INTRODUCTION

Little Saint Germain Lake, Vilas County, is a 980-acre lake comprised of two main drainage lakes (Lower East Bay, East Bay, No Fish Bay, and South Bay) that are fed via Muskellunge Creek, and a seepage lake (West Bay) which groundwater fed and flows from the west-southwest. Water flows out of South Bay via Little Saint Germain Lake into the nearby Wisconsin River (Figure 1). Water levels in the lake are artificially maintained approximately 5.0 feet higher than its natural level by a dam that is maintained by the Wisconsin Valley Improvement Company (WVIC). The WVIC utilizes Little Saint Germain Lake as a storage reservoir.

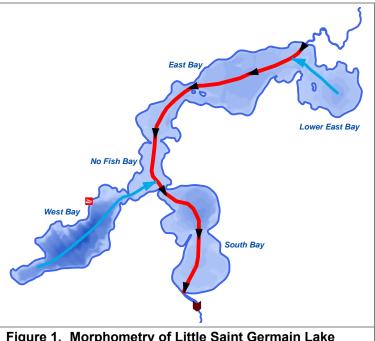


Figure 1. Morphometry of Little Saint Germain Lake

where each winter it releases approximately 1.5 feet of water for use in hydroelectric power generation downstream on the Wisconsin River.

Recent AIS Management

The non-native, invasive plant curly-leaf pondweed (Potamogeton crispus; CLP) was first documented in No Fish Bay in 2000, while fragments of Eurasian water milfoil (Myriophyllum spicatum; EWM) were first discovered floating near the boat landing in West Bay in the spring of 2003. Management actions aimed at reducing lake-wide levels of CLP and EWM have been conducted on Little Saint Germain Lake since 2003. Since its discovery, the LSGLPRD has been active in managing this invasive plant through a combination of localized herbicide spot treatments and manual hand-removal that may include the use of Diver Assisted Suction Harvesting (DASH). Based upon the low quantities of CLP located during the 2016 survey, it is believed that the turion bank on Little Saint Germain has been considerably reduced during the past decade of active management.

The EWM and CLP control program on Little Saint Germain Lake made great strides since 2007, particularly after 2010-2011 when volumetric herbicide dosing was adopted. The EWM and CLP population within Little Saint Germain Lake was at a low level in 2016 and no herbicide treatments were proposed for 2017 although professional hand-harvesting was implemented on a few select areas. The role of hand-harvesting as a tool to manage EWM population in Little Saint Germain Lake continues to be evaluated. Professional harvesting efforts in 2017-2018 showed that seasonal control is attainable with large amounts of effort; however, longer term reductions in EWM populations that extend beyond one growing season has not been demonstrated.

The CLP population was found to be very low in Little Saint Germain Lake in 2018 and no active management was proposed for 2019. Populations of CLP can vary from year to year based on



environmental factors and continued monitoring of this species is important going forward to help understand if populations increase to levels that warrant consideration for active management.

Over the winter of 2018-2019 the LSGLPRD were nearing completion of an update to their comprehensive lake management plan. During the planning process, conversations regarding risk assessment of the various management actions were prominent. Within the planning process, the LSGLPRD has developed a goal along with specific management actions within the implementation plan of the report related to AIS management on the lake:

Management Goal 1:	Control Existing and Prevent Further Aquatic Invasive Species Infestations within Little Saint Germain Lake
Management Action:	Conduct EWM Population Control on Little Saint Germain using Hand-Harvesting and Herbicide Spot Treatments

Following the guidance developed in the management plan, an AIS management plan for 2019 was developed based on the population of EWM and CLP that were mapped in surveys completed during 2018. If the following trigger is met, the LSGLPRD would initiate the collection of pretreatment and planning data necessary to conduct the treatment:

colonized (polygons) areas of EWM, with preference to areas of *dominant* or greater densities, that are of a size/shape/location where management is anticipated to be effective.

Once the trigger has been met and the pretreatment data is collected, the LSGLPRD will review the information in the context of the most current science as it relates to improving the efficacy and minimizing collateral impacts of the control actions.

It is believed that EWM colonies that meet this trigger are too large and dense to be effectively and efficiently controlled using hand-harvesting techniques. It is likely that these areas may be small (3-5 acres) and would need to be conducted with herbicides that require short exposure times (diquat, florpyrauxifen-benzyl [ProcellaCORTM]) or herbicide combinations (diquat/endothall, 2,4-D/endothall, etc.). If large areas and/or sites in protected parts of the lake are to be targeted with an herbicide spot treatment, more traditional systemic herbicides like 2,4-D may be appropriate. If populations exceed spot-treatment thresholds, large-scale (whole-basin) herbicide strategies may be given consideration as was adopted in Lower East Bay during 2014.

Several EWM colonies mapped in late-summer 2018 met the pre-determined trigger for considering herbicide spot-treatments in the lake. These sites were presented to the LSGLPRD in early 2019 to gauge if the process of "considering" a treatment should take place.

Following a period of review, the LSGLPRD elected not to pursue an herbicide control program in 2019 for various reasons that include a lack of pretreatment sub-sample point-intercept data that would assist in evaluating the efficacy and native plant selectivity of the action. Of the five sites that initially met the trigger for considering spot-treatments based on the results of the 2018 Late-Season EWM Mapping Survey, the LSGLPRD elected to target two sites with a professional hand-harvesting control strategy in 2019 rather than herbicide management. The other three sites were monitored in 2019 and if they show signs of EWM expansion, would again be considered for an herbicide control strategy in 2020. This resulted in the collection of sub-sample point-intercept



data within the potential areas during the late-summer of 2019 to serve as a pretreatment dataset, the results of which are discussed later in this report.

The LSGLPRD elected to contract for nine days of professional hand-harvesting efforts in 2019 utilizing DASH. The two sites in West Bay that were selected as the primary hand-harvesting sites in 2019 were prioritized by the LSGLPRD based on their relatively high visibility and high-use location in the lake. Through these harvesting efforts, the LSGLPRD expected to achieve seasonal EWM population suppression in 2019 in the targeted areas, with a goal that the EWM reductions are extended into the following year.

2019 MONITORING AND MANAGEMENT ACTIVITIES

Three EWM mapping surveys were used within this project to qualitatively coordinate and hand-harvesting monitor the efforts (Figure 2). A preliminary hand harvesting strategy was created based on the results of the 2018 Late-Season **EWM** Mapping Survey from which the District obtained a conditional permit from the WDNR for the use of DASH. The first monitoring event on Little Saint Germain Lake in 2019 was the Early Season Aquatic Invasive Species Survey (ESAIS). This late-spring/early-summer survey provides an early look at the lake to help guide the hand-harvesting

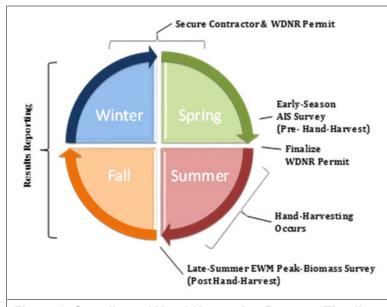


Figure 2. Coordinated Hand-Harvesting Program Timeline.

management to occur on the system. The hand harvesting strategy and DASH permit is finalized based on the results of the ESAIS survey. Following the completion of the hand-harvesting, Onterra ecologists completed the Late-Season EWM Mapping Survey, the results of which serve as a post-harvesting assessment of the hand-removal efforts. The results of the 2019 Late-Season EWM Mapping Survey are compared to the results of the 2018 Late-Season EWM Mapping Survey to qualitatively assess the hand harvesting strategy.

Early Season Aquatic Invasive Species Survey (ESAIS)

Onterra ecologists completed the Early-Season AIS Survey on June 12-13, 2019. The EWM/CLP population was mapped by using either 1) point-based or 2) area-based methodologies. Large colonies >40 feet in diameter are mapped using polygons (areas) and were qualitatively attributed a density rating based upon a five-tiered scale from *Highly Scattered* to *Surface Matting*. Point-based techniques were applied to EWM/CLP locations that were considered as *Small Plant Colonies* (<40 feet in diameter), *Clumps of Plants*, or *Single or Few Plants*.



During the ESAIS survey, the field crews noted fair conditions with a mix of sun and clouds and light to moderate winds. The entire lake was included in the survey extent for the CLP mapping component of the survey. Survey crews documented three *highly scattered* CLP colonies, one in South Bay and two in East Bay as well as a number of relatively sparse and isolated occurrences that were mapped as *single or few plants*, *clumps of plants*, or *small plant colonies* (Map 1). No CLP was located within the West Bay of the lake during the survey.

The EWM population was mapped during the ESAIS survey primarily for the purpose of finalizing the hand-harvesting strategy for 2019. Only the sections of the lake where active management (herbicide spot-treatment or hand harvesting) were being considered in 2019 were included in the extents of the EWM mapping survey. The final EWM hand-harvesting strategy was determined based on the survey results and included targeting three sites in the west bay of the lake totaling 4.92 acres (Map 2). Onterra provided the spatial data from this survey to the professional hand-harvesting firm to aid the control efforts.

Hand-Harvesting Management Activities

The LSGLPRD contracted with Aquatic Plant Management, LLC (APM) to conduct professional hand-harvesting of EWM in 2019. AIS removal specialists from APM conducted hand-harvesting activities on nine days between June 24 and August 2, 2019 and removed approximately 448 cubic feet of EWM. All removal efforts were conducted in site B-19 on the far west end of the west basin of Little Saint Germain Lake. Details of the professional hand-harvesting efforts are included within APM's summary report (Appendix A).

Late-Season EWM Mapping Survey Results

The Late-Season EWM Mapping Survey was conducted on September 11-12 & 17, 2019 to qualitatively assess the hand harvesting efforts as well as to understand the peak growth (peak-biomass) of the EWM population throughout the lake and to determine an appropriate management the strategy for following Conditions during the late-summer survey were variable with a mix of sun and clouds and light to moderate winds. Much of the EWM was growing near the water's surface at the time of the survey.

The 2019 Late-Season EWM Mapping Survey indicated that the EWM population expanded in many areas of the lake compared to 2018. The results of the survey are displayed on Maps 3-6. A total of 68.3 acres of colonized EWM was mapped during the 2019 survey compared to 10.5 acres in 2017 and 44.1 acres in

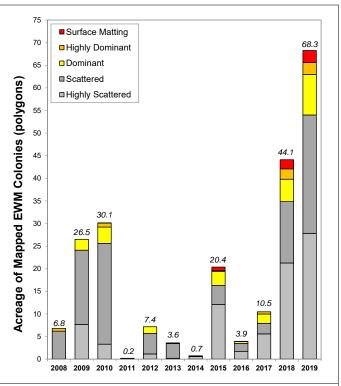


Figure 3. Acreage of EWM colonies in Little Saint Germain Lake from 2008-2019. Data from annual Onterra Late-Season EWM Mapping Surveys.



2018. Total acreage of EWM in 2019 is higher than any survey dating back to 2008 (Figure 3). Please note that the acreages displayed in Figure 3 do not account for any EWM that is marked as point-based occurrences including single plants, clumps of plants, or small plant colonies. Of the 68.3 acres of colonized EWM present in 2019, the majority (54.0 acres) consists of colonies that were of either a *scattered* or *highly scattered* density. These areas likely do not directly impact the ecosystem function of the lake or typically cause nuisance conditions. However, areas mapped as *dominant* or greater in density, which included approximately 14.3 acres in 2019, are more likely to cause localized nuisance conditions.

The site that was targeted for professional harvesting is highlighted in Figure 4 where the left frame shows the pre-harvesting EWM population mapped in September 2018 and the right frame show the post-harvesting EWM population mapped in September 2019. It should be noted that the late-summer survey occurred approximately five weeks after the completion of the professional DASH efforts. This allows for sufficient time for EWM rebound in these areas from root crowns that were not completely removed. The 2018 Late-Season EWM Mapping Survey showed a *highly dominant* and *scattered* density colony present in site B-19 (Figure 4). After nine days of professional hand harvesting efforts during the summer, the 2019 Late-Season EWM Mapping Survey showed a reduction of the EWM population in the site. Most of the remaining EWM population consisted of point-based occurrences described as *single or few plants, clumps of plants*, or *small plant colonies*. Additionally, a small *highly scattered* colony was mapped near shore in the site. The reduction in the EWM population in the site met or exceeded lake managers' expectations for the control strategy.

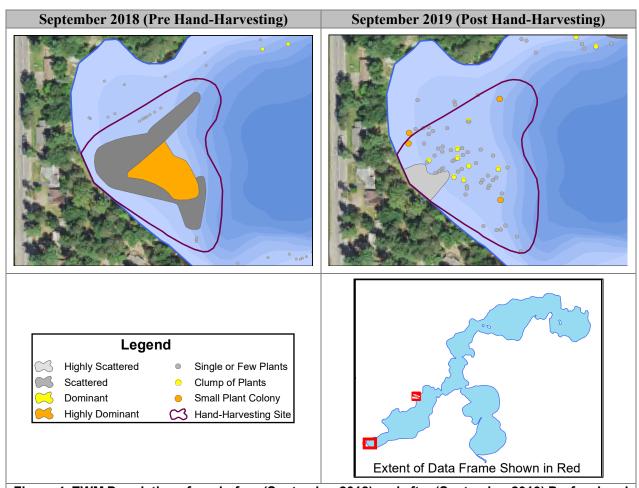


Figure 4. EWM Populations from before (September 2018) and after (September 2019) Professional Hand-Harvesting efforts at site B-19 in Little Saint Germain Lake.

CONCLUSIONS AND DISCUSSION

Aquatic plant monitoring surveys in 2019 showed the EWM population has expanded significantly over the past several years. Active management of EWM in 2019 was limited to one site in West Bay where nine days of professional DASH efforts resulted in a reduction in EWM in the targeted area. With the relatively low CLP population in recent years, no active CLP management has occurred since 2016. The sites that were initially considered for herbicide management in spring 2019 were instead monitored in 2019 through the completion of subset point-intercept surveys and mapping surveys in preparation for potential herbicide treatment in 2020.

2020 AIS Management Strategy Development

Extracted relevant chapters from the WDNR's *APM Strategic Analysis Document*: (https://dnr.wi.gov/topic/EIA/documents/APMSA/APMSA_Final_2019-06-14.pdf) are included with this report as Appendix B to serve as an objective baseline for the LSGLPRD to weigh the benefits of management strategies with the collateral impacts each management action may have on the Little Saint Germain Lake ecosystem.

Herbicide Spot Treatment

Consistent with the management actions and goals that were developed through the management planning project, several areas meet the pre-determined trigger for herbicide control in 2020 based on the 2019 Late-Season EWM Mapping Survey results. The LSGLPRD has completed the collection of pre-treatment quantitative data from three sites that are being considered for herbicide treatment in 2020 (Figure 5). Map 7 displays the proposed 2020 treatment strategy which targets three sites, totaling 32.1 acres in Little Saint Germain Lake. Each of the sites were constructed by applying an approximate 60-foot buffer around the EWM colonies that are being targeted.

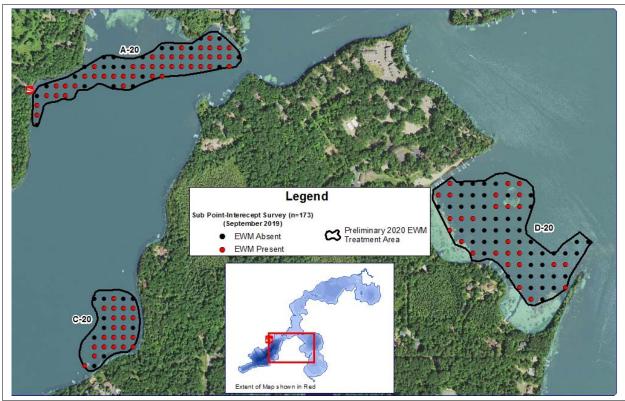


Figure 5. Little Saint Germain Lake Quantitative Monitoring Plan for Proposed 2020 Herbicide Treatments (n=173).

The LSGLPRD is pursuing the option of using a relatively new herbicide called ProcellaCORTM (florpyrauxifen-benzyl) that has shown some promise in other spot treatments in Wisconsin Lakes. This herbicide is specifically designed to control invasive milfoil populations. ProcellaCORTM is in a new class of synthetic auxin mimic herbicides (arylpicolinates) with short concentration and exposure time (CET) requirements compared to other systemic herbicides. Uptake rates of ProcellaCORTM into EWM were two times greater than reported for triclopyr (Haug 2018, Vassios et al. 2017). ProcellaCORTM is primarily degraded by photolysis (light exposure), with some microbial degradation. The herbicide is relatively short-lived in the environment, with half-lives of 4-6 days in aerobic environments and 2 days in anerobic environments (WSDE 2017). The product has a high affinity for binding to organic materials (i.e. high KOC).

Netherland and Richardson (2016) and Richardson et al. (2016) indicated control of select nonnative plant species with the active ingredient in ProcellaCORTM, including invasive watermilfoils (EWM and HWM) at low application rates compared with other registered spot treatment herbicides. The majority of native plants tested to date also suggest greater tolerance to this mode of action. Water lilies, pickerelweed, arrowheads, and native watermilfoils have shown sensitivity to ProcellaCORTM. Coontail may also be impacted at higher application rates. Because this is a new herbicide, data available from field trials is relatively limited.

The use of any aquatic herbicide poses environmental risks to non-target plants and aquatic organisms. The EPA Ecological Risk Assessment places the risk to non-target wildlife into the "no risk concern" category and the impacts to bees, birds, reptiles, amphibians, and mammals in the "practically non-toxic" category. The EPA has also indicated that there are no risks of concern to human health. There are no restrictions on swimming, drinking, fish consumption, or turf irrigation. However, there would be an approximate 1-day waiting period of the proposed application for shoreland irrigation due to concerns of herbicidal impacts. The WDNR's Chemical fact sheet for florpyrauxifen-benzyl is included as Appendix C. The manufacturer of the herbicide (SePRO) recommends a dose of 4.0 prescription dose units (PDU's) in association with the proposed treatment. The maximum application rate of this formulation of ProcellaCORTM is 25 PDU.

The 2020 herbicide treatment would be monitored through the quantitative and qualitative evaluations. The quantitative assessment would be completed through the comparison of the sub point-intercept survey from 2019 (year before treatment), 2020 (year of treatment) and 2021 (year after treatment). The 2020 survey will allow for an understanding of which species were initially impacted by the treatment. Understanding the EWM population in the year of treatment (2020) is important, however the results of a replication of the survey in 2021 (year after treatment) will allow for a better understanding of the efficacy of the treatment and help to understand whether EWM mortality was achieved rather than the treatment simply injuring the plants and suppressing their growth during the year of treatment.

Figure 6 displays the results of the 2019 aquatic plant subset point-intercept survey results. These data were collected on September 11, 2019 visit to Little Saint Germain Lake. Eurasian watermilfoil was the most frequently encountered species during the survey with a littoral frequency of occurrence of 54.3%. EWM was most prevalent in depths between 12-18 feet in the survey area. A number of native aquatic plant species were documented in the site with coontail (42.2%), southern naiad (34.7%), small pondweed (26.0%) and common waterweed (24.3%) being most common (Figure 6). Impacts to some native aquatic plant species are expected to occur to some degree in association with the proposed treatment, particularly coontail and northern watermilfoil.

A qualitative assessment of the 2020 herbicide treatment would include comparing the 2019 Late-Season EWM Mapping Survey (*year before treatment*)) to the 2020 Late-Season EWM Mapping Survey (*year of treatment*) mapping results. The treatment would be considered successful in meeting the EWM control goals if the *year of treatment* survey indicates little to no EWM present in the targeted areas during the year of treatment. Further, reductions in EWM in the targeted areas would be expected to last into 2021.

Herbicide concentration monitoring may occur following the herbicide treatment. The WDNR is evaluating the results of ProcellaCOR concentration monitoring from various similar projects around the state and will determine whether or not future treatments of this nature warrant this type of monitoring.



Additional aquatic plant monitoring is planned in 2020 through the completion of a whole-lake point-intercept survey as a component of a Lake Protection Grant application. The whole-lake point-intercept survey will be valuable in assessing the lake-wide aquatic plant population and results are compared to previous or future surveys to monitor aquatic plant populations in the lake. The whole-lake point-intercept survey is not used to specifically monitor the active management that may occur in 2020.

