1971

Herbicide Residue and Weed Control in Switchgrass

Charles Nicholas Smith Jr.

HERBICIDE RESIDUE AND WEED CONTROL IN SWITCHGRASS

BY

CHARLES NICHOLAS SMITH, JR.

A thesis submitted
in partial fulfillment of requirements for the
degree Doctor of Philosophy, Major in
Agronomy, South Dakota
State University

1971

HERBICIDE RESIDUE AND WEED CONTROL

IN SWITCHGRASS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Committee

Date

HERBICIDE RESIDUE AND WEED CONTROL
IN SWITCHGRASS
Abstract

CHARLES NICHOLAS SMITH, JR.

Under the direction of Drs. Y. A. Greichus and R. A. Moore

Purposes of this study were to find an effective herbicide for control of grassy weeds in a pasture, to adapt known laboratory procedures for analyzing residues and to determine amounts of residues during the growing season in treated plots.

Nine herbicides were screened for controlling grassy weeds, primarily downy brome (Bromus tectorum L.) in a native pasture. Data indicated 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine) applied postemergence at 1 lb/A was the most effective at 85% control. The following year, atrazine, 2-chloro-4,6-bis-(ethylamino)-s-triazine (simazine) and 2,2-dichloropropionic acid (dalapon) each at 1, 2 and 3 lb/A were applied preemergence to switchgrass pasture. Of primary concern was control of grassy weeds; downy brome, green foxtail (Setaria virdis (L.) Beauv.) and yellow foxtail (Setaria glauca (L.) Beauv.). Atrazine effectiveness remained nearly constant through the summer with 50% grassy weed control. Simazine control was not significantly ($P < .05$) different from that of atrazine. Dalapon effectiveness decreased from

90% to 61% and gave significantly ($P < .05$) higher percent control than either triazine. Atrazine and simazine were significantly ($P < .05$) higher in broadleaf weed control than dalapon. Atrazine and simazine caused no injury to the switchgrass. Dalapon, however, resulted in severe injury or death to the desirable grass. All herbicides increased in effectiveness as the rate of application increased. Herbicidal carry over as recorded in July 1970 was evident.

Laboratory procedures for atrazine and simazine residue analysis included column, thin-layer and hydrogen-flame gas chromatography. Dalapon was analyzed using electron capture gas chromatography. No recordable atrazine and simazine residues (less than 5 ppm) were found in vegetative samples beginning with the June harvest. Dalapon applied in May at 1, 2 and 3 lb/A decreased to less than 3 ppm in late summer harvest.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to:

Dr. R. A. Moore, major advisor, for his encouragement and guidance throughout the course of this study and for reviewing the manuscript.

Dr. Y. A. Greichus, thesis advisor, for her many helpful suggestions in laboratory procedures and help in preparation of this thesis.

The Plant Science and Station Biochemistry Departments for financial support and use of their facilities and equipment.

The professors, technicians, secretaries and fellow graduate students in the Plant Science Department and Pesticide Laboratory for their cooperation and advice and especially to Twila Walkes and Lauren Poppen for their assistance in the laboratory.

Dow Chemical Company and Geigy Chemical Company for furnishing the herbicides used for this study.

Dr. Lee Tucker for his statistical assistance.

The remaining members of the graduate committee, Drs. L. O. Fine, C. D. Dybing, A. W. Halverson and D. J. Holden, for their participation and encouragement throughout the program.

The author's wife, Elaine, for her continual encouragement and understanding and for typing the initial copies of the thesis.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

Table | Page

LIST OF TABLES (continued)

LIST OF FIGURES

INTRODUCTION

In 1964, approximately 922 million acres of pasture and range land existed in the United States (U.S.D.A. Agricultural Statistics, 1969). This is 40.7% of the total land area. Klingman (1965) reported that nearly all of the range and pasture land was infested with weeds. These plants include brush, broadleaves and undesirable grasses. According to the Economic Research Service, U.S.D.A. Agricultural Economics Report No. 179 (1969), farmers in 1966 used 10.5 million pounds of herbicide on range and pasture land for weed control. This represents only 9% of all herbicides used by farmers in 1966. Over 90% of the chemical was 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). The Herbicide Handbook (1967) indicated that 2,4-D and 2,4,5-T were used for control of brush and broadleaved weeds and would have little or no effect on grasses. Low-value range lands were seldom treated extensively with chemicals because it was not economically feasible (Muzik, 1970).

The majority of the range and pasture land is composed of cool season grasses that produce during the spring and/or fall but not during the hot summer months of July and August (Dyksterhuis, 1965). A mid-summer supplemental pasture is needed (Derscheid, Moore, and Lewis 1970), which can be composed of either introduced annual species, i.e., sudangrass (Sorghum sudanense (Piper) Stapf), hybrid sudans and sorghum-sudan hybrids, or of native perennials, i.e., big bluestem (Andropogon gerardi Vitman), switchgrass (Panicum vigatum L.), and indiangrass (Sorghastrum nutans L.). Experimental investigation has been concentrated on the introduced annual species, but very little on perennial warm season grasses. Therefore, researchers at the Pasture Research Center near Norbeck, South Dakota, have been investigating the use of native warm season grasses (Moore, 1967).

Switchgrass is a tall, perennial, sodforming grass which occurs naturally in most of the U.S. east of the Rocky Mountains (Hughes, Heath and Metcalfe, 1962). Excellent yields of seed, vigorous seedling growth and high forage yields have made it one of the easiest native grasses to bring under cultivation. While best adapted to fertile, moist soil, it will produce more forage and cover on droughty, infertile, eroded soils than most introduced grasses.

Grassy weeds such as green foxtail (Setaria viridis (L.) Beauv.), yellow foxtail (Setaria glauca (L.) Beauv.) and downy brome (Bromus tectorum L.) are serious weed problems in the warm season grass pasture (Parker, 1967). Cool season grasses can compete quite favorably with the grassy weeds (Klingman, 1965). Green and yellow foxtail are two very common annual grass weeds found growing in cultivated land, lawns and waste places (S. D. Weeds, 1967).

At present, no herbicide is cleared by the Federal Food and Drug Administration for controlling grassy weeds in a warm season pasture to be harvested for forage the same year. Before clearing a herbicide, sufficient residue analysis must be presented to the Federal Food and Drug Administration.

Purposes of this study were to determine an effective herbicide for controlling grassy weeds in a switchgrass sward, to adapt known laboratory procedures for analyzing residues and to determine amounts of residues during the growing season in treated plants.

REVIEW OF LITERATURE

Few methods exist for selective control of weed grasses growing in desirable grasses (Kerr, 1969). The methods available are based upon: 1) annual versus perennial growth habit as the basis for selective grass control in turf, 2) depth of planting or depth of rooting, making it possible to apply relatively insoluble herbicides on the soil surface for selective grass control and 3) physiological selectivity such as that obtained with 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine) or 2-chloro-4,6-bis(ethylamino)-s-triazine (simazine) in corn (*Zea mays* L.).

W. O. Lee (1965) obtained 70-09% control of downy brome and rattail fescue (*Festuca myuros* L.) with 2-methoxy-3,6-dichlorobenzoic acid (dicamba) and with 2,4-bis(isopropylamino)-6-methylmercapto-s-triazine (prometryne) in an irrigated perennial grass field. Chandler and Santelmann (1969) received adequate control of Texas panicum (*Panicum texanum* Buckl.) from α,α,α-trifluro-2,6-dinitro-N,N-dipropyl-p-toluidine (trifluralin) at 3/4 and 1-1/2 lb/A, 3-(m-trifluoromethylphenyl)-1,1-dimethylurea (fluometuron) at 3 lb/A, prometryne at 5 lb/A and 3-amino-2,5-dichlorobenzoic acid (amiben) at 2 and 4 lb/A. McMurphy (1969) evaluated two herbicides for use in seeding range grasses. His results showed that 2-chloro-4, 6-bis(isopropylamino)-s-triazine (propazine) at 3 lb/A controlled broadleaf weeds and large crabgrass (Digitaria sanguinalis (L.) Scop.) and 1-(2-methylcyclohexyl)-3-phenylurea (siduron) at 1-1/2 lb/A controlled large crabgrass. Allen (1969) reported that 2,2-dichloropropionic acid (dalapon) applied between 2 to 5 lb/A in early July suppressed Agrostis stolonifera L. and velvetgrass (Holcus lanatus L.) growing in perennial ryegrass (Lolium perenne L.). Kay (1963) found that dalapon at 2 and 3 lb/A gave excellent medusahead (Taeniatherum asperum (Sim.) Nevski) control while only slightly injuring soft chess (Bromus mollis L.).

Many undesirable grasses, especially annual grasses, can be controlled by a well-timed application of dalapon (Klingman, 1965). Allen (1968) found dalapon applied on July 4 controlled Agrostis stolonifera, Poa trivialis and Holcus lanatus better than when applied on July 16 or 28. Dalapon caused lasting visible injury to desirable grasses on a pasture when applied in April but none when applied in May of July (McGowan, 1970). Warren (1967) found in California that January applications of dalapon were superior to December. He stated that timing was important because grasses that were young and growing well were more easily killed. Hyder and Everson (1968) demonstrated that dalapon varied from year to year in effectiveness and best time application. Dalapon at 3 lb/A caused little decrease in stand of downy brome when applied in the fall of 1958 or spring of 1959, but was effective in the fall of 1959 and spring of 1960 (Robocker, Gates and Kerr, 1965). Some probable reasons for the inconsistant effectiveness of dalapon include 1) the inhibition of the decomposition rate by low soil moisture, low pH, large amounts of organic matter, and temperatures below 20-25 C and 2) by the variability of the microbiological population (Holstum and Loomis, 1956). Other herbicides have been found to be affected by time of application. Jagschitz (1969) found that spring treatments of 4-(methyl-sulfonyl)-2,6-dinitro-N,N-dipropylaniline (nitralin), siduron and 2,6-ditert-butyl-p-tolyl methylcarbamate (terbutol) gave effective crabgrass control with minimum turfgrass injury while fall treatments produced poor control and/or turf injury.

