

AN ABSTRACT OF THE THESIS OF

KENNETH JOHN MIGCHELBRINK for the MASTER OF SCIENCE
(Name) (Degree)

in FARM CROPS presented on June 23, 1969
(Major) (Date)

Title: THE INFLUENCE OF VARIOUS SURFACTANT-HERBICIDE
RATIOS IN THREE VOLUMES OF WATER ON THE
TOXICITY OF DALAPON, PARAQUAT, AND TERBACIL TO
WINTER OATS (*Avena sativa* L.)

Abstract approved: Redacted for Privacy
Arnold P. Appleby

Several studies were conducted to determine if a more consistent predictor of phytotoxicity to winter oats could be obtained with a surfactant-herbicide ratio or a per-unit-volume concentration of surfactant, independent of volume. The herbicides tested were 2,2-dichloropropionic acid (dalapon), 1,1'-dimethyl-4,4'-bipyridinium (paraquat), and 3-tert-butyl-5-chloro-6-methyluracil (terbacil) with the nonionic surfactant X-77 (80% alkylaryl polyoxyethylene glycols, free fatty acids, and isopropanol) in 25, 50, and 75 gallons of water.

All plants were grown in the greenhouse with no supplemental light. Ten plants per pot constituted a replication. All pots were placed in watering trays and irrigated as needed.

Neither a constant surfactant-herbicide ratio nor a per-unit-volume concentration of surfactant proved to be a consistent

predictor of phytotoxicity.

There was a trend of increased phytotoxicity with increasing volumes of water with paraquat and terbacil at the 1/4 lb/acre rate. With the 9 lb/acre rate of dalapon, maximum phytotoxic effects were obtained at the highest volume and the highest rate of surfactant. At the 6 lb/acre rate of dalapon, increased phytotoxic effects were exhibited with a decrease in volume and an increase in surfactant.

High rates of surfactant with terbacil produced necrotic effects one day after spraying. The symptoms were similar to a contact herbicide such as paraquat.

High rates of surfactant without herbicide caused phytotoxic effects. The high rates of surfactant used alone caused an orange appearance in the apical portion of the leaves.

One experiment with terbacil indicated that phytotoxicity may be closely related to drying time of the spray solution on the oat leaf. Using drying time as a criterion for predicting phytotoxicity may encompass the many factors related to successful and consistent surfactant activity. Additional testing of this theory should be pursued.

The Influence of Various Surfactant-Herbicide Ratios
in Three Volumes of Water on the Toxicity of
Dalapon, Paraquat, and Terbacil to Winter
Oats (Avena sativa L.)

by

Kenneth John Migchelbrink

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1970

APPROVED:

Redacted for Privacy

Associate Professor of Agronomy
in charge of major

Redacted for Privacy

Head of Department of Farm Crops

Redacted for Privacy

Dean of Graduate School

Date thesis is presented June 23, 1969

Typed by Donna L. Olson for Kenneth John Migchelbrink

ACKNOWLEDGEMENTS

Dr. Arnold Appleby Accepted me as a graduate student and from
that day supported by endeavors through
financial support and excellent guidance.
The ability to critically evaluate this manu-
script will always be remembered.

Dr. Orvid Lee For serving on my committee and review-
and
Dr. Clifford Smith ing this manuscript.

To my wife Nancy and
sons Paul and Todd

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
LITERATURE REVIEW	4
MATERIALS AND METHODS	18
EXPERIMENT I. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF PARAQUAT TO SEEDLING OATS	22
EXPERIMENT II. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF DALAPON AT 9 POUNDS PER ACRE TO SEEDLING OATS	26
EXPERIMENT III. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF DALAPON AT 6 POUNDS PER ACRE TO SEEDLING OATS	30
EXPERIMENT IV. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF TERBACIL AT 1/2 POUND PER ACRE TO SEEDLING OATS	33
EXPERIMENT V. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF TERBACIL AT 1/4 POUND PER ACRE TO SEEDLING OATS	37
DISCUSSION AND CONCLUSION	43
BIBLIOGRAPHY	48
APPENDIX	52

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Diagram of surfactant molecules forming a film at the interface of an oil droplet and water. (Behrens, 1964).	5
2.	Structural examples of the three types of surfactants.	5
3.	Example of emulsion efficiency varying with HLB (Behrens, 1964).	8
4.	The effect of surfactant-paraquat mixtures to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.	24
5.	The effect of surfactant-dalapon mixtures to seedling oats ten days after application. Dalapon applied at 9 lb/acre.	29
6.	The effect of surfactant-dalapon mixtures to seedling oats ten days after application. Dalapon applied at 6 lb/acre.	32
7.	The effect of surfactant-terbacil mixtures to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre.	36
8.	The effect of drying time and various surfactant-terbacil spray mixtures to seedling oats ten days after spraying. Points refer to ratio quantities from Table 5.	40
9.	Pattern of spray deposition with varying ratios and volumes of spray solution with Experiment V.	41

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Summary of all X-77: paraquat ratio and volume treatment effects. Paraquat applied at 1/64 lb/acre.	23
2. Summary of all X-77: dalapon ratio and volume treatment effects. Dalapon applied at 9 lb/acre.	28
3. Summary of all X-77: dalapon ratio and volume treatment effects. Dalapon applied at 6 lb/acre.	31
4. Summary of all X-77: terbacil ratio and volume treatment effects. Terbacil applied at 1/2 lb/acre.	35
5. Summary of all X-77: terbacil ratio and volume treatment effects. Terbacil applied at 1/4 lb/acre.	

LIST OF APPENDIX TABLES

<u>Table</u>	<u>Page</u>
1. The effect of X-77: paraquat ratios in 25 gallons of water per acre to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.	52
2. The effect of X-77: paraquat ratios in 50 gallons of water per acre to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.	53
3. The effect of X-77: paraquat ratios in 75 gallons of water per acre to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.	54
4. The effect of X-77: dalapon ratios in 25 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 9 lb/acre.	55
5. The effect of X-77: dalapon ratios in 50 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 9 lb/acre.	56
6. The effect of X-77: dalapon ratios in 75 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 9 lb/acre.	57
7. Visual injury ratings of X-77: dalapon ratios on oat seedlings. Dalapon applied at 9 lb/acre.	58
8. The effect of X-77: dalapon ratios in 25 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 6 lb/acre.	59

TablePage

9. The effect of X-77: dalapon ratios in 50 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 6 lb/acre. 60
10. The effect of X-77: dalapon ratios in 75 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 6 lb/acre. 61
11. The effect of X-77: terbacil ratios in 25 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre. 62
12. The effect of X-77: terbacil ratios in 50 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre. 63
13. The effect of X-77: terbacil ratios in 75 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre. 64
14. Visual injury ratings of X-77: terbacil ratios on oat seedlings. Terbacil applied at 1/2 lb/acre. 65
15. The effect of X-77 and X-77: terbacil ratios in 25 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/4 lb/acre. 66
16. The effect of X-77 and X-77: terbacil ratios in 50 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/4 lb/acre. 67

Table

Page

- | | | |
|-----|---|----|
| 17. | The effect of X-77 and X-77:terbacil ratios in 75 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/4 lb/acre. | 68 |
| 18. | Drying time (seconds) of various X-77:terbacil ratios in three volumes of water. | 69 |

THE INFLUENCE OF VARIOUS SURFACTANT-HERBICIDE
RATIOS IN THREE VOLUMES OF WATER ON THE
TOXICITY OF DALAPON, PARAQUAT, AND
TERBACIL TO WINTER OATS
(Avena sativa L.)

INTRODUCTION

Reports of inherent phytotoxicity of surfactant solutions are as old as the history of surfactant additives to pesticidal sprays. An early report on the use of surface-active agents in 1890 showed that the application of arsenical insecticides in strong soapy solutions or in flour-paste suspensions increased insecticide damage to foliage, whereas application in a saponified resin solution was no more damaging than in water alone (Gillette, 1890).

The physical forces operating at interfaces and the free-energy characteristics of surfactant solutions have received the attention of investigators for more than 75 years. In 1915, the contact angle was introduced as a physical measurement which provided a vectoral representation of the interplay between several surface forces (Cooper and Nuttall, 1915). However, no single physical quantity proved adequate for indexing the wetting and spreading characteristics of pesticidal sprays.

Aslander (1927) concluded that the effectiveness of dilute

sulphuric acid as a selective herbicide for cereal crops was dependent on the differential retention of the spray droplets. Subsequently, Blackman and Templeman (1936) showed that the addition of a surface active agent to the spray solution could bring about a greater toxicity of the acid to species with a waxy cuticle owing to the enhanced retention.

The next decade saw an enormous expansion in the development and use of herbicides. With the advent of translocated compounds such as 2,4-dichlorophenoxyacetic acid, the traditional method of spraying a large volume of solution per unit area was abandoned in favor of a much smaller output of relatively concentrated solution per unit area. By this time it was apparent that the phytotoxic effect of a given amount of compound could be markedly influenced by the volume in which it was applied and that this interrelationship changes with the species and the nature of the herbicidal substance (Blackman, 1950).

This study was conducted to determine the influence of spray volume and the nature of herbicidal spray solution on phytotoxicity to seedling oat plants. Three different herbicides were used: 3-tert-butyl-5-chloro-6-methyluracil (terbacil), 2,2-dichloropropionic acid (dalapon), and 1,1'-dimethyl-4,4'-bipyridinium (paraquat). These herbicides were combined with the nonionic surfactant X-77 (80% alkylaryl polyoxyethylene glycols, free fatty acids,

and isopropanol) in each of three volumes of water; 25, 50, and 75 gallons per acre.

An attempt was made to determine if a more consistent predictor of phytotoxicity could be obtained with a per-unit-volume concentration (i. e. percentage of surfactant in solution) or a surfactant-herbicide ratio, independent of volume used. If the per-unit concentration is of greatest importance then a given percentage should provide essentially equivalent control regardless of spray volume. If a surfactant-herbicide ratio is of greatest importance then a given ratio should provide equal control regardless of spray volume. The alternative results are that neither the per-unit-volume concentration nor the surfactant-herbicide ratio are straight line functions.

LITERATURE REVIEW

Surfactants, the name derived from surface-active agent, are chemicals which reduce the surface tension (tendency of the surface molecules of a liquid to be attracted toward the center of the liquid body) of water or increase its wettability (a liquid's ability to moisten a solid). They come in a wide variety of types and each is designed for a particular use. For example, one type of surfactant may be very effective as an emulsifier for oil, usually a particular type of oil. Still another surfactant agent will have cleansing properties, while another has the ability to increase wetting and penetration (Freed, 1958).

Surfactants are molecules which possess both a fairly large oil-soluble group and a water-soluble group. The dual characteristics are termed lipophilic and hydrophilic tendencies, respectively. The combination of these two dissimilar chemical groups in a single substance is responsible for their surface active nature or ability to accumulate at an interface. This causes a reduction in the surface tension of water. It also accounts for the ability of these substances to emulsify oil in water, since the oil-soluble portion of the molecule tends to associate itself with the oil while the water-loving portion of the molecule extends out into the water phase. Behrens (1964) has graphically illustrated this in Figure 1. Both groups are

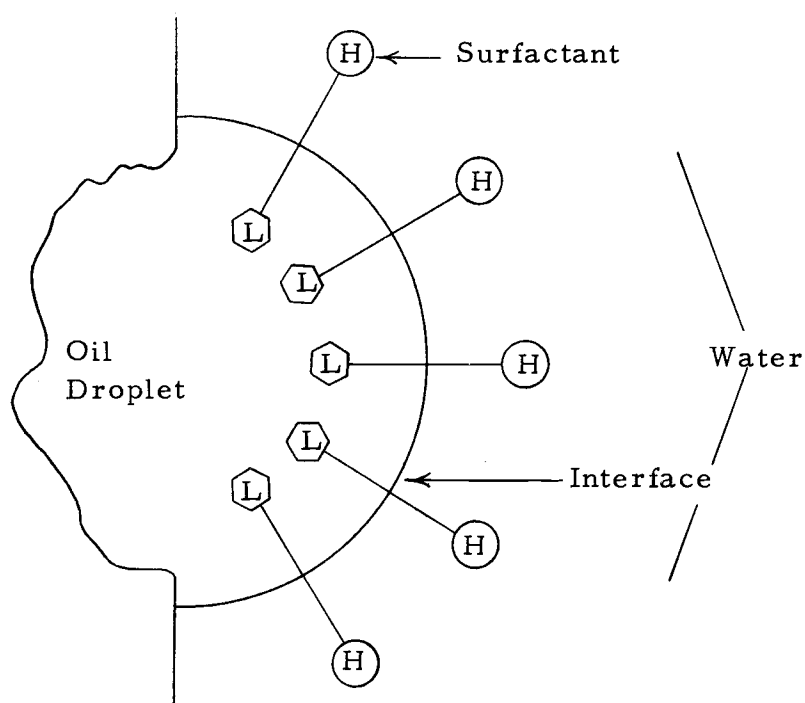


Figure 1. Diagram of surfactant molecules forming a film at the interface of an oil droplet and water. (Behrens, 1964).

