ŧ

THE INFLUENCE OF ENVIRONMENTAL FACTORS ON THE PHYTOTOXICITY AND PERSISTENCE OF TERBUTRYN

Вy

CHU-HUANG WU

Bachelor of Science

National Taiwan University

Taipei, Taiwan

1970

Submitted to the Faculty of the Graduate College of the Oklahoma State University in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE July, 1973

OKLAHOMA STATE UNIVERSITY LIBRARY

NOV 16 1973

54

THE INFLUENCE OF ENVIRONMENTAL FACTORS ON THE

PHYTOTOXICITY AND PERSISTENCE OF TERBUTRYN

Thesis Approved:

lmann Thesis Adviser p

Dean of the Graduate College

ACKNOWLEDGMENTS

4

The author wishes to acknowledge his appreciation and indebtedness to Dr. Paul W. Santelmann, his major adviser, for his valuable training, advice, and consideration during his graduate work. The assistance of the other members of his graduate committee, Dr. Eddie Basler and Dr. Lester W. Reed, is also acknowledged and appreciated.

Special words of appreciation are extended to Prof. Stassen Y. C. Soong and Dr. Ralph S. Matlock for their assistance in furthering the author's education in the United States.

Appreciation is also extended to the Agronomy Department of Oklahoma State University for the use of their facilities and the financial assistance which made this study possible.

The author wishes to express his sincere thanks to his wife, Sue, for her patience, assistance and encouragement.

Appreciation is expressed to Mrs. Kathy Henslick for typing the final copy of this manuscript.

i11

TABLE OF CONTENTS

Chapte:	r Page	5
I,	INTRODUCTION	1
II.	LITERATURE REVIEW , , ,	3
	Temperature Effects	35
		7 7
III.	METHODS AND MATERIALS)
	Soil Factors Studies	4
	Interaction Studies	
IV.	RESULTS AND DISCUSSION	3
	Preliminary Bioassay Studies	1 5
	Moisture and Temperature Interaction Studies	
v.	SUMMARY	2
LIT	ERATURE CITED	4

LIST OF TABLES

Table	Pa	ge
I,	Characteristics of the Different Natural Soils	12
II.	Bioactivity of Terbutryn in Five Model Soils	22
III.	Bioactivity of Terbutryn in Eight Natural Soils	22
IV.	Bioactivity and Adsorption of Terbutryn in Different Soil Types	24
ν.	Correlation of Salt Concentration with Adsorption	26
VI.	Green Weights of 3 Replications of Wheat Foliage as affected by Terbutryn at Five Rates of Application and at three Soil Temperatures	28
VII.	Green Weights of Three Replications of Sorghum Foliage as Affected by Terbutryn at Four Rates of Application	29
VIII.	The Interaction of Temperature and Moisture on Terbutryn Phytotoxicity as Shown by the Average of Four Replications of Green Weights of Wheat,,,,,	31
IX.	The Interaction of Temperature and Moisture on Terbutryn Phytotoxicity as Shown by the Average of Four Replications of Green Weights of Sorghum	31
х.	Effects of Time, Temperature, and Soil Moisture of the Dissipation of Terbutryn on a Silt Loam Soil	37
XI.	Effects of Time, Temperature, and Soil Moisture on the Dissipation of Terbutryn on a Fine Sandy Loam Soil	40

LIST OF FIGURES

Figu	re				Pa	age
1.	Response of Sorghum, Oat, Cucumber, and Wheat to Varyin Terbutryn Concentrations ,	_	•	•	•	19
2.	Response of Velvetleaf and Barnyardgrass to Varying Terbutryn Concentrations	•	•	٠	•	20
3.	Adsorption Isotherms for Terbutryn by Six Different Soils	•	•	•	•	23
4.	The Effect of Soil Moisture on the Phytotoxicity of Terbutryn of Wheat	•	٩	•	•	27
5.	The Effect of Temperature and Moisture on Terbutryn Phytotoxicity	•	•	•	•	32
6.	The Effect of Moisture on Terbutryn Degradation	•	•	•	•	33
7.	The Effect of Temperature on Terbutryn Degradation	•	•	٠	•	34
8.	The Interaction Effect of Moisture and Temperature on Terbutryn Degradation	•	۰	•	•	35
9.	The Effect of Incubation Time on Terbutryn Degradation	•	•	•	•	36

CHAPTER 1

INTRODUCTION

A relatively new s-triazine herbicide 2-(tert-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine (terbutryn) has been introduced for preemergence annual weed control. It shows considerable promise for controlling a wide range of broadleaf weeds in sorghum (<u>Sorghum bicolor</u> L) grown on light soils, and in winter wheat (<u>Triticum aestivum</u> Vill). However, under certain conditions terbutryn injury to the crops has been reported.

Environmental conditions may either increase or decrease the phytotoxicity of herbicides. They can increase a chemical's absorption, translocation or phytotoxicity by altering the physiological and morphological condition of the plant. It is known that susceptibility to a given herbicide is not a constant property of a species but varies according to environmental and intrinsic conditions. It is believed that environmental conditions play a major role in terbutryn phytotoxicity.

From a grower's standpoint, an ideal preemergence herbicide is one that would control weeds and then disappear to prevent an accumulation in the soil and injury to succeeding crops. Whether or not terbutryn does this under our conditions is unknown. Therefore the objectives of this study were twofold: (a) to study environmental factors which influence the phytotoxicity of terbutryn, (b) to determine the influence

of soil temperature and soil moisture levels on the dissipation rate of terbutryn in soil.

CHAPTER II

LITERATURE REVIEW

Terbutryn and 2, 4-bis(isopropylamino)-6-(methylthio)-s-triazine (prometryne) are closely related analogs of methylthio triazines. Terbutryn and 2-chloro-4, 6-bis(ethylamino)-s-triazine (simazine) both belong to the same herbicide family, the symmetrical triazines. However, simazine is a chloro-triazine. Considerable research has been conducted on prometryne and simazine, but only a little work has been done on terbutryn. Consequently, part of the literature review is based on prometryne and simazine. Environmental factors have been shown to affect the response of plants to chemicals. Figuerola and Furtick (5) has shown that many climatic and edaphic factors play an important role in the phytotoxicity of terbutryn.

Edaphic Effects

The amount of soil-applied herbicides required to produce a given level of plant response is variable from soil to soil. It has been shown (20) that many herbicides have a lower herbicidal activity in soils high in clay content or organic matter than in soils low in clay content or organic matter. Harris and Sheets (9) failed to find any single physical or chemical property of the soil that reflected either soil adsorption or the effect of soil on phytotoxicity. However, Talbert and Flelchall (17) concluded that phytotoxicity of the triazines

is inversely correlated with organic matter, clay content, cation exchange capacity, and exchangeable bases, moisture equivalent and other factors contribute to or are indicative of colloidal properties. This variation in the initial toxicity of herbicides with soil is presumably caused by differences in the capacity of soils to adsorb herbicides. Warren and Doherty (20) reported that the adsorption of prometryne by five different soils was in the order Starke mucky sand, Warsaw silty clay loam, Tracy sandy loam, Runnymede loam, Princeton sand, For an approximately fifty-fold increase in organic matter from Princeton sand to Starke mucky sand, there was a thirty-fold increase in relative adsorption. Two other conclusions of theirs were (a) organic matter, cation exchange capacity and specific surface were significantly correlated with adsorption and (b) there was very little correlation between clay percentage and adsorption. Several authors (14, 4, 7, 18) reported a positive correlation of s-triazine adsorption with organic matter in the soil.

