
Eurasian watermilfoil in Christmas Lake, 2011

Literature Review on Controlling Aquatic Invasive Vegetation with Aquatic Herbicides Compared to Other Control Methods: Effectiveness, Impacts, and Costs

Prepared for:
Minnehaha Creek Watershed District

Prepared by:
Steve McComas
Blue Water Science
St. Paul, MN 55116

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Steve McComas, Blue Water Science

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Literature Review on Controlling Aquatic Invasive Vegetation with Aquatic Herbicides Compared to Other Control Methods: Effectiveness, Impacts, and Costs

Introduction

The intent of this report is to present an overview of the literature regarding aquatic plant control with an emphasis on the use of aquatic herbicides as well as addressing mechanical harvesting, water level drawdown, and biological approaches.

The general literature regarding herbicides is broad (over 7 million hits with "herbicide" as a search word), however the literature is more limited regarding the use of aquatic herbicides for the control of aquatic plants. Basically aquatic herbicides are a subset of herbicides in general and terrestrial use of herbicides far exceeds the use of aquatic herbicides in practice (Tables 1 and 2).

With regard to aquatic herbicides, three components are discussed in this report: 1) Identification of the active ingredient associated with the trade name so a user knows what kind of chemical is going into a lake or pond, 2) Description of the mode of action of the herbicides, and 3) The effects of aquatic herbicides on humans and the aquatic environment.

Table 1. Pounds of herbicide used in the US and in Minnesota in a year.

	Terrestrial	Aquatic
Pounds/year Used in US	450,000,000	?
Pounds/year Used in Minnesota (active ingredient)	4,000,000 (MDA 2007)*	138,000 (MnDNR 2008)
Acres Treated in Minnesota	1,555,000 (4 crops)	8,000 (MnDNR 2008)

*(Minnesota Department of Agriculture website)

Table 2. Pounds of herbicide used in Minnesota in a year.

Pounds of Herbicide Used in a Year in Minnesota	
Agricultural (4 crops):	1,850,000 (MDA 2007)
Lawn, Garden, and Turf:	1,625,000 (MDA 2007)
Forestry and Right-of-way:	580,000 (MDA 2007)
Total (terrestrial):	4,055,000
Total (aquatic):	138,000 (MnDNR 2008)

Use of Herbicides as an Aquatic Plant Control Technique

The dominant technique used to control aquatic plants in Minnesota is the use of aquatic herbicides. In research studies, herbicides are shown to impact aquatic plants with the intended purpose of control (usually killing the plant). Sometimes an herbicide application is effective for several years but more frequently, it is an annual control. Rarely does an application result in eradication of the target plant rather annual nuisance control is the typical outcome.

Many variables are involved in a successful application for aquatic plant control and include:

- Water temperature
- Turbidity
- Conductivity
- Plant growth status
- Internal water movements (currents)
- Application dose selection
- Human error

Different types of herbicides are used for different types of aquatic plants. The control agent in an herbicide product is referred to as the active ingredient. Other ingredients in the product are considered to be inert and are present to help the active ingredient come into contact or help to make the active ingredient more effective. A summary of the common active ingredients used in herbicide products is shown in Table 3.

Table 3. The active ingredient in herbicides and the corresponding trade name of the herbicide are listed below. The trade name is the herbicide brand name and the herbicide is usually sold by the brand name. The active ingredient associated with the trade name indicates the type of herbicidal action that will be produced.

Trade Name	Active Ingredient
Navigate (butoxy-ethyl ester), Aqua-Kleen (amine), DMA 4 (amine), Scuplin (amine)	2,4-D
Reward, Weedtrine-D, Littora, Redwing	Diquat
Aquathol K (potassium salt), Hydrothol 191 (amine salt)	Endothall
Clipper	Flumioxazin
Sonar, Avast, WhiteCap	Fluridone
Rodeo, Aquamaster, Touchdown, Aqua Pro, Avocet, ShoreKlear	Glyphosate
Clearcast	Imazamox
Habitat, AquaPier, Gullwing, Polaris	Imazapyr
Galleon	Penoxsulam
Renovate 3 (amine), Renovate OTF (amine), Garlon 3	Trichlopyr

Additional Information on Aquatic Plant Control with Herbicides (full reference is in the reference section of this report):

Brocker and Edwards 1975
Crowell et al 2006
Forsythe et al 1997
Getsinger et al 2008
Gettys et al 2009
Murphy and Barrett 1993
Netherland and Getsinger 1992
Netherland et al 1993
Netherland et al 2000
Parsons et al 2007
Poovey et al 2003
Poovey et at 2007
Skogerboe and Getsinger 2007

How Herbicides Work and Their Mode of Action: Aquatic herbicides kill or injure aquatic plants by effecting plant physiology. Because there are a variety of plant types, there are also a variety of herbicides (Table 4). Herbicide products have a variety of ways they control or kill plants. A summary of herbicide products listing the active ingredient that causes the damage and the processes it impacts, referred to as the mode of action is shown in Table 5.

Table 4. Definitions of plant types and herbicide designations.

Plant Types:
- **Monocotyledon:** monocot (single leaf) parallel venation (example: pondweeds)
- **Dicotyledon:** dicot (two leaves) branching venation (examples: Eurasian watermilfoil, coontail)

Herbicide Types:
- **Systemic herbicide:** herbicide is absorbed and moves within the plant to the site of action. Systemic herbicides act more slowly than contact herbicides (example: 2,4-D).
- **Contact herbicide:** herbicide kills all plant cells they contact. Contact herbicides act quicker than systemic herbicides (example: endothall).

Herbicide Selectivity:
- **Selective herbicide:** kills specific types of plants (example: use of 2,4-D for milfoil)
- **Non Selective herbicide:** broad spectrum (example: diquat for heavy aquatic plant growth in mid-summer)

Table 5. Summary of commonly used herbicides in Minnesota and their mode of action. The active ingredient is listed first and a representative trade name is shown in parentheses in the first column.

Standard Aquatic Herbicides	Mode of Action	Typical Aquatic Plant Species Targeted in Minnesota
2,4-D (Navigate)	Growth regulator	Selective for EWM and dicots
Diquat (Reward)	Cell membrane disrupter	Non selective used for EWM and CLP
Endothall (Aquathol)	Not assigned	Selective for CLP in spring
Fluridone (Sonar)	Pigment inhibitor	Selective at low densities for CLP and EWM
Glyphosate (Rodeo)	Amino acid synthesis inhibitor	Non selective for emergent plants
Trichlopyr (Renovate)	Growth regulator	Selective for EWM and dicots

More Recently Registered Aquatic Herbicides	Mode of Action	
Flumioxazin (Clipper)	Chlorophyll inhibitor	Duckweed, watermeal
Imazamox (Clearcast)	Amino acid synthesis inhibitor	Emergent plants
Imazapyr (Habitat)	Amino acid synthesis inhibitor	Flowering rush, purple loosestrife
Penoxsulam (Galleon)	Amino acid synthesis inhibitor	Submersed, floating, and emergent plants

Information on herbicide selectively and effectiveness for the most common herbicide active ingredients (along with common trade names) are shown in Table 6.

Table 6. Herbicide effectiveness (from APIS, Engineering Research and Development Center, U.S. Army Corp of Engineers website). The active ingredient is listed first and a representative trade name is shown in parentheses.

2,4-D (Navigate): 2,4-D is one of the oldest herbicides registered for aquatic use in the United States. The herbicide is widely used in aquatic environments and is effective against broadleaf species like Eurasian watermilfoil. 2,4-D is a selective systemic herbicide with relatively short contact time but it does not harm narrowleaf pondweeds. 2,4-D is also not effective against hydrilla, elodea, and northern naiad.

Diquat (Reward): Diquat is a fast-acting contact herbicide which is mainly effective against floating plants. It causes rapid die off of plant shoots but is not effective in killing the roots, rhizomes or tubers. Diquat will bind to particulate matter and dissolved organic matter which can restrict use in some situations. The herbicide can also be used effectively with complexed copper compounds.

Endothall (Aquathol): Endothall is a contact herbicide with relatively fast action (12-36 hours). It is thought the herbicide interferes with plant respiration as well as disrupting plant cell membranes. Unlike diquat, endothall is not affected by particulate matter. Endothall should not be used with complex copper compounds due to reactions that affect fish.

Flumioxazin (Clipper): Flumioxazin is a fast acting broad spectrum contact herbicide that controls submersed, floating, and emergent vegetation including duckweed, watermeal, water lettuce, and cabomba. It controls plants by inhibiting an essential enzyme required by plants for chlorophyll biosynthesis.

Fluridone (Sonar): Fluridone is a non-selective systemic aquatic herbicide at high doses and fairly selective at low doses. The herbicide is a carotenoid pigment inhibitor. The loss of carotenoids in plants allows UV light to destroy chlorophyll and eventually kill the plant. Fluridone requires long exposure times of up to 80 or more days but is effective at very low concentrations where it is somewhat selective for Eurasian watermilfoil. Works best for whole lake treatments and is not suited for spot treatments or water bodies with high water exchange.

Glyphosate (Rodeo/Roundup): Glyphosate is not used on submersed aquatic plants, but it is used on emergent and floating leaf wetland and shoreline plants such as spatterdock and cattails. It is a non-selective systemic herbicide that is mainly used to control perennials. The mode of action inhibits the enzyme involved in amino acid production. The herbicide is absorbed through the leaves and translocated to the growing points.

Imazamox (Clearcast): Imazamox is a systemic herbicide used for submerged, emergent, and floating vegetation. It controls both monocots (pondweeds) and dicots (broadleaf plants, like Eurasian watermilfoil).

Imazapyr (Habitat): Imazopyr is a non-selective, systemic herbicide used for emergent and floatingleaf aquatic plants that include cattails and water hyacinth.

Penoxsulam (Galleon): Penoxsulam is a non-selective systemic herbicide that requires a long exposure time. The herbicide works best on very calm waters and if used properly can treat submersed, floating and emergent plants.

Triclopyr (Renovate): Triclopyr is a selective systemic herbicide and like 2,4-D it can control broadleaf plants like Eurasian Watermilfoil. It is applied to the leaves of the plants, including floating plants and emerged plants.

A specific herbicide trade name or brand is associated with a mode action, site of action, and a chemical family. Knowing the type of herbicide allows one to get a quick overview of its potential action. However, within that herbicide group, individual formulations will have specific responses or impacts. Terrestrial herbicides are more numerous than aquatic herbicides and have a wider variety of action in more chemical families than aquatic herbicides (Table 7). Within the aquatic herbicide area there are six site of action groups as described by the Herbicide Resistance Action Committee (HRAC)(shown with letters in Table 8) and six site of action groups described by the Weed Science Society of America (WSSA)(shown with numbers in Table 8). The herbicide classification system was a cooperative effort of the HRAC and WSSA. Additional information for the site of action for all herbicide classes, which includes terrestrial and aquatic herbicides is shown in Appendices A and B. A summary of aquatic herbicides and their characteristics, arranged by the active ingredient is shown in Table 9.

Table 7. Comparison of site of action groups, chemical families and herbicide brands between terrestrial and aquatic herbicides.

	Terrestrial	Aquatic
Site of Action Groups (WSSA)*	28	6
Chemical Families	40+	8
Herbicide Brands	200+	20+

*WSSA = Weed Science Society of America

Table 8. Summary of mode of action and the site of action for aquatic herbicides. Herbicides are arranged in alphabetical order according to the HRAC group. Additional information on the mode of action for each HRAC group is found in Appendices A and B.

