3.7.1 Chemical Control of Aquatic Weeds

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Introduction

Chemical control – the use of registered aquatic herbicides and algaecides – 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 or small clusters of plants up to large-scale treatments from boats or helicopters that may target an invasive weed throughout an entire lake. While the objective of some treatments is broad spectrum control of numerous plant species, most herbicide applications 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 document. In this section we seek to explain some of the rules and regulations associated with aquatic herbicide labeling; explain the difference between trade, chemical and common names; describe key differences between submersed and emergent applications; contrast contact and systemic herbicides; and provide specific information about each registered aquatic herbicide.

All herbicides discussed in this chapter have undergone EPA review (Section 3.7) 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 or 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 16 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, mechanism of action (specific site within the plant affected by the herbicide), mode of action (how they work and symptoms) and time of application in relation to growth of the weed. In this section we 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, weeks, or even months 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 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 or 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 water body, or treatment site within a water body, is used to determine the amount of herbicide needed to control a targeted weed for a submersed (or in-water) application. 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 herbicide dosage is applied. The labels of aquatic herbicides clearly state how these calculations are performed.

Mechanism of action vs. mode of action

The terms "mechanism of action" and "mode of action" are often used interchangeably. The mechanism of action is the actual biochemical site within the plant affected by the herbicide, whereas the mode of action describes the symptoms that occur after herbicide application leading to plant death. The difference is especially important in selecting herbicides for resistance management (Section 3.7.2). Knowing the mode of action is important to see and verify that plants are responding to an herbicide application. Understanding the mechanism of action allows managers to select an herbicide or combinations of herbicides that will provide acceptable plant management results while also providing some measure of resistance management. The Weed Science Society of America (WSSA) groups herbicides according to their mechanism of action providing managers with a better understanding of the potential for resistance development. The following tables list the mechanism and mode of action along with the WSSA Group for each aquatic-registered herbicide.

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 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 treatments of sensitive free-floating plants such as waterlettuce (Section 2.12), duckweed (Section 2.14) and salvinia (Section 2.13) 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 that herbicide before it dissipates or degrades

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 herbicide because they 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. Warm water holds much less dissolved oxygen than cool water. As microbes that decompose plant tissues increase, they can further consume already low oxygen levels below amounts needed for fish to breathe and survive. 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.

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 (Section 3.7.4).

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 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 historical strengths or potential issues associated with the use of these products.

Compound **Date registered for aquatic use**	**Primary use**			**Formulation**	**Mechanism of action (MOA)** **WSSA resistance management group**	**Mode of action / comments**
	Submersed	**Floating**	**Emergent**			
Copper 1950s	X	X		Liquid chelates Granular $CuSO_4$ Granular chelates	Plant cell toxicant WSSA Group is undefined	- Contact herbicide / algaecide - Used alone or in combination with other herbicides - Often used for submersed plant control near potable water intakes - Typical use rate 0.2 to 1 ppm
Endothall 1960	X	X		Liquid Granular	Inhibits protein phosphatase (PP1) enzyme WSSA Group is undefined	- Fast-acting contact herbicide primarily for submersed weeds - Treatment timing affects selectivity - Dipotassium salt for submersed plant control (typical use rate 2 to 3 ppm) - Increased use in irrigation canals (2010) - Dimethyl-alkylamine salt for algae and plants that are more herbicide-tolerant (typical use rate 0.3 to 3 ppm)
Diquat 1962	X	X	X	Liquid	Photosystem 1 inhibitor WSSA Group 22	- Contact, broad spectrum herbicide - Inhibits photosynthesis and destroys cell membranes - Turbidity affects effectiveness - Very fast activity on sensitive plants; faster activity under high light conditions - Typical use rate 0.1 to 0.37 ppm
Peroxides 2002		X		Liquid (PAA/H_2O_2) Granular (SCP)	Oxidizes algal cell membranes WSSA Group is undefined	- Contact algaecide - Affects cell wall permeability, cell membrane integrity - Algae control, particularly cyanobacteria and certain species of filamentous algae
Carfentrazone 2004	X	X	X	Liquid	Inhibits a plant-specific enzyme (PPO) WSSA Group 14	- Contact herbicide - Causes rapid desiccation and necrosis - Waterlettuce and broadleaf weed control - Activity on select submersed species - pH of the water can impact efficacy - Typical submersed rate 50 to 200 ppm - Typical foliar rate 4 oz per ac
Flumioxazin 2011	X	X	X	Liquid Water dispersible granule	Inhibits a plant-specific enzyme (PPO) WSSA Group 14	- Contact herbicide - Causes rapid desiccation and necrosis - Waterlettuce, surface sprays for algae control, submersed plant control - pH of the water can impact efficacy - Typical submersed rate 50 to 200 ppb - Typical foliar rate 4 to 8 oz per ac - Mixed with glyphosate to control some emergent plants

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 is a fast-acting, broad-spectrum, contact herbicide that kills a wide range of algae (Section 2.18) and aquatic plants primarily used in potable waters, irrigation canals, ponds, lakes and reservoirs. Copper sulfate is likely the most widely used copper product. Submersed use rates typically range from 0.2 to 1.0 ppm 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.

