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THE TOXICITY OF DIQUAT, ENDOTHALL, AND FLURIDONE TO

THE EARLY LIFE STAGES OF FISH

by

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## ABSTRACT

While most aquatic herbicides have undergone some toxicity testing for effects on non-target aquatic organisms, little of this testing has been conducted on early life stages of gamefish found in lakes undergoing treatment. Commercial formulations of diquat, endothall, and fluridone were selected for acute toxicity testing using very early life stages of walleye (*Stizostedion vitreum*), largemouth bass (*Micropterus salmoides*), and smallmouth bass (*Micropterus dolomieu*). In addition, the rates of diquat photodegradation and uptake by sediment were determined. These results were used to predict diquat concentrations in lakes of various depths. The results of the toxicity tests were compared to the predicted concentrations. Diquat, with 96-h LC50s of 0.74-4.9 mg/L, was more toxic to these early life stages than endothall or fluridone, with 96-h LC50s of 16-130 mg/L and 1.8-13 mg/L respectively. The LC50s for endothall and fluridone were at least one order of magnitude greater than the labeled application concentrations. As the LC50s for diquat were very close to the predicted concentration, the safety margin for the use of diquat appears to be very small.

## INTRODUCTION

Most aquatic herbicides have undergone some toxicity testing to evaluate effects on non-target aquatic organisms (Urban and Cook 1986). Unfortunately, these tests are rarely conducted on the early life stages of fish commonly found in lakes being treated for "weed control." The continual use of these herbicides has prompted some concern of the effects of these chemicals on the early life stages of fish (Skea et al. 1987). If a herbicide which is toxic to the early life stages of fish is used annually, the herbicide could contribute to a decline in the fishery of a lake. Further study of the toxicity of these chemicals to early life stages is essential to understand the environmental impacts of herbicides.

The persistence of aquatic herbicides in the lake is important as well as their ultimate fate. The length of time which the herbicide remains in the water column determines the length of exposure. The fate of an aquatic herbicide determines whether aquatic life could be exposed at a later time.

Concern about the use of aquatic herbicides prompted the New York State Department of Environmental Conservation (NYSDEC) to conduct a series of toxicity tests as well as a persistence study. Commercial formulations of three commonly used herbicides (diquat, endothall, and fluridone) were selected for these studies. Each year

over one hundred lakes or ponds in New York State are treated with either diquat or endothall. In addition fluridone has been recently registered in New York State. The studies were conducted in two phases. Phase 1 was a series of toxicity tests utilizing early life stages of walleye (*Stizostedion vitreum*), smallmouth bass (*Micropterus dolomieu*), and largemouth bass (*Micropterus salmoides*). This portion of our study was done to confirm and verify earlier unpublished data, provide additional data for walleyes, and provide new toxicity information on fluridone (Hiltibran 1967, Jones 1985, Walker 1963). Phase 2 examined the persistence of diquat in water under various conditions.

## MATERIALS AND METHODS

### Toxicity Testing

Static non-renewal toxicity tests (Weber 1991) were conducted in order to approximate natural conditions following the herbicide treatment of a lake. The toxicity tests were conducted using 2-L glass jars containing 1500 ml of test solution, except for 84-d old walleyes which were tested in 20-L battery jars each containing 16 L of test solution. Test chambers were held in a thermostatically controlled water bath, and the temperature was monitored continuously. All concentrations were tested in triplicate (except for 84-d old walleyes where concentrations were tested in duplicate). All test containers were continuously aerated, and fish were fed brine shrimp nauplii three times per day (except for 84-d old walleye which were fed zooplankton). Test concentrations for diquat and fluridone were confirmed analytically at the beginning and conclusion of each test. Since no differences were found between initial and final concentrations, the initial analytically determined concentrations were used for all statistical calculations. All LC50s were calculated using the probit method (Finney 1978) or the trimmed Spearman-Kärber method (Hamilton et al. 1977), with correction for control mortalities (Abbott 1975). NOAECs (No-Observed-Adverse-Effect Concentrations) and LOAECs (Lowest-Observed-Adverse-Effect Concentrations) were calculated following procedures in Weber (1993) using the TOXSTAT computer program (West Inc. and Gulley 1994).