Propazine applied as a preemergent at 3 lb/A controlled weeds and crabgrass without harming switchgrass (McMurphy, 1969). Simazine applied preemergence to weeds at 2 to 4 lb/A effectively controlled annual weed growth in sprigged bermuda grass (Cynodon dactylon (L.) Pers.) but was found to injure many other seedling pasture grasses (Klingman, 1965).

Atrazine did not harm bermuda grass (Albert, 1965). Tall fescue was found to have more tolerance to simazine and atrazine than orchardgrass (Dactylis glomerata L.), timothy (Phleum pratense L.)

or smooth brome grass (*Bromus inermis* Leyss.) (Fink and Fletchall, 1963). The most successful herbicides for downy brome control in grassland were 3-amino-1,2,4-triazole (amitrole), atrazine, simazine and propazine (Wicks, Fenster and Burnside, 1965) with atrazine being the most consistant. They found intermediate wheatgrass (*Agropyron intermedium* (Host) Beauv.), crested wheatgrass (*Agropyron cristalum* (L.) Beauv.), western wheatgrass (*Agropyron smithii* Rydb.), blue grama (*Bouteloua graciles* (H.B.K.) Lag.) and sedge (*Carex* sp. L.) appeared to be more sensitive to most s-triazines than needle-and thread (*Stipa comata* Trin. and Rupr.) and sand dropseed (*Sporobolus cryptandrus* (Torr.) Gray).

Atrazine at 1 lb/A significantly reduced downy brome at four of five sites (Young, Evans and Eckert, 1969). Investigation by Evans *et al.* (1969) for downy brome control with soil-active herbicides found atrazine at 1 lb/A to be the most effective treatment for three essential characteristics: length of activity, spectrum of weed control, and relative phytotoxicity of both preemergence and postemergence applications. They stated that simazine was not as effective at a 1 lb/A rate with 73% control as atrazine at the same rate with 91% control. Thompson and Slife (1969) concluded that atrazine should be in the soil for root absorption for full kill of giant foxtail (*Setaria faberii* Herrm.). Except under unfavorable seasonal conditions atrazine gave good control of little barley (*Hordeum pusillum* Nutt.) but was ineffective against other established weed species (Albert, 1965).

Atrazine from 1 to 2 lb/A controlled medusahead on the drier upper slope portion of plots while more moist areas required 2 lb/A (Young *et al.*, 1969). Canode, Robocker and Muzik (1962) concluded that both dalapon and simazine were effective in controlling downy brome in intermediate wheatgrass but that simazine was less injurious to wheatgrass and had a longer period of downy brome control. Young *et al.* (1969) found that plots treated with 6 lb/A dalapon in 1964 produced more intermediate wheatgrass and less medusahead in 1966 than the other treatments which included atrazine.

Research has led to the use of the gas chromatograph for dalapon residue analysis (Getzendaner, 1963, and Dow Chemical Company, 1964). Linscott, Hagin and Wright (1970) described their procedures used in determining dalapon residues in alfalfa (*Medicago sativa* L.) using a gas chromatograph. Frank and Demint (1960) described a gas chromatographic analysis of dalapon in water.

Geigy Chemical Corporation issued "Analytical Bulletin No. 7" (1964) concerning the determination of chloro-s-triazines residues in plant material, animal tissue and water using the ultraviolet method. Colorimetric methods for the determination of simazine and related chloro-s-triazines were discussed by Ragab and McCollum (1968). Several investigators have developed gas chromatographic methods for identifying and measuring amounts of various s-triazines in plant, water and/or soil samples (Chilwell and Hughes, 1962, Henkel and Ebing, 1964, Delley et al., 1967, Mattson et al., 1965, and Bengield and Chilwell, 1964). Delley et al. (1967) and Abbott et al. (1965) discussed the use of thin layer chromatography for identification of s-triazines.

MATERIALS AND METHODS

SCREENING EXPERIMENT

In the spring of 1968, a screening study was initiated at the South Dakota Pasture Research Center. The purpose of the experiment was to determine the effect of various herbicides upon grassy weeds, primarily downy brome, in a native pasture. This experiment was designed as a randomized complete block with three replications for a total of 57 plots each measuring 10 x 20 feet (ft). Each replication included a nontreated control plot and 18 treated plots. Treatments included nine herbicides; monosodium acid methanearsonate (MSMA) 3 lb/A, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) 1 lb/A, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (linuron) 1 lb/A, atrazine 1 lb/A, siduron 4 lb/A, B-1455 (U.S. Borax and Chemical Corporation, experimental herbicide) 2 lb/A, dalapon 1 lb/A, CP-44939 (Monsanto Company, experimental herbicide) 4 lb/A and 4-chloro-2-butynyl-m-chlorocarbanilate (barban) 1/3 lb/A, each with and without 1 gallon per acre (gpa) of crop oil (Sun Superior Spay Oil 11E) added to the spray. On April 30, when downy brome was 1 to 2 inches high, herbicides were applied by a tractor-mounted sprayer delivering 20 gpa at the pressure of 42 pounds per square inch (psi). Visual observations were made May 27 to determine the amount of grassy weed control and herbicidal injury to desirable native grasses using the control as a basis for comparison.

Data from the screening study indicated atrazine as a desirable chemical for grassy weed control. Simazine, a compound similar in properties to atrazine, was also selected for study because of its lengthy herbicidal effectiveness. Dalapon was chosen as a third chemical to further study grassy weed control because it has been proven effective on range and pasture land under certain conditions. Although the screening study showed dalapon to be injurious to cool season grasses as well as grassy weeds, it was believed not to be injurious to the later warm season grasses due to its short residual effectiveness.

FIELD EXPERIMENT

In the spring of 1969, a field experiment was started at the South Dakota Pasture Research Center. On May 2, preemergence treatments at 2 locations were made using atrazine, simazine and dalapon (dalapon I) each at 1, 2 and 3 lb/A without oil were applied to "Summer" switchgrass for control of grassy weeds, mainly green and yellow foxtail and downy brome. Crop oils are added to postemergence spray treatments for increased foliar coverage but are seldom used with preemergence applications. On May 18 a second treatment of dalapon (dalapon II) was applied at both locations to previously untreated plots at the 1, 2 and 3 lb/A rate to determine if the time of application would effect weed control, injury to switchgrass or herbicide residue in forage. Each replication consisted of 12 treated plots plus a nontreated control plot. The experiment was designed as a randomized complete block with four replications at two locations. Location I was a three year old switchgrass stand and location II was on a five year old switchgrass area. Visual observations comparing treated plots to control plots based primarily on stand density were made and recorded for grassy weed and broadleaf weed control and injury to switchgrass on June 12, July 7, August 4, 1969, and July 16, 1970. The rating system used for percent weed control was from 0 to 100% with 0 being no control and 100% being complete weed control as compared to check. Switchgrass injury was rated from 0% for no visual injury to 100% for complete elimination of the switchgrass plants. Samples of vegetation from the plots were harvested as follows:

May 2, 1969 - all plots sprayed plus controls

May 18, 1969 - newly sprayed dalapon plots plus controls

June 12, 1969 - all dalapon plots plus control

June 19, 1969 - all plots

August 4, 1969 - all plots

August 20, 1969 - all plots

July 16, 1970 - atrazine and simazine plots plus controls

The May 2 and 18 samples were stored at room temperature for several weeks, whereas all other samples were immediately frozen until analysis for herbicide residue in the Station Biochemistry Department at South Dakota State University.

RESIDUE ANALYSIS

Atrazine and Simazine

Methods for extracting herbicidal residues of atrazine and simazine were modified from procedures published by Mattson et al. (1965) and Geigy Agricultural Chemicals (1964). Thin-layer and gas chromatography procedures were adapted from Delley et al. (1967) and Abbott et al. (1965).

Extraction procedure

Frozen samples were weighed and placed in a forced air oven at 60 C for 24 hours. Upon removal, they were reweighed to determine dry weight, then ground with a Toledo chopper. An erlenmeyer flask containing 15 grams (g) of the ground dried sample and 125 ml chloroform ($CHCl_3$) was placed on a Burrel mechanical shaker at low speed for 30 minutes. The solution was decanted over a Buchner funnel with Whatman No. 2 filter paper, filtered through two inches of anhydrous sodium sulfate to remove any water and brought down to dryness by use of a flash evaporator.

Cleanup procedure

A dry packed column was prepared by adding 25 g of "Woelm" aluminum oxide (Alupharm Chemical Co.) activity 5 (15% H_2O) to a 15 mm o.d. x 40 cm glass column. Glass wool plus a disc of Whatman No. 2 filter paper was used to hold the packing in place. The aluminum oxide activity 5 was prepared by adding 15 ml glass distilled water to each 85 g of aluminum oxide which had been dried in a forced air oven at 160 C for 24 hours. It was thoroughly mixed in a tightly closed glass jar by rolling for 1/2 hour then allowed to stand for 24 hours before using.

