Evaluations Of Controlled Release PVC And Attaclay Formulations Of 2,4-D On Eurasian Watermilfoil[1]

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ABSTRACT

Attaclay granules and polyvinyl chloride (PVC) pellets containing the butoxyethanol ester (BEE) of (2,4-dichlorophenoxy) acetic acid (2,4-D) were evaluated in outside growth pools for efficacy in providing extended control of Eurasian watermilfoil (*Myriophyllum spicatum* L.). Periodic determination of 2,4-D content in the water provides information on the relationships between rate of release from the herbicide carriers, concentration in the water and phytotoxicity. The attaclay granules at 2 ppmw dose rates of 2,4-D produced greater herbicidal injury, longer control, and higher concentrations in water than PVC pellet at 4 ppmw dose rates. Regrowth was not controlled longer than 6 weeks after application because neither formulation was able to maintain phytotoxic herbicide levels (0.25 ppmw 2,4-D).

INTRODUCTION

The conventional method of applying liquid formulations of herbicides for the control of submersed aquatic weeds is to apply a phytotoxic concentration of herbicide in the entire volume of water. Injury to non-target organisms — both plant and animal — caused by this type of treatment can be quite severe, depending upon the toxicity of the herbicide.

This injury may be reduced, however, by applying herbicides in inert carriers to give controlled release. Rather than treating the entire volume of water, it may be possible with selected carriers, to release the herbicide near the soil-water interface where the plant growth originates and where the propagating structures are located. Proper timing of application may prevent dense growths of aquatic plants by inhibiting or preventing growth early in the growing season. Controlled release of a herbicide from a carrier may also prevent regrowth which emerges from propagating structures buried in the bottom muds.

Some early uses of the technique of applying pesticides on inert carriers were in mosquito control (2, 4, 5, 7, 10, 17). The earliest report on the use of herbicides on carriers is by Oborn, *et al.*, 1954 (9), who used (2,4-dichlorophenoxy) acetic acid (2,4-D) pellets for the control of several species of pondweeds (*Potamogeton* spp.). Granular formulations of herbicides are now commonly used in aquatic weed control. These have been either sinking granules which release the herbicides near the bottom for the control of submersed plants (12, 13, 14), or floating granules which release the herbicide at the water surface for control of floating and emerged vegetation (15, 16). The concept of releasing herbicides slowly over long periods of time is relatively new. The precedence for the use of this technique has been in the control of mosquitoes, barnacles, and snails (1, 3, 8, 11, 18).

This study was undertaken to evaluate the efficacy of a polyvinyl chloride (PVC) pelleted formulation of 2,4-D for extended control of Eurasian watermilfoil (*Myriophyllum spicatum* L.).

METHODS AND MATERIALS

The investigation was comprised of laboratory determinations of the rate of herbicide release from experimental formulations, and of bioassay of herbicide formulations

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in outside growth pools. Determinations were also made of 2,4-D content in water of growth pools to provide information on the relationships between rates of herbicide release from carriers, concentration in water, and phytotoxicity.

Release Rate Determinations. Butoxyethanol ester (BEE) of 2,4-D-1-^{14}C herbicide-PVC complexes were prepared from a premixed plastisol by the following general procedure. A PVC plastisol was prepared by mixing 50 g of Geon 135[2] PVC resin with 50 g of dioctylphthalate (DOP) plasticizer. Herbicide-plastisol formulations containing 10, 20 and 30% of herbicide were prepared by adding 0.20, 0.40, and 0.60 g herbicide to 1.80, 1.60 and 1.40 g plastisol, respectively. Five μc of 2,4-D-1-^{14}C herbicide (16 mg) in 1.0 ml of DOP were added to each formulation. The mixtures were stirred, poured into 6 mm I.D. glass tubes, and cured at 125 to 130 C for 30 min. The rod-like products were removed from the glass tubes and cut into pellets weighing approximately 82 mg.

Five pellets were placed in 400 ml of tap water in a screw capped, glass jar and stored at 25 C. Each concentration of 2,4-D-PVC formulation was replicated three times. Aliquots of 1.0 ml were taken at 1, 3, 5, 7 days and at weekly intervals thereafter through 20 weeks.

Each 1.0-ml sample was placed in 14 ml of scintillating fluid for analysis by liquid scintillation counting. Samples were analyzed for radioacticity using a liquid scintillation counter, which had a counting efficiency of 95.6% (unquenched standard).

