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**US Army Corps
of Engineers**

**AQUATIC PLANT CONTROL
RESEARCH PROGRAM**

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**EVALUATION OF 2,4-D/ADJUVANT
MIXTURES IN FLOWING WATER**

by

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20. ABSTRACT (Continued).

compared with herbicide release profiles from conventional 2,4-D formulations (liquid 2,4-D DMA and granular 2,4-D BEE).

All the 2,4-D DMA/adjuvant formulations released 2,4-D for longer periods than did the conventional 2,4-D DMA formulation at 1.5- and 3.0-cm/sec flow velocities. The invert I'vod released for longer periods (180 min) than did the invert Asgrow 403 (24 to 48 min), while the polymer Poly Control released for longer periods (72 to 180 min) than did the polymer Nalquatic (48 to 72 min). Only I'vod and Poly Control released 2,4-D for longer periods (180 min) than the conventional 2,4-D BEE formulation (156 min) at the 1.5-cm/sec flow velocity, and only I'vod released 2,4-D longer (180 min) than BEE (72 min) at the 3.0-cm/sec flow velocity.

At flow velocities within plant stands of ≤ 3 cm/sec, the use of selected 2,4-D DMA/adjuvant formulations will provide longer herbicide release profiles compared with a conventional 2,4-D DMA formulation. The extended release profiles of I'vod and Poly Control make these adjuvants the most promising for use with 2,4-D DMA in flowing water (≤ 3 cm/sec) to control Eurasian watermilfoil.

PREFACE

This study was conducted by personnel of the US Army Engineer Waterways Experiment Station (WES) as part of the US Army Corps of Engineers Aquatic Plant Control Research Program (APCRP). Mr. E. Carl Brown, Office, Chief of Engineers, was Technical Monitor.

This study is being conducted in three phases. Phase I evaluated the release characteristics of hydrophobic herbicide/adjuvant mixtures. Phase II will document the evaluation of release characteristics of hydrophilic herbicide/adjuvant mixtures. Phase III will evaluate the potential role of controlled-release herbicide formulations.

The work was initiated in March 1983 under the general supervision of Dr. John Harrison, Chief, Environmental Laboratory (EL), Mr. Donald L. Robey, Chief, Ecosystem Research and Simulation Division (ERSD), EL, and under the direct supervision of Dr. Thomas L. Hart, Chief, Aquatic Processes and Effects Group (APEG), ERSD. Mr. J. Lewis Decell was the Program Manager for the APCRP. This report was edited by Ms. Jamie W. Leach of the WES Publications and Graphic Arts Division.

The principal investigators for this work were Drs. Kurt D. Getsinger and Howard E. Westerdahl of APEG. They were assisted by Mr. Jerry M. Hall, Dr. Troy Stewart, Ms. Dawn Meeks, and Ms. Nancy Craft of APEG. Herbicide transport modeling was provided by Mr. Mark S. Dortch and Ms. Sandra Bird, Water Quality Modeling Group, ERSD.

Mr. Joe Zolczynski, Alabama Department of Conservation and Natural Resources, provided additional field assistance. The Tennessee Valley Authority, Laboratory Branch, Chattanooga, Tenn., analyzed 2,4-D residues under a cooperative agreement with WES. The Asgrow Florida Company, JLB International Chemical, Nalco Chemical Company, and Union Carbide Agricultural provided the chemicals used in this study.

Director of WES was COL Allen F. Grum, USA. Technical Director was Dr. Robert W. Whalin.

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CONVERSION FACTORS, NON-SI TO SI (METRIC)
UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
gallons	3.785412	cubic decimetres
horsepower (550 foot- pounds (force) per second)	745.6999	watts
pounds (force) per square inch	6.894757	kilopascals

EVALUATION OF 2,4-D/ADJUVANT MIXTURES IN FLOWING WATER

PART I: INTRODUCTION

Background

1. The spread of nuisance submersed aquatic plants into many rivers, streams, and canals has resulted in a need for reliable techniques for controlling the infestation of these plants in flowing water. One approach is to use chemical herbicides with an adjuvant. Adjuvants are ingredients mixed with herbicides designed to minimize drift and maximize placement of herbicides on target species as well as to hold herbicides on the surface of leaves and stems, thus enhancing herbicide uptake into plant tissues (Weed Science Society of America 1982). Examples of adjuvants are surfactants, wetting agents, oils, polymers, stickers, spreaders, thickening agents, and emulsifiers. Adjuvants were initially developed for agricultural uses (McWhorter 1982) and subsequently have been adapted for aquatic weed control as stickers, and drift control and sinking agents (Weldon et al. 1966; Petersen and Bergdorff 1967; Cohee 1967; Stovell 1970; Whortley 1977; Gates 1979).

2. For a herbicide to be effective, a minimum concentration of herbicide must be maintained near the target plant surface, either in the sediment or in the water column, for a minimum contact time. The contact time and concentration needed to control aquatic plants are not easily obtained in flowing water because the water column is continuously moving and herbicides released into the water are transported downstream. Herbicide/adjuvant mixtures have been used effectively for controlling submersed plants in still water (Bitting 1974; Baker et al. 1975); however, only limited data are available on their use in flowing water.

Objective

3. The objective of the herbicide/adjuvant study is to determine which adjuvants, conventional registered herbicides, and controlled-release herbicide formulations may be used effectively for the control of submersed plants in flowing-water environments. The study consists of three phases. Phase I,

as reported in this document, evaluated the release characteristics of 2,4-dichlorophenoxyacetic acid (2,4-D) used as an example of a hydrophobic herbicide. Phase II will evaluate the release characteristics of endothall used as an example of a hydrophilic herbicide. Phase III will evaluate the potential role of controlled-release herbicide formulations.

Purpose and Scope

4. The purpose of Phase I was to:

- a. Determine the release profiles of 2,4-D from selected 2,4-D dimethylamine (DMA)/adjuvant mixtures.
- b. Compare these results with 2,4-D release profiles from conventional liquid and granular 2,4-D formulations when applied in flowing water.
- c. Recommend the best adjuvants for use in flowing water.

5. The information provided in Phase I will be coupled with results from a separate 2,4-D concentration/exposure time study to determine which 2,4-D/adjuvant formulations will control the target species at various flow velocities. Also, results from Phase I will be compared with the results from Phase II to determine if the degree of hydrophilicity of a herbicide affects its release profile from adjuvants.

PART II: MATERIALS AND METHODS

Flume System

6. Herbicide/adjuvant experiments were conducted in a 28-m modified hydraulic flume at the US Army Engineer Waterways Experiment Station (Figure 1). A 7.3-m section of the flume channel was divided lengthwise into two equal areas (0.8 m wide by 0.9 m deep) to accommodate duplicate experiments (Figure 2). Individual, healthy Eurasian watermilfoil (*Myriophyllum spicatum* L.) shoots, collected in the field, were cut into 15-cm lengths and planted in shallow polyethylene flats (23 cm wide by 32 cm long by 10 cm deep) filled with a 60-percent sand/40-percent mud mixture. These flats were arranged in outdoor holding tanks (21 flats per tank) to produce plant stands ≈ 3 m long