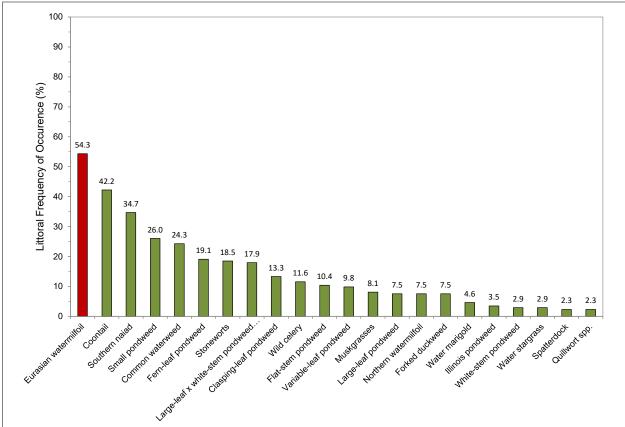
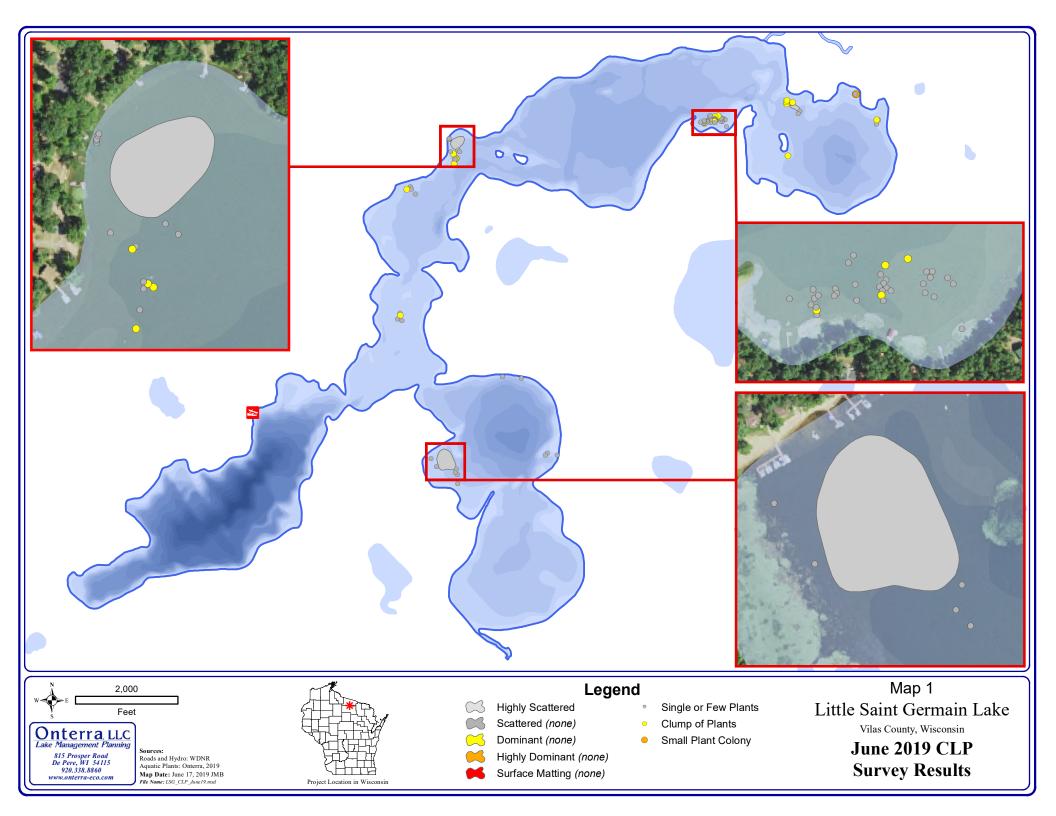


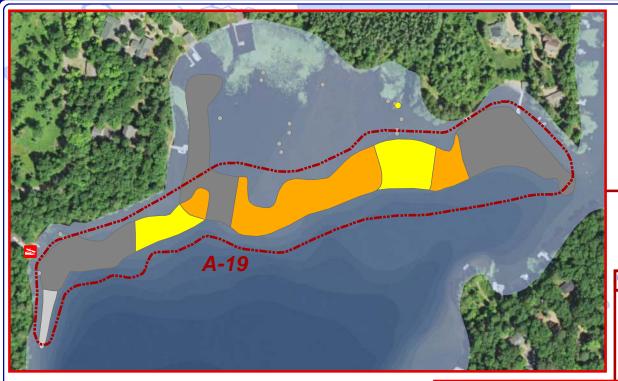
Figure 6. Littoral frequency of occurrence of aquatic plants within sites A-20, C-20, and D-20 in Little Saint Germain Lake. Created using data from Onterra 2019 subset point-intercept survey (n=173).

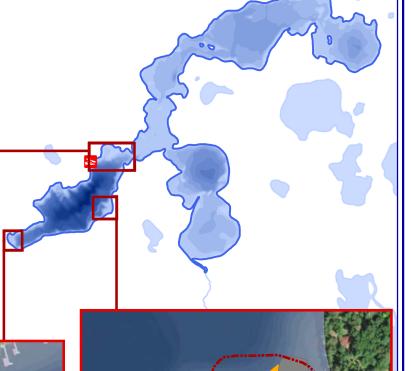
Hand-Harvesting

Based on the EWM management strategy outlined in the management planning project, many areas of the lake could be considered for hand-harvesting actions in 2020. The generally clearer water conditions in West Bay have shown to be more conducive to hand-harvesting methods than other areas of Little Saint Germain Lake. However, any areas in the lake where EWM control is desired, but where herbicide treatments or other control actions are not feasible, may be appropriate for hand-harvesting efforts. The LSGLPRD will prioritize areas of hand-harvesting depending on the overall EWM population, available resources, and strategic location of the EWM populations that meet this criterion.

Over the past several years, the LSGLPRD has gained a greater understanding of the capabilities and limitations of a hand harvesting EWM management strategy and will use this experience in determining a scale-appropriate use for this management technique in Little Saint Germain Lake going forward.

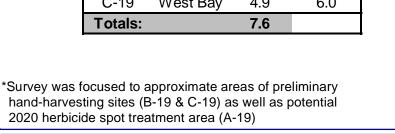


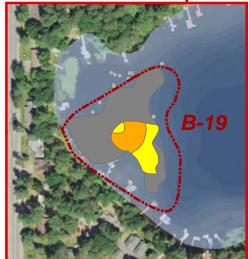


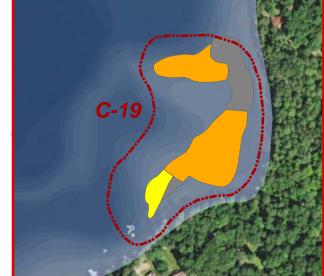


2019 Final EWM Hand-Harvest Areas										
Dive	Diver Assisted Suction Harvest									
			Depth							
Site	Location	(ft)								
B-19	West Bay	2.7	6.0							
C-19	C-19 West Bay 4.9 6.0									
Totala		7.6								

hand-harvesting sites (B-19 & C-19) as well as potential 2020 herbicide spot treatment area (A-19)







Feet

Onterra LLC
Lake Management Planning 815 Prosper Road De Pere, WI 54115 920.338.8860

Roads and Hydro: WDNR Aquatic Plants: Onterra, 2019 Map Date: June 17, 2019 JMB File Name: LSG_EWM_June19.mxd



Highly Scattered

Scattered



Dominant Highly Dominant

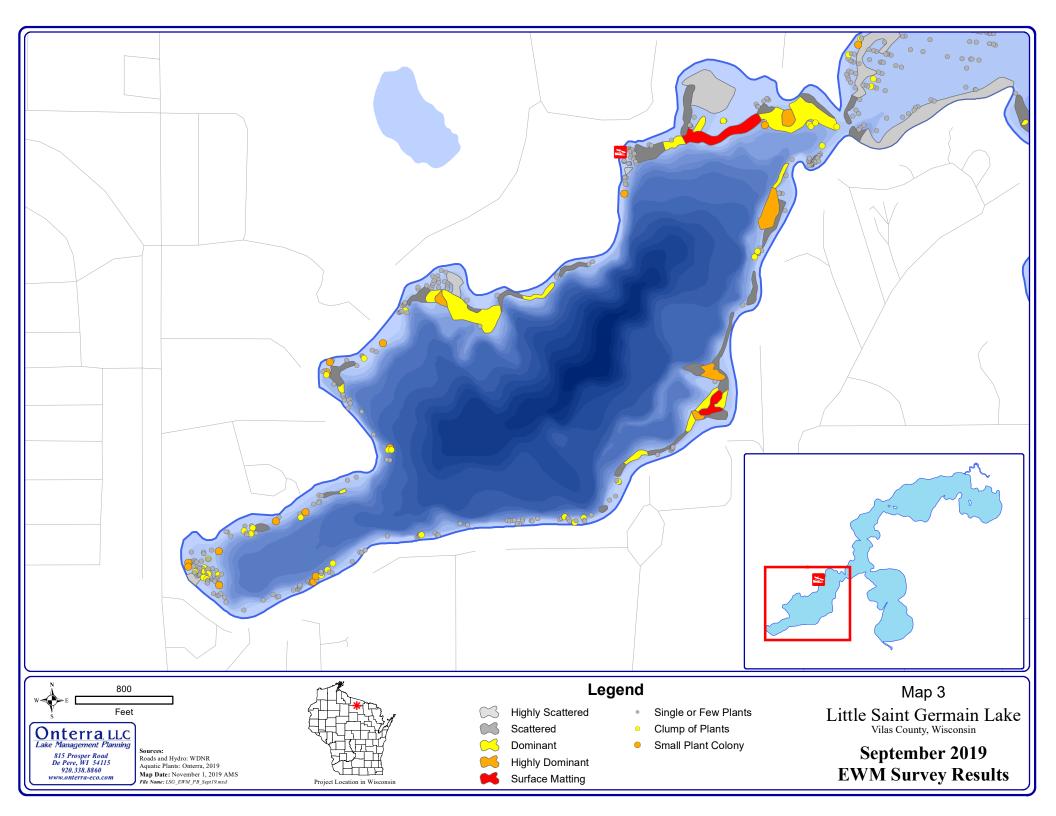
Surface Matting (none)

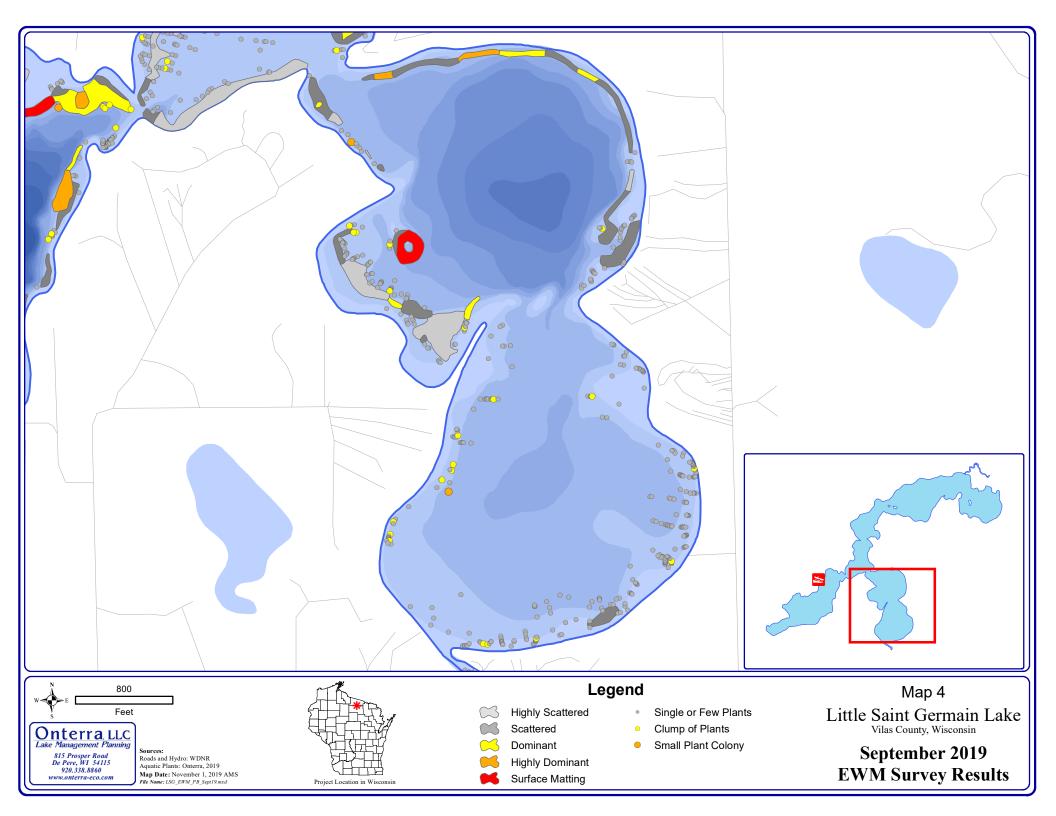
Legend

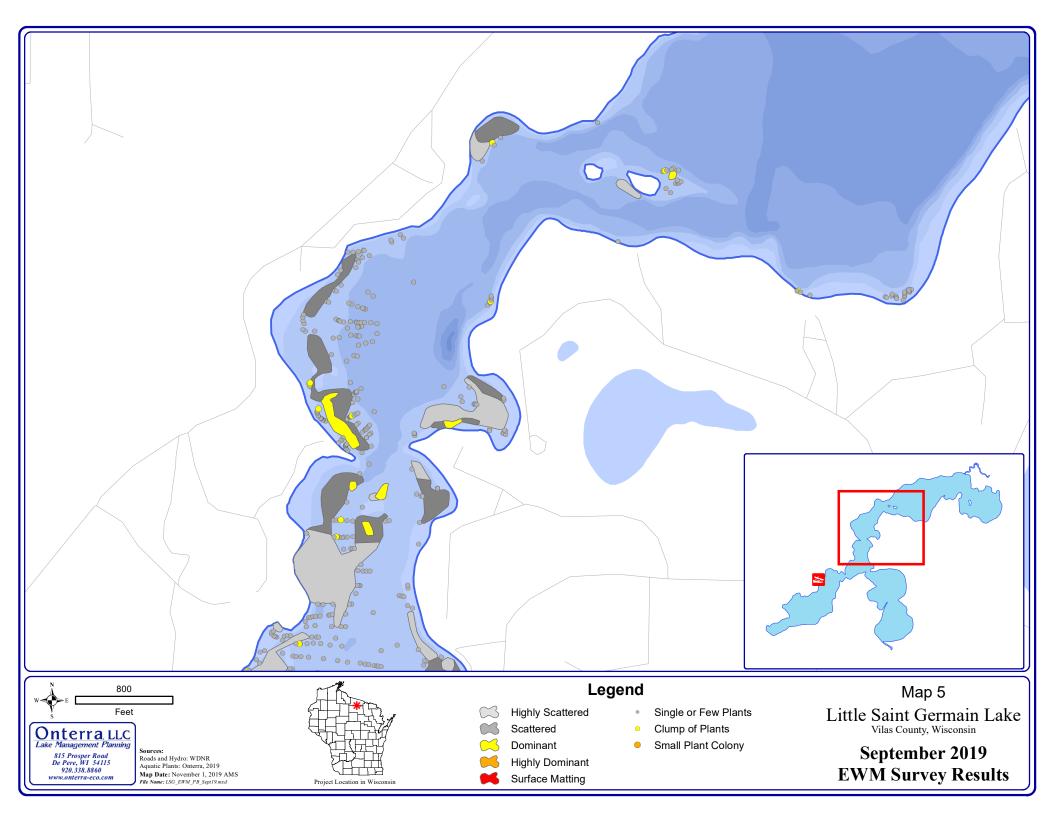
- Single or Few Plants
- Clump of Plants
- Small Plant Colony

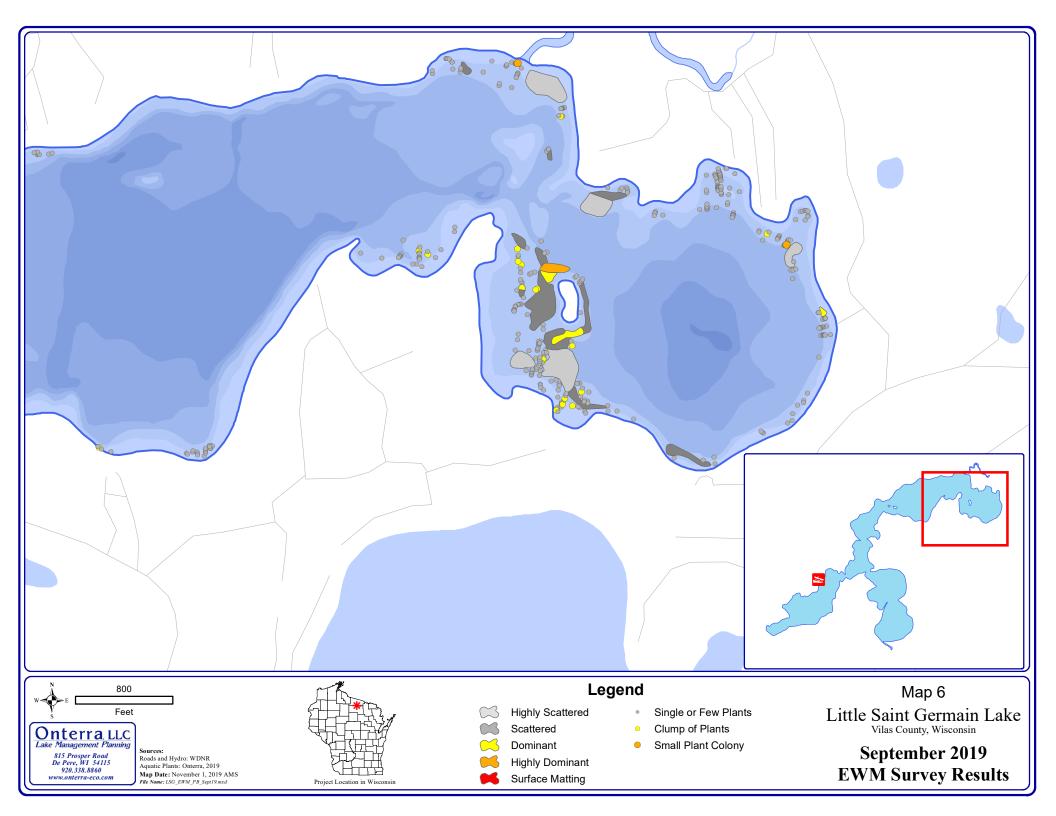
Map 2 Little Saint Germain Lake
Vilas County, Wisconsin

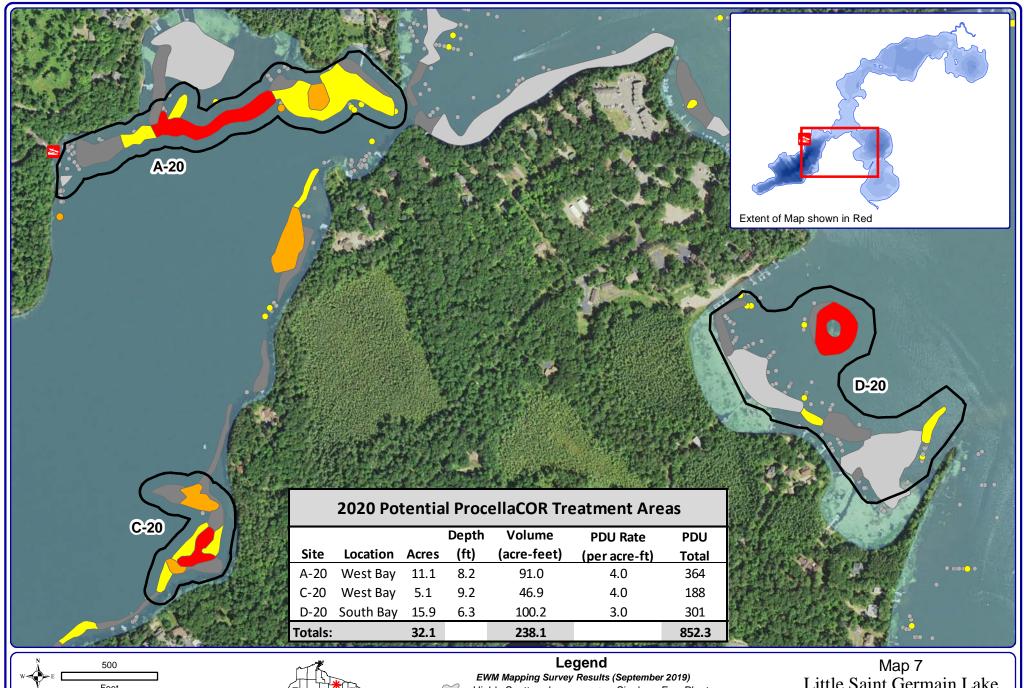
June 2019 EWM Survey Results Focused Areas*





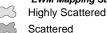












Dominant

Highly Dominant

Surface Matting

- Single or Few Plants
- Clump of Plants
- Small Plant Colony

Preliminary 2020 EWM Treatment Area

Little Saint Germain Lake Vilas County, Wisconsin

Preliminary 2020 EWM Control Strategy v2



APPENDIX A

2019 EWM Hand-Harvesting Report – Aquatic Plant Management, LLC



Little St Germain Lake EWM Treatment Report 2019

PO Box 1134 Minocqua, WI 54548



Little St Germain Lake EWM Treatment Summary 2019

Summary: On June 24th, July 9th, 10th, 11th, 25th, 26th, 29th, 30th and August 2nd, Aquatic Plant Management LLC (APM) conducted Diver Assisted Suction Harvesting (DASH) of Eurasian Watermilfoil (EWM) on Little St Germain Lake in Vilas County, WI. Utilizing maps and GPS coordinates provided by Onterra LLC, the DASH team focused their removal efforts on the highly dominant and scattered plants at site B-19. In total APM was able to remove **448.0 cubic feet of EWM** from Little St Germain Lake.

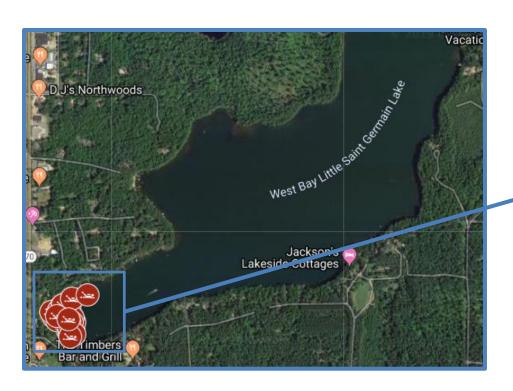
Conditions:

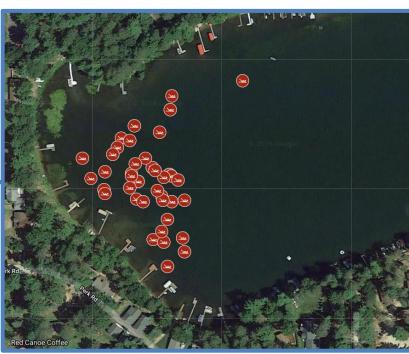
- 6/24/19: Weather was cloudy with an air temperature of 73 degrees; water temperature was 71 degrees with a 9.0 foot clarity reading from the Secchi disk
- 7/9/19: Weather was sunny with an air temperature of 76 degrees; water temperature was 74 degrees with a 9.0 foot clarity reading from the Secchi disk
- 7/10/19: Weather was cloudy with an air temperature of 77 degrees; water temperature was 74 degrees with a 9.5 foot clarity reading from the Secchi disk
- 7/11/19: Weather was sunny with an air temperature of 76 degrees; water temperature was 74 degrees with a 11.5 foot clarity reading from the Secchi disk
- 7/25/19: Weather was sunny with an air temperature of 82 degrees; water temperature was 76 degrees with a 11.5 foot clarity reading from the Secchi disk
- 7/26/19: Weather was cloudy with periods of rain with an air temperature of 73 degrees; water temperature was 76 degrees with a 11.5 foot clarity reading from the Secchi disk
- 7/29/19: Weather was sunny with an air temperature of 77 degrees; water temperature was 76 degrees with a 11.5 foot clarity reading from the Secchi disk
- 7/30/19: Weather was sunny with an air temperature of 78 degrees; water temperature was 76 degrees with a 11.5 foot clarity reading from the Secchi disk
- 8/2/19: Weather was sunny with an air temperature of 82 degrees; water temperature was 76 degrees with a 11.5 foot clarity reading from the Secchi disk

Recommendations: Given proliferation of the EWM population on Little St Germain Lake, targeted DASH efforts at high priority dense locations such as B-19 are effective at reducing the EWM population. Continued monitoring and management efforts are important to prevent proliferation of EWM throughout Little St Germain Lake.