Day et al. (4) estimated the amount of simazine that caused 50% reduction in growth (GR_{50}) of oats (<u>Avena sativa</u> L) under controlled conditions by bioassay. There was negligible correlation of GR_{50} with pH and clay content. They also concluded that there was a marked interrelationship between organic matter, cation exchange capacity, the equilibrium concentration of simazine in the soil solution and GR_{50} . GR_{50} was more closely correlated with percent organic matter than with any other factor. Harris and Sheets (9) studied the simazine dosage required to reduce fresh weights of seedling oats 50% (ED₅₀) and found the extent of adsorption to be most closely correlated to ED₅₀ values.

Temperature Effects

Temperature has been shown to have a pronounced effect upon a plant's response to a herbicide. Burnside and Behrens (2) reported that increasing soil temperature from 15 to 30°C caused increasing simazine toxicity to corn. Figuerola and Furtick (6) found that wheat plants looked unhealthy and lodged in terbutryn treated soil at 24° C and 32° C soil temperatures. At $7^{\circ}C$ and $15^{\circ}C$, the plants were smaller than at high temperature, but the plants treated with terbutryn were very healthy and dark green in color. Houseworth and Tweedy (12) found that when the temperature was increased from a low level (19°C day 14°C night) to a higher level (29°C day, 24°C night), terbutryn toxicity was increased 1.6 times for oats (Avena sativa L) and 1.3 times for cucumber (Cucumis sativus L). Figuerola and Furtick (5) grew wheat plants at 15° C for 1 week and then exposed the plants to temperatures of 20° C or 5° C for 48 hours before terbutryn treatments. Plants at the 20° C temperature developed injury symptoms in 3 or 4 days and exhibited severe injury symptoms after 2 weeks, whereas only slight chlorosis and stunting occurred when plant was exposed at 5°C.

In general, greater herbicidal activity of triazines has been reported at high soil temperatures than at low soil temperatures. Burnside and Behrens (2) explained this phenomena by the accelerating of both translocation and absorption at high temperatures. Leonard (13) observed that high temperatures enhanced the rate of transpiration and thus favored the translocation of photosynthesis-inhibiting herbicides.

Moisture Effects

The moisture content of soils is frequently reported to have an important effect on the phytotoxicity of a herbicide (12). Simazine has been shown to be more phytotoxic under high soil-moisture conditions than low soil-moisture conditions. The effectiveness of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine) was increased when soil moisture was raised from 25% to 31% (16). Grover (8) evaluated the effect of soil moisture on the phytotoxicity of simazine to oats and found that a three-fold increase in simazine concentration was required to give 50% reduction in top growth of oats at 30% soil moisture when compared to 60% soil moisture.

Houseworth and Tweedy (12) showed that at a high soil moisture level, terbutryn was 1.5 and 1.4 times more toxic to cucumbers and oats, respectively, than at low moisture. Figuerola and Furtick (6) studied soil moisture effects on the phytotoxicity of terbutryn to wheat and found similar results. They concluded that injury to wheat grown on terbutryn treated soil was most severe at high soil water content (75 to 100% of field capacity). Cholorosis and necrosis occurred much earlier in plants grown at high soil moisture levels. At 2.24 kg/ha severe wheat injury was observed at the highest moisture levels, but only slight injury was observed at the lowest moisture level (25 to 50% of field capacity). One of their explanations was that low soil moisture may reduce the effectiveness of terbutryn by limiting its absorption and uptake. Another possible reason is that more terbutryn is available for plant uptake in wet soil compared to a dry soil.

Moisture and Temperature

Interaction Effects

Figuerola and Furtick (6) indicated that soil moisture has an important increasing effect on the toxicity of terbutryn to winter wheat when temperatures are high. Houseworth and Tweedy (12) reported that the interaction of moisture and temperature on toxicity of terbutryn to oats and cucumbers was similar. Terbutryn toxicity was more pronounced at high moisture levels regardless of the temperature; however, most injury occurred when both moisture and temperature were at high levels (29°C day and 24°C night; 75 to 100% field capacity).

Dissipation

Preemergence herbicide should not accumulate in the soil over a long period of time and cause injury to succeeding crops. Wiese et al. (21) found 60% of the applied prometryne remained in the soil after 6 months. However, Sheets and Shaw (15) reported that prometryne residues in four soil types were relatively non-toxic to oats 24 weeks after applying at 16 ppmw. They found that 13 weeks after prometryne application, only the residue from the highest concentrations in a Basket silt loam were still present at phytotoxic levels. No detectable residues at any concentration remained in Yahola sandy loam. The two highest concentrations in Basket silt loam were still present in phytotoxic amounts after 31 weeks. Variable soil moisture and temperature conditions can accelerate or retard the rate of degradation. Youngson et al. (23) studied factors influencing the decomposition of 4-amino-3, 5, 6-trichloropicolinic acid (picloram) in soils and

concluded that at above 55.8% of water-holding capacity decomposition of herbicide gradually decreased. Between 55.8 and 18.1%, decomposition decreased over 40% and a further decrease occurred at 9.4% of water holding capacity.

Holly and Roberts (11) applied triazines in different seasons on the same soil type and studied persistence by bioassay. They found that under conditions of high rainfall, disappearance of simazine was relatively rapid. Aelot (1) found in a simazine degradation study that soil type is unlikely to have a significant effect on the rate of simazine degradation. It would thus appear that environmental factors are more important in this respect than soil differences. Harris et al. (10) showed that the relative rates of decomposition for the triazine herbicides varied with temperature and that no lag period was apparent. He also concluded this is not to imply that a lag period may not exist. The rates of degradation of atrazine and simazine were similar and were more responsive to the effects of temperature than that of 2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine (ametryne). When the residual activities of the 12 herbicides in four soils included in the experiment by Sheets and Shaw (15) were considered, the methylthio-derivatives appeared to be slightly more persistent than the chloro-triazines. Harris et al. (10) reported that warm moist climates promote disappearance of triazine herbicides from soils and persistence is more prolonged in cold, dry climates. Burschel (3) showed that the half life of simazine in soil varied indirectly with temperature; at 25°C 50 percent of four ppm disappeared in 20 days, at 18°C in 39 days, and at 8.5°C in 140 days. Wilson and Cole (22) compared the effects of three watering schemes on the persistence of atrazine. Persistance

was greatest in soil that was watered to field capacity once each week, intermediately persistent in soil that was watered to field capacity every 3.5 days and least persistent in soil that was watered daily to field capacity. Soil moisture and soil temperature influence activity of soil microorganisms that degrade herbicides.

CHAPTER III

METHODS AND MATERIALS

In reviewing the literature, there appear to be many complex factors and interactions among factors that can influence the degree of phytotoxicity of terbutryn to wheat or sorghum. Seasonal response are well documented, but experiments under carefully controlled conditions are needed to more fully eludicate the factors involved. This study was directed at studying the effect of soil, temperature, and moisture, separately, and in combination on the phytotoxicity of terbutryn.

