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Aquatic Herbicide Mode of Action and Use Implications

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At present there are more than 200 active ingredients labeled for use as herbicides in the United States. Fifteen of these active ingredients are labeled for aquatic use. These fifteen active ingredients have seven different modes of action (MOA), as defined by the MOA classification system devised by the Weed Science Society of America (WSSA).

What is mode of action? Mode of action is the way in which a herbicide affects a plant at the tissue or cellular level, or the sequence of events from absorption into the plant to the plant's death. Herbicides with the same MOA will have the same movement (translocation) pattern and cause similar injury symptoms. Target plant selectivity and behavior in water and soil are also often similar for herbicides with the same MOA. Mode of action, therefore, has implications for how and when herbicides are applied.

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

Acetolactate synthase is a key enzyme in the biosynthesis of the branched-chain amino acids isoleucine, leucine, and valine. Branched-chain amino acids are critical for plant growth and protein synthesis. When the synthesis of these amino acids is inhibited, cell growth and DNA synthesis are disrupted, which ultimately kills the plant.

ALS inhibitors are symplastically translocated or downwardly mobile. They move from sites of sugar production to sites of metabolic activity, basically from leaves to meristems (root tips and shoot tips), storage organs, and other live tissues.

These herbicides are so potent that they can be effective at very low concentrations of active ingredient. Unfortunately, resistant strains of weeds can quickly become a large percentage of the population. This is presumably because these herbicides have a single mode of action and because many have long residual activity. This reinforces the need to rotate herbicides with different modes of action or use ALS inhibitors in combination with other herbicides. ALS inhibitors are also very slow acting, sometimes requiring up to several weeks to kill plants. ALS inhibitors are effective only on actively growing plants. ALS inhibitors can be used to selectively control targeted plants.

The ALS inhibitors (active ingredients) labeled for aquatic use are imazapyr, imazamox, penoxsulam, and bispyribac-sodium.

Active ingredient	Trade names
Imazapyr	Habitat, Imazapyr 4SL, Ecomazapyr 2SL, GullWing, AquaPier, Polaris AC, AmTide Imazapyr 2SL, others
Imazamox	Clearcast, Clearcast 2.7G
Penoxsulam	Galleon SC
Bispyribac-sodium	Tradewind

Photosystem I Inhibitors

Photosynthesis takes place in two steps—the light reaction and the dark reaction. The light reaction occurs in the grana of chloroplasts where chlorophyll absorbs the light energy. Chlorophylls are of different types and

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absorb different wavelengths of light. Chlorophylls exist in two photosystems, photosystem I and photosystem II.

Photosystem I inhibitors accept electrons from photosystem I. Eventually the energy of these electrons creates hydrogen peroxide and superoxides, generationg hydroxyl radicals that destroy unsaturated lipids, especially the lipids that are part of cell membrane fatty acids and chlorophyll. This causes cytoplasm to leak out from the cells. So instead of light energy being used to create ATP and eventually glucose, it kills cells.

Photosystem I inhibitors are fairly non-selective in the plants they will act upon. Injury symptoms can become apparent within several hours after application. Because they act quickly, the photosystem I inhibitors do not translocate, so there must be extensive plant coverage to kill the plant. Also, symptoms will appear most quickly with bright, sunny, and warm conditions at application. Photosystem I inhibitors work only on actively growing plants.

The only photosystem I inhibitor (active ingredient) legal for aquatic use is diquat.

Active ingredient	Trade names
Diquat	Reward, Aceto Diquat 2L, Harester, Weedtrine-D, Alligare Diquat, Misty Weedtrol CF, Diquat SPC 2L, RedWing, Diquash, Quick Kill, Solera Diquat, Knockout, Tsunami DQ, Tribune, RowRunner ATO, Liberator 711, Misty Weedtrol VF, AquaVet Submerged Weed Control, Ultra PondWeed Defense, others

Protoporphyrinogen Oxidase (PPO or Protox) Inhibitors

Protoporphyrinogen oxidase is an enzyme in the chloroplast responsible for one of the steps in the biosynthesis of protoporphyrinogen (PPGIX) to protoporphyrin IX (PPIX). PPIX is an important precursor for chlorophyll needed for electron transfer chains. Protox inhibitors do more than block chlorophyll synthesis when the enzyme is inhibited. Instead of being converted to PPIX, the PPGIX accumulates out of its normal environment and reacts with oxygen, producing toxic oxygen radicals. The result is the loss of chlorophyll and carotenoids and leaky membranes, leading to cell death.