Preparation of Experimental Formulations for Bioassays. PVC was evaluated as a plastic carrier by preparing herbicide-PVC formulations from a premixed plastisol. Formulations were prepared according to the following precedure. A PVC plastisol was prepared by dispensing 100 g of Geon 135 resin in 150 g of DOP plasticizer. Herbicide was added to the plastisol, the mixture stirred, and poured into aluminum pellet molds. Thermal curing in an oven at 125 to 135 C for 30 min produced pellets weighing approximately 75 mg.

Boiassays. In September, 1969, field-collected cuttings of Eurasion watermilfoil were planted in outside culture tanks which contained 3,700 L of water. These tanks were 2.4 m in diameter and 2 m deep. Treatments of 2,4-D BEE formulated in PVC (30% a.i.) were applied in June, 1970, at concentrations of 1.0, 2.0 and 4.0 ppmw. The 1.0 and 2.0 ppmw rates were compared with a field-tested commercial clay-granule formulation of 2,4-D BEE[3] (12, 13, 14). Each randomized treatment was replicated three times. Herbicidal effects were observed and recorded 1 week after treatment and at 2-week intervals thereafter. Injury was rated on a 0 to 100% scale, which indicates no effect to complete kill.

Residue Analysis. Samples for residue analysis were taken before application of the herbicide and then after 1, 4, 7, 14, 28, 42, and 56 days. The sampling, extraction and analytical procedures used were as follows: three 1.0 L samples were taken at equal intervals around the circumference of the pools. The three samples were composited, mixed, and a 1.0 L subsample of the composite taken for extraction. The pH of the composite sample was adjusted to pH 12 with sodium hydroxide, shaken, and allowed to stand for approximately 30 min to hydrolyze the ester. The pH of the sample was then adjusted to pH 1.5 with concentrated hydrochloric acid and a 500 ml aliquot was extracted twice with two 25 ml volumes of chloroform. The chloroform extracts were then evaporated to remove the chloroform, and the 2,4-D acid was converted to the methyl ester using a Boron trifluoride methylation procedure (6) and analyzed by gas chromatography.

A Micro-Tek Model 150 gas chromatograph with a ^{63}Ni electron capture detector was used for analysis of water extracts. The instrument was equipped with a 2 m by 6 mm glass column packed with 80/90 mesh Chromosorb W coated with 3% OV-1. The operating parameters were: oven temperature 200 C; inlet temperature 235 C; outlet temperature 240 C; detector temperature 250 C; carrier gas N_2; column flow rate 60 cc/min; scavenger flow rate 20 cc/min; and chart speed 0.125 inch/min. The retention time for the methyl ester of 2,4-D relative to aldrin as unity (1) was 0.30. The percent recovery of known amounts of the methyl ester was calculated to be 54.4%. All analyses were corrected for recovery.

RESULTS AND DISCUSSION

Release Rate Determinations. The total amount of 2,4-D released from the formulations increased with increasing pellet concentrations. For example, 9.9 mg, 16.3 mg and 35.9 mg had been released after 28 days from the 10%, 20% and 30% formulations respectively. The initial release rate was greater in the 30% and 20% formulations (Figure 1). After 35 days, the release rate was greater in the 10% formulation. The greatest amount of herbicide was released during the first week in all formulations. This may have been due to immediate rinsing and near-surface release of herbicide from the pellets. The 30% formulation was selected for further evaluation in the bioassays because of the greater amount of herbicide released, and the faster initial release.

Bioassay. The 4.0 ppmw rate was the most effective of the PVC formulations and produced 93% control at 6 weeks (Table 1). The 1.0 and 2.0 ppmw rates of the PVC

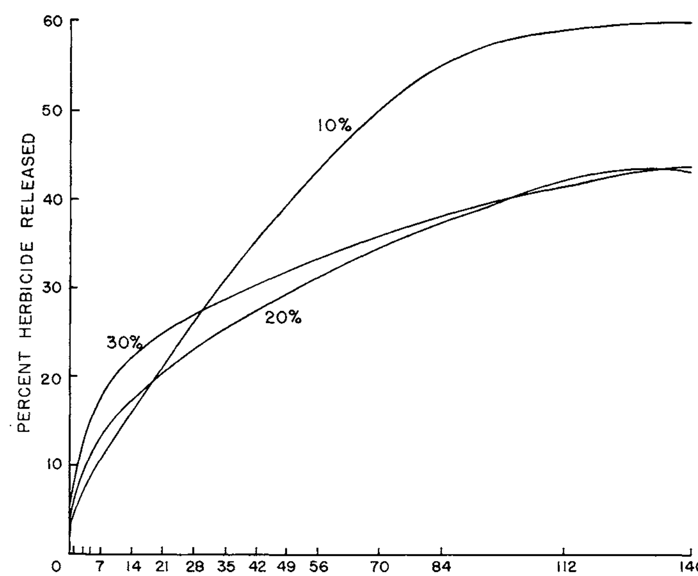

Fig. 1.—Percent herbicide released from 2,4-D BEE PVC formulations.