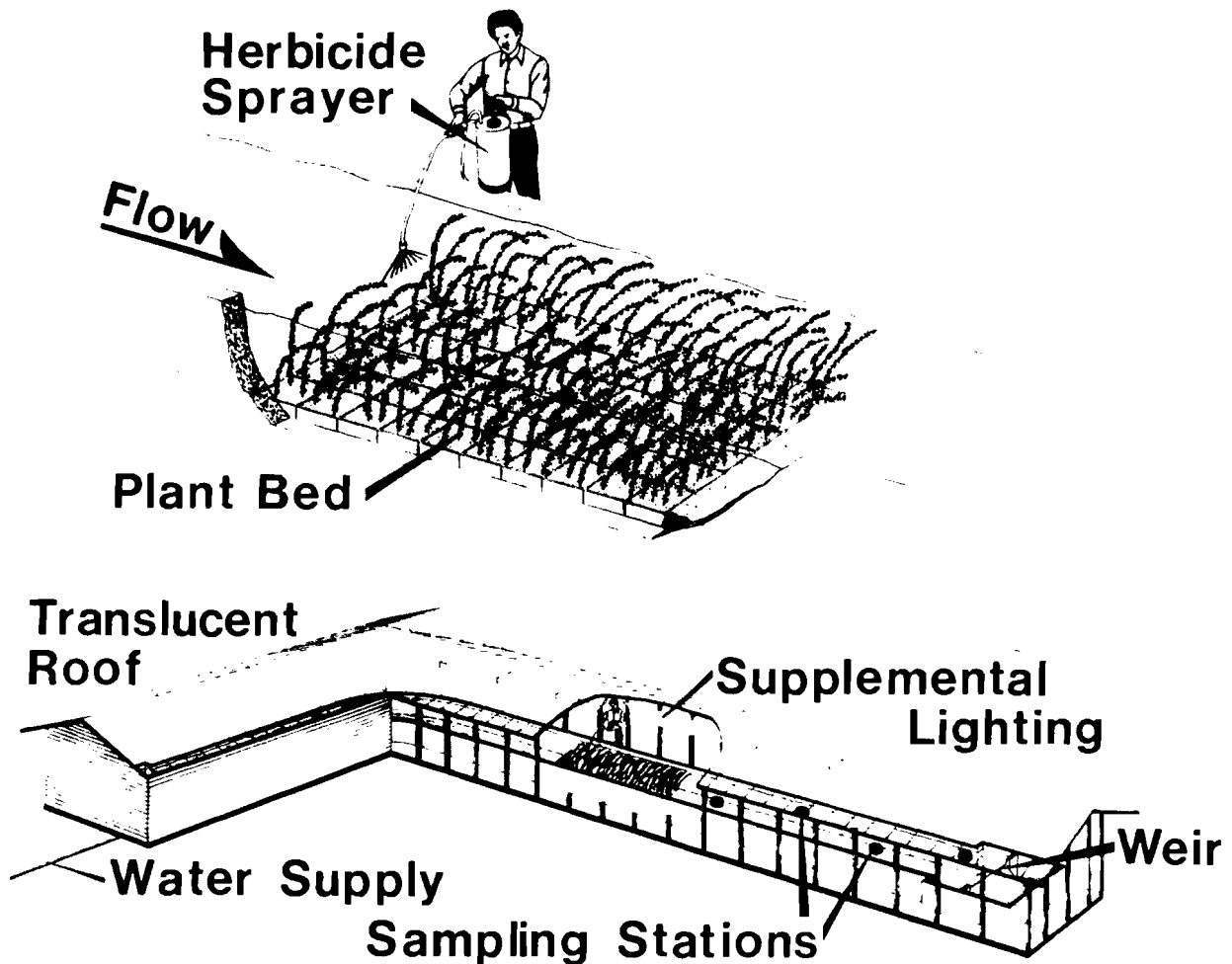


Figure 1. Modified hydraulic flume used in herbicide/adjuvant studies

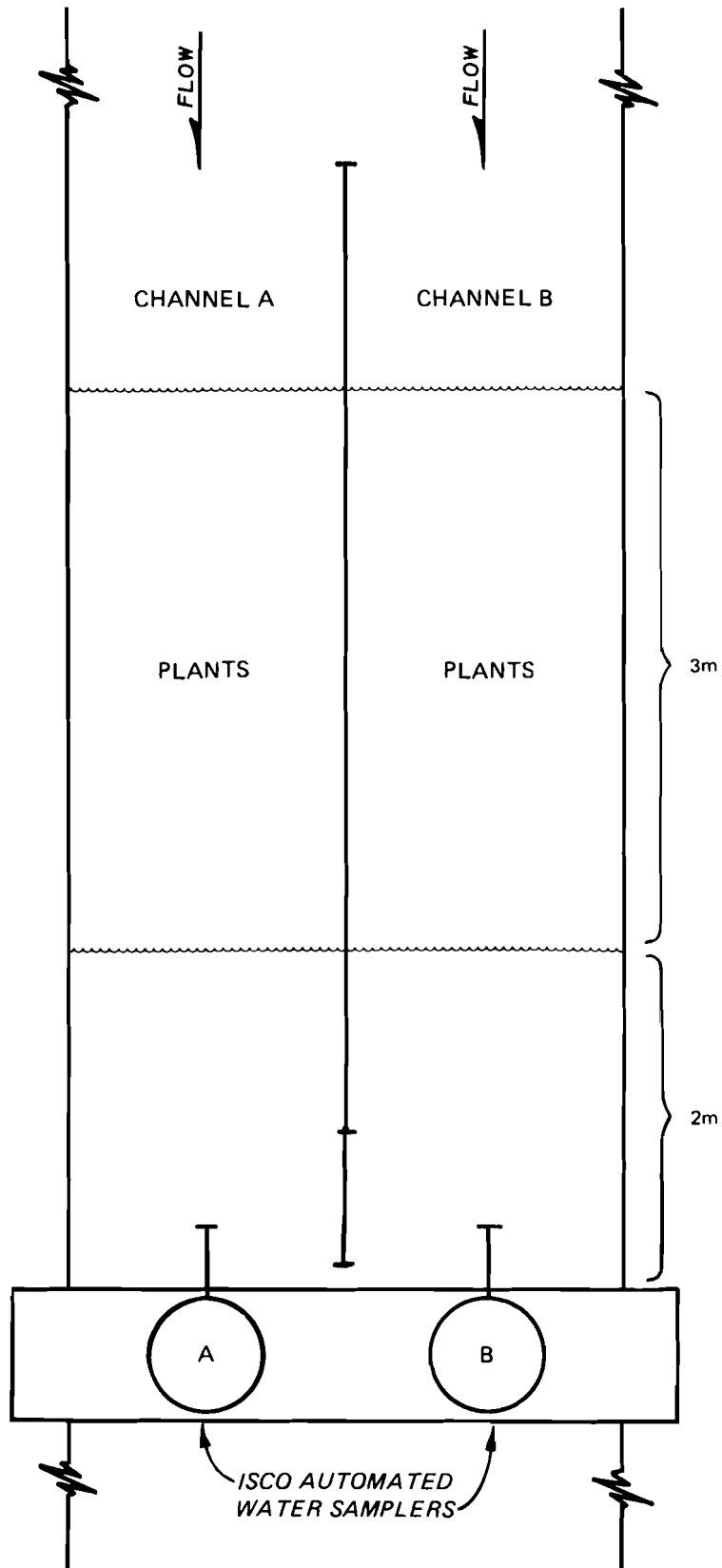


Figure 2. Overhead view of partitioned flume channel

and 0.8 m wide consisting of >1,000 shoots each. Plant stands were allowed to grow in the holding tanks 3 to 4 weeks to a height of ≈ 70 cm. Flats of plants were transferred to the flume channels several days prior to testing. Greenhouse roof panels (90-percent transmittance) covered the plant stands in the flume and supplemental lighting was available, if needed. Water was pumped into the flume system from a small (≈ 1 ha) pond. The submersed species Eurasian watermilfoil was used as the target plant because it has become a problem in flowing water systems in the east (personal observation), west, and Pacific Northwest (Aiken, Newroth, and Wile 1979; Rawson 1982; Killgore 1984).