PPO inhibitors have limited translocation in plants, so extensive plant coverage is essential to kill the plant. PPO inhibitors injure mostly broadleaf plants. PPO inhibitors usually burn plant tissues within hours or days of exposure. Active plant growth is essential for the PPO inhibitors to be effective. Symptoms will appear most quickly with bright, sunny conditions at application.

The PPO inhibitors (active ingredients) labeled for aquatic use are carfentrazone-ethyl and flumioxazin.

Active ingredient	Trade names
Carfentrazone-ethyl	Stingray
Flumioxazin	Clipper

Carotenoid Biosynthesis Inhibitors

Carotenoids play an important role in harvesting light and transferring the captured energy to chlorophyll. Carotenoids also protect the photosynthetic apparatus in three ways, absorbing excess energy and dissipating it as heat. Carotenoids have the ability to quench triplet chlorophyll molecules back to their ground state, quench single (radical) oxygen molecules to a more stable state, and quench the photosystem reaction centers when they are overexcited by very bright light. Without the presence of carotenoids to quench triplet chlorophyll, active oxygen species are generated and destroy the photosynthetic apparatus within the thylakoid membrane. Inhibiting carotenoid biosynthesis leads to the destruction of chlorophyll and the visible bleaching of the plant. The plant dies from starvation.

Carotenoid biosynthesis inhibitors target a narrow range of plants. The active ingredient can be effective at very low concentrations. Resistant strains can become common because of the herbicide's activity on a very narrow biochemical pathway. Carotenoid biosynthesis inhibitors require a very long time before their effects kill plants.

The carotenoid biosynthesis inhibitors (active ingredients) with an aquatic label are fluridone and topramezone.

Active ingredient	Trade names
Fluridone	Sonar AS, Sonar Genesis, SonarOne, Sonar SRP, Sonar Precision Release, Sonar Quick Release, Avast! SC, Restore, Fluridone, Fluridone RTU, Fluridone Granular, WhiteCap
Topramazone	Oasis

Enolpyruvyl Shikimate-3-Phosphate (EPSP) Synthase Inhibitors

EPSP synthase is an important enzyme in the shikimate pathway that produces many aromatic products such as lignins, alkaloids, flavonoids, benzoic acids, and plant hormones, in addition to amino acids needed for protein synthesis. By inhibiting EPSP synthase, the production of the aromatic amino acids phenylalanine, tyrosine, and tryptophan is inhibited. Reduced levels of aromatic amino acids causes significant reductions in protein synthesis, which is necessary for plant growth and development, leading to plant death.

Glyphosate is symplastically translocated or downwardly mobile. It moves from sites of sugar production to sites of metabolic activity, basically from leaves to meristems (root tips and shoot tips), storage organs, and other live tissues. EPSP synthase inhibitors are also rapidly inactivated in the soil.

Glyphosate is a relatively nonselective postemergent herbicide that is inactive in the soil because of high soil adsorption. Agricultural crops have been developed with an alternative EPSP enzyme, allowing the use of glyphosate with no injury. The EPSP inhibitor herbicides are readily absorbed through plant foliage and translocated in the phloem to the growing points. Woody perennials usually are less sensitive to glyphosate than annual plants. Glyphosate injury symptoms are usually apparent within a few days after application.

The only EPSP synthase inhibitor (active ingredient) with an aquatic label is glyphosate.

