Efficacy of Diquat on Submersed Plants Treated Under Simulated Flowing Water Conditions

JOHN G. SKOGERBOE¹, KURT D. GETSINGER² AND LEE ANN M. GLOMSKI³

ABSTRACT

The contact aquatic herbicide, diquat (6,7-dihydrodipyri $do[1,2-\alpha:2',1'-c]$ pyrazinediium ion) was evaluated under simulated flowing water conditions in an outdoor mesocosm facility for efficacy on five submersed aquatic plants: hydrilla (Hydrilla verticillata (L.f. Royle), Eurasian watermilfoil (Myrio*phyllum spicatum* L.), sago pondweed (*Stuckenia pectinata* (L.) Boerner), American pondweed (*Potamogeton nodosus* Poiret), and egeria (Egeria densa Planchon). Diquat was applied at concentrations of 0.37 mg/L ai and 0.185 mg/L ai (cation) under flow-through conditions to provide theoretical 3 and 6 hr herbicide half-lives that produced observed herbicide half-lives of 2.5 and 4.5 hr, respectively. An additional treatment included 0.37 mg/L ai applied under static conditions (no water exchange). Results showed that diquat applications significantly inhibited shoot biomass production from 42 to 100 percent at all application concentrations and exposure times for all species, except hydrilla. Diquat resulted in no measurable control of hydrilla, except under static conditions. Results suggest that Eurasian watermilfoil, egeria, and sago pondweed are highly susceptible to diquat even in areas where herbicide dilution may occur in less than three hours.

Key words: Chemical control, concentration/exposure times, contact herbicide.

INTRODUCTION

Diquat is a contact herbicide that causes rapid plant injury in exposed tissue through disruption of photosynthesis (Black 1988) and, to a lesser extent, respiration (Moreland 1988). It is commonly used to control a wide range of nuisance aquatic plants, including submersed species (Westerdahl and Getsinger 1988). Because diquat is a fast-acting herbicide, it can be used for managing nuisance submersed plants growing in areas where water exchange can shorten aqueous herbicide exposure times, such as small-scale treatments in and around docks, marinas, boat launches, navigation corridors, and swimming areas. Diquat may also be used in situations where rapid control of standing plant mass is desired, and as a tool to spot-treat small stands of target vegetation in lakes and other water bodies. Another potential use of diquat is to control submersed weeds in flowing water canals, such as used in irrigated agriculture, where herbicide exposure times are quite short, commonly less than 12 hours.

Efficacy of herbicides on submersed plants is greatly affected by concentration and exposure time (CET) of the herbicide surrounding the target plant (Green and Westerdahl 1990, Netherland et al. 1991). Duration of exposure or contact time is related to degradation of the parent molecule and, in some cases, dilution of the herbicide out of treatment areas resulting from water exchange patterns driven by flow, wind, waves, and current. As opposed to some other herbicides, efficacy of diquat can be impacted by inorganic turbidity/clay particles in the water column, which can adsorb the diquat cation before sufficient contact time of the product is achieved (Weber et al. 1965, Narine and Guy 1982, Poovey and Getsinger 2001, Hofstra et al. 2001, Poovey and Skogerboe 2004).

Although diquat has been registered for use in U.S. waters since 1962 (Netherland et al. 2005), there is limited information on controlling submersed plants under various CET regimes, particularly at aqueous concentrations <0.5 mg/L and exposure times <24 hours (Barrett and Murphy 1982, Van et al. 1987, Filizadeh and Murphy 2002, Glomski et al. 2005.) Therefore, under simulated flowing water conditions designed to mimic a short-term exposure scenario, diquat was evaluated for efficacy against five submersed plants: hydrilla, Eurasian watermilfoil, egeria, sago pondweed, and American pondweed. The first three plants mentioned are widespread invasive species in U.S. waters, and the two aforementioned pondweeds can cause serious problems in irrigation canals where water flows can greatly reduce herbicide contact times.

