Division of Fish, Wildlife & Marine Resources Bureau of Habitat Technical Memorandum Prepared by T. Sinnott March 17, 2016

Recommendations Regarding the Use of Aquatic Herbicides in Fish-Bearing Waters of the State

March 17, 2016

This document supersedes the Bureau of Habitat Technical Memorandum entitled: "Recommendations Regarding the use of Aquatic Herbicides in Fish-bearing Waters of the State" dated May 20, 2015.

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I. Purpose

The purpose of this document is to provide information to Regional Natural Resource staff (i.e., Regional Fisheries/Habitat Managers/Biologists) to assist them in reviewing permit applications and making recommendations regarding Article 15 permits for the control of aquatic vegetation (i.e., aquatic plants and algae) from an ecological perspective. Aquatic purchase permits¹ are not reviewed by Natural Resources staff. This document is a compilation of technical information from the 1981 Programmatic Environmental Impact Statement (PEIS)² and Statement of Findings, pesticide product labels, chemical-specific Supplemental Environmental Impact Statements (SEIS) and scientific literature.

If additional information is desired, or more detail is needed, consult the product label or request assistance from the Ecotoxicology Section of the Bureau of Habitat (BoH).

II. Division of Fish, Wildlife and Marine Resources interests in aquatic vegetation control

The mission of the Division of Fish, Wildlife and Marine Resources (DFWMR), within the Office of Natural Resources in the New York State Department of Environmental Conservation (NYSDEC, hereafter referred to as the Department), is to serve the interests of current and future New Yorkers by using our collective skills, in partnership with the public, to describe, understand, manage, and perpetuate a healthy and diverse assemblage of fish, wildlife, and ecosystems.

ECL Article 15-0313(4) states that: The Department is authorized to adopt and enforce rules and regulations governing the direct application of chemicals to or in surface waters for the purpose of altering water quality, or the direct application of pesticides to or in surface waters, notwithstanding any of the provisions of this chapter.

a. Such rules and regulations may forbid such direct application or use of pesticides and chemicals except pursuant to a permit issued by the department, or by an appropriate officer or agency authorized by such rules to issue such permits, except that a permit shall not be required for the application of a pesticide to a pond of one acre or less in size which has no outlet to surface water.

b. Such rules and regulations may specify the pesticides and chemicals and quantities and concentrations thereof which may be directly applied or used, which

¹ The Aquatic Pesticide Purchase Permit is issued to a homeowner for the treatment of a water body that lies entirely on the homeowner's property, does not have an outlet and is less than one surface acre in size.

² Final Programmatic Environmental Impact Statement on Aquatic Vegetation Control Program of the Department of Environmental Conservation Division of Lands and Forests, May 1, 1981

specified chemicals and pesticides shall be selected with maximum protection of life, health and property as criteria for their selection, and shall also provide for giving reasonable notice to persons likely to be adversely affected by such use of chemicals and may require consent of persons who may reasonably be expected to suffer substantial damage or injury thereby prior to the issuance of any permit for such use. A fee of one hundred dollars shall accompany each permit.

c. No pesticide or chemical may be introduced into any surface waters of the state classified pursuant to article 17 in violation of such rules and regulations.

6 NYCRR Part 327.3(3) states that: "... permits [for aquatic vegetation control] shall be granted under such limitations as will protect to the greatest extent possible all terrestrial life, aquatic life other than aquatic vegetation intended to be controlled or eliminated, all public and domestic water supplies and irrigation, recreational, agricultural, and industrial water uses."

When this regulation is coupled with the mission statements for the Division of Fish, Wildlife and Marine Resources (DFWMR) and BoH, three principles emerge that can define DFWMR's "interests" in aquatic vegetation control:

- A. Protect aquatic life from direct toxicity and excessive loss of habitat;
- B. Maintain healthy and diverse ecosystems;
- C. Manage fish-bearing waters of the state to support a wide array of uses.

From these three interests, a general "philosophy" emerges to guide Natural Resource staff in making decision regarding the use of aquatic herbicides:

Aquatic plants are an integral part of a healthy aquatic ecosystem, and necessary to maintain a productive fishery. Aquatic herbicide use should therefore be limited to only what is needed to minimize the impact of aquatic vegetation to human activities. Aquatic plants classified as an invasive species³, however, can be targeted for control or eradication by any appropriate means including chemical herbicides, unless such control would cause long term harm to the waterbody or its productive use. Eradication of an invasive aquatic species is particularly important at the initial stages of an infestation, before the species has become wellestablished and widely distributed throughout the water body.

Fish, reptiles, amphibians, aquatic birds, aquatic mammals, and invertebrates rely on aquatic vegetation for shelter, protection, spawning substrate, and food. Aquatic

³ Invasive Species: ECL § 9-1703(10) defines an invasive species as: (a) nonnative to the ecosystem under consideration; and (b) one whose introduction causes or is likely to cause economic or environmental harm or harm to human health. For the purposes of this paragraph, the harm must significantly outweigh any benefits."

vegetation can help improve water quality and clarity by intercepting runoff, sequestering nutrients (which helps to retard algal blooms), and stabilizing sediments.

The sudden and rapid destruction of large beds of aquatic vegetation with an herbicide can reduce water clarity, force fish to graze zooplankton offshore, and stimulate phytoplankton (algae) blooms from the release of nutrients. Aquatic life can be impacted both by the direct action of an herbicide (toxicity), and indirectly, by the removal of aquatic vegetation itself (habitat loss). Widespread ecosystem changes can result from the removal of macrophytes⁴. These changes can in turn impact the enjoyment that people receive from living around and recreating on lakes and other waterbodies.

Aquatic vegetation control is usually desired because it can grow in dense beds that impede boating, fishing, and swimming. Also, decomposing plants can release noxious odors, litter beaches, and remove dissolved oxygen from the water.

III. General Recommendations regarding control of native (non-invasive) aquatic vegetation

Waters open to the public include all of the larger lakes in the state where the bottom of the lake is state-owned up to mean high water line. These include the Great Lakes (Erie, Ontario), Chautauqua Lake, Lake Champlain, Lake George, Oneida Lake and the Finger Lakes (except Hemlock). Other lakes where the ownership of the bottom may be uncertain are considered open to the public whenever there is any publicly-owned land touching the shoreline of the lake (e.g., a public beach, boat launch, or a roadway) and such lands are not posted or regulated against general public access. In all such waters open to the public, the following guidelines should be considered before recommending in favor of the issuance of a permit for use of chemicals in water to control native, or non-invasive aquatic vegetation:

- A. Undeveloped shorelines should not be treated.
- B. Shorelines adjacent to publicly-owned lands may be treated only with the concurrence of the agency having jurisdiction of such lands.
- C. Aquatic plants that are not interfering with human activities such as swimming and boating should not be treated. In waters open to the public, the Bureau of Habitat (BoH) recommends that herbicide treatments should be limited to areas where swimming, boating, and other human activities are adversely impacted because of excessive growth of aquatic vegetation. Herbicide treatments should

⁴ From Engel, S., (1985). Aquatic Community Interactions of Submerged Macrophytes. Technical Bulletin No. 156, Wisconsin Department of Natural Resources, P.O. Box 7921, Madison, Wisconsin 53707

not occur when the targeted aquatic vegetation is in water so deep that it does not interfere with human activities, no matter how close to the shoreline the vegetation is located.

- D. Herbicides should not routinely be permitted in rivers or streams. A site specific environmental impact statement should be required before introducing aquatic herbicides into flowing waters.
- E. The number of treatments allowed in a single year is governed by the pesticide product label, except for diquat dibromide, for which only one application per season is allowed (6 NYCRR 327.6(b)(6)).
- F. Any proposed treatment which could result in demonstrable harm to fisheries or other aquatic resources should be denied, modified, or conditioned as the situation warrants. For example, the proposed area of treatment could be changed, a different herbicide recommended, the timing of the treatment changed to avoid fish spawning, etc.
- G. The use of an aquatic herbicide within a regulated wetland requires an Article 24 permit in addition to an Article 15 pesticide permit. The Article 15 permit would only be required if there was an acre or more of standing or open surface water in the wetland being treated. The Article 24 permit should address concerns and impacts specific to the wetland proposed for treatment.
- A. Killing large masses of vegetation in a waterbody quickly, particularly in the summer when a thermocline exists, could lead to a rapid depletion of dissolved oxygen (DO) in the water as the dead vegetation decays, which could in turn result in fish kills by suffocation. Many, if not most aquatic herbicide and algaecide labels include specific provisions to prevent fish kills resulting from DO depletion. For example, the Nautique label states: "To minimize this hazard, do not treat more than 1/2 of the water body to avoid depletion of oxygen due to decaying vegetation. Wait at least 10 to 14 days between treatments." The Aquathol K label states: "Treatment of aquatic plants can result in oxygen loss from decomposition of dead plants. This loss can cause fish suffocation. Water bodies containing very high plant density should be treated in sections to prevent suffocation of fish." Such label provisions should be carefully adhered to. Even if a specific restriction is not stated on the label, the likelihood of DO depletion should be considered, for example, in backwater embayments or other locations where there is poor water circulation. Similar provisions to prevent DO depletion should be added as permit conditions if deemed necessary.

