# Chapter 11: Chemical Control of Aquatic Weeds

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## Introduction

Chemical control – the use of registered aquatic herbicides and algicides – is a technique that is widely employed by aquatic plant managers in both private and public water bodies throughout the United States. Treatments can range in size from backpack spray applications for individual plants or small clusters of plants up to large-scale treatments from boats or helicopters that may target an invasive weed throughout an entire lake. In addition, the objective of some treatments is broad spectrum control of numerous plant species, while most treatments target a specific invasive plant or algal species. The difference in scale, scope, timing, regulations and management objectives associated with the use of aquatic herbicides makes it a challenge to write an all-encompassing single chapter. In this document we seek to explain some of the rules and regulations associated with aquatic herbicide labeling, explain trade, chemical and common names, describe key differences between submersed and emergent applications, contrast contact and systemic herbicides, and provide specific information on each registered aquatic herbicide.

All herbicides discussed in this chapter have undergone EPA review (Appendix A) and have been approved for aquatic use. This does not mean these herbicides are registered or can be used in every state since most states have their own regulatory and registration procedures. In addition, some states require applicators of aquatic herbicides to be certified and licensed before these products can be purchased and used. Many states also require that permits be obtained before herbicides can be applied to bodies of water – even if the waters are privately owned. Herbicide labels and SDS (safety data sheets) are available online on the registrant's website and are excellent sources of information. ***Always read the label on the herbicide and check with the appropriate regulatory agencies in your state before purchasing or applying pesticides to any body of water***.

Like all pesticides, aquatic herbicides have three names: a trade name, a common name and a chemical name. The trade name of a product is trademarked and is owned by the company, whereas the common name and the chemical name are assigned by the American National Standards Institute and the rules of organic chemistry, respectively. For example, consider the aquatic herbicide Rodeo®. The trade name of this herbicide is Rodeo®, the common name is glyphosate and the chemical name is N-(phosphono-methyl) glycine, isopropylamine salt. If a particular pesticide is protected by a patent, there may be only a single trade name associated with that pesticide. However, if the pesticide is off-patent, there may be multiple trade names that share the same common and chemical name. A number of aquatic herbicides are off-patent and have multiple trade names; therefore, we refer to herbicides by their common names only throughout most of this handbook.

There are approximately 300 herbicides registered in the US, but only 14 are currently registered for use in aquatic systems. Herbicide labels often include a list of the nuisance species controlled by the

product, but applicators may be allowed to use the herbicide to control a target weed not listed on the herbicide label provided the product is labeled for use at the desired site of application. For example, if you wish to use an herbicide to control a weed in your pond and the weed is not listed on the herbicide label, you may still be able to use the product to control this particular weed if the label specifies that the herbicide may be used in ponds. However, it is important to check with state authorities before doing so because some states specify that herbicides can only be used to control weeds that are listed on the product label. Additionally, the user accepts liability for the performance of the product if the specific weed is not included on the label.

Herbicides can be classified in several ways, including by their chemical family, their mode of action (how they work) and their time of application in relation to growth of the weed. In this handbook we will classify aquatic herbicides based upon how they are applied (as foliar or submersed treatments – although some herbicides are both) and on their activity in the plant (systemic or contact).

Products that are applied as foliar treatments are most easily recognized by the public. For example, if you have a weed to control, you select a herbicide based on label directions, mix the product with the prescribed amount of water and apply it directly to the weed. Contact products work quickly and kill the plant rapidly on contact (hence the designation "contact"). Systemic compounds, on the other hand, usually work slowly by affecting biochemical pathways and must be absorbed by the plant before providing control; therefore, systemic compounds may require days or weeks to kill the weed. The application method is the same for both systemic and contact herbicides – the compound is applied directly to the foliage of the plant. Foliar herbicides are used to control floating, floating-leaved and emergent aquatic weeds.

Submersed herbicides are applied as concentrated liquids, granules or pellets. Liquid treatments are often mixed with water to facilitate application and to ensure even distribution and are applied to achieve an entire water volume concentration to control submersed weeds and planktonic algae. Some dry formulations (wettable powders, water dispersible granules) are mixed with water and applied similar to liquids, but many granular and pelleted products are applied using granular spreaders. Aquatic herbicide applicators must determine the volume of the water to be treated before applying submersed herbicides to ensure that the appropriate and effective amount of herbicide is used. The following constants are needed to calculate the volume of water before treatment with submersed herbicides:

• The volume of a body of water is calculated in acre-feet, which is a function of area and depth; for example, a lake with an area of 1 acre and a depth of 6 feet has a volume of 6 acre-feet
• A single acre-foot of water comprises around 326,000 gallons of water and weighs around 2.7 million pounds

The volume (in acre-feet) of a body of water or treatment site is used to determine the amount of herbicide needed to control a particular weed. For example, if the label of a herbicide specifies an application rate of 1 ppm (part per million), then 2.7 pounds of the herbicide's active ingredient must be applied for each acre-foot of the water to effectively control the target weed. This results in a concentration of 1 ppm since 2.7 pounds of herbicide are mixed with 2.7 million pounds of water

in each acre-foot. Most herbicide labels include a table that lists application rates, but it may be necessary to perform calculations similar to those described above to ensure that the correct dosage of herbicide is applied. The labels of aquatic herbicides clearly state how these calculations are performed.

