompanied a change in water clarity. Plants were impossible to collect past the 18th day. Duck weed was dead in 3 days. The rapid plant destruction increased the alkalinity from 30 mg/l to 50 mg/l and dropped the pH from 7.0 to 6.6 on the 14th day. However, the pH recovered to 7.0 by the 21st day. Water hardness increased slightly from 40 mg/l to 45 mg/l. Dissolved oxygen dropped from 4.4 mg/l before treatment to a low of 1.4 mg/l then increased to 2.6 mg/l by the 15th day and remained at that level until the 28th day (Fig. 1).

Phytotoxicity - hardness

Endothall declined from 0.93 mg/l recorded in water 1 day after treatment to 0.11 mg/l on the 4th day and was undetectable on the 9th day in a box with a water hardness of 450 mg/l and

Fig. 4. Dissolved oxygen (O), diquat (D), and endothall (E) from water in (1) a pool with 450 mg/l water hardness and egeria; (2) a pool with 160 mg/l water hardness and egeria; (3) a pool with 31 mg/l water hardness and egeria; (4) a pool with 32 mg/l water hardness and egeria; and (5) a pool with 24 mg/l water hardness.


1
2
3
4
5
D
E
O
HERBICIDE mg/ℓ
DISSOLVED O_2 mg/ℓ
2.0
1.0
0
10.0
5.0
0
6
12
18
24
DAYS

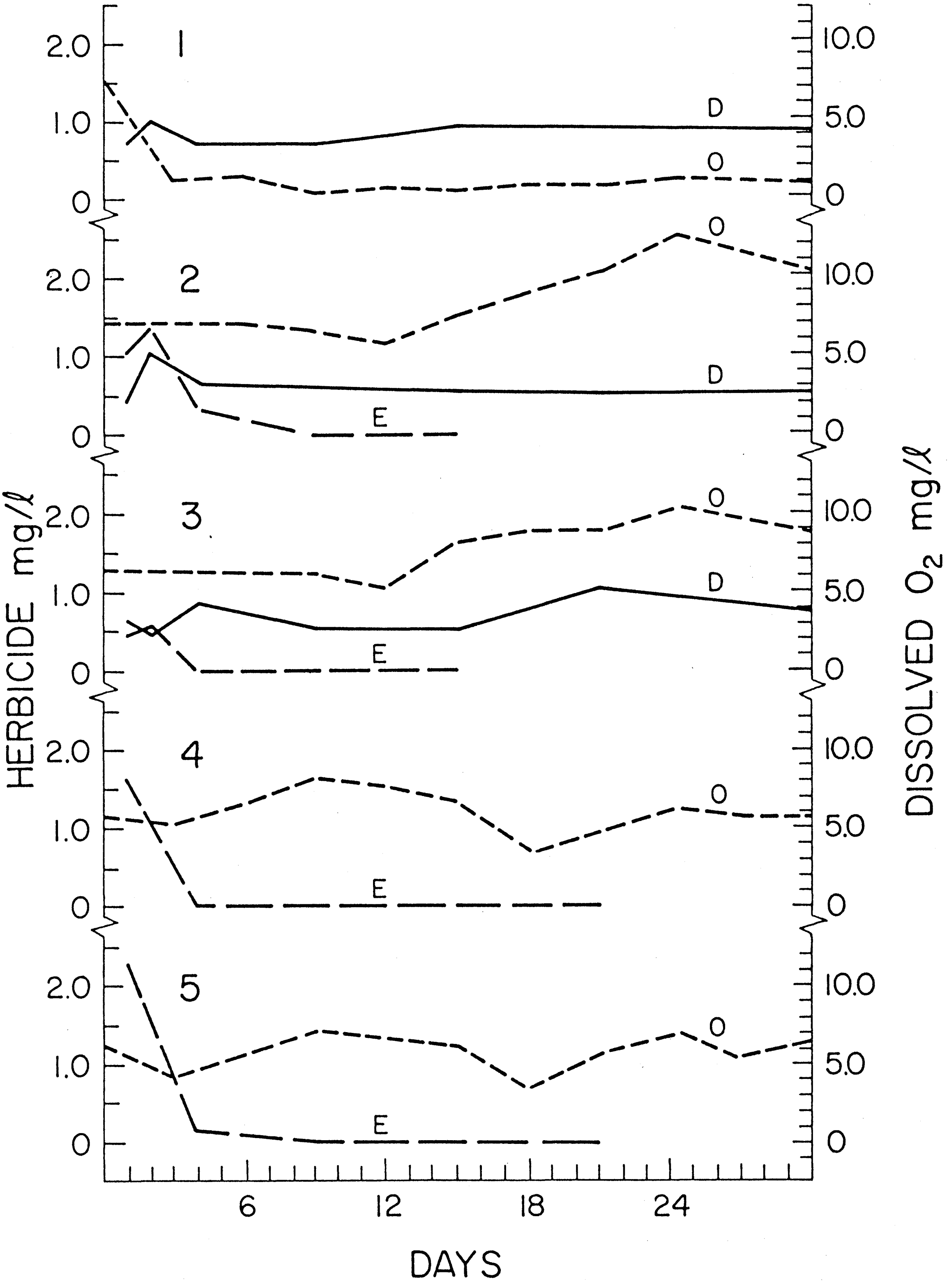
containing egeria (Fig. 1). Diquat maintained a level of approximately 0.70 mg/l through the 21st day and declined to 0.16 mg/l on the 30th day after treatment (Fig. 4). Four days after treatment the egeria began to exhibit chlorosis and loss of turgor, mainly in those plants near the surface, a condition that gradually worsened until disintegration of the leaf materials began approximately 3 wk after treatment. The water remained clear. Evidence of new growth, however, persisted throughout the study at the bottom of the box. Duck weed in the box suffered chlorosis by the 4th day and had died completely by the 14th day. Seventy-five per cent of the stocked plant weight remained after 30 days. Treatment effects caused an increase in alkalinity from 365 mg/l to 400 mg/l and a drop in pH from 8.2 to 7.6. Water hardness increased slightly from 450 mg/l to 460 mg/l probably due to water loss. Dissolved oxygen fell from 9.8 mg/l before treatment to 0.6 mg/l 3 days later and remained at low levels (Fig. 4).