Copper acts 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. High alkalinity or hard water can reduce the effectiveness of copper-based products. Chelated copper compounds were developed in the 1970s to address these problems. Chelate is a chemistry term meaning combining a metal ion, in this case, copper, with an organic molecule, triethanolamine or ethylenediamine. Chelated liquid copper products reportedly remain in solution longer than copper salts when applied to hard water. Copper that is in solution (suspended in the water) for a longer time has greater effect on the aquatic plants and algae. Copper chelates are broken down by hydrolysis and rapidly decline to ambient concentrations with a half-life in water of 2 to 8 days depending on conditions.

All copper formulations are considered toxic to mollusks and can be toxic to some species of fish at relatively low doses, especially if the water has less than 50 ppm of carbonate hardness (soft water). Levels of 1 to 5 ppm are toxic to fish, so copper is applied for aquatic weed and algae control at concentrations of 1.0 ppm or less. Toxicity generally decreases as water hardness increases. 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 acid, first available as an aquatic herbicide in the 1960s, was originally used in agriculture as a plant desiccant. In aquatic sites, endothall is used primarily to control submersed plants and use rates and methods of application vary widely. Endothall is fast-acting and is treated as a contact herbicide but it may be somewhat mobile in plant tissues. Endothall is absorbed by submersed plants in lethal concentrations in 12 to 36 hours depending on the concentration applied. Endothall acid works by interfering with plant respiration, affecting protein and lipid biosynthesis and disrupting plant cell membranes. It causes cellular breakdown of plants within 2 to 5 days. Symptoms of plant damage, including defoliation and brown shriveled tissues, will become apparent within a week of herbicide application. Plants will fall out of the water column within 3 to 4 weeks after application.

Traditional use patterns of endothall have included spot treatments of small target areas generally applied at the highest label rate and where species selectivity is not a major concern. Selective use 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. In recent years, large-scale early-season treatments of the dipotassium salt formulation of endothall have been applied to target invasive plants such as hydrilla (Section 2.2), curlyleaf pondweed (Section 2.4) and Eurasian watermilfoil (Section 2.3) 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 herbicides are applied to dense nuisance populations of weeds in warmer water. Early season, large-scale application rates are generally effective at concentrations as low as 2 to 3 ppm. It is important to treat the entire target area as quickly as possible to avoid herbicide loss through dilution or degradation. Endothall is also widely used in control of submersed weeds and algae in irrigation canals and has irrigation restrictions.

Diquat (1962)

Diquat is a fast-acting contact herbicide that is rapidly absorbed by plant tissues and interferes with photosynthesis in susceptible plant species. Diquat effectively controls many free-floating weeds via foliar applications including duckweed, watermeal (Section 2.14), waterlettuce, waterhyacinth (Section 2.11) and salvinia. Diquat kills the aerial portions of plants in 24 to 36 hours, which occurs too quickly to allow translocation to other parts of the plant. As noted above, good coverage is critical because missing even 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 time that plants are exposed to the herbicide. It diffuses rapidly through the water column during submersed applications and is quickly absorbed into plant tissue.

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. It can also be applied with low rates of endothall to reduce exposure time needed to control some submersed plants, notably hydrilla. 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 desiccate the leaves and vines of potato to increase ease of harvesting.

Peroxides (2002)

Two peroxide formulations are registered for use in aquatic systems to control filamentous and planktonic algae (Section 2.18), especially blue-green algae (also known as cyanobacteria). Granular formulations are composed of sodium carbonate peroxyhydrate (SCP), whereas liquid formulations are peroxyacetic acid (also called peracetic acid or PAA) and hydrogen peroxide. These contact algaecides are used mainly for control of problematic algae and cyanobacteria in domestic water supply sources, with very limited use for control of submersed vascular plants. Granular SCP rapidly transforms via hydrolysis into hydrogen peroxide and sodium carbonate. The sodium carbonate component degrades to inactive sodium and bicarbonate ions, whereas the hydrogen peroxide is the active component. It works by oxidizing critical algal cellular components, resulting in rapid membrane disruption and death. Hydrogen peroxide then rapidly breaks down into water, oxygen and other natural products, and the half-life for this process is approximately 8 hours. Liquid PAA/hydrogen peroxide has two active ingredients: PAA and hydrogen peroxide. PAA is a high-level oxidant; like hydrogen peroxide, it acts on its target through a strong oxidizing reaction, which releases hydroxyl radicals. Liquid PAA/hydrogen peroxide reacts and releases peroxide radicals quickly, leaving acetic acid (vinegar), which is then broken down to acetate. Blowers or granular spreaders should be used to ensure uniform coverage of the water surface when using granular SCP, which can also be utilized to target benthic algae growing at the bottom of the system. Liquid PAA/hydrogen peroxide can be applied using the same methods and equipment as other liquid algaecides. Best results typically occur when treatments are applied on sunny days prior to the onset of a significant algal bloom. Most formulations of SCP and PAA/hydrogen peroxide may be used to control algae and cyanobacteria in potable water supplies. In addition, PAA/hydrogen peroxide is widely used in the medical field to kill bacteria and viruses. The use of peroxides for submersed plant control has been investigated and is generally not considered to be effective.