The herbicides used in all of the tests were commercial formulations registered for use in New York State. Diquat HA (Valent, USA Corp)<sup>b</sup> is a formulation containing 240 g of diquat cation per liter. All diquat concentrations are expressed as mg/L as cation. Aquathol K (AtoChem, North America) is the formulation of potassium endothall which was tested. Aquathol K contains 507 g of potassium endothall per liter. All endothall concentrations are expressed as mg/L potassium endothall. Sonar AS (DowElanco) is an aqueous suspension which contains 479 g of fluridone per liter.

All toxicity tests were conducted at the NYSDEC Rome Field Station. Water used in the tests was Rome Hatchery spring water, Delta Lake water, or South Sandy Creek water. Water quality data are presented in Table 1.

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## Walleyes

Walleyes were obtained from eggs taken at the NYSDEC Oneida Fish Hatchery located on Oneida Lake. Three age groups were tested: 8 to 10-d post hatch, 41 to 43-d post hatch, and 84 to 86-d post hatch.

For the testing of the 8 to 10-d old walleyes, newly hatched fish were transported to the Rome Field Station. These were held in 20-L battery jars and fed brine shrimp until they were 8 to 10-d old. Ten fish were placed in each toxicity test chamber. Tests were conducted for 96 h, and survivors were counted at 24-h intervals. Dead fish were removed from test containers. Test temperature was  $15.6^{\circ} \pm 0.5^{\circ}\text{C}$ .

The 41 to 43-d old walleyes were obtained from a rearing tank at the NYSDEC Rome Fish Hatchery. Since the test temperature and type of water were the same as the test conditions, no holding period was required at the Rome Field Station. Ten fish were placed in each test chamber, and the test was conducted as described above. Test temperature was  $16.1^{\circ} \pm 0.5^{\circ}\text{C}$ .

The 84 to 86-d old walleyes were obtained from rearing ponds at the NYSDEC South Otselic Fish Hatchery. These fish were transported to the Rome Field Station and placed in 20-L battery jars containing 75% South Otselic water/25% Rome Spring Water. These walleyes were fed zooplankton three times per day. The fish were held for 5 d, and each day 25% of the water was exchanged for Rome spring water. The toxicity testing was then conducted using Rome spring water. Ten fish were placed in each test chamber, and the test was conducted as described above. Test temperature was  $17.8^{\circ} \pm 0.5^{\circ}\text{C}$ , which was the temperature of the rearing ponds.

## Smallmouth Bass

Smallmouth bass were collected from approximately 30 nests as sac fry from South Sandy Creek in the Town of Ellisburg, Jefferson County, New York. These fry were held in weighted plastic jars with openings covered with nylon mesh, placed in 20-L plastic buckets, and transported to the Rome Field Station at a constant temperature.

Upon return to the laboratory the plastic buckets containing the sac fry were held at  $17.2^{\circ} \pm 0.5^{\circ}\text{C}$ , and fish began to "swim up" within 3 to 4 h. The young smallmouth bass were fed newly hatched brine shrimp.

On the day following collection, toxicity testing of diquat and endothall began with the smallmouth bass (< 24 h post swim-up). Tests were conducted as described for the 8 to 10-d old walleye. Filtered, South Sandy Creek water was used as dilution water for this set of toxicity tests since these fish had not been acclimated to Delta Lake water.

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<sup>b</sup> Diquat is now being marketed by Zeneca Inc.

Toxicity testing was repeated using diquat and fluridone and smallmouth bass (age 6-8 d post swim-up) during the following week. Test conditions were the same as the first test except that the smallmouth bass had been acclimated (25% exchange/d) to Delta Lake water. Delta Lake water was used as the dilution water for these toxicity tests.

### **Largemouth Bass**

Largemouth bass were collected from Long Pond, Chenango County, New York. These fish were collected with a fine-mesh seine as "schooling" feeding fry, approximately 9 to 13-d post swim-up. The same transport technique was used as with the smallmouth bass. At the Rome Field Station, the plastic buckets containing the largemouth bass were held at  $17.2^{\circ} \pm 0.5^{\circ}\text{C}$ . Fish were fed brine shrimp three times/day and were acclimated to Delta Lake water (25% exchange/d). The bass were held for 5 d prior to testing with each herbicide. Testing began at age 14 to 18-d post swim-up and was conducted as described above with Delta Lake water used as dilution water.