HRAC* Group	Site of Action Group (WSSA)	Mode of Action	Site of Action	Chemical Family	Active Ingredient	Representative Trade Name
B	2	Amino Acid Synthesis Inhibitors	ALS inhibitors	Imidazolinone	Imazamox Imazapyr	Clearcast Habitat
				Triazolopyrimidine	Penoxsulam	Galleon
D	22	Cell Membrane Disrupters	Photosystem I electron diverter	Bipyridilium	Diquat	Reward
E	14	Chlorophyll Inhibitor	Inhibition of PPO	N-phenylphthalimide	Flumioxazin	Clipper
F	12	Pigment Inhibitors	Carotenoid synthesis inhibitors	None generally recognized	Fluridone	Sonar
G	9	Amino Acid Synthesis Inhibitor	EPSP synthase inhibitor	Gylcine	Glyphosate	Rodeo
O	4	Growth Regulators (Synthetic auxins)	Specific site unknown	Phenoxy	2,4-D	Navigate
				Pyridine	Trichlopyr	Renovate
--	Not assigned	Various	Not well understood	None generally accepted	Endothall – dimethylamine salts	Aquathol

* Herbicide Resistance Action Committee

Table 9. Summary of common aquatic herbicides and corresponding characteristics.

Active Ingredient	Trade Name	Formulation and Contact or Systematic	Mode of Action	Advantages	Disadvantages	Systems Where Used Effectively	Plant Species Response	Use Rate (active ingredient)	Half-life
Copper Complexes (an algaecide)	Cutrine-plus Cleatigate Captain Komeen K-tea	Various complexing agents Contact	Plant cell toxicant	Inexpensive rapid action, approved for drinking water	Doesn"t biodegrade, but bio inactivates in sediments	Lakes higher exchange rates	Broad spectrum, acts in 7-10 days, up to 4-6 weeks	1 mg/l	2-8 Days
2-4, D	Navigate Aqua-Kleen	BEE salt DMA, liquid Systemic	Selective- plant growth regulator	Inexpensive, systemic	Non-target may be affected	Lakes and slow flow areas	Selective to broadleaf, acts in 5-7 days or up to 4-6 weeks	to 1.0mg/L	2-6 days
Diquat	Reward Weedtrine-D	Liquid Contact	Disrupts plant cell membrane integrity	Rapid action, limited drift	Does not affect underground portions	Shoreline, localized treatments, higher exchange rate areas	Broad spectrum, acts in 7 days	0.1-0.5 mg/L	< 48 hours
Endothall	Aquathol K Aquathol Super K Hydrothol 191	Liquid or granular Contact	Inactivates plant protein synthesis	Rapid action, limited drift	Does not affect underground portions	Shoreline, localized treatments, higher exchange rate areas	Broad spectrum, acts in 7 days	2-4mg/L	1-7 days
Flumioxazin	Clipper	Contact	Inhibits chlorophyll synthesis	Controls duckweed	New in 2010. Action is being observed.	Ponds and lakes	Broad spectrum	0.1-0.4 mg/l	
Fluridone	Sonar AS, SRP, PR, Q Avast!	Liquid or granular Contact	Disrupts carotenoid synthesis	Very low dosage required, systemic	Very long contact period	Small lakes, slow flow systems	Broad spectrum acts in 30-90 days	0.005-0.020 mg/l	20-80 Days
Glyphosate	Rodeo, AquaPro Aquamaster Aqua Neat Touchdown	Liquid Systemic	Disrupts synthesis of amino acids	Widely used, systemic	Very slow action, no submersed control	Emergent and floating leaf plants only	Broad spectrum, acts in 7-10 days up to 4 weeks	0.5-0.5 mg/L	
Imazamox	Clearcast	Liquid Systemic	Disrupts synthesis of amino acids	Systemic	Growth regulation of submersed plants, not death	Quiescent bodies of water	Growth regulation of submersed plants, acts in 1-2 weeks or more for foliar applications	Up to 0.5 mg/l	7-14 days
Imazapyr	Habitat	Systemic	Disrupts synthesis of amino acids	Systemic	Not recommended for submerged species	Emergent and floatingleaf plants only	Acts in several weeks	1.5 lbs ai/acre	
Penoxsulam	Galleon SC	Liquid Systemic	Disrupts synthesis of amino acids	Selective, few label restrictions, systemic	Very long contact period	Quiescent bodies of water	broad spectrum, acts in 60- 120 days	0.15 mg/l	
Triclopyr	Garlon 3A Renovate 3 Renovate OTF	Liquid Systemic	Selective plant growth regulator	Selective, inexpensive	Can injure other nearby broadleaf species	Lakes and slow flow areas	Selective to broadleaves acts in 5-7 days up to 2 weeks	1.0mg/L	12-72 hours

Additional Information on How Herbicides Work:

Appendix A and B, this report
EXTOXNET 1996
Gettys et al 2009
Gibson 2001
Peterson et al 1994
Retzinger and Mallory-Smith 1997
Siemering et al 2005
Washington State Department of Ecology 2001a
Washington State Department of Ecology 2001b
Washington State Department of Ecology 2001c

Aquatic Herbicide Impacts on Humans and the Ecosystem

Aquatic Herbicide Impacts on Humans: A review of the literature indicates the documented quantifiable adverse impacts of herbicides on humans come primarily from terrestrial herbicide use (Table 10).

Use of aquatic herbicides at concentrations specified by the label for the active ingredients such as endothall, 2,4-D, fluridone, and other aquatic herbicides, do not cause quantifiable adverse impacts to human health. However, there could be subtle, unquantified impacts that have not been detected (Table 10).

Table 10. Examples of terrestrial and aquatic herbicide impacts.

Examples of Terrestrial Herbicide Impacts
Forestry herbicide applicators have been observed to incur short term health impacts.
Non-Hodgkin lymphoma has been associated with the use of glyphosates, 2,4-D, and 2,4,5-T
Parkinson's has been associated with the use of parquat
Attention Deficit Hyperactivity Disorder (ADHD) has been associated organophosphate herbicides (sprayed on crops and fruits)
Terrestrially applied herbicides have been detected in lakes and rivers. Studies are in progress to evaluate their effects.
Examples of Aquatic Herbicide Impacts
General population is not tested for impacts of aquatic herbicides.
Human impacts are difficult to measure based on aquatic herbicide use.
It is rare for aquatic herbicide applicators to be tested for health impacts.
Impacts, if present, could be too low to quantify
If there is an impact, it is likely subtle and indirect
With aquatic herbicide use there is a degree of uncertainty with a declared low risk.
EPA says the risk of aquatic herbicide use is acceptable.
The impact of inert ingredients are sometimes questioned. However, limited test results in the literature do not show harmful effects.
Use of surfactants can make herbicides more toxic.
Synergistic effects of combining several herbicides in an application are rarely tested.

Sometimes the question comes up why if the US EPA allows aquatic herbicide use, it doesn't guarantee that herbicides are safe. The regulatory language of FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act) does not allow language that indicates any registered pesticide is "safe". One reason is because "safe" is a relative term and could be misleading. No agent, natural or man-make, is completely safe. For example, even water can be dangerous if too much is ingested at one time.

At full strength, aquatic herbicides pose acute toxic effects to human health. Acute toxicity refers to the relatively immediate effects (0-7 days) of a chemical and is probably most relevant to an herbicide applicator. The US EPA has a classification for toxicity of herbicides that are referred to as signal words. The signal words are always found on the product's specimen label. The criteria used for toxicity categories are shown in Table 11.

Table 11. Signal words used to classify toxicity categories found on herbicide labels based on US EPA criteria.

	Danger (high toxicity)	Warning (moderate toxicity)	Caution (low toxicity)
Acute Oral LD_{50}	≤ 50 mg/kg	>50-500 mg/kg	>500-5,000 mg/kg
Inhalation LC_{50}	≤ 0.05 mg/kg	>0.05-0.5 mg/kg	>0.5-2.0 mg/kg
Dermal LD_{50}	≤ 200 mg/kg	>200-2,000 mg/kg	>2,000-5,000 mg/kg
Primary Eye Irritation	Corrosive (irreversible destruction of ocular tissue) or corneal involvement or irritation persisting for more than 21 days.	Corneal involvement or eye irritation clearing in 8-21 days.	Corneal involvement or other eye irritation clearing in 7 days or less.
Primary Skin Irritation	Corrosive (tissue destruction into the dermis and/or scarring).	Severe irritation at 72 hours.	Moderate irritation at 72 hours.

Examples of the placement of signal words on an herbicide specimen label are shown in Figure 1. Toxicity does not include chronic hazards such as cancer, endocrine disruption, genetic effects, or behavioral changes that affect species survival.

Figure 1. Specimen labels for Renovate and Rodeo herbicides show where the US EPA signal words are found. Renovate with a "danger" signal word is more acutely toxic than Rodeo which has a "caution" signal word.

Human health impacts should be distinguished from impacts to other test organisms. For example toxicity to humans is based on a lethal dose, defined as a weight of a pesticide per body weight (Table 12). However, the toxicity to aquatic organisms is based on a lethal concentration, defined as a weight of a pesticide per volume of water (Table 12 and Table 13). For example, in Table 14, Aquathol K has a signal word of danger indicating high toxicity if taken orally with a dose of less than 50 mg of active ingredient per kg of body weight being acutely toxic to 50% of a test population. If a 200-pound person ingested 5 grams of the active ingredient, they would likely get sick and could die. However, Aquathol K is not considered to be acutely toxic to fish (based on averaging several fish species tolerances)(Table 14). Some fish species could tolerate 10 mg/l or more of endothall and not be impacted. For a human to get an acutely toxic dose of 5 grams of endothall by drinking lake water with an endothall concentration of 10mg/l, one would have to drink over 130 gallons of water. The recommended dosing concentration of endothall for a lake application for curlyleaf pondweed control is 1.0 mg/l or less. At this concentration, a 200-pound person would have to drink 1,300 gallons of lake water to receive an acute lethal dose.

Table 12. Definitions for discussing the impacts of herbicides on non-target organisms (from: Siemering et al 2005).

EC_{50} = effective concentration of the pesticide that produces a specific measurable effect in 50% of the test organisms.

LC_{50} = concentration (wt of pesticide per volume of water) that is lethal to 50% of the test organisms within the stated time.

LD_{50} = dose (wt of pesticide per body weight) that is lethal to 50% of the test organisms.

LCLo = lowest concentration of pesticide that produces a lethal response in any test animal. As with LDLo, because the LCLo study type is not strictly defined as to the percentage of test animals affected, it is not highly useful for comparing the acute toxicities of different materials.

LDLo = lowest dose of pesticide that produces a lethal response in any test animal. Because the LDLo study type is not strictly defined as to the percentage of test animals affected, it is less useful for comparison purposes than LD50.

LOEC = "lowest observed effect concentration", or the lowest level below which adverse effects are observed. This endpoint depends strongly on the sensitivity of the techniques used to measure the effects.

MATC = "maximum acceptable toxicant concentration" and is a hypothetical threshold concentration that is the geometric mean between the NOEC and the LOEC concentration.

NOEC = "no observed effect concentration", or the level below which no adverse effects are observed. This endpoint depends strongly on the sensitivity of the techniques used to measure the effects.

Table 13. Average acute toxicity ratings for fauna (from Kamrin 1997).

Fauna Toxicity Category	LC_{50} (mg/l)
Very highly toxic	<0.1
Highly toxic	0.1-1.0
Moderately toxic	1-10
Slightly toxic	10-100
Not acutely toxic	>100

Table 14. Human health impacts and impacts to fauna (Colorado State Parks 2003).