Some of the individual items above may conflict with each other. For example, a dense stand of aquatic vegetation that is perceived to be interfering with a human activity may exist adjacent to an undeveloped shoreline. In this instance, the Natural Resources Staff must develop a recommendation that balances the potential benefit to human users against the potential risks to the ecology of the lake.

IV. Recommendations regarding control of Aquatic Invasive Species

Certain aquatic plant species in the waters of New York State are considered to be invasive; that means, they meet the definition of invasive species (see footnote 2, above). The list includes but is not limited to:

- A. Eurasian watermilfoil; *Myriophyllum spicatum*
- B. water chestnut; Trapa natans
- C. hydrilla or water thyme; Hydrilla verticillata;
- D. curly-leaf pondweed; Potamogeton crispus
- E. fanwort; Cabomba caroliniana
- F. European frogs-bit; Hydrocharis morsus-ranae
- G. purple loosestrife; *Lythrum salicaria* (wetland species)
- H. common reed; *Phragmites australis* (wetland species)

Plants such as these alter the natural habitat of New York's water bodies, and usually interfere with boating, fishing, and swimming by growing completely to the surface in thick, dense stands. They usually lack specific predators, pathogens, and parasites that may occur in their native range and are not present in the newly infested habitat. As a result they can often out-compete and displace native vegetation.

DFWMR is generally reluctant to encourage or promote the use of chemical herbicides. However, with invasive species, any possible adverse effects from chemical use must be balanced against the detrimental impacts that would result from the presence of the invasive species. The unchecked growth of an invasive species can be much more damaging to both the ecology of an infested water body and human recreational activities than the generally temporary impacts of chemical use. It is particularly important to aggressively control an aquatic invasive plant species in the earliest stages of an introduction to keep them from completely colonizing a lake. The preceding recommendations for the control of native, or non-invasive vegetation may not be applicable, when the purpose of a proposed herbicide treatment is to eradicate or at least control an invasive species. However, if a water body has been infested with an invasive species for a long period of time, the overall risks to the aquatic ecology of large scale treatment programs must be taken into account, particularly if it seems unlikely that the treatment program will result in the eradication of the invasive species, or if eradicating the invasive species might result in other, undesirable changes.

Large scale, whole lake treatments have been both proposed and accomplished in New York in order to eradicate Eurasian watermilfoil. Such treatments have the potential to dramatically alter lake ecology. The removal of all vegetation will also impact young fish and invertebrates that require vegetation for cover and forage. The macrophyte community could be dramatically altered when recovery does occur. The potential risks of whole lake treatments to eradicate Eurasian watermilfoil (or other invasive plant species) should be carefully evaluated, possibly in a site-specific SEQRA review. A well-designed, carefully monitored whole lake treatment has the potential to eliminate

aggressive invasive species, to restore a native plant community, and may result in an overall benefit to the lake; and, therefore, should be carefully considered.

Such whole lake treatment proposals should be accompanied by a lake management plan that would include topics such as a program to educate boaters, lakefront property owners, and others who use the lake about invasive species, how they are introduced, and what can be done to keep Eurasian watermilfoil or other invasive species from reinvading the lake once it has successfully been removed.

V. SPDES Pesticide General Permit (PGP)

On January 7, 2009, the 6th Circuit Court of Appeals, in <u>The National Cotton Council of America, et al. v. United States Environmental Protection Agency</u>, 553 F.3d 927 (6th Cir., 2009) held that: (1) the Federal Clean Water Act (CWA) unambiguously includes "biological pesticides," and "chemical pesticides" with residuals, within its definition of "pollutant"; and (2) NPDES permits will be required for discharges to waters of the United States of biological pesticides, and of chemical pesticides that leave a residue. As a result, in October 2011, the Division of Water issued the SPDES General Permit for Point Source Discharges to Surface Waters from Pesticide Applications (PGP). Coverage under the PGP is required for the discharge of any pesticide, regardless of whether or not the pesticide application is covered by an Article 15 permit. Information on the Pesticide General Permit can be obtained from the DEC Public website at: <u>http://www.dec.ny.gov/chemical/70489.html</u>.

VI. Harmful Algal Blooms

Certain types of algae, specifically blue-green algae or Cyanobacteria, can proliferate to form dense blooms, usually in mid-to late summer, that can be harmful to other organisms including people, domestic animals, pets, and wildlife. These types of algae produce a variety of potent toxins. When the cells die, they break open and release the toxins into the water. Ingestion of water containing these toxins has produced harmful effects (including death) in fish, dogs, cats, livestock, and humans. Treating a harmful algae bloom with chemical algaecides such as copper compounds or endothall can cause the rapid death and destruction of blue-green algae cells, resulting in the release of a large quantity of toxins that could be potentially dangerous.

Before treating an algal bloom with a chemical herbicide, the applicator should consult with an appropriate expert (for example, a County Health Department, NYSDEC Division of Water, a certified lake manager, etc.) who can determine the type of algae present and whether or not algal toxins would be an issue. If they are, it might be better to forego treatment until the bloom dissipates on its own. Alternatively, if blue-green algae are treated very early in the bloom process, then the number of cells that could potentially release toxins into the water column are greatly reduced, and the bloom might be stopped before becoming a more serious problem. Prevention of harmful algal

blooms is beyond the scope of this document. Look for information and guidance on the topic from the Division of Water (http://www.dec.ny.gov/chemical/77118.html).

VII. Chemical Specific Information and Recommendations

The purpose of this section is to provide information and recommendations to all Regional Natural Resources staff who might be tasked to review Article 15 aquatic vegetation control permit applications, so they may be aware of the chemicals that are approved for use; the allowable dosages or application rates for each chemical; and other concerns and issues related to specific herbicides. If Natural Resources staff have concerns related to the proposed permit, those concerns need to be explained and supported by documentation that can be made available to the applicant of the aquatic permit.

The Pesticide Control Specialist in each region should have available copies of the labels for each pesticide formulation as registered with EPA and the Department. Pesticide labels are also available via the internet using the Department's PIMS (Pesticide Product, Ingredient, Manufacturer System) at http://pims.psur.cornell.edu/. Always consult the label to determine the maximum allowable amount of active ingredient in the chemical proposed for use, water use restrictions, or other pertinent information. Also, 6 NYCRR Part 327.6 imposes specific limitations on the use of copper sulfate for algae control, diquat for submerged and emergent vegetation, and low-volatile esters, salts and amines of 2,4-D for emergent vegetation. The limitations listed in Part 327.6 take precedence over product labels for these compounds.

The following sections describe the active ingredients for aquatic algaecides and herbicides registered for use in New York State.

A. Copper sulfate (pentahydrate) (CuSO₄•5H₂O)

Copper sulfate is the chemical most commonly used for control of algae. The cupric ion (Cu^{+2}) is the primary toxic agent. When applied to water, copper sulfate disassociates rapidly to release cupric ions (Cu^{+2}) , the form of copper that is responsible for most toxicity. However, cupric ions are very reactive, and they don't persist in the water very long. They rapidly bind with soluble anions such as hydroxide (OH^-) , carbonate (CO_3^{-2}) , dissolved organic carbon (DOC) such as humic and fulvic acids, and other substances which remove ionic copper from the water column and mitigate toxicity. Copper sulfate use is regulated both by the approved pesticide label <u>and</u> regulations (6 NYCRR Part 327.6(a)). These regulations describe specific restrictions as to when copper sulfate can be used, how much can be used, how it is applied, how frequently it can be applied, and specific water use restrictions which apply above and beyond those on the product label(s):

327.6(a) Copper sulfate for algae

(1) Active ingredient. CuSO4•5H₂O

(2) Purpose. Authorized for algae control

(3) Periods of treatment. Generally, May to September. Treatments later than Labor Day will require special authorization. Fall treatments may be warranted in some circumstances to reduce potential impacts for human, pet and wildlife exposure to surface scums of cyanobacteria (harmful algae blooms).

(4) Dosage. Not to exceed 0.3 ppm $CuSO_4 \cdot 5H_2O$ in the upper six feet of depth in ponds or lakes with over two acres of surface area. Not to exceed 0.3 ppm $CuSO_4 \cdot 5H_2O$ in the total volume of ponds with two acres or less of surface area. The above is based on water of average alkalinity for the State (100 ppm as $CaCO_3$ or greater). In softer waters, a reduced dosage may be required.

(5) Method of application. No permit shall be issued for the direct broadcasting of crystals or "snow." Copper sulfate should be applied as a liquid using spray equipment or as a solid placed in a burlap bag dragged behind a boat.