The sample residue was dissolved in 10 ml of carbon tetrachloride (CCl_4), and applied to the column allowing it to penetrate into the aluminum oxide. The flask was rinsed with 5 ml CCl_4 which was transferred to the column and allowed to penetrate as before. When all solvent had penetrated into the column, 80 ml of CCl_4 was added and allowed to pass through the column. After the 80 ml of solvent had penetrated the column, all previous elutant was discarded. A clean 250 ml flask was placed as a receiver. A mixture of 100 ml of 5% ethyl ether in CCl_4 was added to the column. The collected sample was evaporated down to 1/2 ml for thin-layer chromatography.

Thin-layer plates covered with silica gel G (Alupharm Chemical Co.)

0.5 mm thick were made by adding 80 ml of H_2O to 60 g silica gel, stirring, then adding an additional 30 ml H_2O and shaking. The slurry was placed on the plates using a Desaga-Brinkman Model "S II" adjustable applicator. The plates were activated by placing in preheated oven at 110-120 C for 30 minutes occasionally opening the door during the first 15 minutes to remove moisture. The activated plates were placed in a dessicator until used.

The sample in 1/2 ml of $CHCl_3$ was applied to the thin layer plate making a line of dots across the plate. The dots were allowed to dry then another row of dots was made placing these between the previous dots. This process was continued until the sample was completely applied and the row of dots looked like one solid line (Figure 1).

The solvent system consisted of nine parts $CHCl_3$ to one part acetone. Heavy filter paper was placed in the chromatographic jar with the solvents to obtain uniform saturation of the atmosphere. The plates were developed for 40 minutes.

The silica gel between the yellow pigment and the line of application (Figure 1) was removed and the residue eluted from the silica gel with a mixture of 50 ml of 5% ethyl ether in CCl_4. The elutant was evaporated to dryness, picked up to 10 ml hexane and analyzed by hydrogen flame gas chromatography.

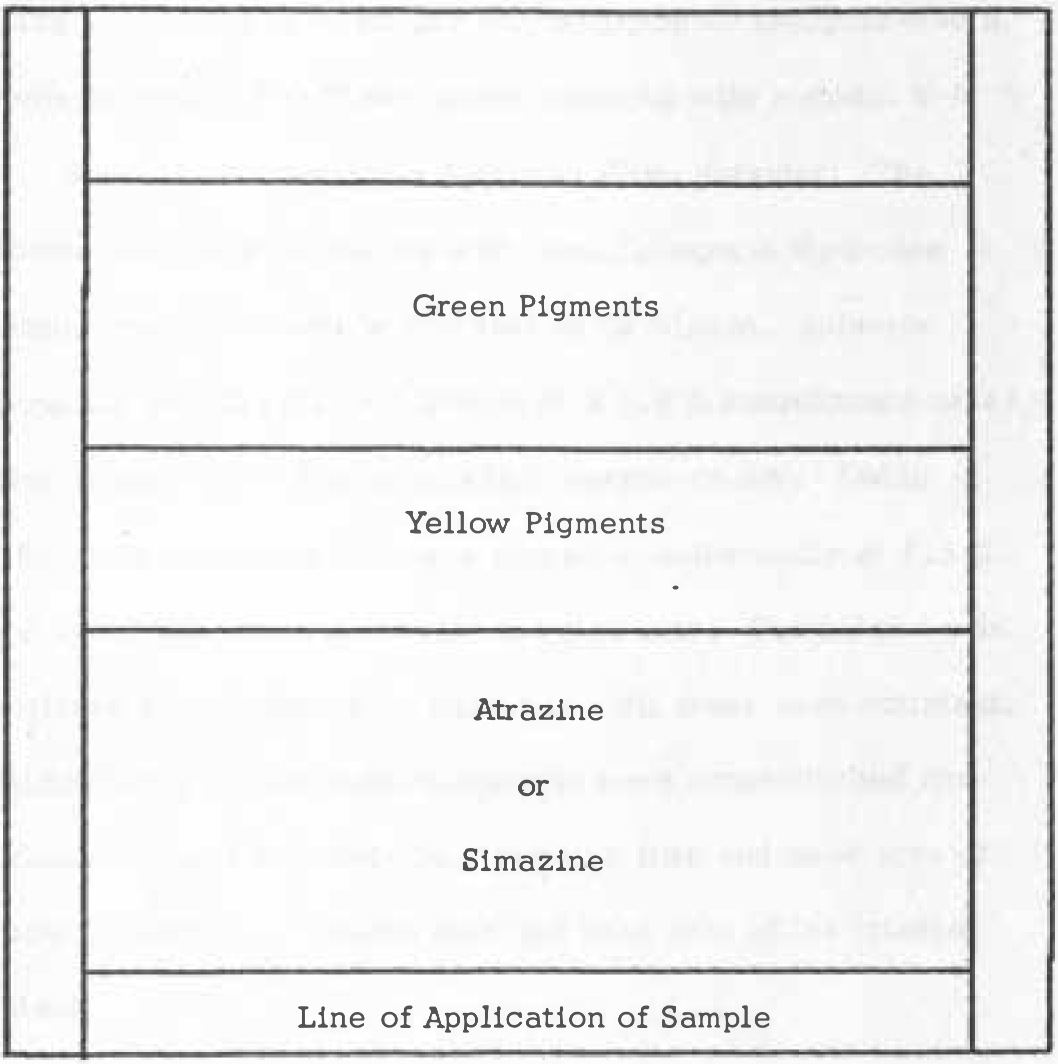

Figure 1. Diagram of the sections of separation for triazine herbicides on thin-layer chromatography plate.

Gas chromatography procedure

The instrument used for gas chromatographic analysis was a Wilkens Aerograph HY-FI model 600 equipped with a model S-R 1-mv. Sargent recorder and a hydrogen flame detector. The hydrogen gas was produced by a Wilkens Aerograph Hydrogen Generator model 650 with a flow rate of 20 ml/min. Injector temperature was 225 C. A 1/8 in o.d. x 2.5 ft borosilicate glass column packed with 8% reoplex 400 polyester on AW. DMAS 80/100 mesh chromosorb W. was operated isothermally at 215 C with a 40 ml/min nitrogen carrier gas flow rate. The column was conditioned by injecting both triazines until areas were constant. Identification and quantitative analysis were accomplished from the chromatograms by comparing retention time and peak area of the sample with the retention time and peak area of the triazine standard.

Dalapon

Methods for extraction and cleanup and gas chromatography procedures published by Getzendaner (1963) and Dow Chemical Company (1964).

Extraction and cleanup procedures

From each sample of frozen switchgrass, duplicate subsamples were taken. One subsample was placed in a forced air oven at 60 C for 24 hr to determine dry weight. The second subsample was cut to approximately 1 cm pieces with a scissors and placed into a blending container. To this was added 47 ml distilled H_2O, 1 ml 85% ortho phosphoric acid (H_3PO_4) and 2 ml 25% phosphotungstic acid and the mixture blended slowly for 10 min on a Sorvall blender. Three grams of celite filter aid were added and the flask shaken by hand. The sample was filtered through Whatman No. 2 filter paper and 5 ml aliquot collected in a test tube. An excess of NaCl was added and the sample shaken until saturated. After addition of 2 ml ethyl ether, the sample was shaken vigorously for 1 min and phases were allowed to separate with dalapon dissolved in the ethyl ether.

Gas chromatography procedure

A Wilkens Aerograph Hy-FI model 600 gas chromatograph with a concentric tube electron capture tritium foil detector using a glass column 1/8 in o.d. x 2.5 ft packed with 3.8% H_3PO_4 on AW. 80/100 mesh chromosorb W. The oven and injector port were 120 C and 175 C, respectively. Nitrogen carrier gas flow rate was 35 ml/min. A standard curve was plotted from peak areas obtained from injecting known amounts of dalapon ranging from .5 to 10 nanograms (ng). If the unknown contained over 10 ng, it was diluted with ethyl ether or smaller amounts were injected into the gas chromatograph so the sample peak area would be within the standard curve.

CALCULATIONS FOR ATRAZINE, SIMAZINE AND DALAPON

Atrazine and Simazine

Parts per million were calculated using the following formula:

$$ppm = \frac{V\ w\ d_2}{W\ v\ d_1\ e}$$

where:

V = volume of extract in milliliters

w = weight of standard injected in nanograms

d_2 = recorder response for sample

W = weight of sample in grams

v = volume of extract injected in microliters

d_1 = recorder response for standard

e = procedure efficiency correction (based on recovery of known quantities of herbicides; see laboratory efficiencies under Results and Discussion).

All atrazine and simazine vegetation had been dried to 60 C for 24 hours before residue analysis. Results were given in ppm on dry weight basis to allow a common basis for comparison.

Dalapon

Parts per million were calculated using the following formula:

$$ppm = \frac{T\ Q\ E\ N}{W\ v\ e}$$

where: T = total volume of aqueaous solvents in milliliters

Q = aliquot of water extracted with ethyl ether in milliliters

E = volume of ethyl ether used to extract dalapon in milliliters

N = weight of dalapon as determined from the standard curve in nanograms

W = dry weight of sample in grams

v = volume of extract injected in microliters

e = procedure efficiency correction (based on recovery of known quantities of herbicide; see laboratory efficiencies under Results and Discussion).

All solvents used in the residue analyses were either Nanograde (Mallinckrodt Chemical Works) or distilled in glass (Burdick and Jackson Laboratories, Inc.).