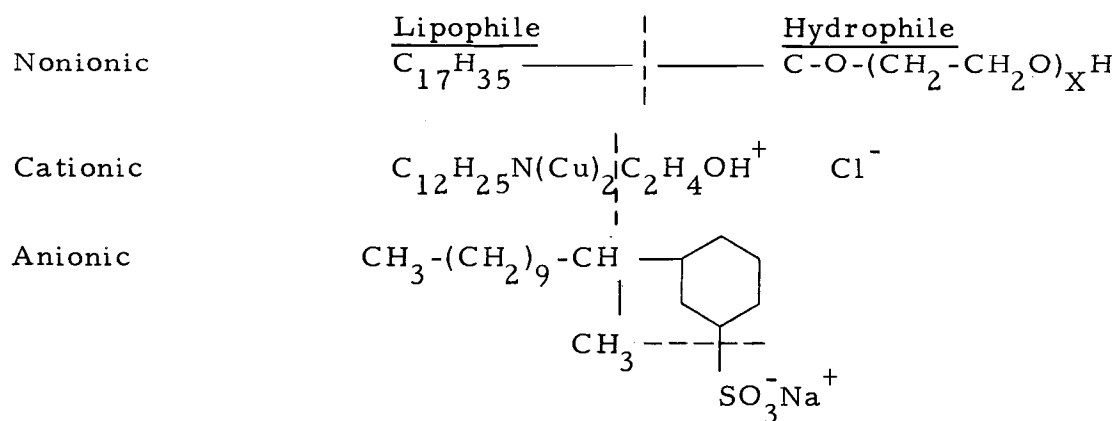


Figure 2. Structural examples of the three types of surfactants.

present in a single molecule. The H represents the group that is polar, largely hydrophilic, and attracted to water; the L group is non-polar, largely lipophilic, and attracted to oil. The characteristics of the molecule can be varied greatly by changing the size and intensity of these groups. Thus a large number of varying properties can be found in the final molecule.

Freed (1958) states that chemists have chosen to classify the surface-active agents into three broad groups depending upon the chemical characteristics of the material. These three groups are called cationic, anionic, and nonionic. The anionic-type surfactant is most familiar because it is commonly encountered as a detergent used as a cleansing agent in the household. A mixture of nonionic surfactant coupled with the anionic surfactant is frequently encountered as an emulsifying agent. The cationic surfactant is more frequently used in germicidal preparations. Structural examples of these groups are given in Figure 2.

The nonionic surfactants obtain their surface active properties without ionization. The hydrophilic portion of the major types of nonionics is conjugated chains of ethylene oxide. Long ethylene oxide chains are highly water soluble, probably due to the multiplicity of hydrogen bonds formed between the oxygen in the hydrophilic chain and the water of the solution. The more common lipophilic portions of nonionic surfactants are derived from the hydrocarbon

portions of alkylphenols, aliphatic acids (especially fatty acids), and corresponding alcohols (Schweizer and McWhorter, 1965).

In the nonionic class, proper choice of the hydrophilic and lipophilic groups provide various degrees of hydrophilic and lipophilic tendencies. The balance of these two characteristics in a single molecule controls the character of the surfactant (Behrens, 1964). This is referred to as the HLB or hydrophilic/lipophilic balance. The HLB is expressed as an arbitrary number and is one way to categorize surfactants. Materials with a high HLB have a predominantly hydrophilic nature and tend to promote oil-in-water emulsions. Materials having a predominantly lipophilic character (low HLB) tend to promote water-in-oil emulsions. Within a family of surfactants of varying HLB's, one member will have an optimum emulsifying efficiency. It appears that each system has a required HLB at which optimum effect will be obtained. Behrens (1964) illustrates this behavior in Figure 3.

Furmidge (1959b) and Jansen (1964) suggest that comparisons of performance characteristics on an HLB basis will show that the "chemical type" of the surfactant is probably more important to herbicide activity and surfactant toxicity than HLB itself. The optimal HLB for enhancing activity of a herbicide on a single species could serve as an initial index for evaluating a large number of chemical types of surfactants systematically. However, the obvious

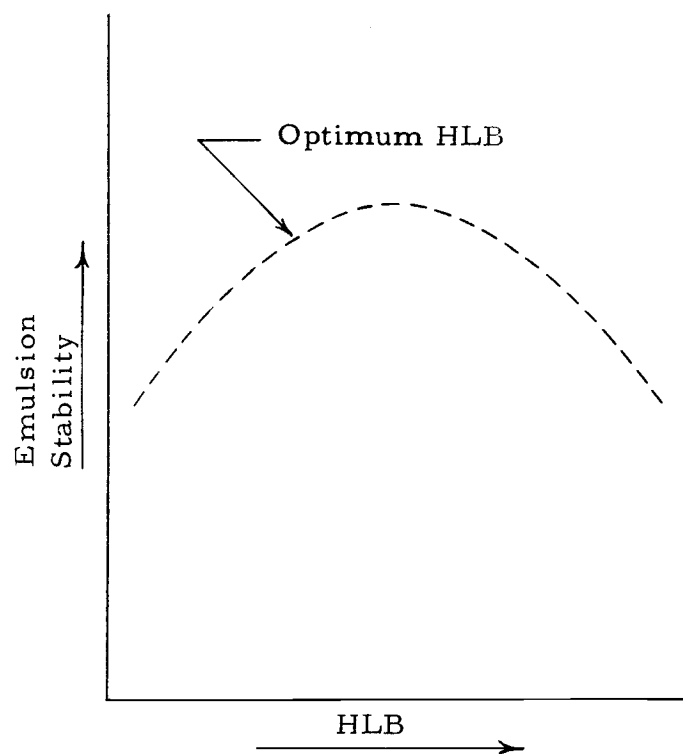


Figure 3. Example of emulsion efficiency varying with HLB (Behrens, 1964).

interaction between herbicides, surfactant, and species suggests that the required HLB could vary with different herbicide/species combinations. It is important to note that HLB numbers are additive which permits blending for adjustment of emulsifiers.

The nonionic surfactants are especially desirable because of their inert qualities and their insensitivity to the presence of hard water. Most are not subject to hydrolysis by acidic or alkaline aqueous solutions. They do not form salts with metal ions. Because of these advantages, nonionic surfactants have received major emphasis in herbicide-surfactant research.

Anionic and cationic surfactants can have either a high or low HLB. They are easily mixed with nonionic surfactants, but not with each other. Their disadvantage is that they are easily influenced by hard water and by acidic or alkaline systems.

In an oil-in-water emulsion, a drop of oil can be seen as surrounded by a film of surfactant molecules with their lipophilic end oriented toward the oil and the hydrophilic end toward the water. If the balance of these tendencies is correct for the oil and water in question, many surfactant molecules can accumulate at the interface. Behrens (1964) has illustrated this behavior in Figure 1.

Behrens (1964) states that an important factor in some emulsion systems is electrical charge. With cationic compounds, the molecules are concentrated at the interface with the hydrophilic end

oriented toward the continuous oil phase. Therefore, the water droplet has many charges at its surface; and since like charges repel one another, the droplets tend to remain suspended.

Currier (1954), Foy (1962), and Jansen, Gentner, and Shaw (1961) indicate that considerable evidence has been accumulated to show that the addition of a surfactant to a solution of a phytotoxic compound can either enhance, diminish, or not affect the herbicidal properties when the resulting solution is applied to the leaves and stems of growing vegetation. The nature and concentration of the herbicide and surfactant, the plant species, the temperature, and the humidity have all been suggested as contributing to the variation in phytotoxicity. While the primary purpose of a surfactant added to a water-soluble herbicide is to promote wetting and coverage of the leaf surfaces, the unique hydrophilic-lipophilic properties of these additives have suggested that they may be capable of more than this one function.

Klingman (1961) indicated that surfactants may: (a) cause more uniform spreading of the spray solution, (b) increase spray retention, (c) bring the spray into more intimate contact with the plant, (d) solubilize non-polar plant substances, (e) cause protein precipitation, and (f) cause denaturation and inactivation of enzymes, viruses, and toxins.

Currier and Dybing (1959) stated that surfactants may enhance

penetration by: (a) improving coverage, (b) removing air films, (c) reducing interfacial tension between relatively polar and apolar submicroscopic regions of the cuticle, (d) inducing stomatal entry, (e) increasing permeability of the plasma membrane, (f) facilitating cell wall movement in the region of the wall-cytoplasm interface, (g) acting as co-solvents, (h) acting directly with the herbicide in some manner, and (i) acting as humectants or hygroscopic agents. Van Overbeek and Blondeau (1954) considered hydrocarbons and surfactants to "solubilize" into the plasma membrane, displacing the fatty molecules and "opening up" the membrane. This hypothesis could explain permeability increases.

Many workers have presented data indicating that surfactants increase herbicide activity. Foy and Smith (1965), McWhorter (1963), and Jansen et al. (1961) found that addition of surfactants increased herbicidal activity of 2,2-dichloropropionic acid (dalapon). The herbicidal activities of 2,4-dichlorophenoxyacetic acid (2,4-D), 4,6-dinitro-o-sec-butylphenol (DNBP), 3-amino-1,2,4-triazole (amitrole), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (linuron), 5-bromo-3-sec-butyl-6-methyluracil (bromacil), 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine), and 2-ethylamino-4-isopropylamino-6-methylmercapto-s-triazine (ametryene) have all been reported to be increased by addition of surfactants (Jansen

et al., 1961; Hill, Belasco, and Ploeg, 1965; McWhorter, 1963; Temple and Hilton, 1963; Freed and Montgomery, 1958).

Inclusion of a suitable surfactant with the post-emergence herbicide, 1,1'-dimethyl-4,4'-bipyridinium salt (paraquat), is essential for maximum herbicidal effect, and in many cases it makes the difference between no toxicity and effective weed control (Elliot, 1962; Smith and Foy, 1967; Evans and Eckert, 1965; Bovey and Davis, 1967; Smith, Foy, and Bayer, 1966).

Hughes and Freed (1961) found that all surfactants tested increased both the rate of absorption and total uptake of chemical when indole-3-acetic acid (IAA) was applied to bean leaves.

Davies et al. (1967) found that appreciable increases in 4-hydroxy-3,5-diiodobenzonitrile (ioxynil) retention by pea and barley occurred with each increase in surfactant concentration. Very little ioxynil was retained when no surfactant was included in the spray.

Smith, Foy, and Bayer (1966) state that when a spray droplet falls on a leaf, it will spread and wet the leaf surface to an extent depending on the leaf surface, the surface tension and the interfacial tension of the spray solution. Evaporation of the water occurs and the concentration of the surfactant and herbicide increases until an equilibrium is reached between the air on the outside and the leaf surface on the inside of the spray deposit. This leaf surface contains many imperfections, i. e., cracks, insect punctures, and

possibly hydrophilic and (or) hydrophobic areas, through which transpiration water escapes and wax precursors move to the leaf surface. It seems reasonable that the surfactant molecules should diffuse from the liquid spray droplet into these areas along the surfaces of the lipophilic cuticle waxes and cutin, the molecules perhaps aligning themselves in monolayers. If true, this would result in the lipophilic end being in or on the cuticle waxes and thus creating a hydrophilic layer or layers in these imperfections. Water molecules would then be attracted to these hydrophilic regions and channels would be formed, conceivably bringing about a slight swelling of the cuticle. Molecules of water-soluble herbicides would be free to diffuse through these "hydrophilic channels" into the cell wall region of the plant cell and thence either into the cytoplasm or via the apoplast into the transpiration stream.

Jansen (1964) proposed a theory of entry of foliar-applied chemicals by separate hydrophilic and lipophilic pathways. He suggested that the primary influence of the surfactant may be promotion of hydration of the cuticle since the cuticle of a leaf swells under humid conditions, resulting in separation of the wax platelets and an increase in the area of the submicroscopic channels through which water moves. Surface wax is just an impediment to droplet contact and appears to have little effect on herbicide entry. Crafts and Robbins (1962) also have suggested polar and apolar routes through

the cuticle.