### **Analytical Methodology**

All chemical analyses for diquat were performed by reverse-phase high performance liquid chromatography (HPLC) using a Hewlett-Packard 1090M, equipped with a diode-array detector set at 308,10 nm. A Hamilton PRP-1 analytical column (5  $\mu\text{m}$ , 150 mm x 4.1 mm) with a  $\text{C}_{18}$  guard column was used. The flow rate of the ion-pair mobile phase was 2.0 ml/min with an oven temperature of  $40^{\circ}\text{C}$ , and the injection volumes were 50  $\mu\text{l}$ . The retention time for diquat was 1.96 ( $\pm 0.03$ ) minutes. All water samples were collected in polypropylene containers and were preserved with sulfuric acid to a pH  $< 2$ , then filtered through a 0.45  $\mu\text{m}$  nylon membrane filter before analysis. The method used for this study was a modification of a draft method used with a recent EPA study (Bashe 1988, Lagman and Hale 1987). The concentration step was not necessary, because the diquat concentrations used in the toxicity tests were detectable.

All chemical analyses for fluridone were performed by HPLC using the Hewlett-Packard 1090M, equipped with a diode-array detector set at 254,4 nm. A Hewlett-Packard ODS Hypersil ( $\text{C}_{18}$ ) analytical column (5  $\mu\text{m}$ , 200 X 2.1 mm) was used. The carrier solvent was methanol:water (65:35,v/v) with a flow rate of 0.300 ml/min. Oven temperature was set at  $40^{\circ}\text{C}$  with a sample injection volume of 15  $\mu\text{l}$ . The retention time for fluridone was approximately 3.7 minutes. Samples were collected in glass bottles and stored at  $4^{\circ}\text{C}$  until analysis. Samples were extracted and concentrated by taking 5 ml of the sample and placing it into a Bakerbond Sep Octadecyl ( $\text{C}_{18}$ ) extraction column and extracting fluridone with 2 ml of methanol. This method is a modification of a method supplied by Eli Lilly and Company (Lilly Research Laboratories 1991).

An HPLC method was not available for analyzing water samples containing endothall. We therefore relied on nominal concentrations to calculate statistics for endothall.

## **Photodegradation**

Diquat was added to eight 20-L glass containers, each filled with 16-L of Rome spring water. Four containers were dosed at approximately 1 mg/L diquat cation, and four were dosed at approximately 4 mg/L. The actual concentration of diquat from each container was determined analytically. Half of the containers (4) were held indoors (fluorescent lighting) and half were held outdoors where they were exposed to sunlight. Dissolved oxygen was measured in each chamber every 24 h and never was less than 9.4 mg/L. Test chambers were held at  $9.4^{\circ} \pm 0.5^{\circ}\text{C}$ .

Each test chamber was sampled at 0, 2, 4, 8, 24, 48, 72, and 96 h from the addition of diquat. All samples were held in the dark and refrigerated ( $4^{\circ}\text{C}$ ) until analysis. All samples were filtered within 7 d of collection.

## **Persistence**

Sediment was collected from a small, unnamed pond near Starr Hill, Oneida County, New York using an Ekman grab. Only the first 5 cm of sediment were collected. The sediment was passed through a 6-mm mesh sieve to remove rocks, sticks, and roots. The remaining material was permitted to settle for 24 h and the supernate was removed, leaving the sediment with only a small quantity of water. The sediment was composed of a mixture of dark grey sand, silt, and clay. Particle size analysis is presented in Figure 1. Total organic carbon of this sediment was 3.5%

Twenty-four 20-L containers were used for this study. Twelve of the containers were filled with 16 L of Rome spring water. The remaining 12 were filled with 15 L of spring water and 1 L of wet sediment. All jars were permitted to sit for 2 d to allow the sediment to settle. Water was aerated using a 1-ml pipette which was 7.5 cm from the bottom of the container. Dissolved oxygen was measured in each test concentration every 24 h.

Diquat was added to each of the test containers and slowly stirred so as not to disturb the material on the bottom. Three diquat concentrations were tested with four replicates of each treatment (with or without sediment). Approximate concentrations used were 1, 4, and 16 mg/l diquat cation. The actual concentrations of the diquat in each container were determined analytically and used for all calculations.

We used regression analysis to compare the rates of disappearance of diquat from the water over time at the three nominal concentrations (Freund and Littell 1986). Each test container was sampled at 0, 2, 4, 8, 24, 48, and 96 h from introduction of diquat. All water samples were held in the dark and refrigerated ( $4^{\circ}\text{C}$ ) until analysis. All samples were filtered within 7 d of collection.