## Contact Herbicides

Several herbicides registered for aquatic use are classified as contact herbicides. This term may lead one to believe that these herbicides kill weeds immediately after contacting them. While contact herbicides tend to result in rapid injury and death of the contacted plant tissues, it is important to realize that the term "contact herbicide" refers to the lack of translocation or mobility of the herbicide in the plant after the herbicide is taken into the plant tissue. Herbicides that are able to move through plant tissues following uptake are said to translocate; these products are called "systemic herbicides." This distinction between contact and systemic herbicides has significant implications for the prescribed use of the products and usually describes how quickly weeds may be controlled.

Contact herbicides are often used for foliar treatment of sensitive free-floating plants such as waterlettuce (Chapter 15.8), duckweed (Chapter 15.10) and salvinia (Chapter 15.9) and good spray coverage is essential to ensure control of all individual plants of these species. Contact herbicides are also used to temporarily control a number of emergent aquatic plants. These treatments are often initially effective, but treating emergent plants with a contact herbicide often results in rapid recovery and significant regrowth from plant tissues that do not come into contact with the herbicide. As a result, systemic products are usually preferred for controlling emergent plants because systemic herbicides move or translocate within the plant and kill underground roots and rhizomes, which reduces or eliminates regrowth.

Contact herbicides that are used to control submersed weeds must remain in the water within the treated area for a few hours to a few days so that plants are exposed to a lethal concentration of the herbicide for a sufficient amount of time. The results of a herbicide application designed to control submersed plants is primarily impacted by two key factors:

      1) the concentration of the herbicide in water that surrounds the target plant
      2) the length of time a target plant is exposed to dissipating concentrations of that herbicide

This dose/response phenomenon is herbicide- and plant-specific and has been defined as a concentration and exposure time (CET) relationship. Contact herbicides have relatively short exposure time requirements (often measured in hours or days), which means that these products are used to target specific areas within a larger water body or in areas where significant dilution is expected. Whether for contact or systemic herbicides, the vast majority of poor treatment results following submersed applications are due to an inability to maintain the herbicide in contact with the target plants at a lethal concentration for an appropriate period of time. Each contact herbicide has a different use rate, exposure requirement and selectivity spectrum. While the registered contact herbicides are often referred to as "broad-spectrum" products, there is a range of plant susceptibilities to each of these contact herbicides based on the species, use rate, treatment timing and exposure period. Proper identification of target and nontarget plants is important when selecting a contact product because herbicides can significantly differ in their selectivity to various plant species.

Susceptible submersed plants that are treated with contact herbicides typically show symptoms of herbicide damage within a day or two of treatment and collapse of the target plants can occur within 3 to 14 days. It is important to note that the use of contact herbicides in areas with dense plant populations and warm water temperatures can lead to a situation where decomposing plant tissue quickly depletes the oxygen from the water column, resulting in conditions that can cause a fish kill. Product labels have directions that provide guidance to avoid oxygen depletion when treatments are made under conditions of dense vegetative cover and warmer water temperatures.

| Compound/ Date registered for aquatic use | Primary use | | | Formulation | Mode of Action | Comments |
|---|---|---|---|---|---|---|
| | Submersed | Floating | Emergent | | | |
| Copper 1950s | X | X | | Liquid chelates Granular CuSO$_4$ Granular chelates | Contact Plant cell toxicant | Algae control Also used in combination with other herbicides Often used for submersed plants near potable water intakes Typical use rates: 0.2 to 1 ppm |
| Endothall 1960 | X | X | | Liquid Granular | Contact Inhibits respiration and protein synthesis | Dipotassium salt for submersed plant control Use in irrigation canals (2010) Dimethyl-alkylamine salt for algae and plants that are more herbicide-tolerant Treatment timing affects selectivity Typical use rates: 0.3 to 3 ppm (submersed) |
| Diquat 1962 | X | X | X | Liquid | Contact Inhibits photosynthesis and destroys cell membranes | Broad spectrum Turbidity affects effectiveness Very fast activity on sensitive plants; faster activity under high light conditions Typical use rates 0.1 to 0.37 ppm |
| Peroxides 1980s | | X | | Liquid Granular | Contact Affects cell wall permeability, cell membrane integrity | Algae control, particularly certain species of floating filamentous algae |
| Carfentrazone 2004 | X | X | X | Liquid | Contact Inhibits plant-specific enzyme (PPO); causes rapid desiccation and necrosis | Waterlettuce and broadleaf weed control Activity on select submersed species pH of the water can impact efficacy Typical submersed use rates – 50 to 200 ppb |
| Flumioxazin 2011 | X | X | X | Water dispersible granule | Contact Inhibits plant-specific enzyme (PPO); causes rapid desiccation and necrosis | Waterlettuce, surface sprays for algae control, submersed plant control pH of the water can impact efficacy Typical submersed use rates – 50 to 200 ppb Mixed with glyphosate for emergent plants |

It is important that contact herbicides be applied and distributed as evenly as possible to the target plant (or throughout the water column for control of submersed plants) to ensure that the entire plant – including the rooted portions of the plant near the sediment – is exposed to the herbicide. Poor mixing of contact herbicides within the water column can result in control of plant tissue growing near the water surface, followed by rapid recovery from the lower portions of the plant that were not exposed to the herbicide. Poor control can also result from summer applications when treating lakes that are thermally stratified (Appendix B).

Contact herbicides are currently used for both small-scale treatments such as along shorelines and for large-scale control efforts. Most of the contact herbicides have been registered for many decades and they tend to be versatile with a wide range of use patterns. Combinations of two or more contact herbicides are often used to target specific invasive or nuisance species. The registered contact herbicides (and dates of registration) are described in more detail below. These brief descriptions are not comprehensive, but are meant to serve as a guide to particular historical strengths or potential issues associated with the use of these products.

