

4.5.10 Summary

Benthic barriers can be an effective treatment for the control macrophytes in small, localized areas of a lake like a dock, boat launch or a swimming beach, but are generally not practical for use in large areas (greater than several acres) as a consequence of cost and maintenance requirements. Materials have included sand and gravel, but the addition of such fill to lakes is not commonly permitted these days, so barriers in use today include mainly porous screen materials and solid sheeting of inert materials. Barriers can be difficult to install, carry substantial initial capital cost, and are labor intensive (particularly if removed, cleaned and replaced for long-term control). Plant control is virtually complete, however, and can enhance overall lake habitat as well as recreational access and safety. Barriers may impact non-target organisms, especially benthic dwellers, and will affect chemistry at the sediment-water interface, but the impacts are limited to the area of installation. As only small areas of lakes are typically exposed to benthic barriers, lake-wide impacts are not expected and have not been observed.

Benthic barriers have many advantages for plant control in small areas. They are unobtrusive and can be installed in areas that are not easily accessible by harvesters, although they can be difficult to apply to areas with obstructions. They are non-toxic, removable and very effective, and usually do not require extensive permitting. The major drawbacks are that they are expensive on an areal basis and require maintenance to be effective for multiple seasons. Gases can get trapped beneath them and cause them to billow up into the water column, but this can be handled by cutting slits or extra weighting. They may impact invertebrates and fish within the treated area, but act as an attractant to many fish and invertebrates.

4.6 HERBICIDES AND ALGAECIDES

4.6.1 Overview

Chemical treatment is one of the oldest methods used to manage nuisance aquatic weeds, and is still the most frequently applied approach. Other than perhaps drawdown, few alternatives to herbicides were widely practiced until relatively recently. With the range of plant management techniques now available, integrated programs are being encouraged by the MDEP and Conservation Commissions. Herbicide use remains a powerful tool in invasive and nuisance plant control, but can be supplemented with other techniques to prolong benefits and minimize adverse effects.

There are few aspects of plant control that breed more controversy than chemical control through the use of herbicides, which are a subset of all chemicals known as pesticides. The controversy is largely a function of perceptions regarding toxicity to non-target organisms, which is a very complicated subject not amenable to generalization. Toxicity is only a part of the equation when discussing pesticides. Exposure potential based on formulation, dilution factors, application rates and application method and the associated risks need to be considered. Risk is a function of product toxicity and the potential for exposure. The registration process employed by the USEPA and the Pesticide Bureau within the Commonwealth of Massachusetts is based on an understanding of the risks posed by these products. The basis for pesticide regulation is that the pesticide does not present an unreasonable risk of adverse impacts to human health or the environment when used in accordance with its label restrictions.

This section will attempt to provide a balanced perspective, but interested readers should seek out additional references on this topic to learn more. References with some depth include Shireman et al. (1982), Westerdahl and Getsinger (1988a; 1988b), WDNR (1989) and Hoyer and Canfield (1997).

Herbicides and algaecides contain active ingredients that provide the toxicity to target plants. For convenience, we will refer to this collective group of chemicals as herbicides in this section, with inclusion of algaecides inferred. Herbicides also contain inert ingredients or auxiliary compounds that aid application or effectiveness but may not themselves provide any toxicity. Consequently, different formulations may contain different percentages of active ingredient. For example, Sonar SRP contains 5% fluridone, the active ingredient, while Sonar AS contains 42% fluridone. Markedly different exposure scenarios can result from use of these two formulations.

Herbicides are typically classified as contact or systemic herbicides based on the action mode of the active ingredient. Contact herbicides are toxic to plants by uptake in the immediate vicinity of external contact, while systemic herbicides are taken up by the plant and are translocated throughout the plant. In general, contact herbicides are more effective against annuals than perennials because they may not kill the roots, allowing perennials to grow back. Seeds are also not likely to be affected, but with proper timing and perhaps several treatments, growths can be eliminated much the same way harvesting can eliminate annual plants. Systemic herbicides tend to work more slowly than contact herbicides because they take time to be translocated throughout the plant. Systemic herbicides generally provide more effective control of perennial plants than contact herbicides, as they kill the entire plant under favorable application circumstances. Systemic herbicides will also kill susceptible annual species, but regrowth from seeds will require additional treatments as with contact herbicides.

Another way to classify herbicides is by whether the active ingredients are selective or broad spectrum. Selective herbicides are more effective on certain plant species than others, with control of that selectivity normally dependent on dose (Langeland, 1993). Plant factors that influence selectivity include plant morphology, physiology and the stage of growth. Even a selective herbicide can kill most plants if applied at high rates. Likewise, contact herbicides may show some selectivity based on dose and plant features, but tend to be more broad spectrum in their effects.

There are only six active ingredients currently approved for use in aquatic herbicides in Massachusetts, with one additional ingredient (triclopyr) recently registered under the federal approval process and likely to be given consideration in Massachusetts soon. Herbicides often come in terrestrial and aquatic formulations, creating some confusion among laypersons over which trade name is applicable to which medium. Examples of aquatic herbicides registered for use in Massachusetts are listed in Table 4-4, grouped by active ingredient. All active ingredients allowable in Massachusetts as of July of 2002 are covered in Table 4-4. However, as products may be registered in any month and must be renewed each June, the list of products in Table 4-4 will probably be incomplete by the time this document is released. An updated list of registered herbicides can be obtained from the Department of Agricultural Resources. Application of

herbicides to lakes in Massachusetts is limited to licensed applicators except under special circumstances.

Additional compounds, mostly peroxides and other membrane-active substances, are in use in some states. These compounds basically rupture algal cell membranes and are marketed as algaecides with low toxicity to other plants and animals. Experience with these compounds in Massachusetts is limited to additions of potassium persulfate and related strong oxidants in the 1970s, and was generally unfavorable. Newer formulations may be more effective and have less impact on non-target organisms, but are not yet registered for use in Massachusetts and are not covered here. Various formulations of the common active ingredients are also in use in other states, but unless they are registered in Massachusetts they can not be used here.