Carfentrazone (2004)

Like a systemic herbicide, carfentrazone affects a plant-specific enzyme, in this case protoporphyrinogen oxidase (PPO); however, the rapid onset of symptoms (membrane destruction, tissue necrosis) is similar to contact herbicides. In contrast to the contact herbicides mentioned above, carfentrazone has a much narrower 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. Carfentrazone is absorbed through the leaves and inhibits the PPO enzyme that is important in chlorophyll synthesis. It needs 1 to 2 hours of contact for good herbicidal activity, but is fairly slow-acting once inside the leaves, causing symptoms in 2 to 5 days and plant necrosis (tissue death) in about 3 to 4 weeks.

Carfentrazone breaks down both through microbial action in soil and through hydrolysis with a half-life of 3 to 5 days in water. It has very low toxicity to fish and waterfowl. Carfentrazone has been used for control of waterlettuce and duckweed, and in combination with other herbicides for selective control of some broadleaf emergent plants. It provides good selectivity since it will not control non-target plants like pickerelweed (*Pontederia cordata*) or grasses that may be mixed with targeted invasive species like waterlettuce. Combinations of carfentrazone and imazamox have provided good control of large-flowered primrosewillow (*Ludwigia grandiflora*). Carfentrazone is also labeled for submersed plant control. However, limited use 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 pH waters may reduce carfentrazone activity on submersed plants due to rapid degradation of the herbicide. Carfentrazone is also used for weed control in turf, corn and other crops.

Flumioxazin (2011)

Flumioxazin was registered by the EPA for aquatic use in 2011. It is a contact herbicide with the same mechanism of action as carfentrazone and the onset of rapid injury is similar to other contact herbicides. However, flumioxazin has a broader spectrum of activity compared to carfentrazone. Like carfentrazone, flumioxazin is a PPO enzyme inhibitor. It moves within treated leaves but does not translocate to other areas of the plant. Flumioxazin disrupts plant cell membranes and the result is cell leakage, inhibited photosynthesis, bleaching of the chloroplasts and cell death. Plant necrosis and death is rapid, taking a few days to a week or two. In general, at least 4 hours of contact time is required for good control. The primary breakdown pathway of flumioxazin in water is by hydrolysis and is highly dependent on water pH. Under high pH values (greater than 9), flumioxazin half-life in water is 15 to 20 minutes. Under more neutral pH values (7 to 8), the half-life in water is around 24 hours.

Flumioxazin controls a wide variety of aquatic weeds and algal species. Submersed plants include Eurasian watermilfoil, cabomba (Section 2.6) and hydrilla. Floating waterlettuce, duckweeds, giant salvinia, watermeal and surface mats of some algae are susceptible to flumioxazin. Typical application rates range from 50 to 200 ppb for submersed plants and 4 to 8 oz per acre applied as a foliar spray for floating plants. Flumioxazin use patterns are still being developed, but rates as low as 2 to 4 oz per acre (foliar spray) or 50 ppb (submersed application) are reportedly effective for waterlettuce control. Field evaluations have shown that surface and submersed flumioxazin applications also provide control of the native species spatterdock (*Nuphar* sp.), waterlily (*Nymphaea* sp.) and American lotus (*Nelumbo lutea*). Flumioxazin can be tank-mixed with other contact or systemic herbicides to enhance control of emergent weeds like large-flowered primrosewillow when used in combination with glyphosate, imazamox or auxin mimic herbicides.

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. Most 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 frequently collapse within 2 to 3 weeks. Like 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. Exposure times of 12 hours or greater may provide good control if the application rate and timing are appropriate. Longer exposure periods (such as 24 to 144 hours) increase the probability that the target weed will be completely controlled. The contact herbicides discussed above are used to control a large number of nuisance and invasive plant species. Auxin mimic herbicides are used for control of a much smaller number of plant species.