[2]Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture, and does not imply its approval to the exclusion of other products that may also be suitable.

[3]Contains 20% (w/w) 2,4-D acid on 8 to 15 mesh attaclay granules.

Table 1. Control of Eurasian Watermilfoil with Two Formulations of 2,4-D BEE in Outside Pools.

Treatment		Percent control[a]					
		Weeks after treatment					
Formulation	Concentration (ppmw)	1	2	4	6	8	10
PVC	1	8	17	18	33	20	18
	2	10	28	30	57	37	25
	4	13	30	90	93	89	89
Attaclay	1	12	38	96	97	95	90
	2	17	43	99	99	100	99
Controls		0	0	3	7	10	12

[a]Injury scale 0—no effect; 100—complete kill.

formulation did not provide effective control of the plants. The 1.0 ppmw rate of the clay granule was approximately equal in effectiveness to the 4.0 ppmw rate of the PVC formulation. The 2.0 ppmw rate of the clay granule was the most effective treatment in the experiment. The near maximum phytotoxic response from all treatments occurred approximately 4 weeks after treatment. Regrowth from below the hydrosoil was observed 6 weeks after treatment in the 4.0 ppmw PVC pellet, and in the 1.0 and 2.0 ppmw clay-granule treatments. A decrease in the average percent control with time in the various treatments indicates that regrowth had occurred (Table 1).

Relationship between herbicide concentration in water and phytotoxicity. The 2 ppmw clay granule treatment produced the highest concentration in water (Table 2). This was also the treatment which produced the greatest phytotoxic effect on Eurasian watermilfoil. The 4.0 ppmw PVC pellet treatment produced 2,4-D levels in water approximately the same as the 1.0 ppmw clay-granule treatment. As was previously mentioned, these two treatments were approximately equal in degree of phytotoxicity to Eurasian watermilfoil.

The herbicide levels of the clay-granule treatments increased more rapidly and were maintained over a longer period of time than were PVC treatments. This may explain the greater overall effectiveness of the clay-granule formulation.

Effective phytotoxic concentrations were not attained in either the 1.0 or 2.0 ppmw PVC treatments. A concentration of at least 0.28 ppmw in the 2.0 ppmw PVC treatment produced a maximum injury of only 57% after 6 weeks. Herbicide levels were not effectively maintained for more than 2 weeks after treatment in either the PVC or clay granule treatments.

Table 2. Concentration of 2,4-D in Eurasian Watermilfoil Pools after Treatment with Controlled Release Formulations.

Treatment		2,4-D concentration (ppmw)						
		Days after treatment						
Formulation	Concentration (ppmw)	1	4	7	14	28	42	56
PVC	1	.040	.060	.074	.064	.003	.001	0
	2	.079	.101	.284	0	0	.005	0
	4	.132	.356	.531	.070	.001	.003	0
Attaclay	1	.400	.421	.566	.103	0	.002	0
	2	.680	.890	.850	.412	0	0	0

The principal advantage of controlled release herbicide formulations is to obtain long-term control of weed problems. In these tests, this objective was not reached, as regrowth occurred 6 weeks after treatment. Eurasian watermilfoil regrowth was not controlled because phytotoxic herbicide levels were not maintained in water. It is not clear at this time why herbicide levels were not maintained; however, the following speculations are suggested.

Laboratory release rate data indicate that the rate of herbicide released from the 30% formulation decreases sharply after 1 week. For example, 17% was released the first week, but less than 5% the second week and less than 4% the third week. This rate of release (less than 1.5% per week) may be too slow to maintain phytotoxic concentrations in water.

It may be possible to maintain phytotoxic herbicide concentrations in water with the present 30% formulation by using higher dose rates, or by altering the formulation to increase the release rate. The laboratory release-rate data suggest that the less concentrated formulations release at a more consistant rate as well as more completely.

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