### Copper (1950s)

Copper is a micronutrient that is needed for healthy growth of animals and is often added to animal feed and to vitamins formulated for human use. Copper is widely used as a fungicide in agricultural systems to control diseases on food crops and copper-based compounds have been used for aquatic plant control since the early 1900s. Copper sulfate is likely the most widely used copper product, but it is corrosive and its effectiveness can be affected by water hardness. Liquid chelated copper compounds were developed in the 1970s to address these problems. Copper compounds are used primarily to control algae and plants growing in irrigation canals, ponds, lakes and reservoirs. Submersed use rates typically range from 0.2 to 1.0 mg/L copper in the water column. There are no restrictions on the use of copper in potable water sources or in waters used for crop irrigation. This allows the immediate use of treated water and helps to explain why copper is widely used to control nuisance plants in drinking water supplies and irrigation canals. Copper acts very quickly on plants and algae and has a short exposure requirement, which can be advantageous when treating small areas or areas subject to rapid dilution. The effectiveness of copper as a herbicide or algicide can be affected by alkalinity or hardness of the water. For example, high alkalinity or hard water can reduce the effectiveness of copper-based products. Despite these limitations, copper remains the major tool for algae control in potable water systems, irrigation canals and in small water bodies. Copper does not biodegrade and regular use can result in increased copper residues in the sediment. Copper is generally considered to be biologically inactive once bound in the sediments.

### Endothall (1960)

Endothall is used primarily to control submersed plants and use rates and methods of application vary widely. Traditional use patterns of endothall have included spot treatments of small target areas in which treatments are generally applied at the highest label rate and species selectivity is not a major concern. Selective use of the product is based on species sensitivity, use rates and treatment timing. The effectiveness of endothall is generally not affected by factors such as alkalinity or turbidity of the water. Within the last several years, large-scale early-season treatments have been applied to target invasive plants such as hydrilla (Chapter 15.1), curlyleaf pondweed (Chapter 15.3) and Eurasian watermilfoil (Chapter 15.2) that persist throughout the winter. These

treatments are conducted before desirable native plants begin to grow in spring, which may allow control of the invasive weeds with limited impact on native species that grow later in the season. It is important to note that these early-season treatments are applied when plant biomass is not at its peak and when water temperatures are cooler. These conditions reduce or prevent oxygen depletion that may occur when fast-acting contact herbicides are applied to dense nuisance populations of weeds in warmer water. Endothall is also widely used in control of submersed weeds and algae in irrigation canals. Endothall has also been used to control weeds in turf and to desiccate cotton and potato plants to aid in harvesting.

## Diquat (1962)

Diquat is a fast-acting contact herbicide that interferes with photosynthesis in susceptible plant species. Diquat effectively controls many free-floating weeds including duckweed, watermeal, waterlettuce and salvinia. As noted above, good coverage is critical when treating these plants because missing a small area or a few individuals can lead to rapid recolonization by these fast-growing floating species. Diquat is also used to control submersed plants in small treatment areas or in areas where dilution may reduce the period of time that plants are exposed to the herbicide. Diquat is generally considered to be a "broad-spectrum" product that kills a wide range of plant species. However, the susceptibility of different submersed species can vary significantly. Diquat can be rapidly inactivated when treating "muddy" or turbid water and the speed of this inactivation can interfere with plant control. There are no hard and fast rules to determine when water is too muddy to treat, but the effectiveness of diquat increases as water clarity increases. Diquat is often mixed with copper-based herbicides to control a broader range of weeds and to improve control of target plants. In addition to its use in aquatic systems, diquat is labeled for weed control in turf and along fence lines and has been used to kill the leaves and vines of potato to increase ease of harvesting.

## Peroxides (1980s)

Several inorganic chemicals produce peroxide (principally hydrogen peroxide) when mixed with water. This contact algicide is used in aquatic systems mainly for control of algae with very limited use for control of submersed vascular plants. Blowers or granular spreaders are used to ensure uniform coverage of the water surface. These compounds produce hydrogen peroxide – which is toxic to some species of algae – when they come into contact with water. Hydrogen peroxide then rapidly breaks down into water, oxygen and other natural products. It is recommended that treatments be applied on sunny days when algal densities remain low. Often used to control algae in potable water supplies, hydrogen peroxide is also widely used in the medical field to kill bacteria.

## Carfentrazone (2004)

Carfentrazone affects a plant-specific enzyme (protoporphyrinogen oxidase); however, the rapid onset of symptoms (membrane destruction, tissue necrosis) is similar to contact herbicides. In contrast to the registered contact herbicides mentioned above, carfentrazone has a much more narrow spectrum of weed control. While this can limit the utility of the product to a few target weeds, it can also result in improved selectivity and reduced damage to nontarget plants. To date, carfentrazone has been used for control of waterlettuce, duckweed and in combination with other herbicides for selective control of some broadleaf emergent plants. Carfentrazone is also labeled for submersed plant control; however, limited use of carfentrazone to date has hampered the development of new use patterns for this product and more research is needed before it will be widely used on submersed weeds. Managers have noted that carfentrazone performance improves

when applications are made on sunny days, but high water pH may reduce carfentrazone activity on submersed plants due to rapid hydrolysis of the herbicide. Carfentrazone is also used for weed control in turf, corn and other crops.