Compound **Date registered for aquatic use**	**Primary use**			**Formulation**	**Mechanism of action (MOA)** **WSSA resistance management group**	**Mode of action / comments**
	Submersed	**Floating**	**Emergent**			
2,4-D Granular ester - 1959 Liquid amine - 1976 Granular amine - 2009 Liquid acid – 2004	X	X	X	Granular ester and amine Liquid amine and acid	Auxin mimic, plant growth regulator WSSA Group 4	- Systemic herbicide - Absorbs into leaves; moves to growth areas - Selective broadleaf plant control - Used for submersed dicots such as Eurasian watermilfoil and for floating waterhyacinth management - Typical submersed rate 0.5 to 4 ppm - Typical foliar rate 2 to 4 pounds per ac
Triclopyr 2002	X	X	X	Liquid amine Liquid acid	Auxin mimic, plant growth regulator WSSA Group 4	- Systemic herbicide - Absorbs into leaves; moves to growth areas - Used for submersed dicots such as Eurasian watermilfoil and for floating and emergent plants - Typical submersed rate 0.25 to 2.5 ppm - Typical foliar rate 1 to 3 pounds per ac
Florpyrauxifen-benzyl 2018	X	X	X	Liquid: Soluble concentrate (SC) Emulsifiable concentrate (EC)	Auxin mimic, plant growth regulator WSSA Group 4	- Systemic herbicide - New mechanism of action for aquatic plant control - Targets a specific receptor in plants - Selective floating, emergent and submersed plant control - Typical submersed rate 2 to 48 ppb - Typical foliar rate 2.7 fl oz/ac (0.026 to 0.052 pounds a.i. per ac)

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 purple loosestrife (Section 2.16), waterhyacinth 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 natural 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.

2,4–D (1959)

2,4-D (2,4-dichlorophenoxyacetic acid) is the oldest organic herbicide registered in the US and was developed to increase crop yields during World War II. It is also the first selective herbicide since it controls broadleaf plants but usually does not control grasses. It is primarily used for weed control in food crops (grains, corn, sorghum, rice, sugarcane), turf, non-crop areas and in certain aquatic environments. 2,4-D was first applied in aquatic systems to control waterhyacinth in the 1950s. It is a systemic, auxin mimic herbicide that is absorbed by roots and leaves, then translocates and accumulates mainly in the growing points of shoots and roots. 2,4-D interferes with the plant's ability to maintain proper hormone balance. Plants undergo uncontrolled growth in some tissues and halted growth in other tissues. The result is injury to the growing regions of the plant and then a gradual death, usually within 1 to 3 weeks.

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 and a low volatile acid formulation have been recently registered. 2,4-D is applied alone or mixed with other herbicides like diquat, flumioxazin or glyphosate to improve efficacy or resistance management. 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. Microbial degradation is the primary breakdown pathway for 2,4-D, resulting in a half-life that ranges from one to several weeks. The half-life is shorter in warmer months and in waters to which 2,4-D has been previously applied, presumably where microbial activity is greater.

2,4-D is sometimes confused with "Agent Orange", a name given to the military's plant defoliant mixture that was developed and used during the Vietnam War. During the manufacture of Agent Orange (2,4-D mixed with 2,4,5-T), it was contaminated with cancer-causing dioxin (tetrachlorodibenzo-p-dioxin), known as TCDD. Although 2,4-D was one of the components of Agent Orange, it is not Agent Orange, nor does it contain TCDD, nor has it been shown to cause cancer. After numerous lifetime feeding studies in rats and mice, the EPA has categorized 2,4-D as Class D compound (Not Classifiable as to Human Carcinogenicity).

Triclopyr (2002)

Triclopyr has been widely used to control herbaceous and woody plants in non-cropland sites, forestry and pastures. It was registered for aquatic use in 2002. Similar to 2,4–D, several plant species are susceptible to triclopyr; however, the historical strength of this auxin mimic herbicide has been selective control of invasives such as Eurasian watermilfoil or purple loosestrife. Triclopyr is absorbed by foliage and translocates throughout the plant. It moves to areas of new growth and causes a disruption in hormone levels, interfering with normal expansion and division of plant cells. It acts like a growth stimulant in some plant tissues and a growth retardant in others. Symptoms include cupped leaves and twisted stems. Vascular tissue becomes crushed, stopping movement of essential nutrients and sugars, and plants essentially grow themselves to death.

Photolysis is the primary breakdown pathway of triclopyr in water. Triclopyr has a short half-life depending on season and water depth (e.g. 2.5 days in warm shallow water during the summer to 14 days in cooler deeper water in winter). Triclopyr does not bind strongly or adsorb to soil particles. It is registered as both liquid and granular amine salt and liquid acid formulations. Some native non-target emergent plants are more susceptible to triclopyr than they are to 2,4-D, so care should be taken to avoid injury to these plants.

Florpyrauxifen-benzyl (2018)

Florpyrauxifen-benzyl is used for broadleaf and grass control in flooded rice fields and was registered by the EPA for aquatic use in 2018. It has been assigned reduced risk status, is practically non-toxic to fish and wildlife and has no drinking, fishing or swimming restrictions. Florpyrauxifen-benzyl represents a new mechanism of action and offers unique properties for aquatic plant control as a member of the arylpicolinate herbicide chemical family. Florpyrauxifen-benzyl is a systemic herbicide with an affinity for aquatic vegetation. It is an auxin mimic that is absorbed through leaves and shoots via foliar treatments or underwater tissues during in-water applications. Following rapid uptake, the herbicide translocates in the xylem and phloem and accumulates in meristematic tissues where it bonds with a specific target receptor. It mimics the effect of a persistent high dose of the natural plant hormone auxin, causing overstimulation of specific auxin-regulated genes, which results in the disruption of several growth processes in susceptible plants.