Assuming a diffusion mechanism of foliar penetration, Temple and Hilton (1963) indicated that the amount of herbicide which would penetrate would depend on: (a) the concentration of herbicide in solution and (b) the length of time the dissolved herbicide is in contact with the leaf. A surfactant would increase the amount of herbicide dissolved in the initial spray solution, and the solubility of the herbicide in pure surfactant may be great enough to keep the herbicide in solution as the water evaporates. Hill et al. (1965) found that surfactants increased the solubility of diuron, linuron, and bromacil. Jansen et al. (1961) also noted increased solubility for dalapon, 2,4-D, DNBP, and amitrole as did Temple and Hilton (1963) for ametryne, diuron, and atrazine. This same characteristic was noted with paraquat (Smith et al., 1965; Evans and Eckert, 1965).

Dorschner and Buchholtz (1956) found that the wetting ability of a herbicide solution appeared to be a significant factor in determining the toxicity of applications of any one herbicide. Freed and Montgomery (1958) reported that reduction in surface tension was an important factor in absorption and translocation, but the relationship of molecular interaction between the surfactant and the herbicide was perhaps of equal or of more importance than the lowering of surface tension. They also reported some indication of

highly specific requirements for surfactant formulations to fit the herbicide in order to achieve maximum effectiveness. Hughes and Freed (1961) reported an interaction between the surfactant and the species of chemical being absorbed which involved not only the ability to reduce surface tension, but also the chemical nature of the surfactant.

Jansen et al. (1961) showed that maximum lowering of surface and interfacial tensions is achieved at concentrations of surfactant considerably below those needed for enhancement of herbicide activity. Above 0.1 percent v/v, the rapid fall in surface tension and interfacial tension begins to level off and little subsequent change is encountered with increasing concentration. This work confirms previous findings of Staniforth and Loomis (1949) that major influences of surfactants upon herbicidal activity are to be found in the range of concentrations beyond which the greatest changes in surface and interfacial tension occur. Foy and Smith (1965) reported that surfactant concentrations of 0.1 - 0.5 percent produced minimum surface tensions and contact angle, but maximum herbicide activity was observed at ten times these levels or greater. Thus above 0.1 - 0.5 percent surfactant concentration, herbicidal enhancement was not correlated with surface tension lowering, contact angle, observed wettability, or initial toxicity of the surfactants. According to these workers, this confirms the view that herbicide-surfactant-plant

interactions, more specific than mere increased wetting, are a part of total surfactant action. There appears to be a close correlation between contact angle and surface tension, but a poor correlation exists with observed herbicidal enhancement by surfactants.

Furmidge (1959a) and Jansen (1964, 1965) discussed structural characteristics of surfactants incorporated with herbicides in the same molecule. At high surfactant concentrations, differences in the toxicity of a herbicide were associated with variation in hydrophilic-lipophilic structure of the surfactant. The formulations were either hydrophilic or lipophilic.

Jansen (1965) established that herbicide toxicity to plants can be influenced as profoundly by structural configuration of ionic surfactants as by those of nonionic surfactants. Jansen et al. (1961) also found many surfactants which showed inherent toxicity at higher concentrations (1.0 percent or above) as well as enhancement of growth at lower surfactant concentrations. Parr and Norman (1964) found that a number of nonionic surfactants inhibited the elongation of the primary cucumber root at concentrations of 0.01 percent. Higher concentrations were more inhibitory and depressed the development of root hairs and lateral roots.

McWhorter (1963) presented data indicating that the percentage of surfactant in solution is not the most important factor nor is the amount applied per plant (or per acre). If the concentration (i. e. ,

percentage of surfactant in solution) is of greatest importance, a given surfactant-herbicide level should provide equal control regardless of spray volume. If the amount of surfactant applied per acre is of primary importance the control obtained with a specific surfactant concentration should decrease in proportion to a reduction in volume. McWhorter (1963) did not find either of these considerations to be valid when put to experimental data.

McWhorter (1964) considered other possibilities. One is that increased activity is a function involving interactions of herbicide level versus volume. The other is that neither the amount of surfactant applied nor the concentration considerations are straight-line functions.

Black and Wilson (1969) feel that each surfactant-herbicide combination will perform best at a fixed ratio under normal spray volumes. For example, some researchers are using 40 to 50 gallons of spray per acre and the farmer may use 15 to 25 gallons of spray per acre. If 1.0 percent surfactant is used on a volume basis, the amount of surfactant in the final spray can vary from 4 pounds to 1.2 pounds of surfactant per acre. With a fixed ratio criteria, the amount of surfactant per acre would be the same regardless of volume. This criteria would be similar to current herbicide recommendations, i. e. applying the same amount of active material per acre regardless of volume.

MATERIALS AND METHODS

All experiments in this thesis research were performed in the greenhouse. Winter oats (Avena sativa L.) were used as the test plants in all experiments. Oats respond to treatments with water-soluble herbicides over a wide range of concentrations. Moreover, they grow readily and uniformly in the greenhouse. Techniques for testing surfactants and herbicides on this species have been standardized. Oats, like most monocotyledons, resist wetting by unmodified aqueous solutions.

The oat seeds were planted in 4x4x4 inch plastic pots containing sandy loam soil. Eight hundred grams of soil were placed in each pot. Fifteen seeds were then placed on the surface and 200 grams of soil were added to cover the seeds. Forty pots were placed in watering trays and subirrigated to field capacity with the excess water drained off. Subsequent irrigations followed as needed. The pots were arranged in a completely randomized design within and among trays. Sixteen days after planting, the oats were thinned to ten plants per pot. The ten plants per pot constituted a treatment replication. Each treatment was replicated four or five times depending on the experiment. At 18 days when the plants were 8 to 11 inches tall, three water-soluble herbicides; 2,2-dichloropropionic acid (dalapon), 1,1'-dimethyl-4,4'-bipyridinium (paraquat), and

3-tert-butyl-5-chloro-6-methyluracil (terbacil) were applied. These herbicides were applied in three volumes of water; 25, 50, and 75 gallons per acre. Varying amounts of the nonionic surfactant X-77 (80% alkylaryl polyoxyethylene glycols, free fatty acids, and isopropanol) were added to each spray mixture at given surfactant-herbicide ratios. Ratio levels were determined in relation to the amount of herbicide in the spray mixture. For example, a 2:1 ratio would include twice the amount of X-77 as herbicide. With paraquat, this would be on a v/v ratio and with dalapon and terbacil, a v/wt ratio.

In initial studies, the herbicides were used at rates which had been determined previously to give a 50 percent reduction in fresh weight of oats when mixed with 5 ml of X-77 diluted with 1000 ml of water described as a 0.5 percent (v/v) solution. These rates were dalapon at 9 lb/acre, terbacil at 1/2 lb/acre, and paraquat at 1/64 lb/acre.

The soil surface in the pots was covered with vermiculite during the spray operation. The vermiculite was removed after the spray deposit had dried. This procedure prevented any herbicide or surfactant from reaching the soil. Growth reduction and toxic effects were thus solely attributable to foliar absorption.

The spraying apparatus used was a greenhouse sprayer which delivered spray from a variable speed cart mounted on an overhead

track. The amount of spray solution applied per unit area was determined by (a) the height of the nozzle from the sprayed surface, (b) the pressure in the spray container, (c) the speed at which the nozzle moved, and (d) the size of the orifice in the nozzle.

The height of the nozzle from the soil surface was adjusted with each volume of spray delivered. The nozzle was 15 inches from the surface at the 75 gal/acre rate, 17 inches at the 50 gal/acre rate, and 19 inches at 25 gal/acre. The speed of the cart moving over the pots increased progressively from the 75 gal/acre rate to 25 gal/acre. A Tee jet 8001-E nozzle was used for the 75 and 50 gal/acre applications. A Tee jet 9501-E nozzle was used for the 25 gal/acre application.

Initial experiments determined that 20 psi was not sufficient pressure to deliver the proper spray pattern with three percent and higher surfactant concentrations. Therefore subsequent applications at all volumes were delivered at 35 psi.

Plant response or toxicity of the surfactant-herbicide solutions was assessed by visual observation of symptoms and fresh weights of the foliage. The phytotoxicity is reported in grams of total green weight and in terms of a toxicity index value, which was calculated by expressing the fresh weight of the plants as a percentage of the control and subtracting this value from 100. The control consisted of the prescribed amount of herbicide, but containing no surfactant

and is reported in the tables as 0:1. Therefore, effects of treatments can be attributed to the amount of X-77 or X-77: herbicide interaction.

Fresh green weights of the above ground portions of ten plants contained in each pot was the parameter used for statistical comparisons in a completely randomized design with a factorial arrangement of varying ratios and volumes. The interaction between ratios and volumes was determined by using a factorial analysis as outlined in LeClerg, Leonard, and Clark (1962). The least significance difference test was used in comparisons of treatment means in all trials of this study.

The greenhouse air temperature averaged 24 C (75 F) most days with a minimum of 15 C (60 F) at night and a maximum of 30 C (87 F) during the day. Relative humidity fluctuated between 40 and 70 percent. No supplemental light was provided for any of the studies.

EXPERIMENT I. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF PARAQUAT TO SEEDLING OATS

The inclusion of a suitable surfactant in paraquat solutions used as a foliar spray is essential for maximum phytotoxic effects. In this study different X-77:paraquat ratios in three different volumes of water were evaluated. Also three levels of X-77 without paraquat were included to determine any phytotoxic effects due to surfactant alone.

Paraquat proved to be a difficult herbicide to work with in this type of experiment. Five identical experiments were conducted at different times. Extremes in variation were encountered because of environmental factors influencing paraquat. Variation in humidity, temperature, and light intensity appeared to be the major factors contributing to the unpredictable results. Results are summarized in Table 1. More complete data are included in Appendix Tables 1 through 3.

The fluctuating values in the 75 gal/acre rate are indicative of all five experiments. It is suspected the additional water may inhibit the direct foliar activity of paraquat in some way. Figure 4 shows that the high rate of surfactant, 64:1, caused the most consistent phytotoxic effects regardless of volume. This was repeated in all five experiments. An untreated control should have been included in

Table 1. Summary of all X-77: paraquat ratio and volume treatment effects. Paraquat applied at 1/64 lb/acre.

X-77: paraquat Ratio	Gallons of diluent/acre			Average effect of ratios
	25	50	75	
0:1	1.70 ^a	1.49	1.21	1.47
1:1	1.60	1.42	1.21	1.43
2:1	1.54	1.36	1.19	1.36
4:1	1.44	1.41	1.35	1.40
8:1	1.50	1.06	1.42	1.33
16:1	1.34	1.26	1.21	1.27
32:1	.90	1.09	1.02	1.00
64:1	.87	.87	.81	.85
16:0	1.62	1.25	1.27	1.38
32:0	1.30	1.62	1.37	1.43
64:0	1.35	1.37	1.22	1.32
Average effect of volumes	1.38	1.29	1.21	

^aValues are average fresh weights of 40 oat plants (4 pots) in grams

Analysis of variance

Source of variation	df	Means square	F value
Treatments	32	.2075	4.65**
Ratios	10	.4980	11.17**
Volumes	2	.3150	7.06**
R x V	20	.0515	1.55
Error	99	.0446	