Table 4-4 Aquatic herbicides and algaecides.¹

USEPA #	USEPA PRODUCT NAMES (% Active Ingredient)	MAX. RATE^{2,3}
	<u>2,4-D (2,4-dichlorophenoxyacetic acid)</u>	
34704-120	CLEAN CROP AMINE (46.5% DMA)	1.0 g
34704-606	SAVAGE DRY SOLUBLE HERBICIDE (95% DMA)	4.0 p
71368-1	WEEDAR® 64 (46.8% DMA)	10.0 g
71368-4	AQUA-KLEEN® (27.6% BEE)	150 p
228-61	RIVERDALE 2,4-D GRANULES (28.9% IOE)	200 p
71368-4-8959	NAVIGATE (27.6% BEE)	150 p
	<u>fluridone</u>	per 2 ft.
67690-3	SONAR™ SRP (5% fluridone)	16.0 p
67690-4	SONAR™ A.S. (41.7% fluridone)	0.2 g
1812-435	AVAST™ SRP (5% fluridone)	16.0 p
1812-447	AVAST™ A.S (41.7% fluridone)	0.2 g
	<u>glyphosate</u>	
524-343	RODEO® AQUATIC HERBICIDE (53.8% IPA)	0.94 g
524-343-71368	AQUANEAT (53.8% IPA)	0.94 g

Table 4-4 Aquatic herbicides and algaecides¹ (continued)

USEPA #	USEPA PRODUCT NAMES (% Active Ingredient)	MAX. RATE ^{2,3}
1278-8 64962-1	<u>copper sulfate (99% CuSO₄5H₂O)</u> TRIANGLE BRAND COPPER SULFATE CRYSTAL EARTHTEC® (20% CuSO ₄ 5H ₂ O)	per 2 ft. 10.6 p 10.8 g
8959-12 AA 8959-12- 10404 8959-10 AA 1812-307 1812-312	<u>copper complexes</u> CUTRINE®-PLUS GRANULAR (3.7% CU EA) LESCOCIDE-PLUS GRANULAR (3.7% CU EA) CUTRINE®-PLUS (9% CU EA) K-TEA™ ALGAECIDE (8% CU TEA) KOMEEN® AQUATIC HERBICIDE (8% CU EDA)	60.0 p 60.0 p per 2 ft. 6.0 g 6.8 g 8.0 g
10182-356- 10807 10182-353 10182-353	<u>diquat dibromide</u> MISTY WEEDTROL (4.35%) DIQUAT HERBICIDE (35.3%) REWARD® (35.3%)	20.0 g 2.0 g 2.0 g
4581-172 4581-174 4581-201 4581-204	<u>endothall</u> HYDROTHOL® 191 GRANULAR (11.2% Amine salt) HYDROTHOL® 191 (53.0% Amine salt) AQUATHOL® GRANULAR (10.1% DP salt) AQUATHOL® K (40.3% DP salt)	per 2 ft. 550 p 13.6 g 269 p 6.4 g

¹ Other aquatic herbicides are available but are not officially registered, or are not designated for use in lakes (see label instructions) and as such are illegal for use in Massachusetts. Triclopyr is not yet registered for aquatic use in Massachusetts.

² The maximum application rate is in pounds or gallons of product per acre. If a variable rate per depth is indicated, a 2-foot depth is assumed, but higher rates may be allowed in deeper depths. For Komeen the rate given is for 1-3 foot depths. Additionally, 2,4-D is in pellet form and is applied in accordance with the number of pounds per surface acre, regardless of the depth; as such, the concentration is not applicable.

³ The maximum application rate is for soft water. See the label for rates in hard water.

It is important to reiterate that only products registered for use in Massachusetts through the Department of Agricultural Resources (DFA) may be used in Massachusetts, and then only by licensed applicators with proper permits (except in some water supply cases and ponds with no outlets). Products registered by the federal government or by other state agencies are not necessarily accepted for registration in Massachusetts. Availability from mail order operations does not signify acceptability for use in Massachusetts or confer approval for unlicensed individuals or organizations to apply such herbicides.

Included are herbicides and algaecides registered in Massachusetts as of July 2002. Note that new products may be added monthly and allowed rates or restrictions may change as products are re-registered. Included are the USEPA registration numbers, the product name, the % active ingredient and the maximum application rate based on one method of calculation. Various salts and complexes are abbreviated: DMA = dimethylamine salt; IOE = isooctyl ester; BEE = butoxyethyl ester; IPA = isopropylamine salt; EA = copper-ethanolamine complexes; EDA = copper-ethylenediamine complex; DP = dipotassium salt. The maximum application rates of the product are from product labels, expressed in either gallons (g) or pounds (p) per acre. When volumetric rates are indicated on the product label, a 2-foot depth is assumed¹.

Herbicides may also contain adjuvants. An adjuvant is any chemical added to the herbicide to increase the effectiveness of the application. There are different classes of adjuvants, which generally function to increase the uptake of the herbicide by the plant, spread the herbicide through the water column, or help the herbicide adhere to the plant. Activator adjuvants include surfactants, wetting agents and oils. These adjuvants can help spread the herbicide in the water, as well as aid in the uptake of the herbicide by the plant.

A second class of adjuvants include the spray-modifier adjuvants, which include spreaders, stickers and spreader-stickers. These adjuvants aid in spreading the herbicide and increasing adherence to the plant. Foaming agents, polymers and inverting oils are also included in this group and are used primarily to control the drift of the herbicide from the target application area.

The final class of adjuvants encompasses the utility-modifier adjuvants. Included in this group are buffering agents, used to increase the dispersion and solubility of an herbicide and anti-foaming agents, used to reduce foam inside the spray tank (McWhorter, 1982; Langeland, 1993). Adjuvants are not expected to be toxic to the target species, but increase the toxicity of the herbicide or otherwise allow the active ingredient to be used more effectively.