Map of Little St Germain Lake Dive Sites

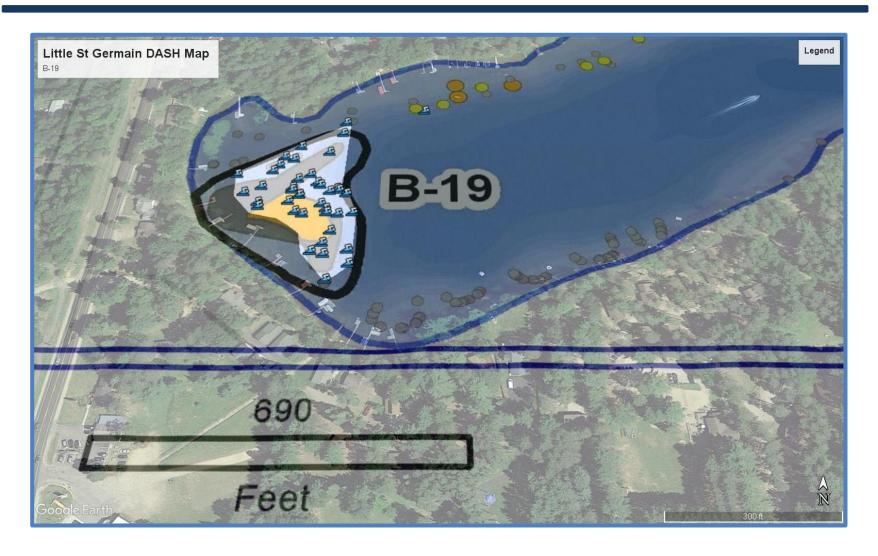








Map of Little St Germain Lake Dive Sites





Detailed Diving Activities

EWM DASH Results:

Date	Dive Location	Latitude	Longitude	Time Under- water	AIS CF Removed	AIS Density	Avg Water Depth	Native By-Catch (CF)	Native Species	Native Density	Substrate Type
6/24/19	B-19	45.90302	-89.48557	2.67	25.0	Medium	5	<0.5	Pondweeds	Medium	Organic/Gravel
6/24/19	B-19	45.90281	-89.48609	2.5	46.5	High	7.5	1.00	None	Medium	Organic/Sand
6/24/19	B-19	45.90207	-89.48544	1.5	19.5	Medium	7	0.50	Pondweeds	High	Organic/Sand
6/24/19	B-19	45.90254	-89.48558	0.75	6.5	Medium	7	0.50	Pondweeds	High	Organic
6/24/19	B-19	45.90254	-89.48558	0.58	6.5	Medium	8	<0.5	Pondweeds	High	Organic
6/24/19	B-19	45.90253	-89.48556	1	22.5	High	8	0.50	Pondweeds	Medium	Organic/Gravel
6/24/19	B-19	45.90253	-89.48556	1.58	7.5	Medium	8	0.50	Pondweeds	Medium	Organic/Gravel
7/9/19	B-19	45.90259	-89.48576	0.92	18.0	High	10	1.50	Pondweeds	Medium	Organic
7/9/19	B-19	45.90252	-89.48564	1.33	33.0	High	10	1.50	Pondweeds	Medium	Organic
7/9/19	B-19	45.90249	-89.48591	1.42	45.0	High	7	1.00	Pondweeds	Medium	Organic
7/9/19	B-19	45.90249	-89.48591	0.75	13.0	High	7	0.50	Pondweeds	Medium	Organic
7/10/19	B-19	45.90235	-89.48542	1.17	14.0	Medium	10	2.00	Chara	High	Organic
7/10/19	B-19	45.90221	-89.48560	0.42	5.0	Medium	10	1.00	Northern Milfoil	High	Organic
7/10/19	B-19	45.90238	-89.48566	1.17	18.0	Medium	10	1.50	Pondweeds	High	Organic
7/10/19	B-19	45.90255	-89.48598	1.33	15.0	Medium	5	1.00	Pondweeds	High	Organic
7/10/19	B-19	45.90253	-89.48598	0.92	12.0	Medium	5.5	1.50	Pondweeds	High	Organic
7/10/19	B-19	45.90257	-89.48573	0.5	9.0	Low	14	<0.5	Pondweeds	High	Organic
Total					316.0						



Detailed Diving Activities

EWM DASH Results:

Date	Dive Location	Latitude	Longitude	Time Under- water	AIS CF Removed	AIS Density	Avg Water Depth	Native By-Catch (CF)	Native Species	Native Density	Substrate Type
7/11/19	B-19	45.90236	-89.48593	1.33	15.0	Medium	6.5	2.00	Pondweeds	High	Organic/Sand
7/11/19	B-19	45.90243	-89.48627	0.5	9.0	Low	5	1.00	Pondweeds	High	Organic/Sand
7/11/19	B-19	45.90244	-89.48600	1	6.0	Low	6	1.00	Pondweeds	High	Organic/Sand
7/11/19	B-19	45.90206	-89.48575	0.92	2.5	Low	5.5	0.50	Pondweeds	High	Organic/Gravel
7/11/19	B-19	45.90204	-89.48564	0.75	2.5	Low	10	0.50	Pondweeds	High	Organic/Sand
7/11/19	B-19	45.90251	-89.48641	1.17	6.0	Low	6.5	1.00	Pondweeds	High	Organic/Sand
7/11/19	B-19	45.9024	-89.48626	1.08	6.0	Low	6.5	1.00	Pondweeds	High	Organic/Sand
7/25/19	B-19	45.90266	-89.48583	1.83	4.5	Medium	10	<0.5	Pondweeds	High	Organic/Sand
7/25/19	B-19	45.90262	-89.48594	1.17	5.0	Low	10	<0.5	Pondweeds	High	Organic/Sand
7/25/19	B-19	45.90234	-89.48586	2.25	4.0	Low	6	<0.5	Pondweeds	High	Organic/Sand
7/25/19	B-19	45.90285	-89.48568	1.67	14.5	Low	13	1.00	Pondweeds	High	Organic/Gravel
7/26/19	B-19	45.90212	-89.48566	1.08	2.0	Low	6	<0.5	Pondweeds	High	Organic/Sand
7/26/19	B-19	45.90266	-89.48650	1.42	5.0	Medium	4.5	0.50	Pondweeds	High	Organic/Sand
7/26/19	B-19	45.90279	-89.48600	1.67	3.0	Low	8.5	1.00	Pondweeds	High	Organic/Sand
7/26/19	B-19	45.90274	-89.48613	1.5	6.5	Low	8.5	1.50	Pondweeds	High	Organic/Sand
7/26/19	B-19	45.90269	-89.48618	1.08	1.5	Low	8.5	<0.5	Pondweeds	High	Organic/Sand
Total					93.0						



Detailed Diving Activities

EWM DASH Results:

Date	Dive Location	Latitude	Longitude	Time Under- water	AIS CF Removed	AIS Density	Avg Water Depth	Native By-Catch (CF)	Native Species	Native Density	Substrate Type
7/29/19	B-19	45.9025	-89.48549	1.5	4.5	Low	14	1.00	Pondweeds	High	Organic
7/29/19	B-19	45.90234	-89.48555	1.25	3.5	Low	16	1.00	Pondweeds	High	Organic
7/29/19	B-19	45.90235	-89.48565	0.67	2.0	Low	10	0.50	Pondweeds	High	Organic
7/29/19	B-19	45.9029	-89.48595	0.92	2.0	Low	10	0.50	Pondweeds	High	Organic
7/29/19	B-19	45.90197	-89.48542	0.58	1.5	Low	8	0.50	Pondweeds	High	Organic
7/29/19	B-19	45.90186	-89.48560	0.58	1.0	Low	5	0.50	Pondweeds	High	Organic
7/30/19	B-19	45.90256	-89.48626	1.5	1.0	Low	8	1.00	Pondweeds	High	Organic
8/2/19	B-19	45.90312	-89.48555	1.25	7.0	Medium	12	0.50	Pondweeds	High	Organic
8/2/19	B-19	45.90323	-89.48480	2.17	13.5	Medium	11	1.50	Chara	High	Organic
8/2/19	B-19	45.90242	-89.48571	0.67	3.0	Medium	11	1.00	Pondweeds	High	Organic
Total					39.0						

B

APPENDIX B

Extracted Relevant Chapters from <u>Strategic Analysis of Aquatic Plant</u> <u>Management in Wisconsin</u> – Final June 2019

The WDNR recently completed a Strategy Analysis which will ultimately mold policies and approaches. The strategy the WDNR is following is outlined on the WDNR's APM Strategic Analysis Webpage:

https://dnr.wi.gov/topic/eia/apmsa.html

Below is a table of contents for the extracted materials for use in risk assessment of the discussed management tools within this project. Please refer to the WDNR's full text document cited above for Literature Cited.

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S.3.4.1. Harvesting: Manual, Mechanical, and DASH

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S.3. Wisconsin's Toolbox for Aquatic Plant Management

Human-caused nutrient addition is the largest threat to water quality in the United States and is a major cause of freshwater impairment worldwide (Parry 1998; Dudgeon et al. 2006). In a watershed, everything flows downstream; fertilizer added to the land moves with runoff water to join the larger surface water drainage network. Wastewater discharged directly into streams also becomes part of the hydrological system. These non-point (runoff) and point (end-of-pipe discharge) pollution sources contribute to increased nutrient levels in freshwater ecosystems. The enrichment of our freshwaters has numerous consequences.

Of relevance for APM is that added nutrients stimulate the growth of aquatic plants and phytoplankton, and in some cases can cause them to grow to high abundance. Decreasing nutrient loads to waterbodies would address the root cause of nuisance algae and plant growth. However, when addressing the ultimate cause of impairment (nutrient loading) is not deemed to be possible (at least in the short-term), it becomes necessary to explore local solutions to temporarily decrease nuisance levels of aquatic plants and phytoplankton.

There are many strategies and tools available to manage aquatic plant communities. Some methods can be selectively applied to a species, while others are non-selectively applied to the larger plant community. The clear majority of aquatic plant and algae management techniques will have effects on non-target elements of the ecosystem. When weighing the decision of whether and how to manage aquatic plant communities, caution is key. It is important to balance the benefit of management with any possible ecological, economic, or social costs. To support informed utilization of the numerous aquatic plant management techniques that are currently available, reviews of the most common techniques and suggestions for appropriate and effective use are included in this Chapter. Lists of susceptible and tolerant plant species are given for many of the management techniques; only species for which control efficacy has been evaluated (in field, mesocosm, or laboratory studies) using each technique are listed. Other species are likely to be tolerant or susceptible to each management technique, for which the effects of each technique have not yet been evaluated. Generally, only plants native to Wisconsin, plants found in states adjacent to Wisconsin, or non-native plants included in ch. NR 40, Wis. Admin. Code, are included in the discussions of species susceptibility and tolerance in this Chapter.

While not discussed in detail in this strategic analysis, other management techniques include:

- Mowing, weed whipping, and scraping (removing sediment or soil along with seeds and rhizomes) in semi-aquatic environments such as some wetlands, along stream banks, and rightof-ways.
- Raking to remove floating or submersed aquatic vegetation.
- Ditch plugs (structures built in drainage ditches to maintain a pre-determined water level in a waterbody for restoration activities).

 Chemical curtains, which are barriers made of semi-impermeable material that may be placed around a targeted treatment area for several days to contain herbicide activity to a specific area (some additional regulatory approvals may be required for deployment of chemical curtains depending on the scenario).

S.3.1. Management Techniques Not Allowed in Wisconsin

Grass carp, triploid grass carp

The use of grass carp (*Ctenopharyngodon idella*) for APM is prohibited in Wisconsin. For more detail, see Supplemental Chapter S.3.5 (Biological Control).

Cutting without Removal

Like mowing a lawn, excess aquatic plant growth can be removed by mechanical harvesting (cutting). Just as some lawn mowers leave cuttings on the grass while others have bagging systems to remove them, aquatic harvesters can be similarly engineered. However, cutting aquatic plants without removing the resulting biomass can cause major impacts on lake biota and water quality (<u>James et al. 2002</u>). As such, cutting plants and leaving the fragments to drift and decay, which releases nutrients, is not permitted in the state of Wisconsin.

S.3.2. Management Techniques for which Permits are Not Issued by Wisconsin DNR's Aquatic Plant Management Program

Sodium Arsenite

Sodium arsenite was used historically for aquatic nuisance plant control, predominantly from the 1920s to the late 1960s. In waterbodies where it was utilized, arsenic can still be detected in the sediment today. Because the compound persists in the environment without breaking down into non-toxic components, the sodium arsenite is no longer used for APM in Wisconsin.

Liming

The application of lime (as $Ca(OH)_2$ or $CaCO_3$) has been used in lake management as a means of addressing acidification in waterbodies, as well as eutrophication to a lesser degree. Like alum treatments (described below), lime can be used to sequester phosphorus, making it less available for uptake by algae and plants. If lime is being used for this purpose, it is regulated under ch. NR 109, Wis. Admin. Code, as a plant inhibitor and a permit is required. Several studies have shown the effects of liming on phosphorus sequestration tend not to persist without repeated treatment, suggesting this approach should not be used as a long-term restoration tool (Reedyk et al. 2001). Laboratory studies have also shown liming to be less effective at reducing phosphorus concentrations than alum (Prepas et al. 2001).

There is little scientific literature related to the use of lime for aquatic plant management. Overapplication of lime can be toxic to aquatic life through alteration of pH, so careful calculation is needed

to maintain pH values within the waterbody's natural range. Studies have shown varying reductions in aquatic plant biomass depending on waterbody characteristics, reductions in chlorophyll *a*, changes in phytoplankton community composition, and increases in turbidity (Prepas et al. 2001; Angeler and Goedkoop 2010). In some Swedish lakes, liming has also been associated with altered food web relationships and decreased fish growth and catch per unit effort (Angeler and Goedkoop 2010; Lau et al. 2017).

"Muck" Removal Products

These products are often bacterial or enzymatic pellets intended to reduce soft sediment or decomposing organic matter on the lake bed. Some sellers suggest they can be used to manage aquatic algae or plants through nutrient digestion by the pellets. There has been little to no reported evaluation of the efficacy and ecological impacts of these products for aquatic plant and algae control, or even the reduction of organic sediments in lakes. If muck removal products are being used as a means of aquatic plant or algae control, or if it is applied as a point-source (i.e., using a pipe or nozzle), a permit is required under ch. NR 107, Wis. Admin. Code and may need U.S. EPA registration.

Weed Rollers

A weed roller is an automated device which uses aluminum or PVC tubes continuously rolling and rotating on a central pivot point to eliminate aquatic vegetation. Because weed rollers rest on the bottom of a waterbody, they are regulated and require a permit from the DNR Waterways and Wetlands Section under <u>s. 30.12 Stats</u>. DNR APM coordinators may review and provide input on applications but are not responsible for approving or denying permits for these types of automated plant removal systems.

Weed rollers have several potential impacts to waterbodies and recreation. They must be placed at an adequate depth so as not to interfere with navigation by passing boats and according to manufacturers, should not be working or plugged in when swimmers are present. Evaluations of weed rollers have found adverse impacts to water quality, macroinvertebrates, fisheries, and potential for erosion by sediment resuspension and removal of plants in the lake littoral zone (Montz 2001; James et al. 2004, 2006). Agitation of plants may also cause fragmentation which can increase plant spread throughout the lake (Smith and Barko 1990).

S.3.3. Herbicide Treatment

Herbicides are the most commonly employed method for controlling aquatic plants in Wisconsin. They are extremely useful tools for accomplishing aquatic plant management (APM) goals, like controlling invasive species, providing waterbody access, and ecosystem restoration. This Chapter includes basic information about herbicides and herbicide formulations, how herbicides are assessed for ecological and human health risks and registered for use, and some important considerations for the use of herbicides in aquatic environments.

A pesticide is a substance used to either directly kill pests or to prevent or reduce pest damage; herbicides are pesticides that are used to kill plants. Only a certain component of a pesticide product is intended to have pesticidal effects and this is called the active ingredient. The active ingredient is listed near the top of the first page on an herbicide product label. Any product claiming to have pesticidal properties must be registered with the U.S. EPA and regulated as a pesticide.

Inert ingredients often make up most of a pesticide formulation and are not intended to have pesticidal activity, although they may enhance the pesticidal activity of the active ingredient. These ingredients, such as carriers and solvents, are often added to the active ingredient by manufacturers, or by an herbicide applicator during use, to allow mixing of the active ingredient into water, make it more chemically stable, or aid in storage and transport. Manufacturers are not required to identify the specific inert ingredients on the pesticide label. In addition to inert ingredients included in manufactured pesticide formulations, adjuvants are inert ingredient products that may be added to pesticide formulations before they are applied to modify the properties or enhance pesticide performance. Adjuvants are typically not intended to have pesticidal properties and are not regulated as pesticides under the Federal Insecticide, Fungicide and Rodenticide Act. However, research has shown that inert ingredients can increase the efficacy and toxicity of pesticides especially if the appropriate label uses aren't followed (Mesnage et al. 2013; Defarge et al. 2016).

The combination of active ingredients and inert ingredients is what makes up a pesticide formulation. There are often many formulations of each active ingredient and pesticide manufacturers typically give a unique product or trade name to each specific formulation of an active ingredient. For instance, "Sculpin G" is a solid, granular 2,4-D amine product, while "DMA IV" is a liquid amine 2,4-D product, and the inert ingredients in these formulations are different, but both have the same active ingredient. Care should always be taken to read the herbicide product label as this will give information about which pests and ecosystems the product is allowed to be used for. Some formulations (i.e., non-aquatic formulations of glyphosate such as "Roundup") are not allowed for aquatic use and could lead to environmental degradation even if used on shorelines near the water. There are some studies which indicate that the combination of two chemicals (e.g., 2,4-D and endothall) applied together produces synergistic efficacy results that are greater than if each product was applied alone (Skogerboe et al. 2012). Conversely, there are studies which indicate that the combination of two chemicals (i.e., diquat and penoxsulam) will result in an antagonistic response between the herbicides, and result in reduced efficacy than when applying penoxsulam alone (Wersal and Madsen 2010b).

The U.S. EPA is responsible for registering pesticide products before they may be sold. To have their product registered, pesticide manufacturers must submit toxicity test data to the EPA that shows that the intended pesticide use(s) will not create unreasonable risks. "Unreasonable" in this context means that the risks of use outweigh the potential benefits. Once registered, the EPA must re-evaluate each pesticide and new information related to its use every 15 years. The current cycle of registration review will end in 2022, with a new cycle and review schedule starting then. In addition, EPA may decide to only register certain uses of any given pesticide product and can also require that only trained personnel can

apply a pesticide before the risks outweigh the benefits. Products requiring training before application are called Restricted Use Pesticides.

As part of their risk assessments, EPA reviews information related to pesticide toxicity. Following laboratory testing, ecotoxicity rankings are given for different organismal groups based on the dosage that would cause harmful ecological effects (e.g., death, reduction in growth, reproductive impairment, and others). For example, the ecotoxicity ranking for 2,4-D ranges from "practically non-toxic" to "slightly toxic" for freshwater invertebrates, meaning tests have shown that doses of >100 ppm and 10-100 ppm are needed to cause 50% mortality or immobilization in the test population, respectively. Different dose ranges and indicators of "harm" are used to assess toxicity depending on the organisms being tested. More information can be found on the EPA's website.

Beyond selecting herbicide formulations approved for use in aquatic environments, there are additional factors to consider supporting appropriate and effective herbicide use in those environments. Herbicide treatments are often used in terrestrial restorations, so they are also often requested in the management and restoration of aquatic plant communities. However, unlike applications in a terrestrial environment, the fluid environment of freshwater systems presents a set of unique challenges. Some general best practices for addressing challenges associated with herbicide dilution, migration, persistence, and non-target impacts are described in Chapter 7.4. More detailed documentation of these challenges is described below and in discussions on individual herbicides in Supplemental Chapter S.3.3 (Herbicide Treatment).

As described in Chapter 7.4, when herbicide is applied to waters, it can quickly migrate offsite and dilute to below the target concentrations needed to provide control (Hoeppel and Westerdal 1983; Madsen et al. 2015; Nault et al. 2015). Successful plant control with herbicide is dependent on concentration exposure time (CET) relationships. In order to examine actual observed CET relationships following herbicide applications in Wisconsin lakes, a study of herbicide CET and Eurasian watermilfoil (Myriophyllum spicatum) control efficacy was conducted on 98 small-scale (0.1-10 acres) 2,4-D treatment areas across 22 lakes. In the vast majority of cases, initial observed 2,4-D concentrations within treatment areas were far below the applied target concentration, and then dropped below detectable limits within a few hours after treatment (Nault et al. 2015). These results indicate the rapid dissipation of herbicide off the small treatment areas resulted in water column concentrations which were much lower than those recommended by previous laboratory CET studies for effective Eurasian watermilfoil control. Concentrations in protected treatment areas (e.g., bays, channels) were initially higher than those in areas more exposed to wind and waves, although concentrations quickly dissipated to below detectable limits within hours after treatment regardless of spatial location. Beyond confining small-scale treatments to protected areas, utilizing or integrating faster-acting herbicides with shorter CET requirements may also help to compensate for reductions in plant control due to dissipation (Madsen et al. 2015). The use of chemical curtains or adjuvants (weighting or sticking agents) may also help to maintain adequate CET, however more research is needed in this area.