RESULTS AND DISCUSSION

SCREENING EXPERIMENT

Analysis of variance for percent downy brome control from the screening experiment initiated in the spring of 1968 indicated a significant ($P < .01$) difference in treatments (Table 1). The treatments on siduron, B-1455 and barban gave no visable control of downy brome. All other herbicides showed some control and were significantly different ($P < .01$) (Table 2). Resulting in over 50% control of downy brome with and without the addition of crop oil, were diuron, linuron and atrazine (Table 2). Addition of 1 gpa crop oil resulted in a significant ($P < .01$) increase in percent downy brome control (Table 1 and Table 2). Considering 50% to be the point between effective and noneffective weed control, dalapon and CP-44939 were also effective with the addition of oil, but noneffective without oil (Table 2). Only the dalapon treatments caused injury to the desirable species in the pasture. Injury was limited to stunting of desirable grasses with no lethal effects except to downy brome.

FIELD EXPERIMENT

The field experiment started in the spring of 1969 was conducted on two different switchgrass pastures (location I and location II).

Table I. Analysis of variance for percent downy brome control as influenced by herbicides and addition of oil.

Source variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replication (R)	2	12.03	6.02	
Treatment (T)	8	564.59	70.57	36.38**
RT	16	30.97	1.94	
Oil (O)	1	18.96	18.96	14.56**
RO	2	1.60	0.80	
OT	8	25.71	3.21	2.47
ROT	16	20.73	1.30	
Total	53	674.59	---	

[a] - values followed by "*" are significant at the $P < 0.05$ level and values followed by "**" are significant at the $P < 0.01$ level.

Table 2. Percent downy brome control in a native pasture. Values are averages of three replications.

Herbicide	Rate/A	Percent downy brome control		
		without oil	with oil 1 gal/A	Average[a]
MSMA	3	5	10	7.5 f
Diuron	1	58	68	63.0 c
Linuron	1	65	78	71.5 b
Atrazine	1	90	92	91.0 a
Siduron	1	0	0	0.0 g
Dalapon	1	20*	59*	39.5 e
CP-44939	4	33	60	46.5 d
B-1455	2	0	0	0.0 g
Barban	1/3	0	0	0.0 g
Average		30.1	40.8	

* - indicates treatment was injurious to grass stand

[a] - values followed by the same letters are not significantly different at $P < 0.01$ by Duncan's new multiple range test

Atrazine, simazine and dalapon were selected for further study. Data from the screening study indicated atrazine as a desirable chemical for grassy weed control. Simazine, a compound similar in properties to atrazine, was selected because of its lengthy herbicidal effectiveness. Dalapon was chosen as a third chemical to further study grassy weed control because it has been proven effective on range and pasture land under certain conditions. Visual observations were made three times during the summer comparing treated plots to untreated control plots at both locations. Observations were also recorded at location I the following July (1970). Data for location I included percent of grassy weed control, broadleaf weed control and amount of switchgrass injury compared to the untreated control plots for all dates. Data for location II included percent of switchgrass injury for all three dates during the 1969 summer, while percent of grassy weed control was recorded only on the first two observation dates.

Grassy Weed Control

Grassy weed control was significantly ($P < .01$) influenced by treatments and dates at location I (Table 3). The atrazine and simazine treatments were not significantly ($P < .05$) different (Table 4). Both triazine treatments were significantly ($P < .05$)

Table 3. Analysis of variance for percent grassy weed control as influenced by four treatments, three rates and four obseravtion dates at location I.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	1	1.04	1.04	
Rates (L)	2	3,408.33	1,704.17	6.59
RL	2	533.33	266.67	
Treatments (T)	3	44,686.46	14,895.48	38.15**
RT	3	928.13	309.38	
LT	6	2,641.67	440.28	1.36
RLT	6	1,937.50	322.92	
Dates (D)	3	18,680.21	6,226.73	54.51**
RD	3	342.71	114.24	
LD	6	2,635.42	439.24	4.41*
RLD	6	597.92	99.65	
TD	9	9,615.63	1,068.40	8.28**
RTD	9	1,161.46	129.05	
LTD	18	4,706.25	261.46	1.38
RLTD	18	3,422.92	190.16	
Total	95	95,298.75		

[a] - values followed by "*" are significant at the $P < 0.05$ level and values followed by "**" are significant at the $P < 0.01$ level.

Table 4. Percent grassy weed control as influenced by four herbicides, four dates, three rates and two replications at location I.

Main factor	Level	Average[a]
Herbicide	Atrazine	38 a
	Simazine	32 a
	Dalapon I	77 b
	Dalapon II	77 b
Date of Observation	6/12/69	66 a
	7/7/69	70 a
	8/4/69	55 b
	7/16/70	32 c
Rate	1 lb/A	44 a
	2 lb/A	57 ab
	3 lb/A	63 b

[a] - values within each main factor followed by the same letters are not significantly different at $P < 0.05$. Herbicide averages were tested using Duncan's new multiple range test. Dates of observation and rate averages were tested using Tukey's test.

lower in grassy weed control than either dalapon treatment (Table 4). The dalapon I and dalapon II treatments averaged over all rates and dates gave approximately twice the grassy weed control as did either triazine treatment (Table 4). Using Tukey's test on the averages for the four dates, the results from the first two dates (6/12/69 and 7/7/69) were not significantly ($P < .05$) different but were both significantly higher in grassy weed control than the last two observation dates (Table 4). The date averages (Table 4) showed that after the 7/7/69 observation, the control of grassy weeds decreased. The 1 lb/A treatments averaged over all other factors was found to be significantly ($P < .05$) lower than the 3 lb/A treatment (Table 4). The rates x dates and treatments x dates interactions were also significant ($P < .05$) (Table 3) indicating no constant direct relationship between the rates at each date or treatments at each date.

At location II analysis of variance were computed on each of the two dates separately. On both dates, the grassy weed control was significantly ($P < .01$) influenced by treatments and rates (Table 5 and Table 6). On both June 12 and July 7, 1969, atrazine and dalapon I treatments gave significantly ($P < .05$) higher grassy weed control than simazine and dalapon II treatments, using Duncan's new multiple range test (Table 7). Applying the dalapon I treatment two weeks earlier than the dalapon II significantly ($P < .05$) increased the percent

Table 5. Analysis of variance for percent grassy weed control as influenced by four treatments and three rates for 6/12/69 date at location II.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	3	535.42	178.47	
Treatments (T)	3	15,539.59	5,179.86	23.83**
RT	9	1,956.24	217.36	
Rates (L)	2	1,757.30	875.65	6.45**
RL	6	817.70	136.28	
TL	6	1,138.53	189.76	1.55
RTL	18	2,203.14	122.40	
Total	47	23,947.92	---	

[a] - values followed by "*" are significant at the $P < 0.05$ level and values followed by "**" are significant at the $P < 0.01$ level.

Table 6. Analysis of variance for percent grassy weed control as influenced by four treatments and three rates for 7/7/69 date at location II.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	3	310.42	103.47	
Treatments (T)	3	4,739.59	1,579.86	10.55**
RT	9	1,347.91	149.77	
Rates (L)	2	12,451.05	6,225.53	15.10**
RL	6	2,473.95	412.33	
TL	6	1,957.28	326.21	2.20
RTL	18	2,667.72	148.21	
Total	47	25,947.92		

[a] - values followed by "*" are significant at the $P < 0.05$ level and values followed by "**" are significant at the $P < 0.01$ level.

Table 7. Percent grassy weed control as influenced by four herbicides, three rates and four replications at location II.

Main factor	Level	Average[a] 6/12/69	Average[a] 7/7/69
Herbicide	Atrazine	93 a	84 a
	Simazine	52 b	55 b
	Dalapon I	86 a	75 a
	Dalapon II	57 b	63 b
Rates	1 lb/A	62 a	45 a
	2 lb/A	76 ab	77 b
	3 lb/A	78 b	85 b

[a] – values within each main factor followed by the same letters are not significantly different at $P < .05$. Herbicide averages were tested using Duncan's new multiple range test. Dates of observation and rate averages were tested using Tukey's test.

of grassy weed control (Table 7). Tukey's test on rate averages showed that over all treatments, the 1 lb/A rate was significantly ($P < .05$) less effective in controlling grassy weeds on 6/12/69 than the 3 lb/A rate (Table 7). On 7/7/69, the 1 lb/A rate was significantly ($P < .01$) less effective than the other two rates (Table 7). The data from the 2 lb/A rate were not significantly ($P < .05$) different from the 3 lb/A rate at either date (Table 7).

This experiment showed no apparent explanation for the higher grassy weed control at location II as compared to location I for the atrazine and dalapon II treatments (Table A Appendix).