Aquatic herbicides must be registered by the USEPA and the Massachusetts Department of Agricultural Resources. The criteria addressed in the registration process include data on forms of toxicity, impacts to non-target organisms, environmental persistence, breakdown products and fate of the herbicide constituents in the aquatic environment (Schmidt, 1984; Appendix III). Herbicide toxicology reports generally report toxicity in terms of LC50 or LD50. The LC50 is usually defined as the concentration (in ppm or mg/L of active ingredient) in water that will result in 50 percent mortality of the test species within the time period (usually 424 to 96 hours) and conditions of the test. The LD50 is defined as the amount of pesticide administered per kg of body weight of the test organism that will result in 50 percent mortality of the test species within

the time period (usually 24 to 96 hours) and conditions of the test. The LC50 tests are usually conducted for aquatic species such as fish and zooplankton, where uptake is generally via gills or direct adsorption. The LD50 tests are usually conducted for birds and/or mammals such as rats or mice, and the tests usually refer to oral doses of the herbicide.

Toxicology data are usually given in metric units of parts per million (ppm), which is equivalent to mg/L. In some toxicology reports, only the mass (weight) of the active cation or the equivalent mass of the acid form of the active anion is considered when reporting units of concentration. The nature and variability in toxicity reporting lend themselves to confusion and ambiguity in herbicide evaluations, and allow both proponents and detractors to make seemingly definitive but opposite statements based on the same data. Detailed information on toxicity and environmental fate of registered herbicides is provided in Appendix III. Additional general information on toxicity tests and ecotoxicology can be found in Hoffman et al. (1995).

While it is generally considered prudent to avoid contact with water immediately after treatment, and some states have their own use restrictions, there are no federal label swimming restrictions for any active ingredient currently in use. Irrigation restrictions of several days or more are common, and prohibition of use in drinking water is applied to all herbicides except copper and fluridone products. Treated waters must be posted as such in accordance with MDEP regulations.

The choice of herbicide to manage an undesirable plant population depends on the properties of the herbicide, the relative sensitivity of the target and non-target plants and other organisms that will be exposed, water use restrictions after herbicide use, and cost. Effectiveness in controlling the target plant species is normally the primary consideration, with the other factors determining a possible choice between two or more potentially effective herbicides, dose, and whether a treatment is actually feasible.

As many as 300 or more Massachusetts lakes were treated per year in the late 1960s and early 1970s, after which the number of treatments fell sharply (G. Smith, ACT, pers. comm., 1996). Concern over possible unintended impacts and availability of alternative techniques and funding were factors. From 1983 through 1991, roughly coinciding with the years of the MDEP Clean Lakes Program, permits for herbicide treatments ranged from 18 to 97, with an increasing trend observed over time (G. Gonyea, MDEP, pers. comm., 1996). From 1992 through 2002, the number of permits ranged from 77 to 231, with continuation of the increasing trend on a yearly basis (G. DeCesare, MDEP, pers. comm., 2003). Each License to Apply Chemicals may authorize one or more chemicals (average of between 2 and 3/license) to be applied to the lake.

In 1995, when treatments involved 257 individual applications of chemicals in Massachusetts, the frequency of use among chemicals was as follows: 2,4-D (10%), endothall as Aquathol K (5%), endothall as Hydrothol 191 (1%), copper sulfate or complexes (31%), diquat (30%), glyphosate (13%), fluridone (7%) and alum compounds and buffering agents (3%) (G. DeCesare, MDEP, pers. comm., 1995). Note that alum is not a herbicide, but requires a License to Apply Chemicals and is therefore included in this database. Copper and diquat accounted for more than half of the treatments in 1995.

In 2002, when treatments involved 605 individual applications of chemicals, the frequency of use among chemicals was as follows: 2,4-D (3%), endothall as Aquathol K (5%), endothall as Hydrothol 191 (1%), copper sulfate or complexes (29%), diquat (29%), glyphosate (19%), fluridone (10%), and alum compounds and buffering agents (4%) (G. DeCesare, MDEP, pers. comm., 2003). Copper and diquat again accounted for over half the treatments. Reduced use of 2,4-D is probably related to the MDEP ruling that limits use of 2,4-D in lakes near active wells. Increased use of fluridone is probably related to advances in formulation and application, with some gain related to the 2,4-D restriction. Increased glyphosate use is probably a function of efforts directed at peripheral emergent or floating leaved plants (e.g., loosestrife, lilies).

For comparison, the State of New York grants an estimated 300 or more permits for lake treatments per year. Fluridone has been used on at least 25 lakes of more than 20 acres with increasing frequency in New York state following 1995 approval for use there (S. Kishbaugh, NYSDEC, pers. comm., 2003). New Jersey issues over 700 permits annually for lake and pond treatments and Connecticut issues over 400 such permits (G. Smith, ACT, pers. comm., 2002).

4.6.2 Effectiveness

Aquatic plants controlled by commonly used herbicides are listed in Table 4-5. The list is not all-inclusive and effective control depends on the rate of application and other factors. Copper, which is primarily an algacide, is not included in Table 4-5, and triclopyr (pending registration for use in Massachusetts) is also excluded. Herbicide effectiveness may be influenced by such factors as timing, rate and method of application, type of species present and weather conditions. Additionally, dose determination should consider basin detention time, morphometry and water hardness to maximize effectiveness

Data in the table are from Nichols (1986), Appendix III and herbicide labels, with the assistance of the staff of ACT, Inc. See labels and text for additional information. C = consistent control (with correct dose, proper formulation and suitable conditions), P = partial control (control sometimes achieved, but may require a higher dose or be affected by conditions that are difficult to control). Re-growth or re-infestation may occur at some time after treatment, but usually not within the same year. The ability to control a plant with a herbicide does not necessarily indicate that the plant requires control in Massachusetts. NE indicates that there is no experience with the management of this species in Massachusetts, while NNM signifies that the species is not normally managed.

The effectiveness of some herbicides, for instance glyphosate, can be increased by the addition of an adjuvant (Harman, 1995). The addition of adjuvants, which may have toxic properties themselves, may increase the toxicity of the herbicide either by an additive or a synergistic effect. Adjuvants may be included under inert ingredients and not be listed explicitly on the label information. Often it is difficult to obtain information regarding adjuvants and truly inert ingredients used in commercial products as it is sometimes considered proprietary information. Toxicological information for many commonly used adjuvants is listed in Appendix III. Approval of an herbicide for use is normally dependent upon testing the complete formulation, however, so surprise toxicity to non-target organisms should be a rare occurrence.