## RESULTS

### Toxicity Tests

For each herbicide, fish mortality continued throughout the 96 h of toxicity tests. In almost every species-age combination diquat had a lower LC50 than endothall or fluridone (Table 2). These tests indicate that diquat is more toxic to the fish tested than fluridone which is more toxic than endothall. The NOAECs/LOAECs (Table 3) indicate similar patterns except that very young walleyes appear to be equally sensitive to diquat and fluridone.

The walleye tests indicate that the very early life stages are the most sensitive. The 8 to 10-d old walleye were more sensitive than the 41 to 43-d old walleyes for both diquat and endothall. In addition the 41 to 43-d old walleyes were more sensitive to diquat than the 84 to 86-d old walleyes.

Both largemouth bass and smallmouth bass were less sensitive than walleyes to all three herbicides. Smallmouth bass were less sensitive than largemouth bass to diquat for up to 48 h, but thereafter were comparable in sensitivity. Largemouth bass were less sensitive than smallmouth bass to endothall and fluridone.

### Photodegradation

Diquat concentrations in the test chambers which were held outside dropped only 3% over the 4-d test period. Diquat concentrations in the test chambers held indoors also remained relatively constant over the same time. Photodegradation did not occur in any of the test containers to any appreciable degree.

### Persistence

Diquat concentrations in the test chambers which contained sediment decreased over time. Diquat concentrations in chambers without sediment remained constant. The mean proportion of the original concentration of diquat over time for each application rate is presented in Figure 2. The rate at which diquat disappeared from the water column was highest initially and decreased over time. Regression analysis of the data yielded the following equations:

$$DC_1 = 1.05 - 0.064(\text{SQRT}(t)) \quad r^2=0.97 \quad p<0.0001$$

$$DC_4 = 1.03 - 0.060(\text{SQRT}(t)) \quad r^2=0.99 \quad p<0.0001$$

$$DC_{16} = 1.02 - 0.043(\text{SQRT}(t)) \quad r^2=0.99 \quad p<0.0001$$

where:  $DC_x$  = the proportion of the original diquat concentration remaining at time t when the initial nominal concentration is X.

t = time from application in hours.

The slopes of each of these equations were significantly different ( $p < 0.05$ ); therefore, the rates of decrease in diquat concentration at the three nominal concentrations were significantly different. The rate of diquat decline was inversely related to the initial application concentration.

## DISCUSSION

Endothall seems to have an adequate margin of safety between application rates used for aquatic macrophyte control and concentrations which are toxic to early life stages of fish. Walker (1963) reported a 96-h LC50 for largemouth bass of 120 mg/L, which is very similar to the 131 mg/L we determined. Young walleyes are much more sensitive with a 96-h LC50 of 16 mg/L. But even this is three times the maximum labelled application rate of 5 mg/L (Aquathol K label EPA Reg. No. 4581-204).

Fluridone also seems to have an adequate margin of safety. Hamelink et al. (1986) determined a range of 96-h LC50s of 4.2-22 mg/L for five different fish species. These fish species did not include bass or walleyes. Our smallmouth and largemouth bass 96-h LC50s fall in the middle of this range. Young walleyes are more sensitive than other fish species which have been tested, yet even the 96-h LC50 of 1.8 mg/L is an order of magnitude greater than the maximum labelled application rate of 0.15 mg/L (Sonar AS label EPA Reg. No. 62719-124).

A review of the toxicity literature for diquat indicates that diquat is highly toxic to some aquatic animals. *Hyaella azteca*, an amphipod, is one of the most sensitive aquatic organisms tested with a 96-h LC50 of 0.048 mg/L (Wilson and Bond 1969). Gilderhus (1967) found a 96-h LC50 of 35 mg/L to bluegills (*Lepomis macrochirus*), and Leung et al. (1983) found a 96-h LC50 of 289 mg/L to mosquitofish (*Gambusia affinis*). Many other aquatic organisms have been tested and fall between the extremes of 0.048 mg/L and 289 mg/L (Hiltibran 1967, Hughes 1975, Johnson and Finley 1980, Simonin and Skea 1977, Williams et al. 1984).

Young walleyes are the most sensitive fish species tested. Gilderhus (1967), also found walleyes to be the most sensitive of the fish species he tested. He reported a 96-h LC50 of 1.2 mg/L for two month old walleyes, which is in close agreement with the LC50s we found.