Product	EPA Signal Word (Human Acute Toxicity) (based on LD_{50})	Human Cancer Risk*	Endocrine Disruptor	Fauna Impacts Average Acute toxicity based on LC_{50} (From Kamrin, M.A. 1997. Pesticide profiles: toxicity, environmental impact, and fate. Lewis Publishers. Boca Raton, FL.)				
				Fish	Crustacean	Zooplankton	Mollusks	Phytoplankton
Glyphosate								
Accord, Aquamaster, Aquaneat, Glyphoste, Rodeo, VMF	Caution (low toxicity)	Inadequate data - EPA	Unknown	ST (Slightly toxic)	MT (Moderately toxic)	ST	--	--
Copper								
Clearigate, Cutrine-Plus	Danger (highly toxic)	Inadequate data EPA	Unknown	ST	NAT (Not acutely toxic)	NAT	--	--
Nauitque								
Komeen	Caution	Inadequate data	Unknown	ST	NAT	NAT	--	--
Diquat								
Reward	Warning (Moderate toxicity)	Not likely	Unknown	NAT	ST	ST	MT	--
Endothall								
Aquathol K, Aquathol	Danger	Not likely	Unknown	NAT	LT	NAT	--	--
Super K								
Hydrothol 191, hydrothol 191 granular	Danger	Not likely	Unknown	HT	--	MT	MT	MT
Fluridone								
Avast! Avast! SRP	Caution	Not likely	Unknown	ST	ST	ST	MT	--
Sonar A.S., Sonar PR								
Sonar SRP								
Triclopyr								
Renovate 3	Danger	Not likely	Unknown	NAT	NAT	--	--	--
2,4-D								
Navigate	Danger	Possible carcinogen IARC, ambiguous data – EPA	Suspected	NAT	NAT	NAT	NAT	--

*cancer risk: determine on weight of evidence – where a panel of scientists evaluates available data for a particular chemical. IARC = International Agency for Research on Cancer

The risk of cancer from contact with aquatic herbicides in water or by ingesting herbicides in lake water is either not likely or data are lacking, although 2,4-D is still being evaluated (Table 14).

In the last decade, it has been observed some chemicals (other than aquatic herbicide chemicals) found in lakes and rivers act as endocrine disrupters (chemicals that affect the hormone system). The only aquatic herbicide in use that is "suspected" of being an endocrine disrupter is 2,4-D. That is a designation assigned by the US EPA. The active ingredients in other aquatic herbicides are listed as "unknown" (Table 14).

Additional Information on Impacts of Aquatic Herbicides on Human Health:

Anderson et al 2002
Durkin 2003
EXTOXNET 1996
Ibrahim et al 1991
Munro et al 1992
Siemering et al 2005
Washington State Department of Ecology 2001a
Washington State Department of Ecology 2001b
Washington State Department of Ecology 2001c

Aquatic Herbicide Impacts on the Ecosystem: With any herbicide application, many variables are involved that produce direct and indirect effects. Under typical conditions and using label criteria, acute impacts to the aquatic ecosystem are few but can occur. Unintended impacts occur, but do not appear to be sustaining. For example, non-target aquatic plant species can be damaged or killed, but they can grow back. In another situation, if zooplankton are rendered less competitive due to an herbicide treatment there can be consequences in several areas of the lake ecosystem (Figure 2). What are unknown are the subtle impacts that cascade through the aquatic ecosystem that have not been quantified because they have not been specifically studied or we have not recognized them.

The impact of aquatic herbicides on the biology of the lake's flora and fauna has been evaluated since the 1960s. A summary of acute (short-term, significant) impacts is shown in Table 15. Although many studies have been conducted on a variety of organisms there are still gaps in our understanding. However, several observations stand out. For example, with endothall, the diamine salt is more toxic than other endothall formulations. With glyphosate, Roundup is more toxic to aquatic organisms than the Rodeo formulation and with 2,4-D the BEE (butoxyethyl ester) formulation is more toxic than the acid formulation (Table 15).

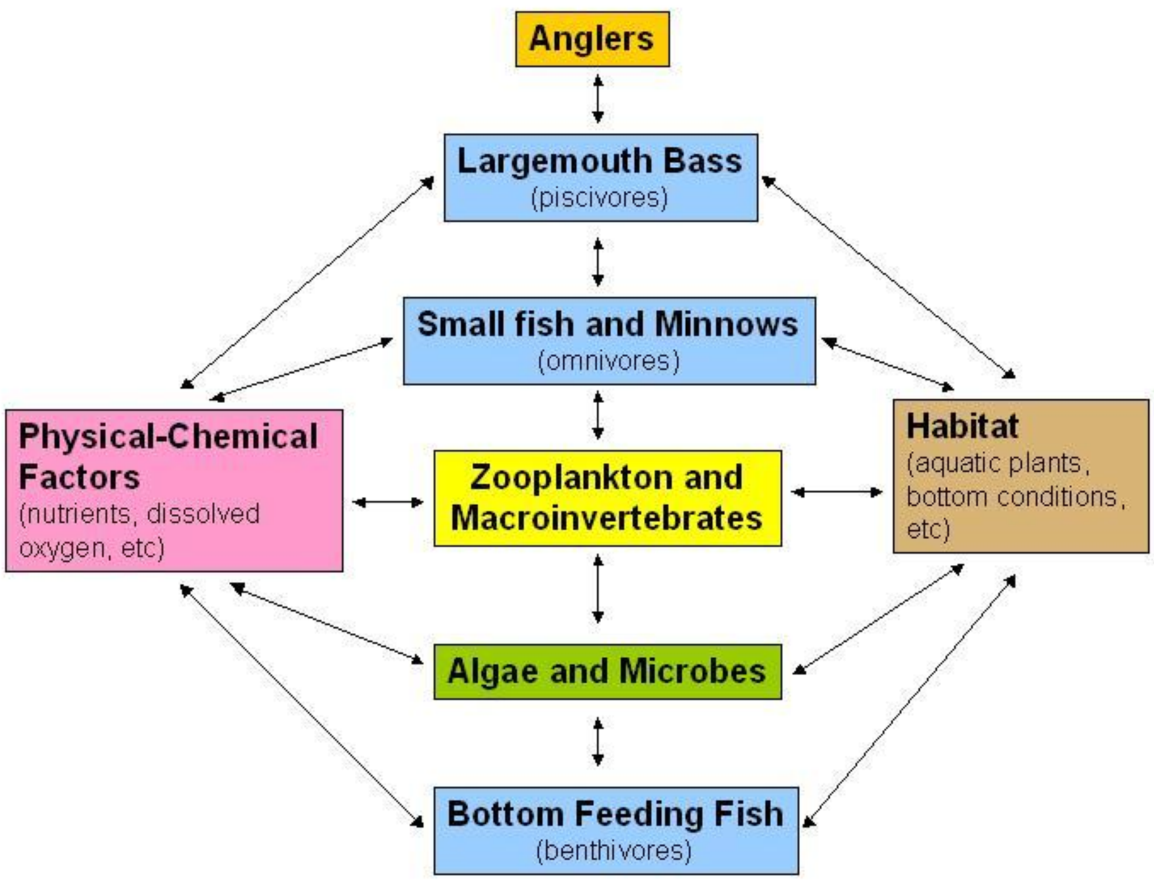


Figure 2. Many components are connected in the web of interactions in a lake. If one component is changed there can be consequences for a number of components within the web.

Table 15. Summary of acute toxicity to fish, amphibians, zooplankton, and invertebrates based on LC_{50} data (Siemering et al 2005). (LC_{50} = a concentration where weight of pesticide per volume of water is lethal to 50% of the test organisms within the stated time).

	Copper		Diquat	Endothall		Fluridone	Glyphosate			Triclopyr	2,4-D	
			p.55	p. 64	Diamine salt	p. 73, 74	Roundup p. 87	Rodeo	Glyphosate		BEE	Acid
Fish												
Largemouth bass			4.9 mg/l LC_{50}: 96 hr (fry survival)	130 mg/l LC_{50}: 96 hr	0.1-0.3 mg/l LC_{50}: hr	13 mg/l LC_{50}: 96 hr (fry survival)						
Walleye			0.75 mg/l LC_{50}: 96 hr (fry survival)	16 mg/l LC_{50}: 96 hr		2.3 mg/l LC_{50}: 72 hr (fry survival)						
Bluegill	46.0 mg/l LC_{50}: 24 hr	12.5 mg/l LC_{50}: 96 hr		0.9 mg/l LC_{50}: 96 hr	0.06-0.2 mg/l LC_{50}: 96 hr	9-17 mg/l LC_{50}: 96 hr	5-34 mg/l LC_{50}: 96 hr		120-140 mg/l LC_{50}: 96 hr	471-891 mg/l LC_{50}: 96 hr		
Golden shiner	630 mg/l LC_{50}: 96 hr (hardwater)	67 mg/l LC_{50}: 96 hr (softwater)										
Fathead minnow			7.6-70 mg/l LC_{50}: 96 hr (fry survival)			>0.5-6.3 mg/l LC_{50} 96 hr	2.3-23 mg/l LC_{50}: 96 hr		97 mg/l LC_{50}: 96 hr	546-947 mg/l LC_{50}: 96 hr		
Amphibians												
Frog							7.7 mg/l LC_{50}: 96 hr	5,515 mg/l LC_{50}: 96 hr				
Zooplankton												
Daphnia magna	0.044 mg/l LC_{50}: 3 wk	0.068- 0.087mg/l LC_{50}: 72 hr	0.032-1.62 mg/l LC_{50}: 48 hr			2.1-6.3 mg/l LC_{50}: 96 hr	3-24 mg/l LC_{50}: 48 hr	218 mg/l LC_{50}:	3.0 mg/l LC_{50}: 48 hr	133-1,110 mg/l LC_{50}: 48 hr	1.7-7.2 mg/l LC_{50}: 48 hr	25-418 mg/l LC_{50}: 48 hr
Ceriodaphnia dubia												236 mg/l LC_{50}: 24 hr
Invertebrates												
Crayfish						>16.9 mg/l LC_{50}: 14 days						
Midge larvae				120 mg/l LC_{50}: 72 hr								
Tubifex												122 mg/l LC_{50}: 96 hr
Amphipod			0.012-0.064 mg/l LC_{50}: 48 hr	320 mg/l LC_{50}: 96 hr								3.2 mg/l LC_{50}: 96 hr

Determining the chronic (long term, subtle adverse impacts) of aquatic herbicides has not been as extensively studied as the acute impacts. A summary of chronic impacts listed in Siemering et al 2005 is shown in Table 16.

Table 16. Summary of chronic toxicity to fish, amphibians, zooplankton, and invertebrates based on NOEC data (Siemering et al 2005). (NOEC = "no observed effect concentration" or the level below where no adverse effects are observed).

	Diquat	Endothall	Fluridone	Glyphosate		2,4-D		
				Roundup	Rodeo		Acid	BEE
Fish								
Largemouth bass	1.8 mg/l 96 hrs – fry survival	50 mg/l 96 hrs						
Walleye	0.480 mg/l 96 hrs – fry survival	5.7 mg/l						
Bluegill	>10 mg/l 12 days – survival							
Golden shiner								
Fathead minnow	0.120 mg/l (34 days)		1.88 mg/l			100 mg/l	63.4 mg/l 32 days	0.3 mg/l 10 months
Amphibians								
Frog				2.4 mg/l 21 days	52 mg/l 21 days			
Zooplankton								
Daphnia	0.036 mg/l 21 days					27.5 mg/l	79 mg/l 21 days	0.29 mg/l 21 days
Invertebrates								
Tubifex							87 mg/l 96 hrs	

Where to Find Specific Information on Herbicide Products and Their Active Ingredients: For information on aquatic herbicides, areas to check are shown below:

Specimen label (search by trade name): Information includes ingredients, directions for use, and amounts to use. All registered herbicides will have a specimen label. For example, Eurasian watermilfoil is being treated in Lake Minnetonka with the herbicide, Renovate. The active ingredient is triclopyr.