Table 4-5 Aquatic plants controlled in Massachusetts by herbicide active ingredients

C = consistent control (with correct dose, proper formulation and suitable conditions),
 P = partial control (control sometimes achieved, but may require a higher dose or be affected by conditions that are difficult to control). Re-growth or re-infestation may occur at some time after treatment, but usually not within the same year. The ability to control a plant with a herbicide does not necessarily indicate that the plant requires control in Massachusetts. NE indicates that there is no experience with the management of this species in Massachusetts, while NNM signifies that the species is not normally managed in Massachusetts.

		Diquat	Endothall	2,4-D	Glyphosate	Fluridone
EMERGENT SPECIES						
<i>Butomus umbellatus</i> (flowering rush)	NE				P	
<i>Alternanthera philoxeroides</i> (alligatorweed)	NE					P
<i>Dianthera americana</i> (water willow)	NE			P		
<i>Eleocharis</i> spp. (spikerush)		P				P
<i>Glyceria borealis</i> (mannagrass)	NE	C				
<i>Juncus</i> spp. (rush)	NNM				P	
<i>Lythrum salicaria</i> (purple loosestrife)					C	
<i>Phragmites</i> spp. (reed grass)					C	
<i>Pontederia cordata</i> (pickerelweed)		P			C	
<i>Sagittaria</i> spp. (arrowhead – emergent forms)					C	
<i>Scirpus</i> spp. (bulrush)					C	
<i>Typha</i> spp. (cattail)		P			C	P
FLOATING/FLOATING LEAF SPECIES						
<i>Brasenia schreberi</i> (watershield)				P	C	P
<i>Eichhornia crassipes</i> (water hyacinth)	NE	C		C		
<i>Hydrocotyle</i> spp. (water pennywort)	NE			P		P
<i>Lemna</i> spp. (duckweed)		P				C
<i>Marsilea quadrifolia</i> (pepperwort)	NE	P			P	
<i>Nelumbo lutea</i> (American lotus)	NNM			P	C	P
<i>Nuphar</i> spp. (yellow water lily)				P	C	P
<i>Nymphaea</i> spp. (white water lily)				P	C	P
<i>Pistia stratiotes</i> (water lettuce)	NE	C		C		
<i>Polygonum amphibium</i> (water smartweed)				P	C	P
<i>Salvinia</i> spp. (Salvinia)	NE					P
<i>Spirodela polyrhiza</i> (big duckweed)	NE					C
<i>Trapa natans</i> (water chestnut)				C		P
<i>Wolffia</i> spp. (watermeal)		P				C
SUBMERGENT SPECIES						
<i>Cabomba caroliniana</i> (fanwort)						C
<i>Ceratophyllum demersum</i> (coontail)		C	C	P		C
<i>Chara</i> spp. (stonewort)		P	P			
<i>Coleogeton pectinatus</i> (sago pondweed, also known by the genera <i>Potamogeton</i> and <i>Stuckenia</i>)		C	C			C
<i>Egeria densa</i> (Brazilian elodea)		C				C
<i>Elodea canadensis</i> (waterweed)		C				C
<i>Elodea nuttallii</i> (slender waterweed)		C				C
<i>Hydrilla verticillata</i> (hydrilla)		C	C			C
<i>Megalodonta beckii</i> (water marigold)	NNM	P	P	C		C

Table 4-5 (continued) Aquatic plants controlled in Massachusetts by herbicide active ingredients

		Diquat	Endothall	2,4-D	Glyphosate	Fluridone
SUBMERGENT SPECIES (continued)						
<i>Myriophyllum aquaticum</i> (parrotfeather)	NE	C	C	C		P
<i>Myriophyllum heterophyllum</i> (variable watermilfoil)		C	P	C		P
<i>Myriophyllum humile</i> (low watermilfoil)		C	P	C		P
<i>Myriophyllum spicatum</i> (Eurasian watermilfoil)		C	C	C		C
<i>Najas flexilis</i> (bushy naiad)		C	C	P		C
<i>Najas guadalupensis</i> (southern naiad)		C	C	P		C
<i>Najas minor</i> (spiny naiad)		C	C	P		C
<i>Nitella</i> spp. (nitella)	NNM	P	P			
<i>Nymphoides cordata</i> (little floating heart)		C		P		P
<i>Nymphoides peltata</i> (yellow floating heart)	NE	C		P		
<i>Polygonum</i> spp. (water smartweed)				P	C	P
<i>Potamogeton amplifolius</i> (largeleaf pondweed)		P	C	P		P
<i>Potamogeton crispus</i> (curlyleaf pondweed)		C	C	P		C
<i>Potamogeton diversifolius</i> (waterthread)		C	C	P		P
<i>Potamogeton epihydrus</i> (pondweed)		C	C	P		P
<i>Potamogeton foliosus</i> (pondweed)		C	C	P		P
<i>Potamogeton gramineus</i> (variable pondweed)		C	C	P		P
<i>Potamogeton illinoensis</i> (Illinois pondweed)		P	C	P		P
<i>Potamogeton natans</i> (floating leaf pondweed)		P	C	P		P
<i>Potamogeton praelongus</i> (boatleaf pondweed)		P	C	P		P
<i>Potamogeton pulcher</i> (heartleaf pondweed)		P	C	P		P
<i>Potamogeton pusillus</i> (pondweed)		C	C	P		P
<i>Potamogeton richardsonii</i> (Richardson's pondweed)		P	C	P		P
<i>Potamogeton robbinsii</i> (Robbins' pondweed)		P	C	P		P
<i>Potamogeton zosteriformis</i> (pondweed)		P	C	P		P
<i>Ranunculus</i> spp. (buttercup)		C				P
<i>Sagittaria</i> spp. (submergent arrowhead)	NNM	P	P			
<i>Utricularia</i> spp. (bladderwort)		C				C
<i>Vallisneria americana</i> (water celery)		P	P			P

Note: *Chara* spp. (stonewort or muskgrass) and *Nitella* spp. can be controlled with copper, which also enhances the performance of Diquat on *Eichhornia crassipes* (water hyacinth) and some other species. Copper is the most common active ingredient in algaecides.