MATERIAL AND METHODS

This study was conducted in outdoor mesocosms at the U.S. Army Engineer Research and Development Center's Lewisville Aquatic Ecosystem Research Facility (LAERF) in Lewisville, TX during June and July 2003. The study design included 18 above ground fiberglass mesocosms (tanks, 1.4 m tall \times 2.6 m diameter; water depth = 1.3 m; vol. = 6700 L) filled with Lake Lewisville water that had been filtered through sand (TD-100, PacFAb, Sanford, NC) to remove algae and particulate matter. Plants were grown in 5-L plastic containers (19.7 cm tall \times 19.7 cm diameter) filled with artificial sediment that consisted of Wal-Mart Special Kitty® litter (67% clay, 18% silt, and 25% sand) amended with 10 g per container of Osmocote® slow-release fertilizer (18-6-12). Hydrilla, Eurasian watermilfoil, American pondweed, and egeria were planted with 3 apical tips per container, whereas

¹U.S. Army Engineer Research and Development Center, Eau Galle Aquatic Research Laboratory, W500 Eau Galle Dam Rd., Spring Valley, WI 54767; skoger@gte.net.

²U.S. Army Engineer Research and Development Center, Environmental Laboratory, 3909 Halls Ferry Rd., Vicksburg, MS 39180.

^sSpecPRO, Inc., U.S. Army Engineer Research and Development Center, Lewisville Aquatic Ecosystem Research Facility, 201 E. Jones St., Lewisville, TX 75057. Received for publication January 18, 2006, and in revised form June 14, 2006.

sago pondweed was planted using 3 tubers per container. Eight planted containers of each species were placed in a mesocosm. Plants were allowed to grow for 5 wks before herbicide applications. Shoot heights ranged from ~120 cm for Eurasian watermilfoil, sago pondweed and American pondweed to <50 cm for hydrilla and egeria at the time of herbicide application. All plants were healthy and actively growing at the time of treatment.

Diquat (Reward®)⁴ was applied at concentrations of 0.185 and 0.37 mg/L ai (active ingredient, cation) to mesocosms with flow-through rates calibrated to deliver a theoretical (or target) half-life of 3 and 6 hr for a conservative tracer material. An additional treatment was diquat applied at 0.37 mg/Lai under static conditions (no water exchange). The experimental design included three blocks of 6 tanks each, and each block included one replicate of each treatment (n = 3). The completely randomized block design was necessary to maintain required flow rates for 48 hr following application of the herbicide by treating blocks on different days. Each mesocosm tank was fitted with a valve calibrated to provide bottom to surface directional flow into each tank. Inflow was from one side of the tank and outflow occurred at the water surface through a standpipe on the opposite side of the tank. Block one was treated on 1 July, block two was treated on 3 July, and block three was treated on 7 July. Diquat concentrate was added to 5 L of water (derived from the same source as water used in the tanks) with a digital pipette (0.01)ml accuracy). This solution was then poured evenly across the surface of each appropriate tank and gently stirred to ensure water-column mixing. All herbicide treatments were applied between the times of 0830 to 0845 hr. Specific treatments and exposure times are shown in Table 1.

Water samples were collected approximately 15 minutes prior to herbicide application, 45 cm below the water surface near the center of each tank and analyzed for pH, alkalinity, temperature, and turbidity. Additional samples were collected at the same location within each tank and analyzed for diquat residues following methods of Bashe (1988) at the LAERF analytical laboratory as follows: a) 6 hr theoretical half-life: pretreatment, 0.5, 1, 3, 6, 9, 24 and 48 hr post-treatment; b) 3 hr theoretical half-life: pretreatment, 0.5, 1, 6, 9, 24 hr post-treatment; c) static (no water exchange): pretreatment, 0.5, 1, 3, 6, 9, 24, and 48 hr post-treatment; and d) untreated reference: pretreatment and 48 hr post-treatment.

At 3 weeks after treatment plant shoots from each container were cut at the sediment surface, placed in an oven and dried (65°C) to a constant weight. Biomass data were log transformed, and compared using analysis of variance (ANO-VA, p < 0.05). The least significant differences method was used for means separation. Data were tested for differences between blocks, and these differences were determined not significant. Initial diquat concentrations were log transformed to preserve the assumptions of equal variance and analyzed using ANOVA (p < 0.05). Observed diquat half-lives (dissipation rates) were determined using linear regression and were statistically compared between treatments using a two-sided t-test (p < 0.05). Dissipation curves were calculated

Target concentrations (mg/L ai cation)	Theoretical half-lives (hr)	Observed initial concentrations ² (mg/L ai cation)	Observed half-lives (hr)	R-sq
0.37	Static ¹	0.33 ± 0.03 A	27.5 A	0.30
0.37	6	$0.31\pm0.02~A$	4.5 B	0.90
0.185	6	$0.16 \pm 0.02 \text{ B}$	4.6 B	0.92
0.37	3	$0.30\pm0.04~A$	2.5 C	0.95
0.185	3	$0.14\pm0.01~B$	2.4 C	0.94

¹No water exchange or flow-through.