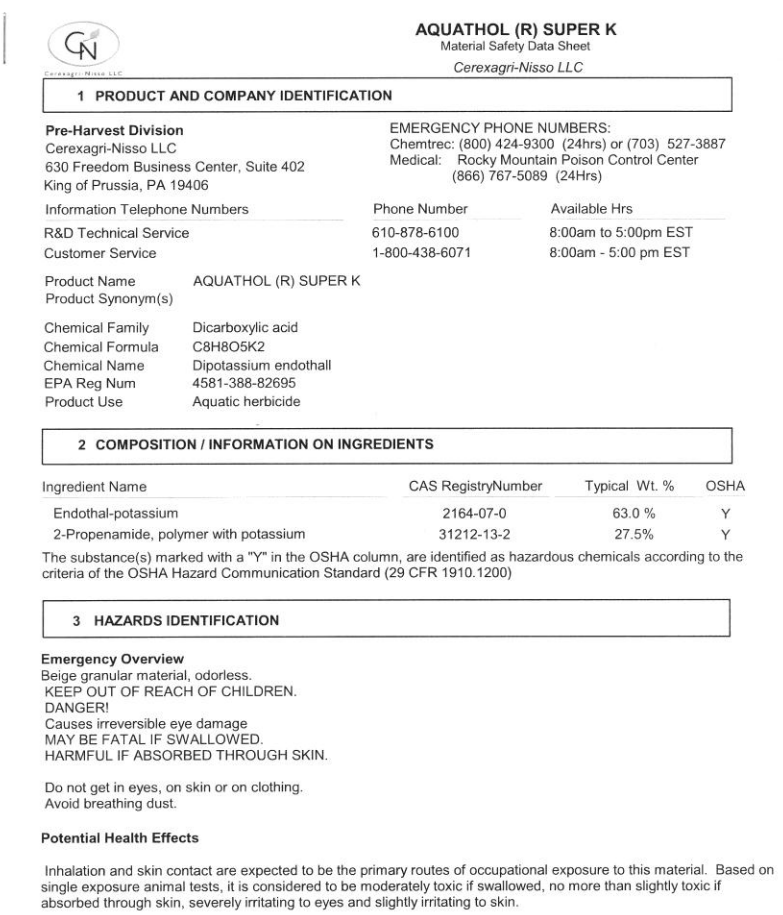
Material Safety Data Sheet (search by active ingredient): Information includes the physical and chemical properties of the active ingredient as well as toxicological information on mammals in terms of LD_{50} and on aquatic fauna and flora in LC_{50} (cover sheet is shown in Figure 3).

EXTOXNET (search by active ingredient): pesticide information profiles have been compiled by the Extension Toxicology Network. This site discusses acute and chronic toxicity and ecological effects of the common active ingredients registered up to the mid-1990s. Aquatic herbicides registered since 2000 are not listed. Aquatic herbicides represented (by active ingredient) include the following:

2,4-D, diquat, endothall, glyphosate, and trichlopyr

Additional Herbicide Product Information:

National Pesticide Information Center
Washington State herbicide assessments (found in references in this report)
WSSA (Weed Science Society of America) website
HRAC (Herbicide Resistance Action Committee) website
PAN Pesticide Database (PAN = Pesticide Action Network) website



AQUATHOL (R) SUPER K
Material Safety Data Sheet
Cerexagri-Nisso LLC

1 PRODUCT AND COMPANY IDENTIFICATION

Pre-Harvest Division
Cerexagri-Nisso LLC
630 Freedom Business Center, Suite 402
King of Prussia, PA 19406

EMERGENCY PHONE NUMBERS:
Chemtrec: (800) 424-9300 (24hrs) or (703) 527-3887
Medical: Rocky Mountain Poison Control Center (866) 767-5089 (24Hrs)

Information Telephone Numbers	Phone Number	Available Hrs
R&D Technical Service	610-878-6100	8:00am to 5:00pm EST
Customer Service	1-800-438-6071	8:00am - 5:00 pm EST

Product Name AQUATHOL (R) SUPER K
Product Synonym(s)

Chemical Family Dicarboxylic acid
Chemical Formula C8H8O5K2
Chemical Name Dipotassium endothall
EPA Reg Num 4581-388-82695
Product Use Aquatic herbicide

2 COMPOSITION / INFORMATION ON INGREDIENTS

Ingredient Name	CAS RegistryNumber	Typical Wt. %	OSHA
Endothal-potassium	2164-07-0	63.0 %	Y
2-Propenamide, polymer with potassium	31212-13-2	27.5%	Y

The substance(s) marked with a "Y" in the OSHA column, are identified as hazardous chemicals according to the criteria of the OSHA Hazard Communication Standard (29 CFR 1910.1200)

3 HAZARDS IDENTIFICATION

Emergency Overview
Beige granular material, odorless.
KEEP OUT OF REACH OF CHILDREN.
DANGER!
Causes irreversible eye damage
MAY BE FATAL IF SWALLOWED.
HARMFUL IF ABSORBED THROUGH SKIN.

Do not get in eyes, on skin or on clothing.
Avoid breathing dust.

Potential Health Effects

Inhalation and skin contact are expected to be the primary routes of occupational exposure to this material. Based on single exposure animal tests, it is considered to be moderately toxic if swallowed, no more than slightly toxic if absorbed through skin, severely irritating to eyes and slightly irritating to skin.

Figure 3. Example of the first page from a Material Safety Data Sheet (MSDS) for the active ingredient, endothall, found in the herbicide with the trade name of Aquathol. Aquathol is commonly used to treat curlyleaf pondweed.

Harvesting, Drawdown, and Biocontrol Aquatic Plant Control Techniques

In addition to the use of herbicides for plant control, other control techniques are options as well. Three of those techniques are discussed here. The information came from several sources including: Cooke et al 2005, Gettys et al 2009, and McComas 2003.

Mechanical Harvesting: Harvesters are the most widely used mechanical control devices in the United States. The Hockney Weed Cutter was produced in 1903 and somewhat resembled the McCormick Reaper. Machines that cut and removed plants were first developed in the 1950's by a Wisconsin company. Harvest and removal harvesters are highly maneuverable around docks and boathouses and the machines can operate in as little as 12 to 18 inches of water. The harvesters cut plants off at depths of 5 feet and in swaths 8 feet wide with a hydraulically operated cutter head and convey the cut plants into a storage bay on the harvester. When the harvester is full, it offloads harvested plants using a conveyor, to a truck trailer for disposal.

Mechanical harvesting of non-native submersed plants, typically curlyleaf pondweed and Eurasian watermilfoil, has been utilized in the Midwest. Plant removal can effectively reduce the standing crop of plants in high use areas and promote general utilization of the water resource. Although mechanical harvesting is often used in northern lakes to control submersed weeds, this method has less utility in southern states due to longer growing seasons and much larger scale coverage of weeds in shallow reservoirs.

Targeted Invasive Plants	Control Effectiveness
All submerged plants within 5 feet of surface	Good to excellent

Advantages and Disadvantages of Harvesting

Advantages of mechanical harvesting include the following:

- Water can be used immediately following harvest treatment. Some aquatic herbicides have restrictions on use of treated water for drinking, swimming, and irrigation.

- Harvesting takes the plant material out of the water so the plants do not decompose slowly in the water column as they do with herbicide treatment. Additionally, oxygen content of the water is generally not affected by mechanical harvesting, although turbidity and water quality may be affected in the short term.

- Nutrient removal can occur but is usually minimal because only small areas of lakes (1 to 2%) are typically harvested. It has been estimated that aquatic plants contain less than 30% of the annual nutrient loading that occurs in lakes.

- The plant community is altered but remains largely intact because most harvesters do not remove submersed plants all the way to the lake bottom. Like mowing a lawn, clipped plants remain rooted in the sediment and regrowth begins soon after the harvest.

- Mechanical harvesting is site specific because plants are only removed where the harvester operates. If a neighbor wants vegetation to remain along his or her lakefront, there is no movement of herbicides out of the intended treatment area.

- Mechanical harvesting is perceived to be environmentally neutral by the public whereas concerns over the safety and long-term toxicology of herbicide applications remain despite widespread research and registration requirements that are enforced by regulatory agencies.

Disadvantages of mechanical harvesting include the following:

- Because of the low demand for commercial harvesting, the equipment has limited production and can be expensive.

- The area that can be harvested in a day depends on the size of the harvester, transport time, distance to disposal site, and density of the plants being harvested. These factors result in a wide range of cost. The cost of harvesting is site-specific, but mechanical harvesting is generally more expensive that other plant control methods.

- Mechanical harvesters are not selective and remove native plants along with target weeds. However, most native plants will likely return by the next growing season or before.

- By-catch, or the harvesting of nontarget organisms such as fish, crayfish, snails, macro invertebrates, along with weeds can be a concern, but the degree or extent of harvesting should be considered. Research on fish catch during mechanical harvesting of submersed vegetation has shown the 15 to 30% of some species of fish can be removed with cut vegetation during a single harvest. If the total area of the lake is 1, 5 or 10% of the lake's area, this will likely be of little consequence, however if the management plan for a 10-acre pond calls for complete harvest 3 times per year, then the issue of by-catch of fish deserves more consideration.

- Regrowth of cut vegetation can occur quickly. For example if Eurasian milfoil can grow 1 to 2 inches per day as reported, a harvest that cuts 5 feet deep could result in plants reaching the water surface again only one to two months after harvesting. Speed of regrowth depends of the target weed, time of year harvested, water clarity, water temperature and other factors.

- Floating plant fragments produced during mechanical harvesting can be a concern because aquatic weeds can regrow vegetatively from even small pieces of vegetation. If initial infestation of aquatic plants is located at a boat ramp, care should be taken to minimize the spread of fragments to uninfested areas of the lakes by maintaining a containment barrier around the area where harvesting will take place. On the other hand if a lake is already heavily infested with a weed, it is unlikely that additional fragments will spread the plants further. However, homeowners downwind of the harvesting site may not appreciate have to regularly rake weeds and floating fragments off their beaches

- Disposal of harvested vegetation can be an expensive and difficult problem after mechanical harvesting. It takes time and additional money to transport the plants to shore, load the material and dispose of the cut material off site.

- Some lakes or rivers may not be suitable for mechanical harvesting. If there is only one public boat ramp on a lake and it is not close to the area to be harvested, the costs of moving the cut vegetation from the harvester to shore will add significantly to the cost of operation. Harvesters move relatively slow, so the extra time traveling to and from the off load site must be factored into the operation. Additionally, the off load site should be paved or a concrete surface because the aquatic plants are wet and unpaved off-loading sites can quickly become a transportation problem.

Drawdown: Drawdown or the lowering of the lake water level can be used to effectively control a number of invasive submersed species. This technique is used in the northern US to expose targeted plants to freezing conditions over winter. Water is either gravity drained using a low-level gate valve or a removable flashboard system on a dam. Siphoning or pumping can also be performed in lakes with insufficient outlet structures.

Plants that are usually controlled by drawdowns include many submersed species that reproduce primarily through vegetative means such as root structures and vegetative fragmentation. Some invasive submersed species most commonly targeted by drawdown include curlyleaf pondweed, Eurasian watermilfoil, variable watermilfoil, fanwart, egeria, and coontail.