A preliminary study evaluating six species showed wheat is a good bioassay species for terbutryn (see Chapter IV). All bioassays were conducted in a growth chamber with the air temperature at 21.1° C. The light intensity was 16140 lux for 12 hours and 21520 lux for another 12 hours of a day. The light was supplied by eight fluorescent tubes and twelve 50 W incandescent bulbs. Fresh weight of foliage was taken 21 days after germination. During the 21 day growth period the plants were fertilized twice with two teaspoons of "Rapid-Gro" solution, which was formulated with 23% N, 19% P₂0₅ and 17% K₂0. To determine the best bioassay species, commercially formulated 80% active ingredient, wettable powder terbutryn was applied to an air-dried Teller sandy loam soil. Terbutryn was dissolved in acetone and diluted to the desired concentration with one liter of water. The terbutryn was mixed into the soil by putting 1000 g of soil into a plastic bag, adding the

terbutryn solution, and then mixing thoroughly with hand-shaking. The soil treatment for a given concentration was mixed in several small amounts of soil and the soil was finally mixed together. In all experiments terbutryn was incorporated with the same hand-mixing method. At least 3 replications were used throughout the studies. Sixteen wheat seeds (Var. Nihoma) were planted in different amounts of soil in different containers depending on the study. One hundred and eighty ml polystyrene foam cups were used in the bioassay and degradation studies. Solid plastic cups with 11 cm diameter and 8 cm depth were used when water baths were used. When the plants were 3 cm tall, the stand was thinned to the 10 most uniform plants. Adequate amount of water was added every 12 hours to provide optimum growth except in the moisture-controlling studies.

Soil Factors Studies

In order to determine the influence of soil texture on the activity of terbutryn, wheat was planted in soils with different textures. Model soils of different textures were prepared by diluting Altus Hollister and Tillman clay loam soil with river sand. Combinations of 100% Altus soil, 75% Altus and 25% sand, 50% Altus and 50% sand, 25% Altus and 75% sand, and 100% sand were used. Each of these soil textures was treated with 0.1, 0.25, 0.5, 0.75 and 1.0 ppm of terbutryn and bioassayed. In another experiment samples of soil from Stillwater, Perkins, Altus, Tipton, Chickasha, Stratford, and Ft. Cobb, Oklahoma were collected and used for treatment with 4 rates of terbutryn and a check. The characteristics of these natural soils are described in Table I.

TABLE I

Material	Organic Matter %	Cation Exchange Capacity (mequiv/100g)	е <u>Ме</u> рН	chanic Clay	al Ana Silt	<u>lysis</u> Sand
Port silty clay loam	1.6	14.6	6.4	46	28	26
Teller sandy loam	1.2	7.3	6.6	20	20	60
Reinach silt loam	1.2	12.9	6.8	26	42	32
Tipton silt loam	1.2	12.4	7.6	22	28	50
Hollister and Tillman clay loam	1.5	25.5	7.5	44	36	20
Stidham fine sandy loam	0.7	3.1	5.2	9	12	79
Dougherty fine sandy laom	0.7	3.3	6.5	7	8	85
Cobb fine sandy loam	0.6	3.0	6.0	9	4	87

CHARACTERISTICS OF THE DIFFERENT NATURAL	SOILS
--	-------

The herbicide concentration which caused 50% inhibition of growth (GR_{50}) was determined for each soil type. The GR_{50} is considered to be the herbicide concentration required to inhibit plant growth by 50% as compared to untreated plants. It was derived by plotting the fresh weight as a percentage of the untreated check plants against the logarithm of the herbicide concentration. The antilogarithm of the point on the concentration axis that corresponded with the point of intersection of the curve and the 50% yield level gave an estimate of the GR₅₀ in ppmw. In order to verify the varying adsorption due to soils textures, adsorption isotherms of Port silty clay loam, Teller sandy loam, Tipton silt loam, Hollister and Tillman clay loam,

Dougherty fine sandy loam and Cobb fine sandy loam soils were determined. Adsorption of the herbicide was determined by mixing a solution of C¹⁴ labelled herbicide with soil. The radioactive herbicide was diluted with unlabelled compound in order to obtain appropriate counting rates. Solutions of varying herbicide concentrations and aqueous CaCl, were prepared. Ten gm dry weight of soil was placed in 50-ml glassstoppered centrifuge tubes and 10 ml of herbicide solution were added. Herbicide concentrations used were 0.25, 0.5, 0.75, 1, 2, and 4 ppmw. The tubes were shaken for 12 hours under constant temperature conditions (25°C). Preliminary experiments had shown that 12 hours is sufficient time to reach the adsorption equilibrium. Shaking was followed by centrifugation at 2500 rpm for 20 min at 25°C. One half m1 of the supernatant was transferred into scintillation vials containing 20 ml of scintillation fluid. The scintillation fluid was a mixture of 770 ml each of xylene and p-dioxane, 464 ml ethanol, 160 g of napthalene, and 10 g of ppo (p-bis)o-Methylstyryl)-Benzene). The radioactivity was measured with a Beckman scintillation counter for 10 min on two seperate counting channels. The counting efficienty was 80%. By comparing counts of the solutions added to the soil with counts of the supernatants, the equilibrium concentration was computed. It was assumed that the difference in concentration was due to adsorption. The distribution coefficient (Kd) was defined as the ratio of the amount of ¹⁴C terbutryn adsorbed to the amount remaining in the solution at equilibrium. The Kd values were calculated from the counting data with the following equation.

Kd= count/min standard-count/min equilibrium solution X ml of solution count/min equilibrium solution X ml of adsorbent

Temperature Studies

In the temperature study, soil temperatures were maintained at three different levels with water baths: 10, 21.1, and 32.2^oC. Terbutryn was incorporated throughly into a Teller sandy loam soil by hand-mixing as mentioned before.

Both a susceptible species (wheat) and resistant species (sorghum) were planted. The rates of terbutryn in soil planted with wheat were 0.5, 1, 2, and 3 ppm. The rates for sorghum were 3, 4, and 6 ppm. Adequate water was added every 12 hours to provide optimum plant growth. The wheat foliage was harvested 3 weeks after planting, while the sorghum foliage was harvested 4 weeks after planting.

Moisture Studies

Wheat was planted in turbutryn treated soil at various moisture levels in a closed system to determine the influence of soil moisture on phytotoxicity. A Teller sandy loam soil was used. A pot of 500 g soil was fully subirrigated and allowed to drain for 6 hours without evaporation. The soil moisture percentage of this pot was determined and used as the maximum moisture level (34.9%).

Soil moisture content at 15 atmospheres was used as the minimum moisture level (7.5%). The three moisture levels used were 25, 50, and 75% of the difference between the maximum and minimum soil water contents. These were 26.2, 17.4 and 8.7% soil moisture respectively. Thus, for example, when the moisture loss from the pot became 25% of the difference between the maximum and minimum, the 25% pots were watered by subirrigation. Plexiglas cups were designed to have uniform vertical density so that a gamma-ray apparatus could be used to

determine the moisture percentage. Soil moisture in each cup was measured on the gamma-ray apparatus twice in 24 hours. The soil moisture content of each cup was computed. Subirrigation of the cups was done if necessary.

Moisture and Temperature Interaction Studies

This investigation was conducted to study the effect of moisture and temperature interactions on the phytotoxicity of terbutryn. Water baths were used to maintain two different soil temperature levels: $15.6^{\circ}C$ and $26.7^{\circ}C$. The available soil moisture was maintained at the desired level by weighing each pot daily and adjusting the moisture as necessary. The two moisture levels were 26.2 and 9.1% soil moisture percentage. The gamma-ray apparatus was used to calculate the amount of water needed to obtain desired soil moisture percentage.

To maintain the 26.2% moisture percentage, the solid plastic cups in which contain 400 gm of Teller sandy loam soil were weighed, sufficient water was added to bring the weight of soil and water to 486 gms. In order to maintain 9.1% soil moisture, the weight was brought up to 442 gms. To correct the calculation for the weight of the growing plants in each cup, extra cups of plants were grown so this plant weight could be determined at 5-day intervals. The weight of the plants were determined by rinsing the soil off and weighing the fresh weight of both roots and tops. The plant weights were considered as daily weighing.