### Flumioxazin (2011)

Flumioxazin has the same mode of action as carfentrazone and the onset of rapid injury is similar to other contact herbicides, but flumioxazin has a broader spectrum of activity compared to carfentrazone. Flumioxazin has only been registered for a short period of time, so use patterns are still being developed. Current uses include control of floating plants such as waterlettuce, duckweed and watermeal, surface mats of filamentous algae (Chapter 13), submersed species such as fanwort (Chapter 15.5), and to enhance control of emergent weeds when used in combination with glyphosate and auxin mimic herbicides. Field use has shown that surface and submersed applications of flumioxazin provide good control of spatterdock (*Nuphar* sp.), waterlily (*Nymphaea* sp.) and American lotus (*Nelumbo lutea*). Water pH significantly affects the activity of this herbicide, particularly in submersed treatments, because flumioxazin degrades very rapidly when water pH is 8 or above, but the role of pH on efficacy of flumioxazin in submersed applications is still being evaluated. Flumioxazin is also widely used in agronomic crops.

## Systemic herbicides – auxin mimics

In contrast to contact herbicides, systemic herbicides are mobile in plant tissue and move through the plant's water-conducting system (xylem) or food-transporting vessels (phloem). Once the herbicide is absorbed into the plant, it can move through one or both of these vessels and throughout the plant tissue to affect all portions of the plant, including underground roots and rhizomes. Auxin mimic herbicides simulate auxin, a naturally occurring plant hormone that regulates plant growth. These herbicides generally target broadleaf plants (dicotyledons or dicots) and are often called "selective herbicides" because many aquatic species (particularly grasses or monocots) are not susceptible to auxin mimic herbicides. In fact, the majority of submersed aquatic plants are monocots, which aids in selectivity when using an auxin mimic. After treatment, the shoot tissue of susceptible plants will often bend and twist (epinasty) and plants will often collapse 2 to 3 weeks after herbicide application. Similar to contact herbicides, auxin mimics that are used to control submersed weeds must remain in the treated area for a few hours to a few days so that plants are exposed to a lethal concentration of the herbicide for a sufficient amount of time. Longer exposure periods (such as 24 to 144 hours) increase the probability that the target weed will be completely controlled, but exposure times of 12 hours or greater may provide good control, provided the application rate and timing are appropriate. The contact herbicides discussed above are used to control a large number of nuisance and invasive plant species, but auxin mimic herbicides are used for control of a much smaller number of plant species.

While there are several aquatic dicotyledons (and some monocots) that show sensitivity to the auxin mimics, these herbicides have historically been used for selective control of a limited number of emergent, floating and submersed plants, including waterhyacinth (Chapter 15.7) and Eurasian watermilfoil. The auxin mimics 2,4–D and triclopyr have very similar use patterns and are used to control broadleaf plants growing among desirable grasses or native submersed plants. This is referred to as "selective control" and is very important in aquatic sites to maintain native species while reducing growth of invasive weeds. These herbicides are also widely used to control weeds in turf, pastures, forestry and other terrestrial sites.

| Compound/ Date registered for aquatic use | Primary use | | | Formulation | Mode of action | Comments |
|---|---|---|---|---|---|---|
| | Submersed | Floating | Emergent | | | |
| 2,4-D 1959 (granular) 1976 (liquid) | X | X | X | Granular ester Granular amine Liquid amine | Systemic Auxin mimic, plant growth regulator | Used for submersed dicots such as Eurasian watermilfoil and for waterhyacinth management Typical use rates: 0.5 to 4 ppm (submersed); 2 to 4 pounds per acre (foliar) |
| Triclopyr 2002 | X | X | X | Liquid Granular | Systemic Auxin mimic, plant growth regulator | Used for submersed dicots such as Eurasian watermilfoil; also for floating and emergent plants Typical use rates: 0.25 to 2.5 ppm (submersed); 1 to 3 pounds per acre (foliar) |

## 2,4–D (1959)

Several nuisance emergent and submersed plants are controlled by 2,4–D, but this herbicide is primarily used for selective control of waterhyacinth and Eurasian watermilfoil. A liquid amine formulation is used to control emergent and submersed plants and a granular ester formulation is used for submersed weed control. In addition, a granular amine formulation has been recently registered. Some native emergent plants – including waterlilies, spatterdock and bulrush – are susceptible to 2,4–D, so care should be taken to avoid injury to these plants. 2,4–D has been used for more than 50 years to control broadleaf weeds in pastures, crops, turf and aquatic systems.

## Triclopyr (2002)

Triclopyr was registered for aquatic use in 2002 and to date the major use of his herbicide has been for selective control of Eurasian watermilfoil. Similar to 2,4–D, there are certainly other plant species that are susceptible to triclopyr; however, the historical strength of auxin mimic herbicides has been selective control of invasives such as Eurasian watermilfoil or waterhyacinth. Triclopyr is registered as both liquid and granular amine formulations. Like 2,4–D, some native non-target emergent plants are susceptible to triclopyr, so care should be taken to avoid injury to these plants. The use of triclopyr in public waters is permitted in some states where 2,4–D use is not allowed. Triclopyr is also labeled for control of broadleaf weeds in turf, forestry and crop production.