**Significant at 1% level

$$\bar{x} = 1.29$$

$$s = .211$$

$$CV = 16.4\%$$

$$\text{Ratio LSD (0.05)} = .17$$

$$\text{Volume LSD (0.05)} = .09$$

$$\text{LSD (0.01)} = .23$$

$$\text{LSD (0.01)} = .12$$

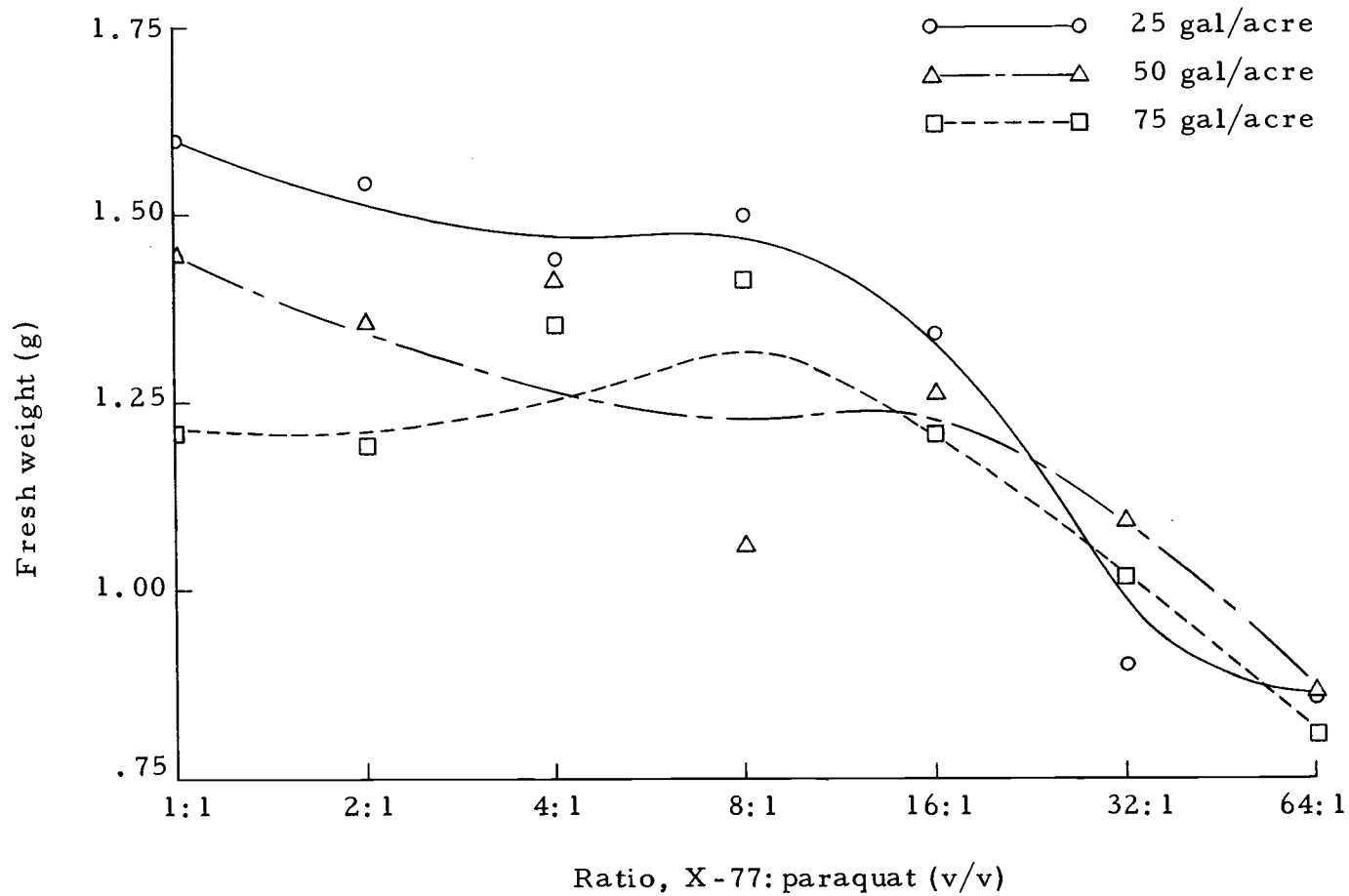


Figure 4. The effect of surfactant-paraquat mixtures to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.

this experiment to determine if, in fact, the low rates of surfactant were stimulatory. However, this cannot be said without an untreated control.

Significant F values were obtained among treatments in each of the volumes tested. When all paraquat treatments were analyzed statistically together, there were significant differences between ratios and between volumes. Significant differences within treatments can be observed by comparing treatment means with LSD values. There was no significant interaction.

EXPERIMENT II. THE EFFECT OF VARIOUS SURFACTANT
CONCENTRATIONS ON THE TOXICITY OF
DALAPON AT NINE POUNDS PER ACRE TO
SEEDLING OATS

The objective of this experiment was to determine if a satisfactory surfactant-to-dalapon ratio would give a more consistent phytotoxic effect than a unit per volume of spray mixture. Injury ratings were given every third day after spraying and were based on visual observations using a scoring system whereby 0 = no injury; 1-3 = little injury, varying degrees of spotting and minor leaf burn; 4-6 = moderate injury, moderate degrees of burn or defoliation; 7-9 = severe injury, severe reductions of foliage; 10 = complete kill. There were five replications per treatment.

Increased surfactant concentrations caused substantial increases in the toxicity of dalapon within each of three volumes tested. Seedling oats receiving 2:1 and 1:1 ratios in the 50 gal/acre rate and the 2:1, 1:1, and 1:2 ratios in the 75 gal/acre rate had an oily appearance one day after application. This was associated with subsequent wilting. Three days after application, these plants were brittle and near death. This would indicate that dalapon entered the plant quicker with these high surfactant rates. Contact injury occurred in scattered flecks over the foliage, usually corresponding to the wetting pattern.

There were significant differences between ratios when all

three volumes were considered together. Increasing amounts of surfactant caused increased phytotoxicity within a given volume. This experiment did not indicate any significant difference between ratios of 1:8, 1:4, 1:2, 1:1, and 2:1 inclusive, or .20 to 10.0 percent of surfactant in all volumes. Results of this experiment are summarized in Table 2. Individual experiment data are in Appendix Tables 4 through 6. Appendix Table 7 records visual observations every third day after spray application. Figure 5 illustrates the pattern of increasing phytotoxicity with an increasing surfactant rate in three volumes of water.

Table 2. Summary of all X-77:dalapon ratio and volume treatment effects. Dalapon applied at 9 lb/acre.

X-77:dalapon Ratio	Gallons of diluent/acre			Average effect of ratios
	25	50	75	
0:1	2.42 ^a	2.40	2.24	2.35
1:64	1.14	1.01	1.30	1.15
1:32	1.08	.95	1.15	1.06
1:16	.82	.65	.90	.79
1:8	.50	.57	.65	.57
1:4	.47	.57	.59	.54
1:2	.62	.44	.38	.48
1:1	.58	.42	.30	.43
2:1	.52	.40	.28	.40
Average effect of volumes	.68	.82	.86	

^aValues are average fresh weights of 50 plants (5 pots) in grams

Analysis of variance

Source of variation	df	Means square	F value
Treatments	26	1.860	24.16**
Ratios	8	5.894	76.55**
Volumes	2	.060	.78
R x V	16	.069	.89
Error	108	.077	

**Significant at 1% level

$$\bar{x} = .87$$

$$s = .28$$

$$CV = 32.18\%$$

$$\text{Ratio LSD (0.05)} = .34$$

$$\text{LSD (0.01)} = .45$$

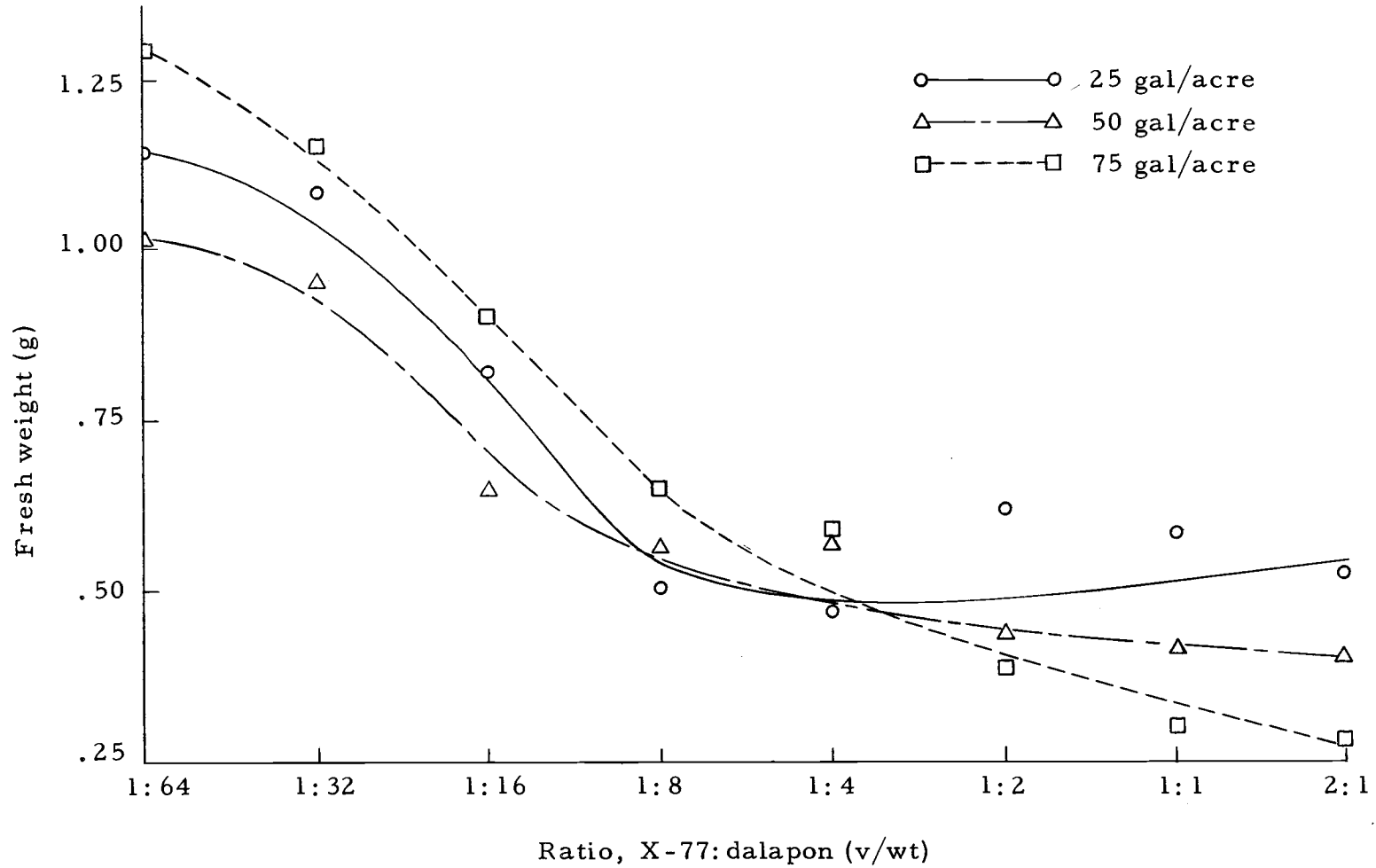


Figure 5. The effect of surfactant-dalapon mixtures to seedling oats ten days after application. Dalapon applied at 9 lb/acre.

EXPERIMENT III. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF DALAPON AT SIX POUNDS PER ACRE TO SEEDLING OATS

Since the 9 lb/acre rate of dalapon caused extreme phytotoxic effects, the experiment was repeated using 6 lb/acre. This produced more significant differences between ratios and volumes.

Since a significant interaction between ratios and volumes was found, the individual treatment means within each volume are the most important consideration. Even though the dalapon dosage was reduced, all fresh green weights were significantly lower than the control of dalapon alone. At the higher surfactant rates, the percent of volume appeared to cause more consistent phytotoxicity than did the ratio criteria. The results of each gallonage experiment are recorded in Appendix Tables 8, 9, and 10.

With the 6 lb/acre rate, there was a general trend for increasing phytotoxic effects with a decrease in volume and an increase in amount of surfactant as indicated in Table 3. This experiment was not repeated to determine if this phenomenon could be duplicated. However, it could be suspected that increased herbicidal effectiveness was not obtained at higher volumes since these plants might have received less toxicant than those sprayed with lower volumes. Figure 6 shows the effect of 3 volumes with dalapon at the 6 lb/acre rate.

Table 3. Summary of all X-77:dalapon ratio and volume treatment effects. Dalapon applied at 6 lbs/acre.