The box adjusted to 160 mg/l water hardness and containing egeria had endothall decline from 0.91 mg/l of water on the 1st day to undetectable levels on the 14th day (Fig. 4). Diquat levels were stable near 0.70 mg/l of water (Fig. 4). Four days after treatment some reduction in turgor and chlorosis was noted in plants near the surface, a trend which continued until affected leaves began to readily disintegrate around 3 wk following treatment. By the 30th day, some stems had become flaccid. Water clarity was excellent. Duck weed at the water's surface was dead by the 14th day following treatment. Alkalinity increased from 99 mg/l to 141 mg/l while the pH dropped from 8.3 to 7.0. Water hardness increased from 160 mg/l to 180 mg/l, due in part to evaporation. Dissolved oxygen declined from 9.2 mg/l before treatment to 0.0 mg/l on the 15th day and did not substantially increase (Fig. 4). The weight of the plants remaining was 75% of the weight introduced.

Endothall declined from 1.00 mg/l of water 1 day after applying the herbicide mixture to undetectable levels by the 4th day in a box containing water with a hardness of 31 mg/l and egeria. Diquat was reduced from 0.96 mg/l of water present 2 days after treatment to 0.37 mg/l on the 30th day (Fig. 4). Egeria showed symptoms of chlorosis and loss of turgor by the 4th day with the most severe conditions near the surface. A number of plants exhibited growth, but by the 14th day all had turned yellow and leaf loss was great. Debris was prevalent in the water column. By the 24th day visibility in the water column was to a depth of 10 cm and H_2S was evident, a condition which had not changed by the 30th day. Duck weed had died completely and sunk from the surface by the 14th day following treatment. Only 40% of the original plant weight remained after 30 days. The treatment caused an increase in alkalinity from 16 mg/l to 57 mg/l and a drop in pH from 7.6 to 6.4. Water hardness increased from 31 mg/l to 40 mg/l. Dissolved oxygen fell from 7.7 mg/l to 0.4 mg/l on the 3rd day after treatment and 0.00 mg/l on the 15th day where it remained (Fig. 4).