Flow Velocity Measurements

7. Flow velocities were measured with a Model 201 Marsh-McBirney Flowmeter (accuracy ± 2 percent). The sensor was attached to a sliding rod and bolted to a platform which enabled measurements to be taken on a horizontal plane. Water depth was held at 70 cm and a constant flow velocity was maintained during all experimental runs. Flow velocities were characterized in each flume channel by taking measurements from surface to bottom at 15-cm intervals and from side to side 5-cm distance from each wall and at mid-channel. These measurements were taken before and after plant stands were established in the flume to determine variation in flow across the channels and with depth.

Mixtures and Application Techniques

8. Herbicides, adjuvants, and herbicide/adjuvant mixtures used in this study are presented in Tables 1 and 2. The herbicide 2,4-D was selected because of its proven efficacy on Eurasian watermilfoil (Smith, Hall, and Stanley 1967; Wojtalik, Hall, and Hill 1971; Elliston and Steward 1972; Whitney et al. 1973; Rawls 1975; Getsinger, Davis, and Brinson 1982). Adjuvants used in the study included inverting oils and polymers compatible with 2,4-D DMA and commonly used for aquatic weed control. Inverting oils are amphipathic molecules with hydrophilic, water-soluble, polar "heads" and lipophilic, water-insoluble, nonpolar "tails" (Steward 1976). Commercially available inverting oils are produced by blending various proportions of oils,

e.g. d'Limonene, and selected emulsifiers. When these oils are mixed with water in an appropriate fashion, an invert is formed. An invert consists of a dispersion of water droplets in oil, where one liquid does not dissolve in the other, i.e. water surrounded by oil or a water-in-oil emulsion (see Appendix A), and functions as sticking and drift control agents when used for aquatic weed control. Polymers used for aquatic weed control are anionic or nonionic, polymeric molecules, blended with selected emulsifiers, and are designed to function as sinking, sticking, and drift control agents. Commercially available polymers, like inverting oils, are produced by blending various proportions of selected polymeric materials and emulsifiers. The exact chemical structures and proportions of components used in the production of commercial inverting oils and polymers are considered proprietary information and are, therefore, unavailable.

9. Inverting oils were blended with water and 2,4-D DMA to form a thick, mayonnaiselike invert material using a 7:1, water-to-inverting oil ratio. Polymers were blended with water and 2,4-D DMA, using 2.5-percent polymer, to form a thick, mucouslike material. These formulations were transferred to a pressurized spray system consisting of a paint pot, hose, and spray wand with a 17-hole multiple-fan-type nozzle.

10. Herbicide/adjuvant and liquid herbicide formulations were injected below the surface, throughout the plant stands, with the pressurized spray system at 1.36 atm (20 psi)* while the granular 2,4-D BEE formulation was broadcast evenly over the surface of the plant stands. All herbicide formulations were prepared to provide a 2,4-D treatment rate of 45 kg ae/ha (40 lb ae/acre).**

Sample Collection and Residue Analysis

11. Water samples were collected in the center of each flume channel, 175 cm downstream from the plant stands, using an ISCO Model 2100 automatic water sampler adapted to sample a water column depth of 10 to 60 cm. The sampler is designed to remove water from the flow stream at approximately

* A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page 3.

** ae = acid equivalent.

30 cm/sec to prevent particles from settling out in the sampling line. This results in an effective withdrawal zone larger than the intake orifice at flow velocities <30 cm/sec. Consequently, theoretical values of herbicide concentration downstream (Appendix B) will be less than the measured concentration at low water velocities. As stream flow velocity increases (approximating 30 cm/sec), the herbicide concentration in the water samples obtained by the ISCO sampler should approximate theoretical estimates, assuming the herbicide is conservative. State-of-the-art sampling equipment and techniques preclude isokinetic water sampling for herbicide analysis from open channel, flowing water (<30 cm/sec) environments. As a result, sampling the water column 175 cm downstream of the treated plants was necessary since the sampling equipment would disrupt the hydraulics of the plant stand and sample herbicide/adjuvant "floc" on the plants within the treatment area. This condition would result in higher than actual herbicide concentrations being measured in the water column.

12. The calculated herbicide transport time from the treatment area to the sampling point was 2 and 4 min at the tested flow velocities of 3 and 1.5 cm/sec, respectively (see Appendix B). Consequently, herbicide concentrations in the water samples approximated the herbicide concentrations in the aqueous phase within the treatment area with a 2- to 4-min time delay. Sampling water at 2-min intervals posttreatment for 180 min and compositing to represent 12-min periods per sample was selected to show the average herbicide residue concentration in the water over this time period. Changes in herbicide release from the adjuvant and other factors affecting herbicide residue levels in water, e.g. uptake and adsorption, occurring within the 2- to 4-min period would be reflected in the water sample. However, it must be realized that the sampling technique and compositing of samples prevent inferring the dynamics of herbicide levels within the 12-min interval. Due to limitations of the sampling technique, determining a mass balance for the herbicide is inappropriate in assessing herbicide concentration per unit time.

13. For most herbicides a contact time >12 min is considered necessary for the control of submersed species. Therefore, a 12-min composite sample was considered reasonable for comparing relative changes in herbicide concentrations over time. Cost constraints associated with herbicide residue analysis in water samples further warranted the compositing of samples.

14. Water samples were also collected 5 m upstream from each plant stand every hour during experimental runs to monitor possible herbicide contamination.

15. Residues of 2,4-D in water were determined by high pressure liquid chromatography standard procedures (American Public Health Association 1976). Recoveries were 92 to 93 percent. The 2,4-D analyses were performed by the Laboratory Branch of the Tennessee Valley Authority, Chattanooga, Tenn.

PART III: RESULTS

Flow Velocities In and Out of Plant Beds

16. Flow velocities from 1.5 to 30 cm/sec in the flume channels, with no plants present, showed little variation across the channel and with depth. However, once plant stands were established in the channels, flow patterns fluctuated. As flow velocities upstream from the plant stands reached 3 cm/sec, the upright plants began to bend with the flow and at 6 cm/sec the plants began to bend into a horizontal position. Flow velocities in the water column above the plants accelerated to 27 to 33 cm/sec, while velocities within the beds remained less than 5 cm/sec (Table 3). Flow velocities within the plant stands remained identical to flow velocities at the upstream edge of the plant stands at 1.5 and 3 cm/sec.

2,4-D Release Rates

17. Herbicide release rates from the liquid 2,4-D DMA formulation and the granular 2,4-D BEE formulation at 1.5- and 3-cm/sec flow velocities are compared in Figures 3 and 4, respectively. The DMA treatments showed a large initial release of 2,4-D with concentrations falling below detection (0.01 mg/l) by 60 min posttreatment at the low velocity and 36 min posttreatment at the high velocity. In contrast, 2,4-D was released from the BEE formulation in smaller increments and 2,4-D concentrations did not fall below detection until 168 min posttreatment at the low velocity and 84 min posttreatment at the high velocity.

18. Herbicide release rates from the 2,4-D DMA formulation are compared with the herbicide release rates from the 2,4-D DMA/invert formulations (Asgrow 403 and I'vod) in Figures 5 and 6, respectively. Both of the invert formulations released 2,4-D more slowly than did the DMA formulation. I'vod maintained 2,4-D residues for the entire 180-min run at both velocities, whereas 2,4-D residues from Asgrow 403 fell below detection by 156 min posttreatment at the low velocity and 72 min posttreatment at the high velocity.