Susceptible plants become brittle and shatter within a few days after exposure. Plants exhibit reduced growth and ultimately turn chlorotic and necrotic, reaching a level of control within 1 to 3 weeks after treatment.

The primary breakdown pathway for florpyrauxifen-benzyl in water is by photolysis. The half-life in shallow water is less than 12 hours and 1 to 2 days in deeper water. Breakdown is slightly enhanced via hydrolysis in waters with pH values greater than 8. Very high turbidity or algal content may subtly reduce florpyrauxifen-benzyl uptake by target aquatic weeds following in-water application due to the herbicide's strong binding to organic matter and merit the use of higher rates within the label range. Florpyrauxifen-benzyl is a highly active herbicide and controls susceptible plants at very low application rates or concentrations. For example, foliar rates for susceptible emergent and floating plants are only 0.026 to 0.052 pounds of active ingredient per acre; in contrast, other Group 4 herbicides are often applied at 1 or more pounds per acre. The auxin herbicides have long been used to control Eurasian watermilfoil and this species is controlled by florpyrauxifen-benzyl at concentrations of 8 ppb or lower. Hydrilla, which is not usually affected by auxin herbicides, is susceptible to florpyrauxifen-benzyl and is controlled at concentrations of 20 to 48 ppb. Floating, floating-leaved and emergent weeds such as floatingheart (Section 2.9), waterprimrose (*Ludwigia* spp.) and waterhyacinth are also listed as susceptible on the product label. Because florpyrauxifen-benzyl is active at such low concentrations, care must be taken to avoid damage to susceptible native or non-target plants and irrigation restrictions must be followed. This product was recently registered for aquatic use so additional data and use patterns are being evaluated in several current and planned field operations.

Systemic herbicides – enzyme specific herbicides for foliar use

The herbicides glyphosate and imazapyr are not labeled for submersed use (both break down rapidly in water and thus are not effective for submersed weed control); instead, they are labeled only for foliar treatment and control of emergent and floating plants. They are systemic and readily move through plant tissue to control aboveground and underground portions of emergent plants. These herbicides target enzymes in pathways found only in plants and they inhibit enzymes that are required for growth, so treated plants slowly "starve" and eventually die. Herbicides that target plant-specific enzymes typically show very low toxicity to non-plant organisms such as mammals, fish and invertebrates. Glyphosate and imazapyr herbicides are truly broad-spectrum, and a very limited number of emergent plant species can tolerate exposure to them. Glyphosate and imazapyr are especially effective at controlling large monotypic stands of invasive and nuisance emergent plants such as phragmites (Section 2.15), cattail (*Typha* sp.) and other perennial plants that have extensive rhizome and root systems. Both herbicides 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**	**Mechanism of action (MOA)** **WSSA resistance management group**	**Mode of action / comments**
	Submersed	**Floating**	**Emergent**			
Glyphosate 1977			X	Liquid	Inhibits plant-specific enzyme (EPSPS) WSSA Group 9	- Systemic herbicide - Broad spectrum for emergent plant control - New growth stunted - Plant death may be slow - Not active in soil or in water
Imazapyr 2003			X	Liquid	Inhibits plant-specific enzyme (ALS) WSSA Group 2	- Systemic herbicide - Broad-spectrum for emergent plant control - Plant death may be slow - Active in soil – cannot be used in irrigation ditches

Glyphosate (1977)

Glyphosate is a broad-spectrum, systemic herbicide used to control annual and perennial broadleaf weeds, grasses, trees and certain floating plants. It is widely used in agriculture, homeowner and specialty markets, including aquatics. Glyphosate is translocated through treated plant tissues. It works by interfering with the plant-specific shikimic acid pathway, which produces the enzyme EPSPS, and inhibiting the synthesis of specialized plant amino acids. Without the ability to manufacture these essential components, plant death occurs slowly over a period of 2 to 3 weeks. Animals do not produce these enzymes, which accounts for the very low toxicity of this herbicide to animals. Visible effects on most annual weeds occur within 4 to 7 days (longer on most perennial weeds), and 30 days or more on most woody plants and trees. Glyphosate has no soil activity and is rapidly deactivated in natural waters via binding to various cations in the water. Therefore, it cannot be used for control of submersed weeds. Because this herbicide is rendered inactive so quickly, the irrigation and 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. Glyphosate breaks down in water microbially with a variable half-life of 12 to 60 days. It binds readily with soil or suspended organic particles, effectively inactivating its herbicidal properties. Also, hard water (containing calcium or magnesium cations) used to make a spray solution may bind some of the glyphosate in the mix tank prior to application. Selective management of plants using glyphosate is achieved only by careful application because, in general, glyphosate damages most plants it contacts. There are an increasing number of glyphosate-resistant weeds reported in agricultural settings. Therefore, it is important to rotate or combine herbicides with different MOAs to the extent possible when applying glyphosate.