In the box containing water at 32 mg/l hardness and egeria, and treated with diquat only, the herbicide declined from 0.53 mg/l of water on the 1st day to 0.24 mg/l on the 30th day (Fig. 4). Following

Fig. 5. Dissolved oxygen (O), diquat (D), and endothall (E) from water in (1) a pool with 465 mg/l water hardness and egeria; (2) a pool with water alone at 162 mg/l water hardness; (3) a pool with water alone at 460 mg/l water hardness; (4) a pool with 460 mg/l water hardness and egeria; and (5) a pool with 24 mg/l water hardness and egeria.


1
2
3
4
5
D
O
E
2.0
1.0
0
10.0
5.0
0
HERBICIDE mg/ℓ
DISSOLVED O_2 mg/ℓ
6
12
18
24
DAYS

treatment, chlorosis and turgor loss were exhibited by the 4th day, with some strands of macrophytes near the surface being completely flaccid. These conditions worsened with time until the 24th day when many of the strands disintegrated. Concurrent with this disintegration particulate matter in the water column increased, the water discolored and the presence of H_2S was apparent. The condition of yellowing growth areas was also apparent. The duck weed had died and sunk to the bottom by the 14th day following treatment. The final plant weight was 40% of the original. Treatment effects increased alkalinity from 20 mg/1 to 55 mg/1 and reduced the pH from 7.9 to 6.5. Water hardness increased from 32 mg/1 to 40 mg/1. Dissolved oxygen fell from 7.7 mg/1 to 0.10 mg/1 on the 12th day after which anoxia prevailed (Fig. 4).

In the box containing egeria, a water hardness of 465 mg/1, and treated with diquat only, the herbicide determinations indicated that diquat remained at approximately 0.80 mg/1 of water over the 30 day trial (Fig. 5). Once more, plant damage was most severe near the surface and included chlorosis and reduced turgor, symptoms which evolved until disintegration had become apparent by the 24th day. Fewer darkened leaves were evident in this box. Water clarity remained good. Growth shoots of a healthy green were apparent even by the 30th day. Duck weed was dead and cleared from the water's surface by the 14th day following treatment. Eighty-six per cent of the plant weight remained. The treatment increased alkalinity from 321 mg/1 to 412 mg/1 and reduced pH from 8.2 to 7.8. Water hardness increased from 162 mg/l to 176 mg/l. Dissolved oxygen fell from 7.7 mg/l to 1.2 mg/l on the 3rd day, and was 0.9 mg/l by the 30th day (Fig. 5).

The box having 460 mg/l water hardness and containing egeria treated with endothall alone had the herbicide declining from 1.62 mg/l of water to undetectable levels by the 4th day (Fig. 5). The impact of the herbicide on the egeria was not noticeable. Plant condition remained unchanged except for new growth and a slight decrease in the intensity of the plant color. Duck weed in the box increased. Alkalinity was not changed by treatment, remaining at 310 mg/l. The pH dropped from 7.9 initially to 7.1 on the 15th day but returned to 7.8 by the 30th day. Water hardness increased from 460 mg/l to 480 mg/l. Dissolved oxygen fluctuated over a range of 3.3 mg/l to 8.2 mg/l (Fig. 5). The plant material remaining in the box was 75% of the original mass.

In the box containing water with a hardness of 24 mg/l, egeria, and receiving only endothall, the herbicide declined from 2.24 mg/l of water (Fig. 5) 1 day after treatment to 0.10 mg/l on the 4th day, and was undetectable on the 9th day. The macrophyte condition following treatment was unchanged except for limited growth and slight fading of color. The duck weed in the box increased. The macrophytes remaining in the box were 25% lower than their original weight. Alkalinity increased from 19 mg/l to 25 mg/l while the pH dropped from 7.6 to 7.0, 15 days after treatment but returned to 7.7 by the 30th day. Water hardness increased from 24 mg/l to 30 mg/l. Dissolved oxygen (Fig. 5) varied over a range of 3.5 mg/l to 7.15 mg/l.

