Endothall concentration exposure time evaluation against horned pondweed in a hydrodynamic system

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ABSTRACT

Standard herbicide efficacy studies conducted in static exposure systems are used to establish application concentrations for the control of nuisance aquatic plants. It is unclear whether such results are applicable to the management of plants growing in riverine environments or irrigation conveyances. A flow-through exposure system was used to determine the efficacious concentration of dipotassium salt of endothall for the control of horned pondweed (Zannichellia palustris L.) in the Quincy-Columbia Basin Irrigation District, part of the Columbia Basin Project in north-central Washington. Seedlings were reared in flowing water to replicate plant structure, leaf morphology, and herbicide contact time observed in irrigation waterways. Water quality parameters were customized to regionspecific water temperature and chemistry. Results confirmed the efficacy of the current recommended application rate of 2.6 mg ae L^{-1} at 9 h, and found similar control at the 6-h exposure time point at the same concentration. This flow-through experiment provided a comprehensive understanding of herbicide delivery and supplied aquatic plant management professionals with applicable data necessary for effective control in flowing systems.

Key words: Cascade[®], endothall, flow-through, irrigation canals, herbicide efficacy, *Zannichellia palustris*.

INTRODUCTION

Overabundance of submerged aquatic macrophytes reduces water velocity and the overall carrying capacity of irrigation canals and laterals (Parochetti et al. 2008, Boman et al. 2012). Fragmentation of these weeds results in clogged siphon tubes and pump intakes, causing ineffective water delivery to agricultural operators. In the western United States, horned pondweed (*Zannichellia palustris* L.) (HPW) is a submerged aquatic perennial that grows up to a length of 1 m and is among the submersed plant communities in the Columbia Basin Project agricultural delivery channels in Washington State (Figure 1). Although classified as a perennial, considerable HPW abundance in the Columbia Basin Project is attributed to residual seed germination from the preceding season. Traditional control techniques for HPW include solvent-based chemistries, including acrolein (2-propenal) and xylene. In 2010, the State of Washington's Department of Ecology approved the use of dipotassium salt of endothall¹ in irrigation canals under their Irrigation System Aquatic Weed Control National Pollution Discharge Elimination System and state Waste Discharge General Permit. Unlike traditional chemistries in the irrigation canal market, recent research indicates endothall to have nontoxic effects on the survival of nontarget aquatic species such as Endangered Species Act–listed anadromous salmonids in the Pacific Northwest within the federal label rate of 5 mg L⁻¹ ai (Courter et al. 2011).

HPW is the dominant aquatic macrophyte in the canals and laterals of the Quincy-Columbia Basin Irrigation District (QCBID), the largest district within Washington's Columbia Basin Project. It is established that endothall is an effective herbicide for the control of HPW (DiTomaso et al 2013). However, anecdotal evidence from the QCBID suggests variable control of HPW with current treatment regimens, and it is unclear what factors affect the efficacy of endothall. Water flow, geochemical characteristics (elemental influences, e.g., calcium, magnesium), water quality, and herbicide tolerance are all plausible factors to influence herbicide efficacy. Flow velocity has the potential to influence plant growth and structural morphology (Sand-Jensen 2003) and has the potential to influence herbicide contact time due to rapidly dissipating concentrations at application sites (cited by Sisneros et al. 1998). Further, water quality parameters such as alkalinity (Whitford et al. 2009) and temperature (Mudge and Theel 2011) can affect an herbicide's efficacy. Although efficacy data has been reported for sago pondweed [Stuckenia pectinatus (L.) Boerner] (Slade et al. 2008), the comparative susceptibility of HPW is currently unknown.

Our experimental approach to optimizing an aquatic management plan for QCBID was to design a concentration and exposure-time efficacy study capturing an irrigation canal's flowing environment. Unique to a standard static assay, our flow-through system allowed for the experimental control of hydrodynamic factors on herbicide efficacy. To further tailor the experiment to QCBID's water quality parameters, region-specific water conditions and chemistry were replicated. Results provided applicable data for the refinement of an irrigation district's aquatic weed management program, leading to more effective control compared to historic strategies.

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Figure 1. The Columbia Basin Project in central Washington, including the Quincy-Columbia Irrigation District. Source: United States Bureau of Reclamation.