19. A comparison of herbicide release rates for 2,4-D DMA and the 2,4-D DMA/polymer formulations Poly Control and Nalquatic at 1.5- and 3-cm/sec flow velocities are shown in Figures 7 and 8, respectively. Herbicide residues

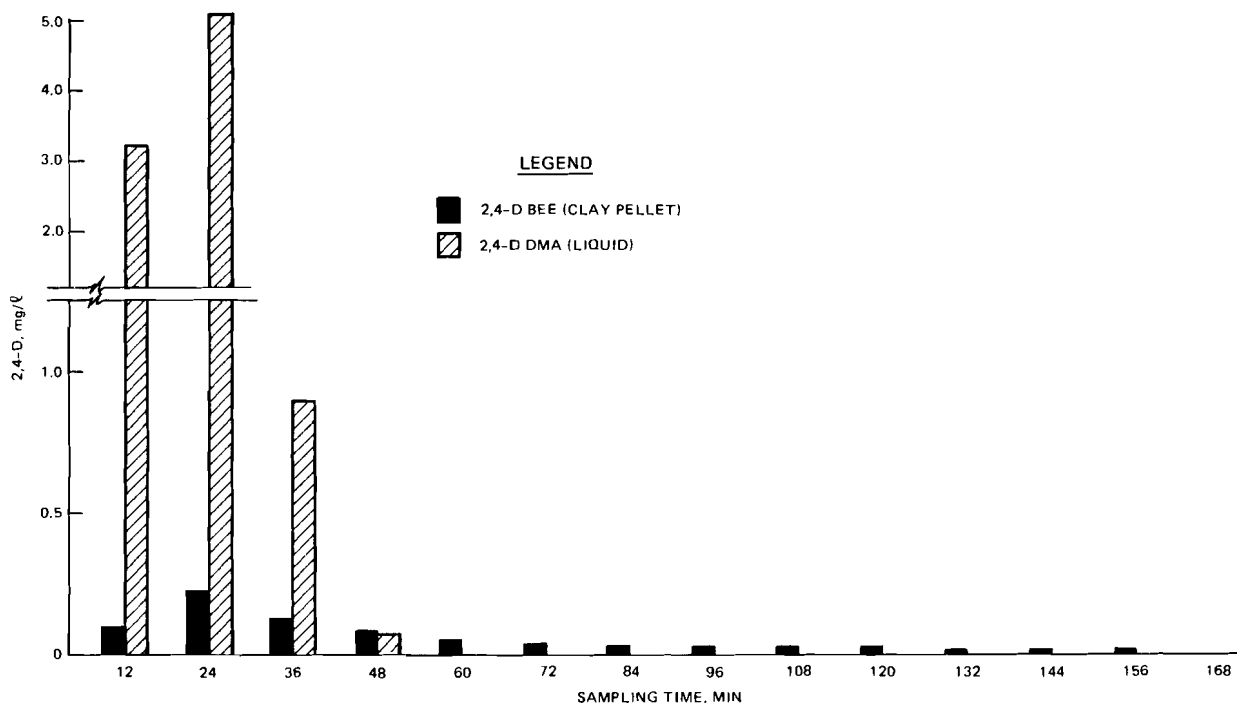


Figure 3. Effect of time on 2,4-D residues 2 m downstream of plant beds using formulations of 2,4-D DMA and 2,4-D BEE at a flow velocity of 1.5 cm/sec

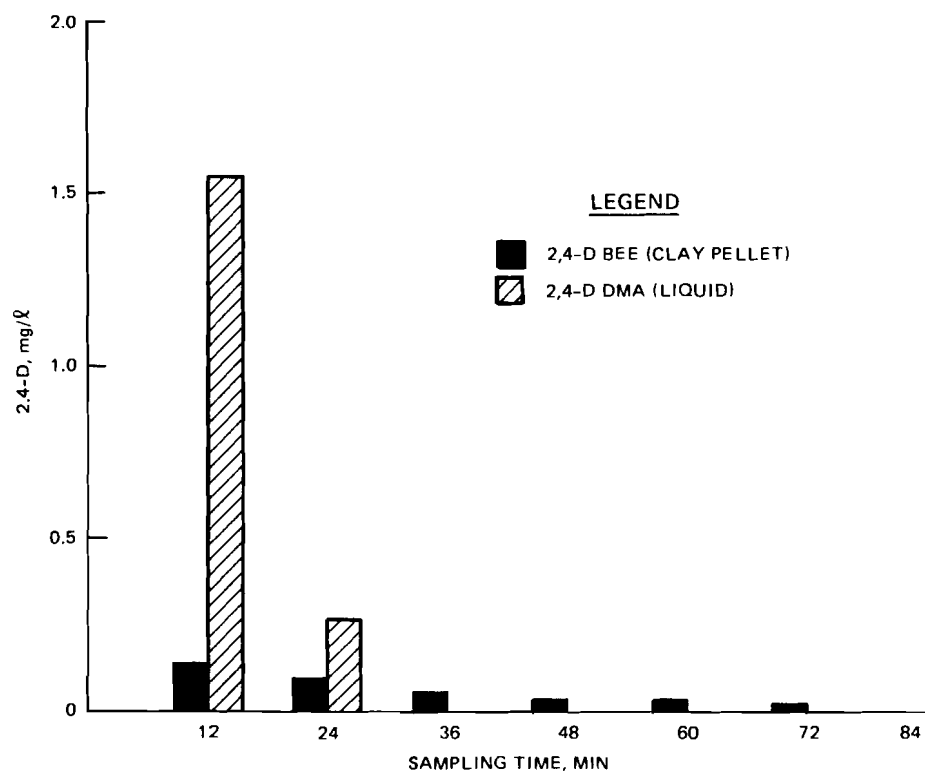


Figure 4. Effect of time on 2,4-D residues 2 m downstream of plant beds using formulations of 2,4-D DMA and 2,4-D BEE at a flow velocity of 3.0 cm/sec

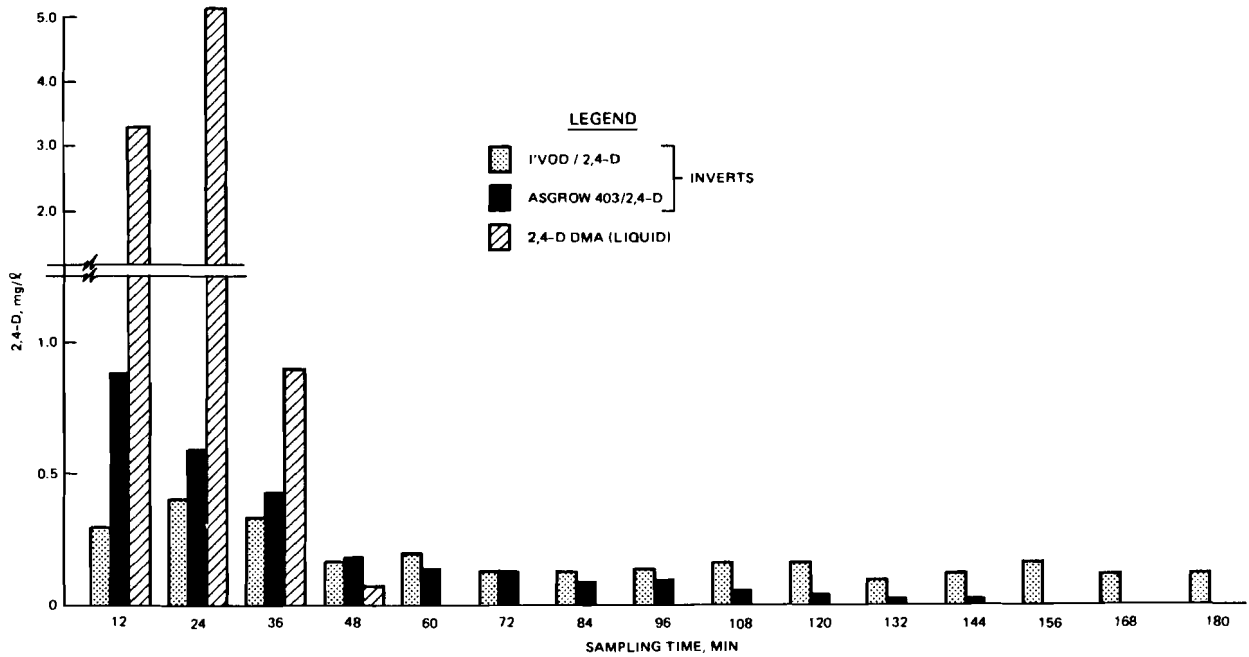


Figure 5. Effect of time on 2,4-D residues 2 m downstream of plant beds using formulations of I'vod/2,4-D DMA, Asgrow 403/2,4-D DMA, and 2,4-D DMA at a flow velocity of 1.5 cm/sec