This rapid dissipation of herbicide off of treatment areas is important for resource managers to consider in planning, as treating numerous targeted areas at a 'localized' scale may actually result in low-concentrations capable of having lakewide impacts as the herbicide dissipates off of the individual treatment sites. In general, if the percentage of treated areas to overall lake surface area is >5% and targeted areas are treated at relatively high 2,4-D concentrations (e.g., 2.0-4.0 ppm), then anticipated lakewide concentrations after dissipation should be calculated to determine the likelihood of lakewide effects (Nault et al. 2018).

Aquatic-use herbicides are commercially available in both liquid and granular forms. Successful target species control has been reported with both granular and liquid formulations. While there has been a commonly held belief that granular products are able to 'hold' the herbicide on site for longer periods of time, actual field comparisons between granular and liquid 2,4-D forms revealed that they dissipated similarly when applied at small-scale sites (Nault et al. 2015). In fact, liquid 2,4-D had higher initial observed water column concentrations than the granular form, but in the majority of cases concentrations of both forms decreased rapidly to below detection limits within several hours after treatment Nault et al. 2015). Likewise, according to United Phosphorus, Inc. (UPI), the sole manufacturer of endothall, the granular formulation of endothall does not hold the product in a specific area significantly longer than the liquid form (Jacob Meganck [UPI], personal communication).

In addition, the stratification of water and the formation of a thermal density gradient can confine most applied herbicides in the upper, warmer water layer of deep lakes. In some instances, the entire lake water volume is used to calculate how much active ingredient should be applied to achieve a specific lakewide target concentration. However, if the volume of the entire lake is used to calculate application rates for stratified lakes, but the chemical only readily mixes into the upper water layer, the achieved lakewide concentration is likely to be much higher than the target concentration, potentially resulting in unanticipated adverse ecological impacts.

Because herbicides cannot be applied directly to specific submersed target plants, the dissipation of herbicide over the treatment area can lead to direct contact with non-target plants and animals. No herbicide is completely selective (i.e., effective specifically on only a single target species). Some plant species may be more susceptible to a given herbicide than others, highlighting the importance of choosing the appropriate herbicide, or other non-chemical management approach, to minimize potential non-target effects of treatment. There are many herbicides and plant species for which the CET relationship that would negatively affect the plant is unknown. This is particularly important in the case of rare, special concern, or threatened and endangered species. Additionally, loss of habitat following any herbicide treatment or other management technique may cause indirect reductions in populations of invertebrates or other organisms. Some organisms will only recolonize the managed areas as aquatic plants become re-established.

Below are reviews for the most commonly used herbicides for APM in Wisconsin. Much of the information here was pulled directly from DNR's APM factsheets (http://dnr.wi.gov/lakes/plants/factsheets/), which were compiled in 2012 using U.S. EPA herbicide

product labels, U.S. Army Corps of Engineers reports, and communications with natural resource agencies in other northern, lake-rich states. These have been supplemented with more recent information from primary research publications.

Each pesticide has at least one mode of action which is the specific mechanism by which the active ingredient exerts a toxic effect. For example, some herbicides inhibit production of the pigments needed for photosynthesis while others mimic plant growth hormones and cause uncontrolled and unsustainable growth. Herbicides are often classified as either systemic or contact in mode of action, although some herbicides are able to function under various modes of action depending on environmental variables such as water temperature. Systemic pesticides are those that are absorbed by organisms and can be moved or translocated within the organism. Contact pesticides are those that exert toxic effects on the part(s) of an organism that they come in contact with. The amount of exposure time needed to kill an organism is based on the specific mode of action and the concentration of any given pesticide. In the descriptions below herbicides are generally categorized into which environment (above or below water) they are primarily used and a relative assessment of how quickly they impact plants.

Herbicides can be applied in many ways. In lakes, they are usually applied to the water's surface (or below the water's surface) through controlled release by equipment including spreaders, sprayers, and underwater hoses. In wetland environments, spraying by helicopter, backpack sprayer, or application by cut-stem dabbing, wicking, injection, or basal bark application are also used.

S.3.3.1. Submersed or Floating, Relatively Fast-Acting Herbicides

Diquat

Registration and Formulations

Diquat (or diquat dibromide) initially received Federal registration for control of submersed and floating aquatic plants in 1962. It was initially registered with the U.S. EPA in 1986, evaluated for reregistration in 1995, and is currently under registration review. A registration review decision was expected in 2015 but has not been released (EPA Diquat Plan 2011). The active ingredient is 6,7-dihydrodipyrido[1,2- α :2',1'-c] pyrazinediium dibromide, and is commercially sold as liquid formulations for aquatic use.

Mode of Action and Degradation

Diquat is a fast-acting herbicide that works through contact with plant foliage by disrupting electron flow in photosystem I of the photosynthetic reaction, ultimately causing the destruction of cell membranes (Hess 2000; WSSA 2007). Plant tissues in contact with diquat become impacted within several hours after application, and within one to three days the plant tissue will become necrotic. Diquat is considered a non-selective herbicide and will rapidly kill a wide variety of plants on contact. Because diquat is a fast-acting herbicide, it is oftentimes used for managing plants growing in areas where water exchange is anticipated to limit herbicide exposure times, such as small-scale treatments. Due to rapid vegetation decomposition after treatment, only partial treatments of a waterbody should

be conducted to minimize dissolved oxygen depletion and associated negative impacts on fish and other aquatic organisms. Untreated areas can be treated with diquat 14 days after the first application.

Diquat is strongly attracted to silt and clay particles in the water and may not be very effective under highly turbid water conditions or where plants are covered with silt (<u>Clayton and Matheson 2010</u>).

The half-life of diquat in water generally ranges from a few hours to two days depending on water quality and other environmental conditions. Diquat has been detected in the water column from less than a day up towards 38 DAT, and remains in the water column longer when treating waterbodies with sandy sediments with lower organic matter and clay content (Coats et al. 1964; Grzenda et al. 1966; Yeo 1967; Sewell et al. 1970; Langeland and Warner 1986; Langeland et al. 1994; Poovey and Getsinger 2002; Parsons et al. 2007; Gorzerino et al. 2009; Robb et al. 2014). One study reported that diquat is chemically stable within a pH range of 3 to 8 (Florêncio et al. 2004). Due to the tendency of diquat to be rapidly adsorbed to suspended clays and particulates, long exposure periods are oftentimes not possible to achieve in the field. Studies conducted by Wersal et al. (2010a) did not observe differences in target species efficacy between daytime versus night-time applications of diquat. While large-scale diquat treatments are typically not implemented, a study by Parsons et al. (2007), observed declines in both dissolved oxygen and water clarity following the herbicide treatment.

Diquat binds indefinitely to organic matter, allowing it to accumulate and persist in the sediments over time (Frank and Comes 1967; Simsiman and Chesters 1976). It has been reported to have a very long-lived half-life (1000 days) in sediment because of extremely tight soil sorption, as well as an extremely low rate of degradation after association with sediment (Wauchope et al. 1992; Peterson et al. 1994). Both photolysis and microbial degradation are thought to play minor roles in degradation (Smith and Grove 1969; Emmett 2002). Diquat is not known to leach into groundwater due to its very high affinity to bind to soils.

One study reported that combinations of diquat and penoxsulam resulted in an antagonistic response between the herbicides when applied to water hyacinth (*Eichhornia crassipes*) and resulted in reduced efficacy than when applying penoxsulam alone. The antagonistic response is likely due to the rapid cell destruction by diquat that limits the translocation and efficacy of the slower acting enzyme inhibiting herbicides (Wersal and Madsen 2010b).

<u>Toxicology</u>

There are no restrictions on swimming or eating fish from waterbodies treated with diquat. Depending on the concentration applied, there is a 1-3 day waiting period after treatment for drinking water. However, in one study, diquat persisted in the water at levels above the EPA drinking water standard for at least 3 DAT, suggesting that the current 3-day drinking water restriction may not be sufficient under all application scenarios (Parsons et al. 2007). Water treated with diquat should not be used for pet or livestock drinking water for one day following treatment. The irrigation restriction for food crops is five days, and for ornamental plants or lawn/turf, it varies from one to three days depending on the concentration used. A study by Mudge et al. (2007) on the effects of diquat on five popular ornamental

plant species (begonia, dianthus, impatiens, petunia, and snapdragon) found minimal risks associated with irrigating these species with water treated with diquat up to the maximum use rate of 0.37 ppm.

Ethylene dibromide (EDB) is a trace contaminant in diquat products which originates from the manufacturing process. EDB is a documented carcinogen, and the EPA has evaluated the health risk of its presence in formulated diquat products. The maximum level of EDB in diquat dibromide is 0.01 ppm (10 ppb). EBD degrades over time, and it does not persist as an impurity.

Diquat does not have any apparent short-term effects on most aquatic organisms that have been tested at label application rates (EPA Diquat RED 1995). Diquat is not known to bioconcentrate in fish tissues. A study using field scenarios and well as computer modelling to examine the potential ecological risks posed by diquat determined that diquat poses a minimal ecological impact to benthic invertebrates and fish (Campbell et al. 2000). Laboratory studies indicate that walleye (Sander vitreus) are more sensitive to diquat than some other fish species, such as smallmouth bass (Micropterus dolomieu), largemouth bass (Micropterus salmoides), and bluegills (Lepomis macrochirus), with individuals becoming less sensitive with age (Gilderhus 1967; Paul et al. 1994; Shaw and Hamer 1995). Maximum application rates were lowered in response to these studies, such that applying diquat at recommended label rates is not expected to result in toxic effects on fish (EPA Diquat RED 1995). Sublethal effects such as respiratory stress or reduced swimming capacity have been observed in studies where certain fish species (e.g., yellow perch (Perca flavescens), rainbow trout (Oncorhynchus mykiss), and fathead minnows (Pimephales promelas)) have been exposed to diquat concentrations (Bimber et al. 1976; Dodson and Mayfield 1979; de Peyster and Long 1993). Another study showed no observable effects on eastern spiny softshell turtles (Apalone spinifera; Paul and Simonin 2007). Reduced size and pigmentation or increased mortality have been shown in some amphibians but at above recommended label rates (Anderson and Prahlad 1976; Bimber and Mitchell 1978; Dial and Bauer-Dial 1987). Toxicity data on invertebrates are scarce and diquat is considered not toxic to most of them. While diquat is not highly toxic to most invertebrates, significant mortality has been observed in some species at concentrations below the maximum label use rate for diguat, such as the amphipod Hyalella azteca (Wilson and Bond 1969; Williams et al. 1984), water fleas (Daphnia spp.). Reductions in habitat following treatment may also contribute to reductions of Hyalella azteca. For more information, a thorough risk assessment for diquat was compiled by the Washington State Department of Ecology Water Quality Program (WSDE 2002). Available toxicity data for fish, invertebrates, and aquatic plants is summarized in tabular format by Campbell et al. (2000).

Species Susceptibility

Diquat has been shown to control a variety of invasive submerged and floating aquatic plants, including Eurasian watermilfoil (*Myriophyllum spicatum*), curly-leaf pondweed (*Potamogeton crispus*), parrot feather (*Myriophyllum aquaticum*), Brazilian waterweed (*Egeria densa*), water hyacinth, water lettuce (*Pistia stratiotes*), flowering rush (*Butomus umbellatus*), and giant salvinia (*Salvinia molesta*; Netherland et al. 2000; Nelson et al. 2001; Poovey et al. 2002; Langeland et al. 2002; Skogerboe et al. 2006; Martins et al. 2007, 2008; Wersal et al. 2010a; Wersal and Madsen 2010a; Wersal and Madsen 2012; Poovey et

al. 2012; Madsen et al. 2016). Studies conducted on the use of diquat for hydrilla (*Hydrilla verticillata*) and fanwort (*Cabomba caroliniana*) control have resulted in mixed reports of efficacy (*Van et al. 1987*; Langeland et al. 2002; Glomski et al. 2005; Skogerboe et al. 2006; Bultemeier et al. 2009; Turnage et al. 2015). Non-native phragmites (*Phragmites australis* subsp. *australis*) has been shown to not be significantly reduced by diquat (Cheshier et al. 2012).

Skogerboe et al. 2006 reported on the efficacy of diquat (0.185 and 0.37 ppm) under flow-through conditions (observed half-lives of 2.5 and 4.5 hours, respectively). All diquat treatments reduced Eurasian watermilfoil biomass by 97 to 100% compared to the untreated reference, indicating that this species is highly susceptible to diquat. Netherland et al. (2000) examined the role of various water temperatures (10, 12.5, 15, 20, and 25°C) on the efficacy of diquat applications for controlling curly-leaf pondweed. Diquat was applied at rates of 0.16-0.50 ppm, with exposure times of 9-12 hours. Diquat efficacy on curly-leaf pondweed was inhibited as water temperature decreased, although treatments at all temperatures were observed to significantly reduce biomass and turion formation. While the most efficacious curly-leaf pondweed treatments were conducted at 25°C, waiting until water warms to this temperature limits the potential for reducing turion production. Diquat applied at 0.37 ppm (with a 6 to 12-hour exposure time) or at 0.19 ppm (with a 72-hour exposure time) was effective at reducing biomass of flowering rush (Poovey et al. 2012; Madsen et al. 2016).

Native species that have been shown to be affected by diquat include: American lotus (*Nelumbo lutea*), common bladderwort (*Utricularia vulgaris*), coontail (*Ceratophyllum demersum*), common waterweed (*Elodea canadensis*), needle spikerush (*Eleocharis acicularis*), Illinois pondweed (*Potamogeton illinoensis*), leafy pondweed (*P. foliosus*), clasping-leaf pondweed (*P. richardsonii*), fern pondweed (*P. robbinsii*), sago pondweed (*Stuckenia pectinata*), and slender naiad (*Najas flexilis*) (Hofstra et al. 2001; Glomski et al. 2005; Skogerboe et al. 2006; Mudge 2013; Bugbee et al. 2015; Turnage et al. 2015). Diquat is particularly toxic to duckweeds (*Landoltia punctata* and *Lemna* spp.), although certain populations of dotted duckweed (*Landoltia punctata*) have developed resistance of diquat in waterbodies with a long history (20-30 years) of repeated diquat treatments (*Peterson et al. 1997*; Koschnick et al. 2006). Variable effects have been observed for water celery (*Vallisneria americana*), long-leaf pondweed (*Potamogeton nodosus*), and variable-leaf watermilfoil (*Myriophyllum heterophyllum*; Skogerboe et al. 2006; Glomski and Netherland 2007; Mudge 2013).

Flumioxazin

Registration and Formulations

Flumioxazin (2-[7-fluoro-3,4-dihydro-3-oxo-4-(2-propynyl)-2H-1,4-benzoxazin-6-yl]-4,5,6,7-tetrahydro-1H-isoindole-1,3(2H)-dione) was registered with the U.S. EPA for agricultural use in 2001 and registered for aquatic use in 2010. The first registration review of flumioxazin is expected to be completed in 2017 (EPA Flumioxazin Plan 2011). Granular and liquid formulations are available for aquatic use.

Mode of Action and Degradation

The mode of action of flumioxazin is through disruption of the cell membrane by inhibiting protoporphyrinogen oxidase which blocks production of heme and chlorophyll. The efficacy of this mode of action is dependent on both light intensity and water pH (<u>Mudge et al. 2012a</u>; <u>Mudge and Haller 2010</u>; <u>Mudge et al. 2010</u>), with herbicide degradation increasing with pH and efficacy decreasing as light intensity declines.

Flumioxazin is broken down by water (hydrolysis), light (photolysis) and microbes. The half-life ranges from approximately 4 days at pH 5 to 18 minutes at pH 9 (EPA Flumioxazin 2003). In the majority of Wisconsin lakes half-life should be less than 1 day.

Flumioxazin degrades into APF (6-amino-7-fluro-4-(2-propynyl)-1,4,-benzoxazin-3(2H)-one) and THPA (3,4,5,6-tetrahydrophthalic acid). Flumioxazin has a low potential to leach into groundwater due to the very quick hydrolysis and photolysis. APF and THPA have a high potential to leach through soil and could be persistent.

Toxicology

Tests on warm and cold-water fishes indicate that flumioxazin is "slightly to moderately toxic" to fish on an acute basis, with possible effects on larval growth below the maximum label rate of 0.4 ppm (400 ppb). Flumioxazin is moderately to highly toxic to aquatic invertebrates, with possible impacts below the maximum label rate. The potential for bioaccumulation is low since degradation in water is so rapid. The metabolites APF and THPA have not been assessed for toxicity or bioaccumulation.

The risk of acute exposure is primarily to chemical applicators. Concentrated flumioxazin doesn't pose an inhalation risk but can cause skin and eye irritation. Recreational water users would not be exposed to concentrated flumioxazin.

Acute exposure studies show that flumioxazin is "practically non-toxic" to birds and small mammals. Chronic exposure studies indicate that flumioxazin is non-carcinogenic. However, flumioxazin may be an endocrine disrupting compound in mammals (EPA Flumioxazin 2003), as some studies on small mammals did show effects on reproduction and larval development, including reduced offspring viability, cardiac and skeletal malformations, and anemia. It does not bioaccumulate in mammals, with the majority excreted in a week.

Species Susceptibility

The maximum target concentration of flumioxazin is 0.4 ppm (400 ppb). At least one study has shown that flumioxazin (at or below the maximum label rate) will control the invasive species fanwort (*Cabomba caroliniana*), hydrilla (*Hydrilla verticillata*), Japanese stiltgrass (*Microstegium vimineum*), Eurasian watermilfoil (*Myriophyllum spicatum*), water lettuce (*Pistia stratiotes*), curly-leaf pondweed (*Potamogeton crispus*), and giant salvinia (*Salvinia molesta*), while water hyacinth (*Eichhornia crassipes*) and water pennyworts (*Hydrocotyle* spp.) do not show significant impacts (<u>Bultemeier et al. 2009</u>;

Glomski and Netherland 2013a; Glomski and Netherland 2013b; Mudge 2013; Mudge and Netherland 2014; Mudge and Haller 2012; Mudge and Haller 2010). Flowering rush (Butomus umbellatus; submersed form) showed mixed success in herbicide trials (Poovey et al. 2012; Poovey et al. 2013). Native species that were significantly impacted (in at least one study) include coontail (Ceratophyllum demersum), water stargrass (Heteranthera dubia), variable-leaf watermilfoil (Myriophyllum heterophyllum), America lotus (Nelumbo lutea), pond-lilies (Nuphar spp.), white waterlily (Nymphaea odorata), white water crowfoot (Ranunculus aquatilis), and broadleaf cattail (Typha latifolia), while common waterweed (Elodea canadensis), squarestem spikerush (Eleocharis quadrangulate), horsetail (Equisetum hyemale), southern naiad (Najas guadalupensis), pickerelweed (Pontederia cordata), Illinois pondweed (Potamogeton illinoensis), long-leaf pondweed (P. nodosus), broadleaf arrowhead (Sagittaria latifolia), hardstem bulrush (Schoenoplectus acutus), common three-square bulrush (S. pungens), softstem bulrush (S. tabernaemontani), sago pondweed (Stuckenia pectinata), and water celery (Vallisneria americana) were not impacted relative to controls. Other species are likely to be susceptible, for which the effects of flumioxazin have not yet been evaluated.

Carfentrazone-ethyl

Registration and Formulations

Carfentrazone-ethyl is a contact herbicide that was registered with the EPA in 1998. The active ingredient is ethyl 2-chloro-3-[2-chloro-4-fluoro-5-[4-(difluoromethyl)-4,5-diydro-3-methyl-5-oxo-1H-1,2,4-trizol-1-yl)phenyl]propanoate. A liquid formulation of carfentrazone-ethyl is commercially sold for aquatic use.

Mode of Action and Degradation

Carfentrazone-ethyl controls plants through the process of membrane disruption which is initiated by the inhibition of the enzyme protoporphyrinogen oxidase, which interferes with the chlorophyll biosynthetic pathway. The herbicide is absorbed through the foliage of plants, with injury symptoms viable within a few hours after application, and necrosis and death observed in subsequent weeks.

Carfentrazone-ethyl breaks down rapidly in the environment, while its degradates are persistent in aquatic and terrestrial environments. The herbicide primarily degrades via chemical hydrolysis to carfentrazone-chloropropionic acid, which is then further degraded to carfentrazone -cinnamic, - propionic, -benzoic and 3-(hydroxymethyl)-carfentrazone-benzoic acids. Studies have shown that degradation of carfentrazone-ethyl applied to water (pH = 7-9) has a half-life range of 3.4-131 hours, with longer half-lives (>830 hours) documented in waters with lower pH (pH = 5). Extremes in environmental conditions such as temperature and pH may affect the activity of the herbicide, with herbicide symptoms being accelerated under warm conditions.

While low levels of chemical residue may occur in surface and groundwater, risk concerns to non-target organisms are not expected. If applied into water, carfentrazone-ethyl is expected to adsorb to suspended solids and sediment.

Toxicology

There is no restriction on the use of treated water for recreation (e.g., fishing and swimming). Carfentrazone-ethyl should not be applied directly to water within ¼ mile of an active potable water intake. If applied around or within potable water intakes, intakes must be turned off prior to application and remain turned off for a minimum of 24 hours following application; the intake may be turned on prior to 24 hours only if the carfentrazone-ethyl and major degradate level is determined by laboratory analysis to be below 200 ppb. Do not use water treated with carfentrazone-ethyl for irrigation in commercial nurseries or greenhouses. In scenarios where the herbicide is applied to 20% or more of the surface area, treated water should not be used for irrigation of crops until 14 days after treatment, or until the carfentrazone-ethyl and major degradate level is determined by analysis to be below 5 ppb.