 $^{\mathrm{2}}\text{Means}$ (±SE) followed by same letter are not significantly different (P < 0.05).

using the exponential model of Microsoft Excel 2000 ($y = a+b \ln [x]$ where a is the y intercept, b is the slope, and ln is the natural logarithm). Half-lives were calculated from -ln [0.5]/b. For simplicity and clarity of presentation, non-transformed data (biomass and diquat half-lives) are presented with statistical interpretations based upon transformed data.

RESULTS AND DISCUSSION

Pretreatment measurements indicated mean (\pm SE) water temperature of 28.3 \pm 0.3°C, pH of 9.11 + 0.08, and alkalinity of 41.7 mg/L + 1.1 CaCO3, all within the range of water quality conditions required for healthy submersed plant growth (Smart and Barko 1985). Mean pretreatment water turbidity values ranged from 0.53 \pm 0.04 to 0.76 \pm 0.19 NTU, indicating extremely low levels of suspended particulates in the water column, which is favorable for diquat applications (Poovey and Getsinger 2002).

A summary of diquat water residue data for each treatment is presented in Table 1. Initial observed diquat concentrations were not significantly different between treatments with similar application rates, including the static treatment. Initial concentrations were 14 to 25% less than target application rates in flowing water treatments, which should be expected due to water flow through the tank. However, the initial diquat concentration in the static treatments was slightly lower (11%) than the target application rate indicating that absorptive processes were probably occurring. Some initial loss of diquat is expected via adsorption processes, such as suspended particulates, sediment, and plant surfaces (Hofstra et al. 2001). Observed diquat half-lives were also slightly lower than theoretical half-lives probably due to degradation and adsorption of the herbicide by sediment and uptake by plants; however regressions of observed half-lives were highly correlated $(R^2 > 0.9)$ for all flowing treatments. There were no significant differences between treatments with observed diquat half-lives that were similar (i.e., 2.5 hr or 4.5 hr), but there were significant differences between observed diquat halflives that were different (i.e., 2.5 hr vs. 4.5 hr).

Under these experimental conditions, submersed plants showed a range of response to diquat (Table 2) and some species were extremely sensitive to the herbicide, even at reduced diquat exposure times (2.5 hr half life) and concentrations (0.185 mg/L). However, evidence of tolerance to diquat was observed with hydrilla at exposure half-lives of 4.5 hours or less.

⁴Citation of trade names does not constitute an endorsement of the use of such commercial products.

TABLE 2. PLANT RESPONSE TO DIQUAT AT VARIOUS CONCENTRATION AN	ND EXPOSURE TIME SCENARIOS AT 3 WEEKS AFTER TREATMENT.
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Target diquat concentration (mg ai/L)	Observed diquat - half-life (hr)	Shoot biomass (g DW) ^{1,2}					
		Hydrilla	Eurasian watermilfoil	Sago pondweed	American pondweed	Egeria	
0	0	$4.50\pm0.60~\mathrm{A}$	32.70 ± 2.45 A	9.23 ± 0.82 A	$0.79\pm0.16\mathrm{A}$	13.7 ± 0.81 A	
0.37	Static ³	$0.01\pm0.01~{\rm C}$	0 E	$0.02\pm0.02~\mathrm{C}$	$0.03\pm0.01~\mathrm{D}$	0 F	
0.37	4.5	$3.91 \pm 0.90 \text{ AB}$	$0.06 \pm 0.01 \text{ D}$	$0.38\pm0.05~\mathrm{B}$	$0.20 \pm 0.10 \text{ C}$	$0.03 \pm 0.02 \text{ E}$	
0.185	4.5	$5.16\pm0.72~A$	$0.14\pm0.03~\mathrm{C}$	$0.31 \pm 0.03 \text{ B}$	$0.12 \pm 0.04 \text{ C}$	$0.67\pm0.24~\mathrm{D}$	
0.37	2.5	$4.63\pm0.62~\mathrm{A}$	$0.10\pm0.03~\mathrm{C}$	$0.31 \pm 0.03 \text{ B}$	$0.42 \pm 0.12 \text{ AB}$	1.43 ± 0.34 C	
0.185	2.5	$6.02\pm0.78~A$	$1.08\pm0.36~\mathrm{B}$	$0.77\pm0.16~B$	$0.28\pm0.05~\mathrm{B}$	$7.96 \pm 1.42 \text{ B}$	

¹Means (± SE) followed by the same letter are not significantly different.