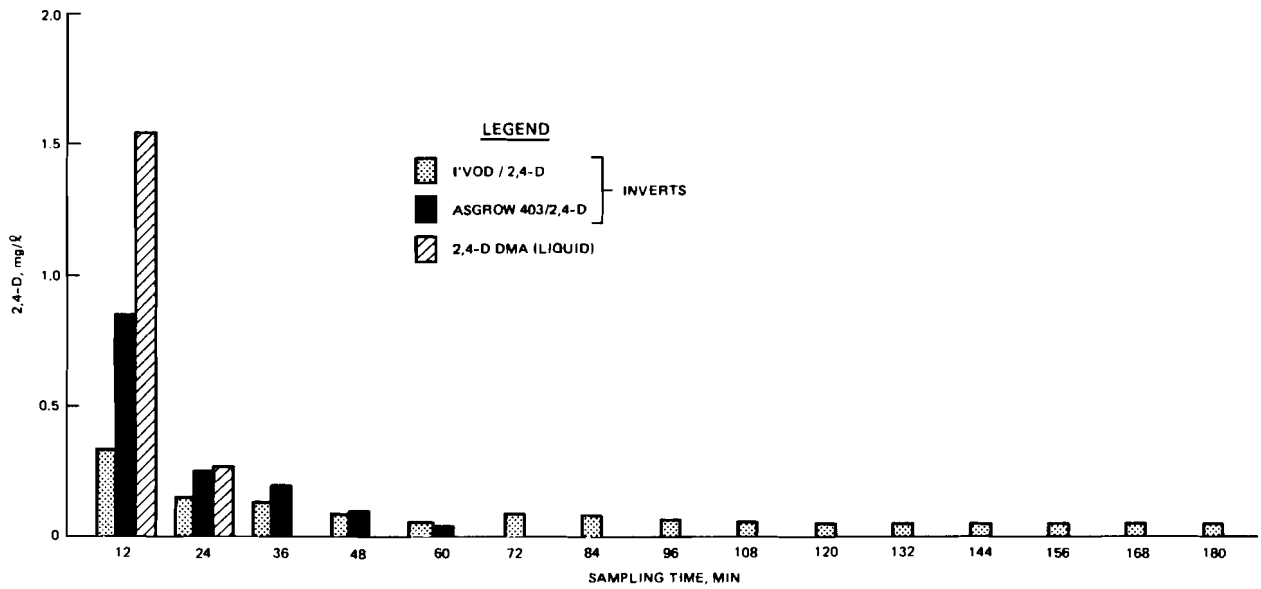


Figure 6. Effect of time on 2,4-D residues 2 m downstream from plant beds using formulations of I'vod/2,4-D DMA, Asgrow 403/2,4-D DMA, and 2,4-D DMA at a flow velocity of 3.0 cm/sec

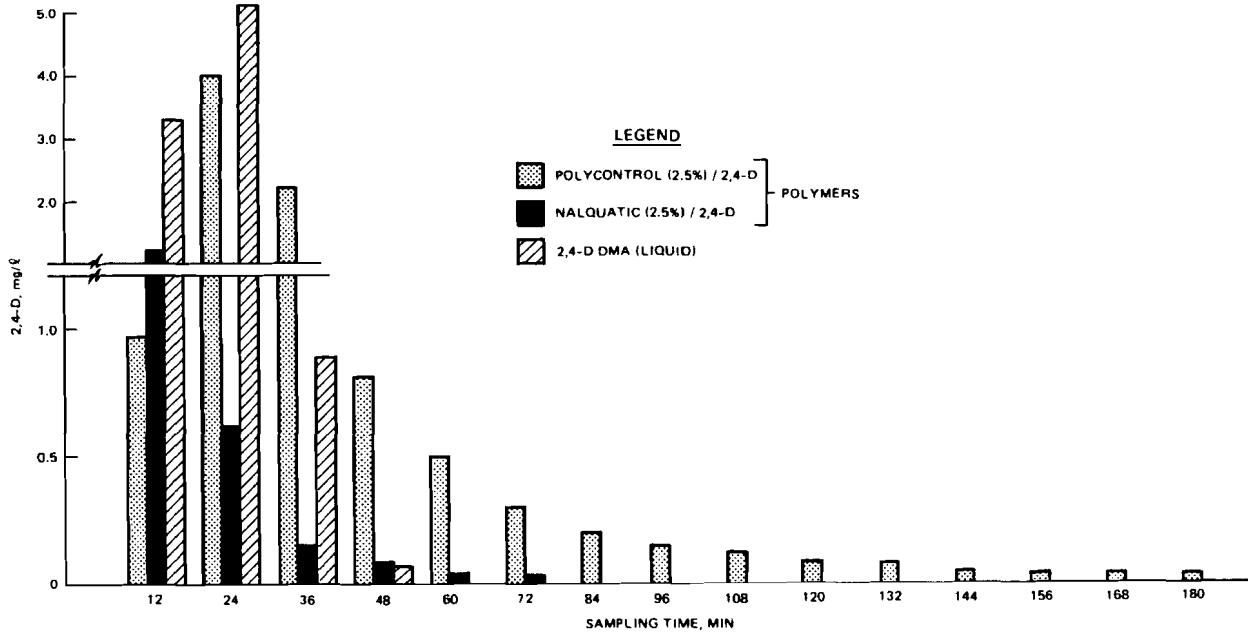


Figure 7. Effect of time on 2,4-D residues 2 m downstream of plant beds using formulations of Poly Control/2,4-D DMA, Nalquatic/2,4-D DMA, and 2,4-D DMA at a flow velocity of 1.5 cm/sec

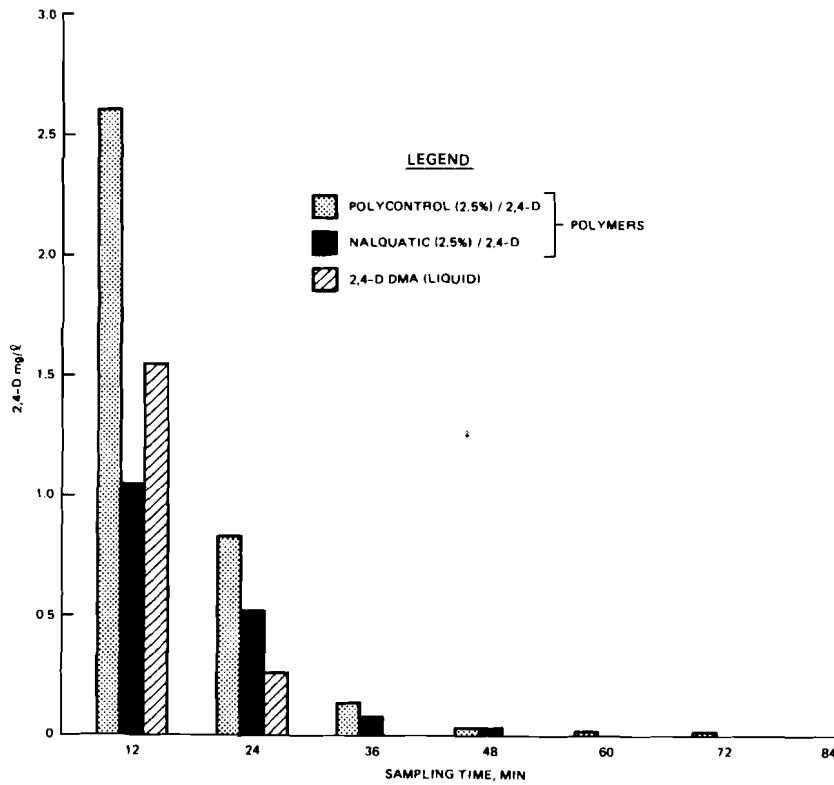


Figure 8. Effect of time on 2,4-D residues 2 m downstream of plant beds using formulations of Poly Control/2,4-D DMA, Nalquatic/2,4-D DMA, and 2,4-D DMA at a flow velocity of 3.0 cm/sec

were present for 180 min posttreatment with Poly Control at 1.5 cm/sec, but below detection with Nalquatic by 84 min posttreatment. At the 3-cm/sec flow velocity, 2,4-D residues were below detection at 84 min posttreatment with Poly Control and 60 min posttreatment with Nalquatic.