To be effective a drawdown condition needs to expose lake sediments to freezing conditions. Excessive snow cover can limit the effectiveness of a winter drawdown. Drawdowns are usually timed to begin during the fall months to avoid stranding amphibians, molluscs and other benthic organisms with limited mobility. Care must also be taken to leave enough water to support fish populations overwinter

Targeted Invasive Plants	Control Effectiveness
Curlyleaf pondweed	Excellent
Eurasian watermilfoil	Good
Purple loosestrife	Poor

Impacts to Aquatic Plants for a Water Level Drawdown Over Winter in Minnesota

Plants That May Increase in Growth

Chara	(*Chara vulgaris*)
Manna grass	(*Glyceria borealis*)
Hydrilla	(*Hydrilla verticillata*)
Rice cutgrass	(*Leersia oryzoides*)
Marsh marigold	(*Megalodonta beckii*) now called (*Bidens Beckii*)
Naiads	(*Najas flexilis*)
Ribbonleaf pondweed	(*Potamogeton epihydrus*)
Leafy pondweed	(*Potamogeton foliosus*)
Variable pondweed	(*Potamogeton gramineus*)
Floatingleaf pondweed	(*Potamogeton natans*)
Claspingleaf pondweed	(*Potamogeton richardsonii*)
Flatstem pondweed	(*Potamogeton zosteriformis*)
Arrowhead	(*Sagittaria latifolia*)
Willow	(*Salix interior*)
Threesquare	(*Scirpus americanus*)
Softstem bulrush	(*Scirpus validus*)
Sago pondweed	(*Stuckenia pectinaus*)

Plants That May Decrease in Growth

Marsh marigold	(*Bidens sp*)
Watershield	(*Brasenia schreberi*)
Cabomba	(*Cabomba caroliniana*)
Coontail	(*Ceratophyllum demersum*)
Water hyacinth	(*Eichhornia crassipes*)
Needlerush	(*Eleocharis acicularis*)
Elodea	(*Elodea canadensis*)
Primrose willow	(*Jussuaea diffusa*)
Duckweed	(*Lemna sp*)
Milfoil	(*Myriophyllum sp*)
Spatterdock	(*Nuphar variegatum*)
White waterlily	(*Nymphaea tuberosa*)
Curlyleaf pondweed	(*Potamogeton crispus*)
Fern pondweed	(*Potamogeton robbinsii*)
Bladderwort	(*Utricularis sp*)

Advantages and Disadvantages of Drawdown

Advantages of a drawdown include the following:

- Inexpensive plant control for lakes with suitable outlet structures.
- Several species of native plants may increase in distribution after the lake is refilled.
- With partial drawdowns, fish are concentrated and gamefish predation on smaller fish may result in an improved fishery.
- Loose, flocculent sediments may consolidate or become more compacted.
- Lake residents may repair or improve docks and shoreland conditions.

Disadvantages of a drawdown include the following:

- If high capacity pumps are needed to drawdown the water level, this option could be expensive.
- Sometimes the lake takes a year or more to refill.
- If sediments don't freeze, curlyleaf control may not be successful. Snowfall before a hard freeze may insulate the sediments and prevent freezing.
- Some aquatic wildlife such as turtle and frogs could be killed with a water level drawdown.
- In a partial drawdown, with a lower water volume, fish could die over winter if the dissolved oxygen levels get too low.
- Sometimes exposing lake sediments results in phosphorus release and algae blooms when the lake is refilled.
- Fringe wetlands could be impacted.
- Water levels may be lower in lakeside water wells during drawdown.

Biocontrol: Biological control (also called biocontrol) is broadly defined as the planned use of one organism (for example, an insect) to control or suppress the growth of another organism such as a weedy plant species. Biocontrol of weeds is primarily the search for, and introduction of, species-specific organisms that selectively attack a single target species such as a non-native weed. Two different approaches are currently used in the biocontrol of aquatic weeds: classical (importation of natural enemies from their native range) and non-classical (augmentation of naturally occurring agents already present, but low in density to control a non-native plant infestation).

Classical biocontrol is the most common biological control method and typically involves the introduction of natural enemies from their native home to control a non-native invasive plant. In classical biocontrol, the planned introduction and release of non-native target-specific organisms (such as beetles or plant pathogens) from the weed's native range should reduce the vigor, reproductive capacity or density of the target weed in its new range. An example of classical biocontrol is the release of the European leaf eating beetle (*Galerucella pusilla*) to control the non-native purple loosestrife.

Non-classical biocontrol involves the mass rearing and periodic release of resident or naturalized non-native aquatic weed biocontrol to increase their effectiveness. Augmentative or repeated releases of native or naturalized insects have occasionally been used for suppression of alligatorweed, water hyacinth, and Eurasian watermilfoil. An example of non-classical biocontrol is the rearing of the native milfoil weevil, *Euhrychiopsis lecontei*, to control Eurasian watermilfoil.

Beetles and weevils have been responsible for most successful biocontrol programs. Adults of these insects tend to remain above the water, which may reduce fish predation, whereas larvae often feed inside the plant. These habits allow them to maintain high density populations in the environment. A number of successful weed biocontrol programs have utilized member of the insect group Coleoptera.

Targeted Invasive Plants	Control Effectiveness
Eurasian watermilfoil	Uneven, research is ongoing.
Purple loosestrife	Fair to good in large dense patches of purple loosestrife.

Advantages

- It is relatively inexpensive to develop and use the plant controlling introduced insects compared to other methods of weed control.

- Biocontrol produces selective, long-term control of the target weed and because biocontrol agents reproduce, they will usually spread on their own throughout the infested area.

Disadvantages

- It may not be possible to find a biocontrol agent that effectively controls a single weed and selectively attacks only that particular weed for every invasive plant species.

- When potential biocontrol agents are identified, their establishment and suppression of the target weed in the introduced area are not guaranteed.

- Even if biocontrol does successfully establish in their introduced areas, control is not immediate and agents may require many years to have a major impact on target weeds.

- Once biocontrol agent is established it cannot be recalled if the agent affects desirable nontarget species.

Summary of Control Techniques for Non-Native Curlyleaf Pondweed and Eurasian Watermilfoil

Herbicides

Herbicides were applied just below the lake surface.

Herbicides: Early season (April or May) application of an endothall herbicide has been used to control curlyleaf pondweed in lakes. Endothall has been used for spot treatments as well as lake-wide curlyleaf control. For Eurasian watermilfoil control, 2,4-D and triclopyr have commonly been used primarily for spot treatments. In special cases, whole-lake treatments for curlyleaf and milfoil have been conducted using fluridone.

Harvesting

Harvesting: Mechanical harvesting is used to control curlyleaf pondweed in May and June and is used to control Eurasian watermilfoil in June, July, and August. When curlyleaf is cut, it generally does not grow back. However, milfoil will grow back at a rate of 1 to 2 inches per day. The cutter bar will cut plants to a depth of about 5 feet below the surface. It takes about 1 to 4 hours per acre to harvest plants.

Drawdown

Drawdown: Exposed lake sediments that freeze over-winter generally kill curlyleaf turions and provide good curlyleaf control for several years. Eurasian watermilfoil is also mostly controlled with a winter drawdown. There is not much information on the effects of summer drawdowns and is rarely used in Minnesota for curlyleaf or milfoil control. The drawdown technique has limitations. Lakes without a drawdown capability will have to be pumped down or siphoned and fish kills are likely unless winter aeration is used.

Biocontrol (Biological Approaches)

Biocontrol: The use of organisms to control Eurasian watermilfoil is ongoing but there is no active program for biological control of curlyleaf pondweed in Minnesota. The milfoil weevil (*Euhrychiopsis lecontei*) is the biological control agent that is used for controlling heavy growth of Eurasian watermilfoil. In other states, milfoil control with the weevil has mixed results. In Minnesota, significant research has been conducted at the University of Minnesota to better understand the capabilities of the milfoil weevil, but milfoil control programs are at an early stage of propagating the local weevils in great enough numbers to reduce heavy milfoil growth.

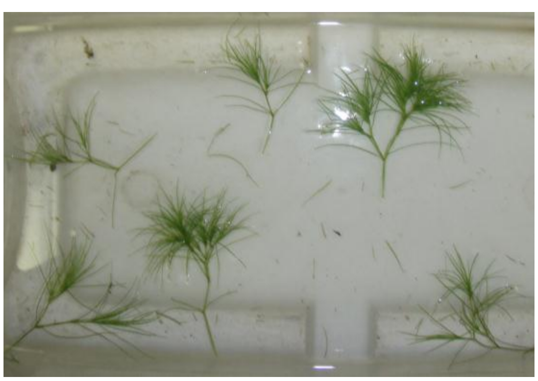
Control Techniques for Other Non-Native Aquatic Plants

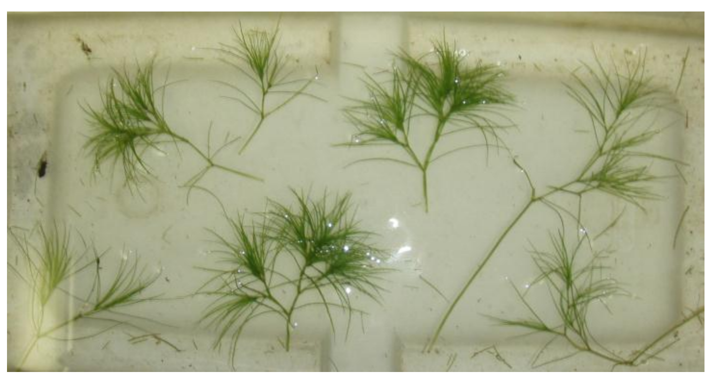
Although curlyleaf pondweed and Eurasian watermilfoil are two of the most common submersed non-native plants, other non-native aquatic plants are found in Minnesota and some, although not present at this time, may became established in the future and control techniques would then be considered.

Several examples of non-native aquatic plants and control options are listed on the next few pages.

***Brazilian Elodea** (found in Powderhorn Lake in 2009 and treated - not established)*
Aquathol – endothall

***Brittle Naiad** (Lac Lavon (Burnsville) and Round Lake (Eden Prairie) only lakes infested in Minnesota)*
Reward – diquat
Hydrothol and Aquathol – endothall





Curlyleaf Pondweed ***(widely distributed)***

Aquathol – endothall

Drawdown
Harvesting

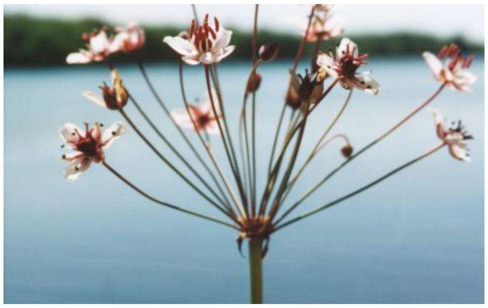
Eurasian Watermilfoil ***(widely distributed)***

Navigate – 2,4-D
Renovate - trichlopyr
Sonar – fluridone

Drawdown
Harvesting
Milfoil weevils

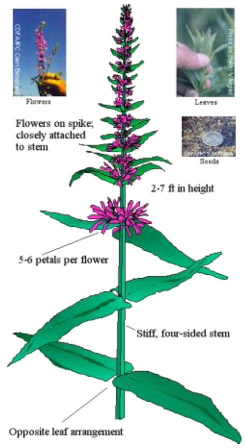
Flowering Rush ***(Lake Minnetonka, Detroit Lake, several other water bodies)***

Habitat – imazapyr (emergent plant)
Aquathol – endothall (submersed plant)
Reward – diquat (submersed plant)
Cutting
Pulling



Purple Loosestrife ***(widely distributed)***

Rodeo – glyphosate
Garlon 3A – trichlopyr
Habitat – imazapyr
Beetles – *Galerucella spp*



Caroline Savage, St. Lawrence Centre

Water Hyacinth ***(occasionally found in Minnesota - not established)***

Navigate – 2,4-D
Reward – diquat
Clearcast – imazamox
Habitat – imazapyr
Galleon – penoxsulam
Renovate - triclopyr

Water Lettuce ***(occasionally found in Minnesota - not established)***

Reward - diquat
Galleon - penoxsulam

Herbicide Options for Future Invasive Species

- **Hydrilla (diquat; fluridone)**
- **Water Chestnut (2,4-D)**
- **Water Soldier (diquat; endothall)**

Minnesota Rules and Regulations for Aquatic Plant Control

(Aquatic plant regulations shown below are from the MnDNR website)

Under Minnesota law, aquatic plants growing in public waters are the property of the state. Because of their value to the lake ecosystem, they may not be destroyed or transplanted unless authorized by the Commissioner of the Department of Natural Resources as stipulated in the Aquatic Plant Management Rules. (A "public water" is generally any body of water 2.5 acres or larger within an incorporated city limit, or 10 acres or larger in rural areas. If you are unsure whether a particular lake is public, please contact your local DNR office).