Broadleaf Weed Control

The broadleaf weeds, wild buckwheat (*Polygonum convolvulus* L.), common sunflower (*Helianthus annuus* L.), and redroot pigweed (*Amaranthus retroflexus* L.), were found only at location I. Analysis of variance showed that results from treatments and dates were significantly ($P < .01$) different and the treatments x dates interaction was significantly different ($P < .05$) (Table 8). There was no significant ($P < .05$) difference in broadleaf weed control from the three rates used (Table 9) according to Tukey's test. Statistical analysis using Duncan's new multiple range test, showed atrazine and simazine to be significantly ($P < .05$) higher in broadleaf weed

Table 8. Analysis of variance for percent broadleaf weed control as influenced by four treatments, three rates and four observation dates at location I.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	1	319.01	319.01	
Rates (L)	2	1,214.06	607.03	6.91
RL	2	175.52	87.76	
Treatments (T)	3	108.954.88	36,318.29	261.00**
RT	3	417.45	139.15	
LT	6	1,944.27	324.04	4.06
RLT	6	478.65	79.77	
Dates (D)	3	7,134.11	2,378.04	84.81**
RD	3	84.11	28.04	
LD	6	840.10	140.02	1.38
RLD	6	611.98	102.00	
TD	9	13,491.91	1,499.10	3.86*
RTD	9	3,500.26	388.92	
LTD	18	2,043.23	113.51	1.38
RLTD	18	1,475.52	81.97	
Total	95	142,684.69		

[a] - values followed by "*" are significant at the P< 0.05 level and values followed by "**" are significant at the P< 0.01 level.

Table 9. Percent broadleaf weed control as influenced by four herbicides, four dates, three rates and two replications at location I.

Main factor	Level	Average[a]
Herbicide	Atrazine	83 a
	Simazine	76 a
	Dalapon I	12 b
	Dalapon II	13 b
Dates of observation	6/12/69	61 a
	7/7/69	44 ab
	8/4/69	39 b
	7/16/70	42 ab
Rate	1 lb/A	42 a
	2 lb/A	49 a
	3 lb/A	48 a

[a] – values within each main factor followed by the same letters are not significantly different at $P < 0.05$. Herbicide averages were tested using Duncan's new multiple range test. Dates of observation and rate averages were tested using Tukey's test.

control than dalapon I and II (Table 9). Results (Table B Appendix) showed that dalapon I and II gave between 35 and 52% control in 6/12/69 but decreased to 11% or less at all other dates. Atrazine and simazine controlled the broadleaf weeds comparatively well throughout all dates.

The 6/12/69 date showed significantly ($P < .05$) higher broadleaf weed control than the 8/4/69 date but were not statistically different from the other dates (Table 9). A possible explanation is that the triazine herbicides remained fairly constant in weed control through 1969 whereas the dalapon treatments decreased through the season (Table B Appendix). Simazine is known to have a slower breakdown after application than atrazine. Therefore, it would be expected that simazine would be capable of a longer control period (Herbicide Handbook, 1967). Dalapon is not regarded as a broadleaf weed chemical but is mainly a grass herbicide. The triazines, however, are known to control both grass and broadleaf type weeds.

Switchgrass Injury

The treatments were significantly ($P < .01$) different in the amount of observed switchgrass injury at location I (Table 10). The two triazine compounds had no visable injury to the switchgrass and were significantly ($P < .05$) less injurious than the two dalapon treatments

Table 10. Analysis of variance for percent switchgrass injury as influenced by four treatments, three rates and four observation dates at location I.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	1	337.50	337.50	
Rates (L)	2	3,384.90	1,692.45	6.51
RL	2	520.31	260.16	
Treatments (T)	3	95,472.88	31,824.29	138.45**
RT	3	689.58	229.86	
LT	6	3,444.27	574.04	2.46
RLT	6	1,396.35	232.73	
Dates (D)	3	5,306.25	1,768.75	23.36*
RD	3	227.08	75.69	
LD	6	998.44	166.41	4.27
RLD	6	233.85	38.98	
TD	9	5,450.00	605.56	4.43
RTD	9	1,229.17	136.57	
LTD	18	1,814.06	100.78	1.00
RLTD	18	1,891.14	105.06	
Total	95	122,395.56		

[a] – values followed by "*" are significant at the $P < .05$ level and values followed by "**" are significant at the $P < .01$ level.

(Table 11). Duncan's new multiple range test indicated no significant difference between the two dalapon treatments (Table 11).

Analysis of variance showed that the data from the dates were significantly ($P < .05$) different (Table 10). Using Tukey's test, the June 12, 1969 rating of all treated plots showed significantly ($P < .05$) less damage to switchgrass than the other three dates (Table 11). There was a trend of increasing injury during 1969.

Tukey's test and the analysis of variance showed no significant ($P < .05$) difference in switchgrass injury from the three rates that the herbicides were applied (Table 12 and Table 11). The treatment x date interactions were significant ($P < .05$) (Table 10). This was possibly caused by the triazine treatments being relatively non-injurious to the switchgrass throughout the experiment, while dalapon I and II treatments tended to increase in injury to the switchgrass throughout 1969.

At location II, the analysis of variance was conducted for each date. Results obtained on 6/12/69 from treatments, and rates were significant ($P < .01$) (Table 12). The triazines showed significantly ($P < .05$) less injury to the switchgrass than either dalapon treatment according to Duncan's new multiple range test (Table 13). The dalapon II treatment was also significantly ($P < .05$) less injurious than the dalapon I treatment. According to Tukey's test, the 1 lb/A

Table 11. Percent switchgrass injury as influenced by four herbicides, four dates, three rates and two replications at location I.

Main factor	Level	Average[a]
Herbicide	Atrazine	0 a
	Simazine	0 a
	Dalapon I	61 b
	Dalapon II	59 b
Dates of observation	6/12/69	20 a
	7/7/69	31 b
	8/4/69	35 b
	7/16/70	35 b
Rates	1 lb/A	23 a
	2 lb/A	31 a
	3 lb/A	36 a

[a] – values within each main factor followed by the same letters are not significantly different at $P < .05$. Herbicide averages were tested using Duncan's new multiple range test. Dates of observation and rate averages were tested using Tukey's test.

Table 12. Analysis of variance for percent switchgrass injury as influenced by four treatments and three rates for 6/12/69 at location II.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	3	506.25	168.75	
Treatments (T)	3	8,835.42	2,945.14	24.71**
RT	9	1,072.92	119.21	
Rates (L)	2	2,038.55	1,019.28	11.08**
RL	6	478.12	79.69	
TL	6	2,061.45	343.58	3.74*
RTL	18	1,655.21	91.96	
Total	47	16,647.92	---	

[a] - values followed by "*" are significant at the $P < .05$ level and values followed by "**" are significant at the $P < .01$ level.

Table 13. Percent switchgrass injury as influenced by four herbicides, three rates and four replications at location II.

Main factor	Level	Average[a] 6/12/69	7/7/69	8/4/69
Herbicide	Atrazine	9 a	1 a	3 a
	Simazine	7 a	1 a	2 a
	Dalapon I	40 c	56 b	57 b
	Dalapon II	27 b	48 b	57 b
Rates	1 lb/A	13 a	9 a	7 a
	2 lb/A	21 b	34 b	40 b
	3 lb/A	28 b	37 b	41 b

[a] - values within each main factor followed by the same letters are not significantly different at $P < .05$. Herbicide averages were tested using Duncan's new multiple range test. Dates of observation and rate averages were tested using Tukey's test.

treatment was significantly ($P < .05$) less injurious to switchgrass than the other two rates (Table 13). The 2 and 3 lb/A rates were not statistically ($P < .05$) different in switchgrass injury. The significant interaction of treatments x rates was probably caused by all triazine rates being relatively equal in injury, while the dalapon I and II treatments increased in injury as the rate increased (Table C Appendix).

On 7/7/69 and similarily on 8/4/69, at location II, switchgrass injury as influenced by treatments and rates was found significant ($P < .01$) in Table 14 and 15 respectively). On both dates, the atrazine and simazine treatments were significantly ($P < .05$) less injurious to the switchgrass than the dalapon I and II treatments. However, unlike the June 12, 1969 date for location II, the results from the two dalapon treatments were not statistically ($P < .05$) different. The 1 lb/A rate on both dates were significantly ($P < .05$) less injurious than the other two rates (Table 13). The significant interaction of rates x treatments was again probably caused by all triazine rates being relatively equal in injury, while the dalapon I and II treatments increased in injury as the rate increased (Table C Appendix).

Dalapon was more effective in controlling grassy weeds than the triazines, however it caused reduction of the number of switchgrass plants. The results indicated that dalapon would not be acceptable as an effective herbicide for controlling grassy weeds in a switchgrass

Table 14. Analysis of variance for percent switchgrass injury as influenced by four treatments and three rates for 7/7/69 at location II.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	3	176.58	58.85	
Treatments (T)	3	32,668.23	10,889.41	109.33**
RT	9	896.36	99.60	
Rates (L)	2	7,604.17	3,802.09	58.87**
RL	6	387.50	64.58	
TL	6	8,820.83	1,470.14	27.26**
RTL	18	970.83	53.94	
Total	47	51,524.48	---	

[a] - values followed by "*" are significant at the $P < .05$ level and values followed by "**" are significant at the $P < .01$ level.

Table 15. Analysis of variance for percent switchgrass injury as influenced by four treatments and three rates for 8/4/69 at location II.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	3	804.17	268.06	
Treatments (T)	3	35,779.17	11,926.39	92.02**
RT	9	1,166.66	129.63	
Rates (L)	2	11,834.38	5,917.19	29.61**
RL	6	1,198.95	199.83	
TL	6	13,711.45	2,285.24	58.33**
RTL	18	705.22	39.18	
Total	47	65,200.00	---	

[a] - values followed by "*" are significant at the $P < .05$ level and values followed by "**" are significant at the $P < .01$ level.

pasture under the conditions of this study. Kay (1963) found that dalapon at 2 and 3 lb/A produced only slight injury to soft chess. Apparently the switchgrass was not as tolerant to dalapon as soft chess.

The two triazines looked promising as a desirable herbicide for weed control in warm season switchgrass. They were less effective in grassy weed control but were more effective in controlling broadleaf weeds and caused little or no damage to switchgrass.