Imazapyr (2003)

Imazapyr was discovered in the 1970s. It is used in forestry and specialty markets, including aquatics, where it was registered for control of aquatic weeds in 2003. Imazapyr is a systemic herbicide that is quickly absorbed by leaves and shoots and moves to areas of new growth where it shuts down plant growth almost immediately. In this regard, imazapyr acts like a contact herbicide. It inhibits the production of the plant-specific acetolactate synthase (ALS) enzyme; plants are not able to grow without this enzyme, so they eventually starve and die. Susceptible plants become reddish at the growing tips within 1 to 2 weeks and control may take 2 to 6 weeks. Imazapyr is absorbed through plant leaves and roots and should be applied when target plants are actively growing in the spring, summer or fall. If applied to mature plants, a higher concentration of herbicide and a longer contact time will be required.

Imazapyr has been used to control invasive plants such as spartina, phragmites and other perennial weeds that have invaded previously unvegetated areas in tidal zones or river flats. Imazapyr is also applied alone or with glyphosate to control cattail and tussocks (floating masses of herbaceous and woody species). 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. Imazapyr is practically non-toxic (the EPA's lowest toxicity category) to fish, invertebrates, birds and mammals. The primary degradation pathway for imazapyr in water is via sunlight with a half-life of about a week or less. Breakdown is via microbial degradation in terrestrial soils and may take weeks to months.

Systemic bleaching herbicides

Compound Date registered for aquatic use	Primary use			Formulation	Mechanism of action (MOA) WSSA resistance management group	Mode of action / comments
	Submersed	Floating	Emergent			
Fluridone 1986	X	X		Liquid Granular	Inhibits plant-specific enzyme (PDS) WSSA Group 12	- Systemic herbicide - New shoot growth is bleached - Large-scale or whole-lake management - Low use rates, long exposure requirements - Treatment timing and rate affect selectivity - Used for some floating plants - Typical submersed rate 5 to 30 ppb
Topramezone 2013	X	X		Liquid	Inhibits plant-specific enzyme (HPPD) WSSA Group 27	- Systemic herbicide - New shoot growth is bleached - Large-scale or whole-lake management - Low use rates, long exposure requirements - Treatment timing and rate affects selectivity - Used to control some floating plants - Typical submersed rate 20 to 40 ppb

Fluridone (1986)

Fluridone is a systemic herbicide that was discovered in the mid-1970s and was initially used for weed control in cotton. It was later shown to be effective for the control of submersed aquatic plants and was registered by the EPA for aquatic use in 1986. Fluridone is a bleaching herbicide that targets the plant-specific enzyme phytoene desaturase (PDS), which protects chlorophyll (the green pigment responsible for photosynthesis in plants) from damage by UV light. Fluridone is used primarily to control submersed [e.g., Eurasian watermilfoil, hydrilla and egeria (Section 2.5)] and floating (e.g., duckweed, watermeal and salvinia) plants by treating the water column. Fluridone symptoms are highly visible, with the new growth of sensitive plants bleaching and turning pink or white as chlorophyll in the plant is destroyed by sunlight. Susceptible plants 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 weeks or months after an initial treatment.

Fluridone can be both selective and broad-spectrum and use rates vary from 4 to 150 ppb, but rates of 12 to 40 ppb are most commonly used. 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 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 two or more months) can allow plants to continue to provide structure for habitat and produce oxygen through photosynthesis. There are limited restrictions for potable water use and no restrictions on fishing or swimming; however, irrigation restrictions are described on the product label. Fluridone is available in several liquid and pellet formulations. All formulations 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 several weeks or more than a month apart to ensure that an effective concentration of the herbicide is maintained. This is especially important for controlling submersed plants. Due to the long-lived nature and critical exposure time requirements, periodic sampling is often conducted to measure fluridone concentrations in treated water and to determine whether further applications are necessary to maintain a lethal concentration of the herbicide in the water. Floating plants are generally controlled much more quickly than submersed species. Fluridone can be used in systems ranging from less than one acre to several thousand acres.

The main degradation pathway for fluridone is via sunlight, but fluridone is also broken down by microbes. Resistance to this herbicide was confirmed at several research institutions in 2000 after repeated failures of large-scale fluridone applications for hydrilla control in Florida in the late 1990s. This was the first occurrence of resistance to a bleaching-type herbicide and the first for a plant species based solely on somatic mutations (Section 3.7.2). As mentioned in Section 2.2, hydrilla reproduces solely by vegetative means (asexually, no seed production) in Florida, leaving no avenue for gene recombination between different plants. Fluridone attacks only one gene location in hydrilla and several genotypes (plants with a specific unique mutation in that gene) have since been reported in Florida, with each genotype having a different level of resistance to fluridone. Repeated fluridone use effectively removed the susceptible hydrilla genotypes, leaving plants with the resistance mutations to expand and become dominant.