Surber and Pickering (1962) determined a 96-h LC50 of diquat to largemouth bass of 7.8 mg/L. This LC50 is also in close agreement with our data. Our NOAECs of 1.6 mg/L (SMB) and 1.8 mg/L (LMB), which were determined at 17°C, are in agreement with Jones (1985) who found that 0.5 mg/L (test temperature 26°C) or 1.0 mg/L (test temperature 22° - 23°C) were the highest diquat concentrations safe to largemouth bass fry. These data suggest that diquat is more toxic at higher temperatures. This contrasts with a report by Johnson and Finley (1980) which noted that the toxicity of diquat to bluegills was not altered by changes in temperature from 7° to 22°C.

According to product literature, "Diquat has a wide margin of safety between recommended dosages and rates necessary to cause signs of toxicity to fish species" (Valent, USA Corp. 1989). The diquat label requires the application of 2 gallons/acre to control certain species of aquatic vegetation (Diquat Label EPA Reg. No. 239-1663-ZA-59639). This results in concentrations of 1.5 mg/L cation in one foot and 0.75 mg/L cation in two feet of water. Both of these concentrations are greater than the 96-h LC50s for young walleyes and certainly do not represent "wide margins of safety." These predicted concentrations assume complete mixing of diquat in the water column. If incomplete mixing occurs, some areas of a lake will have even higher concentrations of diquat.

The labeled application method for submersed weeds is to pour undiluted diquat from the container or underwater injection of slightly diluted diquat. These methods of application are likely to produce regions of high herbicide concentration. Even spray applications can produce uneven diquat concentrations. Berry et al. (1975) detected regions of high herbicide concentration which they termed "hot spots" following an application using a surface spray.

Very little diquat was degraded by sunlight. Only very small decreases in the concentration of diquat occurred following exposure to sunlight over a 4-d period. Photodegradation seems likely to play only a small part in the removal of diquat from the water column.

The possibility for diquat to be present in concentrations which could be lethal to early life stages of several game fish does exist. Jones (1985) stated that bass are sensitive to diquat and recommended that where diquat is used, "great caution" needs to be exercised. The safe use of diquat seems to depend upon the removal of the active ingredient through binding to sediment and/or plant material. Diquat was thought to bind so quickly to clay particles in sediment that it was not present in the water column for very long. Hiltibran et al. (1972) reported that diquat concentrations decreased by 60% after a 4 d exposure to a hydrosol. In our study, we also found 40% of the original concentration of diquat remains after 4 d with sediment present in the test container. The shallow water (23 cm) and aeration of our test chambers should have provided for optimum binding of diquat to the sediment.

Barreiro Lozano and Pratt (1994) used a regression model,  $C = a + b(\ln(t))$ , where C is the diquat concentration, t is time, and a and b are the intercept and slope, respectively, to explain the decrease in diquat concentration over time. Their experiments, however, did not involve the removal of diquat by a sediment, but rather the effect of nutrient concentration on the toxicity of diquat to microbial communities on polyurethane foam substrates in microcosms. We regressed diquat concentration on time using log transformations of time, concentration, and both time and concentration. While these all yielded highly significant models ( $r^2=0.86$  to  $0.97$ ,  $p<.0001$ ) an examination of the residuals indicated a lack of fit by these models (Figure 3). The  $\ln(\text{concentration})$ -time model consistently overestimated the diquat concentration from 8 to 48 h and underestimated the extremes. The  $\ln(\text{concentration})$ - $\ln(\text{time})$  and concentration- $\ln(\text{time})$

models consistently did the opposite, underestimating diquat concentrations from 8 to 48 h and overestimating the extremes. The square root transformation of time yielded highly significant models ( $p < 0.0001$ ), with higher  $r^2$  than the log models. In addition, the residuals did not have any of the patterns noted above (Figure 4) and indicated a better fit to the data.

The toxicity of diquat to walleyes was compared with the diquat concentrations expected during a treatment for aquatic vegetation control, based upon the information from our persistence study (Figure 5). Even after accounting for the removal of diquat from the water column by sediment, the data predict that toxic concentrations will exist in shallow regions of a lake. If incomplete mixing occurs, the concentration of diquat in some regions will even be higher than those predicted. In addition, the predicted concentrations in shallow water (<0.5 m) exceed the NOAECs for young walleyes (ages 8-10 d and 41-43 d) and come very close to exceeding the LOAECs for these fish.

