Evaluation of Request to Apply the Aquatic Herbicide 2,4-Dichlorophenoxy Acetic Acid Butoxyethyl Ester to Selected Massachusetts Ponds for the Control of Water Milfoil (*Myriophyllum* spp.)

Prepared by

The Office of Research and Standards
Massachusetts Department of Environmental Protection
1 Winter Street
Boston, MA 02108

May, 1999

INTRODUCTION AND BACKGROUND

An integral part of the Massachusetts Department of Environmental Protection's strategy to protect the quality of drinking water resources in the state is to manage activities which might adversely impact water quality around waters used directly as sources for public water supplies or contributing to waters intended for such use. One of the activities is application of chemicals for nuisance aquatic weed control. Included in this category are water bodies that fall within areas defined as Zone IIs of public water supplies. In 1993, the DEP Drinking Water Program asked the Office of Research and Standards to review the toxicological and environmental fate characteristics of a number of chemicals used as herbicides (including the butoxyethylester (BEE) form of 2,4-D as Aqua-Kleen) which might be employed for the control of nuisance aquatic vegetation. ORS produced an evaluation (ORS, 1993) which contained its recommendations on each of the chemicals. 2,4-D was not recommended for use because of outstanding concerns about the potential carcinogenicity of this chemical. In the face of this uncertainty, ORS chose to recommend against the use of this chemical, given that there were other chemicals available for the same use that did not have the same uncertainties about their effects.

Since that evaluation was completed, new studies and several recent comprehensive reviews of the mammalian toxicity of 2,4-D have been completed. There has also been continued interest from some applicators and citizens for the use of 2,4-D to control nuisance infestations of water Milfoil in lakes and ponds in the state. ORS has therefore undertaken a review of the recent works and studies and summarized them in an updated review of 2,4-D, presented in their accompanying Background Document and the detailed toxicological evaluation of Harnois (1999).

One of the primary 2,4-D products traditionally used for aquatic weed control has been the butoxyethyl ester form of 2,4-D combined with inert pellets in a granular mixture known as "Aqua-Kleen". Until the last year, this product was manufactured and marketed by Rhone-Poulenc. The product was sold to NuFarm Americas Inc. and is now marketed by them. Applied Biochemists Inc. also markets a product with the same apparent formulation as Navigate.

The purpose of this evaluation is to integrate the current understanding of the toxicity of 2,4-D with the case specific exposures which might result from the intended use of 2,4-D in the Water Supply Program and offer a recommendation on whether or not it should be used for aquatic weed control in Massachusetts water sources intended for use as drinking water resources, or overlying groundwaters serving as source waters.

ISSUES

There are three principal issues which are addressed in this evaluation:

- likely exposure levels versus levels at which human toxicity is seen and exposure limits
- durations of exposures
- potential carcinogenicity of 2,4-D

The toxicological review (Harnois, 1999) has noted that the information available on the human health effects of 2,4-D is insufficient to justify characterizing it as a carcinogen and that the potential adverse health effects from exposures to this chemical can be adequately addressed by using the well documented noncancer toxicity information as a basis for identifying protective exposure limits or assessing health risks.

The potential exposures to humans after treatment of a water body will be examined in the following subsections. The magnitudes and durations of these exposures will then be compared with both exposure route-specific "safe" doses (reference doses, RfDs) for 2,4-D BEE and with media specific concentration limits.

CASE SPECIFIC EXPOSURE EVALUATION

The situation considered in this hypothetical exposure evaluation is one where the BEE form of 2,4-D (i.e., Aqua-Kleen or Navigate) for aquatic weed control will be applied to surface water bodies according to product label specifications to kill water Milfoil.

Product Formulation:	27.6% active ingredient (2,4-D BEE)
Application Rate:	recommended for Milfoil, 45 kg Aqua-Kleen/ha (≡100lb/acre; equivalent to 12.42 kg active ingredient/ha)

Predicted Water Concentrations After Application

In some cases where a treatment chemical is uniformly applied over a surface area of lake or pond, a simple volumetric dilution calculation will give a first approximation to the types of concentrations of the applied chemical which might result in the water column. However, for a product like Aqua-Kleen which is bound to granules which rapidly sink to the bottom, this type of calculation would be inappropriate. There is applicable field experience from controlled applications of this product to lakes and artificial ponds to indicate the types of concentrations of the active ingredient that might result and the chemical transformations which might take place with time (e.g., Birmingham et al., 1981; Hoeppel and Westerdahl, 1983). This information has been summarized in the Background Document included in this review package. Maximum BEE water concentrations one day after application at the above noted application rate were 0.16 and 0.65 mg/L in artificial ponds in the two studies. The 2,4-D acid concentration on day 1 in the same study with the 0.16 mg/L BEE was 1.7 mg/L. The ester is rapidly changed to the acid form of 2,4-D and maximum acid concentrations

were near 3 mg/L within the first two weeks after application. The ester concentration decreased to less than 0.01 mg/L after 15 days and the acid form decreased to about 1 mg/L after 85 days. The ester breaks down in water to butoxyethanol and the acetate form of 2,4-D and then to 2,4-dichlorophenol (Hoeppel and Westerdahl, 1983). Having reviewed results from a number of pre-1980 studies, Bovey and Young (1980) concluded that phenoxy herbicides including 2,4-D BEE do not persist in water bodies after applications, and that "significant" concentrations may only occur for a relatively short time after treatment. Our more recent appraisal would suggest a tempering of those conclusions.