MATERIALS AND METHODS

Sediment and HPW plant material were collected from two sections of the QCBID canal system in Quincy, WA (47°16′6.66″N; 119°36′43.89″W and 47°15′20.28″N; 119°42'12.40"W) on 31 August 2012. Sediment was collected from the top 15 to 16 cm of the W21.3 lateral $(47^{\circ}16'6.66''N)$; 119°36′43.89″W). HPW was collected by raking plant material from the W26 lateral (47°15′20.28″N; 119°42'12.40"W) and transported back to the Center for Lakes and Reservoirs at Portland State University, Portland, OR, where it was dried at ambient greenhouse temperature (approximately 23°C) for 2 wk. Seeds were collected from dried plants and cold-stratified in glass dram vials at 4°C for 6 wk in order to achieve optimum germination (Greenwood and DuBowy 2005). Seeds were sown under 0.5 cm of sediment by fine forceps in 3.8-cm² by 5.8-cm-deep seedling pots in wet, unamended QCBID sediment at eight seeds per pot. A total of 12 pots per time-exposure "treatment" were allocated. Seeds were allowed 24 h at ambient temperature before placing in mesocosm. Pots were submerged 15 cm in static freshwater (Portland city water, Bull Run Reservoir, Oregon). For the germination process, water was maintained at 18°C for approximately 3 wk. The photoperiod was 10:14 h light : dark with natural light supplemented with 400-W sodium halide light bulbs. Temperature in the greenhouse was set at 24°C (day) and 18°C (night). Water

 TABLE 1. WATER QUALITY PARAMETERS THROUGHOUT EXPERIMENT, FROM GERMINATION

 THROUGH HERBICIDE RECOVERY.

	Germination	Rearing ¹	Exposure/recovery ¹
Temperature (°C)	18.3	15.6	15.6
Alkalinity (ppmv)	150 - 160	150 - 160	150-160
pH Flow (0.017 cubic	8.4	8.4	8.4
meter/second)	Static	0.6	0.6

¹Denotes actual water quality parameters during 2013 herbicide application season, as reported by Quincy-Columbia Basin Irrigation District water quality manager.

chemistry was maintained at QCBID conditions (C. Gyselinck, pers. comm.) (Table 1): alkalinity, 150 to 160 ppmv CaCO₃; pH 8.4 (Calcion^{®2}, Alkalin8.3-P^{®3}). Water quality parameters were monitored daily. Alkalinity and pH were monitored by ELOS⁴ KH and pH kits, respectively.

Following germination and initial growth in mesocosms, pots were randomly transferred to 15-cm by 1.83-m by 15cm troughs in a recirculating, flow-through system equipped with self-priming centrifugal pumps⁵ that allowed for desired water velocity, approximately 1 m³ min⁻¹. This flow was simulated to duplicate the flow observed in slowerflowing laterals where HPW presents the largest problem for QCBID. Perforated flat polyvinyl chloride at the water entry and exit points allowed for consistent laminar flow. Plant height averaged 8 to 10 cm upon transfer. Following transfer, water temperature was reduced to 15°C to mimic QCBID lateral and canal temperatures in late spring. Activated carbon filters were placed at the troughs' water exit points to control algal growth. Plants were allowed to achieve 20 to 22 cm in height before endothall exposure.

Prior to each treatment trial, endothall density and trough water volume were calculated and integrated into endothall concentration calculations to accurately ensure the target treatment. The nominal treatments and exposure durations included 1 mg ae L^{-1} (6, 9, and 12 h), 2 mg ae L^{-1} (3, 6, and 9 h), 2.6 mg ae L^{-1} (3, 6, and 9 h), and 3.7 mg ae L^{-1} (3, 6, and 9 h). It is also important to note that dosage rates indicated in this research are described in milligrams acid equivalent per liter of endothall, whereas 2012 product label dosage rates are described in parts per million dipotassium salt. Endothall concentration in each experimental trial was verified by Anatek Laboratories (Moscow, ID); nominal and actual endothall concentrations are listed in Table 2. Endothall was diluted $10\times$ and then administered to a receiving reservoir downstream to allow for effective mixing during recirculation before entry into exposure troughs.

Following desired exposure durations, pots containing plants were gently rinsed with fresh water to eliminate residual endothall contamination and randomly transferred to a parallel flow-through recirculation system with water quality parameters identical to those previously described. Water quality parameters continued to be monitored daily, as described above. At 4 and 8 wk posttreatment (WPT), surviving plants were quantified then harvested for wet weight/mass measurements. Experimental trials were repeated twice.

Generalized linear mixed models (Bates et al. 2011) were fit to the data to evaluate the effects of various endothall concentrations and exposure durations on predicted HPW

TABLE 2. ACTUAL AND NOMINAL ENDOTHALL CONCENTRATIONS BETWEEN EXPERIMENTAL TRIALS.