20. Water samples collected 5 m upstream from each plant stand during experimental runs showed no herbicide contamination.

21. The theoretical herbicide transport curves for a liquid herbicide with an initial distributed source in a flume channel at 1.5 and 3.0 cm/sec are shown in Appendix B.

PART IV: DISCUSSION

22. The herbicide/adjuvant formulations released 2,4-D for longer periods of time than did the conventional, liquid 2,4-D formulation when applied to plants in flowing water, i.e. 1.5- and 3.0-cm/sec flow velocities. In all cases, the I'vod invert formulation released for longer periods than did the Asgrow 403 invert formulation while the Poly Control polymer formulation released for longer periods than did the Nalquatic polymer formulation. It is not apparent from the chemistry of these adjuvants why I'vod and Poly Control released herbicide for longer periods than the others. Commercial adjuvant production involves the blending of selected components; however, the types and proportions of components used in the adjuvant manufacturing process are proprietary and differ with each producer. These differences could explain the variance in performance among adjuvants. Steward (1976) reported that release rates of herbicides from inverts would vary inversely with the stability of the invert and that stabilities of inverts vary according to the kind of components, their relative amounts, and the mechanics of mixing. Differences in the hydrophilic properties of polymers could also affect the release rates of herbicides from those compounds.

23. When herbicide release rates from the 2,4-D DMA/adjuvant formulations were compared with the herbicide release rates from the conventional, granular 2,4-D BEE formulation, only I'vod and Poly Control released 2,4-D for longer periods than BEE at the 1.5-cm/sec flow velocity; and only I'vod released 2,4-D longer than BEE at the 3.0-cm/sec flow velocity. Based on these results, I'vod and Poly Control show the greatest potential as effective adjuvants for the release of 2,4-D in flowing water, particularly in areas where the DMA formulation is desired over the BEE formulation.

24. In theory, adjuvants which release herbicides for extended time periods should be more efficacious than adjuvants which release herbicides for short time periods, provided that a lethal dose of herbicide is maintained for the duration of the exposure period. Therefore, efficacy is obtained by some combination of herbicide concentration and exposure time. Although many of the herbicide formulations released 2,4-D for >60 min posttreatment (most notably Poly Control and I'vod, which released 2,4-D for 180 min), the concentrations of 2,4-D were very low and/or the exposure times relatively short. Since efficacy was not determined in this study, a comparison was made with a

2,4-D DMA concentration/exposure time study which was designed to determine the lethal doses of 2,4-D for Eurasian watermilfoil when exposed to 2,4-D DMA in the water column for different time periods (Hall 1985, unpublished data). Results from the concentration/exposure time study showed control of watermilfoil at 0.1 mg 2,4-D/l for a 336-hr (2 weeks) exposure period and at 2.0 mg 2,4-D/l for at least 15-min exposure periods, versus no control of watermilfoil at 0.1 mg 2,4-D/l for a 2-hr exposure period and at 0.3 mg 2,4-d/l for a 1-hr exposure period. Analysis of herbicide residue data from this study (Figures 7 and 8) and efficacy results from the aforementioned study suggest that a liquid formulation of 2,4-D DMA or a 2,4-D DMA/Poly Control formulation will control Eurasian watermilfoil at a 1.5-cm/sec flow velocity and a 2,4-D DMA/Poly Control formulation may provide control at 3.0 cm/sec. Moreover, the results suggest that watermilfoil will not be controlled with 2,4-D DMA in combination with Asgrow 403, I'vod, or Nalquatic at flow velocities >1.5 cm/sec since the 2.0 mg 2,4-D/l concentration was not maintained for 15 min (Figures 5-8). Analysis of the herbicide release profile from the 2,4-D DMA/I'vod formulation at 3 cm/sec showed release of 2,4-D for at least 3 hr with concentrations >0.1 mg/l for the first 48 min posttreatment and 0.05 mg/l thereafter. Results from the concentration/exposure time study suggested no control with the I'vod formulation at >1.5 cm/sec; however, another efficacy study (more closely matching the herbicide concentrations and exposure times found with I'vod in the flume) would define the efficacy potential of the I'vod formulation. Also, the prolonged herbicide release profile of the I'vod formulation at 3 cm/sec indicates a need to test I'vod at higher flow velocities.

25. No advantage would be gained by using 2,4-D DMA/adjuvant combinations where velocities within plant stands are \leq 1.5 cm/sec. The liquid 2,4-D DMA formulation, when applied to water flowing at 1.5 cm/sec within the plant stand, provided sufficiently high 2,4-D concentrations to achieve control of watermilfoil.

26. When granular 2,4-D BEE was evaluated in the flume system, 2,4-D water residues were below lethal concentrations established in the 2,4-D DMA concentration/exposure time studies (Hall 1985, unpublished data). Since the granule sinks to the sediment, some of the herbicide may enter the plant via sediment/root uptake and play an important role in controlling the plant (Hoepfel and Westerdahl 1983), thus the correlation between 2,4-D

concentration in the water column and watermilfoil control may not be appropriate when using granular 2,4-D formulations.

27. Finally, flow velocity measurements taken in the flume showed that velocities above and around plant stands were much higher than velocities within the stands at flow velocities exceeding 6 cm/sec. This phenomenon has also been reported in field situations (Killgore 1984). Since high flow velocities above or around plant stands will rapidly disperse herbicides away from the treatment area, it is critical that herbicides be placed within the plant stands where flow velocities are lower and contact time can be maximized.

PART V: CONCLUSIONS AND RECOMMENDATIONS

Conclusions

28. The results of Phase I show that at flow velocities within plant stands of ≤ 3 cm/sec, the use of selected 2,4-D DMA/adjuvant formulations will provide longer herbicide release profiles compared with a conventional, liquid 2,4-D DMA formulation. In addition, the invert I'vod and the polymer Poly Control were the only adjuvants which released 2,4-D for longer periods of time than did a conventional, granular 2,4-D BEE formulation. Therefore, the extended herbicide release profiles of I'vod and Poly Control make them the most promising adjuvants for use with 2,4-D DMA and other hydrophobic herbicides in flowing water to control submersed plants.

Recommendations

29. The recommendations suggested by Phase I include the following:
- a. I'vod and Poly Control are recommended for use with 2,4-D DMA in flowing water where velocities within the plant stand are greater than 1.5 cm/sec, but not exceeding 3 cm/sec.
 - b. I'vod needs to be tested at flow velocities within the plant stands exceeding 3 cm/sec.
 - c. A better understanding of flow velocities within plant stands is necessary prior to selecting the appropriate herbicide formulation or herbicide/adjuvant combination.
 - d. Techniques should be developed to apply herbicides in the immediate vicinity of plant stands in flowing water, taking advantage of lower flow velocities found within the stands that maximize herbicide contact time.
 - e. An isokinetic sampling technique should be developed to collect water samples for herbicide analysis in open, flowing water systems. This would result in a better understanding of actual herbicide concentrations within plant stands.
 - f. An economical tracer, which can mimic the characteristics of herbicides, would permit a better understanding of herbicide hydrodynamics within plant stands and eliminate the high costs associated with herbicide residue analysis.
 - g. More information is needed on the chemical characteristics of adjuvants for a better understanding of the behavior of adjuvants in flowing water.

