Persistence and movement of diquat and the effectiveness of limnobarriers after curlyleaf pondweed treatment in Crystal Lake, Connecticut

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ABSTRACT

Diquat (6,7-dihydridopyrido[1,2-α:2’,1’-c] pyrazinediium ion) concentrations in Crystal Lake, Middletown, CT, USA were monitored after diquat was applied in late April to the southern half of the lake to control curlyleaf pondweed (Potamogeton crispus L.). Limnobarriers were installed around a small island and a stretch of shoreline to protect Vasey’s pondweed (Potamogeton vaseyi J. W. Robbins), which is an aquatic plant listed as “threatened” in Connecticut. Surface and bottom water were analyzed for diquat from treated and untreated lake sites, inside and outside limnobarrier sites, and downstream until 24 d after treatment (DAT). Mean diquat concentrations in the treated surface lake sites peaked at 327 µg L⁻¹ 0.2 DAT (5 h) and were no longer detectable 13 DAT. At 5 DAT, the treated and untreated lake surface sites had similar mean diquat concentrations of 32 and 38 µg L⁻¹, respectively. Diquat concentrations in the treated lake surface sites gradually declined until they were no longer detectable 13 DAT. Vertical movement of diquat into the bottom water in the treated lake sites was limited, with a peak concentration of 7 µg L⁻¹ at 7 DAT. Diquat in the lake’s outlet stream followed a pattern similar to the untreated surface water, but the concentration peaked at only 26 µg L⁻¹ at 3 DAT. Inside the limnobarriers, diquat concentrations were significantly reduced but not eliminated. Diquat concentrations peaked inside the island and shore limnobarriers 2 DAT at 75 and 39 µg L⁻¹ respectively, and became nondetectable 13 DAT. Diquat movement into the limnobarriers could have been facilitated by imperfect seals where sections connect. The Vasey’s pondweed inside the limnobarriers did not appear impacted.

Key Words: aquatic weed control, herbicide, pesticide persistence, Potamogeton crispus L.

INTRODUCTION

Crystal Lake in Middletown, CT, like many other northeastern lakes and ponds, contains the nonnative aquatic plant curlyleaf pondweed (Potamogeton crispus L.) (Bugbee et al. 2012). This plant degrades recreational use of lakes and has adverse effects on native plant communities (Woolf 2009). Diquat (6,7-dihydridopyrido[1,2-α:2’,1’-c] pyrazinediium ion) is an aquatic herbicide commonly used to control curlyleaf pondweed (Poovey et al. 2002, Woolf 2009). It is a contact product that rapidly disables the photosynthetic process in exposed plant tissue and has a relatively short residual in aquatic ecosystems (Funderburk and Lawrence 1964, Coats et al. 1966). Previous studies have found that diquat concentrations peak immediately after application and decline to nondetectable levels in 1.5 to 38 d (Grzenda et al. 1966, Langeland and Warner 1986). Rapid deactivation or dissipation of diquat can limit damage to nontarget organisms. Deactivation of diquat can occur rapidly in turbid water (Poovey and Getsinger 2002) or if dense stands of plants are covered with sediment or periphyton (Clayton and Matheson 2010). Water temperature (Netherland et al. 2000) and pH (Florêncio et al. 2004) also can affect the persistence of diquat in aqueous systems. Alkalinity and conductivity might also play a role but documentation is lacking.

Efforts to control nonnative species such as curlyleaf pondweed, can be confounded by the coexistence of desirable or protected native species. Performing partial lake treatments can be a solution if offsite movement is not excessive. To ensure entire plant populations are not harmed, permits sometimes specify that only portions of the water body can be treated. The Connecticut Department of Energy and Environmental Protection’s (CTDEEP) permit for diquat treatment of Crystal Lake specified that only half the lake could be treated. In addition, Crystal Lake had a population of Vasey’s pondweed (Potamogeton vaseyi J. W. Robbins) coexisting with the curlyleaf pondweed. Vasey’s pondweed is listed as “threatened” in Connecticut and therefore is in need of protection. Permitting required protection of Vasey’s pondweed by the installation of limnobarriers. Limnobarriers are made from synthetic sheets that have surface floats and bottom weights. When properly installed, little transfer of water should occur, but information on actual effectiveness is lacking.

