Physiological mechanisms of "selective" aquatic herbicides

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Editors Note: This paper does not follow the BFS tradition of reporting the results of monitoring or basic research. However, it does provide a recap of other researchers' reports regarding the subject. Since this information is not known to be summarized elsewhere, we are including it in this Annual Report.

INTRODUCTION

This paper reviews research articles identifying the physiological mechanisms (modes of action) of the most popular selective aquatic herbicides and discusses implications of those mechanisms to whole lake management. Specific attention is given to fluridone because it is being used widely and it is being considered for even more lakes contending with exotic macrophyte introductions (NYSFOLA 15th Annual Conference, 1998). Such introductions involve a half dozen or so notorious species such as the Eurasian watermilfoil (EWM) (Myriophyllum spicatum) that is now widespread in Otsego Lake (Harman, et al., 1997) and in many other northern U.S. lakes (Crowell, et al., 1996; Welling et al., 1997; Vermont Agency of Natural Resources, 1993; Vermont Agency of Natural Resources, 1996; NYSDEC Lake Services Section, 1997; and Ellis, 1998).

In exploring the literature, it quickly became apparent that specific modes of action are not a focus of interest for limnologists, lake managers, manufacturers or the government. Plant physiologists appear to comprise the group most interested in the modes of action of the herbicides, but most of their herbicide work focuses on terrestrial plants (perhaps because the dynamics of the aquatic environment are more complicated than that of soil and atmosphere).

Limnologists and lake managers considering the use of herbicides are typically driven to such consideration by the introduction of an exotic plant which disrupts the biological relationships between naturally occurring aquatic plants. Exotics typically arrive without natural predators and pathogens and, if they survive their introduction, tend to dominate. (If they do not survive the introduction, their introduction in unlikely to be noted.) When confronted with such situations, lake managers and limnologists look for an herbicide or a natural enemy that will kill off the exotic with minimum "collateral damage" to growth and relationships amongst naturally occurring plants. How the

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"solution" targets the exotic is not nearly as germane as the fact that the solution does target the exotic while permitting native plants to survive and to continue nutrient absorption, food production, and habitat development for other organisms (NYSFOLA Conf., 1998; Peverly and Johnson, 1979; Carpenter and Adams, 1978; and Jewell, 1970). Myriad examples of research documenting the practical selective effects and consequences of using various aquatic herbicides are found in the literature (Welling et al., 1997; Crowell, et al., 1996; Vermont Agency of Natural Resources, 1996; Vermont Agency of Natural Resources, 1993; Brooker and Edwards, 1975; and Maloney and Palmer, 1956 as examples).

While the U.S. government has not demanded to know how chemical herbicides do their job, it has mandated strict testing for herbicides involving residues, toxicity (acute and chronic), carcinogenicity, mutagenicity, neurotoxicity, reproductive effects, skin and eye irritation and impacts on other various animals (mammals, birds, and insects) as well as its fate when left in the environment. Industry has responded and those attributes for each aquatic herbicide have been provided to the government (Oregon State University, 1998 and Hoyer and Canfield, 1998) and often "repackaged" and provided to the public in advertising literature touting the herbicides. (For examples, see SePRO Corporation®, undated; Elf Atochem North America, Inc. ®, 1996; and Monsanto Company®, 1990.)

Legal aquatic herbicide active ingredients, other than those whose use is limited to irrigation ditches, include:

- copper,
- 2,4-D,
- dichlobenil,
- diquat,
- endothall,
- fluridone, and
- glyphosate (Hoyer and Canfield, 1998).

Aquatic herbicides that have been described as selective include:

- **Fluridone** (1-methyl-3-phenyl-5(3-(trifluoromethyl)phenyl)-4(1H)-pyridone [C_{19}H_{14}F_{3}NO]) marketed commercially as Sonar® by SePRO® (SePRO Corporation®, undated; Hoyer and Canfield, 1998; Crowell et al., 1996 and Humburg et al., 1989);
- **2,4-D** (2,4-dichlorophenoxy acetic acid [C_8H_6Cl_2O_3]) marketed commercially as Aqua-Kleen, Weedar®, and Landmaster® (Hoyer and Canfield, 1998, Vermont Department of Environmental Conservation, 1993; Gallagher, 1992; and Humburg et al., 1989);
- **Diquat** (1,1'-ethylene-2,2'-bipyrididylium dibromide salt [C_{12}H_{12}N_{2}Br_{2}]) marketed commercially as Aquacide®, Aquakill®, Dextrone®, Diquat®,

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\[2\] In both 1975 and 1998 the UK had eight plant growth inhibiting chemicals authorized for use in or around water (Brooker and Edwards, 1975; and Barret, 1998).
Reglone®, Reglox®, Reward®, Tag®, Torpedo®, Vegetrole®, and Weedtrine-D® (the last by Aquatic Ecosystems, Inc. ®) (Anonymous, 1998; Hoyer and Canfield, 1998; and Oregon State University, 1998 and Humburg et al., 1989);