In scenarios where the herbicide is applied as a spot treatment to less than 20% of the waterbody surface area, treated water may be used for irrigation by commercial turf farms and on residential turf and ornamentals without restriction. If more than 20% of the waterbody surface area is treated, water should not be used for irrigation of turf or ornamentals until 14 days after treatment, or until the carfentrazone-ethyl and major degradate level is determined by analysis to be below 5 ppb.

Carfentrazone-ethyl is listed as very toxic to certain species of algae and listed as moderately toxic to fish and aquatic animals. Treatment of dense plants beds may result in dissolved oxygen declines from plant decomposition which may lead to fish suffocation or death. To minimize impacts, applications of this herbicide should treat up to a maximum of half of the waterbody at a time and wait a minimum of 14 days before retreatment or treatment of the remaining half of the waterbody. Carfentrazone-ethyl is considered to be practically non-toxic to birds on an acute and sub-acute basis.

Carfentrazone-ethyl is harmful if swallowed and can be absorbed through the skin or inhaled. Those who mix or apply the herbicide need to protect their skin and eyes from contact with the herbicide to minimize irritation and avoid breathing the spray mist. Carfentrazone-ethyl is not carcinogenic, neurotoxic, or mutagenic and is not a developmental or reproductive toxicant.

Species Susceptibility

Carfentrazone-ethyl is used for the control of floating and emergent aquatic plants such as duckweeds (*Lemna* spp.), watermeals (*Wolffia* spp.), water lettuce (*Pistia stratiotes*), water hyacinth (*Eichhornia crassipes*), and salvinia (*Salvinia* spp.). Carfentrazone-ethyl can also be used to control submersed plants such as Eurasian watermilfoil (*Myriophyllum spicatum*).

S.3.3.2. Submersed, Relatively Slow-Acting Herbicides

2,4-D

Registration and Formulations

2,4-D is an herbicide that is widely used as a household weed-killer, agricultural herbicide, and aquatic herbicide. It has been in use since 1946 and was registered with the U.S. EPA in 1986 and evaluated and reregistered in 2005. It is currently being evaluated for reregistration, and the estimated registration review decision date was in 2017 (EPA 2,4-D Plan 2013). The active ingredient is 2,4-dichlorophenoxyacetic acid. There are two types of 2,4-D used as aquatic herbicides: dimethyl amine salt (DMA) and butoxyethyl ester (BEE). The ester formulations are toxic to fish and some important invertebrates such as water fleas (*Daphnia* spp.) and midges at application rates. 2,4-D is commercially sold as a liquid amine as well as ester and amine granular products for control of submerged, emergent, and floating-leaf vegetation. Only 2,4-D products labeled for use in aquatic environments may be used to control aquatic plants.

Mode of Action and Degradation

Although the exact mode of action of 2,4-D is not fully understood, the herbicide is traditionally believed to target broad-leaf dicotyledon species with minimal effects generally observed on numerous monocotyledon species, especially in terrestrial applications (WSSA 2007). 2,4-D is a systemic herbicide which affects plant cell growth and division. Upon application, it mimics the natural plant hormone auxin, resulting in bending and twisting of stems and petioles followed by growth inhibition, chlorosis (reduced coloration) at growing points, and necrosis or death of sensitive species (WSSA 2007). Following treatment, 2,4-D is taken up by the plant and translocated through the roots, stems and leaves, and plants begin to die within one to two weeks after application, but can take several weeks to decompose. The total length of target plant roots can be an important in determining the response of an aquatic plant to 2,4-D (Belgers et al. 2007). Treatments should be made when plants are growing. After treatment, the 2,4-D concentration in the water is reduced primarily through microbial activity, off-site movement by water, or adsorption to small particles in silty water.

Previous studies have indicated that 2,4-D degradation in water is highly variable depending on numerous factors such as microbial presence, temperature, nutrients, light, oxygen, organic content of substrate, pH, and whether or not the water has been previously exposed to 2,4-D or other phenoxyacetic acids (Howard et al. 1991). Once in contact with water, both the ester and amine formulations dissociate to the acid form of 2,4-D, with a faster dissociation to the acid form under more alkaline conditions. 2,4-D degradation products include 1,2,4-benzenetriol, 2,4-dichlorophenol, 2,4-dichlorophenol, 2,4-dichlorophenol, 2,4-dichlorophenol, and volatile organics.

The half-life of 2,4-D has a wide range depending on water conditions. Half-lives have been reported to range from 12.9 to 40 days, while in anaerobic lab conditions the half-life has been measured at 333 days (EPA RED 2,4-D 2005). In large-scale low-concentration 2,4-D treatments monitored across numerous Wisconsin lakes, estimated half-lives ranged from 4-76 days, and the rate of herbicide

degradation was generally observed to be slower in oligotrophic seepage lakes. Of these large-scale 2,4-D treatments, the threshold for irrigation of plants which are not labeled for direct treatment with 2,4-D (<0.1 ppm (100 ppb) by 21 DAT) was exceeded the majority of the treatments (Nault et al. 2018). Previous historical use of 2,4-D may also be an important variable to consider, as microbial communities which are responsible for the breakdown of 2,4-D may potentially exhibit changes in community composition over time with repeated use (de Lipthay et al. 2003; Macur et al. 2007). Additional detailed information on the environmental fate of 2,4-D is compiled by Walters 1999.

There have been some preliminary investigations into the concentration of primarily granular 2,4-D in water-saturated sediments, or pore-water. Initial results suggest the concentration of 2,4-D in the pore-water varies widely from site to site following a chemical treatment, although in some locations the concentration in the pore-water was observed to be 2-3 times greater than the application rate (Jim Kreitlow [DNR], *personal communication*). Further research and additional studies are needed to assess the implications of this finding for target species control and non-target impacts on a variety of organisms.

Toxicology

There are no restrictions on eating fish from treated waterbodies, human drinking water, or pet/livestock drinking water. Based upon 2,4-D ester (BEE) product labels, there is a 24-hour waiting period after treatment for swimming. Before treated water can be used for irrigation, the concentration must be below 0.1 ppm (100 ppb), or at least 21 days must pass. Adverse health effects can be produced by acute and chronic exposure to 2,4-D. Those who mix or apply 2,4-D need to protect their skin and eyes from contact with 2,4-D products to minimize irritation and avoid inhaling the spray. In its consideration of exposure risks, the EPA believes no significant risks will occur to recreational users of water treated with 2,4-D.

There are differences in toxicity of 2,4-D depending on whether the formulation is an amine (DMA) or ester (BEE), with the BEE formulation shown to be more toxic in aquatic environments. BEE formulations are considered toxic to fish and invertebrates such as water fleas and midges at operational application rates. DMA formulations are not considered toxic to fish or invertebrates at operational application rates. Available data indicate 2,4-D does not accumulate at significant levels in the tissues of fish. Although fish exposed to 2,4-D may take up very small amounts of its breakdown products to then be metabolized, the vast majority of these products are rapidly excreted in urine (Ghassemi et al. 1981).

On an acute basis, EPA assessment considers 2,4-D to be "practically non-toxic" to honeybees and tadpoles. Dietary tests (substance administered in the diet for five consecutive days) have shown 2,4-D to be "practically non-toxic" to birds, with some species being more sensitive than others (when 2,4-D was orally and directly administered to birds by capsule or gavage, the substance was "moderately toxic" to some species). For freshwater invertebrates, EPA considers 2,4-D amine to be "practically non-toxic" to "slightly toxic" (EPA RED 2,4-D 2005). Field studies on the potential impact of 2,4-D on benthic macroinvertebrate communities have generally not observed significant changes, although at least one

study conducted in Wisconsin observed negative correlations in macroinvertebrate richness and abundance following treatment, and further studies are likely warranted (<u>Stephenson and Mackie 1986</u>; <u>Siemering et al. 2008</u>; <u>Harrahy et al. 2014</u>). Additionally, sublethal effects such as mouthpart deformities and change in sex ratio have been observed in the midge *Chironomus riparius* (<u>Park et al. 2010</u>).

While there is some published literature available looking at short-term acute exposure of various aquatic organisms to 2,4-D, there is limited literature is available on the effects of low-concentration chronic exposure to commercially available 2,4-D formulations (EPA RED 2,4-D 2005). The department recently funded several projects related to increasing our understanding of the potential impacts of chronic exposure to low-concentrations of 2,4-D through AIS research and development grants. One of these studies observed that fathead minnows (*Pimephales promelas*) exposed under laboratory conditions for 28 days to 0.05 ppm (50 ppb) of two different commercial formulations of 2,4-D (DMA® 4 IVM and Weedestroy® AM40) had decreases in larval survival and tubercle presence in males, suggesting that these formulations may exert some degree of chronic toxicity or endocrine-disruption which has not been previously observed when testing pure compound 2,4-D (DeQuattro and Karasov 2016). However, another follow-up study determined that fathead minnow larval survival (30 days post hatch) was decreased following exposure of eggs and larvae to pure 2,4-D, as well as to the two commercial formulations (DMA® 4 IVM and Weedestroy® AM40), and also identified a critical window of exposure for effects on survival to the period between fertilization and 14 days post hatch (Dehnert et al. 2018).

Another related follow-up laboratory study is currently being conducted to examine the effects of 2,4-D exposure on embryos and larvae of several Wisconsin native fish species. Preliminary results indicate that negative impacts of embryo survival were observed for 4 of the 9 native species tested (e.g., walleye, northern pike, white crappie, and largemouth bass), and negative impacts of larval survival were observed for 4 of 7 natives species tested (e.g., walleye, yellow perch, fathead minnows, and white suckers; Dehnert and Karasov, *in progress*).

A controlled field study was conducted on six northern Wisconsin lakes to understand the potential impacts of early season large-scale, low-dose 2,4-D on fish and zooplankton (Rydell et al. 2018). Three lakes were treated with early season low-dose liquid 2,4-D (lakewide epilimnetic target rate: 0.3 ppm (300 ppb)), while the other three lakes served as reference without treatment. Zooplankton densities were similar within lakes during the pre-treatment year and year of treatment, but different trends in several zooplankton species were observed in treatment lakes during the year following treatment. Peak abundance of larval yellow perch (*Perca flavescens*) was lower in the year following treatment, and while this finding was not statistically significant, decreased larval yellow perch abundance was not observed in reference lakes. The observed declines in larval yellow perch abundance and changes in zooplankton trends within treatment lakes in the year after treatment may be a result of changes in aquatic plant communities and not a direct effect of treatment. No significant effect was observed on peak abundance of larval largemouth bass (*Micropterus salmoides*), minnows, black crappie (*Pomoxis nigromaculatus*), bluegill (*Lepomis macrochirus*), or juvenile yellow perch. Larval black crappie showed

no detectable response in growth or feeding success. Net pen trials for juvenile bluegill indicated no significant difference in survival between treatment and reference trials, indicating that no direct mortality was associated with the herbicide treatments. Detection of the level of larval fish mortality found in the lab studies would not have been possible in the field study given large variability in larval fish abundance among lakes and over time.

Concerns have been raised about exposure to 2,4-D and elevated cancer risk. Some epidemiological studies have found associations between 2,4-D and increased risk of non-Hodgkin lymphoma in high exposure populations, while other studies have shown that increased cancer risk may be caused by other factors (Hoar et al. 1986; Hardell and Eriksson 1999; Goodman et al. 2015). The EPA determined in 2005 that there is not sufficient evidence to classify 2,4-D as a human carcinogen (EPA RED 2,4-D 2005).

Another chronic health concern with 2,4-D is the potential for endocrine disruption. There is some evidence that 2,4-D may have effects on reproductive development, though other studies suggest the findings may have had other causes (<u>Garry et al. 1996</u>; <u>Coady et al. 2013</u>; <u>Goldner et al. 2013</u>; <u>Neal et al. 2017</u>). The extent and implications of this are not clear and it is an area of ongoing research.

Detailed literature reviews of 2,4-D toxicology have been compiled by Garabrant and Philbert (2002), Jervais et al. (2008), and Burns and Swaen (2012).

Species Susceptibility

With appropriate concentration and exposure, 2,4-D is capable of reducing abundance of the invasive plant species Eurasian watermilfoil (*Myriophyllum spicatum*), parrot feather (*M. aquaticum*), water chestnut (*Trapa natans*), water hyacinth (*Eichhornia crassipes*), and water lettuce (*Pistia stratiotes*; Elliston and Steward 1972; Westerdahl et al. 1983; Green and Westerdahl 1990; Helsel et al. 1996, Poovey and Getsinger 2007; Wersal et al. 2010b; Cason and Roost 2011; Robles et al. 2011; Mudge and Netherland 2014). Perennial pepperweed (*Lepidium latifolium*) and fanwort (*Cabomba caroliniana*) have been shown to be somewhat tolerant of 2,4-D (Bultemeier et al. 2009; Whitcraft and Grewell 2012).

Efficacy and selectivity of 2,4-D is a function of concentration and exposure time (CET) relationships, and rates of 0.5-2.0 ppm coupled with exposure times ranging from 12 to 72 hours have been effective at achieving Eurasian watermilfoil control under laboratory settings (<u>Green and Westerdahl 1990</u>). In addition, long exposure times (>14 days) to low-concentrations of 2,4-D (0.1-0.25 ppm) have also been documented to achieve milfoil control (<u>Hall et al. 1982</u>; <u>Glomski and Netherland 2010</u>).

According to product labels, desirable native species that may be affected include native milfoils (*Myriophyllum* spp.), coontail (*Ceratophyllum demersum*), common waterweed (*Elodea canadensis*), naiads (*Najas* spp.), waterlilies (*Nymphaea* spp. and *Nuphar* spp.), bladderworts (*Utricularia* spp.), and duckweeds (*Lemna* spp.). While it may affect softstem bulrush (*Schoenoplectus tabernaemontani*), other species such as American bulrush (*Schoenoplectus americanus*) and muskgrasses (*Chara* spp.) have been shown to be somewhat tolerant of 2,4-D (Miller and Trout 1985; Glomski et al. 2009; Nault et al. 2014;

<u>Nault et al. 2018</u>). Wild rice (*Zizania palustris*) is sensitive to 2,4-D when applied to young, actively growing plants (<u>Nelson et al. 2003</u>).

In large-scale, low-dose (0.073-0.5 ppm) 2,4-D treatments evaluated by Nault et al. (2018), milfoil exhibited statistically significant lakewide decreases in posttreatment frequency across 23 of the 28 (82%) of the treatments monitored. In lakes where year of treatment milfoil control was achieved, the longevity of control ranged from 2-8 years. However, it is important to note that milfoil was not 'eradicated' from any of these lakes and is still present even in those lakes which have sustained very low frequencies over time. While good year of treatment control was achieved in all lakes with pure Eurasian watermilfoil populations, significantly reduced control was observed in most lakes with hybrid watermilfoil (Myriophyllum spicatum x sibiricum) populations. Eurasian watermilfoil control was correlated with the mean concentration of 2,4-D measured during the first two weeks of treatment, with increasing lakewide concentrations resulting in increased Eurasian watermilfoil control. In contrast, there was no significant relationship observed between Eurasian watermilfoil control and mean concentration of 2,4-D. In lakes where good (>60%) year of treatment control of hybrid watermilfoil was achieved, 2,4-D degradation was slow, and measured lakewide concentrations were sustained at >0.1 ppm (>100 ppb) for longer than 31 days. In addition to reduced year of treatment efficacy, the longevity of control was generally shorter in lakes that contained hybrid watermilfoil versus Eurasian watermilfoil, suggesting that hybrid watermilfoil may have the ability to rebound quicker after large-scale treatments than pure Eurasian watermilfoil populations. However, it is important to keep in mind that hybrid watermilfoil is broad term for multiple different strains, and variation in herbicide response and growth between specific genotypes of hybrid watermilfoil has been documented (Taylor et al. 2017).

In addition, the study by Nault et al. (2018) documented several native monocotyledon and dicotyledon species that exhibited significant declines posttreatment. Specifically, northern watermilfoil (*Myriophyllum sibiricum*), slender naiad (*Najas flexilis*), water marigold (*Bidens beckii*), and several thin-leaved pondweeds (*Potamogeton pusillus*, *P. strictifolius*, *P. friesii* and *P. foliosus*) showed highly significant declines in the majority of the lakes monitored. In addition, variable/Illinois pondweed (*P. gramineus*/*P. illinoensis*), flat-stem pondweed (*P. zosteriformis*), fern pondweed (*P. robbinsii*), and sago pondweed (*Stuckenia pectinata*) also declined in many lakes. Ribbon-leaf pondweed (*P. epihydrus*) and water stargrass (*Heteranthera dubia*) declined in the lakes where they were found. Mixed effects of treatment were observed with water celery (*Vallisneria americana*) and southern naiad (*Najas guadalupensis*), with some lakes showing significant declines posttreatment and other lakes showing increases.

Since milfoil hybridity is a relatively new documented phenomenon (<u>Moody and Les 2002</u>), many of the early lab studies examining CET for milfoil control did not determine if they were examining pure Eurasian watermilfoil or hybrid watermilfoil (*M. spicatum* x *sibiricum*) strains. More recent laboratory and mesocosm studies have shown that certain strains of hybrid watermilfoil exhibit more aggressive growth and are less affected by 2,4-D (<u>Glomski and Netherland 2010</u>; <u>LaRue et al. 2013</u>; <u>Netherland and Willey 2017</u>; <u>Taylor et al. 2017</u>), while other studies have not seen differences in overall growth patterns

or treatment efficacy when compared to pure Eurasian watermilfoil (<u>Poovey et al. 2007</u>). Differences between Eurasian and hybrid watermilfoil control following 2,4-D applications have also been documented in the field, with lower efficacy and shorter longevity of hybrid watermilfoil control when compared to pure Eurasian watermilfoil populations (<u>Nault et al. 2018</u>). Field studies conducted in the Menominee River Drainage in northeastern Wisconsin and upper peninsula of Michigan observed hybrid milfoil genotypes more frequently in lakes that had previous 2,4-D treatments, suggesting possible selection of more tolerant hybrid strains over time (<u>LaRue 2012</u>).

Fluridone

Registration and Formulations

Fluridone is an aquatic herbicide that was initially registered with the U.S. EPA in 1986. It is currently being evaluated for reregistration. The estimated registration review decision date was in 2014 (EPA Fluridone Plan 2010). The active ingredient is (1-methyl-3-phenyl-5-[3-(trifluoromethyl) phenyl]-4(1H)-pyridinone). Fluridone is available in both liquid and slow-release granular formulations.

Mode of Action and Degradation

Fluridone's mode of action is to reduce a plant's ability to protect itself from sun damage. The herbicide prevents the plant from making a protective pigment and as a result, sunlight causes the plant's chlorophyll to break down. Treated plants will turn white or pink at the growing tips a week after exposure and will begin to die one to two months after treatment (Madsen et al. 2002). Therefore, fluridone is only effective if plants are actively growing at the time of treatment. Effective use of fluridone requires low, sustained concentrations and a relatively long contact time (e.g., 45-90 days). Due to this requirement, fluridone is usually applied to an entire waterbody or basin. Some success has been demonstrated when additional follow-up 'bump' treatments are used to maintain the low concentrations over a long enough period of time to produce control. Fluridone has also been applied to riverine systems using a drip system to maintain adequate CET.

Following treatment, the amount of fluridone in the water is reduced through dilution and water movement, uptake by plants, adsorption to the sediments, and via breakdown caused by light and microbes. Fluridone is primarily degraded through photolysis (<u>Saunders and Mosier 1983</u>), while depth, water clarity and light penetration can influence degradation rates (<u>Mossler et al. 1989</u>; <u>West et al. 1983</u>). There are two major degradation products from fluridone: n-methyl formamide (NMF) and 3-trifluoromethyl benzoic acid.

The half-life of fluridone can be as short as several hours, or hundreds of days, depending on conditions (West et al. 1979; West et al. 1983; Langeland and Warner 1986; Fox et al. 1991, 1996; Jacob et al. 2016). Preliminary work on a seepage lake in Waushara County, WI detected fluridone in the water nearly 400 days following an initial application that was then augmented to maintain concentrations via a 'bump' treatment at 60 and 100 days later (Onterra 2017a). Light exposure is influential in controlling degradation rate, with a half-life ranging from 15 to 36 hours when exposed to the full spectrum of natural sunlight (Mossler et al. 1989). As light wavelength increases, the half-life increases too,

indicating that season and timing may affect fluridone persistence. Fluridone half-life has been shown to be only slightly dependent on fluridone concentration, oxygen concentration, and pH (Saunders and Mosier 1983). One study found that the half-life of fluridone in water was slightly lower when the herbicide was applied to the surface of the water as opposed to a sub-surface application, suggesting that degradation may also be affected by mode of application (West and Parka 1981).

The persistence of herbicide in the sediment has been reported to be much longer than in the overlying water column, with studies showing persistence ranges from 3 months to a year in sediments (<u>Muir et al. 1980</u>; <u>Muir and Grift 1982</u>; <u>West et al. 1983</u>). Persistence in soil is influenced by soil chemistry (<u>Shea and Weber 1983</u>; <u>Mossler et al. 1993</u>). Fluridone concentrations measured in sediments reach a maximum in one to four weeks after treatment and decline in four months to a year depending on environmental conditions. Fluridone adsorbs to clay and soils with high organic matter, especially in pellet form, and can reduce the concentration of fluridone in the water. Adsorption to the sediments is reversible; fluridone gradually dissipates back into the water where it is subject to chemical breakdown.