The instructions on the diquat label should include cautions regarding water depth when recommending application rates. Application rates in shallow water (<1 m) should be reduced. In addition, we recommend that diquat be applied as a dilute spray, since the likelihood of hot spots would be reduced. Finally, the use of diquat should be discouraged in lakes containing sensitive fish species at times when early life stages will be present.

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Table 1. Selected characteristics of dilution waters used  
in toxicity tests. (NA = not available; ranges of values in parentheses)

Water	pH	Alkalinity mg/L CaCO <sub>3</sub>	Hardness mg/L CaCO <sub>3</sub>
Rome Spring	7.71 (7.1-8.0)	114 (98-130)	132 (122-138)
Delta Lake	7.4 (7.1-7.8)	53 (38-69)	65 (46-81)
South Sandy Creek	7.2	NA	81

Table 2. LC50s and associated 95% confidence intervals for diquat, endothall, and fluridone.  
(SMB = Smallmouth Bass, LMB = Largemouth Bass, and NA = not available)

Chemical	Species	Age (d)	LC50 (mg/L) (95% CI)			
			24 h	48 h	72 h	96 h
Diquat	Walleye	8-10	2.9 (2.3-3.5)	1.6 (1.2-1.9)	1.0 (0.76-1.2)	0.75 (0.29-0.86)
	Walleye	41-43	3.1 (2.5-4.1)	1.9 (1.6-2.2)	1.6 (1.5-1.8)	1.5 (1.4-1.7)
	Walleye	84-86	7.8 (6.6-9.3)	4.9 (4.4-5.6)	4.9 (4.3-5.5)	4.9 (4.3-5.5)
	SMB	6-8	110 (98-120)	28 (22-34)	10 (8.5-12)	3.9 (2.9-5.0)
	LMB	9-13	15 (13-17)	11 (9.7-11)	8.0 (6.8-9.7)	4.9 (4.2-5.8)
Endothall	Walleye	8-10	66 (42-140)	30 (24-37)	27 (22-33)	16 (11-21)
	Walleye	41-43	140 (100-1000)	73 (58-100)	62 (49-80)	54 (42-68)
	SMB	< 1	> 91 (NA)	60 (54-69)	59 (55-64)	47 (42-54)
	LMB	9-13	> 400 (NA)	280 (NA)	170 (150-190)	130 (120-150)
Fluridone	Walleye	8-12	3.6 (3.2-4.1)	2.8 (2.4-3.1)	2.3 (2.0-2.6)	1.8 (1.4-2.0)
	SMB	4-8	19 (17-21)	11 (9.7-13)	9.5 (8.5-11)	7.6 (6.9-8.7)
	LMB	10-14	16 (NA)	16 (NA)	14 (13-16)	13 (12-15)

Table 3. NOAECs and LOAECs (mg/L) for diquat, endothall, and fluridone.  
(SMB = Smallmouth Bass and LMB = Largemouth Bass)

Chemical/ Species	Age (d)	24 h		48 h		96 h	
		NOAEC	LOAEC	NOAEC	LOAEC	NOAEC	LOAEC
Diquat							
Walleye	8-10	0.93	2.0	0.93	2.0	0.48	0.93
Walleye	41-43	0.90	1.9	0.90	1.9	0.90	1.9
Walleye	84-86	4.4	8.4	2.6	4.4	2.6	4.4
SMB	6-8	68	130	14	34	1.6	3.4
LMB	9-13	7.1	18	7.1	18	1.8	3.6
Endothall							
Walleye	8-10	5.7	11	5.7	11	5.7	11
Walleye	41-43	45	91	23	45	23	45
SMB	<1	45	91	23	45	23	45
LMB	9-13	200	400	100	200	50	100
Fluridone							
Walleye	8-12	1.2	2.0	1.2	2.0	0.78	1.2
SMB	4-8	8.7	19	6.2	8.7	4.5	6.2
LMB	10-14	12	21	12	21	9.6	12

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FIGURE 1. Percent composition of particle sizes of sediment used in the diquat persistence study.