(6) Repeat treatments. Shall not be authorized at any interval of less than two weeks.

(7) Water use restrictions. Bathing and livestock watering shall be prohibited for at least 24 hours following a treatment.

Because these restrictions are in regulation, they must be observed even if they conflict with the approved label, and they take precedence over the label. A concentration of 0.3 ppm copper sulfate pentahydrate is equivalent to a concentration of 0.076 ppm ionic, or elemental copper. 6 NYCRR Part 327.6(a)(4) states that "The above [0.3 ppm] is based upon water of average alkalinity for the State (100 ppm or more). In softer waters, a reduced dosage may be required." The Bureau of Habitat has interpreted this limitation in the following manner: In water of 100 ppm hardness or greater, allow 0.3 ppm copper sulfate (0.815 pounds per acre foot of water). If the hardness is between 50 - 100 ppm hardness, allow 0.2 ppm copper sulfate (0.543 pounds per acre foot of water). If the hardness is less than 50 ppm, allow only 0.1 ppm copper (0.272 pounds per acre foot of water). Water supply reservoirs may be treated for algae without a permit, but applications must still comply with label conditions. If a pesticide application is determined to be exempt from permitting under Parts 327, 328, or 329, the regulations in those Parts do not apply to the application.

Copper sulfate use can lead to the depletion of dissolved oxygen (DO) as killed algae settle to the bottom and are decomposed. Many copper sulfate labels require that only a third to a half of a lake or pond be treated at a time to avoid DO depletion, and a 7-14 day period should separate treatments (the regulations above require a minimum of a two week interval between repeat treatments). Users of copper-based products should be aware that much of the copper applied to the water will settle to the bottom and accumulate in the sediments. It may eventually cause toxicity to bottom-dwelling benthic organisms. If Natural Resources Staff have concerns that a buildup of copper in lake bottom sediments might be causing adverse impacts to the benthos, the sediments should be tested. There are no other water use restrictions on the label⁵.

B. Chelated Copper Compounds⁶

These are other copper-based compounds that are registered for use to control both algae and aquatic macrophytes. These products use organically chelated copper (i.e., copper that is bound, or complexed, with other substances usually referred to as ligands) as the active ingredients. Chelated copper products differ considerably from copper sulfate. The organic copper complexes are nonpolar, and can pass through plant membranes and into algae cells more easily than ionic copper, where they trigger a toxic effect. Ionic copper harms aquatic animals by binding to the gills and interfering with the passage of other ions such as sodium. Since chelated copper complexes are nonpolar, they are less likely to bind to the gills of fish and aquatic invertebrates. As a result, chelated copper compounds generally exhibit lower toxicity to fish and most invertebrates than copper sulfate. 6 NYCRR Part 327.6(a) specifically addresses the use of *copper sulfate* for control of algae. The use of chelated copper compounds, to control algae or other aquatic plants is not addressed by this regulation.

Toxicity studies⁷ have shown that copper sulfate is about four times more toxic than Cutrine Plus, a mixed copper ethanolamine complex. Laboratory studies conducted at the NYSDEC Rome Field Station⁸ showed that the chelated copper product Captain

⁵ Labels do contain the statement: If treated water is to be used as a source of potable water, the metallic residual must not exceed 0.2 ppm copper; however, use rates that high are not allowed in <u>any</u> water in New York State.

⁶ This section refers to ethylenediamine complexes, mixed ethanolamine complexes, triethanolamine complexes of copper, and similar active ingredient formulations.

⁷ Murray-Gulde, C. L., J. E. Heatley, A. L. Schwartzman, and J. H. Rodgers, Jr. 2002. Algicidal effectiveness of Clearigate, Cutrine-Plus, and Copper Sulfate and margins of safety associated with their use. Arch. Environ. Contam. Toxicol. 43:19-27.

⁸ Klosson, K.R. and E.A. Paul, 2014. Comparison of the toxicity of two chelated copper algaecides and copper sulfate to non-target fish. Bulletin of Environmental Contamination and Toxicology 93(6):660-665.

Wagner, J.L., A.K. Townsend. A.E. Velzis, and E.A. Paul (2015). Relative toxicity of copper herbicides Nautique[™], Captain[™] and copper sulfate to non-target fathead minnows and brook trout. (Manuscript).

was about two times less toxic than copper sulfate to fathead minnows (warmwater fish), but both were about equally toxic to brook trout (coldwater fish). Captain XTR is the same chelated copper product formulated with a surfactant. In laboratory tests, Captain XTR exhibited about the same toxicity to fathead minnows as copper sulfate. A third chelated copper product, Nautique was significantly less toxic to fish under laboratory conditions than either Captain, Captain XTR, or copper sulfate.

In natural waters, toxicity from copper can be mitigated by the presence of dissolved organic carbon and other organic and inorganic ligands that can complex copper ions. The Rome Field Station conducted a caged fish study under field conditions in conjunction with the use of Nautique to control brittle naiad. At treatment concentrations as high as 0.6 ppm copper, very little toxicity was observed, and what little was observed may have been at least partially attributable to very high water temperatures.

Some chelated copper product labels (e.g. Cutrine) bear the warning: "This product may be toxic to trout and other species of fish. Fish toxicity is dependent upon the hardness of the water and the sensitivity of the fish species present. Do not use in water if the carbonate hardness⁹ of water does not exceed 50 ppm. [Do not use in waters containing Koi and hybrid goldfish¹⁰]." Other chelated copper products (e.g., Nautique, Captain) state: "Do not use in waters containing trout or other fish species that are highly sensitive to copper if the <u>alkalinity</u> is less than 50 ppm. Fish toxicity generally decreases when the hardness of water increases. This product must not be used in ornamental ponds containing Koi." Alkalinity and hardness are related water quality characteristics. In this context, both are referring to the presence of carbonate ions that can bind with and reduce the toxicity of copper ions to fish.

The recent laboratory studies conducted at the Rome Field Station clearly demonstrate that some chelated copper products have the potential to be toxic to fish at water concentrations consistent with label application rates. Conversely, field studies suggest that similar fish toxicity is not evident in natural water, particularly harder water with abundant dissolved and particulate organic carbon in the water column. Based on the most recent toxicity data relating to chelated copper products, the Bureau of Habitat provides the following recommendations:

A. If the label for the specific product proposed for use has a requirement that either carbonate hardness or alkalinity of the water to be treated must be \geq 50 ppm, then the hardness or alkalinity must be measured and confirmed prior to treatment.

⁹ The carbonate hardness of water includes the portion of total hardness associated with bicarbonate and carbonate in the water column. This has been called "temporary" hardness, because it disappears as water is softened by boiling and the ensuing precipitation of calcium carbonate and magnesium carbonate. From <u>Textbook of Limnology</u>, 2nd ed., by Gerald A. Cole, 1979.

¹⁰ The section in brackets appears on the Cutrine Ultra and Cutrine Plus Algaecide/Herbicide labels. It may appear on others as well.

B. All applications should comply with label instructions limiting treatments to only 1/3 - 1/2 of the total surface area of the pond under conditions of heavier infestation or low oxygen levels.

C. Chelated copper herbicides are often labeled for control of submerged macrophytes at application rates of 0.5 ppm or higher. Based on the results of recent laboratory fish toxicity studies, the Bureau of Habitat does not object to the use of Nautique at the full labeled rate. Other chelated copper products, specifically Captain and Captain XTR (formulated with a surfactant) showed toxicity to fish in the laboratory at concentrations similar to those that could be used for macrophyte control. More studies with chelated copper products are being planned, particularly in field conditions, where environmental factors absent in laboratory testing may alter the toxicity to fish and invertebrates. In the meantime, the Bureau of Habitat prefers that chelated copper products other than Nautique not be used for macrophyte control, except perhaps when required for rapid response to infestations of *Hydrilla*.

D. For non-fish bearing waters, or ponds completely owned by the applicant with little or no outflow, the products should be used as labeled.

C. 2,4-D

This herbicide is marketed in numerous formulations, including low volatile esters such as iso-octyl ester and butoxyethyl ester (BEE); diethyl- and dimethylamines, and salts. Despite the numerous formulations, the active ingredient of 2,4-D is measured as the 2,4-dichlorophenoxy acetic acid equivalent, which is generated when the products are applied to the water. The Bureau of Habitat considers all 2,4-D formulations acceptable for use, as long as all products are applied in accordance with their label and the limitations listed in regulation.

Regulations were promulgated in 6 NYCRR Part 327.6(c) that specifically govern the use of 2,4-D in New York State above and beyond the product labels. Those regulations include the following restrictions:

A. Authorized only for the control of emergent plants having a large part of their leafy growth projecting above or lying flat on the water surface;

B. Use restricted to late spring or early summer when the chemical is most effective;

C. Use of chemical solutions (i.e., liquid formulations) for dosage of up to eight pounds active ingredient per acre may be permitted in the treatment of dense stands. Use of pellets for subsurface application requires special authorization.