A box containing water alone at 32 mg/l hardness was treated with the mixture of herbicides. Endothall (Fig. 5) declined from 0.89 mg/l of water the day after treatment to 0.35 mg/l 4 days after treatment and was undetectable on the 9th day. Diquat averaged approximately 0.74 mg/l of water over the 30 day trial (Fig. 5). Alkalinity increased from 18 mg/l through the first 2 wk to 22 mg/l on the 30th day. The pH dropped from 7.6 to 6.9 on the 15th day. Water hardness did not change. Dissolved oxygen remained close to 7.0 mg/l until the last week when an increase in algae present in the water increased the oxygen to 8.3 mg/l (Fig. 5).

A second box containing only water but at a hardness of 162 mg/l was treated with the herbicide mixture. Endothall was measured at a maximum 1.06 mg/l of water 1 day after treatment, 0.31 mg/l after 4 days, and undetectable on the 9th day (Fig. 5). Diquat declined from 1.04 mg/l of water measured on the second day after treatment to 0.55 mg/l on the 30th day (Fig. 5). Alkalinity increased from 107 mg/l to 126 mg/l and the pH rose from 8.1 to 8.4. Hardness increased from 162 mg/l to 176 mg/l. Dissolved oxygen values were 7.3 mg/l initially, 5.9 mg/l on the 12th day, and an increasing algae population raised it to 10.2 mg/l by the 30th day.

In a box containing only water with a hardness of 460 mg/l and treated with the mixture, endothall declined from 0.58 mg/l of water measured on the 2nd day to 0.00 mg/l on the 4th day (Fig. 5). Diquat persisted at approximately 0.74 mg/l of water throughout the 30 day trial. Alkalinity increased from 330 mg/l to 412 mg/l while pH decreased from 8.6 to 8.3. Water hardness increased from 460 mg/l to 480 mg/l. Dissolved oxygen fell from 6.5 mg/l to 5.4 mg/l by the 12th day then increased to 8.8 mg/l on the 30th day due to the presence of increasing numbers of green algae.

In the trial to test the effects of the light regime and container materials on endothall decline, the herbicide in the lighted box declined from 0.17 mg/l of water 2 days after treatment to 0.07 mg/l on the 5th day and undetectable levels on the 12th day. Endothall was 0.22 mg/l of water on the 2nd day and 0.15 mg/l on the 5th day following treatment in the darkened box, but the herbicide was below the level of detection on the 12th day. In the illuminated glass container, endothall declined from 0.18 mg/l on the 2nd day after treatment to 0.02 mg/l on the 12th day and was undetectable on the 20th day.

DISCUSSION

Under the treatment conditions and application rates used in the box decline studies, endothall was never detectable in water 8 days following the administration of the herbicide. The egeria did not assimilate enough endothall from the water column to permit detection, except in the pool treated with endothall alone. In this case the herbicide was just above the limit of detectability and not toxic enough to control the macrophyte. No hydrosoils contained endothall in concentrations above the limit of detectability, hence it is impossible to determine if decomposing egeria increases herbicide levels in the hydrosoils.

Diquat persisted in water at the limit of detection up to 20 days following treatment in artificial pools containing sediments and egeria. Eighteen days after treatment, herbicide concentrations in egeria ranged from 25 to 70 times the original concentrations in the water column. In sediments, diquat reached concentrations 10 to 20 times original water column concentrations by the 28th day after treatment. There was insufficient data to determine if diquat was released by dying macrophytes to the water column or sediments as suggested by Davies and Seaman (1968).

Diquat applied to water alone declined only 50% of its treatment concentration in 28 days, indicating that the presence of plants and sediment increases the herbicide's decline rate as noted by Coates et al. (1964). Endothall, however, when applied in the mixture did not decline from water in the presence of plants and sediments more rapidly than it did from water alone as reported by Hiltibran (1962). However, the rapid decline of endothall from water in the pool treated with endothall alone indicates that plants and sediments may decrease the herbicide's persistence in water if diquat is not present.