Dissipation Studies

Most of the persistence studies with triazine herbicides have been conducted in the field. The relation of triazine persistence to soil properties and to soil temperature and soil moisture can best be assessed where conditions can be controlled. In order to study the influence of the interaction of soil temperature and soil moisture levels on terbutryn dissipation, treated soil samples were stored in plastic bags at different soil moisture levels and different air temperatures. Bioassay procedures were used to detect terbutryn residues in soils after varying time periods.

Tipton silt loam and Dougherty fine sandy loam soils were used. Plastic bags of terbutryn treated soil at three different moisture levels were stored under three different temperature conditions. At three week intervals after storage, samples were taken and bioassayed for the terbutryn. Each sample for bioassay was placed in a separate plastic bag. The three storage temperatures were approximately 10°C in a cold room, approximately 21.1°C in a laboratory room, and one in a greenhouse in which temperatures fluctuated from 10° C to 60° C during the storage period. Three different moisture levels were air dry soil, soil with 7% water by weight, and soil with 14% water by weight. The moisture was not changed much in bags which were stored in 10°C and 21.1°C. However, the moisture in bags stored in the greenhouse was completely evaporated after ten weeks storage. Therefore, another 7% or 14% by weight of water was added to appropriate bags at that time. The environmental conditions for the bioassays were maintained the same throughout the experiment. The experiment was designed as factorial which contained factors of two soil textures, three storage

temperatures, three different moistures and three different rates.

CHAPTER IV

RESULTS AND DISCUSSION

Preliminary Bioassay Studies

Various species were evaluated as to their usefulness for a terbutryn bioassay (Figures 1 and 2), Wheat and barnyardgrass were injured at herbicide concentration greater than 1/2 ppmw. Oats exhibited some resistence at herbicide concentration up to 3 ppmw but were moderately susceptible to terbutryn. Cucumber was another moderately susceptible species. Sorghum was the most resistant of all plant species tested, and barnyardgrass was the most susceptible species. Barnyardgrass plants were completely killed at 2 ppmw. Although barnyardgrass was more susceptible than wheat, it was too sensitive to be a bioassay species. Oats and cucumber exhibited somewhat more tolerance to terbutryn but were chlorotic and plant heights were reduced at herbicide concentrations greater than 2 ppmw. The response of velvetleaf to terbutryn was sporadic. Wheat was susceptible to terbutryn at herbicide concentrations as low as 0.5 ppmw. Leaf chlorosis and apical necrosis developed after one week. Chlorosis was evident at all herbicde concentrations greater than 0.5 ppmw, and plant height was reduced at 0.5 ppmw. Lodging was observed when the herbicide concentrations were greater than 1 ppmw. Only a slight sorghum plant height reduction was observed at the 4 ppmw concentration.

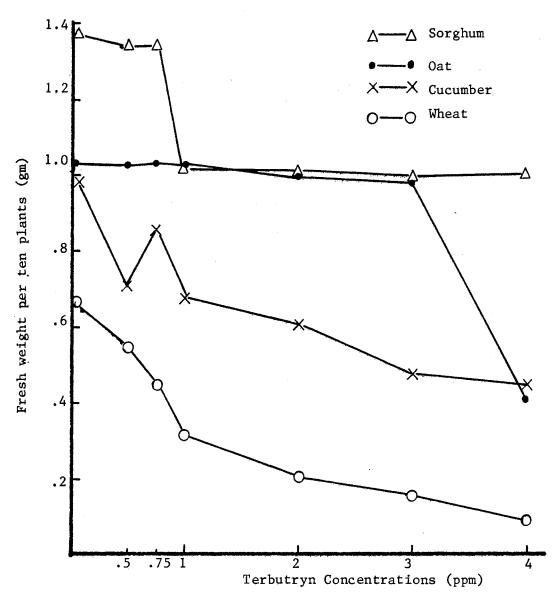


Figure 1, Response of Sorghum, Oat, Cucumber, and Wheat to Varying Terbutryn Concentrations

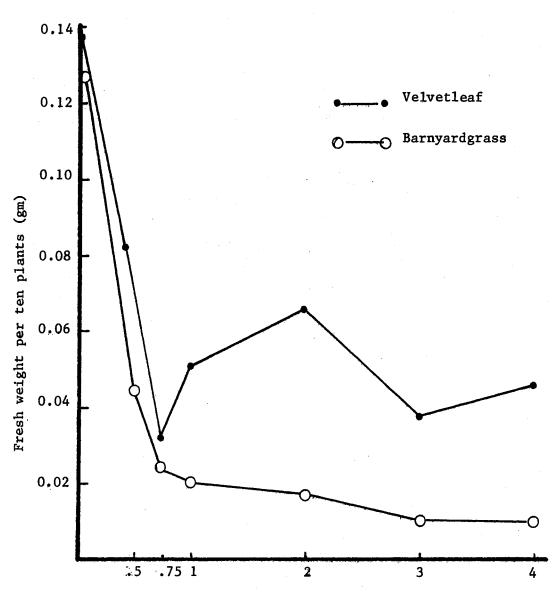


Figure 2, Response of Velvetleaf and Barnyardgrass to Varying Terbutryn Concentrations

On the basis of these results wheat was chosen as a susceptible species and sorghum as a resistant species for future studies. Sorghum was selected because of its resistance to terbutryn at herbicide concentrations greater than 4 ppmw. Wheat showed susceptibility at terbutryn concentration as low as 0.5 ppmw.

Soil Factors Studies

Wheat was planted on five model soils which were prepared by combining different ratios of a clay loam and river sand. Table II shows the response of wheat to terbutryn as affected by model soil texture. It appeared that more terbutryn was needed to cause wheat injury in a clay soil than in the sand-diluted soil. Wheat grown on different textures of natural Oklahoma soils showed similar results. In general, more wheat injury was observed on light soil than on heavy soil. GR₅₀ values of the natural soils are shown in Table III.

Any change in GR_{50} found in different soils might be due to adsorption on the colloidal complex. Figure 3 shows the terbutryn adsorption isotherms found for six natural soils. The curves were drawn on semilog graph paper. The influence of terbutryn phytotoxicity due to soil types may be explained satisfactorily by the difference of adsorption of terbutryn to these soils. Differences in the colloidal properties of soils may exert their influence on herbicidal toxicity through the mechanism of removing part of the herbicide from the soil solution by adsorption. The higher the adsorption of terbutryn to a soil, the higher amount of terbutryn necessary to achieve the same degree of phytotoxicity. Therefore, the higher the GR_{50} value. It is evident from data in Table IV that the

TABLE II

	Terbutryn conc, (ppmw)						GR 50
Model Soils	0	0.1	0.25	0.5	0.75	1	(ppmw)
100% Hollister & Tillman							
clay loam 75% H.T. clay loam and	6.1*	5.7	5.6	4.6	2.7	0.9	0.56
25% river sand 50% H.T. clay loam &	5.0	4.8	4.4	3.1	1.4	0.4	0.46
50% river sand 25% H.T. clay loam &	4.5	5.1	4.3	1.0	0.3	0.2	0.39
75% river sand		4.0		0.3	0.2	0.1	0.21
100% river sand	3.7	1.2	0.2	0,2	0.2	0,1	0.04

BIOACTIVITY OF TERBUTRYN IN FIVE MODEL SOILS

*Data is gms of plant weight obtained from an average of 4 replications which had 10 wheat plants in each replication.