D. The treatment area shall not extend beyond 200 feet from shore or beyond a maximum depth of six feet, whichever gives the greater distance from shore.

E. Use of waters for irrigation shall be prohibited for a period sufficient to permit the decay of phytotoxicity (i.e., plant toxicity). The treated waters and those waters affected by the treatment shall not be used for other purposes during the treatment and for at least 24 hours thereafter.

In addition to truly emergent plants, such as water chestnut, water shield, water lilies, etc., 2,4-D is often proposed for use to control Eurasian watermilfoil. Eurasian watermilfoil is technically not considered to be "emergent" vegetation, however, the use of 2,4-D has been justified because at full growth, milfoil gives the appearance of being emergent because it can produce mats of leafy growth projecting above or lying flat on the water surface.

NYCRR Part 327.6 does not explain what constitutes the "special authorization" needed for the use of granular, pelletized formulations of 2,4-D. In the absence of other guidance, the approval of an Article 15 permit application to use granular 2,4-D products by the Regional Pesticide Control Specialist should be construed as the necessary special authorization required by the regulations.

Application rates of these granular formulations should not exceed 20 - 40 lb. active ingredient (acid equivalent) per acre, depending on the susceptibility of the target vegetation. Aqua-Kleen and Navigate are examples of granular 2,4-D product commonly used in New York. The application rate ranges from 100 - 200 lbs. of formulated granular product per acre. These products contain 27.6% active ingredient, which is the butoxyethyl ester (BEE) formulation. When applied to water, the BEE formulation disassociates to form 2,4-D acid, which has a smaller molecular weight than the BEE Active ingredient, so it actually contains only 19% of the active ingredient acid equivalent (ae). Two hundred pounds of these products, when applied to an acre of water, would only contain 19%, or 38 lbs. of 2,4-D. So, an application of 200 lbs. formulated product per acre is consistent with the above guidance not to exceed 40 lbs. Al(ae) per acre.

Note again that 6 NYCRR Part 327.6(c)(4) specifically limits the use of 2,4-D to within 200 feet of shore or water less than six feet deep, whichever gives the greatest distance from shore. Regardless of the need or desirability of a treatment outside these limits, they are specifically prohibited by regulation. To treat aquatic vegetation outside of these limits, a different aquatic herbicide product must be used.

D. Diquat Dibromide

Diquat is a contact herbicide¹¹ that is absorbed through the foliage of submerged plants. It is a "knockdown" product; it kills standing vegetation but it does not kill the entire plant, and regrowth of treated plants should be anticipated. All diquat products are registered in New York State under a Special Local Needs (SLN) registration that provides for more stringent use conditions than are in effect in other states or under the EPA-registered label. Concerns were raised about diquat when toxicity testing conducted at the Bureau of Habitat's Rome Field Station showed that diquat was very toxic to very young fish. Diquat product labels allow undiluted herbicide to be poured directly out of the container into the water from the back of a boat. When applied in this manner, "hot spots", or high concentrations of diquat, can occur. These hot spots might persist within the dense weed beds long enough to potentially be lethal to juvenile fish sheltered there. The best way to prevent "hot spots" is to dilute diquat and apply it only as a surface spray.

The SLN establishes the conditions under which diquat can be used in New York State:

A. For application only to ponds, lakes, and drainage ditches where there is little or no outflow of water and which are totally under the control of the product's user.

B. Do not apply to water where depth is three feet or less.

C. Dilute all applications by mixing with water prior to a treatment at a dilution of 1 part product to at least 200 parts water.

- D. Apply only by spray to the surface of a lake with a boom sprayer.
- E. Do not use diquat for algae control in New York.
- F. Do not combine copper with diquat in New York¹².
- G. Do not apply by air in New York.
- H. Do not use for control of water lettuce in New York.

I. Do not apply under conditions involving possible drift to food, forage, or other plantings that might be damaged or the crops thereof rendered unfit for sale, use, or consumption.

¹¹ A contact herbicide kills only the plant tissue with which they make direct contact. They are applied directly to weeds and are not translocated. A systemic herbicide is one that is translocated throughout the plant, and can cause a toxic injury anywhere in the plant or throughout the entire plant.

¹² Toxicity tests with diquat and copper together shows that the combination is highly synergistic; that is, together, the two compounds are much more toxic than either compound is alone.

J. Application rates:

	Target plant species	Gallons/surface acre
	Bladderwort	1-2
	Coontail	2
	Elodea	2
Submerged weeds	Naiad	1
	Potamogeton spp (except	2
	P. robbinsii)	
	Eurasian watermilfoil	1-2
	Pennywort	1/2 - 3/4
Electing woods	Salvinia	1/2 - 3/4
Floating weeds	Water hyacinth	1/2 - 3/4
	Duckweed	1
Marginal weeds	Cattails	1

Any application of diquat must be consistent with the requirements of the SLN registration. In addition to the limitations required with the SLN registration, Diquat is also specifically regulated in 6 NYCRR Part 327.6(b). All of the restrictions listed in that regulation, however, are addressed by the SLN with two exceptions, the treatment area and water use restrictions (see section VII, below). According to 6 NYCRR Part 327.6(b)(5), diquat treatment areas shall not extend beyond 200 feet from shore or beyond a maximum depth of six feet, whichever gives the greater distance from shore.

As of May 2015, the Bureau of Habitat is proposing changes to the diquat SLN. Specifically, BOH is proposing to drop the requirement to apply only by <u>boom</u> sprayer, and to reduce the required dilution from 200:1 to 50:1. Check PIMS for the most current SLN registration for Diquat to see if these changes have occurred.

E. Endothall

Endothall, like diquat, is a contact herbicide that will "knock down" standing vegetation, but not necessarily kill the plant or prevent regrowth the following season, or even later in the same season. One difference between endothall and diquat is that endothall appears to work more slowly than diquat. This is significant because a large, rapid dieoff of plant material could lead to a depletion of dissolved oxygen, particularly below the thermocline.

Like 2,4-D, there are several different formulations of this herbicide. When applied to water, the active ingredient formulations disassociate to release the acid form. The most common formulations are the dipotassium or disodium salts, and the dimethylalkylamine, or amine formulation. Both disassociate in water to produce the endothall acid, however, the dipotassium and disodium salts disassociate much more

rapidly. Ionic compounds, such as endothall acid, do not pass through biological membranes very easily, so endothall acid is not taken up to any great degree by aquatic animals. The dimethylalkylamine formulation does not disassociate as rapidly, and can be taken up by aquatic animals to a much greater degree than the salt formulations. This is reflected in toxicity. For fish and aquatic invertebrates, the LC₅₀s for the salt formulation of endothall range from 6.25 - 325 mg/L, but the LC₅₀s for the amine formulation range from 0.18 - 1.3 mg/L. Therefore, the Bureau of Habitat recommends that only salt formulations of endothall be used in fish-bearing waters.

Aquathol K uses the dipotassium salt of endothall in liquid form as its active ingredient. Aquathol Super K Granular is the same chemical in granular form and provides a slow release of the active ingredient at the lake or pond bottom thus having less impact on the entire water column. The label calls for application rates from 0.5 - 5.0 ppm, depending on the species of vegetation targeted for control. The label provides a chart so the user can determine how much product needs to be applied in order to achieve a particular active ingredient concentration in parts per million in different volumes of water.

Hydrothol 191 (Liquid) and Hydrothol 191 (Granular) are formulated with the dimethylalkylamine salt of endothall as the active ingredient. These chemicals can cause fish kills at dosages slightly above 0.3 ppm. The Hydrothol label states that the product is generally effective at controlling algae at application rates between 0.05 - 0.3 ppm; however, the label allows for application rates as high as 1.5 ppm for algae control. For control of aquatic macrophytes, the label application rates are as high as 5 ppm. Fish appear to avoid amine salts of endothall if given the opportunity. However, young-of-the-year and other juvenile life stage fish sheltered in vegetation in shallow water, three feet or less, might not have the opportunity to avoid the chemical treatment, as these fish are not likely to venture out into open water. The lack of a sizeable safety margin between efficacious application rates and toxicity thresholds suggests this product ought not be used where early life stage fish are likely to be present. The Bureau of Habitat recommends against the use of Hydrothol products in fish-bearing waters. If deemed necessary in a fish-bearing water, the Bureau of Habitat recommends that in order to prevent fish toxicity, Hydrothol products should only be used for algae control at concentrations of 0.3 ppb or less, or for control of infestations of hydrilla, if other herbicides have proven to be ineffective.