- h. Herbicide concentration/exposure time studies should be continued to identify the most probable effective combinations at various flow velocities.

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Table 1

Herbicide and Adjuvant Compounds Used in Flowing Water Study

<u>Compound</u>	<u>Active Ingredient</u>	<u>Manufacturer</u>
Herbicides		
Weedar 64 (liquid)	Dimethylamine salt of 2,4-Dichlorophenoxyacetic acid (2,4-D DMA) 0.45 kg ae/l (3.8 lb ae/gal)	Union Carbide Agricultural Products Company, Inc.
Aqua-Kleen (granular)	2,4-Dichlorophenoxyacetic acid, butoxyethyl ester (2,4-D BEE) 19% ae by weight	Union Carbide Agricultural Products Company, Inc.
Inverting oils		
Asgrow 403	Water-in-oil emulsifiers and selected solvents, 100%	Asgrow Florida Company
I'vod	d'Limonene [d-1,8(9)-p- menthadiene] 50% plus selected emulsifiers, 50%	JLB International Chemical, Inc.
Polymers		
Nalquatic	Polycarboxylate polymer, 30% Constituents ineffective as a spray adjuvant, 70%	Nalco Chemical Company
Poly Control	Polyacrylamide copolymer, 30% Nonpolymer dispersant constit- uents, 70%	JLB International Chemical, Inc.

Note: ae = acid equivalent.

Table 2
Herbicide/Adjuvant Mixtures Used in the Flowing Water Study

<u>Adjuvant</u>	<u>Proportions</u>	<u>2,4-D DMA</u>
Inverting oils		
Asgrow 403	7:1, water to oil	45 kg ae/ha
I'vod	7:1, water to oil	45 kg ae/ha
Polymers		
Nalquatic	2.5%	45 kg ae/ha
Poly Control	2.5%	45 kg ae/ha

Table 3
Flow Velocities Measured in Flume System Containing Plant Beds

<u>Flow Velocity at Indicated Location, cm/sec</u>			
<u>Upstream Edge of Plant Beds</u>	<u>Within Plant Beds</u>	<u>Above Plant Beds</u>	<u>Downstream Edge of Plant Beds</u>
1.5	1.5	1.5	1.5
3.0	3.0	3.0	3.0
6.0	3.9	11.7	6.0
12.0	3.9	27.0	13.5
18.0	4.5	33.0	16.6
24.0	*	*	*

* Plants uprooted from sediment.

APPENDIX A: INVERT PREPARATION WITH FIELD-SCALE EQUIPMENT

1. A pilot study was conducted in the flume system to evaluate the herbicide release rates from invert formulations prepared with an operational-scale spray system. Several 2,4-D DMA/invert mixtures (7:1 water to oil) were prepared using a Minnesota Wanner (MW) Pump Pak designed for aquatic spraying. The principal components of this system included a Briggs Stratton 11-hp engine, a Wanner 10-gpm positive displacement piston pump, an MW mechanical inverter, and a large hand-held spray wand (3- to 6-m hose) containing six single-orifice nozzle tips.

2. When prepared correctly, an invert emulsion consists of water surrounded by oil and has a mayonnaiselike consistency (Kirch 1967; Petersen and Bergdorff 1967; Stovell 1970).* The herbicide is dissolved within the water phase of the emulsion. Inverts have the appearance of snowflakes when sprayed under the surface of the water and flakes of invert stick to leaves and stems of submersed plants.

3. The preparation of a high quality invert is related to the experience of the applicator and environmental factors. Selecting appropriate metering orifices for water, herbicide, and inverting oil; maintaining adequate pressure; and eliminating fitting and line air leaks are critical for blending a good invert when using a system such as the MW Pump Pak Mechanical Inverter. Water hardness may also affect the quality of the invert. A deficiency in any one of these factors can result in a poor invert.

4. A desirable 2,4-D DMA/Asgrow 403 invert formulation (thick, mayonnaiselike consistency) and a 2,4-D DMA Asgrow 403 noninvert mixture (thin, milky consistency) were blended in the MW Pump Pak system and sprayed into a 20-l container. The formulations were transferred to the small-scale pressurized spray system and applied onto plant stands in the flume (see Part II of main text). The high pumping rate and subsequent water pressure from the MW spray system resulted in a disruption and uprooting of the plant stands in the flume; therefore, the small-scale system was used for flume applications. A liquid formulation of 2,4-D DMA and a granular 2,4-D BEE formulation were tested for comparative purposes.

* See References at the end of the main text.

5. All formulations were prepared to provide a herbicide application rate of 45 kg ae/ha* and were applied on duplicate plant stands. Stream velocity was controlled at 3 cm/sec with a water depth of 70 cm. Preliminary observations in the flume system showed that herbicide/adjuvant mixtures were extremely difficult to apply and were rapidly stripped away from the plants at incoming flow velocities >6 cm/sec. Mid-depth water samples were collected 2 m downstream from each plant stand at 2-min intervals posttreatment for 60 min. Samples were composited to represent 12-min periods and analyzed for 2,4-D residue. Water samples collected 5 m upstream from each plant stand during experimental runs showed no herbicide contamination.

6. Herbicide residues (Figure A1) showed that the noninvert mixture and the liquid 2,4-D DMA formulation released 2,4-D into the water in a similar fashion, with both formulations releasing a large pulse of herbicide during the first 12 min and herbicide residues falling below detection by 48 min posttreatment. These results indicate that no advantage is gained by using an improperly prepared, noninvert mixture over a conventional liquid formulation. In contrast, the desirable invert emulsion and the granular 2,4-D BEE formulation showed slower herbicide release rates. Based on the concentration/exposure time studies (see Part IV of main text), none of these formulations would have given desired efficacy on Eurasian watermilfoil at the 3.0-cm/sec flow velocity.

* ae = acid equivalent.