An herbicide treatment can be an effective short-term management procedure to produce a rapid reduction in algae or vascular plants for periods of weeks to months. Although long-term effectiveness from herbicide treatments is possible, in most cases herbicide use is considered a short-term control technique. Herbicides are generally applied seasonally to every two years to achieve effective control. Systemic herbicides, which kill the entire plant including the roots, generally provide results with greater longevity than contact herbicides, which can leave roots alive to regrow. In many cases, use of a herbicide will reduce the amount of regrowth the following season. In some cases involving fluridone or 2,4-D, as many as five years of control can be gained (G. Smith, ACT, pers. comm., 1995). In other cases, however, several applications per year may be necessary to achieve control goals.

Herbicide treatments are presently the most viable means of opening the vast acreage of water infested with the exotic water hyacinth (*Eichhornia crassipes*) in Florida and other southeastern states (Shireman et al. 1982). This is a case in which chemicals for management are a necessity until some other more long-term control, such as plant-eating insects, can be established. A similar case could be made for control of Eurasian watermilfoil or fanwort in Massachusetts. The use of herbicides to get a major plant nuisance under control is a valid element of long-term management when other means of keeping plant growths under control are then applied. However, failure to apply alternative techniques on a smaller scale once the nuisance has been abated places further herbicide treatments in the cosmetic maintenance category; such techniques tend to have poor cost-benefit ratios over the long-term.

Effectiveness of individual herbicidal active ingredients in use today is further discussed in association with each active ingredient in subsequent sub-sections of this herbicide review.

4.6.3 Impacts to Non-Target Organisms

Herbicides are intended to reduce the abundance of at least one plant species, and will usually cause a reduction in overall algal or plant biomass on at least a temporary basis. By their very nature then, herbicides may have an indirect impact on species dependent upon the affected plants for food or cover. This is no different than the corresponding impact of any other plant control technique. Where such changes in the plant community are temporary, only minor effects on non-target organisms are expected. Where the change in the plant community is more permanent, greater impacts are possible and represent a trade-off for conditions perceived to be more favorable to other lake users, human and non-human. If such indirect impacts to non-target species are considered intolerable, the project may not be permitted, but the desirability of plant control where an invasive species or excessive plant biomass is present is usually accepted.

Concern over impacts to non-target flora centers on protected species and overall impacts to the plant community that may affect habitat for fish and wildlife. Herbicides are intended to kill plants, and while advances in selectivity have been achieved through new or altered formulation, reduced dose, or timing and location of application, more plants than just the target species are normally at risk. In cases of excessive native plant growth, the herbicide may be intended to reduce the overall abundance of plants without targeting one species above all others. Usually, however, the herbicide is matched with the dominant species, and impacts to at least some other species will be less.

Where light and nutrients are sufficient, plants will grow. This applies to planktonic algae or floating vascular plants in the water column and rooted vascular plants and algal mats associated with benthic habitat. This will limit the longevity of benefits and the duration of impacts derived from herbicide use. Where protected plant species are threatened or even temporary loss of cover is viewed as an unacceptable impact, herbicide use may not be permitted, but usually the benefits of plant control by herbicides are perceived to outweigh temporary impacts to non-target flora.

Of greater concern with respect to herbicides is the potential for direct toxic effects on non-target fauna. To eliminate direct impacts to non-target organisms, the application rate must be below the rate that will impact the most sensitive non-target organism. While long-term chronic toxicity studies may be suitable to evaluate the impacts of repeated application of herbicides, most short-term effects are usually evaluated by means of the common LC50 lethality tests on fish, invertebrates and sometimes other aquatic organisms (see Appendix III). Note that the fish used in the tests may be less sensitive than those found in the lake to be treated. In most cases aquatic herbicides have relatively short aquatic half-lives and thus the standard 96-hour (or sometimes 24-hour) LC50 is commonly used. It is difficult to judge sub-lethal effects or estimate the No Observable Effects Level or the Maximum Acceptable Toxicant Concentration based on LC50 data alone. Commonly the Maximum Acceptable Toxicant Concentration is set at $\leq 10\%$ of the LC50 for any given herbicide to provide a margin of safety.

Other mitigating factors such as the form (granular or liquid), timing, temperature, water hardness and other environmental conditions are taken into account in testing and dose planning. The comparison of the initial environmental herbicide concentrations to the LC50 levels assumes there is no reduction in herbicide concentration due to adsorption to sediments or degradation during the 24- or 96-hour period after introduction. Larval or juvenile fish and invertebrates are often used in testing to maximize the effect, as older organisms tend to have higher resistance to impacts. A number of other conservative assumptions are typically made and are intended to result in allowable doses being lower than those that would actually cause observable effects on fauna in the aquatic environment. Field experience is taken into consideration during the re-registration process that herbicides must periodically undergo.

The degree of safety increases as the applied concentration decreases relative to the LC50. Each herbicide is evaluated individually based on the formulation and the expected concentration as a function of the percent active ingredient, application rate and depth of water. It is important to note that the concentrations allowed as application rates are much higher than those to which the public would be exposed under normal circumstances. The granular products may only slowly dissolve in the water over time and dissipate. Many of the compounds are rapidly removed from the water. Use in accordance with label instructions and restrictions is therefore not expected to result in toxicity to non-target fauna, including humans, other mammals, waterfowl, fish and invertebrates. Only in rare cases have herbicide treatments induced mortality in Massachusetts (R. Hartley, MDFG, pers. comm., 2003), but the chronic effects of frequent exposure are not truly known in many cases.

Chemical improvements of the last 30 years have greatly reduced non-target faunal toxicity, and testing advancements have allowed much more detailed evaluation of possible impacts. Fish kills are very rarely observed with use of herbicides today. Herbicide-induced fish kills that have

occurred in the US in recent years have mainly been a consequence of lowered oxygen during plant die-off, although overapplication in confined waters has also occurred (Hoyer and Canfield, 1997). Human error cannot be eliminated, and we can never be sure that chronic impacts will not occur, but herbicide formulations and applications have been greatly improved since the 1950s and 1960s.