- **Endothall** (3,6-endoxohexahydrophthalic acid (technical endothall) \([C_8H_{10}O_5]\); disodium-3,6-endoxohexahydrophthalate (disodium endothall); and 3,6-endoxohexahydrophthalic acid amine salt (amine salt of endothall)) marketed commercially as Accelerate®, Des-i-cate®, Aquathol® and Hydrothol® by Elf Atochem North America, Inc. ® (Hoyer and Canfield, 1998; Elf Atochem North America, Inc. ®, 1996; and Humburg et al., 1989);

- **Triclopyr** (3,5,6-trichloro-2-pyridinyloxyacetic acid combined with triethylamine salt \([C_7H_4Cl_3N_2O_2]\)) marketed commercially as Garlon 3A® by Dow Elanco® (and as Access®, Crossbow®, ET®, Grazon®, PathFinder®, Redeem®, Rely®, Remedy®, and Turflon® by others) which is being tested for aquatic environments in seven states with an EPA experimental use permit (Vermont Department of Environmental Conservation, 1993; and Humburg et al., 1989); and

- **Tordan 202C** (2,4-D plus picloram \([C_6H_3Cl_3N_2O_2]\)) also marketed as Grazon® (Forsyth et al., 1997; and Humburg et al., 1989).

Herbicides work by interfering with "growth, respiration, or photosynthesis" (Laws, 1993). In the following few pages we attempt to delineate what is known about the modes of action for the approved selective aquatic herbicides.

**Fluridone**

Fluridone appears to be the most aggressively marketed of the approved aquatic herbicides. In spite of this, it was missing from the most valuable on-line database dealing with aquatic herbicides as (potentially) toxic chemicals (Oregon State University, 1998).

Its categorization and action as a selective herbicide is challenged by the Vermont Agency of Natural Resources (1996). Nevertheless, the manufacturer touts the selective nature of fluridone in a 24 page glossy publication in which testimonials to the effectiveness of fluridone are included. According to the manufacturer, most native plants tolerate fluridone, but exotics such as EWM, hydrilla, and curlyleaf pondweed are susceptible to its chemistry. In those plants, fluridone interferes with carotenoid production leaving chlorophyll unprotected from decomposition by sunlight. The loss of chlorophyll leads to chlorosis on apical meristems and plant death (SePRO Corporation®, undated; and Humburg et al., 1989). The effects of fluridone are relatively long-lasting since it is a systemic herbicide (Hoyer and Canfield, 1998; and Vermont Agency of Natural Resources, 1996).
2,4-D

2,4-D is a long used herbicide with more testing and documentation associated with it than any other herbicide. Initial research on 2,4-D began under wartime secrecy during World War II (Page, 1998 and; Humburg et al., 1989). It may be the most widely used aquatic herbicide in the U.S. (Vermont Agency of Natural Resources, 1996). It is a chlorinated phenoxy compound which operates systemically to control various broadleaf weeds (terrestrial even more so than aquatic) (Hoyer and Canfield, 1998). It is an auxin that apparently resists breakdown by IAA oxidase (Levitt, 1969). It is readily broken down by sunlight, dissolved oxygen, sediment load and dissolved organic carbon. Nevertheless, minute amounts of 2,4-D have been detected in surface and groundwater (Oregon State University, 1998) even though the federal government prohibits its use in water intended for consumption. 2,4-D works quickly which can jeopardize aquatic oxygen levels when copious amounts of target macrophytes are in the treated area (Vermont Agency of Natural Resources, 1996).

As noted, much research has been focused on 2,4-D. Many enzyme functions are disturbed by 2,4-D which increases ethylene production. Nevertheless, it is believed the major mode of action for 2,4-D starts with a series of reactions that turn off the gene controlling RNase synthesis. Cell synthesis results if other hormones are available. RNA and protein movement to stems result in blockages effecting both transpiration and translocation. Additionally, 2,4-D interferes with oxidative phosphorolation (Forsyth, et al., 1997; Humburg et al., 1989; Ashton and Crafts, 1973; and Abeles, 1973).

Diquat

Diquat is considered selective only because it is a contact herbicide and its effects can be localized by careful application. It is a fast-acting herbicide and plant growth regulator. It is used in terrestrial agricultural operations as a desiccant (potatoes, seed crops, and sugar cane). A key advantage to its use is that it is ephemeral and leaves no residual trace in water, soil, or plants. It is broken down by photochemical degradation. Diquat's fast action is made possible by its absorption into plant leaves. It is so short-lived that it does not have direct impacts on plant tissues not exposed to its effects (Hoyer and Canfield, 1998; Oregon State University, 1998; and AGS Computer Services®, 1998). Because it kills so quickly, its use raises concerns about phosphorous regeneration and oxygen levels in the aquatic environment (Peverly and Johnson, 1979).