Pretreatment endothall $(mg ae L^{-1})^1$	Nominal endothall (mg ae L^{-1})	Actual endothall (mg ae L^{-1})	Statistical group identification ²
Trial 1			
0	0	0	1 (0)
0	1	0.99	2(1)
0	2	2.05	3 (2)
0	3.7	2.71	4 (2.7)
Trial 2			
0	0	0	1 (0)
0.01	1	1.40	2 (1)
0.01	2	2.57	4 (2.7)
0.01	3.7	3.73	5 (3.7)

¹"Pretreatment" indicates residual endothall from previous trial present in troughs during plant placement for rearing.

²"Statistical group identification" column denotes the statistical group each exposure was assigned to for statistical analysis, see Materials and Methods for further details on differences in treatments between trials and statistical grouping. Parenthetical numbers indicate to which statistical group data was assigned based on actual endothall concentrations.

viability. Surviving plants at 4 or 8 WPT were identified as "viable." Potential variation from different trials in the study was modeled as an additive random effect. Specific examples include subtle variation in chemical exposure levels and flow rates, and changes in plant size between trials. Incorporating random effects allowed us to account for these small differences, which may otherwise have biased statistical results. A single variable whose levels were comprised of each unique combination of duration and endothall exposure was included as a fixed effect. This approach was adopted because preliminary analyses indicated that the unbalanced nature of the exposure and endothall duration treatments provided poor convergence for both additive and multiplicative mixed models.

RESULTS AND DISCUSSION

At 4 WPT, HPW viability decreased by 40% at exposure concentrations $\geq 2 \text{ mg}$ as L^{-1} for all durations $\geq 3 \text{ h}$, compared with 86% viability in untreated control (P < 0.05; all nine exposure level-time combinations) (Figure 2). At 8

WPT, viability decreased to an average of 25% (2.7 mg ae L^{-1} ; all three exposure level-time combinations; P < 0.05) and 4% (3.7 mg ae L^{-1} ; $P \le 0.01$: all three exposure level-time combinations) across all exposure durations, compared with control (74%) (Figure 2). A dose-response decrease in HPW predicted viability was observed following 2.7 mg ae L^{-1} , where we found viability to range between approximately 40% at 3 h and 15% at 9 h, in contrast to results observed in 1- and 2-mg ae L^{-1} treatments (Figure 3). At 8 WPT at the highest treatment concentration (3.7 mg ae L^{-1}), we observed no difference in predicted viability (approximately 0%) across all exposure durations. Consistent with these results at 8 WPT, a dose-dependent decrease in mean HPW biomass was found in surviving plants (Figure 4).

From 2009 until 2013, QCBID has followed the current recommended application rate for the control of HPW of 2.6 mg ae L^{-1} endothall at 9 h. Our results confirm that this is an efficacious control concentration in QCBID's canals and laterals (Figure 3), where mean HPW viability in our study was found at 10%. However, the results also provide evidence that similar treatment of 2.7 mg ae L^{-1} at 6 h delivers comparable control (24%) (Figure 3). According to QCBID managers, this is an acceptable rate of HPW control for their water delivery responsibilities. Acceptable control of aquatic macrophytes will be unique to an irrigation district, since system demand for irrigation water varies by region due to crop and weather patterns.

To identify a more accurate endothall application strategy for HPW control in QCBID, we developed an exposure system that considered flow, temperature, and water chemistry. HPW and other submersed macrophytes develop morphological changes in order to circumvent potential mechanical damage generated by flowing water (as reviewed by Madsen et al. 2001). Such hydrodynamic conditions known to influence plant morphology include changes in water level, depth, and current (Roberts and Ludwig 1991, Sand-Jensen 2003). Therefore, we reared HPW seedlings in a hydraulic flume with a consistent laminar flow rate at approximately 1 m³ min⁻¹ to consider potential structural adaptations that would occur during rearing and development. Compared with more static environments, submersed macrophytes in riverine systems have been shown to experience less herbicide contact time, thereby



Figure 2. Horned pondweed predicted viability at 4 and 8 wk posttreatment (WPT) following 3, 6, 9 or 12 h exposure to endothall at varying concentrations. Data points are a representative average of predicted viability across all exposure time points; error bars represent \pm SEM. Linear regression is denoted by formula.