Aquathol K (or other salt formulation products) are the preferred endothall products for fish-bearing waters because they are inherently less toxic. Only as much endothall should be applied as is needed to control the target vegetation. For example, curly-leaf pondweed is controlled at an application rate of 1.5 - 3.0 ppm; Eurasian watermilfoil is controlled at an application rate of 3.0 - 4.0 ppm. Very few targeted aquatic plant species would require treatment at rates as high as 5.0 ppm.

F. Flumioxazin

Flumioxazin is a new aquatic herbicide that was first registered for use in New York in 2013. It is available under the product name "Clipper." Flumioxazin was registered for use on terrestrial plants since 2003. Like diquat and endothall, it is a contact herbicide. Floating and emergent vegetation are treated with a maximum application rate of 141 ppb. Submerged vegetation can be treated at a maximum application rate of 400 ppb. Up to six applications can be made to the same section of water after an interval of 28 days between applications. Submerged vegetation can be treated by surface spray or subsurface application. Floating and emergent vegetation can be treated by surface spray or subsurface application. Flumioxazin can only be used in slow moving or quiescent water; it cannot be applied to flowing water. There is no post-application restriction against the use of treated water for drinking, swimming, or fishing. Treated water cannot be used for irrigation for at least five days after application. Clipper cannot be used in water utilized for crawfish farming.

Flumioxazin degrades very rapidly through hydrolysis, particularly in waters of higher pH. The label warns that in waters with a pH above 8.5, the effectiveness of flumioxazin in controlling aquatic vegetation might be diminished because of rapid degradation.

G. Fluridone

Fluridone (most commonly known as Sonar), is a systemic herbicide that comes in two forms, an aqueous suspension (AS) and several varieties of granular formulations. The federal label allows liquid fluridone to be applied in concentrations as high as 150 ppb. Because of concerns raised by the Department of Health, liquid formulations of fluridone are registered under a Special Local Needs (SLN) registration, which states that no single application can exceed a concentration of 50 ppb, and the sum of multiple applications during the same season cannot exceed a total of 150 ppb. The concentration limits are based on the volume that is applied, and <u>not</u> on concentration as measured in the water column. The restriction that application rates of the aqueous suspension of fluridone not exceed a water column concentration of 50 ppb is also stated in 6 NYCRR Part 326.2(b)(4)(i). Lower application rates (20 ppb) are required within 1/4 mile of potable drinking water intakes.

Multiple applications during the same season can be an important factor for successful fluridone treatments. A concentration of fluridone that is lethal to target plants must be maintained for a 30 to 90 day period, depending on the dose applied and other environmental factors. The current protocol for extended fluridone treatments is to apply the product, then periodically measure the fluridone concentration in the water column using FasTEST, which is an enzyme-linked immunoassay (ELISA) test. This test allows for a rapid measurement of the fluridone concentration in the water. If the fluridone concentration starts to fall below efficacious levels in the treatment area, a

booster application or continuous application of a low dosage "drip" is made to restore the effective lethal concentration.

Fluridone is generally described as a selective herbicide, because some plants such as Eurasian watermilfoil (EWM) are killed at concentrations as low as 6 - 8 ppb, and continual exposure to concentrations as low as 3-5 ppb, although at this low concentration, the duration of the treatment needed for success is quite long and the margin for efficacy is small. The experience with fluridone use in New York, particularly in whole lake treatments to eradicate EWM at higher dosages, is that <u>all</u> vegetation is likely to be killed during the treatment, although some selectivity may be achieved at very low dosage rates and early season or late fall applications. Ideally, native plants that grow from seeds will regrow in subsequent years, and some regrowth of native plants from seeds can also occur during the same year as the treatment.

Granular, "slow release" formulations are the preferred tool for partial lake treatments. Pelletized products are not limited to the same conditions on the SLN label for the liquid suspension product. The same approach of multiple treatments based on the use of fasTEST results in order to maintain a lethal concentration can be accomplished with pelletized formulations as well. However, given the high solubility of the fluridone pellets, tightly controlled treatments solely within small treatment areas may be difficult to achieve.

6 NYCRR Part 326.2(b)(4)(ii) states that pelletized formulations may only be applied in water two feet deep or greater, however, the use of pellet formulations in waters less than two feet deep may be authorized for the control of invasive species through SLN permits. That same regulation also prohibits swimming in waters treated with fluridone for 24 hours following treatment, but that prohibition has been dropped for the liquid suspension only.

Fluridone's mode of action is to disrupt the synthesis of enzymes that are needed by a plant for photosynthesis. Because this mode of toxicity is so specialized for plants, fluridone exhibits very little, if any, direct toxicity to fish or aquatic invertebrates at concentrations allowed on the product labels. The greatest concern related to fluridone use is that with whole lake treatments, <u>all</u> vegetation is likely to be killed, not just the target species, and there is no guarantee what kind of, and how much, aquatic vegetation will grow back. Dramatic changes in the plant community may result in similarly significant changes in the fish community. Partial lake treatments with pelletized formulations are not likely to have significant lake-wide impacts, particularly if the general recommendations (Section III., above), above, are observed.

Eurasian watermilfoil is particularly susceptible to fluridone, both because it is highly sensitive to low concentrations, and because it doesn't generally reproduce from seeds. Eurasian watermilfoil is also an aquatic invasive species (Section IV., above). Ridding a lake of this invasive, nonindigenous plant can lead to a restored native plant community that is less likely to adversely affect human activities. However, if the lake is populated by fish species that are highly dependent upon vegetation, and if impairment to that fish

population is unacceptable, then smaller, partial lake treatments should be considered for EWM control rather than whole lake treatments, or a more selective product should be used.

H. Glyphosate

Glyphosate is a systemic herbicide that causes toxicity by interfering with the plant's ability to synthesize proteins and produce new plant tissue. It is an effective herbicide for controlling emergent and floating vegetation. It is not effective against submerged vegetation because it is rapidly diluted and dissipated in the aquatic environment. It must be applied to foliage in order to be absorbed. Glyphosate should not be applied to vegetation ½ mile upstream of a drinking water intake in flowing waterbody, or within ½ mile of a drinking water intake in a ponded waterbody. Applications should be made to actively growing plants to maximize effectiveness, and spray nozzle settings must be set to avoid fine mists which are capable of drifting. Aquatic animals are generally not sensitive to glyphosate, and the normal application rates are well below toxicity thresholds.

Glyphosate products come labeled for terrestrial and aquatic uses. It is very important that only glyphosate products labeled for aquatic uses are used for aquatic or wetland applications. Glyphosate products labeled for terrestrial use come premixed with a surfactant. The surfactant used is toxic to amphibians. Glyphosate products labeled for aquatic uses must be mixed with a surfactant. To insure that a similar problem of surfactant toxicity does not result from the use of glyphosate labeled for aquatic uses, only surfactants classified by the EPA as slightly toxic or practically non-toxic should be used with glyphosate. Appendix A contains more information and a partial list of surfactants that meet this criteria.

I. Imazamox

Imazamox is the active ingredient in the aquatic herbicide Clearcast. It is available in both liquid and granular formulations. The mode of action for Imazamox is that it interferes with the synthesis of three important amino acids, thus disrupting the plant's metabolism. Target plants usually die within 4-12 weeks after application. Like all herbicides, it works best when applied as early as possible, when the plants are actively growing. The approved SEIS for Imazamox states that it provides selective control of gramineous (i.e., grass-like) and broadleaf species and that it is very useful for controlling monocot species such as *Hydrilla verticillata*. However, to date, this herbicide has not been used to control any of the monoecious hydrilla infestations in the northeastern US.

Imazamox must be applied to the foliage, from where it is absorbed and transported to the roots. Sensitive species include bladderwort, Eurasian watermilfoil, variable leaf milfoil, curly leaf pondweed, and Hydrilla. Dicots are generally less sensitive than

monocots. Application rates generally range from 50 to 200 ppb, although the label allows applications as high as 500 ppb.

Imazamox is moderately persistent. It degrades primarily by photolysis, with a halflife in the laboratory of 6.8 hours. It is also degraded by microbes under aerobic conditions, but it is resistant to degradation under anaerobic conditions. In water, where imazamox is not likely to experience continuous exposure to high light conditions, it generally dissipates with a halflife of between 30-50 days, from photolysis, microbial degradation, and dilution.

Imazamox is classified by the EPA as practically non-toxic to fish and aquatic invertebrates. There are no restrictions on livestock watering, swimming, fishing, domestic use, or treated water for agricultural sprays although there are some restrictions on the use of treated water for irrigation (see Section VIII.). Imazamox may be applied to potable water sources at concentrations up to 500 ppb to within a distance of 1/4 mile from an active potable water intake. Within 1/4 mile, applications of Imazamox cannot exceed 50 ppb.

Imazamox appears to have some advantage over fluridone, in that it is more selective. Experience in New York (albeit limited) has shown that it is very effective for control of water chestnut, and has fewer water use restrictions. Persistence could be a concern in deeper or more turbid waters where light penetration might not be sufficient to support photolysis. Treatments can be authorized in accordance with the label, but monitoring for the disappearance of Imazamox and for any potential adverse impacts would be useful.