Activities not allowed:

- Excavating the lake bottom for aquatic plant control
- Use of hydraulic jets
- Destroying or preventing the growth of aquatic plants by using lake bottom barriers.
- Removing aquatic vegetation within posted fish-spawning areas.
- Removing aquatic plants from an undeveloped shoreline.

Removing aquatic plants where they do not interfere with swimming, boating, or other recreation.

Control methods which must have a permit

- Destruction of any emergent vegetation (for example, cattails and bulrushes).
- Cutting or pulling by hand, or by mechanical means, submerged vegetation in an area larger than 2,500 square feet.
- Applying herbicides or algicides.
- Moving or removing a bog of any size that is free-floating or lodged in any area other than its place of origin in public waters.
- Transplanting aquatic plants into public waters.
- Use of automated aquatic plant control devices (such as the Crary WeedRoller).
- Physical removal of floating-leaf vegetation from an area larger than a channel 15 feet wide extending to open water.

When a permit is not needed

If you are a lakeshore-property owner who wants to create or maintain a swimming or boat-docking area, you may cut or pull submerged vegetation, such as Elodea, without a DNR permit under certain conditions:

- First, the area to be cleared must be no larger than 2,500 square feet.
- Second, the cleared area must not extend more than 50 feet along the shoreline or one-half the length of your shoreline, whichever is less.

A boat channel up to 15 feet wide, and as long as necessary to reach open water, may also be cleared, through submerged vegetation. (The boat channel is in addition to the 2,500 square feet allowed). The cutting or pulling may be done by hand or with hand-operated or powered equipment that **does not significantly alter the course, current, or cross-section of the lake bottom**. Such control cannot be done with draglines, bulldozers, hydraulic jets, suction dredges, and automated untended aquatic plant control devices, or other powered earth-moving equipment. After you have cut or pulled aquatic plants, you must dispose of them on land to prevent them from drifting onto your neighbor's property or washing back into the lake. In addition, a channel 15 feet wide through floating-leaf vegetation (except yellow lotus, a protected wildflower) extending to open water may be maintained by mechanical means without a permit. Any other destruction of floating-leaf vegetation requires a permit. If you have questions on control activities that do not require a permit, please contact your local DNR office.

A DNR permit is not needed to gather aquatic plants for personal use (except for wild rice and yellow lotus) or for constructing a shooting or observation blind.

Applying for a permit

To apply for a permit, contact the Aquatic Plant Management Program or the closest regional office. The DNR does not grant permits automatically. Site inspections are required for first time permits. Applications may be denied or modified for several reasons: because the plant beds in question are too valuable for fish or wildlife or because the plants are part of protected natural areas. To ensure that plant control is done correctly and with proper care for the environment, take these three steps:

1. If herbicides are permitted carefully read the product label and follow all instructions.
2. Notify the DNR before control operations begin, as specified on the permit.
3. Post signs that identify the area that will be treated with an herbicide. (These signs are included with the permit or are furnished by the DNR to the commercial applicator.) There may be water use restrictions required on the product label for swimming, fish consumption, irrigation, or household use until the herbicide is broken down or has been diluted to safe levels. You will be asked to report the actual size of the controlled area and the amount of chemical used. This will help the DNR monitor statewide use of aquatic herbicides.

[*Note: All herbicide applications need a permit. However, some herbicides can be applied by the homeowner (with a permit). Diquat products (like Reward) and some endothall products (like Hydrothal 191) can be applied only by a licensed applicator. Make sure to read the product label before using.*]

Cost of Control Methods

Aquatic plant control costs vary greatly. For herbicides, costs depend on the size of the treatment area and water depths. For harvesting costs depend on the size of the treatment area, density of the plants, and ease of access. Drawdown costs are dependent on the method used to lower water levels. Biological approaches can be inexpensive if lake users volunteer to raise beetles for purple loosestrife control, but at this time, it can be expensive to raise milfoil weevils for milfoil control primarily because techniques are being developed. A range of aquatic plant control costs are shown in Table 16.

Table 16. Range of costs of aquatic plant control on a per acre basis.

	Costs	Comments
Herbicides	$290 - $550	Lakewide treatments, will be less expensive than spot treatments on a cost per acre basis.
Harvesting	$350 - $700	Hourly rates for harvesters vary. Small harvesters cost $120-$180 per hour and large harvesters cost $200-$270 per hour. However, the cost per acre is similar. Less dense plant growth is less expensive than heavy growth on a per acre basis.
Drawdown	$0 - $300	A lake with a controlled outlet (dam) is the easiest and cheapest to drawdown. Lakes that do not have a dam will likely have to be pumped down using big pumps and pipes and hoses. In some cases, a siphon can be used and pumps are not needed.
Biological Approaches	$0 - $1,000	Using commercially supplied milfoil weevils from out of state to control Eurasian watermilfoil is not allowed by the MnDNR.

Discussion of the Herbicide Literature

Factors to consider regarding the herbicide literature are wide-ranging and several are outlined below.

Wide variety of literature published in peer reviewed papers and in the gray literature have different conclusions: The basic science is better in peer reviewed papers compared to non-peer reviewed papers (also called the gray literature). Results from peer-reviewed articles found in scientific journals should be considered more heavily than articles from the gray literature that are not peer reviewed.

Terrestrial vs aquatic herbicide use: The results of research based on terrestrial studies are not always applicable to aquatic settings. Frequently, the active ingredients of an herbicide of a terrestrial study are not used in aquatic environments.

Dose and concentration definitions: Toxicity of herbicides are presented in a number of ways. In regard to humans and mammals, toxicity is typically described as a dose in terms of the amount of the active ingredients (in mg) per weight of the subject (in kg). This toxicity category relates to the product coming out of the container at full strength and is most relevant for applicators or herbicide handlers. In the case of aquatic organisms toxicity is described as a concentration in terms of the amount of the active ingredient (in mg) in a volume (in liters). The herbicide concentrations that would be toxic to a fish would not likely be toxic to a human.

Different formulations using the same active ingredient: Some herbicides have the same active ingredient, but with a different formulation. For example, 2,4-D has an ester formulation and an amine formulation. The ester formulation is considered to be a little "hotter" or more lethal to target plants, but has a higher toxicity than the amine formulation. Navigate, a common 2,4-D herbicide used for Eurasian watermilfoil control, uses an ester formulation, butoxyethyl ester, abbreviated as BEE.

Exposure associated with studies of herbicide effects: As part of the testing process, exceptionally high concentrations of the active ingredients are used to bring about effects in the test organisms. These concentrations should not be encountered in standard operating conditions. However, results are sometimes subjective. Its possible herbicide exposure impacts could be underestimated or overestimated.

Impacts change as new data are received: In 1992, 2,4-D was not considered to be an endocrine disrupter. In 2009, US EPA says 2,4-D is suspected to be an endocrine disrupter. As new information is acquired impacts of herbicides will be reevaluated.

Ecological risk: Risk is an assessment of the potential for adverse effects that result from some activity. The toxicity of a product alone does not indicate risk. Risk is sometimes quantified by assigning statistical outcomes to various probabilities and then combining the data. However uncertainty regarding the impacts of using herbicides is still present and uncertainty is immeasurable.

In summary, the herbicide literature is broad and extensive. Most of the herbicide literature is geared toward terrestrial conditions and not aquatic. Risk analysis has been used to gage the impacts of a herbicide in general. The risk analysis prepared by EPA has found herbicide applications have an acceptable risk for use. However, there is still uncertainty associated with herbicide use and uncertainty is not measurable. Therefore there will be concerns by some who view the risk to be too high and the uncertainty to be significant, although not quantifiable.

Ultimately the decision to use herbicides for aquatic plant control is a personal decision. Regulatory agencies allow the use of herbicides indicating it is an acceptable risk. However, uncertainty remains regarding subtle or undocumented impacts of aquatic herbicides to plants and animals (including humans).

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APPENDIX

Appendix A: HRAC Classification of Herbicides

Appendix B: How Various Herbicides Work, Grouped by the HRAC Classification

Appendix A: ***The Herbicide Resistance Action Committee (HRAC) classification of terrestrial and aquatic herbicides is shown below. Herbicides are arranged alphabetically by HRAC groups, A-Z. Included in the table are the Site of Action, the Chemical family, the Active Ingredient, and the WSSA (Weed Science Society of America) group number designation (source: HRAC website).***

Classification of Herbicides According to Site of Action

Farmers, advisors and researchers should know which herbicides are best suited to combat specific resistant weeds. To support the use of herbicides suitable for resistance management the enclosed classification of herbicides is proposed.

The herbicides are classified alphabetically according to their target sites, sites of action, similarity of induced symptoms or chemical classes.

If different herbicide groups share the same site of action only one letter is used. In the case of photosynthesis inhibitors subclasses C_1, C_2 and C_3 indicate different binding behavior at the binding protein D_1 or different classes. Bleaching can be caused by different ways. Accordingly subgroups F_1, F_2 and F_3 are introduced. Growth inhibition can be induced by herbicides from subgroups K_1, K_2 and K_3. Herbicides with unknown sites of action are classified in group Z as "unknown" until they can be grouped exactly.

Classification of Herbicides

Since the system was in part developed in co-operation with the "Weed Science Society of America (WSSA)" new herbicides should be categorized jointly by HRAC and WSSA.

For reference the numerical system of the WSSA is listed, too.

The aim of HRAC is to create a uniform classification of herbicide sites of action in as many countries as possible.

Such a classification system can be useful for many instances but there are cases where weeds exhibit multiple resistance across many of the groups listed and in these cases the key may be of limited value.

The system itself is *not* based on resistance risk assessment but can be used by the farmer or advisor as a tool to choose herbicides in different sites of action groups, so that mixtures or rotations of active ingredients can be planned.

The WSSA and HRAC systems differ in minor ways. Herbicides in *italics* are listed on the HRAC classification system but are not listed on the WSSA classification.

January 2005

HRAC: Herbicide classification

HRAC Group	Site of Action	Chemical Family	Active Ingredient	WSSA Group
A	Inhibition of acetyl CoA carboxylase (ACCase)	Aryloxyphenoxy-propionate „FOPs"	clodinafop-propargyl cyhalofop-butyl diclofop-methyl fenoxaprop-P-ethyl fluazifop-P-butyl haloxyfop-R-methyl propaquizafop quizalofop-P-ethyl	1
		Cyclohexanedione „DIMs"	alloxydim butroxydim clethodim cycloxydim *profoxydim* sethoxydim *tepraloxydin* tralkoxydim	
		Phenylpyrazoline „DEN"	pinoxaden	
B	Inhibition of acetolactate synthase ALS (acetohydroxyacid synthase AHAS)	Sulfonylurea	amidosulfuron azimsulfuron bensulfuron-methyl chlorimuron-ethyl chlorsulfuron cinosulfuron cyclosulfamuron ethametsulfuron-methyl ethoxysulfuron flazasulfuron flupyrsulfuron-methyl-Na foramsulfuron halosulfuron-methyl *imazosulfuron* iodosulfuron mesosulfuron metsulfuron-methyl nicosulfuron *oxasulfuron* primisulfuron-methyl prosulfuron pyrazosulfuron-ethyl rimsulfuron sulfometuron-methyl sulfosulfuron thifensulfuron-methyl triasulfuron tribenuron-methyl trifloxysulfuron triflusulfuron-methyl *tritosulfuron*	2
		Imidazolinone	imazapic imazamethabenz-methyl **imazamox*** **imazapyr*** imazaquin imazethapyr	
		Triazolopyrimidine	cloransulam-methyl diclosulam florasulam flumetsulam *metosulam* ***penoxsulam****	