²g DW = grams dry weight.

³No water exchange or flow-through.

Comparison of hydrilla data showed that only the static diquat treatment was significantly less than the untreated reference, providing nearly 100% reduction in biomass (Table 2). In the flowing water scenarios there were no significant differences between treatments, with biomass ranging from a 34% increase (0.185 mg/L diquat at a 2.5-hr half life) to a 13% reduction (0.37 mg/L diquat at a 4.5-hr half life). Based on these findings, a diquat exposure longer than that provided by a 4.5-hr half life would be required to achieve acceptable control of hydrilla. Other investigators have reported a wide range of hydrilla control when using diquat. Van et al. (1987) reported 81% control of hydrilla with 2 mg/L ai diquat following a 12-hr exposure time, while Langeland et al. (2002) reported 62 to 91% control of hydrilla with 0.25 mg/ L ai diquat following static exposure. Comparing a range of diquat concentrations and exposure times (0.09 to 0.37 mg/L ai and 4 to 12 hr), Glomski et al. (2005) reported no significant difference in biomass between treated and untreated hydrilla. It should be noted that operational use of diquat against hydrilla, particularly in combination with copper, has proven to be an effective herbicide for controlling that plant in the field (Westerdahl and Getsinger 1988, Pennington et al. 2002, Poovey and Skogerboe 2004).

In contrast to hydrilla, data for egeria, a close taxonomic relative, indicated that all diquat treatments resulted in greater than 90% reduction in biomass compared to the untreated reference, with the exception of the 0.185 mg/L ai, 2.5-hr half-life treatment which provided only a 42% reduction in biomass (Table 2). Glomski et al. (2005) reported excellent control of another closely related species, elodea (*Elodea canadensis* L.), with diquat. As with the dipotassium salt formulation of the contact herbicide, endothall (7-oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid), against these same species (Corning and Prosser 1969, Skogerboe and Getsinger 2002, MacDonald et al. 2002), diquat seems to yield variable control of three morphologically similar and related members of the Hydrocharitaceae family: hydrilla, egeria, and elodea.

Comparison of Eurasian watermilfoil biomass data indicated that all diquat treatments reduced biomass by 97 to 100% compared to the untreated reference (Table 2). Eurasian watermilfoil is very susceptible to diquat, as it is with endothall (Netherland et al. 1991, Skogerboe and Getsinger 2002), 2,4-D (2,4-dichlorophenoxyacetic acid) (Green and Westerdahl 1990), triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) (Netherland and Getsinger 1992), and fluridone (1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone) (Netherland et al. 1993; 1997).

Since pondweeds are primary target species in many flowing-water canals in the western U.S., a high susceptibility to diquat at short exposure times might be an option for managing weeds in these systems. Data comparisons of sago pondweed indicated that all diquat treatments provided between 92 and 100% reduction in biomass compared to the untreated reference (Table 2). Like egeria and Eurasian watermilfoil, sago pondweed seems to be very susceptible to diquat, even at the lowest concentration and shortest exposure time evaluated. However, American pondweed responded in an intermediate fashion to diquat with biomass reduction compared to the untreated reference ranging between 46 and 85%, following 2.5 and 4.5-hr diquat half-life exposures at concentrations of 0.185 and 0.37 mg/L.

While diquat is generally regarded and used as a broad spectrum herbicide, submersed plant control using that product varied somewhat between species under the treatment conditions employed in this study (concentration and exposure times). The plant susceptibility noted in this study indicates that diquat would be effective for controlling Eurasian watermilfoil, egeria, and sago pondweed in situations where water exchange processes reduce herbicide exposure times. However, acceptable control of American pondweed, and particularly hydrilla, with diquat will likely require longer contact times. While the low turbidity conditions in this study should have favored the efficacy of diquat for all the plants evaluated, these results suggest that individual plant species can show a wide range of response to diquat. In addition to factors such as water exchange and turbidity, inherent species susceptibility plays a role in target plant response, as well as the selectivity achieved when using diquat for submersed plant control.

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