**Systemic herbicides – enzyme specific herbicides for foliar use**
Two aquatic herbicides – glyphosate and imazapyr – are labeled only for foliar treatment and control of emergent and floating plants. Both are systemic and readily move through plant tissue to control aboveground and underground portions of the plant. These herbicides inhibit enzymes that plants need to produce proteins that are required for growth, so plants treated with these systemic herbicides slowly "starve" and eventually die. These herbicides target enzymes in a pathway that is found only in plants. Herbicides that target plant-specific enzymes typically show very low toxicity to non-plant organisms such as mammals, fish and invertebrates. Both of these herbicides are truly broad-spectrum and a very limited number of emergent plant species can tolerate exposure to them. These herbicides are especially effective at controlling large monotypic stands of nuisance

emergent plants such as phragmites (Chapter 15.11), cattail and other invasive perennial plants that have extensive rhizome and root systems. Both products result in fairly slow control of target weeds and are often mixed together for plants that are particularly hard to control.

| Compound/ Date registered for aquatic use | Primary use | | | Formulation | Mode of action | Comments |
|---|---|---|---|---|---|---|
| | Submersed | Floating | Emergent | | | |
| Glyphosate 1977 | | | X | Liquid | Systemic Inhibits plant-specific enzyme (EPSP) New growth stunted | Broad spectrum for emergent plant control Plant death may be slow Not active in soil |
| Imazapyr 2003 | | | X | Liquid | Systemic Inhibits plant specific enzyme (ALS) | Broad-spectrum for emergent plant control Plant death may be slow Active in soil – cannot be used in irrigation ditches |

### Glyphosate (1977)

Glyphosate is widely used in agriculture, homeowner and specialty markets, including aquatics. Glyphosate is translocated through treated plant tissues; new growth is disrupted and plants die 1 to 4 weeks after herbicide application. Glyphosate has no soil activity and is rapidly deactivated in natural waters via binding to various cations in the water and therefore it cannot be used for control of submersed weeds. Because this herbicide is rendered inactive so quickly, the irrigation or potable water restrictions associated with the use of glyphosate are minimal. Treatment timing can impact the effectiveness of glyphosate and nuisance species should be treated during late summer or fall when plants are moving sugars to storage organs such as roots or rhizomes in preparation for overwintering. This treatment timing can increase the translocation of glyphosate into the storage organs and often results in enhanced control of the target plant during the following growing season.

### Imazapyr (2003)

Imazapyr is also used in forestry and specialty markets, including aquatics, where it was registered for control of aquatic weeds in 2003. Imazapyr inhibits the plant-specific enzyme acetolactate synthase (ALS), which plays a critical role in protein production in plants. This herbicide has been used to control invasive plants such as spartina or phragmites that have invaded previously unvegetated areas in tidal zones or river flats. Similar to glyphosate, imazapyr readily translocates throughout the plant and new growth is inhibited due to the lack of protein production. Imazapyr should be applied when the plants are actively growing in the spring, summer or fall and is absorbed through plant leaves and roots. Unlike glyphosate, imazapyr is active in the soil so care should be taken to avoid treating areas around the root zones of desirable plants, particularly near trees along the water's edge.

**Systemic bleaching herbicides**

| Compound/ Date Registered for aquatic use | Primary use | | | Formulation | Mode of action | Comments |
|---|---|---|---|---|---|---|
| | Submersed | Floating | Emergent | | | |
| Fluridone 1986 | X | X | | Liquid Granular | Systemic Inhibits plant-specific enzyme (PDS) New shoot growth is bleached | Large-scale or whole-lake management Low use rates, long exposure requirements Treatment timing and use rate affects selectivity Used for some floating plants Typical use rates: 5 to 30 ppb (submersed) |
| Topramezone 2013 | X | X | | Liquid | Systemic Inhibits plant-specific enzyme (HPPD) New shoot growth is bleached | Large-scale or whole-lake management Low use rates, long exposure requirements Treatment timing and use rate affects selectivity Used for some floating plants Typical use rates: 20 to 40 ppb (submersed) |

## Fluridone (1986)

Fluridone is a bleaching herbicide that targets a plant-specific enzyme (phytoene desaturase) that protects chlorophyll, the green pigment responsible for photosynthesis in plants. Fluridone is used primarily to control submersed [e.g., Eurasian watermilfoil, hydrilla and egeria (Chapter 15.4)] and floating plants (e.g., duckweed, watermeal and salvinia) by treating the water column. Fluridone symptoms are highly visible, with the new growth of sensitive plants bleaching or turning white as chlorophyll in the plant is destroyed by sunlight. Susceptible plants will show bleaching symptoms in new shoot growth; however, it is important to note that bleaching symptoms don't always equal control and actual plant death may not occur for months after an initial treatment. Fluridone can be both selective and broad-spectrum and use rates vary from 4 to 150 ug/L. Higher rates often provide broad-spectrum control, whereas lower rates increase selectivity.

Unlike the contact or auxin mimic herbicides that require hours or days of exposure, the fluridone label states that target weeds must be exposed to fluridone for a minimum of 45 days. The extended exposure requirement typically calls for treatment of the entire aquatic system or treatment of protected embayments of lakes or reservoirs. Required exposure periods will often depend on the plant species, stage of plant growth and treatment timing. During the exposure period, new shoot growth of susceptible plants becomes bleached and this continuous bleaching of new growth depletes the plant's reserves of carbohydrates needed for growth. This slow death (which may take 2 or more months) can allow plants to continue to provide structure for habitat and produce oxygen through photosynthesis. Despite the extended herbicide exposure requirements associated with fluridone treatments, there are no restrictions for potable water use, fishing or swimming; however, irrigation restrictions are described on the product label. Fluridone has been used for numerous whole-lake management treatments throughout the United States targeting invasive submersed weeds such as hydrilla and Eurasian watermilfoil.