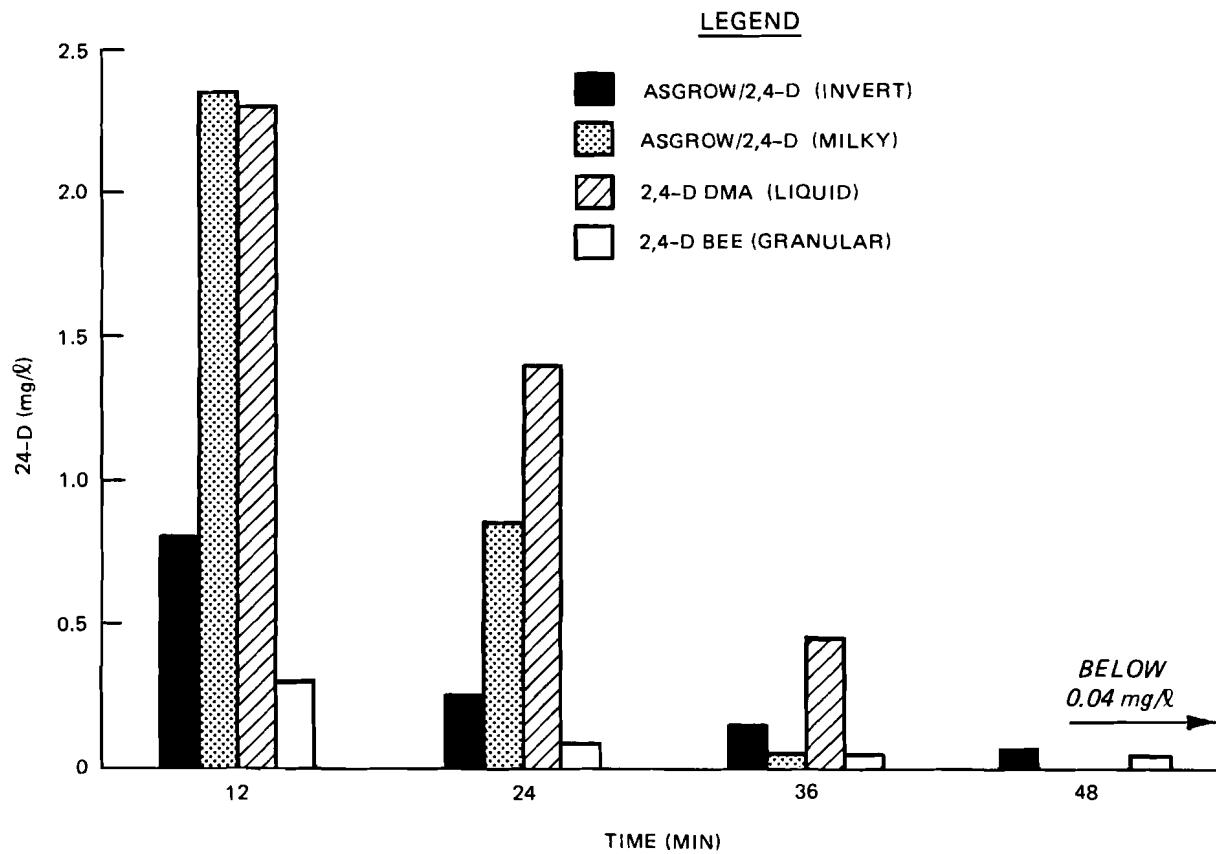


Figure A1. Effect of time on 2,4-D residues 2 m downstream of plant beds using formulations of Asgrow 403/2,4-D DMA, 2,4-D DMA, and 2,4-D BEE at a flow velocity of 3.0 cm/sec

APPENDIX B: TRANSPORT OF HERBICIDES IN A FLUME CHANNEL

1. It is assumed that the uninhibited continuum transport of a conservative constituent in the flume channel can be described by the one-dimensional advective diffusion equation

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} \quad (B1)$$

where

C = constituent concentration, M/L^3

t = time

u = cross sectionally averaged velocity in x-direction, L/T

D = longitudinal (x-direction) diffusion coefficient, L^2/T

2. The solution of Equation B1 for a steady, uniform flow and with an initial distributed source (from Fisher et al. 1979)* is.

$$C(x,t) = \int_{-\infty}^{\infty} \frac{f(\xi)}{\sqrt{4\pi Dt}} \exp \left[\frac{-(x - ut - \xi)^2}{4Dt} \right] d\xi \quad (B2)$$

where $f(\xi)$ is the initial distribution function and ξ is the location in the x domain.

3. Applying the initial condition

$$C(x,0) = \begin{cases} 0, & x < 0 \\ C_0, & 0 \leq x \leq L \\ 0, & x > L \end{cases}$$

where C_0 is an initial cross-sectional uniform concentration over channel Length L , Equation B2 becomes

$$C(x,t) = \int_0^L \frac{C_0}{\sqrt{4\pi Dt}} \exp \left[\frac{-(x - ut - \xi)^2}{4Dt} \right] d\xi \quad (B3)$$

* See References at the end of the B1 main text.

Equation B3 can be integrated* to yield

$$C(x,t) = \frac{C_o}{z} \left[\operatorname{erf} \left(\frac{x - ut}{4Dt} \right) - \operatorname{erf} \left(\frac{x - ut - L}{4Dt} \right) \right] \quad (\text{B4})$$

where erf is the error function defined as

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\xi^2) d\xi$$

4. The theoretical transport curves of a liquid herbicide measured 175 cm downstream from an initial distributed source (305 cm in length) in a flume channel (70 cm by 76 cm) containing no plants at flow velocities 1.5 and 3.0 cm/sec are plotted in Figure B1. The transport curves show that most of the herbicide, approximately 75 percent, would pass the sampling point (175 cm downstream) at 2 min posttreatment at 3.0 cm/sec and at 4 min posttreatment at 1.5 cm/sec. By 12 min posttreatment nearly all of the herbicide would have passed the sampling point at both velocities. A comparison of theoretical versus actual downstream herbicide concentrations from composite water samples is shown in Table B1. This comparison suggests that the actual transport pattern of 2,4-D from a liquid formulation (e.g. 2,4-D DMA) applied in the flume with plants present was similar to the theoretical transport pattern of 2,4-D in the flume with no plants present. Since water samples were not obtained isokinetically, the actual herbicide concentrations should represent conservative estimates.

* Personal Communication, 1985, Mark S. Dortch, Hydraulic Engineer, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

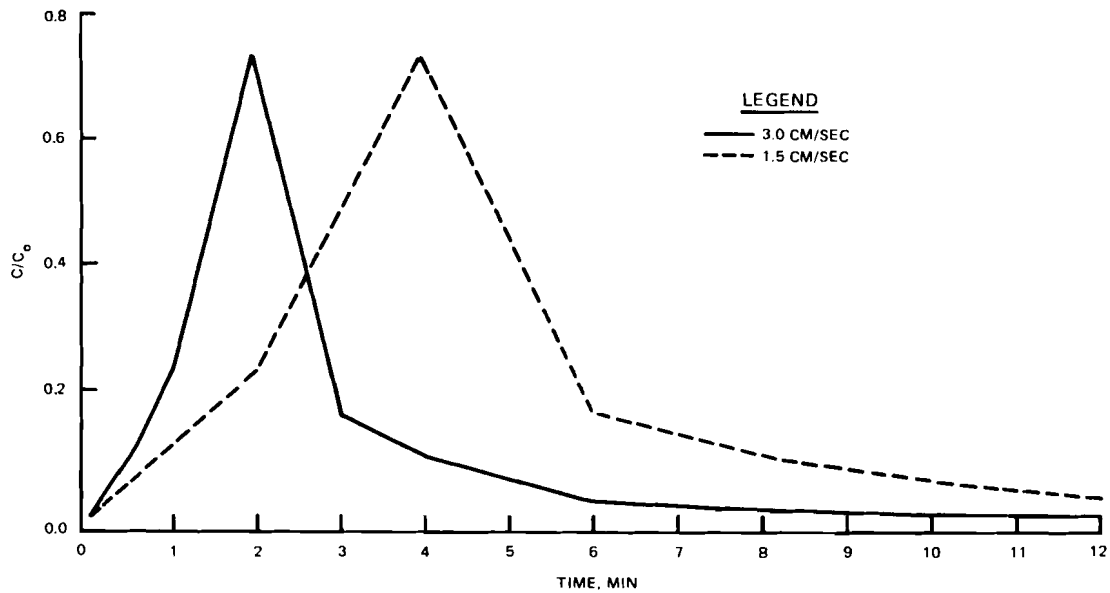


Figure B1. Theoretical transport pattern of a liquid herbicide measured from an initial distributed source at 1.5- and 3.0-cm/sec flow velocities (— 3 cm/sec, - - - - - 1.5 cm/sec)

Table B1

Downstream Herbicide Concentrations From Composite Water Samples*

<u>Velocity</u> <u>cm/sec</u>	<u>Time</u> <u>min</u>	<u>Theoretical</u> <u>Concentration</u> <u>No Plants</u> <u>mg/l</u>	<u>Actual</u> <u>Concentration</u> <u>Plants</u> <u>mg/l</u>
3.0	12	1.06	1.55
	24	~0	0.26
	36	~0	~0
1.5	12	1.63	3.30
	24	0.04	5.10
	36	~0	0.89
	48	~0	0.05
	60	~0	0.02
	72	~0	~0

* Represents a sample every 2 min for a 12-min period.