RESIDUE ANALYSIS

Laboratory Efficiencies

Laboratory techniques were developed for the recovery of atrazine, simazine and dalapon from switchgrass. Utilizing these procedures, laboratory efficiencies were determined by fortifying individual untreated switchgrass samples with known amounts of a herbicide. Four replications were analyzed for each chemical. Atrazine recovery was found to average 80% with a range from 76 to 86%. Mattson *et al.* (1965) recovered an average of 84% atrazine from wheat (*Triticum aestivum* L.) straw and 90% from soybeans (*Glycine max* (L.) Merrill). Average simazine recovery was 50% with a range of 48 to 55%. Recovery of the dalapon ranged between 87 to 92% with an average of 90%. Getzendaner (1963) obtained 80 to 100% recovery of dalapon from fortified samples of plant materials.

When the samples from the field experiment were analyzed, a control fortified with a known amount of herbicide was processed to check consistency of laboratory procedures. These checks fell within the ranges previously obtained.

Residue Loss in Storage

A study was conducted to determine the amount of herbicide lost while in frozen storage. Known amounts of atrazine, simazine and dalapon were applied uniformly to separate switchgrass samples. Subsamples were taken from each sample immediately and analyzed for amount of residue present. The remainder of the sample was placed in frozen storage. Further subsamples at one, two, four, six and eight months were analyzed for the particular herbicide. Results indicated that atrazine and simazine lost approximately 20% of the total amount applied to the foliage while in frozen storage for the first month period (Figure 2). It was assumed that once frozen, any loss occurring during the first month would continue throughout storage but at a decreasing rate. However, since there was no loss after the first month, perhaps the loss which did occur took place before reaching freezing temperature. This loss may have resulted

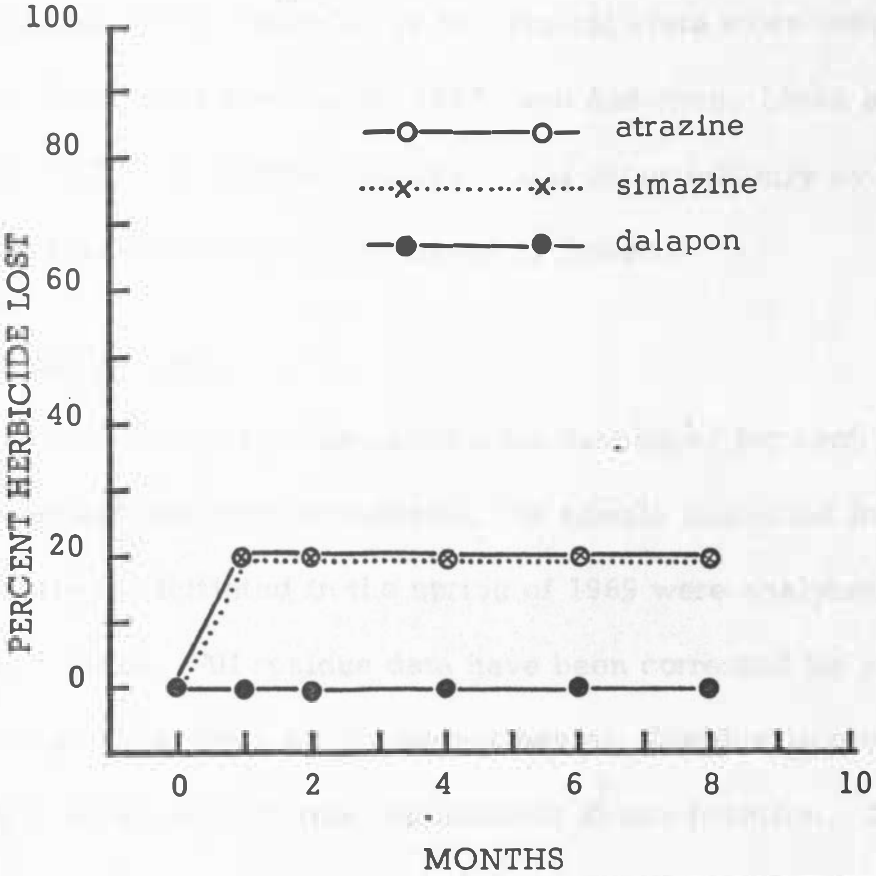

Figure 2. Percent herbicide lost during frozen storage (-20 C). Values are averages of three replications.

from switchgrass metabolism of the triazine or in the freezing process.

Dalapon loss was considered negligible during the eight months of frozen storage (Figure 2). Dalapon, unlike atrazine and simazine, is not metabolized but remains in its original state when taken up by plants (Herbicide Handbook, 1967, and Anderson, Linck and Behrens, 1962). Therefore, no loss would occur initially by plant metabolic breakdown before the tissue is frozen.

Atrazine and Simazine

Once the laboratory techniques were developed for each herbicide and the percent recovery determined, the sample collected from the field experiment initiated in the spring of 1969 were analyzed for chemical residue. All residue data have been corrected for procedure efficiency and are given on dry weight basis. Residue is given in ppm and is an average of four replications at one location. The May 2 harvest was done within two hours after herbicide application to the respective plots which consisted of dry upright stems from the previous years growth. Analysis of samples harvested on May 2 showed approximately 5, 10 and 17 ppm of atrazine and simazine on plots receiving treatments of 1, 2 and 3 lb/A, respectively (Table D Appendix). Atrazine and simazine were not significantly ($P < .05$) different (Table 16 and Table 17). Duncan's new multiple range

Table 16. Analysis of variance for atrazine and simazine residue (ppm) as influenced by two treatments and three rates on May 2 harvest date.

Source of variance	Degrees of freedom	Sums of squares	Mean square	F[a]
Replications (R)	3	15.26	5.09	
Treatments (T)	1	0.03	0.03	0.30
RT	3	0.30	0.10	
Rates (L)	2	639.11	319.55	191.79**
RL	6	10.00	1.67	
TL	2	4.56	2.28	3.23
RTL	6	4.23	0.71	
Total	23	675.50	---	

[a] - values followed by "*" are significant at the $P < .05$ level and values followed by "**" are significant at the $P < .01$ level.

Table 17. Residue (ppm) found in switchgrass immediately after application as influenced by two herbicides, three rates and four replications at location I.

Main factor	Level	Average[a]
Herbicide	Atrazine	11 a
	Simazine	11 a
Rate	1 lb/A	5 a
	2 lb/A	10 b
	3 lb/A	18 c

[a] - values within each main factor followed by the same letters are not significantly different at $P < 0.05$. Herbicide averages were tested using Duncan's new multiple range test. Rate averages were tested using Tukey's test.

test indicated that residue from each rate of the herbicides was significantly ($P < .05$) different from each other (Table 17). Analysis of triazine treated samples from all other harvest dates throughout the season indicated less than 5 ppm.

Wheeler and Hamilton (1968) found that corn had less than 4 ppm atrazine in tissue after 24 days when grown in nutrient solution containing 10 ppm. Ten ppm would be greater than an application of 3 lb/A sampled to a soil depth of 3 inches. This may explain why no recordable atrazine or simazine residue was found in the growing vegetation during the summer.

The U.S.D.A. Pesticides Regulation Division, Agricultural Research Service (1968) stated that perennial ryegrass may have up to 15 ppm atrazine and be safely used for forage. Simazine may range up to 15 ppm in grass crops to be used for seed and 15 ppm in alfalfa for forage consumption. If similar tolerance limits were set for these triazines in switchgrass, data from this study would indicate that atrazine and simazine are below the government limit of 15 ppm at all periods during the growing season. Only at the 3 lb/A rate immediately following spraying (May 2), were residues over 15 ppm (Table 17). Usually switchgrass isn't ready for grazing or harvesting in South Dakota until mid-summer.

Dalapon

Analysis of variance showed that residue of dalapon in plant tissue varied significantly ($P < .05$) between dates, rates and rates x dates interactions (Table 18). Samples taken immediately after spraying (May 2 for dalapon I and May 18 for dalapon II) had approximately 200 ppm for 1 lb/A, 400 ppm for 2 lb/A and 1000 ppm for 3 lb/A on both dalapon I and II and at both locations (Table 19). These values were about half the amount reported by Linscott et al. (1970) for dalapon residue in alfalfa. Perhaps less foliage was present to catch the spray. Also, Linscott et al. sprayed growing alfalfa plants 40 cm high while this study was initiated early in spring and only the previous years growth was harvested on May 2 and 18. Using Tukey's test, the residue on May 2 and 18 was significantly ($P < .05$) higher than at all other dates (Table 20). Dalapon treated plots were again harvested June 12 when there was ample switchgrass growth to facilitate sampling of green vegetation. Data from this harvest were significantly ($P < .05$) less than the application dates having a greater than 10 fold decrease (Table 19 and Table 20). Statistically the two June residues were not different ($P < .05$). However, the June 12 residue was significantly ($P < .05$) higher than the July 7 and all later dates (Table 20). The last two harvest dates, August 4 and 20 had significantly ($P < .05$) less

Table 18. Analysis of variance for dalapon residue (ppm) as influenced by two locations, two treatments, three rates and six dates.