Some studies have shown variable release time of the herbicide among different granular fluridone products (Mossler et al. 1993; Koschnick et al. 2003; Bultemeier and Haller 2015). In addition, pelletized formulations may be more effective in sandy hydrosoils, while aqueous suspension formulations may be more appropriate for areas with high amounts of clay or organic matter (Mossler et al. 1993)

Toxicology

Fluridone does not appear to have short-term or long-term effects on fish at approved application rates, but fish exposed to water treated with fluridone do absorb fluridone into their tissues. However, fluridone has demonstrated a very low potential for bioconcentration in fish, zooplankton, and aquatic plants (McCowen et al. 1979; West et al. 1979; Muir et al. 1980; Paul et al. 1994). Fluridone concentrations in fish decrease as the herbicide disappears from the water. Studies on the effects of fluridone on aquatic invertebrates (e.g., midge and water flea) have shown increased mortality at label application rates (Hamelink et al. 1986; Yi et al. 2011). Studies on birds indicate that fluridone would not pose an acute or chronic risk to birds. In addition, no treatment related effects were noted in mice, rats, and dogs exposed to dietary doses. No studies have been published on amphibians or reptiles. There are no restrictions on swimming, eating fish from treated waterbodies, human drinking water or pet/livestock drinking water. Depending on the type of waterbody treated and the type of plant being watered, irrigation restrictions may apply for up to 30 days. There is some evidence that the fluridone degradation product NMF causes birth defects, though NMF has only been detected in the lab and not following actual fluridone treatments in the field, including those at maximum label rate (Osborne et al. 1989; West et al. 1990).

Species Susceptibility

Because fluridone treatments are often applied at a lakewide scale and many plant species are susceptible to fluridone, careful consideration should be given to potential non-target impacts and changes in water quality in response to treatment. Sustained native plant species declines and

reductions in water clarity have been observed following fluridone treatments in field applications (O'Dell et al. 1995; Valley et al. 2006; Wagner et al. 2007; Parsons et al. 2009). However, reductions in water clarity are not always observed and can be avoided (Crowell et al. 2006). Additionally, the selective activity of fluridone is primarily rate-dependent based on analysis of pigments in nine aquatic plant species (Sprecher et al. 1998b).

Fluridone is most often used for control of invasive species such as Eurasian and hybrid watermilfoil (Myriophyllum spicatum x sibiricum), Brazilian waterweed (Egeria densa), and hydrilla (Hydrilla verticillata; Schmitz et al. 1987; MacDonald et al. 1993; Netherland et al. 1993; Netherland and Getsinger 1995a, 1995b; Cockreham and Netherland 2000; Hofstra and Clayton 2001; Madsen et al. 2002; Netherland 2015). However, fluridone tolerance has been observed in some hydrilla and hybrid watermilfoil populations (Michel et al. 2004; Arias et al. 2005; Puri et al. 2006; Slade et al. 2007; Berger et al. 2012, 2015; Thum et al. 2012; Benoit and Les 2013; Netherland and Jones 2015). Fluridone has also been shown to affect flowering rush (Butomus umbellatus), fanwort (Cabomba caroliniana), buttercups (Ranunculus spp.), long-leaf pondweed (Potamogeton nodosus), Illinois pondweed (P. illinoensis), leafy pondweed (P. foliosus), flat-stem pondweed (P. zosteriformis), sago pondweed (Stuckenia pectinata), oxygen-weed (Lagarosiphon major), northern watermilfoil (Myriophyllum sibiricum), variable-leaf watermilfoil (M. heterophyllum), curly-leaf pondweed (Potamogeton crispus), coontail (Ceratophyllum demersum), common waterweed (Elodea canadensis), southern naiad (Najas guadalupensis), slender naiad (N. flexilis), white waterlily (Nymphaea odorata), water marigold (Bidens beckii), duckweed (Lemna spp.), and watermeal (Wolffia columbiana) (Wells et al. 1986; Kay 1991; Farone and McNabb 1993; Netherland et al. 1997; Koschnick et al. 2003; Crowell et al. 2006; Wagner et al. 2007; Parsons et al. 2009; Cheshier et al. 2011; Madsen et al. 2016). Muskgrasses (Chara spp.), water celery (Vallisneria americana), cattails (Typha spp.), and willows (Salix spp.) have been shown to be somewhat tolerant of fluridone (Farone and McNabb 1993; Poovey et al. 2004; Crowell et al. 2006).

Large-scale fluridone treatments that targeted Eurasian and hybrid watermilfoils have been conducted in several Wisconsin lakes. Recently, five of these waterbodies treated with low-dose fluridone (2-4 ppb) have been tracked over time to understand herbicide dissipation and degradation patterns, as well as the efficacy, selectivity, and longevity of these treatments. These field trials resulted in a pre- vs. post-treatment decrease in the number of vegetated littoral zone sampling sites, with a 9-26% decrease observed following treatment (an average decrease in vegetated littoral zone sites of 17.4% across waterbodies). In four of the five waterbodies, substantial decreases in plant biomass (≥10% reductions in average total rake fullness) was documented at sites where plants occurred in both the year of and year after treatment. Good milfoil control was achieved, and long-term monitoring is ongoing to understand the longevity of target species control over time. However, non-target native plant populations were also observed to be negatively impacted in conjunction with these treatments, and long-term monitoring is ongoing to understand their recovery over time. Exposure times in the five waterbodies monitored were found to range from 320 to 539 days before falling below detectable limits. Data from these recent projects is currently being compiled and a compressive analysis and report is anticipated in the near future.

Endothall

Registration and Formulations

Endothall was registered with the U.S. EPA for aquatic use in 1960 and reregistered in 2005 (Menninger 2012). Endothall is the common name of the active ingredient endothal acid (7-oxabicyclo[2,2,1] heptane-2,3-dicarboxylic acid). Granular and liquid formulations are currently registered by EPA and DATCP. Endothall products are used to control a wide range of terrestrial and aquatic plants. Two types of endothall are available: dipotassium salt and dimethylalkylamine salt ("mono-N,N-dimethylalkylamine salt" or "monoamine salt"). The dimethylalkylamine salt form is toxic to fish and other aquatic organisms and is faster-acting than the dipotassium salt form.

Mode of Action and Degradation

Endothall is considered a contact herbicide that inhibits respiration, prevents the production of proteins and lipids, and disrupts the cellular membrane in plants (MacDonald et al. 1993; MacDonald et al. 2001; EPA RED Endothall 2005; Bajsa et al. 2012). Although typical rates of endothall application inhibit plant respiration, higher concentrations have been shown to increase respiration (MacDonald et al. 2001). The mode of action of endothall is unlike any other commercial herbicide. For effective control, endothall should be applied when plants are actively growing, and plants begin to weaken and die within a few days after application.

Uptake of endothall is increased at higher water temperatures and higher amounts of light (<u>Haller and Sutton 1973</u>). Netherland et al. (<u>2000</u>) found that while biomass reduction of curly-leaf pondweed (*Potamogeton crispus*) was greater at higher water temperature, reductions of turion production were much greater when curly-leaf pondweed was treated a lower water temperature (18 °C vs 25 °C).

Degradation of endothall is primarily microbial (Sikka and Saxena 1973) and half-life of the dipotassium salt formulations is between 4 to 10 days (Reinert and Rodgers 1987; Reynolds 1992), although dissipation due to water movement may significantly shorten the effective half-life in some treatment scenarios. Half of the active ingredient from granular endothall formulations has been shown to be released within 1-5 hours under conditions that included water movement (Reinert et al. 1985; Bultemeier and Haller 2015). Endothall is highly water soluble and does not readily adsorb to sediments or lipids (Sprecher et al. 2002; Reinert and Rodgers 1984). Degradation from sunlight or hydrolysis is very low (Sprecher et al. 2002). The degradation rate of endothall has been shown to increase with increasing water temperature (UPI, unpublished data). The degradation rate is also highly variable across aquatic systems and is much slower under anaerobic conditions (Simsiman and Chesters 1975). Relative to other herbicides, endothall is unique in that is comprised of carbon, hydrogen, and oxygen with the addition of potassium and nitrogen in the dipotassium and dimethylalkylamine formulations, respectively. This allows for complete breakdown of the herbicide without additional intermediate breakdown products (Sprecher et al. 2002).

Toxicology

All endothall products have a drinking water standard of 0.1 ppm and cannot be applied within 600 feet of a potable water intake. Use restrictions for dimethylalkylamine salt formulations have additional irrigation and aquatic life restrictions.

Dipotassium salt formulations

At recommended rates, the dipotassium salt formulations appear to have few short-term behavioral or reproductive effects on bluegill (*Lepomis macrochirus*) or largemouth bass (*Micropterus salmoides*; Serns 1977; Bettolli and Clark 1992; Maceina et al. 2008). Bioaccumulation of dipotassium salt formulations by fish from water treated with the herbicide is unlikely, with studies showing less than 1% of endothall being taken up by bluegill (Sikka et al. 1975; Serns 1977). In addition, studies have shown the dipotassium salt formulation induces no significant adverse effects on aquatic invertebrates when used at label application rates (Serns 1975; Williams et al. 1984). A freshwater mussel species was found to be more sensitive to dipotassium salt endothall than other invertebrate species tested, but significant acute toxicity was still only found at concentrations well above the maximum label rate. However, as with other plant control approaches, some aquatic plant-dwelling populations of aquatic organisms may be adversely affected by application of endothall formulations due to habitat loss.

During EPA reregistration of endothall in 2005, it was required that product labels state that lower rates of endothall should be used when treating large areas, "such as coves where reduced water movement will not result in rapid dilution of the herbicide from the target treatment area or when treating entire lakes or ponds."

Dimethylalkylamine salt formulations

In contrast to the respective low to slight toxicity of the dipotassium salt formulations to fish and aquatic invertebrates, laboratory studies have shown the dimethylalkylamine formulations are toxic to fish and macroinvertebrates at concentrations above 0.3 ppm. In particular, the liquid formulation will readily kill fish present in a treatment site. Product labels for the dimethylalkylamine salt formulations recommend no treatment where fish are an important resource.

The dimethylalkylamine formulations are more active on aquatic plants than the dipotassium formulations, but also are 2-3 orders of magnitude more toxic to non-target aquatic organisms (EPA RED Endothall 2005; Keckemet 1969). The 2005 reregistration decision document limits aquatic use of the dimethylalkylamine formulations to algae, Indian swampweed (Hygrophila polysperma), water celery (Vallisneria americana), hydrilla (Hydrilla verticillata), fanwort (Cabomba caroliniana), bur reed (Sparganium sp.), common waterweed (Elodea canadensis), and Brazilian waterweed (Egeria densa). Coontail (Ceratophyllum demersum), watermilfoils (Myriophyllum spp.), naiads (Najas spp.), pondweeds (Potamogeton spp.), water stargrass (Heteranthera dubia), and horned pondweed (Zannichellia palustris) were to be removed from product labels (EPA RED Endothall 2005).

Species Susceptibility

According to the herbicide label, the maximum target concentration of endothall is 5000 ppb (5.0 ppm) acid equivalent (ae). Endothall is used to control a wide range of submersed species, including non-native species such as curly-leaf pondweed and Eurasian watermilfoil (*Myriophyllum spicatum*). The effects of the different formulations of endothall on various species of aquatic plants are discussed below.

Dipotassium salt formulations

At least one mesocosm or lab study has shown that endothall (at or below the maximum label rate) will control the invasive species hydrilla (Netherland et al. 1991; Wells and Clayton 1993; Hofstra and Clayton 2001; Pennington et al. 2001; Skogerboe and Getsinger 2001; Shearer and Nelson 2002; Netherland and Haller 2006; Poovey and Getsinger 2010), oxygen-weed (Lagarosiphon major; Wells and Clayton 1993; Hofstra and Clayton 2001), Eurasian watermilfoil (Netherland et al. 1991; Skogerboe and Getsinger 2002; Mudge and Theel 2011), water lettuce (Pistia stratiotes; Conant et al. 1998), curly-leaf pondweed (Yeo 1970), and giant salvinia (Salvinia molesta; Nelson et al. 2001). Wersal and Madsen (2010a) found that parrot feather (Myriophyllum aquaticum) control with endothall was less than 40% even with two days of exposure time at the maximum label rate. Endothall was shown to control the shoots of flowering rush (Butomus umbellatus), but control of the roots was variable (Poovey et al. 2012; Poovey et al. 2013). One study found that endothall did not significantly affect photosynthesis in fanwort with 6 days of exposure at 2.12 ppm ae (2120 ppb ae; Bultemeier et al. 2009). Large-scale, low-dose endothall treatments were found to reduce curly-leaf pondweed frequency, biomass, and turion production substantially in Minnesota lakes, particularly in the first 2-3 years of treatments (Johnson et al. 2012).

Native species that were significantly impacted (at or below the maximum endothall label rate in at least one mesocosm or lab study) include coontail (Yeo 1970; Hofstra and Clayton 2001; Hofstra et al. 2001; Skogerboe and Getsinger 2002; Wells and Clayton 1993; Mudge 2013), southern naiad (Najas guadalupensis; Yeo 1970; Skogerboe and Getsinger 2001), white waterlily (Nymphaea odorata; Skogerboe and Getsinger 2001), leafy pondweed (Potamogeton foliosus; Yeo 1970), Illinois pondweed (Potamogeton illinoensis; Skogerboe and Getsinger 2001; Shearer and Nelson 2002; Skogerboe and Getsinger 2002; Mudge 2013), long-leaf pondweed (Potamogeton nodosus; Yeo 1970; Skogerboe and Getsinger 2001; Shearer and Nelson 2002; Mudge 2013), small pondweed (P. pusillus; Yeo 1970), broadleaf arrowhead (Sagittaria latifolia; Skogerboe and Getsinger 2001), sago pondweed (Stuckenia pectinata; Yeo 1970; Sprecher et al. 1998a; Skogerboe and Getsinger 2002; Slade et al. 2008), water celery (Vallisneria americana; Skogerboe and Getsinger 2001; Skogerboe and Getsinger 2002; Shearer and Nelson 2002; Mudge 2013), and horned pondweed (Yeo 1970; Gyselinck and Courter 2015).

Species which were not significantly impacted or which recovered quickly include watershield (*Brasenia schreberi*; Skogerboe and Getsinger 2001), muskgrasses (*Chara* spp.; Yeo 1970; Wells and Clayton 1993; Hofstra and Clayton 2001), common waterweed (Yeo 1970; Wells and Clayton 1993; Skogerboe and

Getsinger 2002), water stargrass (Skogerboe and Getsinger 2001), water net (Hydrodictyon reticulatum; Wells and Clayton 1993), the freshwater macroalgae Nitella clavata (Yeo 1970), yellow pond-lily (Nuphar advena; Skogerboe and Getsinger 2002), swamp smartweed (Polygonum hydropiperoides; Skogerboe and Getsinger 2001), pickerelweed (Pontederia cordata; Skogerboe and Getsinger 2001), softstem bulrush (Schoenoplectus tabernaemontani; Skogerboe and Getsinger 2001), and broadleaf cattail (Typha latifolia; Skogerboe and Getsinger 2002).

Field trials mirror the species susceptibility above and in addition show that endothall also can impact several high-value pondweed species (*Potamogeton* spp.), including large-leaf pondweed (*P. amplifolius*; Parsons et al. 2004), fern pondweed (*P. robbinsii*; Onterra 2015; Onterra 2018), white-stem pondweed (*P. praelongus*; Onterra 2018), small pondweed (Big Chetac Chain Lake Association 2016; Onterra 2018), clasping-leaf pondweed (*P. richardsonii*; Onterra 2018), and flat-stem pondweed (*P. zosteriformis*; Onterra 2017b).

Dimethylalkylamine salt formulations

The dimethylalkylamine formulations are more active on aquatic plants than the dipotassium formulations (EPA RED Endothall 2005; Keckemet 1969). At least one mesocosm study has shown that dimethylalkylamine formulation of endothall (at or below the maximum label rate) will control the invasive species fanwort (Hunt et al. 2015) and the native species common waterweed (Mudge et al. 2015), while others have shown that the dipotassium formulation does not control these species well.

Imazamox

Registration and Formulations

Imazamox is the common name of the active ingredient ammonium salt of imazamox (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-(methoxymethl)-3-pyridinecarboxylic acid. It was registered with U.S. EPA in 2008 and is currently under registration review with an estimated registration decision between 2019 and 2020 (EPA Imazamox Plan 2014). In aquatic environments, a liquid formulation is typically applied to submerged vegetation by broadcast spray or underwater hose application and to emergent or floating leaf vegetation by broadcast spray or foliar application. There is also a granular formulation.

Mode of Action and Degradation

Imazamox is a systemic herbicide that moves throughout the plant tissue and prevents plants from producing a necessary enzyme, acetolactate synthase (ALS), which is not found in animals. Susceptible plants will stop growing soon after treatment, but plant death and decomposition will occur over several weeks (Mudge and Netherland 2014). If used as a post-emergence herbicide, imazamox should be applied to plants that are actively growing. Resistance to ALS-inhibiting herbicides has appeared in weeds at a higher rate than other herbicide types in terrestrial environments (Tranel and Wright 2002).

Dissipation studies in lakes indicate a half-life ranging from 4 to 49 days with an average of 17 days. Herbicide breakdown does not occur readily in deep, poorly-oxygenated water where there is no light. In this part of a lake, imazamox will tend to bind to sediments rather than breaking down, with a half-life of approximately 2 years. Once in soil, leaching to groundwater is believed to be very limited. The breakdown products of imazamox are nicotinic acid and di- and tricarboxylic acids. It has been suggested that photolytic break down of imazamox is faster than other herbicides, reducing exposure times. However, short-term imazamox exposures have also been associated with extended regrowth times relative to other herbicides (Netherland 2011).

<u>Toxicology</u>

Treated water may be used immediately following application for fishing, swimming, cooking, bathing, and watering livestock. If water is to be used as potable water or for irrigation, the tolerance is 0.05 ppm (50 ppb), and a 24-hour irrigation restriction may apply depending on the waterbody. None of the breakdown products are herbicidal nor suggest concerns for aquatic organisms or human health.

Most concerns about adverse effects on human health involve applicator exposure. Concentrated imazamox can cause eye and skin irritation and is harmful if inhaled. Applicators should minimize exposure by wearing long-sleeved shirts and pants, rubber gloves, and shoes and socks.

Honeybees are affected at application rates so drift should be minimized during application. Lab tests using rainbow trout (*Oncorhynchus mykiss*), bluegill (*Lepomis macrochirus*), and water fleas (*Daphnia magna*) indicate that imazamox is not toxic to these species at label application rates. Imazamox is rated "practically non-toxic" to fish and aquatic invertebrates and does not bioaccumulate in fish. Additional studies on birds indicate toxicity only at dosages that exceed approved application rates.

In chronic tests, imazamox was not shown to cause tumors, birth defects or reproductive toxicity in test animals. Most studies show no evidence of mutagenicity. Imazamox is not metabolized and was excreted by mammals tested. Based on its low acute toxicity to mammals, and its rapid disappearance from the water column due to light and microbial degradation and binding to soil, imazamox is not considered to pose a risk to recreational water users.

Species Susceptibility

In Wisconsin, imazamox is used for treating non-native emergent vegetation such as non-native phragmites (*Phragmites australis* subsp. *australis*) and flowering rush (*Butomus umbellatus*). Imazamox may also be used to treat the invasive curly-leaf pondweed (*Potamogeton crispus*). Desirable native species that may be affected could include other pondweed species (long-leaf pondweed (*P. nodosus*), flat-stem pondweed (*P. zosteriformis*), leafy pondweed (*P. foliosus*), Illinois pondweed (*P. illinoensis*), small pondweed (*P. pusillus*), variable-leaf pondweed (*P. gramineus*), water-thread pondweed (*P. diversifolius*), perfoliate pondweed (*P. perfoliatus*), large-leaf pondweed (*P. amplifolius*), watershield (*Brasenia schreberi*), and some bladderworts (*Utricularia* spp.). Higher rates of imazamox will control Eurasian watermilfoil (*Myriophyllum spicatum*) but would also have greater non-target impacts on

native plants. Imazamox can also be used during a drawdown to prevent plant regrowth and on emergent vegetation.

At low concentrations, imazamox can cause growth regulation rather than mortality in some plant species. This has been shown for non-native phragmites and hydrilla (*Hydrilla verticillata*; Netherland 2011; Cheshier et al. 2012; Theel et al. 2012). In the case of hydrilla, some have suggested that this effect could be used to maintain habitat complexity while providing some target species control (Theel et al. 2012). Imazamox can reduce biomass of non-native phragmites though some studies found regrowth to occur, suggesting a combination of imazapyr and glyphosate to be more effective (Cheshier et al. 2012; Knezevic et al. 2013).

Some level of control of imazamox has also been reported for water hyacinth (*Eichhornia crassipes*), parrot feather (*Myriophyllum aquaticum*), Japanese stiltgrass (*Microstegium vimineum*), water lettuce (*Pistia stratiotes*), and southern cattail (*Typha domingensis*; Emerine et al. 2010; de Campos et al. 2012; Rodgers and Black 2012; Hall et al. 2014; Mudge and Netherland 2014). Imazamox was observed to have greater efficacy in controlling floating plants than emergents in a study of six aquatic plant species, including water hyacinth, water lettuce, parrot feather, and giant salvinia (*Salvinia molesta*; Emerine et al. 2010). Non-target effects have been observed for softstem bulrush (*Schoenoplectus tabernaemontani*), pickerelweed (*Pontederia cordata*), and the native pondweeds long-leaf pondweed, Illinois pondweed, and coontail (*Ceratophyllum demersum*; Koschnick et al. 2007; Mudge 2013).

Giant salvinia, white waterlily (*Nymphaea odorata*), bog smartweed (*Polygonum setaceum*), giant bulrush (*Schoenoplectus californicus*), water celery (*Vallisneria americana*; though the root biomass of wide-leaf *Vallisneria* may be reduced), and several algal species have been found by multiple studies to be unaffected by imazamox (<u>Netherland et al. 2009</u>; <u>Emerine et al. 2010</u>; <u>Rodgers and Black 2012</u>; <u>Mudge 2013</u>; <u>Mudge and Netherland 2014</u>). Other species are likely to be susceptible, for which the effects of imazamox have not yet been evaluated.