HRAC Group	Site of Action	Chemical Family	Active Ingredient	WSSA Group
B		Pyrimidinyl(thio)benzoate	bispyribac-Na pyribenzoxim *pyriftalid* pyrithiobac-Na *pyriminobac-methyl*	
		Sulfonylaminocarbonyl-triazolinone	flucarbazone-Na propoxycarbazone-Na	
C1	Inhibition of photosynthesis at photosystem II	Triazine	ametryne atrazine cyanazine desmetryne *dimethametryne* prometon prometryne propazine simazine simetryne terbumeton terbuthylazine *terbutryne* trietazine	5
		Triazinone	hexazinone metamitron metribuzin	
		Triazolinone	Amicarbazone	
		Uracil	bromacil *lenacil* terbacil	
		Pyridazinone	pyrazon = chloridazon	
		Phenyl-carbamate	desmedipham phenmedipham	
C2	Inhibition of photosynthesis at photosystem II	Urea	*chlorobromuron* chlorotoluron *chloroxuron* dimefuron diuron *ethidimuron* *fenuron* fluometuron (see F3) isoproturon *isouron* linuron methabenzthiazuron *metobromuron* metoxuron monolinuron *neburon* siduron tebuthiuron	7
		Amide	propanil *pentanochlor*	
C3	Inhibition of photosynthesis at photosystem II	Nitrile	*bromofenoxim* bromoxynil ioxynil	6
		Benzothiadiazinone	Bentazon	
		Phenyl-pyridazine	pyridate *pyridafol*	
D	Photosystem-I-electron diversion	Bipyridylium	<u>**diquat***</u> paraquat	22

HRAC Group	Site of Action	Chemical Family	Active Ingredient	WSSA Group
E	Inhibition of protoporphyrinogen oxidase (PPO)	Diphenylether	acifluorfen-Na bifenox *chlomethoxyfen* *fluoroglycofen-ethyl* fomesafen *halosafen* lactofen oxyfluorfen	**14**
		Phenylpyrazole	*fluazolate* pyraflufen-ethyl	
		N-phenylphthalimide	cinidon-ethyl **flumioxazin*** flumiclorac-pentyl	
		Thiadiazole	fluthiacet-methyl *thidiazimin*	
		Oxadiazole	oxadiazon oxadiargyl	
		Triazolinone	azafenidin *carfentrazone-ethyl* *sulfentrazone*	
		Oxazolidinedione	*pentoxazone*	
		Pyrimidindione	*benzfendizone* butafenacil	
		Other	*pyraclonil* *profluazol* flufenpyr-ethyl	
F1	Bleaching: Inhibition of carotenoid biosynthesis at the phytoene desaturase step (PDS)	Pyridazinone	norflurazon	**12**
		Pyridinecarboxamide	diflufenican picolinafen	
		Other	beflubutamid **fluridone*** flurochloridone flurtamone	
F2	Bleaching: Inhibition of 4-hydroxyphenyl-pyruvate-dioxygenase (4-HPPD)	Triketone	mesotrione sulcotrione	**27**
		Isoxazole	*isoxachlortole* isoxaflutole	
		Pyrazole	benzofenap pyrazolynate pyrazoxyfen	
		Other	*benzobicyclon*	
F3	Bleaching: Inhibition of carotenoid biosynthesis (unknown target)	Triazole	amitrole (in vivo inhibition of lycopene cyclase)	**11**
		Isoxazolidinone	clomazone	**13**
		Urea	fluometuron (see C2)	
		Diphenylether	aclonifen	

HRAC Group	Site of Action	Chemical Family	Active Ingredient	WSSA Group
G	Inhibition of EPSP synthase	Glycine	**glyphosate*** *sulfosate*	9
H	Inhibition of glutamine synthetase	Phosphinic acid	glufosinate-ammonium *bialaphos = bilanaphos*	10
I	Inhibition of DHP (dihydropteroate) synthase	Carbamate	asulam	18
K1	Microtubule assembly inhibition	Dinitroaniline	benefin = benfluralin *butralin* *dinitramine* ethalfluralin oryzalin pendimethalin trifluralin	3
		Phosphoroamidate	*amiprophos-methyl* *butamiphos*	
		Pyridine	dithiopyr thiazopyr	
		Benzamide	propyzamide = pronamide *tebutam*	
		Benzoic acid	DCPA = chlorthal-dimethyl	3
K2	Inhibition of mitosis / microtubule organisation	Carbamate	*chlorpropham* *propham* carbetamide	23
K3	Inhibition of VLCFAs (see Remarks) (Inhibition of cell division)	Chloroacetamide	acetochlor alachlor butachlor	15
			dimethachlor dimethanamid metazachlor metolachlor *pethoxamid*	
			pretilachlor propachlor *propisochlor* thenylchlor	
		Acetamide	*diphenamid* napropamide *naproanilide*	
		Oxyacetamide	flufenacet mefenacet	
		Tetrazolinone	fentrazamide	
		Other	anilofos *cafenstrole* *piperophos*	
L	Inhibition of cell wall (cellulose) synthesis	Nitrile	dichlobenil *chlorthiamid*	20
		Benzamide	isoxaben	21
		Triazolocarboxamide	*flupoxam*	
		Quinoline carboxylic acid	quinclorac (for monocots) (also group O)	26
M	Uncoupling (Membrane disruption)	Dinitrophenol	*DNOC* *dinoseb* dinoterb	24

HRAC Group	Site of Action	Chemical Family	Active Ingredient	WSSA Group
N	Inhibition of lipid synthesis - not ACCase inhibition	Thiocarbamate	butylate cycloate *dimepiperate* EPTC esprocarb molinate *orbencarb* pebulate prosulfocarb thiobencarb = benthiocarb *tiocarbazil* triallate vernolate	**8**
		Phosphorodithioate	bensulide	
		Benzofuran	*benfuresate* ethofumesate	
		Chloro-Carbonic-acid	*TCA* *dalapon* *flupropanate*	**26**
O	Action like indole acetic acid (synthetic auxins)	Phenoxy-carboxylic-acid	clomeprop **2,4-D*** 2,4-DB dichlorprop = 2,4-DP MCPA MCPB mecoprop = MCPP = CMPP	**4**
		Benzoic acid	chloramben dicamba TBA	
		Pyridine carboxylic acid	clopyralid fluroxypyr picloram **triclopyr***	
		Quinoline carboxylic acid	quinclorac (also group L) quinmerac	
		Other	benazolin-ethyl	
P	Inhibition of auxin transport	Phthalamate Semicarbazone	naptalam diflufenzopyr-Na	**19**
Z	Unknown Note: While the site of action of herbicides in Group Z is unknown it is likely that they differ in site of action between themselves and from other groups.	Arylaminopropionic acid	Flamprop-M-methyl /-isopropyl	**25**
		Pyrazolium	difenzoquat	**26**
		Organoarsenical	DSMA MSMA	**17**
		Other	*bromobutide* *(chloro)-flurenol*	
			cinmethylin	
			cumyluron	
			dazomet	

HRAC Group	Site of Action	Chemical Family	Active Ingredient	WSSA Group
Z			*dymron = daimuron* *methyl-dimuron=* *methyl-dymron* *etobenzanid* fosamine *indanofan* metam *oxaziclomefone* *oleic acid*	
			pelargonic acid pyributicarb	
	Unknown		**endothall***	Not assigned

Remarks: According to information and comments following herbicides are classified in the January 2005 version in HRAC (WSSA) groups.

*Active ingredient used in aquatic herbicides. All other listed active ingredients are found in herbicides used in terrestrial applications.

Appendix B: ***Descriptions of how herbicides work on terrestrial and aquatic plants based on the Herbicide Resistance Action Committee (HRAC). HRAC groups are shown with capital letters in colored boxes with the Weed Science Society of America (WSSA) groups shown with numbers in superscript in parentheses (source: WSSA website).***

Summary of Herbicide Mechanism of Action According to the Herbicide Resistance Action Committee (HRAC) and Weed Science Society of America (WSSA) Classification[1]

$A^{(1)}$

Acetyl CoA Carboxylase (ACCase) Inhibitors

Aryloxyphenoxypropionate (FOPs) and cyclohexanedione (DIMs) herbicides inhibit the enzyme acetyl-CoA carboxylase (ACCase), the enzyme catalyzing the first committed step in *de novo* fatty acid synthesis (Burton 1989; Focke and Lichtenthaler 1987). Inhibition of fatty acid synthesis presumably blocks the production of phospholipids used in building new membranes required for cell growth. Broadleaf species are naturally resistant to cyclohexanedione and aryloxyphenoxy propionate herbicides because of an insensitive ACCase enzyme. Similarly, natural tolerance of some grasses appears to be due to a less sensitive ACCase (Stoltenberg 1989). An alternative mechanism of action has been proposed involving destruction of the electrochemical potential of the cell membrane, but the contribution of this hypothesis remains in question.

$B^{(2)}$

Acetolactate Synthase (ALS) or Acetohydroxy Acid Synthase (AHAS) Inhibitors

Imidazolinones, pyrimidinylthiobenzoates, sulfonylaminocarbonyltriazolinones, sulfonylureas, and triazolopyrimidines are herbicides that inhibit acetolactate synthase (ALS), also called acetohydroxyacid synthase (AHAS), a key enzyme in the biosynthesis of the branched-chain amino acids isoleucine, leucine, and valine (LaRossa and Schloss 1984). Plant death results from events occurring in response to ALS inhibition and low branched-chain amino acid production, but the actual sequence of phytotoxic processes is unclear.

$C_1^{(5)}$ $C_2^{(7)}$ $C_3^{(6)}$

Photosystem II Inhibitors

Phenylcarbamates, pyridazinones, triazines, triazinones, uracils (Group $C_1^{(5)}$), amides, ureas ($C_2^{(7)}$), benzothiadiazinones, nitriles, and phenylpyridazines (Group $C_3^{(6)}$), are examples of herbicides that inhibit photosynthesis by binding to the Q_B-binding niche on the D1 protein of the photosystem II complex in chloroplast thylakoid membranes. Herbicide binding at this protein location blocks electron transport from Q_A to Q_B and stops CO_2 fixation and production of ATP and $NADPH_2$ which are all needed for plant growth. However, plant death occurs by other processes in most cases. Inability to reoxidize Q_A promotes the formation of triplet state chlorophyll which interacts with ground state oxygen to form singlet oxygen. Both triplet chlorophyll and singlet oxygen can abstract hydrogen from unsaturated lipids, producing a lipid radical and initiating a chain reaction of lipid peroxidation. Lipids and proteins are attacked and oxidized, resulting in loss of chlorophyll and carotenoids and in leaky membranes which allow cells and cell organelles to dry and disintegrate rapidly. some compounds in this group may also inhibit carotenoid biosynthesis (fluometuron) or synthesis of anthocyanin, RNA, and proteins (propanil), as well as effects on the plasmalemma (propanil) (Devine et al. 1993).

[1] The capitalized letter in the colored boxes represents the Herbicide Resistance Action Committee (HRAC) classification and the number superscripted in parentheses represents the Weed Science Society of America classification.

Summary of Herbicide Mechanism of Action According to HRAC and WSSA Classification

$D^{(22)}$ Photosystem I Inhibitors

Bipyridyliums are examples of herbicides that accept electrons from photosystem I and are reduced to form an herbicide radical. This radical then reduces molecular oxygen to form superoxide radicals. Superoxide radicals then react with themselves in the presence of superoxide dismutase to form hydrogen peroxides. Hydrogen peroxides and superoxides react to generate hydroxyl radicals. Superoxides and, to a lesser extent, hydrogen peroxides may oxidize SH (sulfhydryl) groups on various organic compounds within the cell. Hydroxyl radical, however, is extremely reactive and readily destroys unsaturated lipids, including membrane fatty acids and chlorophyll. Hydroxyl radicals produce lipid radicals which react with oxygen to form lipid hydroperoxides plus another lipid radical to initiate a self-perpetuating chain reaction of lipid oxidation. Such lipid hydroperoxides destroy the integrity of cell membranes allowing cytoplasm to leak into intercellular spaces which leads to rapid leaf wilting and desiccation. These compounds can be reduced/oxidized repeatedly (Dodge 1982).