X-77:dalapon Ratio	Gallons of diluent/acre			Average effect of ratios
	25	50	75	
0:1	1.05 ^a	.96	1.10	1.04
1:32	.58	.55	.95	.69
1:16	.46	.49	.59	.51
1:8	.43	.58	.45	.49
1:4	.37	.48	.36	.40
1:2	.33	.40	.55	.43
1:1	.28	.35	.50	.38
2:1	.25	.25	.32	.27
4:1	.15	.26	.29	.23
Average effect of volumes	.43	.48	.57	

^aValues are average fresh weights of 50 plants (5 pots) in grams

Analysis of variance

Source of variation	df	Means square	F value
Treatments	26	.3173	26.89**
Ratios	8	.9037	76.58**
Volumes	2	.2100	17.80**
R x V	16	.0375	3.18**
Error	108	.0118	

**Significant at 1% level

$$\bar{x} = .49$$

$$s = .11$$

$$CV = 22.2\%$$

$$\text{Interaction LSD (0.05)} = .13$$

$$\text{LSD (0.01)} = .18$$

$$\text{Ratio LSD (0.05)} = .04$$

$$\text{LSD (0.01)} = .06$$

$$\text{Volume LSD (0.05)} = .08$$

$$\text{LSD (0.01)} = .10$$

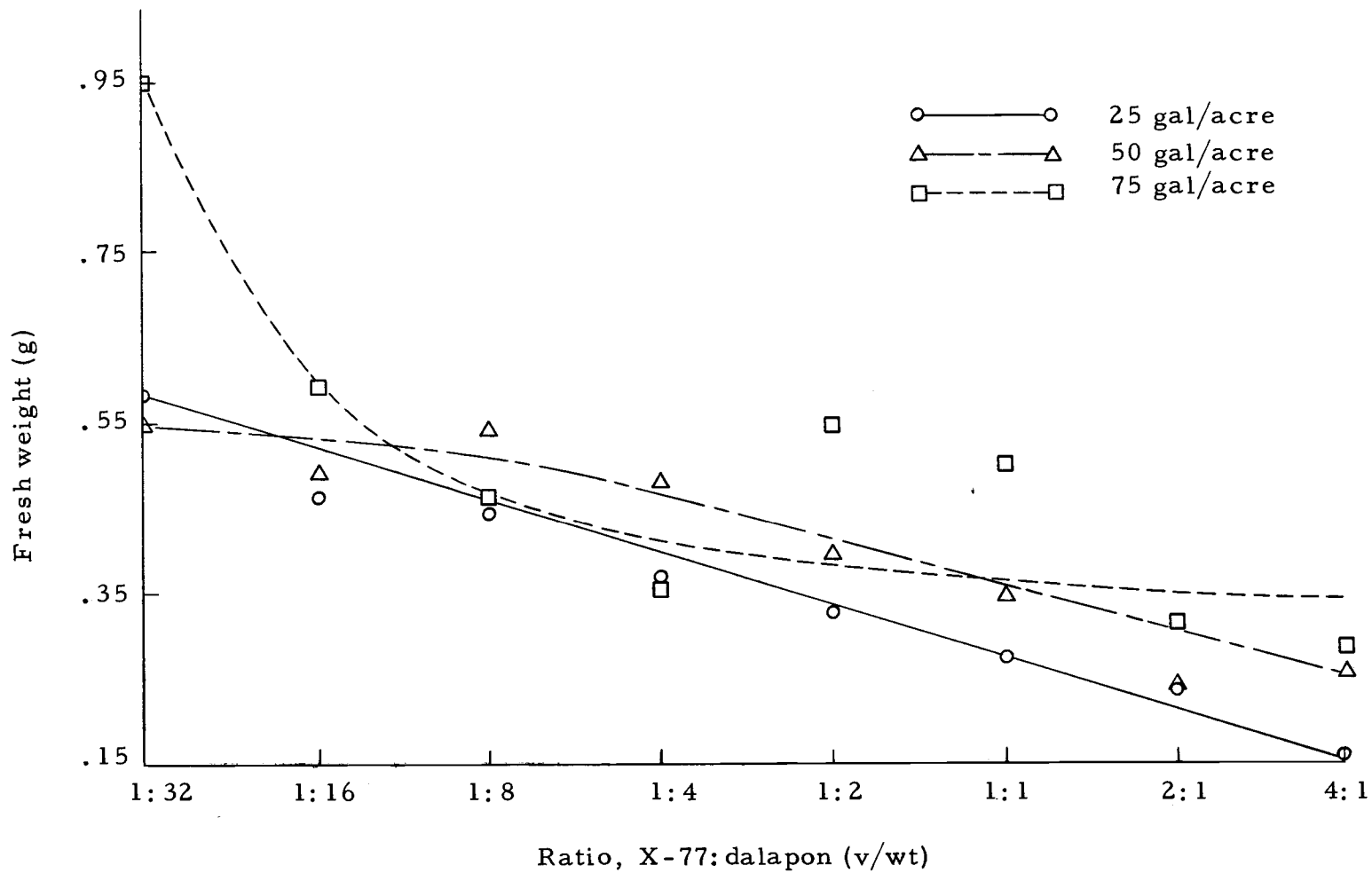


Figure 6. The effect of surfactant-dalapon mixtures to seedling oats ten days after application. Dalapon applied at 6 lb/acre.

EXPERIMENT IV. THE EFFECT OF VARIOUS SURFACTANT
CONCENTRATIONS ON THE TOXICITY OF
TERBACIL AT 1/2 POUND PER ACRE TO
SEEDLING OATS

Terbacil, a member of the uracil herbicide family, was tested to determine phytotoxicity enhancement with the addition of a surfactant to the spray mixture. Terbacil has commonly been used as a soil-applied herbicide. Recently, there has been interest in terbacil's use as a foliar-applied herbicide. The objective of this experiment was to determine if terbacil could be used effectively as a foliar-applied material and whether the inclusion of a surfactant at a given ratio to the herbicide or a percentage of the volume of water was a more consistent predictor of phytotoxicity.

Injury ratings were given to the plants every third day after spraying. The injury scale used in experiment II was also used in this experiment.

Severe injury was noted within three days with high surfactant rates added to terbacil at 1/2 lb/acre (Appendix Table 14). Ratios of 32:1 and 64:1 produced necrotic effects one day after spraying. These ratios produced effects very similar to a paraquat application, i. e. symptoms appeared to be of a contact nature rather than the anticipated symptoms of inhibition of the Hill reaction expected of terbacil. Some oat plants showed signs of regrowth six days after spraying with rates of 32:1 and 64:1 at 50 gal/acre. Contact injury

alone was suspected with these high surfactant dosages. However, these plants were retained after harvesting and regrowth did not occur. This would indicate that translocation of the herbicide did, in fact, occur. Appendix Tables 11, 12, and 13 show the results of each study.

At low surfactant rates (1:1 and 2:1) highly significant differences occurred between volumes. At high surfactant rates (64:1 and 32:1) there were no significant differences between volumes. This would indicate that volume is an important consideration depending on the rate of surfactant, whether it be on a ratio or percent basis. When the data were pooled, there was a significant interaction between volumes and ratios as indicated in Table 4. Figure 7 illustrates the effect of different X-77:terbacil combinations in three volumes of water.

Table 4. Summary of all X-77:terbacil ratio and volume treatment effects. Terbacil applied at 1/2 lb/acre.

X-77:terbacil Ratio	Gallons of diluent/acre			Average effect of ratios
	25	50	75	
0:1	2.66 ^a	2.70	2.56	2.63
1:1	.80	.64	1.23	.89
2:1	.87	.57	1.23	.89
4:1	.63	.54	.82	.67
8:1	.65	.52	.81	.66
16:1	.66	.49	.44	.53
32:1	.45	.36	.41	.40
64:1	.36	.35	.38	.36
Average effect of volumes	.88	.77	.98	

^aValues are average fresh weights of 50 plants (5 pots) in grams

Analysis of variance

Source of variation	df	Means square	F value
Treatments	23	2.580	60.0**
Ratios	7	8.104	188.5**
Volumes	2	.450	10.5**
R x V	14	.122	2.84**
Error	96	.043	

**Significant at 1% level

$$\bar{x} = .88$$

$$x = .21$$

$$CV = 23.9\%$$

$$\text{Interaction LSD (0.05)} = .26$$

$$\text{LSD (0.01)} = .34$$

$$\text{Ratio LSD (0.05)} = .15$$

$$\text{LSD (0.01)} = .20$$

$$\text{Volume LSD (0.05)} = .09$$

$$\text{LSD (0.01)} = .12$$

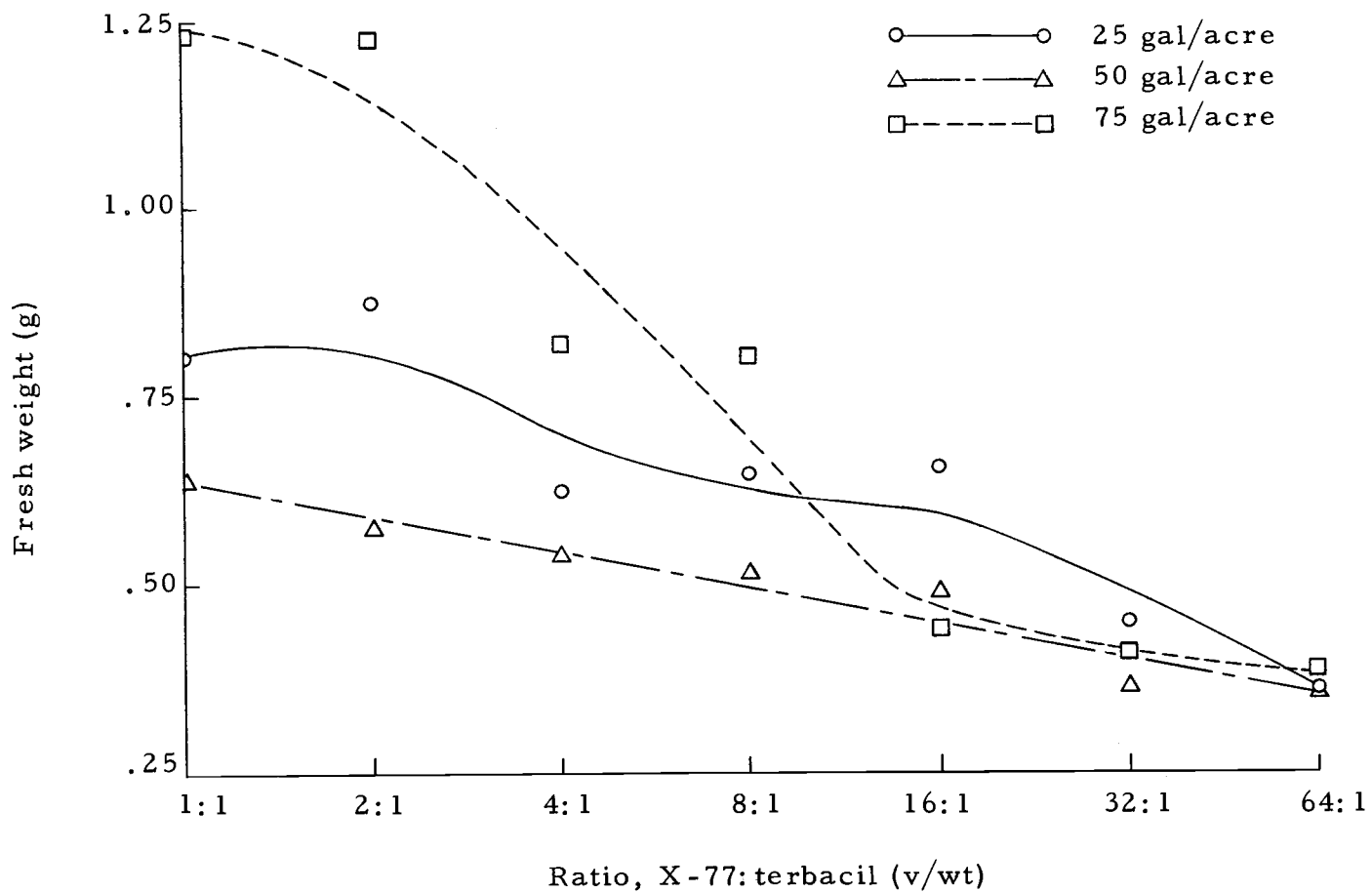


Figure 7. The effect of surfactant-terbacil mixtures to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre.

EXPERIMENT V. THE EFFECT OF VARIOUS SURFACTANT CONCENTRATIONS ON THE TOXICITY OF TERBACIL AT 1/4 POUND PER ACRE TO SEEDLING OATS

Since the 1/2 lb/acre rate of terbacil caused extreme phytotoxic effects, it was repeated with terbacil at 1/4 lb/acre. It was anticipated this would provide more significant differences between ratios and volumes.

Since the phytotoxic effects were so pronounced with high surfactant rates in experiment IV, this experiment included high surfactant rates without any terbacil to determine if X-77 had phytotoxic effects.

The literature contains many explanations as to how and why surfactants work, resulting in various authors agreeing, half-agreeing, or not agreeing at all. Since these varied opinions do exist, a study was conducted to determine how long the spray mixture remains on the leaf of the oat plant after it has been sprayed. Various methods of magnification were evaluated. Use of the naked eye was deemed most useful in determining length of drying time. This was done by selecting two oat leaves at approximately a 70 degree angle to the soil prior to moving the spray apparatus over the plants. As the sprayer passed over the leaves, a hand stop watch was started. The watch was stopped when the last droplet dried from the leaf surface. Drying time was best determined at an

angle of 5-15 degrees between the eye and the leaf surface. Care was taken to calculate the drying time for the liquid in the same environment from the moment of spray contact till the liquid had dried.

Highly significant differences in fresh weights were obtained between ratios and volumes as indicated in Table 5. Significant interaction differences were recorded.

Increased phytotoxic effects were obtained with increasing volumes of spray mixture and increasing surfactant rates. Individual volume results are reported in Appendix Tables 15, 16, and 17. High surfactant rates without terbacil (8:0, 16:0, 32:0, and 64:0) also exhibited phytotoxic effects. Oat leaves exhibited an increasing degree of apical orange coloration as the surfactant increased without terbacil. The angle of incidence of the leaf at the time of spraying corresponded to degree of orange color. As the angle between the leaf and sprayer increased, the degree of orangeness increased. This would indicate that increased surfactant entered the leaf as the angle increased and the amount of surfactant applied increased.