Source of variation	Degrees of freedom	Sums of squares	Mean square	F[a]
Locations (P)	1	2,160.55	2,160.55	0.74
Dates (D)	5	10,234,251.06	2,046,850.21	704.06**
PD	5	7,265.22	1,453.04	0.50
Replications (R)	3	2,075.22	691.74	
PR	3	2,964.46	988.15	
DR	15	15,445.71	1,029.71	
PDR	15	19,652.65	1,310.18	
Treatments (T)	1	0.18	0.18	
PT	1	511.15	511.15	0.18
DT	5	798.10	159.62	0.05
PDT	5	5,602.73	1,120.55	0.39
RT	3	2,299.06	766.35	
PRT	3	4,247.15	1,415.72	
DRT	15	7,548.90	503.26	
PDRT	15	20,541.28	1,369.42	
Rates (L)	2	1,284,935.16	642,467.58	220.99**
PL	2	374.27	187.13	0.06
DL	10	4,152,593.95	415,259.40	142.84**
PDL	10	16,168.57	1,616.86	0.56
RL	6	3,853.00	642.17	
PRL	6	4,050.96	675.16	
DRL	30	24,917.25	830.58	
PDRL	30	23,593.28	786.44	
TL	2	376.44	188.22	0.06
PTL	2	939.82	469.91	0.16
DTL	10	1,826.54	182.65	0.06
PDTL	10	4,112.14	411.21	0.14
RTL	6	2,804.28	467.38	
PRTL	6	17,112.57	2,852.10	
DRTL	30	14,682.28	489.41	
PDRTL	30	87,216.85	2,907.28	
Total	287	15,964,920.77		

Table 18. (continued)

a - values followed by "*" are significant at the $P < .05$ level and values followed by "**" are significant at the $P < .01$ level.

Table 19. Dalapon residue found in switchgrass from treated plots.

Herbicide	Rate lb/A	Harvest Dates May 2	May 18	June 12	June 19	July 7	August 4	August 20
					ppm, dry weight			
Location I								
Dalapon I	1	194.94	---	14.87	10.62	6.68	1.91	1.88
	2	375.57	---	34.97	18.42	18.42	4.91	2.45
	3	1,000.29	---	84.29	36.59	27.53	8.21	3.28
Dalapon II	1	---	201.38	13.41	11.20	11.33	2.32	2.29
	2	---	387.52	29.67	20.90	18.12	6.14	2.69
	3	---	1,025.61	60.50	40.67	47.89	7.73	5.58
Location II								
Dalapon I	1	202.27	---	14.79	20.18	8.66	2.29	2.02
	2	413.44	---	34.17	31.13	19.10	3.52	3.14
	3	992.42	---	97.50	83.82	52.81	5.76	5.39
Dalapon II	1	---	208.01	18.06	13.83	12.46	3.22	1.40
	2	---	391.43	46.20	49.47	20.98	5.41	2.85
	3	---	928.72	101.75	78.40	49.32	8.31	5.55

Table 20. Dalapon residue found in switchgrass as influenced by six dates, three rates and four replications at two locations.

Main factor		Average[a] (ppm)
Date of observations	May 2 and 18	527 a
	June 12	46 b
	June 19	35 bc
	July 7	25 c
	August 4	5 d
	August 20	3 d
Rate	1 lb/A	41 a
	2 lb/A	81 b
	3 lb/A	198 c

[a] - values within each main factor followed by the same letters are not significantly different at $P < .05$. Dates of observation and rate averages were tested using Tukey's test.

residue than all other harvest dates. At the last sampling, values were below 6 ppm for even the 3 lb/A rate of dalapon. There was a significant ($P < .05$) decrease in dalapon residue in forage during the season (Table 20).

Analysis of variance showed that the two locations and the two dates of dalapon application had no significant ($P < .05$) effect on the residue found in the plants (Table 18). There was a direct and significant ($P < .05$) relationship between the rate of dalapon applied and the amount of residue recovered from the vegetation on the treated plots (Table 18 and Table 20). Residue was significantly ($P < .05$) increased according to Tukey's test, as the rate/A of the dalapon was increased (Table 20). The significance of the dates x rates interaction was probably caused by the irratic decrease in residue from one date to another and the fact that each rate seemed to have a different time at which it would decrease or remain constant (Table 19).

At present there is no tolerance limit for dalapon use on pasture by U.S.D.A. Pesticide Regulation Division (1968).

SUMMARY

Purposes of this study were to find an effective herbicide for control of grassy weeds in a pasture, to adapt known laboratory procedures for analyzing residues and to determine amounts of residues during the growing season in treated plots.

Nine herbicides were evaluated for downy brome control in a native pasture by a screening experiment at the Pasture Research Center, near Norbeck, South Dakota, in 1968. Each chemical was applied postemergence with and without the addition of 1 gpa crop oil. Of the herbicides tested, atrazine was the most effective giving 90 and 92% downy brome control without and with oil respectively.

Atrazine was selected for further study because of the positive results obtained from the screening experiment. Simazine has properties similar to atrazine with a longer soil residual effect therefore making it an evident choice. Dalapon, an effective grassy weed herbicide, was further tested to determine its effects on grassy weeds and on the desirable switchgrass under the conditions of this experiment.

In the spring of 1969, atrazine, simazine and dalapon each at 1, 2 and 3 lb/A without oil were applied preemergence to

switchgrass at two locations (location I and II). Grassy weeds at location I and II were primarily downy brome and green and yellow foxtail. Broadleaf weeds found only at location I were wild buckwheat, common sunflower and redroot pigweed. Visual observations were made in June, July and August 1969 at both locations with an additional observation July 1970 at location I. At location I during 1969, atrazine effectiveness remained nearly constant through the summer with 38% grassy weed control. Simazine effectiveness was not significantly ($P < .05$) different from that of atrazine. Dalapon effectiveness decreased from 90% to 61% and gave significantly ($P < .05$) higher percent control than either triazine. At location II, atrazine and dalapon I (applied May 2) were not significantly ($P < .05$) different in grassy weed control. Simazine and dalapon II (applied May 18) were significantly ($P < .05$) less effective in grassy weed control than atrazine and dalapon I.

Analysis of the broadleaf weed control at location I during 1969 found the triazines significantly ($P < .05$) effective while dalapon was ineffective. No broadleaf weeds were present at location II.

Atrazine and simazine caused no injury to the desirable switchgrass at location I and only slight damage at location II. Dalapon significantly ($P < .05$) injured the switchgrass. At both locations the first indications were stunting leading to a lethal effect in many cases. Herbicidal carry over to July 1970 at location I was evident. This residue resulted in broadleaf control but little grassy weed control or switchgrass injury from the triazines. Dalapon carry over showed opposite effects with little broadleaf weed control, adequate grassy weed control and extensive injury to switchgrass.

Vegetation was sampled from the field experiment plots during the growing season and frozen until analyzed for residue in the laboratory. May 2 and 18 samples consisting of the previous year's growth were harvested immediately after spraying and stored at room temperature.

Laboratory procedures for atrazine and simazine residue analysis included column, thin-layer and hydrogenflame gas chromatography. Recovery efficiencies for atrazine and simazine were 80% and 50%, respectively. Electron capture gas chromatography was used to detect dalapon residue. Average percent recovery for dalapon was 90%.

Herbicidal loss during frozen storage was 20% for atrazine and simazine during the first month and remained constant thereafter. Dalapon had no detectable loss through the eight months. All residue data for harvested samples were corrected for laboratory procedure effectiveness and storage loss.

Analysis of samples harvested on May 2 showed approximately 5, 10 and 15 ppm of atrazine and simazine on plots receiving treatments of 1, 2 and 3 lb/A, respectively. Data from atrazine and simazine residue analysis were not significantly ($P < .05$) different. Residue in samples from all other harvest dates was less than 5 ppm for both atrazine and simazine. Dalapon residues ranged from approximately 200 ppm for 1 lb/A to 1,000 ppm for 3 lb/A at both the May 2 and 18 application dates. Residues at 1, 2 and 3 lb/A were significantly ($P < .05$) different. The residue decreased through the summer to a low ranging from 1.4 to 5.6 ppm at August 20.

Results of the study indicated that atrazine and simazine were most effective for controlling grassy weeds without injury to the desirable switchgrass. Laboratory analysis showed little if any triazine residue in the vegetation collected at times when the pasture would be harvested. Dalapon under the conditions of this experiment could not be considered desirable because of the severe injury and death to switchgrass and the residue in vegetation throughout the summer harvest. At the present time, there are no herbicides cleared by the Federal Food and Drug Administration for controlling grassy weeds in pastures grazed the same year. With over 900 million acres of pasture and range land in the United States, the need for a herbicide labeled for grassy weed control is apparent.

LITERATURE CITED

Abbott, D. C., J. A. Bunting and J. Thomson. 1965. The thin-layer chromatographic determination of triazine herbicides in soil and water. Analyst 90:356-364.

Albert, W. B. 1965. Control of little barley in Coastal Bermuda-grass with atrazine and paraquat. Weeds 13:375-376.

Allen, G. P. 1968. The effect of July applications of dalapon on the growth and botanical composition of an Agrostis lolium pasture. Weed Res. 8:309-320.

Allen, G. P. 1969. The influence of nitrogen on a pasture treated with dalapon for the selective suppression of Agrostis stolonifera and Holcus lanatus in perennial rye-grass. J. Br. Grassld. Soc. 24:138-145.

Andersen, R. N., A. J. Linck and R. Behrens. 1962. Absorption, translocation, and fate of dalapon in sugar beets and yellow foxtail. Weeds 10:1-3.

Benfield, C. A., and E. D. Chilwell. 1964. The determination of some triazine herbicides by gas-liquid chromatography with particular reference to atraton in soil. Analyst 89:475-479.