Active ingredient	Trade names
Glyphosate	Rodeo, AquaPro, Shore-Klear, Shore-Klear Plus, Alligare Glyphosate 5.4, Cinco, AquaMaster, AquaNeat, PondMaster, GlyphoMate 41, Avocet, Avocet PLX, Catt Plex, Eraser AQ, Roundup Custom, Imitator Aquatic, AquaVet Shoreline Weeds, Shoreline Defense, others

Synthetic Auxins or Auxin Mimics

Indole-3-acetic acid (IAA) is the most common, naturally occurring plant hormone of the auxin class. IAA is predominantly produced in cells of the apex (bud) and very young leaves of a plant. IAA has many different effects, as all auxins do, such as inducing cell elongation and cell division with the result of plant growth and development. On a larger scale, IAA serves as a signaling molecule necessary for development of plant organs and coordination of growth.

Once the auxin mimic gets into the plant and reaches a living cell, it is thought to bind to the same receptor that recognizes the natural hormone, IAA. This acts as a signal for the cell to turn on several genes. A classic response to an auxin mimic is cell elongation. Another is to induce a gene that helps loosen the cell-wall region and this loosening causes differential lengthening on one side of a stem compared to another, resulting in characteristic twisting (epinasty). Another example of a gene that auxin mimics can turn on is for the enzyme (ACC synthase) that helps synthesize ethylene, another plant hormone. Ethylene can be involved in plant injury because ethylene causes epinasty or bending and twisting as well. Ethylene can also turn on the production of abscisic acid in sensitive plants; abscisic acid, another plant hormone, will close stomata so the plant can not access carbon dioxide for photosynthesis. Another byproduct of the ethylene synthesis pathway is cyanide, which injures sensitive grasses.

Auxin mimics are symplastically translocated or downwardly mobile. They move from sites of sugar production to sites of metabolic activity, basically from leaves to meristems (root tips and shoot tips), storage organs, and other live tissues.

These herbicides are very important agrochemicals for selective weed management in grass and cereal crops and are generally phytotoxic to broadleaf plants, causing little or no damage to monocots (grasses, for example). Monocot plants are tolerant, in general, because of restricted translocation, enhanced metabolism, and the lack of a vascular cambium in their phloem tissue. The killing action of synthetic auxins is not due to any single factor but to the disruption of several growth processes in susceptible plants. This indicates that resistant strains are less likely to occur.

The auxin mimics (active ingredients) with an aquatic label are 2,4-D and triclopyr.

Active ingredient	Trade names
2,4-D	Navigate, Sculpin G, DMA 4 IVM, TernStyle, Alligare 2,4-D Amine, Helena 2,4-D Amine 4, Unison, Weed Rhap A-4D, HardBall, Loveland Amine 4 2,4-D, Savage, Clean Amine, WEEDestroy AM-40, Platoon, Riverdale 2,4-D 6 Amine, Riverdale Solution Water Soluble, Riverdale Solution Water Soluble IVM, Tenkoz Amine 4 2,4-D, Hi-Yield 2,4-D Amine No. 4, Winfield 2,4-D Amine 4, Tacoma 2,4-D Amine 4, Sentry Amine 4, Defy Amine 4, Rugged, Shredder Amine 4, De-Amine 4, others
Triclopyr	Renovate 3, Renovate OTF, Renovate Max G (triclopyr and 2,4-D), Triclopyr 3, Element 3A, Garlon 3A, Trycera, Kraken, Navitrol, Navitrol DPF, others

Mode of Action Not Classified

Endothall

Endothall has many modes of action, unlike other herbicides that have only one. In some plants, endothall inhibits lipid and protein biosynthesis. Its inhibitory effect on mRNA synthesis suggest an action similar to actinomycin D. It has been reported that endothall inhibits lipid synthesis by inhibiting the incorporation of malonic acid into the lipids. In other plants, endothall can also affect membrane integrity by disrupting respiratory processes. This results in a collapse of the membrane electrical gradient because of a lack of energy, the formation of leaky membranes, and a rapid desiccation of tissue. Endothall has also been shown to reduce the activity of proteolytic enzymes that hydrolyze dipeptides during seed germination. The result is defoliation and brown, desiccated tissue.