The conclusion that the presence of diquat affected the persistence of endothall in the water column is supported by data indicating that not only was the decline of endothall most rapid in the absence of diquat, but endothall was recovered from plants under these conditions. Diquat may affect the ability of egeria to remove endothall from the water column because endothall was not found in any plants from pools treated with the herbicide mixture. Endothall may exert a similar effect on diquat because the pool containing only diquat had the most rapid decline of diquat from the water column and conversely the highest concentrations of diquat in sediments and plants. Sediments and plants were more effective at removing diquat from the water column in the absence of endothall. Replicates of this study may confirm the possibility that each herbicide affects the ability of egeria to assimilate the other herbicide.

Visual observations documenting the inability of endothall to control egeria when used alone and confirming that control was achieved in the boxes containing the mixture and diquat alone were supported by the water quality data. Effective treatment increased alkalinity, drastically reduced dissolved oxygen, and usually reduced pH slightly, effects also noted by Strange (1975) as accompanying plant control. The inefficacy of endothall was reflected in more stable water quality determinations. These data suggest that plant control achieved by the mixture were achieved principally through the phytotoxic activities of diquat alone, and indicate that the use of endothall in the mixture to control egeria should be reevaluated. No differences in the decline of diquat or endothall in water or plants from the flowing water pool and still water pool were apparent. Diquat concentrations in sediment from the lotic pool were higher than those from the lentic pool, perhaps due to the increased herbicide contact with sediment created by the flowing water. Concomitant changes in water concentrations may have been too subtle to detect. Phytotoxicity, however, was not influenced by lotic conditions.

Endothall did not persist until the 9th day following treatment in any of the various water hardness regimes with or without the presence of egeria, indicating that water hardness had no apparent effect on endothall decline. Diquat persisted in the water column over each 30 day trial period with no evident differences in decline due to water hardness. The average amount of diquat left in boxes without egeria on the 30th day was 0.68 mg/l while those containing plants averaged 0.44 mg/l providing additional confirmation that plants remove diquat from the water column.

Each hardness regime treated with diquat had visual evidence of plant control and exhibited increases in alkalinity and decreases in pH and dissolved oxygen. The data indicate that herbicide phytotoxicity was reduced by increasing water hardness, a relationship which appears to be independent of herbicide decline rates from water or uptake rates by plants. The range of hardness tested was great, and lesser differences might obscure any changes in herbicide phytotoxicity. Endothall failed to control egeria in both soft and hard water situations. Consequently, water quality factors remained stable, supporting the contention that endothall's use with diquat in a mixture to control E. densa should be reevaluated. Further, some justification may exist for adjusting recommended field treatment concentrations where differences in water hardness are great.

In the trials testing the effects of light regimes and container materials on herbicide persistence, the decline of endothall varied with different pool types and light conditions employed. The persistence of endothall was more prolonged in water from a glass jar than in water from a wooden pool treated at the same concentration. The decline of endothall in a lighted pool was more rapid than in a darkened pool. Variability existing in the literature on the decline of endothall may be attributed in part to differences in the types of artificial pools used and the lighting systems employed for each pool. One such variable may explain the differences between the rate of decline of endothall in water alone as reported by Hiltibran (1962) and the results reported here. Diquat was not evaluated in this study because decline curves reported earlier in this paper approximated those existing in the literature.

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APPENDIX

Table 1. Persistence of endothall (mg/l) in water at Chickahominy Reservoir study stations.