Fresh weights appeared to be closely related to drying time after spraying. Drying time of various X-77:terbacil ratios appears in Appendix Table 18. Figure 8 graphically demonstrates the relationship between times, expressed in seconds, and final fresh weights. Figure 9 shows the characteristic pattern of spray droplets

Table 5. Summary of all X-77 and X-77:terbacil ratio and volume treatment effects. Terbacil applied at 1/4 lb/acre.

X-77:terbacil Ratio	Gallons of diluent/acre			Average effect of ratios
	25	50	75	
0:1	1.27 ^a	1.16	.95	1.13
1:1	.84	.79	.57	.73
2:1	.78	.74	.54	.69
4:1	.77	.62	.46	.62
8:1	.68	.59	.27	.52
16:1	.58	.40	.29	.43
32:1	.44	.33	.21	.33
64:1	.30	.28	.34	.31
8:0	.75	.49	.67	.64
16:0	.96	.45	.58	.67
32:0	.67	.80	.35	.61
64:0	.58	.60	.36	.52
Average effect of volumes	.72	.61	.47	

^aValues are average fresh weights of 40 plants (4 pots) in grams

Analysis of variance

Source of variation	df	Means square	F value
Treatments	35	.2506	9.47**
Ratios	11	.5600	21.13**
Volumes	2	.7600	28.68**
R x V	22	.0495	1.87*
Error	108	.0265	

*Significant at 5% level

**Significant at 1% level

$$\bar{x} = .60$$

$$s = .16$$

$$CV = 27.2\%$$

$$\text{Ratio LSD (0.05)} = .13$$

$$\text{LSD (0.01)} = .17$$

$$\text{Volume LSD (0.05)} = .06$$

$$\text{LSD (0.01)} = .09$$

$$\text{Interaction LSD (0.05)} = .23$$

$$\text{LSD (0.01)} = .30$$

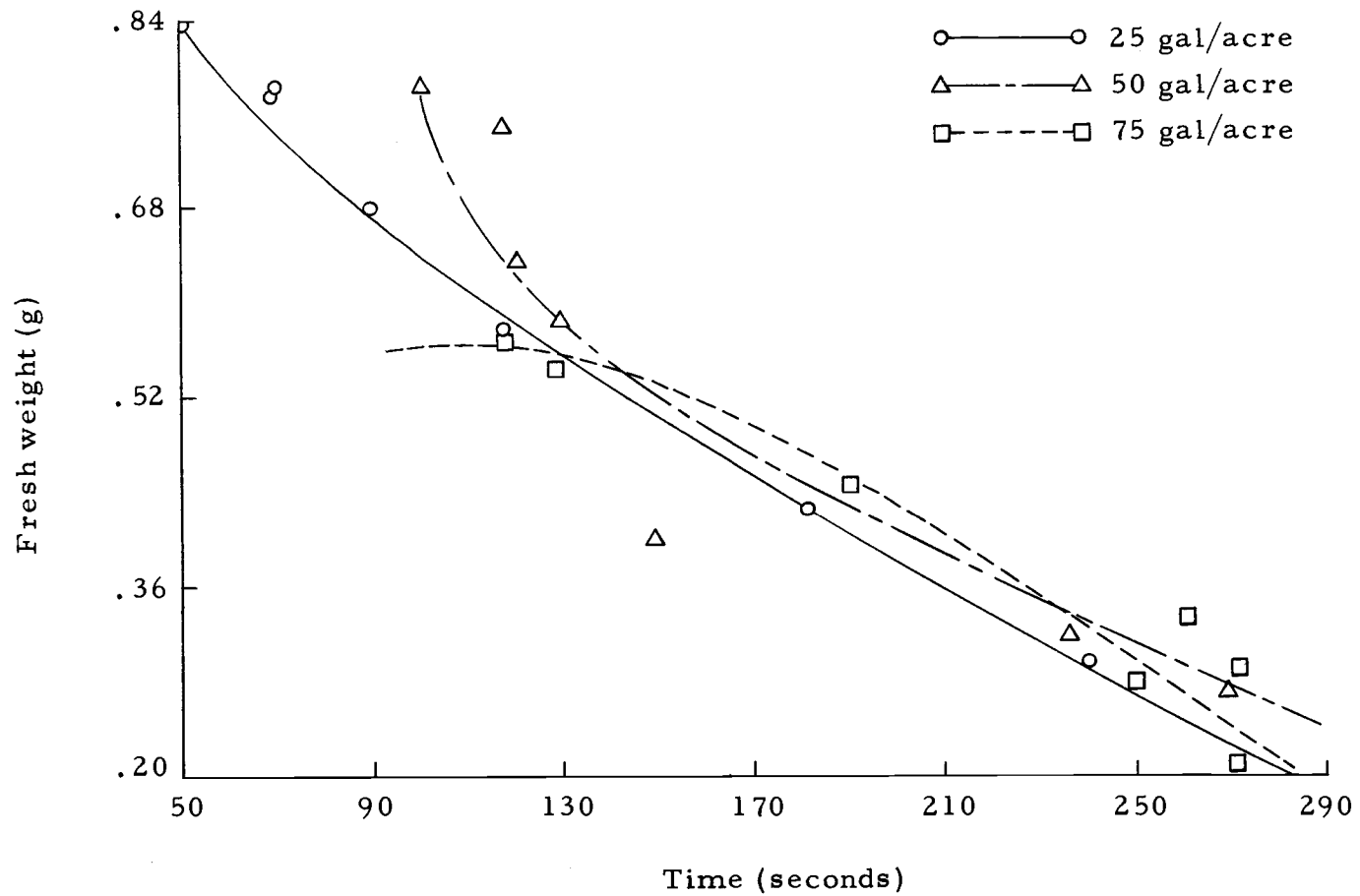


Figure 8. The effect of drying time and various surfactant-terbacil spray mixtures to seedling oats ten days after spraying. Points refer to ratio quantities from Table 5.



	Ratios
25 gal/acre	2:1, 4:1, 8:1
50 gal/acre	1:1, 2:1

(a) Spray droplets adhere to leaf margin



	Ratios
25 gal/acre	16:1, 32:1
50 gal/acre	4:1, 8:1, 16:1
75 gal/acre	1:1, 2:1, 4:1

(b) Spray droplets adhere to center of leaf and margins



	Ratios
25 gal/acre	64:1
50 gal/acre	32:1, 64:1
75 gal/acre	8:1, 16:1, 32:1, 64:1

(c) Spray droplets coalesce and create a film over leaf surface

Figure 9. Pattern of spray deposition with varying ratios and volumes of spray solution with Experiment V.

on the surface of the oat leaf at different ratios, volumes, and times. From Table 5 and Appendix Table 18 along with Figures 8 and 9, it would appear that the herbicide should remain in a liquid state on the leaf surface for at least one minute to receive the minimum benefit of foliar-applied terbacil. Maximum results were obtained when the X-77: terbacil solution remained on the leaf surface for at least three minutes.

Table 5 data indicate that similar degrees of phytotoxicity were achieved with a 4:1 ratio in 75 gal/acre as with the 16:1 ratio in 50 gal/acre or the 32:1 ratio in 25 gal/acre. This would follow that a lesser amount of surfactant is needed in 75 gal/acre to achieve the same degree of phytotoxicity as with 50 gal/acre. Following this would be a lesser amount of surfactant is needed in 50 gal/acre to achieve the same degree of phytotoxicity as with 25 gal/acre. This may lead one to concluded that it is the degree of coverage which determines levels of phytotoxicity, rather than a prescribed surfactant-herbicide ratio or per-unit percentage of total volume.

DISCUSSION AND CONCLUSIONS

Studies were conducted to determine if more consistent phytotoxic effects could be obtained with a surfactant-herbicide ratio independent of volume or a per-unit-volume concentration (i. e. percent of surfactant in solution).

The literature review indicated that surfactants may enhance penetration of a herbicide by several means. X-77 enhanced the phytotoxicity of the three foliar-applied herbicides (paraquat, dalapon, and terbacil) in this study. However, the volume of water, as well as the level of surfactant, was found to influence herbicidal activity.

Paraquat proved to be a difficult herbicide to test in this type of study. Because of its extreme sensitivity to environmental factors, the results often responded to the environmental factor which predominated while the study was in progress. This finding should be kept in mind while reviewing similar studies of paraquat action. Only the high surfactant ratio of 64:1 proved to cause consistent phytotoxicity in three different volumes of water.

Neither a surfactant-to-herbicide ratio nor a percent of volume provided a consistent basis for predicting phytotoxic effects with dalapon at the 9 lb/acre or 6 lb/acre rate. Higher phytotoxic effects were recorded within each volume as the amount of surfactant

increased in each study. When the average effect of volume is considered in each experiment, there is an increase of phytotoxicity with a decrease in volume. It could be suspected that increased herbicidal effectiveness was not obtained at higher volumes because these plants may have received or retained less toxicant than those sprayed with lower volumes. Furmidge (1962) states that after droplets have adhered to the target surface, the spray retained increases proportionately with the volume applied until the surface becomes saturated with spray. At this point "run-off" commences and, on continued spraying, the volume retained tends to decrease. It is at the point of incipient run-off maximum deposit will occur which in turn should result in maximum phytotoxicity.

High ratios of surfactant-to-terbacil (32:1 and 64:1) produced necrotic effects one day after spraying. The symptoms were of a contact nature similar to paraquat injury. It was suspected that a "burning" or dessication of the leaf was occurring resulting in no translocation of the terbacil. These plants were retained after harvest and regrowth did not occur indicating that translocation did occur.

The greatest phytotoxicity with X-77 and terbacil at 1/2 lb/acre was with 50 gal/acre of water. At 1/4 lb/acre of terbacil, there was increasing phytotoxicity from 25 gal/acre to 75 gal/acre of water.

Increased levels of surfactant within a given volume most often

tended to increase phytotoxic effects. The accuracy with which one can predict phytotoxicity seems to increase with increasing surfactant levels. As the level of surfactant decreases, the accuracy of predicting phytotoxicity appears to diminish accordingly and also volume of carrier is more critical. The greater effect of increased surfactant may be due, in part, to the greater retention of the herbicide by more efficient wetting and increased spray load. It appears the additional surfactant has sealing or humectant properties so that it slows down droplet drying. This would provide an aqueous continuum from the leaf surface to the protoplast creating a more favorable microclimate for prolonged penetration through the cuticle.

This could lead to the hypothesis that it is the degree of coverage which will determine herbicidal effectiveness, not a set criteria of surfactant-herbicide ratios nor a per-unit concentration of surfactant in a given volume of water. Although a degree of coverage can be attained based upon these kinds of criteria, a more workable and practical method should be determined. The method selected should encompass most factors which are known to influence surfactant and/or herbicide entry into a plant. This would include species differences and environmental influences.

It appears the degree of flowability of the spray mixture resulting in maximum coverage of the leaf surface is vitally important for enhancing herbicidal activity. One trial in this study indicated

that the length of time the spray solution remains on the leaf surface could possibly encompass the many factors influencing foliar-applied herbicidal effectiveness (i. e. volume of carrier, herbicidal properties, species differences, leaf angle, environmental differences, etc.)

This theory would indicate that a surfactant should be added to the spray mixture, at the time of spraying, until the spray solution remains on the leaf surface for a predetermined amount of time. For example, it is well known that phenoxy compounds cause greater phytotoxic effects in the early morning hours than the late afternoon hours. This is because of the leaf's increased retention characteristics in the early morning hours. However, if additional surfactant were added in the late afternoon to the point where the spray solution remained on the leaf surface as long as it does in the early morning hours, quite possibly the same degree of phytotoxicity could be achieved.

This study indicated that a 1/4 lb/acre foliar application of terbacil should remain on the leaf surface for at least one minute to receive the minimum benefit of the surfactant-herbicide combination. Maximum results were obtained when the spray solution remained on the leaf surface for about three minutes. This should not be interpreted that spray retention of periods longer than three minutes will produce increased herbicidal activity. Quite the contrary!

Conceivably, herbicidal activity may decrease as a result of runoff.

If these findings can be successfully repeated in the greenhouse and in the field with other herbicides, the practical implications could become wide-spread. Instead of a given quantity of surfactant being recommended for all situations, a recommendation could conceivably be developed that would tell a farmer to continue adding surfactant until the spray solution remained on the leaf surface for at least one minute. Supposedly, this would account for most factors influencing herbicidal effectiveness at the time of spraying.

It appears from this study that consistency of phytotoxic results can be attributed to increased deposition and more uniform spreading of the herbicidal solution, which in turn, could possibly be best measured by time.