Acute toxicity data for fish bioassays and rat ingestion studies are presented in Table 4-6, along with expected half-life in the aquatic environment, limits on maximum concentration and use restrictions. This simple table does not take the place of more detailed information available for each compound, and should not be taken out of context. Key points to be gleaned from this table include:

1. The maximum applicable concentration is less than the most sensitive fish LC50 for all but one 2,4-D formulation and two copper formulations. This does not mean that 2,4-D and copper will be toxic to fish, but that the possibility exists under the most extreme conditions tested. Toxicity of herbicides as assessed by the most sensitive fish bioassay is within an order of magnitude of the maximum applicable concentration.
2. The maximum applicable concentration is far less than the rat LD50 in every case. A 0.25 kg rat (about half a pound) would have to consume 5 liters of water containing the maximum concentration of endothal as the Aquathol-K salt (the ingredient in Table 4-6 most toxic to rats) to get a toxic reaction. For fluridone, the least toxic ingredient in Table 4-6, a 0.25 kg rat would have to consume more than 16,700 liters of water to get a toxic reaction.
3. Limitation on use in drinking water supplies generally follows the rat LD50 results. Restrictions apply to all herbicides, but greater restrictions or prohibition applies to those with lower ratios of LD50 to maximum concentration.
4. Half-life tends to be a matter of days for herbicides. The half-life is the time necessary for the concentration to be cut in half by natural degradation processes. Consequently, some herbicides may remain in the lake at low concentrations for many weeks if flushing is low. No impacts from chronic exposure to low doses of herbicides are generally known, and the synergistic effects of low doses of herbicides and other stresses in the aquatic environment are difficult to study in detail.
5. Aquashade is not an herbicide, but as it is treated as one in the regulatory process, toxicity information is provided here. It is interesting to note that the blue dye most responsible for the properties of Aquashade is more toxic to rats than some of the active ingredients in herbicides.

By way of further comparison, the rat LD50 values for two commonly ingested household chemical compounds are: table salt (NaCl), 3750 mg/kg (Merck, 1983); and aspirin (salicylic acid acetate), 1,500 mg/kg (Merck, 1983). Risk is a function of both toxic properties of the compound and exposure; information on either toxicity or exposure alone is insufficient to make risk predictions. It is important to consider both toxicity of the compound and likely level of exposure when evaluating herbicide risks.

Table 4-6 Massachusetts aquatic herbicide acute toxicity

ACTIVE INGREDIENT¹	Half-Life (days)	Max. Conc.² (ppm)	Fish LC50³ (ppm)	Rat LD50⁴ (mg/kg)	Use Restrictions⁵
2,4-D BEE {AE}	14-30	5.3	1.1	565	NU for D/I
2,4-D DMA {AE}	0.5-6.6	7.1	>100.0	490	D/I (3w)
2,4-D IOE {AE}	<14	7.1	7.2	>449	NU for D/I
GLYPHOSATE	1.5-14	0.70	86.0	>5,000	D (1/2 mile from intake)
COPPER EDA {Cu}	1-7	1.0	NA	498	D (1 ppm conc. limit)
COPPER TEA {Cu}	1-7	1.0	NA	1,312	
COPPER EA {Cu}	1-7	1.0	0.2	650-2,400	
COPPER SULFATE {Cu}	1-7	0.5	0.02	300	
DIQUAT	≤1	0.72	2.4	>194	D (3d), I (5d)
ENDOTHALL (AQUA-K salt)	≤10	5.0	47.0	99	F (3d), D/I (7-25d)
ENDOTHALL (HYDRO-191 ion)	≤10	5.0	0.1	233.4	
FLURIDONE	21-40	0.15	7.6	>10,000	D (1/4 mile from intake), I (7-30d)
TRICLOPYR	1.5-29	2.5	101.0	2,140	Not yet set
AQUASHADE (dye)	28	1.0	96.0	2,000	NU for D

¹The data are based on ion or salt concentrations {} as indicated.

²Maximum concentration assumes 2-foot water depth unless noted.

³The most sensitive fish 96-hour LC50s are listed except for Diquat, which was a 24-hour test.

⁴The LD50 is based on oral dose to rats.

⁵Key for restriction types: F=Fishing, S=Swimming, D=Drinking, I=Irrigation. Key for restriction limits: NU=Not to be Used, h=hours, d=days, w=weeks. See Appendix III and product labels for additional details.

Information on the nature of toxicity from herbicides is provided in Table 4-7. This summary, prepared by D. Manganaro of the MDEP, provides an appraisal of the mutagenicity and carcinogenicity of active ingredients and breakdown residuals and the level of certainty of possible effects. Note that no active ingredient in aquatic herbicides approved for use in Massachusetts is rated as having sufficient or substantial evidence of mutagenicity, and only three even qualify with suggestive evidence. Five active ingredients have limited or non-positive evidence of such effects. With regard to human carcinogenicity, no active ingredients or their breakdown residuals are known to be probable or possible carcinogens.

The Oral Reference Dose (RfD) indicates the amount that can be ingested per kg of body weight on a daily basis without apparent effect. RfDs for active ingredients in Massachusetts are far in excess of what a person or aquatic animal might be expected to consume on a daily basis. Risk of effects appears very low, but cannot be considered non-existent, however. Additional information on the Oral Reference Dose, the mutagenicity, carcinogenicity and developmental and reproductive effects of the herbicides are described in Appendix III and in documents prepared by the MDEP (1990) and USEPA (1986; 1995).

Fish impacts garner the most attention after herbicide treatments, but are rarely a function of direct toxicity. Most often it is low oxygen caused by decaying vegetation that leads to an herbicide-induced fish kill (Hoyer and Canfield, 1997). Invertebrate impacts are rarely reported, but may occur. Dead snails have been observed after treatments in some cases (e.g., Hoosac Lake in 1988, G. Gonyea, MDEP, pers. comm., 2002), but it should be noted that die off of snails is very common in eutrophic water bodies (L. Lyman, Lycott, pers. comm., 1997), partly as a function of abundance and the annual life cycle of some species (Jokinen, 1992). The difficulty in assigning causes to faunal mortality can be substantial.

4.6.4 Impacts to Water Quality

Direct impacts to water quality vary with the type of chemical and are discussed for each herbicide separately below. A general summary of usage restrictions for waters used for swimming, fishing, drinking and irrigation is provided in Appendix III. Most restrictions are based on potential toxicity to non-target organisms, especially humans, and may vary among formulations. Some herbicide labels warn about the depletion of oxygen in water bodies after treatment due to the decomposition of dead plants. The potential for major oxygen depression in Massachusetts waters is limited by the lower average water and air temperatures in the northern United States, but oxygen depletion is still possible. Increases in suspended solids and many dissolved constituents are possible as plants decay, with impacts varying with the amount of vegetation killed and specific lake features.