Date		Deep Water		Shallow Water	
VII -	8	0.00	0.00	0.00	0.00
(4 hr)	10	0.05		3.29	
(12 hr)	11	0.00	0.00	0.26	0.20
(20 hr)		0.03	0.04	0.13	0.17
(28 hr)		0.04	0.02	0.14	0.09
	12	0.11	0.06	0.18	0.19
	13	0.01	0.01	0.06	0.00
	14	0.02	0.01	0.10	0.04
	15	0.00		0.04	0.03
	16	0.04	0.01	0.03	
	17	0.02	0.02	0.00	0.03
	18	0.01	0.00	0.03	0.02
	19	0.00	0.01	0.00	0.04
	20	0.00	0.00	0.04	
	21	0.00	0.00	0.03	0.01
	22	0.00	0.00	0.00	0.00
	24	0.00	0.00	0.00	
	25	0.00		0.00	
	27			0.00	
	28	0.00		0.00	
	30	0.00			
VIII -	3	0.00		0.00	
	15	0.00		0.00	
	22	0.00		0.00	

Table 2. Persistence of diquat (mg/l) in water at Chickahominy Reservoir study stations.

	Deep Water			Shallow Water		
Date	1	2	Chevron*	1	2	Chevron*
VII - 8	0.00	0.00		0.00	0.02	
(4 hr)10	0.00		0.02	0.66	0.46	1.07
(12 hr)11	0.03	0.04	0.02	0.20	0.00	0.13
(20 hr)	0.03	0.00	0.00	0.04	0.06	0.10
(28 hr)	0.00	0.00		0.00	0.00	
12	0.01	0.03		0.00	0.00	0.02
13	0.01	0.04	0.00	0.00	0.02	0.01
14	0.02	0.00	0.00	0.05	0.00	0.00
15	0.00		0.00	0.01	0.00	0.00
16	0.04	0.00	0.00	0.00	0.03	0.00
17	0.00	0.00	0.00	0.01	0.00	0.00
18	0.00	0.00	0.00	0.03	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.08	0.00	0.00	0.00	0.00
22	0.04	0.03		0.02	0.00	
24	0.01	0.00	0.00	0.00	0.00	0.00
25			0.00			0.00
28	0.00	0.01		0.00	0.00	
30	0.00	0.00		0.00	0.00	
VIII - 3	0.00	0.00		0.00	0.00	
8	0.00	0.00		0.00	0.00	
22	0.00			0.00		

*Analysis done by Chevron Corp., Richmond, Calif.

Table 3. Endothall residues (mg/l) in water samples collected at sites associated with the water supply system of Newport News, Virginia.

Date	In Pump	Off Pump				Other	
		Surface		12 ft. deep			
VII - 8	0.00	0.00					
9	0.04	0.00	0.06				
10	0.00	0.02	0.00				
	0.00	0.10	0.14			Lee Hall	0.00
11		0.00				Lee Hall	0.00
12		0.00		0.00		Harwood Mill	0.00
13						Harwood Mill	0.00
14				0.00	0.02		
15		0.00	0.00				
16		0.00		0.00			
17		0.00		0.00			
18		0.04		0.00			
19		0.00					
20		0.00		0.00		Lee Hall	0.00
21		0.00		0.00			
22		0.00		0.00			
23				0.00			
24		0.00		0.00			
25		0.00					

Table 4. Diquat residues (mg/l) in water samples collected at sites associated with the water supply system of Newport News, Virginia.

			Off Pump						
	In Pump		Surface			12 ft. deep		Other	
Date	1	2	1	2	Chevron*	1	Chevron*		Chevron*
VII - 8	0.00	0.00	0.00						
9	0.00	0.05	0.04		0.02				
10	0.00	0.00	0.03		0.00				
			0.45	0.00	0.83				
11								Lee Hall	0.00
12					0.00		0.00		
13			0.00					Lee Hall	0.00
14			0.00					Harwood Mill	0.00
15			0.01			0.00			
16			0.02			0.00			
17			0.00			0.04			
18			0.08						
19			0.00			0.03		Lee Hall	0.00
20			0.00			0.06			
21			0.00			0.00			
22			0.00			0.00			
24			0.00			0.01			
26			0.04			0.00			
28			0.00			0.00		Harwood Mill	0.00
30			0.00			0.00			
1			0.00			0.00			
3			0.00			0.00		Harwood Mill	0.003

*Analyses done by Chevron Corp., Richmond, Calif.