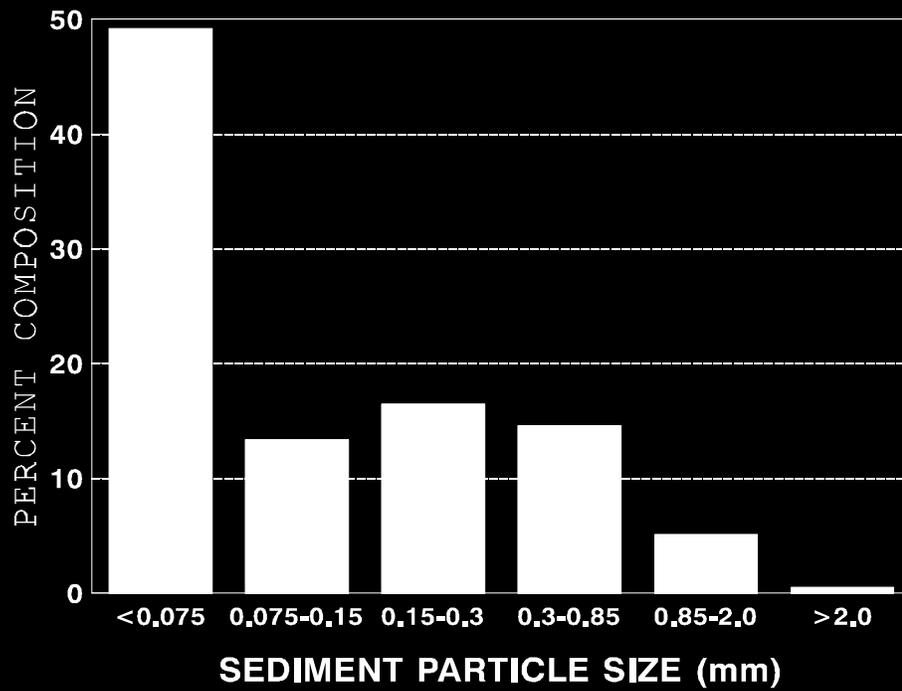


Figure 2. Percentage of the original diquat concentration remaining in containers with sediment over time.

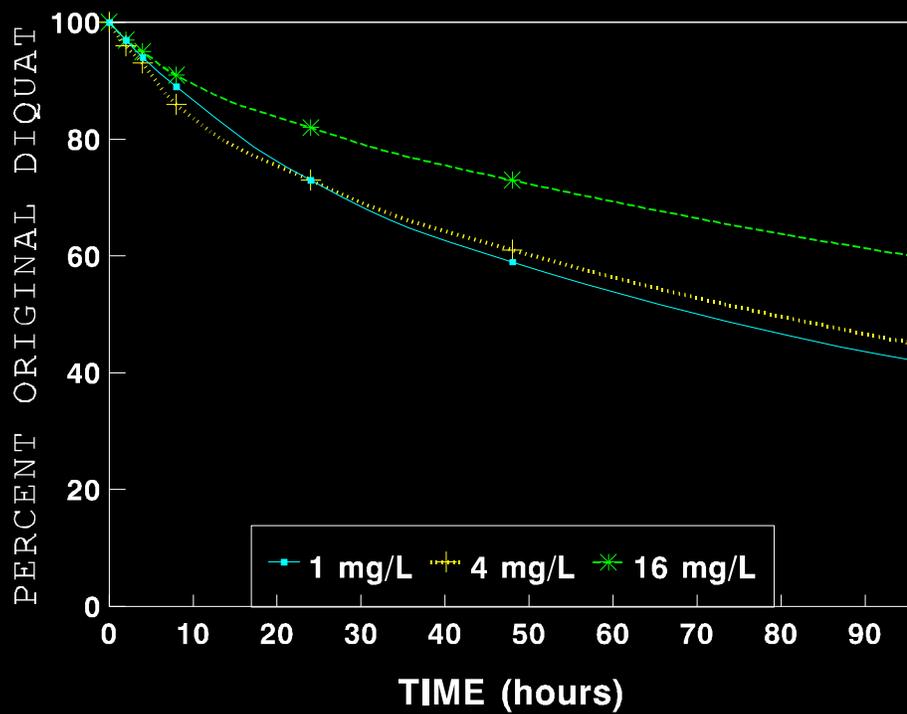


FIGURE 3. Residual plot from regression of diquat concentration (DC) on the natural log of time (t). (a and b are regression coefficients.)