J. Sodium Carbonate Peroxyhydrate

This is the active ingredient of a new, non-copper based algaecide, GreenClean Granular Algaecide. When applied to water, the active ingredient reacts to generate hydrogen peroxide, which is a potent oxidizer. Hydrogen peroxide is highly unstable, and it quickly dissipates from the water. The label states: "Apply GreenClean Granular to any water or surface sites except treated, finished drinking water reservoirs or drinking water receptacles." This product is also intended to remove algae from surfaces that are in contact with water and are likely to accumulate algal growth, such as non-painted floors, walkways, storage areas, patios, decks, siding, boats, piers, docks, ramps, etc. Other commercial and horticultural sites identified on the label include water gardens, power washing, landscapes, drainage systems, impounded waters, wastewater, and irrigation systems. It can be applied directly in its granular form, as a liquid solution, or as a foam. The label application rates for treating water bodies are 90 - 500 lbs./million gallons of water for heavy algae growth and 9 - 50 Ibs./million gallons of water for low algae growth/maintenance (a pond with a mean depth of three feet and a diameter of 63 feet would constitute a volume of 1,000,000 gallons of water). This product is a restricted use pesticide (actually all pesticides applied to surface waters are restricted use). Because the product is individually

classified as restricted use, even those applications that are not made to surface water bodies can only be made by certified pesticide applicators. The only environmental hazards identified on the label are that the product is toxic to birds and highly toxic to honeybees.

The Bureau of Habitat has no experience with this product and cannot make recommendations other than that the product be used strictly in accordance with the label. A technical review of this product and its toxicity to non-target organisms suggests that this product will not be harmful to fish or aquatic invertebrates. Field studies have shown that the hydrogen peroxide generated by application of the active ingredient is nearly completely degraded within 12-24 hours of application.

K. Simazine

Simazine is available as an active ingredient in New York as a terrestrial herbicide. Currently, no pesticide products containing simazine as the active ingredient are registered for aquatic outdoor use in New York State. Simazine is used to control algae in home aquaria. Accordingly, no permit applications for the aquatic outdoor use of simazine products should be approved.

L. Triclopyr

Triclopyr is the active ingredient in the aquatic herbicide product Renovate. Triclopyr has been available for a long time in New York as a terrestrial herbicide (Garlon), but was registered for aquatic uses only recently. Triclopyr's mode of action is to mimic plant growth hormones, causing uncontrolled and disorganized plant growth that leads to plant death. Triclopyr works fairly quickly. Bending and twisting of leaves and stems occurs almost immediately, with chlorosis (bleaching) occurring at apices within three days, and defoliation and sinking occurring over the next two weeks.

Triclopyr is highly selective. It is effective against Eurasian watermilfoil and many other (but not all) aquatic dicots. Triclopyr has little or no effect on a large number of the more common monocots, such as naiads (*Najas* spp.), pondweeds (*Potamogeton* spp.), common waterweed (*Elodea canadensis*), and freshwater eelgrass (*Vallisneria americanum*) (wild celery or tapegrass). These species often constitute the more valued native species in New York aquatic plant communities. Monocots that are sensitive to triclopyr include: *Phragmites*, arrowhead (*Sagittaria spp.*), water hyacinth (*Eichhornia crassipes*), American frogsbit (*Limnobium spongia*), and water stargrass (*Heteranthera dubia*). Dicots that are generally not sensitive to triclopyr include narrowleaf dicots such as coontail (*Ceratophyllum*), fanwort (*Cabomba*), and bladderwort (*Utricularia* spp.).

Triclopyr is available in both liquid and granular formulations. The maximum application rate is 2.5 ppm. The primary means of degradation is photolysis, which can occur very

rapidly in bright light and clear water, with a halflife of less than one day. Other degradation pathways, such as aerobic microbial degradation, are much slower. In the SEIS, examples are provided in which triclopyr dissipated from water with a halflife ranging from 3-5 days, however, in Cazenovia Lake, triclopyr has proven to be quite persistent, although at very low concentrations.

The EPA classified triclopyr as slightly to practically nontoxic to aquatic fish and invertebrates. The labeled application rate is many times lower than toxicity thresholds. Triclopyr cannot be applied at labeled application rates within the vicinity of an active drinking water intake. The label provides information for determining the setback distance from an active drinking water intake, depending on the area of a lake surface to be treated, and the application rate. To apply triclopyr closer to a drinking water intake, the intake must be turned off and it cannot be turned on until the concentration immediately around the intake is determined to be 50 ppb or less (New York SLN Label).

Triclopyr has been used numerous times in New York State, including Saratoga Lake, Waneta Lake, Lamoka Lake, Cazenovia Lake, and Lake Luzerne. It has very effectively controlled infestations of Eurasian watermilfoil while leaving large areas of native vegetation unharmed. In Lake Luzerne, a large number of dead snails were observed within the treatment area following the treatment. However, the herbicide treatment does not appear to be the cause. Before a triclopyr treatment was approved for Cazenovia Lake, toxicity testing with snails was required because water from Cazenovia flows down Chittenango Creek and over Chittenango Falls, which is the home of the Chittenango amber ovate snail, an endangered species. Toxicity testing was conducted with two species of snails, and triclopyr was found to be practically nontoxic to both species. The snail species found dead in Lake Luzerne was the banded mystery snail, and this snail is known to experience regular die-offs of adults in late spring or early summer, which coincided with the timing of the triclopyr application¹³.

The Renovate product labels state that: "Water treated with Renovate 3 may not be used for irrigation purposes for 120 days after application or until residue levels of Renovate 3 are determined by laboratory analysis, or other appropriate means of analysis, to be 1 ppb or less." This has proven to be a difficult problem with the use of triclopyr, because the photolytic degradation can be slow in deeper or turbid waters. In lakes with an outlet, it is possible for triclopyr residues to move a considerable distance downstream before being degraded to the 1 ppb level.

M. 2,4,5-TP (Silvex)

¹³ Jokenin, E.H., H. Guerette, and R.W. Kortmann, 1982. The natural history of an ovoviviparous snail, *Viviparus georgianus*, in a soft-water Eutrophic lake. Freshwater Invertebrate Biology, 1(4):2-17, November 1982.

This chemical is not registered for use in New York. No herbicides containing this active ingredient may be authorized due to the potential for dioxin contaminants.

N. Water Colorants

Certain products function to control aquatic plants and algae by adding dyes to the water. These dyes block critical wavelengths of light and inhibit photosynthesis. They are not pesticides *per se*, because they are not toxic to plants. However, if their label makes pesticidal claims (i.e., <u>control</u> aquatic weeds, etc.) then they must be registered as pesticides, and permits are required before they can be applied to waters of the state. The products registered for use in New York use tartrazine (acid yellow 23) and erioglaucine (acid blue 9) as the active ingredients. They are generally applied at rates that result in a water column concentration of 1 - 2 ppm (mg/L). Both dyes are food grade dyes. A search of EPA's ECOTOX database revealed that the *Ceriodaphnia dubia* 48 hour EC₅₀ for tartrazine was 5,706 mg/L. No fish toxicity data were listed. For erioglaucine, the 48 hour EC₅₀ for *Daphnia magna* was > 97 mg/L¹⁴. The rainbow trout 96 hour LC₅₀ for erioglaucine was between 412 – 1,474 mg/L. Toxicity thresholds for these dyes are several of orders of magnitude higher than the concentrations at which they are used.

VIII. Water Use Restrictions

Water use restrictions are specific limitations placed on water that has been treated with a pesticide. The following table identifies the water use restrictions generally associated with each active ingredient. There might be differences on individual product labels. Not all individual product labels were checked.

One common water use restriction relates to the possibility of an aquatic herbicide contaminating drinking water, or more specifically, the presence of an aquatic herbicide in the vicinity of a drinking water intake pipe or structure. New York State has established water quality standards for the protection of water as a source of water supply for drinking, culinary, or food processing purposes (H(WS) standard) for many aquatic pesticides. These values have been adopted in regulation, in 6 NYCRR Part 703.5. The values are as follows:

Pesticide Active Ingredient	NYSDEC H(WS) value, μg/L (ppb)
2,4-D	50
Copper (dissolved)	200
Diquat	20
Endothall	50
Glyphosate	50

¹⁴ When a LC₅₀ or EC₅₀ is described as "greater than (>)", it signifies that little or no mortality (or effect) occurred, and the LC₅₀ or EC₅₀ is higher than the highest concentration tested.