Table 5. Diquat residues (mg/l) in water from Johnson' Creek as determined by Chevron Corporation to measure downstream movement of herbicide streaming study.

VII - 8	Upstream	Downstream
11	0.00	0.02
12	0.00	0.00
13	0.00	0.00
14	0.00	0.00
15	0.00	0.00
16	0.00	0.00
17	0.00	0.00
18	0.00	0.00
19	0.00	0.00
20	0.00	0.01
21	0.00	0.00
22	0.00	0.00
24	0.00	0.00

Table 6. Persistence of diquat (μg/g) in plants from Chickahominy study stations.

Date	Shallow Water			Deep Water	
VII - 8	0.13			0.03	
11	2.68	21.60	5.88	9.77	
12	4.81	35.60		4.37	
13	7.00	10.91		16.40	4.36
14	10.86	2.38		5.79	
15	5.71	9.03		2.97	
16	8.31	4.05		2.63	
17	8.80	24.20		3.21	
18	19.40			2.92	
19	2.53				
20	6.56			1.62	
22	.72			0.91	0.62
24	.82	3.40		1.00	0.42
26	3.34			1.14	
28	.56			3.08	
30	5.89			1.30	
VIII- 3	0.82	0.21		1.73	
8	9.42	0.00			
15	5.15				
22	0.70	0.00			
31	3.07	2.97			

Table 7. Persistence of endothall (μg/g) in plants from Chickahominy study stations.

Date	Shallow Water		Deep Water	
VII - 8				
11	2.81	1.24	2.25	
12			1.52	0.91
13	1.02		0.00	
14	2.37		0.85	
15	1.80		1.12	
16	1.73		1.53	0.94
17			1.06	
18	1.40		0.54	
19	0.00			
20	1.16	0.00	1.05	
22	1.54			
24	0.00		0.00	
28	trace		1.04	
30			0.00	
VII 3	0.00	0.00		
22				

Table 8. Herbicide persistence (μg/g) in hydrosoils from Chickahominy Reservoir study stations.

	Deep water		Shallow water	
Date	Diquat	Endothall	Diquat	Endothall
1973				
VII - 11	3.77	0.00	3.80	0.00
			1.26	
16	1.81	0.00	3.40	0.00
20	3.26	0.00	3.40	0.00
VII - 8			17.37	0.00
15	3.32	0.00	11.09	
22	0.90	0.00	4.84	
IX - 20	5.45		0.39	
X - 14	0.00	0.00	15.86	0.00
XII - 14	2.08	0.00	1.72	0.00
1974				
I - 25	1.16			
III - 14	0.76			
V - 9	5.54			
VI - 24	0.00			

DISSIPATION OF THE HERBICIDES ENDOTHALL, DIQUAT, AND A 1:1 MIXTURE IN WATER, SEDIMENT AND *EGERIA DENSA*

by

Scott Lee Van Horn

(ABSTRACT)

A herbicidial mixture of diquat and endothall used for control of aquatic macrophytes was evaluated to determine the environmental persistence of the combination and its components and phytotoxicity for egeria (*Egeria densa*). The tests were conducted in wooden pools illuminated with a 15 hr photoperiod with flourescent lights. Diquat was assayed by a spectrophotometric procedure and endothall was quantified using a gas-liquid chromatographic technique. Persistence of diquat in water was decreased by the addition of plants and sediments to the system; whereas the decline of endothall in water was independent of the presence of plants and sediments at the concentrations tested. No measurable differences existed between the persistence of the mixture under lentic and lotic conditions. The presence of each herbicide in the mixture appeared to decrease the uptake in plants and sediments and increase the persistence of the other herbicide in water. Results of testing the mixture and its components individually under various water hardnesses (32 mg/1 to 460 mg/1) indicate the phytotoxicity of the mixture and diquat decreased as water hardness increased, while the phytotoxicity of endothall remained unchanged. Herbicide concentration decline in water appeared

independent of water hardness. While diquat was effective in controlling egeria, endothall was not, indicating that the role of the mixture for treating egeria should be reevaluated.