Canode, C. L., W. C. Robocker and T. J. Muzik. 1962. Grass seed production as influenced by chemical control of downy brome. Weeds 10:216-219.

Chandler, J. M., and P. W. Santelmann. 1969. Growth characteristics and herbicide susceptibility of Texas Panicum. Weeds 17:91-93.

Chilwell, E. D., and D. Hughes. 1962. Detection of traces of some triazine herbicides by gas-liquid chromatography. J. Sci. Food Agric. 13:425-427.

Delley, R. K., Friedrich, B. Karlhuber, G. Szekely and K. Stammbach. 1967. The identification and determination of various triazine herbicides in biological materials. J. of Anal. Chem. 288:23-38.

Derscheid, L. A., R. A. Moore, J. K. Lewis. 1970. A pasture system for you. F.S. 307. South Dakota State University.

Dow Chemical Company. 1964. Residue determination method of dalapon residues by gas chromatography. Midland, Michigan. 6 p.

Dyksterhuis, E. J. 1965. Graze longer and feed less roughage. Systems to balance native and tame pasture with seasonal needs. F.S. 223. South Dakota State University.

Evans, R. A., R. E. Eckert, Jr., B. L. Kay and J. A. Young. 1969. Downy brome control by soil-active herbicides for revegetation of rangelands. Weeds 17:166-169.

Fink, R. J., and O. H. Fletchall. 1963. Forage crop establishment in soil containing atrazine or simazine residues. Weeds 11:81-83.

Frank, P. A., and R. J. Demint. 1969. Gas chromatographic analysis of dalapon in water. Environ. Sci. Technol. 3:69-71.

Geigy Agricultural Chemicals. 1964. The determination of chlorotriazine residues in plant material, animal tissue and water using the ultraviolet method. Anal. Bull. No. 7. Ardsley, New York. 13 p.

Getzendaner, M. E. 1963. Gas chromatographic determination of dalapon residue. J. Off. Agric. Chem. 46:269-275.

Henkel, H. G., and W. Ebing. 1964. A contribution to the gas chromatography of triazine herbicides. J. Gas Chrom. 2:215-218.

Herbicide Handbook of the Weed Society of America. 1967. W. F. Humphery Press, Inc., Geneva, New York. 293 p.

Holstun, J. T., Jr. and W. E. Loomis. 1956. Leaching and decomposition of 2,2-dichloropropionic acid in several Iowa soils. Weeds 4:205-217.

Hughes, H. D., M. E. Heath and D. S. Metcalfe. 1962. Forages. 2nd ed. Iowa State University Press, Ames, Iowa. p. 330-331 and 384-385.

Hyder, D. N., and A. C. Everson. 1968. Chemical fallow of abandoned croplands on the short-grass plains. Weeds 16:531-533.

Jagschitz, J. A. 1969. Fall and spring use of preemergence crabgrass control chemicals in turfgrass. NEWCC 23:398-403.

Kay, B. L. 1963. Effects of dalapon on a medusahead community. Weeds 11:207-209.

Kerr, H. D. 1969. Selective grass control with siduron. Weeds 17:181-186.

Klingman, G. C. 1965. Weed Control: As a Science. John Wiley and Sons, Inc., New York. 421 p.

Lee, W. O. 1965. Selective control of downy brome and rattail fescue in irrigated perennial grass seed fields of central Oregon. Weeds 13:205-208.

Linscott, D. L., R. D. Hagin and M. J. Wright. 1970. Dalapon residues in alfalfa as affected by harvesting and dehydrating. Agron. J. 62:405-407.

Mattson, A. M., R. A. Kahrs and J. Schneller. 1965. Use of microcoulometric gas chromatograph for triazine herbicides. J. Agr. Food Chem. 13:120-122.

McGowan, A. A. 1970. The effect of four herbicides on pasture yield and composition. Weed Abstracts 19:1980.

McMurphy, W. E. 1969. Preemergence herbicides for seeding range grasses. J. Range Mngt. 22:427-429.

Moore, R. A. 1967. Personal communication. Plant Science Dept., South Dakota State University, Brookings, South Dakota.

Muzik, T. J. 1970. Weed Biology and Control. McGraw-Hill Book Company. New York. p 162.

Parker, R. 1967. Personal communication. Plant Science Dept., South Dakota State University, Brookings, South Dakota.

Ragab, M. T. H., and J. P. McCollum. 1968. Colorimetric methods for the determination of simazine and related chloro-s-triazines. J. Agr. Food Chem. 16:284-289.

Robocker, W. C., D. H. Gates and H. D. Kerr. 1965. Effects of herbicides, burning and seeding date in reseeding an arid range. J. Range Mngt. 18:114-118.

South Dakota Weeds. 1967. Agricultural Extension Service, South Dakota State University. South Dakota State Weed Control Commission. 216 p.

Steel, R. G. D., and J. H. Torrie. 1960. Principles and Procedures of Statistics. McGraw-Hill Book Company, Inc., New York. 481 p.

Thompson, L, Jr. and F. W. Slife. 1969. Foliar and root absorption of atrazine applied postemergence to giant foxtail. Weeds 17:251-256.

U. S. Department of Agriculture, Pesticides Regulation Division, Agricultural Research Service. 1968. Summary of registered Agricultural Pesticides Chemical Uses. Vol 1, 3rd ed.

U. S. Department of Agriculture. 1969. Economic Research Service Quantities of Pesticides Used by Farmers in 1966. Agricultural Economics Report No. 179.

U. S. Department of Agriculture. 1969. Land Utilization. Agricultural Statistics. p 429.

Warren, L. E. 1967. Effect of rate, time of treatment, use of additives and spray volume on control of winter annual grasses with Dowpon. Down to Earth 23:12-13.

Wheeler, H. L., and R. H. Hamilton. 1968. The leaf concentrations of atrazine in cereal crops as related to tolerance. Weeds 16:7-10.

Wicks, G. A., C. R. Fenster and O. C. Burnside. 1965. Chemical control of downy brome in grasslands of western Nebraska. Weeds 13:202-205.

Young, J. A., R. A. Evans and R. E. Eckert, Jr. 1969. Wheatgrass establishment with tillage and herbicides in a mesic medusahead community. J. Range Mngt. 22:151-155.

APPENDIX

Appendix Table A. Effects of four herbicides at three rates on the percent grassy weed control. Values at location I are averages of two replications and values at location II are averages of four replications.

Herbicide	Rate lb/A	6/12/69 Location I	6/12/69 Location II	7/7/69 Location I	7/7/69 Location II	8/4/69 Location I	8/4/69 Location II	7/16/70 Location I	7/16/70 Location II
		%	%	%	%	%		%	
Atrazine	1	45	92	40	71	30	--	0	--
	2	50	93	40	90	50	--	0	--
	3	55	95	40	90	65	--	0	--
Simazine	1	25	47	25	30	37	--	0	--
	2	30	53	40	57	40	--	0	--
	3	50	55	70	78	72	--	0	--
Dalapon I	1	75	73	85	50	52	--	30	--
	2	95	93	90	85	75	--	80	--
	3	100	91	92	91	55	--	90	--
Dalapon II	1	90	42	87	30	45	--	42	--
	2	90	56	95	78	75	--	70	--
	3	90	72	95	80	65	--	75	--
LSD .05		29.4	16.4	29.4	18.1	29.4		29.4	

Dates of Visual Observations

Appendix Table B. Effects of four herbicides at three rates on the percent broadleaf weed control at location I. Values at location I are averages of two replications.

Herbicide	Rate lb/A	Dates of Visual Observations			
		6/12/69	7/7/69	8/4/69	7/16/70
		%	%	%	%
Atrazine	1	87	90	72	60
	2	95	92	82	70
	3	95	85	87	85
Simazine	1	45	75	37	92
	2	77	70	85	97
	3	70	85	85	97
Dalapon I	1	35	0	5	0
	2	50	7	10	0
	3	40	0	0	0
Dalapon II	1	52	10	0	0
	2	45	5	2	0
	3	40	5	0	0
LSD .05		19.0	19.0	19.0	19.0

Appendix Table C. Effects of four herbicides at three rates on the percent switchgrass injury. Values at location I are averages of two replications and values at location II are averages of four replications.

		Dates of Visual Observations							
		6/12/69 Location		7/7/69 Location		8/4/69 Location		7/16/70 Location	
Herbicide	Rate lb/A	I	II	I	II	I	II	I	II
		%	%	%	%	%	%	%	
Atrazine	1	0	10	0	0	0	0	0	--
	2	0	10	0	2	0	7	0	--
	3	0	7	0	0	0	3	0	--
Simazine	1	0	5	0	2	0	5	0	--
	2	0	7	0	0	0	0	0	--
	3	0	10	0	0	0	0	0	--
Dalapon I	1	40	21	30	16	52	3	65	--
	2	40	40	75	67	75	75	72	--
	3	50	60	85	86	55	93	90	--
Dalapon II	1	30	15	40	17	68	22	47	--
	2	40	28	52	66	82	78	55	--
	3	40	37	85	62	87	70	90	--
LSD .05		21.1	14.7	21.1	10.7	21.1	9.2	21.1	

Appendix Table D. Atrazine and simazine residue found in switchgrass immediately after application. Values are averages of four replications.

Main factor	Level	Average (ppm)
Atrazine	1 lb/A	5
	2 lb/A	10
	3 lb/A	17
Simazine	1 lb/A	5
	2 lb/A	9
	3 lb/A	18