Fluridone is available in both liquid and pellet formulations. Both products require that plants be exposed to sufficient concentrations of fluridone for an appropriate period of time. As a result, sequential fluridone treatments – often called "bumps" – are usually applied over a period of time to ensure that an effective concentration of the herbicide is maintained. Due to the long-lived nature and critical exposure time requirements, fluridone treatments are often monitored to measure fluridone concentrations in the treated water. This helps to determine if further applications are necessary to maintain a lethal concentration of the herbicide. The main degradation pathway for fluridone is via photolytic processes, or breakdown by ultraviolet wavelengths in sunlight.

Fluridone is also applied to the water column to control floating plants such as duckweed, salvinia and watermeal in small water bodies. Floating plants are generally controlled much more quickly than submersed species. Fluridone can be used in systems of less than one acre and in systems that exceed several thousand acres. Regardless of the size of the treatment, target plants must be exposed to sufficient concentrations of fluridone for an appropriate period of time in order to effectively control target plants.

### Topramezone (2013)

Topramezone is a recently registered bleaching herbicide that targets a plant-specific enzyme (4-hydroxyphenyl-pyruvate dioxygenase) that protects chlorophyll, the green pigment responsible for photosynthesis in plants. Although use patterns are still being developed, it is likely that topramezone will share many of the characteristics described for fluridone.  This includes: 1) low use rates (20 to 40 ppb); 2) extended exposure requirement of > 45 days; 3) rate-based selectivity; 4) bleaching of new plant growth; 5) slow death of target plants; 6) water sampling to manage long-term herbicide concentrations; 7) no use restrictions on drinking, swimming and fishing; and 8) whole-lake or large-scale use patterns. The current topramezone label includes submersed weeds such as hydrilla and Eurasian watermilfoil and floating plants such as duckweed and waterhyacinth. New use patterns will be developed for both small and large water bodies over time as resource managers become familiar with this product. The main degradation pathway for topramezone is via photolysis.

### Systemic herbicides – ALS herbicides

Several recently registered herbicides include compounds that target the plant-specific enzyme acetolactate synthase (ALS). As noted above for imazapyr, this enzyme plays a key role in the production of amino acids needed for protein synthesis in plants and the affected pathway does not occur in animals. In contrast to the broad-spectrum activity described for glyphosate and imazapyr above, the newly registered ALS herbicides tend to be much more selective. Despite a similar mode of action, use patterns vary substantially among these products. Similar to other enzyme specific inhibitors, these herbicides are applied at comparatively low use rates and result in a slow kill of the target weed. Susceptible floating plants are often controlled much more quickly than large emergent rooted plants or submersed plants. Although systemic ALS herbicides do not result in bleaching of new plant growth, they are similar to the bleaching herbicides since they require 1 to 3 or more months of exposure to achieve control of submersed weeds.

| Compound/ Date registered for aquatic use | Primary use | | | Formulation | Mode of action | Comments |
|---|---|---|---|---|---|---|
| | Submersed | Floating | Emergent | | | |
| Penoxsulam 2007 | X | X | | Liquid | Systemic Inhibits plant-specific enzyme (ALS) New growth stunted | Large-scale control of hydrilla and other submersed plants Floating plant control Extended exposure required for submersed plant control Typical use rates: 10 to 30 ppb (submersed) |
| Imazamox 2008 | X | X | X | Liquid | Systemic Inhibits plant-specific enzyme (ALS) New growth stunted | Selective emergent plant control Waterhyacinth control Growth regulation and control in hydrilla Typical use rates: 25 to 75 ppb (submersed) |
| Bispyribac-sodium 2012 | X | X | | Wettable powder | Systemic Inhibits plant-specific enzyme (ALS) New growth stunted | Large-scale control of hydrilla and other submersed plants Floating plant control Extended exposure required for submersed plant control Typical use rates: 20 to 40 ppb (submersed) |

### Penoxsulam (2007)

Penoxsulam was registered for aquatic use in 2007 and is currently applied to control floating species such as waterhyacinth, waterlettuce and salvinia and submersed plants such as hydrilla. Treatments may include foliar application of penoxsulam directly to the target floating plants or submersed application for control of both submersed and floating plants. Penoxsulam use rates and exposure requirements for submersed applications are generally similar to those of fluridone and plant death may occur over a period of 60 to 100+ days depending on the plant species, stage of plant growth and treatment timing. During the exposure period, new shoot growth is inhibited and plants can turn red in color due to stress. The extended exposure requirement typically necessitates treatment of the entire aquatic system or application to protected embayments of lakes or reservoirs where dilution from water exchange is minimized. Combining penoxsulam with the contact herbicide endothall can greatly increase the speed of control and may reduce the penoxsulam exposure requirements. Despite the extended herbicide contact time associated with penoxsulam treatments, there are no restrictions on use of water for drinking, fishing or swimming, but irrigation restrictions are described on the product label. Penoxsulam is also registered for weed control in rice and turf. The main degradation pathway is via photolytic processes.

### Imazamox (2008)

Imazamox was registered for aquatic use in 2008 and is currently used for selective control of large emergent species such as phragmites, Chinese tallow, cattail and wild taro, and for floating species such as waterhyacinth. Emergent and floating plant use patterns are very similar to imazapyr; however, imazamox is often used in situations where greater selectivity is desired. Use of imazamox for submersed plant control has been somewhat limited and has focused on growth suppression of

hydrilla and control of curlyleaf pondweed. Selective use patterns for emergent and submersed applications of imazamox in aquatic systems are still being developed. There are no restrictions on the use of the imazamox-treated water for drinking, fishing, swimming and minimal restrictions for irrigation. Imazamox is also registered for weed control in turf and rice. The main degradation pathway for imazamox is via photolytic processes.