These potable water use restrictions should be applied when an herbicide is applied to a waterbody (or could flow into a downstream waterbody) classified for use as a potable water supply (Class AA or A). In a Class AA or A water, these values take precedence over other values that might appear on pesticide labels as water use restrictions for pesticides applied in the vicinity of drinking water intakes. For example, the 2,4-D label states: "Unless an approved assay indicates the 2,4-D concentration is 70 ppb or less, Do not use water from treated areas for potable water (drinking water)." Because the NYSDEC H(WS) value is lower, water from treated areas cannot be used for potable water until an approved assay indicates the 2,4-D concentration is 50 ppb or less.

These regulatory restrictions do not be apply to herbicide treatments in waterbodies (or downstream waterbodies) not classified for use as sources of potable water (that is, Class B, C, or D waters).

Active Ingredient	Water Use Restriction	Source
Copper sulfate	Bathing and livestock watering shall be prohibited for at least 24 hours following a treatment	6 NYCRR Part 327.6(a)(7)
Chelated copper compounds	None	
2,4-D	Do not swim in treated water for a minimum of 24 hours after application. Use of the waters for irrigation shall be prohibited for a period sufficient to permit the decay of phytotoxicity. The treated waters and those waters affected by the treatment shall not be used for other purposes during the treatment and for at least 24 hours thereafter. Unless an approved assay indicates the 2,4-D concentration is 100 ppb or less, or, only growing crops and non-crop areas labeled for direct treatment with 2,4-D will be affected, do not use water from treated areas for irrigating plants or mixing sprays for agricultural or ornamental plants. Unless an approved assay indicates the 2,4-D concentration is 70 ppb or less, Do not use water from treated areas for potable water (drinking water). (In New York, the drinking water standard for 2,4-D of 50 ppb takes precedence in Class AA or A waters).	6 NYCRR Part 327.6(c)(6) 2,4-D liquid BEE labels (Navigate)

Active Ingredient	Water Use Restriction	Source
Diquat dibromide	Treated waters shall not be used for irrigation, bathing, fishing, or by man or animals for drinking or food processing for a period of 14 days after treatment	6 NYCRR Part 327.6(b)(7)
Endothall, (mono (N,N- dimethylalkylamine salt)	Do not use in brackish or saltwater. In order to allow for sufficient mixing of this product after application to bodies of water, swimming in the treated area is restricted until the day after application. Do not contaminate water intended for domestic purposes. Do not use treated water for animal consumption or for domestic purposes within the following periods: 0.3 ppm – 7 days after application; 3.0 ppm – 14 days after application; 5.0 ppm – 25 days after application. For applications of endothall, the drinking water setback distance from functioning potable water intakes is greater than or equal to 600 feet. The drinking water restrictions on this label are to ensure that consumption of water by the public is allowed only when the concentration of endothall in the water is less than 0.1 ppm (This is the value on the label. In New York, the drinking water standard of 50 ppb takes precedence in Class AA or A waters).	Hydrothol 191 Label and Hydrothol 191 granular label

Active Ingredient	Water Use Restriction	Source
Fluridone	Aqueous suspension formulations may be applied at application rates not to exceed 50 parts per billion. Swimming is prohibited for 24 hours following applications ¹⁵ . Pelletized formulations may only be applied in water two feet deep or greater, however, the use of pellet formulations in waters less than two feet deep may be authorized for the control of invasive species. Irrigation from a fluridone AS application may result in injury to the irrigated vegetation. The label suggests the following time frames to avoid irrigation with treated water to reduce the potential for injury: established tree crops - 7 days after application; established row crops/turf/plants - 14 to 30 days after application; newly seeded crops/seed beds or areas to be planted - assay required. Do not apply any formulation of fluridone (liquid or granular) at concentrations greater than 20 ppb within 1/4 mile of a potable water intake. At application rates between 4-20 ppb, liquid fluridone may be applied within 1/4 mile of a functioning potable water intake providing potable use of the water is delayed by 24 hours.	6 NYCRR Part 326.2(b)(4)(iii), SLN Label
Glyphosate	Do not apply within 1/2 mile of a potable water intake. Do not use treated water for drinking until the glyphosate level is below 0.7 ppm (This is the value on the label. In New York, the drinking water standard of 50 ppb takes precedence).	Rodeo label
Imazamox	Do not use treated water to irrigate greenhouses, nurseries, or hydroponics. Do not use any imazamox-treated waters from still or quiescent sources for irrigation purposes less than 24 hours after imazamox application was completed. Waters receiving imazamox may be used for irrigation as long as the concentrations are \leq 50 ppb. There are no restrictions on livestock watering, swimming, fishing, domestic use, or use of treated water for agricultural sprays.	Clearcast label

¹⁵ The 24 hr swimming restriction still applies to the aqueous formulation, still appears on the aqueous SLNs, and was not removed from Part 326. However, it was erroneously removed from the last printing of Part 326. The web version of Part 326 will be corrected.

Active Ingredient	Water Use Restriction	Source
Sodium carbonate peroxyhydrate		
Triclopyr	Water treated with triclopyr may not be used for irrigation purposes for 120 days after application or until triclopyr residues are determined by laboratory analysis, or other appropriate means of analysis, to be 1.0 ppb or less. To apply triclopyr within the labeled setback distance from a functioning potable water intake, the intake must be turned off until the triclopyr level in the intake water is determined to be 50 ppb or less (NOTE – this is a significant difference between the New York SLN Registration for triclopyr and the standard product label). There are no restrictions on livestock consumption of water from the treatment area. There are no restrictions on use of water in the treatment area for recreational purposes, including swimming and fishing for liquid formulations, but swimming is restricted for 3 hours following application with the granular (OTF) formulation.	Renovate label SLN Label
Water colorants	None	

IX. Ecological Impacts from Water Holding or Flow Restrictions

In situations where the movement of an herbicide out of the lake via an outflow is a potential concern, applicators could propose to limit, restrict, or totally block the flow of water out of the lake. Such blockage or restrictions of flow could have adverse impacts to water quality and/or aquatic life in the outfall stream. The Department adopted a water quality standard for flow, which states: "No alteration that will impair the waters for their best usage."

Natural Resources staff in cooperation with Division of Water staff must determine if blocking the outflow of a lake would be consistent with the flow standard, or whether it would constitute an alteration to flow that would impair the best uses of the outflow stream. Also, an Article 15 Stream Protection permit might be required, particularly if restricting the flow would necessitate installing a structure. So the issues to be considered are: 1) determining if a flow restriction is necessary; 2) deciding if blocking the flow out of a lake is ecologically acceptable for both the outflow stream that will lose

flow, and the lake itself that must retain the additional water; and 3) If so, how long must the flow be blocked or restricted? Some lakes have dams already installed, and flow restrictions are a common occurrence. Some outflows are very slow, quiescent waters, and restricting the flow out of the lake might not have much downstream impact, particularly for a short period of time. Outflow tributaries might receive flow from other lakes or tributaries, thus restricting the flow from one upstream source might not have a significant downstream affect. If restricting the flow would pose a threat to aquatic life in the outflow stream, then the flow restriction should not be allowed.

Flow restrictions should be in place for as short as possible that is consistent with the label.

Natural resources staff should be concerned that an herbicide applied in a lake or pond might leave the pond via the outflow, and have effects downstream. Some aquatic herbicides specifically state on the label that they are intended for use in ponds "... with little or no outflow". The likelihood of the herbicide leaving the treatment area via an outflow should always be addressed during the permit application process. The applicant should explain why this is not a concern; e.g., the treated areas are far away from the outflow, they are using a granular formulation that will not cause a significant concentration of herbicide in the water column, treated areas are small relative to the surface area of the lake, the lake has a relatively small outflow, the herbicide in use has a relatively short half-life in water, or there are no water use restrictions with this product. If there are substantive concerns, such as in a long-duration, lake wide Sonar treatment for Eurasian watermilfoil eradication, then a site-specific EIS for the proposed treatment should be required or recommend that the permit be denied.

X. Pond Restoration/Water Quality Improvement Products

Pond restoration/water quality improvement products are products or materials applied to waterbodies to improve the quality of the water, usually by limiting the availability of excess nutrients, specifically, phosphorus and nitrogen. The reduction of nutrients can result in a substantially lower level of algae production, and a concomitant reduction in turbidity. There is a considerable variety of such materials, including alum (aluminum sulfate hydrate, Al₂(SO₄)₃•14 H₂O), Phoslock, various bacterial products, barley straw, and several others.

Ultimately, the end result of the use of these materials/products is a reduction in the production of algae. Even though none of these products/materials are toxic to algae, they have recently (September 2014) been construed by the Office of General Counsel as pesticides, consistent with their interpretation of the ECL, because by suppressing the availability of nutrients they are in effect "preventing" algae¹⁶. None of these materials are registered as pesticides. In the past, these products have been used (through either SPDES or Article 24 permits) because the applicant(s) were careful to

¹⁶ A pesticide is defined in ECL 33-0101(35)(a) as any substance or mixture of substances intended for <u>preventing</u>, destroying, repelling, or mitigating any pest.

state that the purpose of the application was water quality improvement, or reduction of phosphorus without mentioning any potential impact to algae. However, in recent years, it has become common knowledge within the Department that the use of these products/materials is aimed primarily at reducing the abundance of algae.