Florpyrauxifen-benzyl

Registration and Formulations

Florpyrauxifen-benzyl is a relatively new herbicide, which was first registered with the U.S. EPA in September 2017. The active ingredient is 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoro-pyridine-2-benzyl ester, also identified as florpyrauxifen-benzyl. Florpyrauxifen-benzyl is used for submerged, floating, and emergent aquatic plant control (e.g., ProcellaCORTM) in slow-moving and quiescent waters, as well as for broad spectrum weed control in rice (*Oryza sativa*) culture systems and other crops (e.g., RinskorTM).

Mode of Action and Degradation

Florpyrauxifen-benzyl is a member of a new class of synthetic auxins, the arylpicolinates, that differ in binding affinity compared to other currently registered synthetic auxins such as 2,4-D and triclopyr (Bell et al. 2015). Florpyrauxifen-benzyl is a systemic herbicide (Heilman et al. 2017).

Laboratory studies and preliminary field dissipation studies indicate that florpyrauxifen-benzyl in water is subject to rapid photolysis (Heilman et al. 2017). In addition, the herbicide can also convert partially via hydrolysis to an acid form at high pH (>9) and higher water temperatures (>25°C), and microbial activity in the water and sediment can also enhance degradation (Heilman et al. 2017). The acid form is noted to have reduced herbicidal activity (Netherland and Richardson 2016; Richardson et al. 2016). Under growth chamber conditions, water samples at 1 DAT found that 44-59% of the applied herbicide had converted to acid form, while sampling at 7 and 14 DAT indicated that all the herbicide had converted to acid form (Netherland and Richardson 2016). The herbicide is short-lived, with half-lives ranging from 4 to 6 days in aerobic aquatic environments, and 2 days in anaerobic aquatic environments (WSDE 2017). Degradation in surface water is accelerated when exposed to sunlight, with a reported photolytic half- life in laboratory testing of 0.07 days (WSDE 2017).

There is some anecdotal evidence that initial water temperature and/or pH may impact the efficacy of florpyrauxifen-benzyl (Beets and Netherland 2018). Florpyrauxifen-benzyl has a high soil adsorption coefficient (KOC) and low volatility, which allows for rapid plant uptake resulting in short exposure time requirements (Heilman et al. 2017). Florpyrauxifen-benzyl degrades quickly (2-15 days) in soil and sediment (Netherland et al. 2016). Few studies have yet been completed for groundwater, but based on known environmental properties, florpyrauxifen-benzyl is not expected to be associated with potential environmental impacts in groundwater (WSDE 2017).

Toxicology

No adverse human health effects were observed in toxicological studies submitted for EPA herbicide registration, regardless of the route of exposure (<u>Heilman et al. 2017</u>). There are no drinking water or recreational use restrictions, including swimming and fishing, and no restrictions on irrigating turf. There is a short waiting period (dependent on application rate) for other non-agricultural irrigation purposes.

Florpyrauxifen-benzyl showed a good environmental profile for use in water, and is "practically non-toxic" to birds, bees, reptiles, amphibians, and mammals (<u>Heilman et al. 2017</u>). No ecotoxicological effects were observed on freshwater mussel or juvenile chinook salmon (<u>Heilman et al. 2017</u>). Florpyrauxifen-benzyl will temporarily bioaccumulate in freshwater organisms but is rapidly depurated and/or metabolized within 1 to 3 days after exposure to high (>150 ppb) concentrations (WSDE 2017).

An LC₅₀ value indicates the concentration of a chemical required to kill 50% of a test population of organisms. LC₅₀ values are commonly used to describe the toxicity of a substance. Label recommendations for milfoils do not exceed 9.65 ppb and the maximum label rate for an acre-foot of water is 48.25 ppb. Acute toxicity results using rainbow trout (*Oncorhynchus mykiss*), fathead minnow (*Pimephales promelas*), and sheepshead minnows (*Cyprinodon variegatus variegatus*) indicated LC₅₀ values of greater than 49 ppb, 41 ppb, and 40 ppb, respectively when exposed to the technical grade active ingredient (<u>WSDE 2017</u>). An LC₅₀ value of greater than 1,900 ppb was reported for common carp (*Cyprinus carpio*) exposed to the ProcellaCOR end-use formulation (<u>WSDE 2017</u>).

Acute toxicity results for the technical grade active ingredient using water flea ($Daphnia\ magna$) and midge ($Chironomus\ sp.$) indicated LC_{50} values of greater than 62 ppb and 60 ppb, respectively ($WSDE\ 2017$). Comparable acute ecotoxicity testing performed on $D.\ magna$ using the ProcellaCOR end-use formulation indicated an LC_{50} value of greater than 8 ppm (80,000 ppb; $WSDE\ 2017$).

The ecotoxicological no observed effect concentration for various organisms as reported by Netherland et al. (2016) are: fish (>515 ppb ai), water flea (*Daphnia* spp.; >21440 ppb ai), freshwater mussels (>1023 ppb ai), saltwater mysid (>362 ppb ai), saltwater oyster (>289 ppb ai), and green algae (>480 ppb ai). Additional details on currently available ecotoxicological information is compiled by WSDE (2017).

Species Susceptibility

Florpyrauxifen-benzyl is a labeled for control of invasive watermilfoils (e.g., Eurasian watermilfoil (*Myriophyllum spicatum*), hybrid watermilfoil (*M. spicatum* x *sibiricum*), parrot feather (*M. aquaticum*)), hydrilla (*Hydrilla verticillata*), and other non-native floating plants such as floating hearts (*Nymphoides* spp.), water hyacinth (*Eichhornia crassipes*), and water chestnut (*Trapa natans*; Netherland and Richardson 2016; Richardson et al. 2016). Natives species listed on the product label as susceptible to florpyrauxifen-benzyl include coontail (*Ceratophyllum demersum*; Heilman et al. 2017), watershield (*Brasenia schreberi*), and American lotus (*Nelumbo lutea*). In laboratory settings, pickerelweed (*Pontederia cordata*) vegetation has also been shown to be affected (Beets and Netherland 2018).

Based on available data, florpyrauxifen-benzyl appears to show few impacts to native aquatic plants such as aquatic grasses, bulrush (*Schoenoplectus* spp.), cattail (*Typha* spp.), pondweeds (*Potamogeton* spp.), naiads (*Najas* spp.), and water celery (*Vallisneria americana*; WSDE 2017). Laboratory and mesocosm studies also found water marigold (*Bidens beckii*), white waterlily (*Nymphaea odorata*), common waterweed (*Elodea canadensis*), water stargrass (*Heteranthera dubia*), long-leaf pondweed (*Potamogeton nodosus*), and Illinois pondweed (*P. illinoensis*) to be relatively less sensitive to florpyrauxifen-benzyl than labeled species (*Netherland et al. 2016*; *Netherland and Richardson 2016*). Non-native fanwort (*Cabomba caroliniana*) was also found to be tolerant in laboratory study (*Richardson et al. 2016*).

Since florpyrauxifen-benzyl is a relatively new approved herbicide, detailed information on field applications is very limited. Trials in small waterbodies have shown control of parrot feather (*Myriophyllum aquaticum*), variable-leaf watermilfoil (*M. heterophyllum*), and yellow floating heart (*Nymphoides peltata*; Heilman et al. 2017).

S.3.3.3. Emergent and Wetland Herbicides

Glyphosate

Registration and Formulations

Glyphosate is a commonly used herbicide that is utilized in both aquatic and terrestrial sites. It was first registered for use in 1974. EPA is currently re-evaluating glyphosate and the registration decision was

expected in 2014 (EPA Glyphosate Plan 2009). The use of glyphosate-based herbicides in aquatic environments that are not approved for aquatic use is very unsafe and is a violation of federal and state pesticide laws. Different formulations of glyphosate are available, including isopropylamine salt of glyphosate and potassium glyphosate.

Glyphosate is effective only on plants that grow above the water and needs to be applied to plants that are actively growing. It will not be effective on plants that are submerged or have most of their foliage underwater, nor will it control regrowth from seed.

Mode of Action and Degradation

Glyphosate is a systemic herbicide that moves throughout the plant tissue and works by inhibiting an important enzyme needed for multiple plant processes, including growth. Following treatment, plants will gradually wilt, appear yellow, and will die in approximately 2 to 7 days. It may take up to 30 days for these effects to become apparent for woody species.

Application should be avoided when heavy rain is predicted within 6 hours. To avoid drift, application is not recommended when winds exceed 5 mph. In addition, excessive speed or pressure during application may allow spray to drift and must be avoided. Effectiveness of glyphosate treatments may be reduced if applied when plants are growing poorly, such as due to drought stress, disease, or insect damage. A surfactant approved for aquatic sites must be mixed with glyphosate before application.

In water, the concentration of glyphosate is reduced through dispersal by water movement, binding to the sediments, and break-down by microorganisms. The half-life of glyphosate is between 3 and 133 days, depending on water conditions. Glyphosate disperses rapidly in water, so dilution occurs quickly, thus moving water will decrease concentration, but not half-life. The primary breakdown product of glyphosate is aminomethylphosphonic acid (AMPA), which is also degraded by microbes in water and soil.

Toxicology

Most aquatic forms of glyphosate have no restrictions on swimming or eating fish from treated waterbodies. However, potable water intakes within ½ mile of application must be turned off for 48 hours after treatment. Different formulations and products containing glyphosate may vary in post-treatment water use restrictions.

Most glyphosate-related health concerns for humans involve applicator exposure, exposure through drift, and the surfactant exposure. Some adverse effects from direct contact with the herbicide include temporary symptoms of dermatitis, eye ailments, headaches, dizziness, and nausea. Protective clothing (goggles, a face shield, chemical resistant gloves, aprons, and footwear) should be worn by applicators to reduce exposure. Recently it has been demonstrated that terrestrial formulations of glyphosate can have toxic effects to human embryonic cells and linked to endocrine disruption (Benachour et al. 2007; Gasnier et al. 2009).

Laboratory testing indicates that glyphosate is toxic to carp (*Cyprinus* spp.), bluegills (*Lepomis macrochirus*), rainbow trout (*Oncorhynchus mykiss*), and water fleas (*Daphnia* spp.) only at dosages well above the label application rates. Similarly, it is rated "practically non-toxic" to other aquatic species tested. Studies by other researchers examining the effects of glyphosate on important food chain organisms such as midge larvae, mayfly nymphs, and scuds have demonstrated a wide margin of safety between application rates.

EPA data suggest that toxicological effects of the AMPA compound are similar to that of glyphosate itself. Glyphosate also contains a nitrosamine (n-nitroso-glyphosate) as a contaminant at levels of 0.1 ppm or less. Tests to determine the potential health risks of nitrosamines are not required by the EPA unless the level exceeds 1.0 ppm.

Species Susceptibility

Glyphosate is only effective on actively growing plants that grow above the water's surface. It can be used to control reed canary grass (*Phalaris arundinacea*), cattails (*Typha* spp.; Linz et al. 1992; Messersmith et al. 1992), purple loosestrife (*Lythrum salicaria*), phragmites (*Phragmites australis* subsp. *australis*; Back and Holomuzki 2008; True et al. 2010; Back et al. 2012; Cheshier et al. 2012), water hyacinth (*Eichhornia crassipes*; Lopez 1993; Jadhav et al. 2008), water lettuce (*Pistia stratiotes*; Mudge and Netherland 2014), water chestnut (*Trapa natans*; Rector et al. 2015), Japanese stiltgrass (*Microstegium vimineum*; Hall et al. 2014), giant reed (*Arundo donax*; Spencer 2014), and perennial pepperweed (*Lepidium latifolium*; Boyer and Burdick 2010). Glyphosate will also reduce abundance of white waterlily (*Nymphaea odorata*) and pond-lilies (*Nuphar* spp.; Riemer and Welker 1974). Purple loosestrife biocontrol beetle (*Galerucella calmariensis*) oviposition and survival have been shown not to be affected by integrated management with glyphosate. Studies have found pickerelweed (*Pontederia cordata*) and floating marsh pennywort (*Hydrocotyle ranunculoides*) to be somewhat tolerant to glyphosate (Newman and Dawson 1999; Gettys and Sutton 2004).

Imazapyr

Registration and Formulations

Imazapyr was registered with the U.S. EPA for aquatic use in 2003 and is currently under registration review. It was estimated to have a registration review decision in 2017 (EPA Imazapyr Plan 2014). The active ingredient is isopropylamine salt of imazapyr (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid). Imazapyr is used for control of emergent and floating-leaf vegetation. It is not recommended for control of submersed vegetation.

Mode of Action and Degradation

Imazapyr is a systemic herbicide that moves throughout the plant tissue and prevents plants from producing a necessary enzyme, acetolactate synthase (ALS), which is not found in animals. Susceptible plants will stop growing soon after treatment and become reddish at the tips of the plant. Plant death and decomposition will occur gradually over several weeks to months. Imazapyr should be applied to

plants that are actively growing. If applied to mature plants, a higher concentration of herbicide and a longer contact time will be required.

Imazapyr is broken down in the water by light and has a half-life ranging from three to five days. Three degradation products are created as imazapyr breaks down: pyridine hydroxy-dicarboxylic acid, pyridine dicarboxylic acid (quinolinic acid), and nicotinic acid. These degradates persist in water for approximately the same amount of time as imazapyr (half-lives of three to eight days). In soils imazapyr is broken down by microbes, rather than light, and persists with a half-life of one to five months (Boyer and Burdick 2010). Imazapyr does not bind to sediments, so leaching through into groundwater is likely.

Toxicology

There are no restrictions on recreational use of treated water, including swimming and eating fish from treated waterbodies. If application occurs within a ½ mile of a drinking water intake, then the intake must be shut off for 48 hours following treatment. There is a 120-day irrigation restriction for treated water, but irrigation can begin sooner if the concentration falls below 0.001 ppm (1 ppb). Imazapyr degradates are no more toxic than imazapyr itself and are excreted faster than imazapyr when ingested.

Concentrated imazapyr has low acute toxicity on the skin or if ingested but is harmful if inhaled and may cause irreversible damage if it gets in the eyes. Applicators should wear chemical-resistant gloves while handling, and persons not involved in application should avoid the treatment area during treatment. Chronic toxicity tests for imazapyr indicate that it is not carcinogenic, mutagenic, or neurotoxic. It also does not cause reproductive or developmental toxicity and is not a suspected endocrine disrupter.

Imazapyr is "practically non-toxic" to fish, invertebrates, birds and mammals. Studies have also shown imazapyr to be "practically non-toxic" to "slightly toxic" to tadpoles and juvenile frogs (<u>Trumbo and Waligora 2009</u>; <u>Yahnke et al. 2013</u>). Toxicity tests have not been published on reptiles. Imazapyr does not bioaccumulate in animal tissues.

Species Susceptibility

The imazapyr herbicide label is listed to control the invasive plants phragmites (*Phragmites australis* subsp. *australis*), purple loosestrife (*Lythrum salicaria*), reed canary grass (*Phalaris arundinacea*), nonnative cattails (*Typha* spp.) and Japanese knotweed (*Fallopia japonica*) in Wisconsin. Native species that are also controlled include cattails (*Typha* spp.), waterlilies (*Nymphaea* sp.), pickerelweed (*Pontederia cordata*), duckweeds (*Lemna* spp.), and arrowhead (*Sagittaria* spp.).

Studies have shown imazapyr to effectively control giant reed (*Arundo donax*), water hyacinth (*Eichhornia crassipes*), manyflower marsh-pennywort (*Hydrocotyle umbellata*); yellow iris (*Iris pseudacorus*), water lettuce (*Pistia stratiotes*), perennial pepperweed (*Lepidium latifolium*), Japanese stiltgrass (*Microstegium vimineum*), parrot feather (*Myriophyllum aquaticum*), and cattails (<u>Boyer and Burdick 2010</u>; <u>True et al. 2010</u>; <u>Back et al. 2012</u>; <u>Cheshier et al. 2012</u>; <u>Whitcraft and Grewell 2012</u>; <u>Hall et al. 2012</u>; <u>Mack et a</u>

<u>al. 2014; Spencer 2014; Cruz et al. 2015; DiTomaso and Kyser 2016</u>). Giant salvinia (*Salvinia molesta*) was found to be imazapyr-tolerant (Nelson et al. 2001).

S.3.3.4. Herbicides Used for Submersed and Emergent Plants

Triclopyr

Registration and Formulations

Triclopyr was initially registered with the U.S. EPA in 1979, reregistered in 1997, and is currently under review with an estimated registration review decision in 2019 (EPA Triclopyr Plan 2014). There are two forms of triclopyr used commercially as herbicides: the triethylamine salt (TEA) and the butoxyethyl ester (BEE). BEE formulations are considered highly toxic to aquatic organisms, with observed lethal effects on fish (Kreutzweiser et al. 1994) as well as avoidance behavior and growth impairment in amphibians (Wojtaszek et al. 2005). The active ingredient triethylamine salt (3,5,6-trichloro-2-pyridinyloxyacetic acid) is the formulation registered for use in aquatic systems. It is sold both in liquid and granular forms for control of submerged, emergent, and floating-leaf vegetation. There is also a liquid premixed formulation that contains triclopyr and 2,4-D, which when combined together are reported to have synergistic impacts. Only triclopyr products labeled for use in aquatic environments may be used to control aquatic plants.

Mode of Action and Degradation

Triclopyr is a systemic plant growth regulator that is believed to selectively act on broadleaf (dicot) and woody plants. Following treatment, triclopyr is taken up through the roots, stems and leaf tissues, plant growth becomes abnormal and twisted, and plants die within one to two weeks after application (Getsinger et al. 2000). Triclopyr is somewhat persistent and can move through soil, although only mobile enough to permeate top soil layers and likely not mobile enough to potentially contaminate groundwater (Lee et al. 1986; Morris et al. 1987; Stephenson et al. 1990).

Triclopyr is broken down rapidly by light (photolysis) and microbes, while hydrolysis is not a significant route of degradation. Triclopyr photodegrades and is further metabolized to carbon dioxide, water, and various organic acids by aquatic organisms (McCall and Gavit 1986). It has been hypothesized that the major mechanism for the removal of triclopyr from the aquatic environment is microbial degradation, though the role of photolysis likely remains important in near-surface and shallow waters (Petty et al. 2001). Degradation of triclopyr by microbial action is slowed in the absence of light (Petty et al. 2003). Triclopyr is very slowly degraded under anaerobic conditions, with a reported half-life (the time it takes for half of the active ingredient to degrade) of about 3.5 years (Laskowski and Bidlack 1984). Another study of triclopyr under aerobic aquatic conditions yielded a half-life of 4.7 months (Woodburn and Cranor 1987). The initial breakdown products of triclopyr are TCP (3,5,6-trichloro-2-pyridinol) and TMP (3,5,6-trichloro-2-methoxypridine).

Several studies reported triclopyr half-lives between 0.5-7.5 days (<u>Woodburn et al. 1993</u>; <u>Getsinger et al. 2000</u>; <u>Petty et al. 2001</u>; <u>Petty et al. 2003</u>). Two large-scale, low-dose treatments were reported to have

longer triclopyr half-lives from 3.7-12.1 days (Netherland and Jones 2015). Triclopyr half-lives have been shown to range from 3.4 days in plants, 2.8-5.8 days in sediment, up to 11 days in fish tissue, and 11.5 days in crayfish (Woodburn et al. 1993; Getsinger et al. 2000; Petty et al. 2003). TMP and TCP may have longer half-lives than triclopyr, with higher levels in bottom-feeding fish and the inedible parts of fish (Getsinger et al. 2000).

Toxicology

Based upon the triclopyr herbicide label, there are no restrictions on swimming, eating fish from treated waterbodies, or pet/livestock drinking water use. Before treated water can be used for irrigation, the concentration must be below 0.001 ppm (1 ppb), or at least 120 days must pass. Treated water should not be used for drinking water until concentrations of triclopyr are less than 0.4 ppm (400 ppb). There is a least one case of direct human ingestion of triclopyr TEA which resulted in metabolic acidosis and coma with cardiovascular impairment (Kyong et al. 2010).

There are substantial differences in toxicity of BEE and TEA, with the BEE shown to be more toxic in aquatic settings. BEE formulations are considered highly toxic to aquatic organisms, with observed lethal effects on fish (Kreutzweiser et al. 1994) as well as avoidance behavior and growth impairment in amphibians (Wojtaszek et al. 2005). Triclopyr TEA is "practically non-toxic" to freshwater fish and invertebrates (Mayes et al. 1984; Gersich et al. 1984). It ranges from "practically non-toxic" to "slightly toxic" to birds (EPA Triclopyr RED 1998). TCP and TMP appear to be slightly more toxic to aquatic organisms than triclopyr; however, the peak concentration of these degradates is low following treatment and depurates from organisms readily, so that they are not believed to pose a concern to aquatic organisms.

Species susceptibility

Triclopyr has been used to control Eurasian watermilfoil (*Myriophyllum spicatum*) and hybrid watermilfoil (*M. spicatum* x *sibiricum*) at both small- and large-scales (<u>Netherland and Getsinger 1992</u>; <u>Getsinger et al. 1997</u>; <u>Poovey et al. 2004</u>; <u>Poovey et al. 2007</u>; <u>Nelson and Shearer 2008</u>; <u>Heilman et al. 2009</u>; <u>Glomski and Netherland 2010</u>; <u>Netherland and Glomski 2014</u>; <u>Netherland and Jones 2015</u>). Getsinger et al. (<u>2000</u>) found that peak triclopyr accumulation was higher in Eurasian watermilfoil than flat-stem pondweed (*Potamogeton zosteriformis*), indicating triclopyr's affinity for Eurasian watermilfoil as a target species.