## Bispyribac-sodium (2012)

Bispyribac-sodium was registered for aquatic use in 2012 and it is currently being applied for whole-lake and large-scale treatments of hydrilla. This product is newly registered and a number of use patterns are being evaluated, but use patterns of bispyribac-sodium are likely to be similar to those of penoxsulam. These similarities include: 1) low use rates in the 15 to 40 ppb range; 2) extended exposure requirements of 60 to 100+ days; 3) same mode of action; 4) rapid cessation of new plant growth and slow death of target plants; 5) water sampling to manage long-term herbicide concentrations; 6) no use restrictions on drinking, swimming and fishing; and 7) whole-lake or large-scale use patterns. Bispyribac-sodium is currently being evaluated in combination with flumioxazin and carfentrazone for control of waterhyacinth and other weedy species.

## Herbicide resistance and resistance management

Aquatic plant management has been largely unaffected by issues related to herbicide resistance. Nonetheless, the discovery of large-scale resistance of formerly sensitive populations of hydrilla to the herbicide fluridone in Florida during 2000 and 2001 was an unexpected development that has made aquatic managers much more sensitive to this issue. The biochemical basis for resistance development is beyond the scope of this document; however, factors that are known to foster development of resistance include:

1) repeated use of the same herbicide within and over multiple seasons
2) use of herbicides that target plant-specific enzymes (e.g., ALS inhibitors)

When possible, managers should consider rotation of herbicides to reduce the potential for resistance development. In addition, if a manager observes a formerly sensitive target plant population showing a significant change in response to a herbicide, they should immediately contact an aquatic weed specialist for further evaluation of the situation.

## Herbicide dissipation and half-lives

The length of time a herbicide remains in contact with target plants following a submersed application is critical to achieving desired results. The two key processes that dictate the required exposure of plants to herbicides are herbicide dispersion and degradation. Once applied to the water, herbicides are subject to dispersion or movement both within and away from the treated area. Dispersion initially has a positive influence on the treatment because it facilitates mixing of the herbicide in the water column. The rate of movement of herbicide residues from the treatment area is likely the largest single factor affecting treatment success, especially for those treatments applied to a small area in a larger water body. For example, application of a herbicide to a 10-acre protected cove in a large reservoir may result in limited movement outside of the treatment area and a subsequent long exposure period. In contrast, a 10-acre plot applied along an unprotected shoreline of the same reservoir on the same day may result in the herbicide moving out of the target area and becoming diluted to less-than-lethal concentrations within a few hours of

treatment. Conditions on the day of treatment can also be very important, especially for treatments applied to unprotected areas of larger lakes. High winds or high water flow associated with recent precipitation can have a strong negative influence on treatment results. As the potential range of exposure periods can vary significantly at the same site from day to day, even greater variation between sites is likely. This variation in the expected exposure period will often influence both choice and application rate of the selected herbicide.

In addition to dispersion, herbicide degradation plays a significant role in the effectiveness of a treatment. With the exception of copper (a natural element), all herbicides are subject to degradation pathways that ultimately lead to breakdown products that include carbon, hydrogen and other simple compounds. These degradation pathways result in decomposition of the herbicide to simpler products that lack herbicidal activity via processes such as photolysis (breakdown by ultraviolet rays in sunlight), microbial degradation (breakdown via action of the microbial community) or hydrolysis (breakdown via the action of water splitting the herbicide molecule). Environmental conditions such as temperature, hours of sunlight, trophic status of the water body and pH can all influence the rate of degradation of the different herbicides. In terms of herbicidal effectiveness, degradation pathways are particularly important for products like fluridone or penoxsulam that require long exposure periods of 30 to 100 days. In these situations, the entire water body is often treated and therefore dispersion or dilution is not an issue, but the rate of degradation will often dictate product effectiveness. The role of pH for products that are degraded via hydrolysis such as flumioxazin and carfentrazone is relatively new to aquatic plant management, and managers need to consider pH as a significant factor in product performance. It is also important to mention the phenomenon of herbicide binding in relation to herbicide effectiveness. Several herbicides can bind with various ions in the water column, which can result in a reduction or loss of herbicidal activity. Binding is not a degradation pathway, but it can have an important influence on herbicide effectiveness. The best examples of product binding are the immediate binding of glyphosate to positively charged cations in the water column and the binding of diquat to negatively charged particles such as clay or organic matter in the water column. In both of these cases, the herbicide molecule remains intact but no longer has any herbicidal activity. The bound particles eventually settle to the sediments where microbial degradation takes place. Herbicides that are chemically bound in the sediment no longer have herbicidal activity and undergo microbial degradation over time.

The tables on pages 87 and 88 provide general information about exposure time requirements, typical aqueous half-lives that result from product degradation and the key degradation pathways for aquatic herbicides.

### Herbicide Concentration Monitoring
The above discussion of herbicide dissipation and half-lives is relevant to current use patterns of many aquatic herbicides. Operational monitoring of herbicide concentrations has increased significantly over the past 10 years. The advent of enzyme-linked immunoassays (ELISA) for several of the registered aquatic herbicides (including fluridone, endothall, triclopyr, 2,4–D, penoxsulam and bispyribac-sodium) has largely been responsible for this trend. While monitoring used to be very costly and was associated almost exclusively with regulatory studies or field research trials, several groups now offer monitoring support for operational treatments. When managers select herbicides such as fluridone and bispyribac, the extended exposure requirements and large-scale use patterns

are often supported by monitoring programs. In this case the monitoring can be used to manage the concentrations and exposure periods and to determine when and if additional herbicide applications are necessary to achieve optimal target plant control. In addition, monitoring can be used to determine when herbicide concentrations become low enough that use restrictions on water can be lifted (e.g. irrigation, potable water use). There are numerous potential uses for operational monitoring of aquatic herbicide concentrations and given the value of the information that can be obtained, it is likely this trend will increase in the future.