Topramezone (2013)

Topramezone has been used to control broadleaf and grass species in corn as well as in conifer and other non-crop areas. It was registered for aquatic use by the EPA in 2013. Topramezone is the first aquatic-registered herbicide belonging to the chemical class called pyrazolones and can be used in rotation with other modes of action in resistance management programs. It is a systemic herbicide that is applied to the water column for submersed or floating plant control, or directly to foliage of floating and emergent vegetation. In sensitive plant species, topramezone inhibits the enzyme 4-hydroxy-phenyl-pyruvate-dioxygenase (4-HPPD), which leads to a disruption of the synthesis and function of chloroplasts. Consequently, chlorophyll is destroyed by oxidation, resulting in bleaching symptoms (white or pink coloration) of the growing shoot tissue within 7 to 10 days after exposure and subsequent death of the plant.

Topramezone shares many of the characteristics described for fluridone. These include: 1) low use rates (20 to 40 ppb); 2) extended exposure requirement of greater than 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 some floating plants. Applications are made to actively growing plants early in the growing season before mature plants can build carbohydrate reserves, mat at the water surface, and slow growth and subsequent herbicide response. Applying early in the growth stage reduces the amount of herbicide and the exposure period necessary to control hydrilla. Waterhyacinth has been controlled via root uptake of topramezone in waters treated for hydrilla control. The main degradation pathway for topramezone is via photolysis with a half-life in water ranging from 4 to 6 weeks. Microbial degradation is a minor breakdown pathway for topramezone, which may also weakly adhere to suspended clay particles.

Systemic herbicides – ALS herbicides

Several recently registered herbicides include compounds that target the plant-specific enzyme acetolactate synthase (ALS). As noted above for imazapyr, ALS inhibitors stop the production of three amino acids (isoleucine, leucine and valine) which then inhibits the production of ALS enzymes and other proteins that are built from these amino acids. Although the exact mechanism is not understood, when ALS is inhibited, plants die. Animals do not produce these enzymes, so penoxsulam has low toxicity to animals. In contrast to the broad-spectrum activity described for glyphosate and imazapyr, the ALS herbicides tend to be much more selective. Despite a similar mode of action, use patterns vary substantially among the ALS 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. They require 1 to 3 or more months of exposure to achieve control of submersed weeds since the plants slowly deplete their carbohydrate reserves.

Compound Date registered for aquatic use	Primary use			Formulation	Mechanism of action (MOA) WSSA resistance management group	Mode of action / comments
	Submersed	Floating	Emergent			
Penoxsulam 2007	X	X		Liquid	Inhibits plant-specific enzyme (ALS) WSSA Group 2	- Systemic herbicide - New growth stunted - Large-scale control of hydrilla and other submersed plants - Extended exposure required for submersed plant control - Typical submersed rate 10 to 30 ppb - Floating plant control - Typical foliar rate 2 to 5.6 oz/ac
Imazamox 2008	X	X	X	Liquid Granular	Inhibits plant-specific enzyme (ALS) WSSA Group 2	- Systemic herbicide - New growth stunted - Selective emergent plant control - Typical foliar rate 32 to 128 oz/ac - Growth regulation and control in hydrilla - Typical submersed rate 25 to 75 ppb
Bispyribac-sodium 2012	X	X		Wettable powder	Inhibits plant-specific enzyme (ALS) WSSA Group 2	- Systemic herbicide - New growth stunted - Large-scale control of hydrilla and other submersed plants - Extended exposure required for submersed plant control - Typical submersed rate 20 to 40 ppb - Floating plant control - Typical foliar rate 1 to 2 oz/ac

Penoxsulam (2007)

Penoxsulam was originally registered in 2004 for broadleaf, grass and sedge control in rice and turf. It was registered for aquatic use in 2007 and is currently used to manage floating species including 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 is a systemic herbicide that is absorbed by plant tissues and moves to areas of new growth. 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. 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 broken down primarily via photolysis and to a lesser extent by microbes. Its half-life in waters ranges from 7 to more than 30 days and is dependent on water depth and light intensity. Enzyme inhibiting herbicides act very slowly and control is highly dependent on contact time. Penoxsulam use rates and exposure requirements for submersed applications are generally similar to those of fluridone, topramezone and bispyribac-sodium and plant death may occur over a period of 60 to 100 or more days depending on the plant species, stage of plant growth and treatment timing. This may necessitate split or multiple applications to keep the herbicide concentration at at 20 to 40 ppb for up to 100 days for optimum performance.

Resistance to ALS herbicides has been reported in terrestrial plants, so mixing these products with a second active ingredient with a different mechanism of action can reduce the likelihood of resistance development. Combining penoxsulam with the dipotassium salt formulation of endothall substantially decreases the exposure time needed to control hydrilla to about 7 to 14 days, which reduces the effects of degradation and dissipation and the need for additional applications to maintain appropriate penoxsulam concentrations in the water column. Applying these herbicides in combination provides a measure of resistance management, requires less of each herbicide to control hydrilla and may increase selectivity to conserve non-target native plants. Likewise, applying penoxsulam in combination with flumioxazin or carfentrazone has provided an effective waterhyacinth management tool with increased resistance management benefit over penoxsulam alone.