According to product labels, triclopyr is capable of controlling or affecting many emergent woody plant species, purple loosestrife (*Lythrum salicaria*), phragmites (*Phragmites australis* subsp. *australis*), American lotus (*Nelumbo lutea*), milfoils (*Myriophyllum* spp.), and many others. Triclopyr application has resulted in reduced frequency of occurrence, reduced biomass, or growth regulation for the following species: common waterweed (*Elodea canadensis*), water stargrass (*Heteranthera dubia*), white waterlily (*Nymphaea odorata*), purple loosestrife, Eurasian watermilfoil, parrot feather (*Myriophyllum aquaticum*), variable-leaf watermilfoil (*M. heterophyllum*), watercress (*Nasturtium officinale*), phragmites, flat-stem pondweed (*Potamogeton zosteriformis*), clasping-leaf pondweed (*P. richardsonii*),

stiff pondweed (P. strictifolius), variable-leaf pondweed (P. gramineus), white water crowfoot (Ranunculus aquatilis), sago pondweed (Stuckenia pectinata), softstem bulrush (Schoenoplectus tabernaemontani), hardstem bulrush (S. acutus), water chestnut (Trapa natans), duckweeds (Lemna spp.), and submerged flowering rush (Butomus umbellatus; Cowgill et al. 1989; Gabor et al. 1995; Sprecher and Stewart 1995; Getsinger et al. 2003; Poovey et al. 2004; Hofstra et al. 2006; Poovey and Getsinger 2007; Champion et al. 2008; Derr 2008; Glomski and Nelson 2008; Glomski et al. 2009; True et al. 2010; Cheshier et al. 2012; Netherland and Jones 2015; Madsen et al. 2015; Madsen et al. 2016). Wild rice (Zizania palustris) biomass and height has been shown to decrease significantly following triclopyr application at 2.5 mg/L. Declines were not significant at lower concentrations (0.75 mg/L), though seedlings were more sensitive than young or mature plants (Madsen et al. 2008). American bulrush (Schoenoplectus americanus), spatterdock (Nuphar variegata), fern pondweed (Potamogeton robbinsii), large-leaf pondweed (P. amplifolius), leafy pondweed (P. foliosus), white-stem pondweed (P. praelongus), long-leaf pondweed (P. nodosus), Illinois pondweed (P. illinoensis), and water celery (Vallisneria americana) can be somewhat tolerant of triclopyr applications depending on waterbody characteristics and application rates (Sprecher and Stewart 1995; Glomski et al. 2009; Wersal et al. 2010b; Netherland and Glomski 2014).

Netherland and Jones (2015) evaluated the impact of large-scale, low-dose (~0.1-0.3 ppm) granular triclopyr) applications for control of non-native watermilfoil on several bays of Lake Minnetonka, Minnesota. Near complete loss of milfoil in the treated bays was observed the year of treatment, with increased milfoil frequency reported the following season. However, despite the observed increase in frequency, milfoil biomass remained a minor component of bay-wide biomass (<2%). The number of points with native plants, mean native species per point, and native species richness in the bays were not reduced following treatment. However, reductions in frequency were seen amongst individual species, including northern watermilfoil (*Myriophyllum sibiricum*), water stargrass, common waterweed, and flat-stem pondweed.

Penoxsulam

Registration and Formulations

Penoxsulam (2-(2,2-difluoroethoxy)--6-(trifluoromethyl-N-(5,8-dimethoxy[1,2,4] triazolo[1,5-c]pyrimidin-2-yl))benzenesulfonamide), also referred to as DE-638, XDE-638, XR-638 is a post-emergence, acetolactate synthase (ALS) inhibiting herbicide. It was first registered for use by the U.S. EPA in 2009. It is liquid in formulation and used for large-scale control of submerged, emergent, and floating-leaf vegetation. Information presented here can be found in the EPA pesticide fact sheet (EPA Penoxsulam 2004).

Mode of Action and Degradation

Penoxsulam is a slow-acting herbicide that is absorbed by above- and below-ground plant tissue and translocated throughout the plant. Penoxsulam interferes with plant growth by inhibiting the AHAS/ALS

enzyme which in turn inhibits the production of important amino acids (<u>Tranel and Wright 2002</u>). Plant injury or death usually occurs between 2 and 4 weeks following application.

Penoxsulam is highly mobile but not persistent in either aquatic or terrestrial settings. However, the degradation process is complex. Two degradation pathways have been identified that result in at least 13 degradation products that persist for far longer than the original chemical. Both microbial- and photo-degradation are likely important means by which the herbicide is removed from the environment (Monika et al. 2017). It is relatively stable in water alone without sunlight, which means it may persist in light-limited areas.

The half-life for penoxsulam is between 12 and 38 days. Penoxsulam must remain in contact with plants for around 60 days. Thus, supplemental applications following initial treatment may be required to maintain adequate concentration exposure time (CET). Due to the long CET requirement, penoxsulam is likely best suited to large-scale or whole-lake applications.

Toxicology

Penoxsulam is unlikely to be toxic to animals but may be "slightly toxic" to birds that consume it. Human health studies have not revealed evidence of acute or chronic toxicity, though some indication of endocrine disruption deserves further study. However, screening-level assessments of risk have not been conducted on the major degradates which may have unknown non-target effects. Penoxsulam itself is unlikely to bioaccumulate in fish.

Species Susceptibility

Penoxsulam is used to control monocot and dicot plant species in aquatic and terrestrial environments. The herbicide is often applied at low concentrations of 0.002-0.02 ppm (2-20 ppb), but as a result long exposure times are usually required for effective target species control (Cheshier et al. 2011; Mudge et al. 2012b). For aquatic plant management applications, penoxsulam is most commonly utilized for control of hydrilla (*Hydrilla verticillata*). It has also been used for control of giant salvinia (*Salvinia molesta*), water hyacinth (*Eichhornia crassipes*), and water lettuce (*Pistia stratiotes*; Richardson and Gardner 2007; Mudge and Netherland 2014). However, the herbicide is only semi-selective; it has been implicated in injury to non-target emergent native species, including arrowheads (*Sagittaria* spp.) and spikerushes (*Eleocharis* spp.) and free-floating species like duckweed (Mudge and Netherland 2014; Cheshier et al. 2011). Penoxsulam can also be used to control milfoils such as Eurasian watermilfoil (*Myriophyllum spicatum*) and variable-leaf watermilfoil (*M. heterophyllum*; Glomski and Netherland 2008). Seedling emergence as well as vegetative vigor is impaired by penoxsulam in both dicots and monocots, so buffer zone and dissipation reduction strategies may be necessary to avoid non-target impacts (EPA Penoxsulam 2004).

When used to treat salvinia, the herbicide was found to have effects lasting 10 weeks following treatment (<u>Mudge et al. 2012b</u>). The herbicide is effective at low doses and while low-concentration applications of slow-acting herbicides often result in temporary growth regulation and stunting, plants

are likely to recover following treatment. Thus, complementary management strategies should be employed to discourage early regrowth (Mudge et al. 2012b). In particular, joint biological and herbicidal control with penoxsulam has shown good control of water hyacinth (Moran 2012). Alternately, a low concentration may be maintained over time by repeated low-dose applications. Studies show that maintaining a low concentration for at least 8-12 weeks provided excellent control of salvinia, and that a low dose followed by a high-dose application was even more efficacious (Mudge et al. 2012b).

S.3.4. Physical Removal Techniques

There are several management options which involve physical removal of aquatic plants, either by manual or mechanical means. Some of these include manual and mechanical cutting and hand-pulling or Diver-Assisted Suction Harvesting (DASH).

S.3.4.1. Manual and Mechanical Cutting

Manual and mechanical cutting involve slicing off a portion of the target plants and removing the cut portion from the waterbody. In addition to actively removing parts of the target plants, destruction of vegetative material may help prevent further plant growth by decreasing photosynthetic uptake, and preventing the formation of rhizomes, tubers, and other growth types (<u>Dall Armellina et al. 1996a</u>, <u>1996b</u>; <u>Fox et al. 2002</u>). These approaches can be quick to allow recreational use of a waterbody but because the plant is still established and will continue to grow from where it was cut, it often serves to provide short-term relief (<u>Bickel and Closs 2009</u>; <u>Crowell et al. 1994</u>). A synthesis of numerous historical mechanical harvesting studies is compiled by <u>Breck et al. 1979</u>.

The amount of time for macrophytes to return to pre-cutting levels can vary between waterbodies and with the dominant plant species present (Kaenel et al. 1998). Some studies have suggested that annual or biannual cutting of Eurasian watermilfoil (Myriophyllum spicatum) may be needed, while others have shown biomass can remain low the year after cutting (Kimbel and Carpenter 1981; Painter 1988; Barton et al. 2013). Hydrilla (Hydrilla verticillata) has been shown to recover beyond pre-harvest levels within weeks in some cases (Serafy et al. 1994). In deeper waters, greater cutting depth may lead to increased persistence of vegetative control (Unmuth et al. 1998; Barton et al. 2013). Higher frequency of cutting, rather than the amount of plant that is cut, can result in larger reductions to propagules such as turions (Fox et al. 2002).

The timing of cutting operations, as for other management approaches, is important. For species dependent on vegetative propagules, control methods should be taken before the propagules are formed. However, for species with rhizomes, cutting too early in the season merely postpones growth while later-season cutting can better reduce plant abundance (Dall Armellina et al. 1996a, 1996b). Eurasian watermilfoil regrowth may be slower if cutting is conducted later in the summer (June or later). Cutting in the fall, rather than spring or summer, may result in the lowest amount of Eurasian watermilfoil regrowth the year after management (Kimbel and Carpenter 1981). However, managing early in the growing season may reduce non-target impacts to native plant populations when early-

are likely to recover following treatment. Thus, complementary management strategies should be employed to discourage early regrowth (Mudge et al. 2012b). In particular, joint biological and herbicidal control with penoxsulam has shown good control of water hyacinth (Moran 2012). Alternately, a low concentration may be maintained over time by repeated low-dose applications. Studies show that maintaining a low concentration for at least 8-12 weeks provided excellent control of salvinia, and that a low dose followed by a high-dose application was even more efficacious (Mudge et al. 2012b).

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The timing of cutting operations, as for other management approaches, is important. For species dependent on vegetative propagules, control methods should be taken before the propagules are formed. However, for species with rhizomes, cutting too early in the season merely postpones growth while later-season cutting can better reduce plant abundance (Dall Armellina et al. 1996a, 1996b). Eurasian watermilfoil regrowth may be slower if cutting is conducted later in the summer (June or later). Cutting in the fall, rather than spring or summer, may result in the lowest amount of Eurasian watermilfoil regrowth the year after management (Kimbel and Carpenter 1981). However, managing early in the growing season may reduce non-target impacts to native plant populations when early-

growing non-native plants are the dominant targets (<u>Nichols and Shaw 1986</u>). Depending on regrowth rate and management goals, multiple harvests per growing season may be necessary (<u>Rawls 1975</u>).

Vegetative fragments which are not collected after cutting can produce new localized populations, potentially leading to higher plant densities (<u>Dall Armellina et al. 1996a</u>). Eurasian watermilfoil and common waterweed (*Elodea canadensis*) biomass can be reduced by cutting (<u>Abernethy et al. 1996</u>), though Eurasian watermilfoil can maintain its growth rate following cutting by developing a moredensely branched form (<u>Rawls 1975</u>; <u>Mony et al. 2011</u>). Cutting and physical removal tend to be less expensive but require more effort than benthic barriers, so these approaches may be best used for small infestations or where non-native and native species inhabit the same stand (<u>Bailey and Calhoun 2008</u>).

Ecological Impacts of Manual and Mechanical Cutting

Plants accrue nutrients into their tissues, and thus plant removal may also remove nutrients from waterbodies (Boyd 1970), though this nutrient removal may not be significant among all lake types. Cutting and harvesting of aquatic plants can lead to declines in fish as well as beneficial zooplankton, macroinvertebrate, and native plant and mussel populations (Garner et al. 1996; Aldridge 2000; Torn et al. 2010; Barton et al. 2013). Many studies suggest leaving some vegetated areas undisturbed to reduce negative effects of cutting on fish and other aquatic organisms (Swales 1982; Garner et al. 1996; Unmuth et al. 1998; Aldridge 2000; Greer et al. 2012). Recovery of these populations to cutting in the long-term is understudied and poorly understood (Barton et al. 2013). Effects on water quality can be minimal but nutrient cycling may be affected in wetland systems (Dall Armellina et al. 1996a; Martin et al. 2003). Cutting can also increase algal production, and turbidity temporarily if sediments are disturbed (Wile 1978; Bailey and Calhoun 2008).

Some changes to macroinvertebrate community composition can occur as a result of cutting (Monahan and Caffrey 1996; Bickel and Closs 2009). Studies have also shown 12-85% reductions in macroinvertebrates following cutting operations in flowing systems (Dawson et al. 1991; Kaenel et al. 1998). Macroinvertebrate communities may not rebound to pre-management levels for 4-6 months and species dependent on aquatic plants as habitat (such as simuliids and chironomids) are likely to be most affected. Reserving cutting operations for summer, rather than spring, may reduce impacts to macroinvertebrate communities (Kaenel et al. 1998).

Mechanical harvesting can also incidentally remove fish and turtles inhabiting the vegetation and lead to shifts in aquatic plant community composition (Engel 1990; Booms 1999). Studies have shown mechanical harvesting can remove between 2%-32% of the fish community by fish number, with juvenile game fish and smaller species being the primary species removed (Haller et al. 1980; Mikol 1985). Haller et al. (1980) estimated a 32% reduction in the fish community at a value of \$6000/hectare. However, fish numbers rebounded to similar levels as an unmanaged area within 43 days after harvesting in the Potomac River in Maryland (Serafy et al. 1994). In addition to direct impacts to fish populations, reductions in fish growth rates may correspond with declines in zooplankton populations in response to cutting (Garner et al. 1996).

S.3.4.2. Hand Pulling and Diver-Assisted Suction Harvesting (DASH)

Hand-pulling and DASH involve removing rooted plants from the bottom sediment of the water body. The entire plant is removed and disposed of elsewhere. Hand-pulling can be done at shallower depths whereas DASH, in which SCUBA divers do the pulling, may be better suited for deeper aquatic plant beds. As a permit condition, DASH and hand-pulling may not result in lifting or removal of bottom sediment (i.e., dredging). Efforts should be made to preserve water clarity because turbid conditions reduce visibility for divers, slowing the removal process and making species identification difficult. When operated with the intent to distinguish between species and minimize disturbance to desirable vegetation, DASH can be selective and provide multi-year control (Boylen et al. 1996). One study found reduced cover of Eurasian watermilfoil both in the year of harvest and the following year, along with increased native plant diversity and reduced overall plant cover the year following DASH implementation (Eichler et al. 1993). However, hand harvesting or DASH may require a large time or economic investment for Eurasian watermilfoil and other aquatic vegetation control on a large-scale (Madsen et al. 1989; Kelting and Laxson 2010). Lake type, water clarity, sediment composition, underwater obstacles and presences of dense native plants, may slow DASH efforts or even prohibit the ability to utilized DASH. Costs of DASH per acre have been reported to typically range from approximately \$5,060-8,100 (Cooke et al. 1993; Mattson et al. 2004). Additionally, physical removal of turions from sediments, when applicable, has been shown to greatly reduce plant abundance for multiple subsequent growing seasons (Caffrey and Monahan 2006), though this has not been implemented in Wisconsin due to the significant effort it requires.

Ecological Impacts of Hand-Pulling and DASH

Because divers are physically uprooting plants from the lake bed, hand removal may disturb benthic organisms. Additionally, DASH may also result in some accidental capture of fish and invertebrates, small amounts of sediment removal, or increased turbidity. It is possible that equipment modifications could help minimize some of these unintended effects. Because DASH is a relatively new management approach, less information is available about potential impacts than for some more established techniques like large-scale mechanical harvesting.

S.3.4.3. Benthic Barriers

Benthic barriers can be used to kill existing plants or prevent their growth from the outset. They are sometimes referred to as benthic mats, or screens, and involve placing some sort of covering over a plant bed, which provides a physical obstruction to plant growth and reduces light availability. They may be best used for dense, confined infestations or along shore or for providing boat lanes (Engel 1983; Payne et al. 1993; Bailey and Calhoun 2008). Reductions in abundance of live aquatic plants beneath the barrier may be seen within weeks (Payne et al. 1993; Carter et al. 1994). The target plant species, light availability, and sediment accumulation have been shown to influence the efficacy of benthic barriers for aquatic plant control. Effects on the target plants may be more rapid in finer sediments because anoxic conditions are reached more quickly due to higher sediment organic content and oxidization by bacteria (Carter et al. 1994). Benthic barriers may be more expensive but less time intensive than some



APPENDIX C

WDNR Chemical Fact Sheet

• Florpyrauxifen-benzyl (ProcellaCOR™)

Florpyrauxifen-benzyl Chemical Fact Sheet

Formulations

Florpyrauxifen-benzyl was registered with the EPA for aquatic use in 2017. The active ingredient is 2-pyridinecarboxylic acid, 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoro-, phenyl methyl ester. The current Wisconsin-registered formulation is a liquid (ProcellaCOR™ EC) solely manufactured by SePRO Corporation.

Aquatic Use and Considerations

Florpyrauxifen-benzyl is a systemic herbicide that is taken up by aquatic plants. The herbicide is a member of a new class of synthetic auxins, the arylpicolinates, that differ in binding affinity compared to other currently registered synthetic auxins. The herbicide mimics the plant growth hormone auxin that causes excessive elongation of plant cells that ultimately kills the plant. Susceptible plants will show a mixture of atypical growth (larger, twisted leaves, stem elongation) and fragility of leaf and shoot tissue. Initial symptoms will be displayed within hours to a few days after treatment with plant death and decomposition occurring over 2 – 3 weeks. Florpyrauxifenbenzyl should be applied to plants that are actively growing; mature plants may require a higher concentration of herbicide and a longer contact time compared to smaller, less established plants.

Florpyrauxifen-benzyl has relatively short contact exposure time (CET) requirements (12 – 24 hours typically). The short CET may be advantageous for localized treatments of submersed aquatic plants, however, the target species efficacy compared to the size of the treatment area is not yet known.

In Wisconsin, florpyrauxifen-benzyl may be used to treat the invasive Eurasian watermilfoil (*Myriophyllum spicatum*) and hybrid Eurasian watermilfoil (*M. spicatum* X *M. sibiricum*). Other invasive species such as floating hearts

(Nymphoides spp.) are also susceptible. In other parts of the country, it is used as a selective, systemic mode of action for spot and partial treatment of the invasive plant hydrilla (Hydrilla verticillata). Desirable native species that may also be negatively affected include waterlily species (Nymphaea spp. and Nuphar spp.), pickerelweed (Pontederia cordata), and arrowhead (Sagittaria spp.).

It is important to note that repeated use of herbicides with the same mode of action can lead to herbicide-resistant plants, even in aquatic plants. Certain hybrid Eurasian watermilfoil genotypes have been documented to have reduced sensitivity to aquatic herbicides. In order to reduce the risk of developing resistant genotypes, avoid using the same type of herbicides year after year, and utilize effective, integrated pest management strategies as part of any long-term control program.

Post-Treatment Water Use Restrictions

There are no restrictions on swimming, eating fish from treated waterbodies, or using water for drinking water. There is no restriction on irrigation of turf. Before treated water can be used for non-agricultural irrigation besides turf (such as shoreline property use including irrigation of residential landscape plants and homeowner gardens, golf course irrigation, and non-residential property irrigation around business or industrial properties), follow precautionary waiting periods based on rate and scale of application, or monitor herbicide concentrations until below 2 ppb. For agricultural crop irrigation, use analytical monitoring to confirm dissipation before irrigating. The latest approved herbicide product label should be referenced relative to irrigation requirements.

Herbicide Degradation, Persistence and Trace Contaminants

Florpyrauxifen-benzyl is broken down quickly in the water by light (i.e., photolysis) and is also subject to microbial breakdown and hydrolysis. It has a half-life (the time it takes for half of the active ingredient to degrade) ranging from 1 – 6 days. Shallow clear-water lakes will lead to faster degradation than turbid, shaded, or deep lakes.

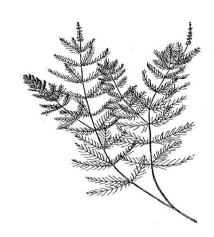
Florpyrauxifen-benzyl breaks down into five major degradation products. These materials are generally more persistent in water than the active herbicide (up to 3 week half-lives) but four of these are minor metabolites detected at less than 5% of applied active ingredient. EPA concluded no hazard concern for metabolites and/or degradates of florpyrauxifen-benzyl that may be found in drinking water, plants, and livestock.

Florpyrauxifen-benzyl binds tightly with surface sediments, so leaching into groundwater is unlikely. Degradation products are more mobile, but aquatic field dissipation studies showed minimal detection of these products in surface sediments.

Impacts on Fish and Other Aquatic Organisms

Toxicity tests conducted with rainbow trout, fathead minnow, water fleas (*Daphnia* sp.), amphipods (*Gammarus* sp.), and snails (*Lymnaea* sp.) indicate that florpyrauxifen-benzyl is not toxic for these species. EPA concluded florpyrauxifen-benzyl has no risk concerns for non-target wildlife and is considered "practically non-toxic" to bees, birds, reptiles, amphibians, and mammals.

Florpyrauxifen-benzyl does not bioaccumulate in fish or freshwater clams due to rapid metabolism and chemical depuration.



Human Health

EPA has identified no risks of concern to human health since no adverse acute or chronic effects, including a lack of carcinogenicity or mutagenicity, were observed in the submitted toxicological studies for florpyrauxifen-benzyl regardless of the route of exposure. EPA concluded with reasonable certainty that drinking water exposures to florpyrauxifen-benzyl do not pose a significant human health risk.

For Additional Information

Environmental Protection Agency Office of Pesticide Programs www.epa.gov/pesticides

Wisconsin Department of Agriculture, Trade, and Consumer Protection http://datcp.wi.gov/Plants/Pesticides/

Wisconsin Department of Natural Resources 608-266-2621 http://dnr.wi.gov/lakes/plants/

National Pesticide Information Center 1-800-858-7378 http://npic.orst.edu/

Washington State Department of Ecology. 2017. https://fortress.wa.gov/ecy/publications/documents/1710020.pdf