$E^{(14)}$ Protoporphyrinogen Oxidase (PPG oxidase or Protox) Inhibitors

Diphenylethers, *N*-phenylphthalimides, oxadiazoles, oxazolidinediones, phenylpyrazoles, pyrimidindiones, thiadiazoles, and triazolinones are herbicides that appear to inhibit protoporphyrinogen oxidase (PPG oxidase or Protox), an enzyme of chlorophyll and heme biosynthesis catalyzing the oxidation of protoporphyrinogen IX (PPGIX) to protoporphyrin IX (PPIX). Protox inhibition leads to accumulation of PPIX, the first light-absorbing chlorophyll precursor. PPGIX accumulation apparently is transitory as it overflows its normal environment in the thylakoid membrane and oxidizes to PPIX. PPIX formed outside its native environment probably is separated from Mg chelatase and other pathway enzymes that normally prevent accumulation of PPIX. Light absorption by PPIX apparently produces triplet state PPIX which interacts with ground state oxygen to form singlet oxygen. Both triplet PPIX and singlet oxygen can abstract hydrogen from unsaturated lipids, producing a lipid radical and initiating a chain reaction of lipid peroxidation. Lipids and proteins are attacked and oxidized, resulting in loss of chlorophyll and carotenoids and in leaky membranes which allows cells and cell organelles to dry and disintegrate rapidly (Duke 1991).

$F_1^{(12)}$ $F_2^{(28)}$ $F_3^{(11)}$ Carotenoid Biosynthesis Inhibitors

Amides, anilidex, furanones, phenoxybutan-amides, pyridiazinones, and pyridines ($F_1^{(12)}$) are examples of compunds that block carotenoid biosynthesis by inhibition of phytoene desaturase (Bartels and Watson 1978; Sandmann and Böger 1989). Carotenoids play an important role in dissipating the oxidative energy of singlet O_2 ($^1O_2$). In normal photosynthetic electron transport, a low level of photosystem II reaction center chlorophylls in the first excited singlet state transform into the excited triplet state (^{3}Chl). This energized ^{3}Chl can interact with ground state molecular oxygen (O_2)to form $^1O_2$. In healthy plants, the energy of $^1O_2$ is safely quenched by carotenoids and other protective molecules. Carotenoids are largely absent in fluridone-treated plants, allowing $^1O_2$ and ^{3}Chl to abstract a hydrogen from an unsaturated lipid (e.g. membrane fatty acid, chlorophyll) producing a lipid radical. The lipid radical interacts with O_2 yielding a peroxidized lipid and another lipid radical. Thus, a self-sustaining chain reaction of lipid peroxidation is initiated which functionally destroys chlorophyll and membrane lipids. Proteins also are destroyed by $^1O_2$. Destruction of integral membrane components leads to leaky membranes and rapid tissue desiccation.

Callistemones, isoxazoles, pyrazoles, and triketones (F_2[(28)]) are examples of herbicides that inhibit *p*-hydroxyphenyl pyruvate dioxygenase (HPPD), which converts *p*-hydroxymethyl pyruvate to homogentisate. This is a key step in plastoquinone biosynthesis and its inhibition gives rise to bleaching symptoms on new growth. These symptoms result from an indirect inhibition of carotenoid synthesis due to the involvement of plastoquinone as a cofactor of phytoene desaturase.

Recent evidence suggests that clomazone (F_3[(11)]) is metabolized to the 5-keto form of clomazone which is herbicidally active. The 5-keto form inhibits 1-deoxy-D-xyulose 5-phosphate synthase (DOXP), a key component to plastid isoprenoid synthesis. Clomazone does not inhibit geranylgeranyl pyrophosphate biosynthesis (Croteau 1992; Weimer 1992).

Amitrole (F_3[(11)]) inhibits accumulation of chlorophyll and carotenoids in the light (Ashtakala, 1989), although the specific site of action has not been determined. Precursors of carotenoid synthesis, including phytoene, phytofluene, carotenes, and lycopene accumulate in amitrole-treated plants (Barry and Pallett 1990), suggesting that phytoene desaturase, lycopene cyclase, imidazoleglycerol phosphate dehydratase, nitrate reductase, or catalase may be inhibited. Other research (Heim and Larrinua 1989), however, indicates that the histidine, carotenoid, and chlorophyll biosynthetic pathways probably are not the primary sites of amitrole action. Instead, amitrole may have a greater effect on cell division and elongation than on pigment biosynthesis.

Aclonifen (F_3[(11)]) appears to act similar to carotenoid inhibiting/bleaching herbicides; but the exact mechanism of action in unknown.

G[(9)]

Enolpyruvyl Shikimate-3-Phosphate (EPSP) Synthase Inhibitors

Glycines (glyphosate) are herbicides that inhibit 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase (Amrhein 1980) which produces EPSP from shikimate-3-phosphate and phosphoenolpyruvate in the shikimic acid pathway. EPSP inhibition leads to depletion of the aromatic amino acids tryptophan, tyrosine, and phenylalanine, all needed for protein synthesis or for biosynthetic pathways leading to growth. The failure of exogenous addition of these amino acids to completely overcome glyphosate toxicity in higher plants (Duke and Hoagland 1978; Lee 1980) suggests that factors other than protein synthesis inhibition may be involved. Although plant death apparently results from events occurring in response to EPSP synthase inhibition, the actual sequence of phytotoxic processes is unclear.

H[(10)]

Glutamine Synthetase Inhibitors

Phosphinic acids (glufosinate and bialophos) inhibit activity of glutamine synthetase (Lea 1984), the enzyme that converts glutamate and ammonia to glutamine. Accumulation of ammonia in the plant (Tachibana 1986) destroys cells and directly inhibits photosystem I and photosystem II reactions (Sauer 1987). Ammonia reduces the pH gradient across the membrane which can uncouple photophosphorylation.

I[(18)]

Dihydropteroate Synthetase Inhibitors

The carbamate herbicide, asulam, appears to inhibit cell division and expansion in plant meristems, perhaps by interfering with microtubule assembly or function (Fedtke 1982; Sterrett and Fretz 1975). Asulam also inhibits 7,8-dihydropteroate synthase, an enzyme involved in folic acid synthesis which is needed for purine nucleotide biosynthesis (Kidd et al. 1982; Veerasekaran et al. 1981).

Summary of Herbicide Mechanism of Action According to HRAC and WSSA Classification

$K_1^{(3)}$ $K_2^{(23)}$ $K_3^{(15)}$

Mitosis Inhibitors

Benzamide, benzoic acid (DCPA), dinitroaniline, phosphoramidate, and pyridine herbicides ($K_1^{(23)}$)are examples of herbicides that bind to tubulin, the major microtubule protein. The herbicide-tubulin complex inhibits polymerization of microtubules at the assembly end of the protein-based microtubule but has no effect on depolymerization of the tubule on the other end (Vaughn and Lehnen 1991), leading to a loss of microtubule structure and function. As a result, the spindle apparatus is absent, thus preventing the alignment and separation of chromosomes during mitosis. In addition, the cell plate can not be formed. Microtubules also function in cell wall formation. Herbicide-induced microtubule loss may cause the observed swelling of root tips as cells in this region neither divide nor elongate.

The carbamate herbicides, carbetamide, chlorpropham, and propham ($K_2^{(23)}$), are examples of herbicides that inhibit cell division and microtubule organization and polymerization.

Acetamide, chloroacetamide, oxyacetamide, and tetrazolinone herbicides ($K_3^{(15)}$)are examples of herbicides that are currently thought to inhibit very long chain fatty acid (VLCFA) synthesis (Husted et al. 1966; Böger et al. 2000). These compounds typically affect susceptible weeds before emergence, but do not inhibit seed germination.

$L^{(20)}$ $L^{(21)}$ $L^{(27)}$

Cellulose Inhibitors

Benzamides (WSSA Group 21), nitriles (Group 20), quinclorac (Group 27), and triazolocarboxamides (Group 27) are herbicides that inhibits cell wall biosynthesis (cellulose) in susceptible weeds (Heim et al. 1990).

$M^{(24)}$

Oxidative Phosphorylation Uncouplers

Dinitrophenols (dinoterb) are herbicides that uncouple the process of oxidative phosphorylation causing almost immediate membrane disruption and necrosis.

$N^{(8)}$ $N^{(16)}$ $N^{(26)}$

Fatty Acid and Lipid Biosynthesis Inhibitors

Benzofuranes (WSSA Group 16), chlorocarbonic acids (Group 26), phosphorodithioates (Group 8), and thiocarbamates (Group 8) are examples of herbicides that are known inhibitors of several plant processes including: 1) biosynthesis of fatty acids and lipids which may account for reported reductions in cuticular wax deposition, 2) biosynthesis of proteins, isoprenoids (including gibberellins), and flavonoids (including anthocyanins), and 3) gibberellin synthesis inhibition which may result from the inhibition of kaurene synthesis. Photosynthesis also may be inhibited (Gronwald 1991). A currently viable hypothesis that may link all these effects involves the conjugation of acetyl coenzyme A and other sulfhydryl-containing biomolecules by thiocarbamate sulfoxides (Casida 1974; Fuerst 1987). The sulfoxide forms may be the active herbicides (Ashton and Crafts 1981).

Summary of Herbicide Mechanism of Action According to HRAC and WSSA Classification

O (4)

Synthetic Auxins

Benzoic acids, phenoxycarboxylic acids, pyridine carboxylic acids, and quinoline carboxylic acids (O(4) and L(27))are herbicides that act similar to that of endogenous auxin (IAA) although the true mechanism is not well understood. The specific cellular or molecular binding site relevant to the action of IAA and the auxin-mimicking herbicides has not been identified. Nevertheless, the primary action of these compounds appears to affect cell wall plasticity and nucleic acid metabolism. These compounds are thought to acidify the cell wall by stimulating the activity of a membrane-bound ATPase proton pump. The reduction in apoplasmic pH induces cell elongation by increasing the activity of enzymes responsible for cell wall loosening. Low concentrations of auxin-mimicking herbicides also stimulate RNA polymerase, resulting in subsequent increases in RNA, DNA, and protein biosynthesis. Abnormal increases in these processes presumably lead to uncontrolled cell division and growth, which results in vascular tissue destruction. In contrast, high concentrations of these herbicides inhibit cell division and growth, usually in meristematic regions that accumulate photosynthate assimilates and herbicide from the phloem. Auxin-mimicking herbicides stimulate ethylene evolution which may in some cases produce the characteristic epinastic symptoms associated with exposure to these herbicides.

P (19)

Auxin Transport Inhibitors

Phthalamates (naptalam) and semicarbazones (diflufenzopyr) are compounds that inhibit auxin transport. These compounds inhibit polar transport of naturally occurring auxin, indoleacetic acid (IAA) and synthetic auxin-mimicking herbicides in sensitive plants. Inhibition of auxin transport causes an abnormal accumulation of IAA and synthetic auxin agonists in meristematic shoot and root regions, disrupting the delicate auxin balance needed for plant growth. When diflufenzopyr is applied with dicamba, it focuses dicamba's translocation to the meristematic sinks, where it delivers effective weed control at reduced dicamba rates and across a wider range of weed species. Sensitive broadleaf weeds exhibit rapid and severe plant hormonal effects (e.g., epinasty) after application of the mixture; symptoms are visible within hours, and plant death usually occurs within a few days. Symptomology, in sensitive annual grasses, is characterized by a stunted growth. Tolerance in corn occurs through rapid metabolism of diflufenzopyr and dicamba.

Z (17) **Z (27)**

Potential Nucleic Acid Inhibitors or Non-descript mode of action

Several herbicides have been identified as having an unknown mode of action including the pyrazoliums (WSSA Group 8), organic arsenicals (Group 17), arylaminopropionic acids (Group 25), and other non-classified herbicides (Group 27).

NC

Not Classified

These herbicides have not been classified by HRAC or WSSA.

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