TABLE III

BIOACTIVITY OF TERBUTRYN IN EIGHT NATURAL SOILS

Natural Soils	GR ₅₀ (ppmw)
Port silty clay loam	
Teller sandy loam	1.26
Reinach silty loam	1.24
Tipton silt loam	1.15
Hollister and Tillman clay loam	0.93
Stidham fine sandy loam	0.87
Dougherty fine sandy loam	0.83
Cobb fine sandy loam	0.36

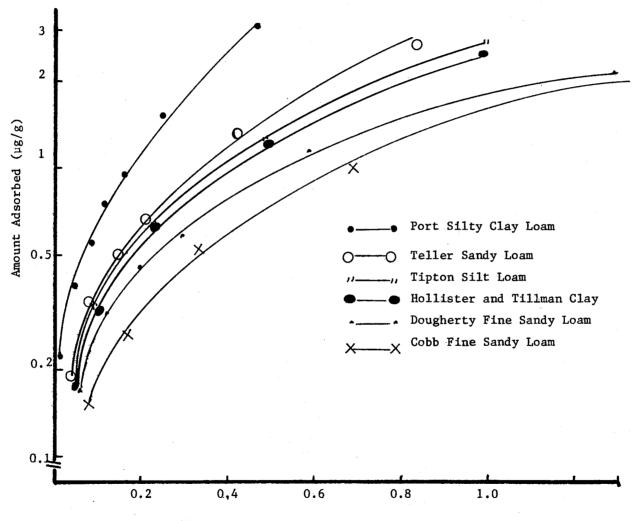


Figure 3. Adsorption Isotherms for Terbutryn by Six Different Soils

trend of GR_{50} values correlated with adsorption of the six natural soils.

TABLE IV

BIOACTIVITY AND ADSORPTION OF TERBUTRYN IN DIFFERENT SOIL TYPES

Soil Type	GR ₅₀ (ppmw)	Kd
Port silty clay loam		6,22
Teller sandy loam	1.26	3.16
Tipton silt loam	1.15	2.56
Hollister and Tillman clay loam	0.93	2.52
Dougherty fine sandy loam	0.83	2.01
Cobb fine sandy loam	0.34	1,55
Cobb fine sandy loam	0.34	1,55

However, GR_{50} and Kd (distribution coefficient) values are not necessarily correlated to soil classifications. The fact that wheat grown in Hollister and Tillman clay loam showed more terbutryn phytotoxicity than in Teller sandy loam or Tipton silt loam indicated that less herbicide was adsorbed in Hollister and Tillman clay loam. This can be shown in comparing the Kd values of these three soils. It is apparent that the order of adsorption on Hollister and Tillman clay loam was in agreement with the order of its GR_{50} value despite its textural ranking

The adsorption isotherm study also revealed that the adsorption of

terbutryn by different soils was generally correlated with the soil organic matter percentage, cation exchange capacity and specific colloidal area. There was little correlation between adsorption and clay content. However, the Hollister and Tillman clay loam adsorbed terbutryn less than both Teller sandy loam and Tipton silt loam, even though its organic matter content, cation exchange capacity, and clay content were greater. One explanation could be the high salt concentration of Hollister and Tillman clay loam (Table V). The salt molecules might compete with herbicide for adsorption sites, so that the higher the salt concentrations of a soil, the less adsorption would take place. In fact, Hollister and Tillman clay loam has a history of being irrigated with water high in total salts. This indicated that the specific available surface of a soil could be an important factor on affecting the adsorption of terbutryn. The results of these studies support the view that organic matter is more adsorptive than clay and that clay has little predictive value about degree of adsorption. Doherty and Warren (20) suggested that correlation coefficients of organic matter percentage, clay percentage, cation exchange capacity and specific surface with adsorption were organic matter, 0.98; clay, 0.35; CEC, 0.95; specific surface, 0.92.

Moisture Studies

The influence of soil moisture levels on terbutryn phytotoxicity is shown in Figure 4. Terbutryn injury to wheat was most severe at high soil water content (26.2%). The plants at this high moisture level developed chlorosis within the first week of growth at rates of 1 ppmw or greater. At 1 ppmw wheat showed severe injury at the highest

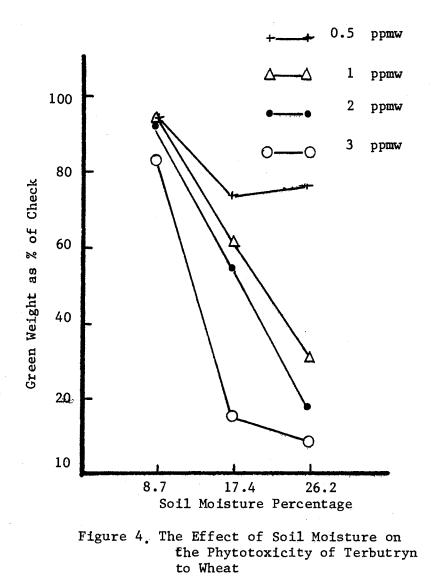
moisture level but little injury at the lowest moisture level. Although plants grown at the lowest moisture level were much smaller, only a slight apical necrosis or lodging occurred on wheat grown at the lowest moisture level even at the 2 and 3 ppmw terbutryn rates. No significant plant growth difference was observed between medium and the highest moisture levels at either the 0.5 or the 3 ppmw of terbutryn. At rates of 1 and 2 ppmw, significant differences were observed among the three moisture levels.

These studies suggest that phytotoxicity of terbutryn is more pronounced at high than at low soil moisture levels. At high soil moisture level not only the phytotoxicity of terbutryn was increased, but the wheat revealed injury symptoms much earlier.

TABLE V

Soil Type	Kd	Salt content (mhos)
Port silty clay loam	6.22	376.5
Teller sandy loam	3.16	110.0
Tipton silt loam	2.56	-
Hollister & Tillman clay loam	2.52	507.2
Cobb fine sandy loam	1,55	309.1

CORRELATION OF SALT CONCENTRATION WITH ADSORPTION



Temperature Studies

Significant differences in terbutryn phytotoxicity were obtained at soil temperatures of 21.1° and 32.2° C (Table VI). Chlorosis and necrosis were the common symptoms observed. At the low soil temperature plants were very healthy, with only slight chlorosis and stunting in the plants treated with the highest rate of terbutryn. Wheat which was treated with 3 ppmw and grown at 32.2° C died 10 days after planting. Injury symptom occurred much later at low temperatures than at high temperatures.

TABLE VI

GREEN WEIGHT OF 3 REPLICATIONS OF WHEAT FOLIAGE AS AFFECTED BY TERBUTRYN AT FIVE RATES OF APPLICATION AND AT THREE SOIL TEMPERATURES

			Soil Tem	peratu		
Rate	10 ⁰ C		21.1°	3	32,2°C	
(ppmw)	(g)		(g)		(g)	
0	5.15	e*	10.97	g	8.36 f	Eh
0.5	5.88	е	8.56	h	7.80 f	Е
1	5.23	e	3.07	bc	4,32 d	1
2	3.63	с	1.66	Ъ	1.69 1	D
3	3.11	bc	0.86	a	0.74 a	a

*Any values in the table followed by the same letter do not differ at the 5% level of significance.

It is evident from Table VI that high temperature caused more terbutryn phytotoxicity to wheat. However, no significant difference was observed between 21.1°C and 32.2°C. Wheat grown at 10°C exhibited increased tolerance to terbutryn.