Applicators are required to follow label instructions when applying aquatic herbicides. The diquat label (Reward®, USEPA Reg. No. 100-1091) states that the effectiveness of diquat could be improved with bottom placement...
with weighted hoses if vegetation has “reached the water surface and/or where the water is slowly moving through the weed growth.” Neither of these conditions are usually present when early season diquat applications are performed to control curlyleaf pondweed in quiescent water bodies such as Crystal Lake. This study investigates the horizontal and vertical movement of diquat in Crystal Lake when label instructions are followed and diquat is applied as a partial lake treatment. In addition, this study determines the effectiveness of limnobarriers at limiting diquat movement to areas containing a protected plant species.

**MATERIALS AND METHODS**

Crystal Lake is a 13.1-ha man-made impoundment located in Middletown, CT. It has a mean depth of 2.2 m and an estimated volume of 290 megaliters (ML). Flow is from south to north where water exits via a surface spillway (Figure 1). The southern section of the lake averages 2 m deep and supports dense stands of curlyleaf pondweed. The northern section has a rocky shoreline which rapidly drops to a depth of over 4 m and supports sparse vegetation.

In 2006, areas along the southern shoreline and a small island were found to contain the state-protected plant Vasey’s pondweed. The CTDEEP required limnobarriers be installed to protect this plant. On April 25, 2010, 5 d before the diquat application, experienced personnel installed limnobarriers along a 26-m section of shoreline and around a 0.04-ha island (Figures 1 and 2). Limnobarriers were made from impervious synthetic material with floats at the surface and chain weights along bottom. The barriers extended out approximately 3 m from shore into water 1.5 m deep. The shoreline limnobarrier was comprised of two sections, and the island limnobarrier was comprised of four sections. Sections were stitched together with rope through grommets located approximately 25 cm apart and secured at the base with cement blocks. The limnobarriers were removed 21 d after treatment (DAT). Plant growth inside the limnobarriers was not directly measured because of the sensitive nature of sites containing state-protected species; however, the sites were inspected in the summer prior to treatment and the summer after treatment by biologists from CTDEEP to assess the general condition of the Vasey’s pondweed.

**Diquat Application**

Diquat was applied to the southern half of the lake (6.5 ha) on April 30, 2010, at the label suggested rate of 7.8 kg ai ha⁻¹. This equates to a diquat cation concentration in the treatment area of approximately 224 µg L⁻¹. The application was made during the early afternoon with sunny skies, calm winds, and an air temperature of 26 C. A 1 : 1 ratio of diquat formulation to water was injected 0.5 m beneath the surface with a 95-L electric sprayer. An onboard global positioning system (GPS) was used to assure the boat paths were approximately 15 m apart. One-half of the herbicide was applied in a north–south direction and the other half was applied in an east–west direction. The lake received similar diquat treatments in 2007 and 2009. Each treatment yielded nearly complete control in the treatment year but substantial regrowth in the following year.

**Water Testing**

Water samples were obtained from north (TN) and south (TS) treated lake sites, and north (UTN) and south (UTS) untreated lake sites from 0.5 m beneath the surface and 0.5 m above the bottom (Table 1, Figure 1). The effectiveness of the limnobarriers were determined by obtaining water samples at north, middle, and south locations inside and outside the shore limnobarrier (S-IN, S-IM, S-IS, S-ON, S-OM, S-OS) and island limnobarrier (I-IN, I-IM, I-IS, I-ON, I-OM, I-OS). The inside and outside locations were approximately 1.5 m from the limnobarrier.

To assure consistency in the sampling locations, each site was located with a GPS with submeter accuracy. The UTN and UTS sites were approximately 410 and 70 m from the treatment edge, respectively. Water samples were also taken from a downstream site (DS) that was approximately 70 m from the edge of the lake and 500 m from the treatment edge. The streams outflow was determined 10 DAT by calculating the filling rate of a 7.5 L bucket with all the water flowing from the spillway pipe. This procedure was repeated five times and the mean flow rate was calculated. No severe weather occurred during the study to appreciably change the flow rate. Rainfall during the period was 0.6, 0.5, 0.2, 1.0, 1.3, and 1.0 cm at 8, 13, 14, 15, 19 and 20 DAT, respectively (weather records, Brainard Field, Connecticut).