At present, Division of Materials Management has determined that the use of alum should not be allowed because it is being used as an unregistered pesticide. That assessment has not formally been applied to any other materials besides alum. If an application for the use of a pond restoration/water quality improvement product states or implies that the goal of the treatment is algae control, then it cannot be approved. Alum and other water quality improvement tools continue to be evaluated by an Agency workgroup, comprised of DFWMR, DOW, DMM, and DER, to determine if consistent alternative permitting vehicles can be identified and implemented.

XII. Additional Comments

A. Diquat, endothall, and flumioxazin are contact herbicides or "knockdown" products. They do not kill the entire plant, but they will knock down the standing plant biomass. The herbicides are not translocated throughout the plant, and only the foliage that comes into direct contact the herbicides in the water column is killed. Aquatic vegetation treated with these compounds will regrow shortly after treatment. However, they can provide seasonal control.

B. Copper, 2,4-D, fluridone, glyphosate, imazamox, and triclopyr are "systemic" herbicides that are distributed throughout the entire plant, allowing for exposed plants to be killed completely. Targeted plants treated with these compounds are not as likely to grow back and populations take a much longer time to recover, as stands of treated aquatic vegetation can regrow from seeds or be reintroduced. Targeted plants that did not receive a lethal dose can recover. After the targeted plants have been largely removed, unsusceptible plants can recolonize these treatment zones and further delay the return of target plants.

C. It should be noted that many algaecide treatments are short-lived due to the rapid re-introduction of algae and the sustained nutrient base supporting their growth.

D. Eurasian watermilfoil and *Hydrilla* reproduce asexually by fragmentation. A one inch fragment can settle to the sediment and grow into a new plant. Mechanical harvesting of these plants is likely to produce fragments that can re-seed areas where vegetation was removed by harvesting or herbicides.

E. When large masses of vegetation are killed suddenly by herbicides, they will sink to the bottom and be degraded by bacteria. Microbial degradation of large masses of dead aquatic vegetation can deplete the water column of dissolved oxygen, particularly in the summer under the thermocline, or when the lake is shallow. In deeper lakes, the biochemical oxygen demand (BOD) associated with microbial degradation in the bottom waters can ultimately lead to nutrient release from bottom sediments, triggering algae

blooms. To preclude this problem, treatments should occur as early in the growing season as possible. The lake could also be divided up into sections which are treated at different times. This is frequently a label requirement.

F. Whole lake or large-scale partial lake treatments are generally restricted to fluridone and triclopyr applications to eradicate Eurasian watermilfoil. Regional Natural Resources staff should carefully consider the worst-case impacts when reviewing such proposals. The worst case scenario is that all vegetation will be removed, and only limited re-growth will occur in subsequent years. There could be a dramatic shift in the aquatic vegetation community, which could in turn dramatically change the fish community. For example, in Chautauqua lake, milfoil disappeared in the early 1990s, probably because of herbivorous insects. Milfoil was replaced in part by eelgrass¹⁷. This change in vegetation was a factor in a concomitant shift in the fishery from sunfish to white perch, as eelgrass favors the white perch's reproductive process of broadcasting eggs over vegetation. The potential for such changes in a lake ecosystem need to be considered and balanced against the obvious benefit of eradicating the Eurasian watermilfoil. Any such whole lake treatment proposal should include a comprehensive, long term plan for keeping Eurasian watermilfoil from being re-introduced.

¹⁷ Chautauqua County Federation of Sportsmen, Ad Hoc Chautauqua Lake Vegetation Control Committee, Position Statement, Chautauqua Lake Vegetation Control Program, April 27, 1999.

Appendix A: Surfactants Recommended for use with Aquatic Applications of Glyphosate

The herbicide glyphosate requires the addition of a surfactant. The surfactant enhances the speed by which plant tissues absorb the herbicide. There are two general formulations of glyphosate products. The product Roundup comes premixed with a surfactant, and is labeled only for terrestrial applications. The Rodeo and Accord¹⁸ products are labeled for aquatic uses, and a surfactant must be added.

Studies have demonstrated that the surfactant premixed with Roundup products is toxic to amphibians (Relyea and Jones 2009). The toxicity of Roundup raises the question as to whether or not other surfactants, when mixed with Rodeo or Accord formulations, could be toxic as well. The type of surfactant premixed with Roundup that is known to be toxic to amphibians is known as a polyethoxylated tallowamine (POEA) surfactant. That class of surfactants should not be used with Rodeo or Accord.

The surfactant issue is discussed in McLaren/Hart (1995). Surfactants, like any pesticide, are classified according to their toxicity. Those classifications are:

LC ₅₀ or EC ₅₀ *	Classification
< 1mg/L	Highly toxic
1 – 10 mg/L	Moderately toxic
10 – 100 mg/L	Slightly toxic
100 – 1,000 mg/L	Practically non-toxic
> 1,000 mg/L	Insignificant Hazard

Table 1. Classification of chemicals based on toxicity (Christensen 1976)

* The LC₅₀ is the concentration that is lethal to 50% of the exposed test organisms. The EC₅₀ is the concentration at which a particular effect, such as immobilization, is observed in 50% of the test organisms. A toxicity test for fish is typically run for 96 hours. A toxicity test for *Daphnia magna* is typically run for 48 hours.

McLaren/Hart (1995) list the toxicity of several surfactants grouped by their toxicity classification. Nine surfactants are listed as moderately toxic to fish, three are listed as slightly toxic to fish, and two are listed as practically non-toxic to fish (see Table 2).

The Bureau of Habitat recommends that a surfactant be selected that has been classified as either practically non-toxic or slightly toxic. The classifications in McLaren/Hart (1995) are based on toxicity to fish. It is highly unlikely that amphibian toxicity data will be available, so the assumption is made that fish toxicity data would also reflect amphibian toxicity data. By selecting a surfactant that is practically non-

¹⁸ Rodeo and Accord are the two primary products that were reviewed when glyphosate was originally registered. Numerous other pesticide formulators have been licensed to produce their own glyphosate products with their own individual product names. The label must always be checked to be sure that the glyphosate product proposed for use is 1) registered for aquatic uses, and 2) does not come premixed with a surfactant.

toxic or slightly toxic insures that a margin of safety would exist even if amphibians are more sensitive than fish.

If a surfactant is proposed for use that is not listed in McLaren/Hart (1995), the Bureau of Habitat can review the toxicity data and make a determination. Toxicity data must be requested from the manufacturer and submitted to the Bureau of Habitat for review. At least one 96 hour LC_{50} for a fish species should be submitted, however, the preferred data would include two fish, a cold water species and a warm water species (most typically rainbow trout and bluegill) and a 48 hour EC_{50}/LC_{50} for *Daphnia magna*. Occasionally, this information can be found in section 12 (Ecological or Ecotoxicity Information) of a product's MSDS. Table 2 lists surfactants that are either listed in McLaren/Hart (1995) or have been reviewed by the Bureau of Habitat, and are therefore recommended for use with glyphosate products labeled for aquatic applications.

Surfactant	Toxicity classification	Basis
Agri-Dex	Practically non-toxic	McLaren/Hart (1995)
LI-700	Practically non-toxic	McLaren/Hart (1995)
Spreader-Sticker	Slightly toxic	McLaren/Hart (1995)
Passage	Slightly toxic	McLaren/Hart (1995)
Liqua-Wet	Slightly toxic	McLaren/Hart (1995)
Cygnet Plus	Slightly toxic	Reviewed by BOH
Surflex AQ-80	Slightly toxic	Reviewed by BOH
Arborchem Clean Cut	Unknown but	Reviewed by BoH, tentatively
	appears to be of	approved on the basis of the
	limited toxicity	characteristics of the active
		ingredient. Toxicity data not
		submitted or reviewed.

Table 2.	Surfactants	recommended for	or use with	aquatic	applications	of alvphosate

Literature Cited:

Christensen, H.E., 1976. Registry of Toxic Effects of Chemical Substances. U.S. Department of Health, Education, and Welfare. National Institute for Occupational Safety.

McLaren/Hart, 1995. Use of the Registered Aquatic Herbicide Fluridone (Sonar) and Use of the Registered Aquatic Herbicide Glyphosate (Rodeo and Accord) in the State of New York, Final Generic Environmental Impact Statement. McLaren/Hart Environmental Engineering Corporation, 25 Independence Boulevard, Warren, New Jersey 07059, January 10, 1995, Version 5.0.

Relyea, R.A., and D.K. Jones, 2009. The toxicity of Roundup Original Max to 13 species of larval amphibians. Environ. Toxicol. Chem. 28(9):2004-2008