BIBLIOGRAPHY

- Aslander, A. L. 1927. Sulphuric acid as a weed spray. *Journal of Agricultural Research* 34:1065.
- Bayer, D. E. and H. R. Drever. 1965. The effects of surfactants on efficiency of foliar-applied diuron. *Weeds* 13:222-225.
- Behrens, R. W. 1964. The physical and chemical properties of surfactants and their effects on formulated herbicides. *Weeds* 12:255-258.
- Black, F. S. and H. P. Wilson. 1969. Performance of herbicide adjuvant-sprays as effected by the time of day, by the ratio of herbicide to adjuvant, and by the chemical type of the adjuvant. *Abstracts of the Weed Science Society of America, 1969*, p. 1.
- Blackman, G. E. 1950. Selective toxicity and the development of selective weedkillers. *Journal of the Royal Society of Arts* 98:500.
- Blackman, G. E., R. S. Bruce and K. Holly. 1958. Studies in the principles of phytotoxicity. V. Interrelationships between specific differences in spray retention and selective toxicity. *Journal of Experimental Botany* 9:175-205.
- Blackman, G. E. and W. G. Templeman. 1936. The eradication of weeds in cereal crops by sulphuric acid and other compounds. *Journal of Agricultural Science* 26:368.
- Bovey, R. W. and F. S. Davis. 1967. Factors affecting the phytotoxicity of paraquat. *Weed Research* 7:281-289.
- Cooper, W. F. and W. H. Nuttall. 1915. The theory of wetting, and the determination of the wetting power of dipping and spraying fluids containing a soap basis. *Journal of Agricultural Science* 7:219-239.
- Crafts, A. S. and W. W. Robbins. 1962. *Weed control*. New York, McGraw-Hill. 660p.
- Currier, H. B. 1954. Wetting agents and other additives. *Proceedings of the 6th California Weed Conference* 6:10-15.

- Currier, H. B. and C. D. Dybing. 1959. Foliar penetration - review and present status. *Weeds* 7:195-213.
- Davies, P. J., D. S. H. Drennan, J. D. Fryer and K. Holly. 1967. The basis of the differential phytotoxicity of 4-hydroxy-3,5-di-iodobenzonitrile. *Weed Research* 7:220-233.
- Dorschner, K. P. and K. P. Buchholtz. 1956. Wetting ability of aqueous herbicidal sprays as a factor influencing stands of alfalfa seedlings. *Agronomy Journal* 48:59-63.
- Elliot, J. G. 1962. Chemical possibilities in grassland. *Proceedings of the British Weed Control Conference* 6:31-36.
- Ennis, W. B., Jr., R. E. Williamson and K. P. Dorschner. 1952. Studies on spray retention by leaves of different plants. *Weeds* 1:274-286.
- Evans, R. A. and R. E. Eckert, Jr. 1965. Paraquat-surfactant combinations for control of downy brome. *Weeds* 13:150-151.
- Freed, V. H. 1958. Use of surfactants with agricultural chemicals. *Agricultural Chemicals* 13:31-32.
- Freed, V. H. and H. M. Montgomery. 1958. The effect of surfactants on foliar absorption on 3-amino-1,2,4-triazole (amitrole). *Weeds* 6:386-389.
- Foy, C. L. 1962. Penetration and initial translocation of 2,2-dichloropropionic acid (dalapon) in individual leaves of Zea mays L. *Weeds* 10:35-39.
- Foy, C. L. and L. W. Smith. 1965. Surface tension lowering, wettability of paraffin and corn leaf surfaces, and herbicidal enhancement of dalapon by seven surfactants. *Weeds* 13:15-18.
- Furmidge, C. G. L. 1959a. Physico-chemical studies on agricultural sprays. I. General principles of incorporating surface-active agents as spray supplements. *Journal of the Science of Food and Agriculture* 10:267-273.
- Furmidge, C. G. L. 1959b. Physico-chemical studies on agricultural sprays. III. Variation of phytotoxicity with the chemical

- structure of surface-active agents. *Journal of the Science of Food and Agriculture* 10:419-425.
- Furmidge, C. G. L. 1962. Physico-chemical studies on agricultural sprays. IV. The retention of spray liquids on leaf surfaces. *Journal of the Science of Food and Agriculture* 13:127-140.
- Gillette, C. P. 1890. Experiments with arsenites. Ames. p. 401-420. (Iowa. Agricultural Experiment Station. Bulletin 10)
- Hill, G. D., I. J. Belasco and H. L. Ploeg. 1965. Influence of surfactants on the activity of diuron, linuron, and bromacil as foliar spray on weeds. *Weeds* 13:103-104.
- Hughes, R. E. and V. H. Freed. 1961. The role of surfactants in the foliar absorption of indole-3-acetic acid (IAA). *Weeds* 9:54-60.
- Jansen, L. L. 1964. Surfactant enhancement of herbicide entry. *Weeds* 12:251-254.
- Jansen, L. L. 1965. Effects of structural variations in ionic surfactants on phytotoxicity and physical-chemical properties of aqueous sprays of several herbicides. *Weeds* 13:117-122.
- Jansen, L. L., W. A. Gentner and W. C. Shaw. 1961. Effects of surfactants on the herbicidal activity of several herbicides in aqueous spray systems. *Weeds* 9:381-405.
- Klingman, G. C. 1961. *Weed control as a science*. New York, Wiley. 421p.
- LeClerg, E. L., W. H. Leonard and A. G. Clark. 1962. *Field plot technique*. 2d ed. Minneapolis, Burgess. 373p.
- McWhorter, C. G. 1963. Effects of surfactants on the herbicidal activity of foliar sprays of diuron. *Weeds* 11:265-270.
- McWhorter, C. G. and E. E. Schweizer. 1964. The use of surfactants to increase herbicidal activity. *Proceedings of the Northeastern Weed Control Conference* 18:6-13.
- Parr, J. F. and A. G. Norman. 1964. Effects of nonionic surfactants on root growth and cation uptake. *Plant Physiology* 39:502-507.

- Schweizer, E. E. and C. G. McWhorter. 1965. Surfactants: how they work. *Weeds, Trees, and Turf* 4:8-11.
- Smith, L. W. and C. L. Foy. 1967. Interactions of several paraquat-surfactant mixtures. *Weeds* 15:67-72.
- Smith, L. W., C. L. Foy and D. E. Bayer. 1966. Structure-activity relationships of alkyphenol ethylene oxide ether non-ionic surfactants and three water-soluble herbicides. *Weed Research* 6:233-242.
- Staniforth, D. W. and W. E. Loomis. 1949. Surface action in 2,4-D sprays. *Science* 109:628-629.
- Temple, R. E. and W. Hilton. 1963. The effect of surfactants on the water solubility of herbicides, and the foliar phytotoxicity of surfactants. *Weeds* 11:297-300.
- Van Overbeek, J. and R. Blondeau. 1954. Mode of action of phytotoxic oils. *Weeds* 3:55-65.

Appendix Table 1. The effect of X-77: paraquat ratios in 25 gallons of water per acre to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.

Surfactant concentration		Fresh weights per pot in grams					Toxicity index
Ratio	Percent	I	II	III	IV	Avg.	
0:1		2.30	1.40	1.90	1.20	1.70	
1:1	.03	1.20	1.70	2.30	1.20	1.60	5.9
2:1	.06	1.30	1.60	1.85	1.40	1.54	9.4
4:1	.12	1.60	1.55	1.20	1.40	1.44	15.3
8:1	.24	1.70	2.00	1.20	1.10	1.50	11.8
16:1	.48	1.70	1.00	1.40	1.25	1.34	21.2
32:1	.96	.80	.80	.90	1.10	.90	47.1
64:1	1.92	1.10	.70	.90	.80	.87	48.8
16:0	.48	1.50	1.75	1.74	1.50	1.62	4.7
32:0	.96	1.10	1.45	1.45	1.20	1.30	23.5
64:0	1.92	1.55	1.25	1.25	1.35	1.35	20.6

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	3	.997	13.29**
Within treatments	40	.075	

**Significant at 1% level

$$\bar{x} = 1.38$$

$$s = .27$$

$$CV = 19.6\%$$

$$LSD (0.05) = .38$$

$$LSD (0.01) = .51$$

Appendix Table 2. The effect of X-77: paraquat ratios in 50 gallons of water per acre to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.

Surfactant concentration		Fresh weights per pot in grams					Toxicity index
Ratio	Percent	I	II	III	IV	Avg.	
0:1		1.50	1.50	1.35	1.60	1.49	
1:1	.015	1.40	1.50	1.40	1.40	1.42	5.4
2:1	.03	1.20	1.30	1.55	1.40	1.36	9.3
4:1	.06	1.50	1.25	1.60	1.30	1.41	6.0
8:1	.12	1.05	.90	1.20	1.10	1.06	29.3
16:1	.24	1.20	1.25	1.40	1.20	1.26	16.0
32:1	.48	1.25	1.05	1.15	.90	1.09	27.4
64:1	.96	.75	.95	.90	.90	.87	42.0
16:0	.24	1.35	1.30	1.25	1.10	1.25	16.7
32:0	.48	1.60	1.30	1.40	2.20	1.62	-8.0
64:0	.96	1.55	1.40	1.30	1.25	1.37	8.7

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	3	.620	26.95**
Within treatments	40	.023	

**Significant at 1% level

$$\bar{x} = 1.29$$

$$s = .15$$

$$CV = 11.6\%$$

$$LSD (0.05) = .22$$

$$LSD (0.01) = .30$$

Appendix Table 3. The effect of X-77: paraquat ratios in 75 gallons of water per acre to seedling oats ten days after application. Paraquat applied at 1/64 lb/acre.

Surfactant concentration		Fresh weights per pot in grams					Toxicity index
Ratio	Percent	I	II	III	IV	Avg.	
0:1		1.20	1.35	1.10	1.20	1.21	
1:1	.01	1.10	1.40	1.25	1.10	1.21	0
2:1	.02	1.20	1.35	1.10	1.10	1.19	.8
4:1	.04	1.40	1.25	1.30	1.45	1.35	-12.5
8:1	.08	1.40	1.50	1.25	1.55	1.42	-18.3
16:1	.16	1.25	1.25	1.30	1.05	1.21	0
32:1	.32	1.00	1.00	.90	1.20	1.02	15.0
64:1	.64	.85	.85	.75	.80	.81	32.5
16:0	.16	1.10	1.20	1.50	1.30	1.27	- 4.9
32:0	.32	1.50	1.40	1.40	1.20	1.37	-13.2
64:0	.64	1.35	1.20	1.30	1.05	1.22	- .8

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	3	.390	32.5**
Within treatments	40	.012	

**Significant at 1% level

$$\bar{x} = 1.21$$

$$s = .11$$

$$CV = 9.09\%$$

$$LSD (0.05) = .16$$

$$LSD (0.01) = .21$$

Appendix Table 4. The effect of X-77:dalapon ratios in 25 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 9 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		1.96	2.54	2.48	2.50	2.64	2.42	
1:64	.08	1.72	.88	.96	1.72	.42	1.14	52.9
1:32	.16	1.11	.30	1.15	1.43	1.40	1.08	55.4
1:16	.32	.37	.62	1.07	1.32	.72	.82	66.1
1:8	.64	.28	.62	.42	.52	.66	.50	79.3
1:4	1.27	.31	.78	.59	.22	.45	.47	80.6
1:2	2.54	.76	.71	.50	.60	.52	.62	74.4
1:1	5.08	.55	.74	.67	.42	.50	.58	76.0
2:1	10.16	.40	.58	.48	.54	.58	.52	78.6

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	3.870	45.52**
Within treatments	40	.085	

**Significant at 1% level

$$\bar{x} = .90$$

$$s = .29$$

$$CV = 32.2\%$$

$$LSD(0.05) = .36$$

$$LSD(0.01) = .49$$

Appendix Table 5. The effect of X-77:dalapon ratios in 50 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 9 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		2.80	2.42	2.40	2.30	2.40	2.46	
1:64	.04	1.48	.98	.32	.65	1.60	1.01	57.9
1:32	.08	1.44	.67	.88	1.37	.39	.95	60.4
1:16	.16	.96	.53	.37	.81	.59	.65	72.9
1:8	.32	.30	.89	.40	.68	.60	.57	76.3
1:4	.64	.87	.62	.23	.68	.60	.57	76.3
1:2	1.27	.33	.37	.47	.43	.58	.44	81.7
1:1	2.54	.43	.60	.29	.30	.49	.42	82.5
2:1	5.08	.37	.32	.35	.40	.58	.40	83.3

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	4.230	57.16**
Within treatments	40	.074	

**Significant at 1% level

$$\bar{x} = .83$$

$$s = .27$$

$$CV = 32.53\%$$

$$LSD (0.05) = .35$$

$$LSD (0.01) = .47$$

Appendix Table 6. The effect of X-77:dalapon ratios in 75 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 9 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		1.80	2.40	2.32	2.26	2.40	2.24	
1:64	.025	1.63	.72	1.10	1.58	1.49	1.30	42.0
1:32	.05	1.10	.89	1.08	1.69	.98	1.15	48.7
1:16	.11	.78	1.12	1.03	.63	.96	.90	59.8
1:8	.21	.30	.63	.98	.90	.43	.65	71.0
1:4	.42	.40	.76	.53	.62	.66	.59	73.7
1:2	.85	.43	.43	.57	.28	.19	.38	83.0
1:1	1.69	.20	.22	.37	.28	.42	.30	86.6
2:1	3.39	.33	.41	.21	.12	.34	.28	87.5

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	3.747	74.94**
Within treatments	40	.050	

**Significant at 1% level

$$\bar{x} = .87$$

$$s = .22$$

$$CV = 25.3\%$$

$$LSD (0.05) = .28$$

$$LSD (0.01) = .38$$

Appendix Table 7. Visual injury ratings of X-77: dalapon on oat seedlings. Dalapon applied at 9 lb/acre.