Diquat concentrations at the treated and untreated lake sites were measured 1 d prior to treatment (−1 DAT), 0.2 (5 h), 0.9 (22 h), and at 1.2, 2, 3, 5, 7, 10, 13, 17, and 24 DAT. Sampling at the limnobarriers occurred on the same schedule except for 24 DAT because the limnobarriers had been removed. The diquat samples were collected in 15-mL polypropylene tubes. Surface samples were obtained by hand by immersing a collection tube 0.5 m below the surface. Water samples from 0.5 m above the bottom were obtained with an electric pump. Only samples from the 0.5 m depth were taken inside and outside the limnobarriers because of the shallow nature of the sites. The samples were immediately frozen in dry ice and stored in a cooler until delivery to the laboratory. In the laboratory, the samples were equilibrated to room temperature and passed through a 45 micron syringe filter. Samples that could not be immediately analyzed were stored at −20 C. Diquat concentrations were quantified using an HPLC-MS/MS with a diquat cation quantitation limit of 3.3 µg L⁻¹ (Robb and Eitzer 2011). Mean diquat concentrations from the lake sites were calculated from the two treated surface sites, the two treated bottom sites, the two untreated surface sites, and the two untreated bottom sites. Mean diquat concentrations from the shore and island limnobarrier sites were calculated from the three inside sites and the three outside sites. Differences in diquat concentration between the inside and outside of the shore and island limnobarrier were evaluated using repeated measures analysis and significant differences were based on the multivariate F-statistic and P value.
Water transparency, temperature, and dissolved oxygen concentration were measured in situ on the same schedule as the diquat concentrations. Transparency was measured at the deeper water sites (UTS, UTN) with a Secchi disk. Treated sites (TS, TN) were not measured with a Secchi disk because of insufficient depth. Temperature and dissolved oxygen were measured with a calibrated digital meter or sonde at 0.5 m below the surface and 0.5 m above the

Figure 1. Treatment area and location of water sampling sites in Crystal Lake, Connecticut.

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bottom. The pH, alkalinity, and conductivity of the water samples were determined at −1, 5, 13, and 24 DAT. Samples for pH, alkalinity, and conductivity were placed in 250 ml Nalgene® bottles, stored on ice in a cooler, refrigerated, and analyzed within 7 d. Water pH was determined with a calibrated digital pH meter and alkalinity (calcium carbonate [CaCO₃]) was quantified by titration with 0.016 M sulfuric acid (H₂SO₄) to a pH 4.5 endpoint. Conductivity was measured with a calibrated digital conductivity meter.

RESULTS AND DISCUSSION

Diquat movement and persistence at treated and untreated lake sites

No diquat was found at any sites prior to treatment (−1 DAT, Figure 3). Shortly after treatment (0.2 DAT), the mean diquat concentrations in the treated surface lake sites rose to 327 µg L⁻¹ as compared to 9 µg L⁻¹ in the untreated surface lake sites. All diquat detected in untreated surface lake sites 0.2 DAT occurred in the site that was closest to the treatment area (UTS). From 0.9 to 10 DAT, diquat concentrations in the treated surface lake sites gradually declined until they were no longer detectable 13 DAT. Mean diquat concentrations in the untreated surface lake sites peaked 1.2 DAT at 67 µg L⁻¹. At 5 DAT, the treated and untreated surface lake sites had similar mean diquat concentrations of 32 and 38 µg L⁻¹, respectively. At 10 DAT, mean diquat concentrations declined to 4 µg L⁻¹ in the treated surface lake sites and 3 µg L⁻¹ in the untreated surface lake sites. By 13 DAT, diquat was no longer detectable in the treated surface lake sites, but 2 µg L⁻¹ was still present in the untreated surface lake sites, suggesting that the natural water flow from treated to untreated lake sites could be influencing residual concentrations. Diquat was not detected in any lake site 17 DAT or thereafter.