Temperature had less influence on the phytotoxicity of terbutryn to sorghum (Table VII). Optimum growth was obtained at 26.7° C and 32.2° C. Stunting and chlorosis were the common injury symptoms to sorghum. Plants grew much less at 15.6° C. Plant growth was reduced only at herbicide concentrations of 6 ppmw or greater. Only a few dead plants were observed even at 15 ppmw. The difference between temperatures was because low temperature inhibited sorghum growth. The effect of temperature on terbutryn phytotoxicity to sorghum is -negligible.

TABLE VII

		RATES OF APPL	ICATION*		
Rate	<u>Soil</u> 21.1°C	Temperature 32.2°C	Rate	<u>Soil</u> 15.6°C	Temperature 26.7°C
(ppmw)		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	(ppmw)	**************************************	
0	3.25 a	10.66 c	0	3.35 d	8.64 a
3	3.07 a	10.35 c	6	2.14 e	6.73 b
4	2.52 a	9.60 c	12	1.83 e	4.81 c
6	1.95 b	8.07 d	15	1.57 e	4.59 c

GREEN WEIGHTS OF THREE REPLICATIONS OF SORGHUM FOLIAGE AS AFFECTED BY TERBUTRYN AT FOUR RATES OF APPLICATION*

*Data show two different experiments which were conducted in the same controlled environmental conditions.

Moisture and Temperature Interaction Studies

Studies were conducted in a growth chamber in which environmental conditions were controlled as those listed in Chapter III. The interaction effects of moisture and temperature on terbutryn phytotoxicity to wheat are shown in Table VIII. The data were recorded as percent of checks and corrected to arc sins for statistical analysis data. Both temperature and moisture significantly affected terbutryn phytotoxicity. However, the interaction effects between temperature and moisture had no statistically significant difference at the 5% level. The most severe injury was observed when both moisture and temperature were at the high levels. Apparently the effects of temperature and moisture to terbutryn phytotoxicity are cumulative. The insignificant interaction in these studies does not imply that an interaction of temperature and moisture would not exist in the field, Figure 5 shows this interaction effect by three dimensional drawing.

The effects of temperature and moisture to sorghum are shown in Table IX. No significant effects to sorghum were observed due to either temperature or moisture. Neither was interaction effect. The height of sorghum plants grown in favorable conditions was slightly reduced at terbutryn concentrations 6 and 10 ppmw.

Dissipation Studies

Incubation time, incubation temperature, and soil moisture influence the degradation of terbutryn is shown in Figures 6, 7, 8, and 9 and Table X. Data in Figures 6, 7, and 8 were obtained from averages of all incubation intervals. Wheat was used as indicator plant.

TABLE VIII

THE INTERACTION OF TEMPERATURE AND MOISTURE ON TERBUTRYN PHYTOTOXICITY AS SHOWN BY THE AVERAGE OF FOUR REPLICATIONS OF GREEN WEIGHTS OF WHEAT

Temp, variables	Moisture variables	0		Rates 3/4	(ppi	n) ^a 2	
15.6°C	9.1%	3.17	bc	2.97	bc	2.18 c	
15.6°C	26.2%	4.85	а	3.25	Ъ	1.56 d	
26.7 [°] C	9.1%	2.83	Ъс	1.64	d	1.16 de	
26.7 [°] C	26.2%	3.40	Ъ	1.33	d	0.32 e	

^AValues followed by different letters are significantly different at 5% levels of Duncan's Multiple Range Test. F Values: Rates, 45.44*; Treatments, 34.69*; Temperature, 51.91*; Moisture, 51.33*; Moisture X Temperature, 0.84; Rates X Moisture, 1.36; Rates X Temperature, 0.86.

* Significant at 5% level of F-test.

TABLE IX

THE INTERACTION OF TEMPERATURE AND MOISTURE ON TERBUTRYN PHYTOTOXICITY AS SHOWN BY THE AVERAGE OF FOUR REPLICATIONS OF GREEN WEIGHTS OF SORGHUM

		Ra	tes (pp	nw)
Temp. Variables	Moisture Variabl	les O	6	10
15.6°C	9.1%	1.67	1.31	1.00
15.6°C	26.2%	1.72	0,99	0.72
26.7 [°] C	9.1%	2.64	2.31	2.02
26.7 ⁰ C	26.2%	5.48	4.98	2,54

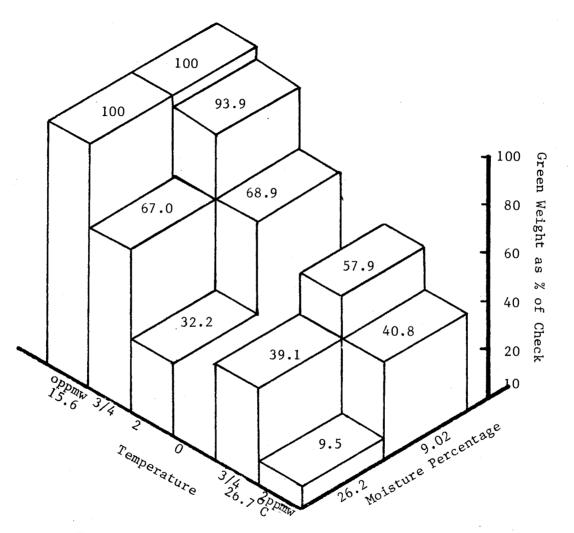


Figure 5. The Effect of Temperature and Moisture on Terbutryn Phytotoxicity

32

.