## Summary

This chapter lists fourteen products that are registered by the EPA for aquatic plant control in aquatic systems. These herbicides are very different from one another; some have been used for decades, whereas others have only recently been approved for use in water. More specific directions regarding the use of these products are on the label and are also available from the companies that manufacture, sell or distribute these herbicides.

## For more information:

•Aquatic Plant Management Society. http://www.apms.org
•University of Florida Center for Aquatic and Invasive Plants. http://plants.ifas.ufl.edu
•US Army Corps of Engineers. http://www.erdc.usace.army.mil/pls/erdcpub/docs

**Contact herbicides: contact exposure requirements, half-lives and degradation pathways**

| Compound | General Exposure Requirements | Typical half-life in water | Key degradation pathway and comments |
|---|---|---|---|
| Copper | Hours to 1 day | Hours to 1+ day | Copper is a natural element and is therefore not subject to degradation. Following application, copper ions are typically bound to particles or chemical ions in the water or sediment, which results in the loss of biological activity. Active copper ions in the water column are more readily inactivated in hard water systems. Concerns have been expressed regarding buildup of copper residues in sediments. |
| Endothall | Hours to days | 2 to 14+ days | Endothall is a simple acid that is degraded via microbial action. Water temperature and the level of microbial activity can have a strong influence on the rate of degradation. Cooler water temperatures typically result in slower rates of degradation. |
| Diquat | Hours to days | ½ to 7 days | Diquat is rapidly bound to negatively charged particles in the water column. Higher turbidity water can result in very fast deactivation of the diquat molecule. The ionic bonds between diquat and charged particles negate herbicidal activity. Once biologically inactivated, diquat is then slowly degraded via microbial action. |
| Peroxides | Minutes to hours | Rapid | Peroxide based algaecides are short lived in the water column and quickly breakdown via abiotic and biotic processes. Degradation is enhanced in warm alkaline waters. The peroxides result in rapid membrane disruption of algal cells. Best results typically occur prior to the onset of a significant bloom. Use of peroxides for submersed plant control is being investigated. |
| Carfentrazone | Hours to 1+ day | Hours to 1 + day | Carfentrazone is degraded via hydrolysis. The rate of hydrolysis is pH–dependent, with faster degradation occurring in higher pH waters. |
| Flumioxazin | Hours to 1+ day | Minutes to 1+ day | Flumioxazin is degraded via hydrolysis and the half-life has been calculated as ~5 days, 24 hours, and 22 minutes at pH of 5, 7, and 9 respectively. The pH can have a strong influence on efficacy of flumioxazin. |

## Systemic herbicides: contact exposure requirements, half-lives and degradation pathways

| Compound | General Exposure Requirements | Typical half-life in water | Key degradation pathway and comments |
|---|---|---|---|
| 2,4-D | Hours to days | 4 to 21+ days | The key degradation pathway for 2,4-D is via microbial action. Water temperature and rate of microbial activity can have a strong influence on the rate of degradation. Photolysis also plays a role in degradation. |
| Triclopyr | Hours to days | 4 to 14+ days | The key degradation pathway for triclopyr is via photolysis or sunlight. Time of year, water depth and water clarity can influence the rate of photodegradation. There is also some microbial action that results in degradation. |
| Glyphosate | Not used for submersed | Hours to 1+ day | Glyphosate is rapidly deactivated once it contacts the water column due to immediate binding with positively charged ions in the water. Once bound to cations, glyphosate is biologically inactive. Microbial action ultimately degrades the glyphosate molecule in the sediment. |
| Imazapyr | Not used for submersed | 7 to 14+ days | The key aqueous degradation pathway for imazapyr is via photolysis. Time of year, water depth and water clarity can influence the rate of photodegradation. Microbial degradation can also play a role. |
| Fluridone | 45+ days | 7 to 30+ days | The key degradation pathway for fluridone is via photolysis. Factors such as water depth, water clarity and season of application can influence photolytic degradation. Microbial activity can also play a supporting role in degradation. |
| Topramezone | 45+ days | 14 to 30+ days | The key degradation pathway for topramezone is via photolysis. Factors such as water depth, water clarity and season of application can influence the rate of photolytic degradation. Microbial activity can also play a supporting role in degradation. |
| Penoxsulam | 45+ days | 7 to 30+ days | The key degradation pathway for penoxsulam is via photolysis. Factors such as water depth, water clarity and season of application can influence photolytic degradation. Microbial activity can also play a supporting role in degradation. |
| Imazamox | 14+ days | 7 to 14+ days | The key degradation pathway for imazamox is via photolysis. Factors such as water depth, water clarity and season of application can influence photolytic degradation. Microbial activity can also play a supporting role in degradation. |
| Bispyribac-sodium | 45+ days | 30+ days | Bispyribac-sodium is degraded via microbial action. Factors such as water temperature, trophic status, and plant density can influence the rate of degradation. Bispyribac-sodium generally has a long half-life; however, faster rates of degradation have been noted in a limited number of sites. |