Figure 3. Horned pondweed viability at 4 and 8 wk posttreatment (WPT) with varying exposure times and concentrations of the dipotassium salt endothall. Proceeding symbols represent endothall concentrations; \circ , 0; \blacksquare , 1; \blacktriangle , 2; \blacktriangledown , 2.7; \times , 3.7 mg are L⁻¹.

reducing herbicide uptake and treatment effectiveness (Netherland 1991a,b). However, we found that the potential reduction in herbicide efficacy due to water flow may have been ameliorated. We observed water flow to facilitate breakage of plants weakened by herbicide treatment. In the field, this could potentially create seed dispersal and undesirable germination downstream of the treatment site if treatment is applied to more mature, seed-developing plants. In our study, however, we found effective control of HPW at the preseeding developmental stage with 2.6 mg ae L^{-1} at 6 h. Based on these laboratory results, QCBID district managers amended their application strategy for the 2013 irrigation season, thereby effectively controlling HPW. Figure 5 presents OCBID's historical treatment strategies (2007 through 2013) based on total herbicide usage. QCBID's revised 2013 endothall treatment strategy involved the following: 1) a nominal rate of 2.6 mg as L^{-1} (actual field rate range: 2.45 to 3.13 mg ae L^{-1}) for 6 h; 2) treatment earlier in the season on younger, less mature plants (approximately 30 cm in height); and 3) treatment in two different conveyance locations in the system (northern and southern reaches), compared with one location at the northern reach of the conveyance system. Qualitative field observations during the 2013 irrigation season included physiological disturbances, such as uniform discoloration and plant collapse at approximately 7 WPT (C. Gyselink, unpub. data). With a more effective endothall treatment

strategy, QCBID also faced the economic benefit of reduced application of solvent-based herbicides (Figure 5), which is often implemented as a secondary control approach later in season following endothall treatment.

Endothall concentration and field exposure time recommendations for irrigation conveyances and other hydrodynamic systems will depend on plant management objectives. We suggest that caution should be exercised with the direct application of our findings in the field, as region-specific factors might influence efficacy results. Hydraulic exchanges should be considered, such as those caused by precipitation, infiltration, runoff, and agricultural drawdowns and return flows, which all affect canal volume, thereby impacting desired herbicide concentrations downstream of application sites. Dense aquatic vegetation and ditch and canal conditions (e.g., concrete, soil) impact flow and carrying capacity (Boman et al 2012); therefore, varied laminar herbicide distribution throughout the water column could be expected. Varied plant morphology caused by flow velocity differences (Sand-Jensen 2003) in different segments of the conveyance system may further yield varied herbicide contact time and efficacy. Lastly, water quality parameters (e.g., alkalinity, pH, temperature) and a herbicide's chemical properties should be considered to account for potential effects on herbicide dissipation and degradation, which directly affect herbicide availability.

By simulating conditions specific to the QCBID water delivery system, the results from this study provided guidance for district managers with an improved endothall



Figure 4. Horned pondweed mean biomass at 8 wk posttreatment with varying exposure times and concentrations of the dipotassium salt endothall. Mean biomass value across both trials incorporates 0 mg for 0% surviving plants. Proceeding symbols represent endothall concentrations; \circ , 0; \blacksquare , 1; \blacktriangle , 2; \triangledown 2.7;, \times , 3.7 mg a.e. L⁻¹.

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Figure 5. Quincy-Columbia Basin Irrigation District's historical herbicide treatment strategies for irrigation seasons 2007 to 2013.

treatment strategy for the effective control of HPW. We recommend similar herbicide treatment strategies be developed and incorporated in aquatic weed management plans to maximize herbicide effectiveness against species found in irrigation conveyances. This approach would allow water delivery managers to achieve their goals of effective weed control, environmental stewardship, and reduced operation and maintenance costs. Future research should be directed toward establishing endothall concentration and exposure-time relationships for other aquatic macrophytes found in irrigation waterways to further improve predictions of aquatic weed control in such hydrodynamic systems.

SOURCES OF MATERIALS

¹Cascade[®], United Phosphorus Inc., 630 Freedom Business Center Dr., King of Prussia, PA 19406.

²Calcion[®], Brightwell Aquatics, 115 Industrial Park Road, Elysburg, PA 17824.

³Alkalin8.3-P, Brightwell Aquatics, 115 Industrial Park Road, Elysburg, PA 17824.

⁴PrimaLine, ELOS, Via Evangelista Torricelli, 32, Valeggio sul Mincio, Verona, Italy.

 $^{5}\mathrm{1-1/2}$ HP Dragon Series Wave Pump; W. Lim Corporation, 11095 Inland Ave, Mira Loma, CA 91752.

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