Shireman et al. (1982) caution that the following lake characteristics can produce undesirable water quality changes after treatment with herbicides for weed control, especially when they occur in combination:

- High water temperature
- High plant biomass to be controlled
- Shallow, nutrient-rich water

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Table 4-7 Herbicide toxicity summary (Manganaro, MDEP, unpublished compilation of data)

COMPOUND	RfD ¹	MUT. ²	CARC. ³	DEVELOPMENTAL/REPRODUCTIVE ⁴	SUMMARY
Aquashade	---	---	ID ⁵	-----	slightly irritating to skin and eyes; GI tract effects; not well characterized
Copper Sulfate	---	C	D (Cu salts)	(Copper) increased fetal mortality, developmental abnormalities, fertility effects in lab animals	(Cu) GI tract, liver, kidney effects; suggestive evidence of mutagenicity; not classifiable as to human carcinogenicity; some evidence of developmental or reproductive effects
2,4-D	0.003 mg/kg /day	D	D	embryotoxic, fetotoxic, weakly teratogenic in laboratory animals	effects on GI tract, liver, kidney, brain, pituitary, adrenal, lung, thyroid, CNS; limited evidence of mutagenicity; not classifiable as to human carcinogenicity; some evidence of developmental effects
Diquat	0.005 mg/kg /day	C	E	no significant teratogenicity in rats, mice or rabbits although teratogenic effects produced in animals dosed intravenously (iv) or intraperitoneally (ip); fetotoxicity in rats and mice given a single iv or ip dose	cataract formation; decreased organ weights; suggestive evidence of mutagenicity; no evidence of carcinogenicity in humans; some evidence of developmental effects
Endothall	0.02 mg/kg /day	D	ID ⁵	fetotoxicity in mice at 40 mg/kg/day (gavage) in presence of maternal toxicity; rat NOAELs (oral) of 12.5 mg/kg/day for maternal effects, 25 mg/kg/day for fetal effects; rat NOAEL of 150 ppm for maternal reproductive effects in a 2-generation study	effects on GI tract, liver, kidney; limited evidence of mutagenicity; insufficient data on carcinogenicity; inconclusive evidence of developmental or reproductive effects
Fluridone	0.08 mg/kg /day	E	E	no teratogenic effects noted at levels to 2000 ppm; fetotoxicity (in the presence of maternal toxicity) in rats at 1000 mg/kg/day and in rabbits at 300 mg/kg/day	skin and eye irritation; effects on kidney, testes; liver enzyme changes; organ/body weight changes; keratitis of eye; no positive evidence of mutagenicity; no evidence of carcinogenicity in humans; inconclusive evidence of developmental or reproductive effects
Glyphosate	2.0 mg/kg /day	E	D	fetal toxicity in male 3rd generation rat pups with parents exposed to 30 mg/kg/day; no teratogenicity in absence of maternal toxicity; fetal toxicity (in presence of maternal toxicity) at 3500 mg/kg/day	organ/body weight changes; no positive evidence of mutagenicity; not classifiable as to human carcinogenicity; inconclusive evidence developmental or reproductive effects
Triclopyr	0.005 mg/kg /day	C	ID ⁵	mild fetotoxic effects in offspring of rats dosed with 200 mg/kg/day (gavage); not teratogenic to rabbits at 100 mg/kg/day (gavage)	liver and kidney effects; suggestive evidence of mutagenicity; insufficient data on carcinogenicity; some evidence of developmental effects

Table 4-7 (continued) Herbicide toxicity summary

1. Oral Reference Dose (RfD) developed by the USEPA Office of Pesticide Programs (USEPA, 1995). An RfD is defined as an estimate, (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

2. Mutagenicity weight of evidence score determined using methodology defined in the Chemical Health Effects Assessment Methodology and the Method to Derive Allowable Ambient Limits (CHEM/AAL, 1990). Scoring scheme is defined as follows:

LETTER	MUTAGENICITY
<u>SCORE</u>	<u>WEIGHT OF EVIDENCE</u>
A	Sufficient
B	Substantial
C	Suggestive
D	Limited
E	Non-Positive
ND	No Data

3. Carcinogenicity weight of evidence as designated by the Office of Pesticide Programs (USEPA, 1995). Scoring scheme is defined as follows:

LETTER	CARCINOGENICITY
<u>SCORE</u>	<u>WEIGHT OF EVIDENCE</u>
A	Human Carcinogen
B	Probable Human Carcinogen
C	Possible Human Carcinogen
D	Not Classifiable as to Human Carcinogenicity
E	Evidence of Noncarcinogenicity to Humans
ND	No Data

* The USEPA Guidelines for Carcinogen Risk Assessment define "E" as having "No Evidence of Carcinogenicity to Humans".

4. Information on developmental/reproductive toxicity as summarized in herbicide toxicological profiles contained in Appendix to this document.

5. ID - Insufficient Data

- High percentage of lake area treated
- Closed or non-flowing system

These conditions occur in many Massachusetts waters that are treated, but various mitigative strategies have been developed over the last two decades to facilitate treatment while minimizing risk of adverse water quality impacts.

4.6.5 Applicability to Saltwater Ponds

Little information was found on the use of herbicides in saltwater ponds. Glyphosate is sometimes used on reed grass, but aqueous applications of other herbicides are uncommon. It would be expected that application would be comparable to freshwater systems, although toxicity to organisms (and possibly effectiveness) may be reduced somewhat as a function of increased dissolved solids content.

4.6.6 General Implementation Guidance

4.6.6.1 Key Data Requirements

Data requirements will vary depending on the nature of the problem and the specifics of each situation. Data collected prior to treatment should include accurate plant identification during the initial biological survey, with distributions and plant densities indicated on a map of the lake. The area to be treated should be clearly indicated. Adequate oxygen levels and relatively cool water temperature should ideally be present to avoid rapid plant decomposition and associated depletion of dissolved oxygen. Other data requirements include whether the water is used for drinking, swimming or irrigation and the proximity of drinking water wells. These issues should also be evaluated downstream in a lake with a flowing outlet. Many herbicides (especially copper) vary in toxicity with hardness (calcium and magnesium content) of the water, so this should be evaluated prior to setting dose rates. Estimates of short- and long-term effectiveness should be provided in terms of percent cover or biomass of target and non-target species.