Diquat interferes with cell respiration and energy production. Even low concentrations of this herbicide can control aquatic weeds. Apparently, diquat anions form stable free radicals in water which, in turn, form unstable peroxide free radicals which provide the herbicidal effect (Humburg et al., 1989). While diquat is sold by a variety of vendors under various names as noted above, its basic manufacturer is Zeneca Ag Products®, 1800 Concord Pike Wilmington, DE 19897 (Oregon State University, 1998; and MacDonald, et al., 1992).
Endothall

Endothall is a contact selective herbicide that works well in muddy and flowing water (Elf Atochem North America, Inc.®, 1996; Hoyer and Canfield, 1998; and Oregon State University, 1998). It is used terrestrially both as an herbicide to control broadleaf weeds and annual grasses and as a desiccant to prepare alfalfa, potatoes, cotton, and clover for harvest. Aquatic herbicides are made from the potassium and amine salts of endothall and are used to control phytoplankton, Potamogeton spp., Ceratophyllum spp., Myriophyllum spp. (including EWM), Elodea spp. and others (Oregon State University, 1998; and MacDonald, et al., 1992). Because it is a contact herbicide, its effects on target species are relatively short-lived (Vermont Agency of Natural Resources, 1996).

Endothall promotes ethylene production (Abeles, 1973) and works on target species by inhibiting lipid and protein synthesis and protein breakdown and by, apparently, inhibiting respiration. This was determined by MacDonald, et al. (1992) in a series of experiments with cucumber (Cucumis sativa L.) in which they evaluated ion leakage in light and dark, inflorescence of leaf disks, and oxygen consumption of leaf disks. While some plants metabolize endothall acid, others die from exposure to this compound which is comprised solely of carbon, hydrogen, and oxygen. Endothall does not move past the symplast in aquatic plants. Degradation in the environment is attributed to metabolism by microorganisms (Elf Atochem North America, Inc.®, 1996). The basic manufacturer of endothall is ELF Atochem North America®, Three Parkway, Room 619 Philadelphia, PA 19102 (Oregon State University, 1998 and MacDonald, et al., 1992).

Triclopyr

Triclopyr is similar to 2,4,5-T which is notorious for dioxin impurities. Dioxin has not been found associated with triclopyr, which is a fast-acting selective and systemic herbicide used to control various woody and broadleaf plants in terrestrial applications. It is an auxin type herbicide that accumulates in meristem tissues. There is little written about its performance as an aquatic herbicide although the Vermont Agency of Natural Resources claims that it is more EWM selective than fluridone. The lack of literature is almost certainly due to its conditional use permit status. Since it is fast acting, it cannot be used in whole lake applications because of the potential for oxygen depletion associated with the die-off of the macrophytes effected. Because it is systemic, it can prevent target macrophyte regrowth for periods in excess of a year. The basic manufacturer of triclopyr is Dow Elanco®, 9330 Zionsville Road, Indianapolis, IN 46268-1054 (Oregon State University, 1998 and Humburg et al., 1989).

Tordon 202C

As noted previously, tordon 202C is a mixture of 2,4-D with picloram which produces an apparent herbicidal "synergistic effect" (Forsyth, et al., 1997). Inasmuch as 2,4-D is discussed above, picloram will be discussed here. Picloram is included in a number of commercial products including Access®, Grazon®, Pathway®, and Tordon®.
and is regularly combined with other herbicides such as bromoxynil, diuron, 2,4-D, MCPA, triclorpyr, and atrazine (Oregon State University, 1998).

Picloram is a systemic herbicide used to control various woody and broadleaf plants in terrestrial applications, particularly those intended to foster grass growth. It stimulates ethylene synthesis which inhibits flowering and has other effects. Picloram is absorbed by all plant parts, but less so by foliage than by roots. It remains in the plants for a considerable period of time. The basic manufacturer of picloram is Dow Elanco®, 9330 Zionsville Road, Indianapolis, IN 46268-1054 (Oregon State University, 1998; Forsyth, et al., 1992; and Abeles, 1973).

Discussion and Conclusions

The herbicides described in the preceding vary in their suitability for aquatic environments that vary in

- water movement rates;
- suspended particles;
- macrophyte communities.

Since aquatic environments vary so widely, the variety of choices is fortunate. What is unfortunate is that there appears to be little consensus on the selectivity of the various herbicides.

Results of partial and whole lake tests demonstrate trends in selectivity for various aquatic herbicides (Mol, 1994; Vermont Agency of Natural Resources, 1996; Crowell, et al., 1996; and Welling, et al., 1997), but the variation in results underscores our lack of understanding of the mechanisms by which these herbicides work. Aquatic chemistry is complex. It is easily hypothesized that varying lake chemistries interact with selective herbicides in ways that influence their selectivity. We need more focus and research on the specific mechanisms by which the selective herbicides select.
Literature Cited


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