Imazamox (2008)

Imazamox was registered by the EPA in 1997 for broadleaf and grass control and has been used in agricultural sites including soybeans, rice, sunflowers and wheat. It was registered for aquatic use in 2008. Imazamox is a systemic herbicide that is applied to plant foliage to control floating or emergent plants, or to the water for submersed plant control. Imazamox is broken down in the water by photolysis and microbial degradation and its half-life in water is 7 to 14 days.

Imazamox is available in liquid and granular formulations and should be applied to actively growing plants, preferably early in the season to young plants with lower carbohydrate reserves. It is rapidly absorbed into plant tissues and growth of susceptible plants is generally inhibited within a few hours after application. In this regard, it acts somewhat like a contact-type herbicide, requiring a short exposure period. However, plant death is relatively slow. Meristematic tissues become chlorotic in 1 to 2 weeks; this is followed by general chlorosis and death in 2 to 6 weeks. Primary aquatic plant management uses of imazamox include foliar applications to control cattail, wild taro (*Colocasia esculenta*), Uruguayan primrose willow complex (*Ludwigia grandiflora/hexapetala*) and waterhyacinth. Imazamox may be applied alone or in combination with other herbicides like glyphosate or carfentrazone. Applying imazamox alone provides a measure of selectivity for comingled non-target plants. Combining with glyphosate or carfentrazone results in more rapid and thorough control but is usually limited to monocultural stands of target plants or other areas where selectivity is not a concern. Imazamox may provide up to a year of control of waterhyacinth via root uptake from in-water applications.

Bispyribac-sodium (2012)

Bispyribac-sodium has been labeled and used for weed control in rice for many years and was registered by the EPA for aquatic plant control in 2012. It is a systemic herbicide that is absorbed into and moves within the affected plant. Like most systemic aquatic herbicides, control is highly dependent on contact time or exposure of the plant to the herbicide. The primary degradation pathway for bispyribac-sodium is microbial metabolism and the half-life in water is about 30 days.

Bispyribac-sodium is applied alone via subsurface injection at 30 to 45 ppb to manage hydrilla and requires 60 to 90 days of exposure to achieve control. With a half-life in water of about 30 days, monitoring and reapplication to maintain the original desired concentration and exposure period without exceeding the label maximum of 45 ppb. Combining lower rates of bispyribac-sodium with as little as 1 ppm of dipotassium salt of endothall not only reduces the exposure time required to control hydrilla, but also provides a measure of resistance management by utilizing two different mechanisms of action.

These three ALS-inhibiting herbicides clearly demonstrate that each herbicide is different since the use rates and the spectrum of plants controlled are very different, particularly between imazamox and the other two herbicides in this section.

Herbicide dissipation, degradation, deactivation and half-life

The length of time a herbicide remains in contact with target plants following a submersed application is critical to achieving desired results. Two key processes that dictate the required exposure of plants to herbicides are 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 treatments applied to a small area in a large water body. For example, application of a herbicide to a 10-acre protected cove in a large reservoir may result in limited movement outside 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 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. Since 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. Except for 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 (Section 1.1) 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, penoxsulam, topramezone or bispyribac-sodium that require long exposure periods of 45 to 100 or more 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 and may require additional “bump” treatments to maintain lethal concentrations for the required exposure times.

The role of pH for products that are degraded via hydrolysis such as flumioxazin and carfentrazone is a relatively new factor in 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 deactivation 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 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 177 and 178 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-sodium, the extended exposure requirements and large-scale use patterns are often supported by monitoring programs. In this case, 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; given the lower analytical costs and the value of the information that can be obtained, it is likely this trend will increase in the future.

Summary

This chapter lists 16 chemicals 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.

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 2-3 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	0.5 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 ~8 hours	Peroxide based algaecides are short-lived in the water column and quickly breakdown via biotic and abiotic processes including hydrolysis. Degradation is enhanced in warm alkaline waters.
Carfentrazone	Hours to 1+ day	Hours to 3 to 5 days	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 has 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. Warmer water temperatures increase the rate of microbial activity and can have a strong influence on the rate of degradation. Photolysis also plays a role in degradation.
Triclopyr	Hours to days	3 to 14+ days	The key degradation pathway for triclopyr is via photolysis or sunlight. Time of year, water depth and water clarity influence the rate of photodegradation. There is also some microbial action that results in degradation.
Florpyrauxifen-benzyl	Hours	0.5 to 2 days	The key degradation pathway for florpyrauxifen-benzyl in water is by photolysis or sunlight. Breakdown is faster in shallower or clearer water. Breakdown is slightly enhanced via hydrolysis in basic (pH > 8) waters.
Glyphosate	Several hours to 1 day	Hours to 1+ day to inactivate Degradation in soil: 12 to 60 days	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	At least 1 hour for foliar applications 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 an important 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	Several hours	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.