Evaluation of Potential Human Exposures

The primary exposure route of concern after treatment of surface waters is through ingestion of water. The magnitude of these potential exposures will be estimated by comparing likely concentrations of the chemical in lake water or in groundwater under a treated lake with exposure route specific concentrations and also considering durations of potential exposure in relation to the time periods associated with toxicity values (e.g., subchronic or acute).

For the purposes of this evaluation, no distinction will be made between the chemical forms of 2,4-D since the drinking water limits and RfDs are given for 2,4-D and not the various forms of the parent compound 2,4-D. In addition, the level of information on differential uptake rates of the various forms of 2,4-D is not sufficient, nor is the level of analysis in this evaluation intended to incorporate this aspect of exposure. Once in the body, most forms are rapidly changed to the acid form.

The preceding paragraphs indicate that maximum concentrations of 2,4-D seen in surface water after application may reach 3 mg/L (acid form) within two weeks after application and decline thereafter. The studies reporting this information plus another by Aly and Faust (1964 cited in Bovey and Young, 1980) indicate that low concentrations of the acid form may be detected for up to 180 days. It should be noted that the study by Birmingham et al. (1981) which provided the concentration data used here was conducted in southern Ontario, Canada. Weather conditions in Massachusetts would generally be warmer than those of Ontario and a temperature related increased rate of decay of the 2,4-D BEE and its decay products after application would be expected in Massachusetts compared to Ontario.

The potential for harm to human health from drinking water which has been treated with Aqua-Kleen or Navigate can be estimated in two ways: directly comparing expected concentrations in water to drinking water guidelines for this chemical; and calculating average daily doses of 2,4-D from ingesting the water and comparing them to reference doses. Risks to both children and adults can be assessed.

The best estimate available of the maximum exposure from a single day's exposure (an acute exposure) would be to 3 mg/L 2,4-D. This concentration is greater than the

applicable acute drinking water exposure guideline termed a One-Day Health Advisory for children for this chemical (Table 1). The acute dose (expressed in mg 2,4-D/kg human body weight/day) associated with ingesting water containing this concentration of 2,4-D is greater than the acute RfD for children, and about the same for adults. Similarly, for a daily exposure during the period when concentrations might be highest (est. 34 days after application), the time weighted average concentration for children would be greater than the 10 day Health Advisory Value for children. These approaches suggest that if children's or adult's average drinking water requirements were met by treated lake or pond water for up to several weeks after treatment, then there is a possibility that some might experience adverse health effects.

Table 1. Potential Human Health Drinking Water Exposures, Doses and Applicable Criteria

Exposure Duration (d)	Type of Duration	Conc. (mg/L)	EPA Guidance (mg/L)	Daily Dose* (adult/child) (mg/kg/d)	RfD (mg/kg/d)	Daily Dose/RfD (adult/child)
1	acute	3.0 (max.)	1 (1d child HA)	0.09/0.3	0.1 (acute)[1]	0.9/3
34	subacute	~2 (TWA)[3]	0.3 (10d child HA)	0.06/0.2	-	-
180	subchronic	1.0 (TWA) [3]	0.1 (Longer-Term HA, child) 0.4 (Longer-Term HA, adult)	0.03/0.1	0.01 (subchronic)[2]	3/10

* Daily dose calculated as: conc (mg/L) * water ing. rate (2L/d adult, 1 L/d child) * 1/ body wt (70 kg adult, 10 kg child)

[1] RfD from US EPA (1987)

[2] RfD derived from US EPA (1987). Based on same 90 d study used by EPA for chronic RfD where they did not apply Adjustment Factor of 10 for subchronic to chronic study results.

[3] time-weighted average of 2,4-D acid decay curve in water for period indicated from Birmingham et al. (1981).

An evaluation of potential risks from use of the water for drinking over the period during which 2,4-D residues might persist (180d) can be performed in much the same way as was done for the acute exposures. In this case, the exposures are termed subchronic. Drinking water guidelines and subchronic RfDs are the appropriate comparative values for use in the evaluation. Since the concentration of 2,4-D decreases exponentially over time, a time weighted average concentration is calculated for this period using the decay curve for the 2,4-D acid form in water from Ontario experimental ponds (Birmingham et al., 1981). This average daily concentration of 1 mg/L is shown in Table 1 and is greater than both the adult Longer-Term Health Advisory (intended for exposures lasting up to 7 years) and an advisory level for this same subchronic exposure period (Table 1)

calculated for children using children's default exposure parameters. Average daily doses associated with these exposures are greater than the subchronic reference dose. This evaluation also suggests that there would be a possibility of adverse health effects from daily ingestion of treated lake water for up to 180 days after treatment.