Endothall is a selective contact herbicide that has been used to manage submerged aquatic vegetation for more than 50 years. The herbicide is absorbed rapidly and damages the cells of susceptible plants at the point of contact, but does not affect areas untouched by the herbicide, like roots or tubers (underground storage structures). This means extensive coverage of the target plant is required for maximum effectiveness. It is selective in the sense that some plants show greater susceptibility to endothall treatment than others. Plant damage will be apparent within a week.

Active ingredient	Trade names
Endothall	Aquathol K, Aquathol Super K, Cascade, Hydrothol 191, Hydrothol 191 Granular, Teton

Copper Compounds (Copper Sulfate & Copper Chelate)

Copper algaecides/herbicides fall into two categories based upon the copper compound(s) included as the active ingredient. These categories are copper sulfate and the chelated copper compounds, primarily copper ethylenediamine and copper triethanolamine. Copper sulfate is widely available in crystalline form, often called bluestone, and is increasingly available as a premixed liquid formulation. Chelated copper compounds are almost exclusively marketed as liquid formulations.

Very low concentrations of copper are necessary for plant growth. However, excess copper, concentrations as little as 0.2 to 1.0 parts per million in water, can kill algae and several species of rooted aquatic plants. Copper is believed to work by causing an imbalance with other vital enzyme metal cofactors, resulting in blocked enzyme activity. Copper is believed to target the specific physiological processes electron transport in photosystem I, cell division, and nitrogen.

While copper compounds can be effective in killing most types of algae, some of the filamentous algae species can be tougher to control. Mixing copper with other herbicides such as diquat can enhance control.

The chelated copper compounds copper ethylenediamine and copper triethanolamine are effective for controlling algae species, but are also marketed as herbicides rather than algaecides for the control of hydrilla, egeria, and several other higher plants. Chelated copper compounds alone can be effective, but they become extremely potent when combined with another herbicide such as diquat, endothall, or flumioxazin. In these instances, the chelated copper compound acts both as a herbicide and as an adjuvant.

Plants choose specific microbial species and give them access to the root so that they form a microbial film. In this way plants host a unique, carefully selected bacterial community from which they benefit in a variety of ways. The exact herbicidal mechanism of copper is unknown, but it is widely speculated that the bactericidal properties of copper destroy the microbial communities that form a film around the plant, thus reducing the ability of the plant to absorb required nutrients, weakening the plant immune system, and leaving the plant vulnerable to pathogenic and parasitic bacteria. The adjuvant properties of copper are similar. As copper kills bacteria and algae growing on the surface of the plant, it allows increased absorption of the other herbicide's active ingredients.

Copper can be toxic to fish in soft water (<50ppm alkalinity). Before applying copper sulfate, the water should be tested to ensure the alkalinity is above 20 mg/L, preferably above 50 mg/L. The rate is adjusted based on the receiving water's alkalinity. The chelated copper formulations are said to be much less toxic to fish in soft water situations as long as label directions are followed.

Active ingredient	Trade names (for formulations other than crystals)
Copper sulfate crystals	Crystal Blue, AB Brand Copper Sulfate Crystals, Southern Ag Copper Sulfate, Applied Biochemists Copper Sulfate Crystals, Blue Mix, Sanco Crystal Blue, Copper sulfate (generic crystals)
Liquid copper sulfate	Crystal Plex, Stock Plex, EarthTec, Algae X, Current, SeClear, AgriTec-2 Algicide, Altivia Liquid Copper Sulfate, AquaVet Algae Control, Pond Boss Pro, Copper Cat
Liquid chelated copper compounds (ethylenediamine, triethanolamine)	Alligare 8% Copper, PondMaster Aquatic Algaecide, Harpoon, Symmetry, Mizzen, Komeen, Nautique, Captain, Captain XTR, KTea, Cutrine Ultra, CutrinePlus, Stocktrine II
Granulated chelated copper compound (ethylenediamine, triethanolamine)	Harpoon Granular, Cutrine Plus Granular

Suggested readings

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