Compared to the rapid and thorough horizontal mixing of diquat observed in the surface water, vertical mixing into either the treated or untreated lake bottom sites was minimal (Figure 3). This accounts for the peak 327 µg L⁻¹ surface diquat concentration in the treated lake sites being greater than the 224 µg L⁻¹ target concentration that would have occurred if the diquat had mixed throughout the water column. Mean diquat concentrations in the treated bottom lake sites were nondetectable through 3 DAT and peaked at 7 µg L⁻¹ at 7 DAT. At 13 DAT, no diquat was detected in treated bottom lake sites. Diquat was never detected in the untreated bottom lake sites. Poor vertical mixing of diquat is recognized but not well documented. Parsons et al. (2007) performed a similar treatment in Battle Ground Lake, Washington, USA and found the maximum diquat concentration near the surface was 90 µg L⁻¹ as compared to 11 µg L⁻¹ at a depth of 3 m. Langeland et al. (1994) studied the vertical distribution of diquat and observed that the greatest mixing occurred when temperatures in the water column were uniform. Limited vertical mixing therefore could be related to thermal stratification present during this study. There was a 3 to 5 C temperature difference between the treated surface and bottom lake sites from 0.2 to 7 DAT.

<table>
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and less than a 2 C difference from 13 to 24 DAT (Figure 4). Both surface and bottom water temperatures were within the reported range for diquat efficacy on curlyleaf pondweed (Netherland et al. 2000, Poovey et al. 2002).

Characteristics of the herbicide formulation might also cause it to stay near the surface. Bitting (1974) recognized that diquat might need an adjuvant to facilitate its ability to sink, and suggested the use of an invert emulsion. The diquat label mentions the possible need for an invert emulsion, but the practice is rarely employed (B. Burns, Syngenta, USA, pers. comm., October 28, 2013). Alternatively, diquat applications could be enhanced by bottom placement with weighted hoses; however, the label indicates it is not necessary when vegetation has not reached the surface. Limited vertical mixing has the disadvantage of limiting herbicide contact to target plants near the bottom but could reduce the impacts on desirable low-growing plants that are just beginning their yearly growth cycle.

**Diquat persistence and movement at the downstream site**

The downstream site had lower diquat concentrations than any surface site and followed a similar pattern to the untreated surface water (Figure 3). Diquat peaked 3 DAT at 26 µg L⁻¹ and was no longer detectable 10 DAT. The stream’s flow rate was 0.09 ML d⁻¹ which constitutes 0.03% of the lake volume per day, or 0.7% of the lake volume over the 24-d study period. Given this small discharge rate and the low concentrations of diquat in the stream, losses via this route were considered negligible.

Concern exists over the presence of diquat in outlet streams, particularly if adverse downstream effects are not factored into the overall treatment plan. The U.S. Environmental Protection Agency currently has a 20 µg L⁻¹ maximum contaminant level (MCL) for diquat in drinking water. This was slightly exceeded 3 DAT when 26 µg L⁻¹ was detected. Downstream concentrations of diquat were well below levels shown to harm aquatic organisms (Wilson and Bond 1969, Paul et al. 1994) and ornamental plants (Mudge et al. 2007).

**Diquat persistence and movement at the limnobarriers sites**

Diquat was first detected inside the island limnobarrier sites 0.2 DAT at a mean concentration of 11 µg L⁻¹ (Figure 4). Inside the shore limnobarrier, the first detection did not occur until 0.9 DAT, at a mean concentration of 30 µg L⁻¹. Outside the island and shore limnobarriers, mean diquat concentrations peaked 0.2 DAT at 291 µg L⁻¹ and 316 µg L⁻¹, respectively. The limnobarriers reduced the mean peak diquat concentrations to 75 µg L⁻¹ and 39 µg L⁻¹ in the island and shore sites, respectively, and slowed its occurrence until 2 DAT. Diquat was no longer detectable inside either limnobarrier 13 DAT and outside 17 DAT. When the concentration and movement of diquat were compared using repeated measures analysis, significant differences were detected between the inside and outside of the barriers for both sites. The island site exhibited a significant trend over time, where the diquat concentration was significantly lower inside the limnobarrier compared to outside (F = 738.17, P < 0.001). This same pattern was found for the
shoreline limnobarrier site ($F = 54.94, P = 0.002$). Movement of diquat across the limnobarriers appeared to be facilitated by leaks where barrier sections were attached and a few small tears in the material. Imperfect seals to the bottom were possible but not apparent.