Diluent/acre	Ratio	Days following spray application		
		3	6	9
25 gallons	1:64	2	5	6
	1:32	2	5	6
	1:16	4	6	8
	1:8	6	7	9
	1:4	7	7	9
	1:2	7	8	9
	1:1	7	8	9
	2:1	7	9	9
50 gallons	1:64	2	3	5
	1:32	3	6	8
	1:16	5	7	10
	1:8	6	7	9
	1:4	7	8	9
	1:2	8	10	10
	1:1	9	10	10
	2:1	9	10	10
75 gallons	1:64	2	2	5
	1:32	3	5	7
	1:16	4	6	9
	1:8	6	7	9
	1:4	7	8	9
	1:2	8	10	10
	1:1	9	10	10
	2:1	9	10	10

Appendix Table 8. The effect of X-77:dalapon ratios in 25 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 6 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		1.10	1.02	1.12	1.02	.98	1.05	
1:32	.11	.54	.56	.52	.54	.74	.58	44.7
1:16	.21	.52	.38	.50	.40	.52	.46	56.2
1:8	.42	.32	.52	.50	.36	.44	.43	59.1
1:4	.84	.30	.46	.32	.40	.38	.37	64.8
1:2	1.68	.50	.22	.14	.30	.50	.33	68.6
1:1	3.39	.50	.32	.10	.14	.32	.28	73.3
2:1	6.78	.28	.28	.06	.28	.34	.25	76.2
4:1	13.56	.10	.26	.18	.04	.18	.15	85.7

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	.690	69.0**
Within treatments	40	.010	

**Significant at 1% level

$$\bar{x} = .43$$

$$s = .10$$

$$CV = 23.3\%$$

$$LSD (0.05) = .13$$

$$LSD (0.01) = .17$$

Appendix Table 9. The effect of X-77:dalapon ratios in 50 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 6 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		.80	1.04	.96	.82	1.20	.96	
1:32	.05	.62	.52	.52	.40	.70	.55	42.7
1:16	.11	.50	.38	.44	.58	.56	.49	49.0
1:8	.21	.58	.40	.68	.70	.56	.58	39.6
1:4	.42	.54	.60	.40	.34	.52	.48	50.0
1:2	.84	.42	.50	.30	.26	.50	.40	58.3
1:1	1.68	.50	.30	.16	.32	.48	.35	63.5
2:1	3.39	.22	.30	.30	.18	.26	.25	74.0
4:1	6.78	.20	.20	.34	.30	.24	.26	73.0

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	.470	41.78**
Within treatments	40	.011	

**Significant at 1% level

$$\bar{x} = .48$$

$$s = .11$$

$$CV = 21.8\%$$

$$LSD (0.05) = .14$$

$$LSD (0.05) = .18$$

Appendix Table 10. The effect of X-77:dalapon ratios in 75 gallons of water per acre to seedling oats ten days after application. Dalapon applied at 6 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		.88	1.02	1.18	1.32	1.12	1.10	
1:32	.03	.84	.82	1.00	.90	1.18	.95	13.6
1:16	.07	.58	.52	.72	.54	.58	.59	46.6
1:8	.14	.40	.50	.40	.46	.50	.45	59.1
1:4	.28	.34	.32	.20	.48	.44	.36	67.3
1:2	.57	.52	.50	.56	.58	.60	.55	50.0
1:1	1.13	.50	.50	.40	.40	.68	.50	54.5
2:1	2.26	.50	.18	.28	.20	.42	.32	70.9
4:1	4.52	.30	.30	.30	.30	.24	.29	73.6

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	.797	75.9**
Within treatments	40	.011	

**Significant at 1% level

$$\bar{x} = .57$$

$$s = .10$$

$$CV = 17.5\%$$

$$LSD (0.05) = .13$$

$$LSD (0.01) = .17$$

Appendix Table 11. The effect of X-77:terbacil ratios in 25 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		2.53	2.28	2.86	2.72	2.92	2.66	
1:1	.29	.89	.72	1.15	.44	.80	.80	69.9
2:1	.59	.50	.70	.98	1.07	1.12	.87	67.3
4:1	1.18	.69	.62	.42	.82	.61	.63	76.3
8:1	2.36	.45	1.00	.52	.69	.57	.65	75.6
16:1	4.73	.62	.59	.57	.63	.87	.66	75.2
32:1	9.47	.43	.49	.47	.35	.50	.45	83.1
64:1	18.9	.46	.48	.26	.20	.39	.36	86.5

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	4.670	111.19**
Within treatments	35	.042	

**Significant at 1% level

$$\bar{x} = .88$$

$$s = .20$$

$$CV = 22.3\%$$

$$LSD (0.05) = .26$$

$$LSD (0.01) = .35$$

Appendix Table 12. The effect of X-77:terbacil ratios in 50 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		3.08	2.46	2.72	2.68	2.54	2.56	
1:1	.15	.52	.80	.43	.97	.49	.64	76.3
2:1	.29	.57	.46	.69	.72	.43	.57	78.6
4:1	.59	.92	.37	.46	.45	.52	.54	80.0
8:1	1.18	.73	.51	.43	.43	.49	.52	80.7
16:1	2.36	.89	.40	.37	.40	.40	.49	81.8
32:1	4.73	.32	.31	.39	.43	.33	.36	86.7
64:1	9.47	.30	.50	.29	.37	.30	.35	87.0

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	5.390	199.63**
Within treatments	35	.027	

**Significant at 1% level

$$\bar{x} = .77$$

$$s = .16$$

$$CV = 20.8\%$$

$$LSD(0.05) = .20$$

$$LSD(0.01) = .27$$

Appendix Table 13. The effect of X-77:terbacil ratios in 75 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/2 lb/acre.

Surfactant concentration		Fresh weights per pot in grams						Toxicity index
Ratio	Percent	I	II	III	IV	V	Avg.	
0:1		1.95	2.62	2.72	2.70	2.80	2.56	
1:1	.10	1.63	1.22	1.04	.81	1.43	1.23	52.0
2:1	.20	.87	1.14	1.43	1.48	1.22	1.23	52.0
4:1	.40	1.08	.67	.64	1.07	.66	.82	68.0
8:1	.79	.76	.88	.83	.98	.62	.81	68.4
16:1	1.58	.29	.44	.70	.35	.40	.44	82.8
32:1	3.17	.38	.18	.37	.38	.72	.41	84.0
64:1	6.34	.42	.29	.42	.44	.33	.38	85.2

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	4	4.562	95.0**
Within treatments	35	.048	

**Significant at 1% level

$$\bar{x} = .98$$

$$s = .22$$

$$CV = 22.5\%$$

$$LSD (0.05) = .28$$

$$LSD (0.01) = .38$$

Appendix Table 14. Visual injury ratings of X-77: terbacil on oat seedlings. Terbacil applied at 1/2 lb/acre.

Diluent/acre	Ratio	Days following spray application		
		3	6	9
25 gallons	1:1	1	6	7
	2:1	2	7	7
	4:1	4	8	9
	8:1	6	8	9
	16:1	7	9	9
	32:1	9	10	10
	64:1	9	10	10
50 gallons	1:1	1	4	6
	2:1	2	6	8
	4:1	4	8	10
	8:1	6	8	10
	16:1	8	9	10
	32:1	9	10	10
	64:1	9	10	10
75 gallons	1:1	1	2	4
	2:1	1	2	4
	4:1	3	4	6
	8:1	3	4	6
	16:1	7	8	10
	32:1	8	9	10
	64:1	9	10	10

Appendix Table 15. The effect of X-77 and X-77:terbacil ratios in 25 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/4 lb/acre.

Surfactant concentration		Fresh weights per pot in grams					Toxicity index
Ratio	Percent	I	II	III	IV	Avg.	
0:1		1.40	1.00	1.24	1.44	1.27	
1:1	.15	.95	.70	.80	.92	.84	33.9
2:1	.30	.60	.84	.78	.90	.78	38.6
4:1	.60	1.00	.50	.98	.60	.77	39.4
8:1	1.20	.88	.70	.54	.60	.68	46.5
16:1	2.40	.46	.76	.50	.60	.58	54.3
32:1	4.80	.78	.24	.30	.46	.44	66.0
64:1	9.51	.40	.18	.42	.22	.30	76.4
8:0	1.20	.92	.90	.48	.70	.75	40.5
16:0	2.40	.70	1.20	.90	1.06	.96	24.4
32:0	4.80	1.00	.40	.62	.66	.67	47.3
64:0	9.51	.48	.48	.60	.76	.58	54.3

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	3	.900	32.14**
Within treatments	44	.028	

**Significant at 1% level

$$\bar{x} = .72$$

$$s = .17$$

$$CV = 23.6\%$$

$$LSD (0.05) = .24$$

$$LSD (0.01) = .32$$

Appendix Table 16. The effect of X-77 and X-77:terbacil ratios in 50 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/4 lb/acre.

Surfactant concentration		Fresh weights per pot in grams					Toxicity index
Ratio	Percent	I	II	III	IV	Avg.	
0:1		1.38	1.30	.86	1.12	1.16	
1:1	.07	.80	.70	.80	.84	.79	31.9
2:1	.15	.70	.82	.62	.80	.74	36.2
4:1	.30	.74	.64	.58	.52	.62	46.5
8:1	.60	.64	.54	.58	.60	.59	49.1
16:1	1.20	.60	.32	.22	.48	.40	65.5
32:1	2.40	.20	.30	.44	.40	.33	71.5
64:1	4.80	.28	.38	.22	.24	.28	75.8
8:0	.60	.30	.40	.60	.66	.49	57.7
16:0	1.20	.20	.46	.38	.78	.45	61.2
32:0	2.40	.70	1.10	.64	.78	.80	31.1
64:0	4.80	.82	.46	.62	.50	.60	48.3

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	3	.880	46.32**
Within treatments	44	.019	

**Significant at 1% level

$$\bar{x} = .61$$

$$s = .14$$

$$CV = 22.9\%$$

$$LSD (0.05) = .20$$

$$LSD (0.01) = .26$$

Appendix Table 17. The effect of X-77 and X-77:terbacil ratios in 75 gallons of water per acre to seedling oats ten days after application. Terbacil applied at 1/4 lb/acre.

Surfactant concentration		Fresh weights per pot in grams					Toxicity index
Ratio	Percent	I	II	III	IV	Avg.	
0:1		1.20	.80	.80	1.02	.95	
1:1	.05	.60	.56	.48	.62	.57	40.0
2:1	.10	.40	.40	.56	.80	.54	43.2
4:1	.20	.34	.72	.60	.20	.46	51.6
8:1	.40	.38	.28	.18	.26	.27	71.6
16:1	.80	.26	.24	.52	.16	.29	69.5
32:1	1.60	.30	.20	.24	.12	.21	77.9
64:1	3.18	.20	.32	.34	.50	.34	64.2
8:0	.40	.84	1.02	.52	.32	.67	29.5
16:0	.80	.62	1.00	.30	.40	.58	39.0
32:0	1.60	.50	.20	.52	.20	.35	63.2
64:0	3.18	.42	.54	.20	.30	.36	62.1

Analysis of variance

Source of variation	df	Means square	F value
Among treatments	3	.640	35.6**
Within treatments	44	.018	

**Significant at 1% level

$$\bar{x} = .47$$

$$s = .13$$

$$CV = 27.7\%$$

$$LSD (0.05) = .19$$

$$LSD (0.01) = .26$$

Appendix Table 18. Drying time (seconds) of various X-77:terbacil ratios in three volumes of water.

Ratio	Gallons of diluent/acre		
	25	50	75
1:1	50	100	122
2:1	70	117	128
4:1	70	121	193
8:1	90	130	250
16:1	120	153	274
32:1	180	236	271
64:1	240	267	260
8:0	83	170	200
16:0	116	200	290
32:0	180	268	306
64:0	248	242	306