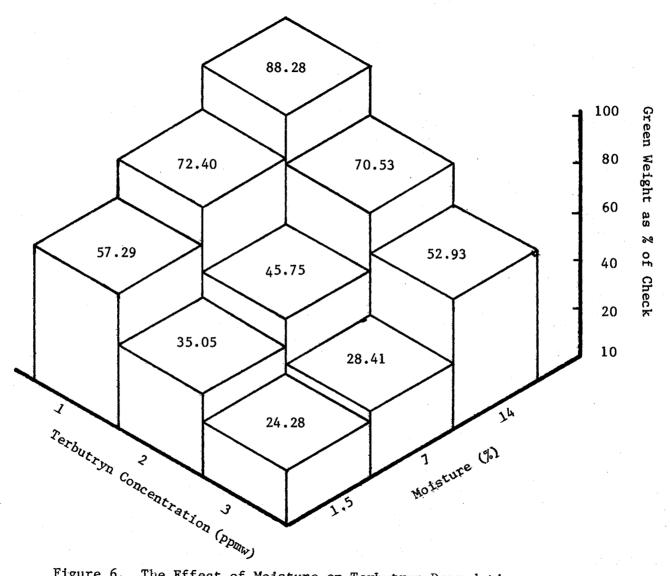


Figure 6. The Effect of Moisture on Terbutryn Degradation

ω ω

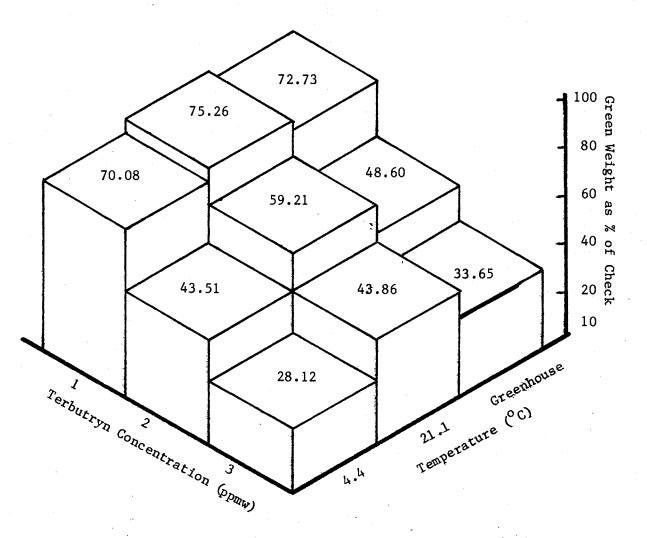


Figure 7. The Effect of Temperature on Terbutryn Degradation

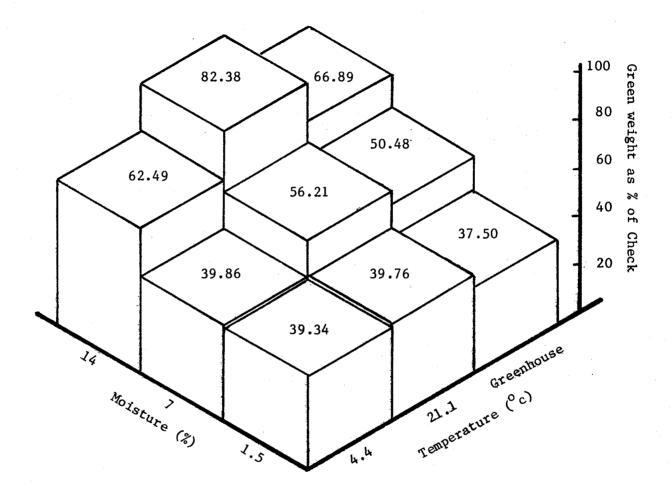


Figure 8. The Interaction Effect of Moisture and Temperature on Terbutryn Degradation

ώ. Un

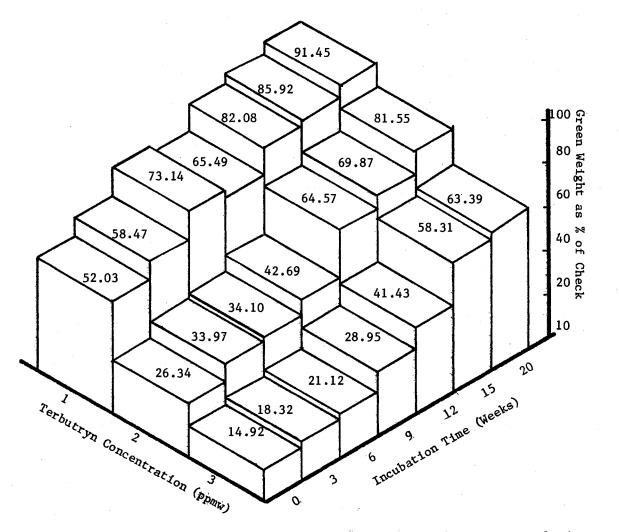


Figure 9. The Effect of Incubation Time on Terbutryn Degradation

TABLE X

ppmw	Treatments			Weeks	of Inc	ubatio	n	
Terbutryn	Soil Variables	0	3	6	9	12	15	20
1	A-1.5%, B-4.4 ⁰ C	52	51	51	53	59	70	73
2		26	24	21	18	46	47	56
3		14	19	17	17	27	37	39
1	A-1.5%, B-21.1°C	52	53	60	39	53	69	70
2		26	24	25	24	38	64	69
3		14	19	11	10	19	44	42
1	A-1.5%, B-gh	52	53	63	50	59	49	65
2		26	27	17	22	36	37	53
3		14	23	18	18	16	39	43
1	A-7%, B-4,4°C	52	57	51	55	58	72	78
2		26	16	13	26	55	51	60
3		14	17	14	16	13	35	47
1	A-7%, B-21.1°C	52	57	88	72	9 9	103	105
2		26	19	20	44	74	80	92
3		14	11	16	19	37	70	71
1	A-7%, B-gh	52	55	90	61	67	90	98
2		26	40	41	47	48	66	81
3		14	18	13	10	23	51	63
1	A-14%, B-4.4 [°] C	52	60	69	91	119	132	110
		26	56	21	48	75	93	99
		14	18	10	34	46	65	66

EFFECTS OF TIME, TEMPERATURE, AND SOIL MOISTURE ON THE DISSIPATION OF TERBUTRYN ON A SILT LOAM SOIL

			•					
ppmw Terbutryn	Treatments Soil Variables	0	3	6	9	12	15	20
1	A-14%, B-21.1 [°] C	52	65	80	78	120	93	112
2		26	60	83	85	138	93	121
3		14	19	64	. 88	127	102	98
1	A-14%, B-gh	52	71	104	86	100	92	108
2		26	36	62	65	67	92	97
3		14	16	23	45	61	78	98

TABLE X (CONTINUED)

^aData are presented as % of check of three replications

A = % of water by weight added to the soil, B = Temperature (gh was under greenhouse condition), D = Time, E = Herbicide levels.

F values: Treatment = 15.85*, D = 77.04*, B = 20.72*, A = 143.34* DXB = 2.82 DXA = 7.08*, BXA = 5.81*, DXBXA = 2.39*, C.V. = 20.44% *Significant at 5% level of F-test Environmental conditions were controlled consistently throughout the whole sampling period as listed in the Methods and Materials section. Data are presented as bioassay growth as % of check, based on the growth of check plants of each sampling date. At 14% soil moisture by weight and at high storage temperatures, no phytotoxic level of terbutryn was observed after 9 weeks of storage. After 20 weeks of incubation the terbutryn had apparently dissipated from soils stored under the following conditions:

7% soil moisture at $21.1^{\circ}C$ (at 1, 2 ppmw); 7% stored in the greenhouse (at 1 ppmw); 14% soil moisture stored at $4.4^{\circ}C$ (at 1, 2 ppmws) 14% moisture stored either at $21.1^{\circ}C$ or in the greenhouse (at 1, 2, 3 ppmws).

Moisture played a more important role than temperature on the rate of dissipation. Soil moisture showed significant influence at 6 weeks of storage. Although temperature did affect the disappearance of terbutryn, significant differences in dissipation of terbutryn due to temperature began to become apparent after 12 weeks incubation. Terbutryn was slightly degraded even in air dry soil at 4.4°C.

Table XI shows the effects of time, temperature, and soil moisture on terbutryn dissipation on Dougherty fine sandy loam soil. The dissipation of terbutryn in this light soil followed the same pattern of that on Tipton silt loam soil. No significant difference was found due to the difference of soil type.

TABLE XI

ppmw	Treatments	Weeks of Incubation ^a							
Terbutryn	Soil Variables	0	3	6	9	15	20		
1	A-1.5%, B-4.4 [°] C	41	38	33	38	47	50		
2		17	24	28	24	39	46		
3		11	12	14	16	21	34		
1	A-1.5%, B-21.1 [°] C	41	31	45	45	46	70		
2		17	24	38	34	29	55		
3		11	11	13	22	21	39		
1	A-1.5%, B-gh	41	36	31	35	36	71		
2		17	20	16	20	23	52		
3		11	17	12	20	14	45		
1	A-7%, B-4.4°C	41	58	51	53	60	68		
2		17	22	19	26	38	57		
3		11	18	13	20	29	40		
1	A-7%, B-21.1 [°] C	41	57	78	81	77	101		
2		17	24	26	32	45	105		
3		11	19	15	17	48	63		
1	A-7%, B-gh	41	54	64	68	78	117		
2		17	39	36	40	66	81		
3		11	10	12	13	43	74		
1	A-14%, B-4.4 [°] C	41	43	44	64	59	78		
2		17	24	37	50	52	77		
3		11	15	12	28	52	54		

EFFECTS OF TIME, TEMPERATURE, AND SOIL MOISTURE ON THE DISSIPATION OF TERBUTRYN ON A FINE SANDY LOAM SOIL

ppm Terbutryn	<u>Treatments</u> Soil Variables	0	3	6	9	15	20	
1	A-14%, B-21.1 [°] C	41	61	80	81	86	98	
2		17	64	85	75	78	91	
3		11	23	65	68	70	75	
1	A-14%, B-gh	41	73	89	79	78	9 4	
2		17	36	67	64	84	78	
3		11	13	17	20	73	71	

TABLE XI (CONTINUED)

^aData are presented as % of check of three replications

CHAPTER V

SUMMARY

Growth chamber studies using wheat and sorghum were conducted to determine the influence of environmental factors on the phytotoxicity and degradation of terbutryn.