**Diquat persistence and water parameters**

In addition to dispersion, the persistence of diquat in lake water might be reduced by adsorption to suspended particulate matter and living organisms (turbidity, periphyton) and degradation by microbial activity or photolysis (Simsiman and Chesters 1976, Hofstra et al. 2001, Poovey and Getsinger 2002, Clayton and Matheson 2010). Water chemistry parameters such as pH, alkalinity, conductivity, and dissolved oxygen could also facilitate chemical reactions that remove diquat from aquatic environments (Emmett 2002). Although we did not directly measure suspended particulate matter or other forms of turbidity, comparisons of water transparencies measured via Secchi disk with direct turbidity show high correlations (Steel and Neuhauser 1999). The Secchi disk measurements of 2 to 3 m (Figure 5) suggest turbidity was minimal. Because the treatment area had a large biomass of aquatic vegetation, adsorption to particulates adhering to the vegetation, periphyton, or the plants themselves was likely (Simsiman and Chesters 1976). Diquat has been reported to be photolytically stable in aquatic systems (EPA 1995); however, laboratory work by Smith and Grove (1969) showed photolysis by natural sunlight accounted for a 90% loss of diquat from pure water after 5 wk. The weather until 3 DAT was generally sunny, thus maximizing the potential for photo-degradation, particularly because most of the herbicide remained near the surface. The remainder of this study featured a mixture of sunny and cloudy days typical for this area of Connecticut (weather records, Brainard Field, Connecticut).

The pH of all sites ranged from 6.4 to 7.6 and the alkalinity ranged from 26 to 33 mg L$^{-1}$ CaCO$_3$ (Figure 5). Diquat is stable within a pH range of 3 to 8 (Florêncio et al. 2004), making losses due to pH unlikely. Little information is available on the effects of alkalinity on the fate of diquat. Dissolved oxygen could favor microbial activity that can metabolize pyridine ring structures similar to those in diquat (Kaiser et al. 1996). Both surface and bottom water in the treated area remained highly aerobic during this study (Figure 4), and insufficient oxygen was not likely to have limited microbial activity.

Vasey’s pondweed was found growing inside the limnobarrier when inspected in August along with other native plants such as snailseed pondweed (*Potamogeton bicupulatus* Fernald) and nonnative minor naiad (*Najas minor* All.) With the exception of Vasey’s pondweed, the other native plants were common in treated and untreated areas outside the limnobarriers. It is possible that a considerable amount of protection came from treating early in the season before the native plants began growing.

Partial lake diquat treatments and limnobarrier exclusion zones provide mechanisms to protect nontarget species. Diquat concentrations rapidly decline outside the treatment zone and with time from the treatment date. Limnobarriers did not eliminate diquat penetration but reduced the maximum concentration and exposure time to levels not likely to harm plants. Vertical movement of
diquat is limited, suggesting greater emphasis on using weighted hoses is needed. Future studies on the persistence and movement of diquat, when applied with weighted hoses, would clarify if bottom applied diquat migrates to the surface and if better long-term weed control can be achieved.

Figure 5. Water chemistry in the surface and bottom water of Crystal Lake, Connecticut over time (DAT 0 = April 30, 2010). Bars indicate standard error.

**SOURCES OF MATERIALS**

3. ProXT®, Trimble Inc., 935 Stewart Dr., Sunnyvale, CA 94085.
4. GeoXT®, Trimble Inc., 935 Stewart Dr., Sunnyvale, CA 94085.
ACKNOWLEDGEMENTS

Many members of Connecticut Agricultural Experiment Station Invasive Aquatic Plant Program (CAES IAPP) have helped with this research, and they are gratefully acknowledged: Martha Barton, Michael Cavadini, Jennifer Fanzutti, Michelle Marko, Annette Russell, and Rachel Soufrine. We greatly appreciated Nancy Murray of the CTDEEP for her help with locating Vasey’s pondweed. We also would like to thank John Milardo of the City of Middletown and Chris Hart of the Crystal Lake Association for their assistance. This research was funded by the U.S. Department of Agriculture Cooperative Agreement 58-6629-2-205 and Hatch CONH00768.

LITERATURE CITED