The federal drinking water standard (Maximum Contaminant Level, MCL) for 2,4-D of 0.07 mg/L is probably not the most appropriate basis for comparison in this evaluation. For public water supplies, MCLs are compared to running quarterly average concentrations of chemicals in the water. In the case of 2,4-D, potential exposures up to one third of a year (180 days) are possible. The MCL is set to protect against chronic toxicity from chronic exposures. The more appropriate comparison values for less than chronic exposures are duration-specific toxicity values (acute and subchronic RfDs) and equivalent water concentrations for exposure durations being considered (One or Ten Day or Longer-Term Health Advisories).

The Health Advisories and the risk assessment using RfDs only account for the potential noncarcinogenic effects of this chemical. The MCL is set such that it reflects the U.S. EPA's judgement that this chemical is not a carcinogen (specifically: not classifiable as to its carcinogenicity) and therefore exposure limits need not reflect allowance for this type of effect. ORS has recommended that, pending the availability of additional test data, the recognized NOAEL which is the basis of the MCL and subchronic and chronic RfDs (Table 1) be used as a basis for identifying environmental concentrations protective of human health.

Contamination of groundwater serving as a drinking water supply source under lakes and ponds is the other potential outcome of herbicide use that is of concern. The potential for this event happening was evaluated in the Background Document provided with this review packet. For the purposes of this evaluation, there do not appear to be adequate numerical data to permit projection of likely 2,4-D residue concentrations in groundwater after application to surface waters at label rates. The evidence for whether or not this happens is divided. Conditions favoring groundwater contamination as a result of recharge through lake and pond bottoms would seem to exist where bottom sediments are porous or where there are fractured bedrock bottoms. The first condition exists in the southeastern part of Massachusetts where the geology of sandy sediments with low organic content would be conducive to recharge along with residual 2,4-D from application to lakes. .

The conclusions derived above for human drinking water exposures are consistent with the use guidelines for this product which specify that it should **not** be applied to water used for drinking (humans or livestock), nor should treated water be ingested. The evaluation above suggests that the drinking water prohibition should extend up to perhaps six months. The guidance also consists of a one-day exclusion of swimming after application.

There would also appear to be a reasonable potential for applied 2,4-D to contaminate groundwater under and downgradient from some lakes and ponds.

RECOMMENDATION

ORS recommends, consistent with federal guidance, that 2,4-D BEE containing granular aquatic herbicides not be applied for aquatic weed control to lakes or ponds in Massachusetts which serve as source water for drinking water or which contribute within a third of a year and with no substantial dilution, through surface water flow, to other source waters.

This recommendation is made because previous field experience has shown that concentrations of 2,4-D in water after application of this type of product can persist for several months at concentrations above health-based exposure limits. For the particular purposes of MA DEP Drinking Water Program, there also seems to be a reasonable potential to contaminate groundwater resources underlying some types of lakes or ponds, including those in the southeastern part of the state. Therefore, **application is not recommended to surface water bodies where waters may substantially contribute to groundwater which might serve as a drinking water sources. These situations would most likely exist as a result of recharge through porous, sandy sediments on lake bottoms or fractured bedrock lake bottoms.**

REFERENCES

Birmingham, B.C., M. Thorndyke and B. Colman. 1981. The dynamics and persistence of the herbicide Aqua-Kleen in small artificial ponds and its impact on non-target aquatic microflora and microfauna. p. 12-23. In, N.K. Kaushik and K.R. Solomon, eds. Proceedings of the Eighth Annual Aquatic Toxicity Workshop: November 2-4, 1981, Guelph, Ontario. Can. Tech. Rep. Fish. Aquat. Sci. No. 1151.

Bovey, R.W., and A.L. Young. 1980. The Science of 2,4,5-T and Associated Phenoxy Herbicides. John Wiley & Sons. New York.

Harnois, M. 1999. Toxicological Profile for 2,4-Dichlorophenoxyacetic acid (2,4-D). Office of Research and Standards, Massachusetts Department of Environmental Protection. Boston, MA

Hoeppel, R.E., and H.E. Westerdahl. 1983. Dissipation of 2,4-D DMA and BEE from water, mud and fish at Lake Seminole, Georgia. Water Resources Bull. 19:197-204.

Mattson, M.D., P.J. Godfrey, R.A. Barletta and A Aiello. 1998. Eutrophication and Aquatic Plant Management in Massachusetts. Final Generic Environmental Impact Report. Report prepared by the Water Resources Research Center, the University of Massachusetts. Amherst. For the MA Department of Environmental Protection and the Department of Environmental Management.

ORS. 1993. Memorandum from Nicholas Anastas to Tara Gallagher. "ORS recommendations on the use of aquatic herbicides within Zone II Water Supply Areas". Office of Research and Standards. Massachusetts Department of Environmental Protection. Boston, MA

Rodriguez, E.M., M. Schuld, and L. Romano. 1994. Chronic histopathological effects of parathion and 2,4-D on female gonads of *Chasmagnathus granulata* (Decapoda, Brachyura). Fd. Chem. Toxic 32:811-818.

U.S. EPA. 1987. Health Advisory for 2,4-Dichlorophenoxyacetic acid. U.S. Environmental Protection Agency. Washington, DC.