Preliminary bioassay studies with several species showed that wheat and barnyardgrass were susceptible to terbutryn at herbicide concentration of 0.5 ppmw; while sorghum was susceptible to terbutryn at herbicide concentration of 6 ppmw.

Many edaphic factors and climatic factors were found to play a role in the phytotoxicity of terbutryn. The phytotoxicity of terbutryn was not closely correlated to soil texture classification. It appears that organic matter percentage, cation exchange capacity, and hygroscopic surface area (salt content of colloids) can only give an indirect guide to degree of adsorption. None of these factors alone would be the best single soil property on which to base recommendation rates for field application. Distribution coefficient (Kd value), which indicates the degree of herbicide adsorption, is a more accurate indicator for the degree of phytotoxicity of terbutryn.

Soil moisture and soil temperature have an important effect on the phytotoxicity of terbutryn to wheat. The effects are additive. The highest degree of terbutryn phytotoxicity was obtained when the soil was at both high temperature and high moisture, which were required for

optimum wheat growth. Soil temperature did not significantly affect the phytotoxicity of terbutryn to sorghum. The interaction study of these two factors also showed no significant effect to sorghum. However, sorghum plants heights were reduced at herbicide concentration larger than 6 ppmw.

At soil incubation temperature of 21.1°C and soil moisture of 7% or 14% by weight, no phytotoxic level of terbutryn in the soil was observed after 20 weeks of incubation. Under air dry soil (soil moisture 1.5%) conditions phytotoxic levels of terbutryn still existed after 20 weeks of incubation. In Oklahoma terbutryn is recommended for sorghum. The farmers might grow winter wheat immediately after sorghum, If low rainfall and low temperature conditions occurred in that year the farmers might need to be cautious about the possibility of terbutryn carry-over. If there is enough soil moisture and high temperature, worry about terbutryn carry-over or residue problem is of doubtful concern.

LITERATURE CITED

- Allott, D. J. 1969. The Persistence of Simazine applied Annually in the Prolonged Absence of Soil Cultivation. Weed Res. 9:279-287.
- Burnside, O. C. and R. Behrens. 1961. Phytotoxicity of Simazine. Weeds 9:145.
- 3. Burschel, P. 1961. Untersuchunger uber das Verhalten Von Simazin im Boden. Weed Res. 1:131.
- Day, B. E. and L. S. Jordan, and V. A. Jolliffe. 1968. The Influence of Soil Characteristics on the Adsorption and Phytotoxicity of Simazine. Weed Sci. 16:209-213.
- Figuerola, L. F. and W. R. Furtick. 1972. Effect of Climatic Conditions on Phytotoxicity of Terbutryn. Weed Sci. 20:60-63.
- 6. Figuerola, L. F. and W. R. Furtick. 1972. Edaphic Factors Affecting the Activity of Terbutryn, Weed Sci. 20:28-30.
- Grover, R. 1966. Influence of Organic Matter Texture and Available Water on the Toxicity of Simazine in Soil. Weeds 15:157-160.
- Grover, R. 1966. Influence of Organic Matter, Texture and Available Water on the Toxicity of Simazine in Soil. Weeds 15:148-151.
- 9. Harris, C. I. and T. J. Sheets. 1965. Influence of Soil Properties on Adsorption and Phytotoxicity of CIPC, diuron, and Simazine. Weeds 13:215-219.
- 10. Harris, C. I., E. A. Woodson, and B. E. Humner. 1969. Dissipation of Herbicides at Three Soil Depths. Weed Sci, 17:27.
- Holly, K. and H. A. Roberts. 1963. Persistence of Phytotoxic Residues of Triazine Herbicides in Soil. Weed Res. 3:1-10.
- 12. Houseworth, L. D. and B. G. Tweedy. 1971. Interaction of Light Temperature and Moisture on Terbutryn Toxicity. Weed Sci. 19:732-734.

- 13. Leonard, O. A. 1967. Action and Effectiveness of Certain Classes of Herbicides. Weeds, 14:237-239.
- Sheets, T. J. 1959. The Comparative Toxicities of Monuron and Simazine in Soil. Weeds. 7:189-194.
- Sheets, T. J. and W. C. Shaw. 1963. Herbicidal Properties and Persistence in Sorts of S-triazines, Weeds. 11:15-21.
- 16. Stickler, R. L., E. L. Knake and T. D. Hinesey. 1969. Soil Moisture and Effectiveness of Preemergence Herbicide. Weed Sci. 17:259.
- Talbert, R. E. and O. H. Flelchall. 1965. The Adsorption of Some S-triazines in Soils. Weeds. 13:46-52.
- Upchurch, R. P. and D. D. Mason. 1962. The Influence of Soil Organic Matter on the Phytotoxicity of Herbicides. Weeds. 10:9-14.
- 19. Upchurch, R. P. 1957. The influence of Soil-Moisture Content on the Response of Cotton to Herbicides. Weeds. 5:112-120.
- 20. Warren, G. F. and P. J. Doherty. 1969. The adsorption of Four Herbicides by Different Types of Organic Matter and a Bentonite Clay. Weed Res. 9:20-26.
- 21. Wiese, A. F., D. E. Lavake, E. W. Chenault and D. T. Smith. 1971. Toxicity and Persistence of Trifluralin, Fluometuron, and Prometryne in Four Soils. Proc. Southern Weed Contr. Conf. 24:365.
- 22. Wilson, H. P., and R. H. Cole. 1964. Effect of Formulation, Rate, and Soil Moisture on Atriaine Persistence. Proc. N. E. Weed Contr. Conf. 18:358.
- 23. Youngson, C. R., R. W. Merkle and J. D. Griffith. 1968. Factors Influencing the Decomposition of Tordon Herbicides in Soils. Down to Earth. 23:3-11.

VITA

Chu-huang Wu

Candidate for the Degree of

Master of Science

Thesis: THE INFLUENCE OF ENVIRONMENTAL FACTORS ON THE PHYTOTOXICITY AND PERSISTENCE OF TERBUTRYN

Major Field: Agronomy

Biographical:

- Personal Data: Born in December 18, 1947, at Tainan, Taiwan, the son of Mr. and Mrs. H. Y. Wu.
- Education: Graduated from the First Tainan High School, Tainan, Taiwan, in 1964; received the Bachelor of Science degree from National Taiwan University, Taipei, Taiwan, with a major in agronomy, in June, 1970; graduate study at Oklahoma State University, August, 1971 to July, 1973.

Experience: Acted as a personnel officer in the Chinese Air Force in July, 1970 to July, 1971; Graduate Research Assistant, Oklahoma State University, September, 1971, to June, 1973.