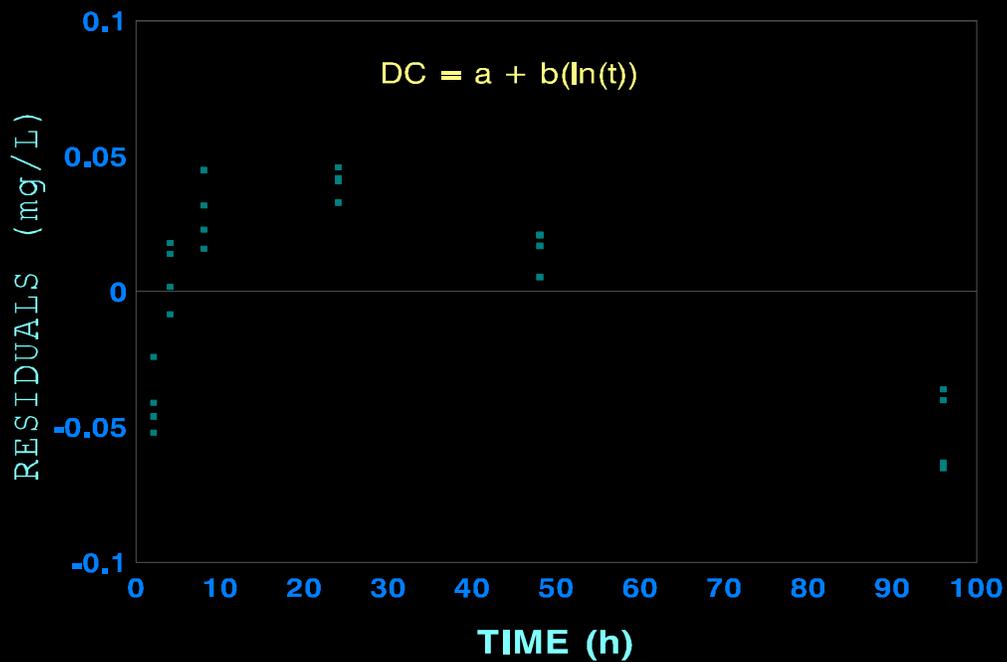
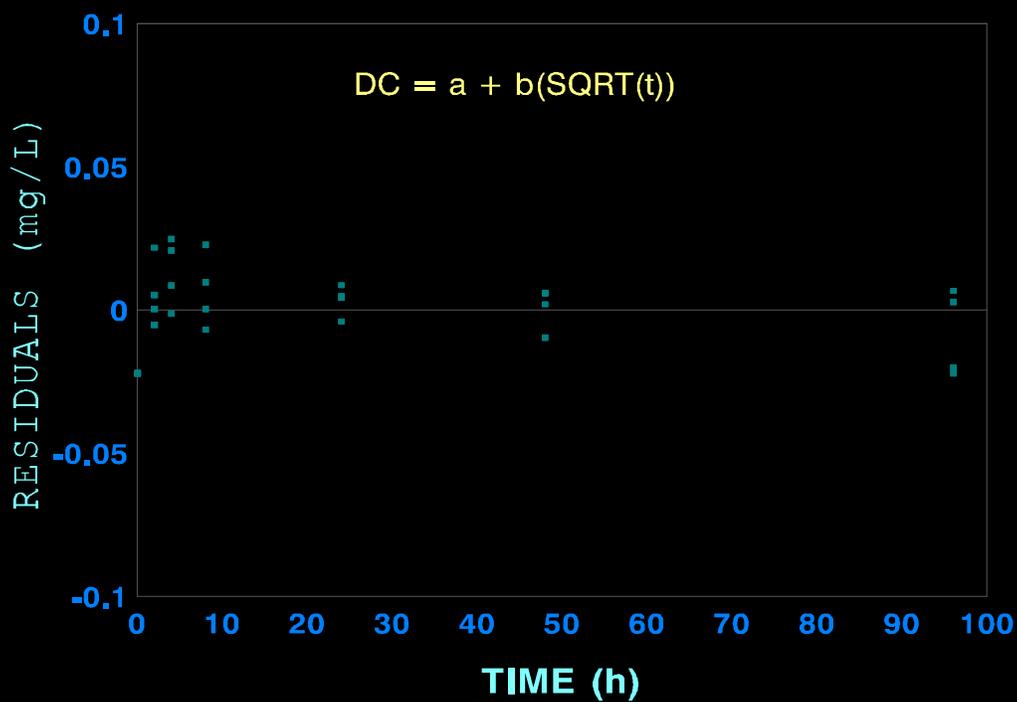


FIGURE 4. Residual plot from regression of diquat concentration (DC) on the square root of time (t). (a and b are regression coefficients.)



**FIGURE 5. Toxicity of diquat 8-10 d old walleye (*Stizostedion vitreum*) compared to the expected diquat concentration during treatment of shallow waters.**