4.6.6.2 Factors that Favor this Approach

The following considerations are indicative of appropriate application of herbicides and algaecides for the management of plants in lakes:

1. Periodic algal blooms impair recreation or water supply use, but are not a frequent occurrence (algaecides, mainly copper).
2. An invasive plant species has been detected at non-dominant levels but is not amenable to physical control techniques.
3. An invasive plant species has become dominant and is greatly reducing the diversity of native species, affecting habitat and water uses.
4. Overall vegetative density is excessive over a large portion of the lake, negatively affects habitat and water uses, is not amenable to alternative control methods, but requires management to meet reasonable intended uses. In such cases it is recommended that herbicides be considered as part of a long-term plan that seeks to prolong the benefits of an individual treatment.

4.6.6.3 Performance Guidelines

Planning and Implementation

There are many factors to consider when choosing and applying an herbicide that will determine the effectiveness and impacts of the application. Key factors to consider include the type and distribution of plants, water chemistry, lake area and volume, water depth, depth to any thermocline, sediment type, turbidity, fish populations, benthic and planktivorous fauna, presence of rare or endangered species and recreational uses. Based on these lake conditions, a careful evaluation of herbicide formulation, application rates, adjuvant addition, timing of the treatment and application method should be adjusted to increase effectiveness and minimize impacts.

Important questions to be answered before adopting a management program involving herbicides include:

- What is the acreage and volume of the area(s) to be treated? Proper dosage is based upon these facts.
- What plant species are to be controlled? This will determine the herbicide and dose to be used.
- How is this water body used and does the management plan have reasonable goals that balance the uses? Many herbicides have restrictions of a day to two weeks on water use following application, and most cannot be used in water supplies.
- What will the long-term costs of this decision be? Most herbicides must be reapplied annually, with a range of about two times per growing season to once per five years possible.

Where application of some herbicides (such as 2,4-D and diquat) to lakes heavily infested with plants has a clear potential for lakewide impacts to water quality and habitat, it may be recommended that the lake be treated in strips or sectors and that about 14 days be allowed between treatments. This method of application will minimize oxygen depletion from decomposing plants (RCC Undated a,b,c; National Chemsearch, 1987), and untreated areas can offer a refuge for fish. If desired, partial treatment of a lake might be done in a cross-hatch pattern to provide both open water and plant cover for fish. Such partial treatment approaches depend on low mobility of the herbicide, however. Active ingredients such as fluridone are highly mobile and not well suited to partial lake treatment unless the lake can be partitioned in some fashion, usually with limno-curtains.

It is often appropriate to dilute liquid herbicides and apply them evenly over the area to be treated in order to avoid areas of high concentrations that could impact non-target organisms. Pelletized formulations should also be spread evenly over the target area, but cannot be diluted prior to application. Competent applicators have developed approaches to meet a variety of plant management goals.

Lake managers who choose herbicidal chemicals need to exercise all proper precautions. As shown in Table 4-5, effectiveness of a given herbicide varies by plant species and therefore the nuisance plants must be carefully identified. Users should follow the herbicide label directions carefully, use only a herbicide registered by USEPA and the Massachusetts Pesticide Bureau for aquatic use, wear personal protective equipment as appropriate during application, and protect

desirable plants to the extent practical. Most states, including Massachusetts, require applicators to be licensed and to have adequate insurance.

Monitoring and Maintenance

Monitoring of the concentration of fluridone is becoming standard, but no such monitoring of other herbicides is commonly practiced. Most of the effort goes into planning and conducting the actual treatment. This is especially necessary for effective algaecide use, as the types and density of algae should be tracked to determine the appropriate treatment type and timing.

A visual survey for any large impacts (e.g., macroinvertebrate or fish kills) should be carried out and reported. MDEP should work with applicators to develop case studies to inform subsequent decisions on the appropriateness of various herbicides for specific applications. Depending on the scope and nature of the problem to be addressed, case study information might include the USEPA registration number, the maximum expected concentration of the active ingredient, and vegetation surveys (species and density). Surveys should be conducted before and after treatment to assess effectiveness. Where algaecides are used, assessments should include species identification and densities of algae and zooplankton. Basic water quality (pH, dissolved solids, temperature, and dissolved oxygen) should also be assessed. Where sensitive fauna are present, assessment of selected indicator populations would be helpful.

The cost issue for case history development is a bigger obstacle for herbicide treatment than most other techniques. While it is possible to perform at least a rudimentary assessment as noted above for <\$10,000, the cost of most chemical treatments is less than anticipated monitoring costs for such assessments. Herbicides are chosen not just for effectiveness, but based on cost, and a doubling of that cost is not well received by lake associations or others financing the project. An organized effort at the state level is necessary to gather the desired data for an overall evaluation of treatment impacts in Massachusetts, both for purposes of affordability and to achieve an appropriate level of coverage for treatment types and plant problems.

Other than possible re-application, there is little maintenance involved in herbicide treatments.

Mitigation

Once an herbicide is applied, there is little opportunity for mitigation. However, applicators can mitigate impacts during application by varying the timing of application to treat during times of active target plant growth, cool water, and higher oxygen content, as well as staggering the applications in space and time, applying a different application form of the herbicide (e.g., pellets, spray, wiper) to specific target areas or by using selective herbicides when this is an option.

4.6.7 Copper

Copper is a contact herbicide that is generally considered non-selective (Langeland, 1993). However, when copper is used at a continuous low dose it can be considered selective in some cases (Hansen et al., 1983). The active ingredient in copper sulfate and copper complexes is the copper ion. The mode of action of copper is to inhibit photosynthesis and may affect nitrogen metabolism (Kishbaugh et al., 1990; Olem and Flock, 1990). Copper is by far the most used active ingredient in algaecides. Copper is one of the only algaecides approved for use in potable