ENVIRONMENTAL AND SOIL FACTORS AFFECTING THE DISSIPATION, PHYTOTOXICITY AND MOBILITY OF DIPROPETRYN

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CHAPTER I

INTRODUCTION

With present agricultural trends to increase food and fiber quantity and quality, many growers have turned to chemicals for controlling weeds. The s-triazine herbicide family has been found to be a valuable tool for controlling a wide variety of weed species in various crops. Within this herbicide family there are three general structural groups--the chloro-, methoxy- and thio-triazines. Between these groups there is a rather wide range of influence on biological characteristics such as selectivity, physiological activity, persistence and various soil characteristics. There is also variability of many of these aspects within one group.

Prometryn, a methylthio-s-triazine, has been a herbicide used in cotton (*Gossypium hirsutum* L.) for weed control. Its use on sandy soils has resulted in some injury to the crop. Dipropetryn (GS-16068), an ethylthio-s-triazine, is a new herbicide being evaluated for weed control in cotton grown on sandy soils. Initial reports indicate that the ethylthio analog is less phytotoxic to cotton than the methylthio analog.

The purpose of this research was to evaluate some of the physiological and edaphic conditions which affect the biological activity of dipropetryn.

The objectives were:

(1) Compare the inherent phytotoxicity of two thio-s-triazine herbicides (dipropetryn and prometryn),

(2) Determine the influence of environmental factors on dipropetryn phytotoxicity and dissipation,

(3) Determine the amount of dipropetryn absorbed and translocated by various species, and

(4) Evaluate the effects of various soil properties on dipropetryn adsorption-desorption processes and mobility.

CHAPTER II

LITERATURE REVIEW

The s-triazines dipropetryn and prometryn are structurally quite similar (Figure 1). Prometryn is three times more soluble in water than dipropetryn, 48 and 16 ppm respectively. The ionization constants (pK) are similar, 4.05 and 4.30 for prometryn and dipropetryn respectively.

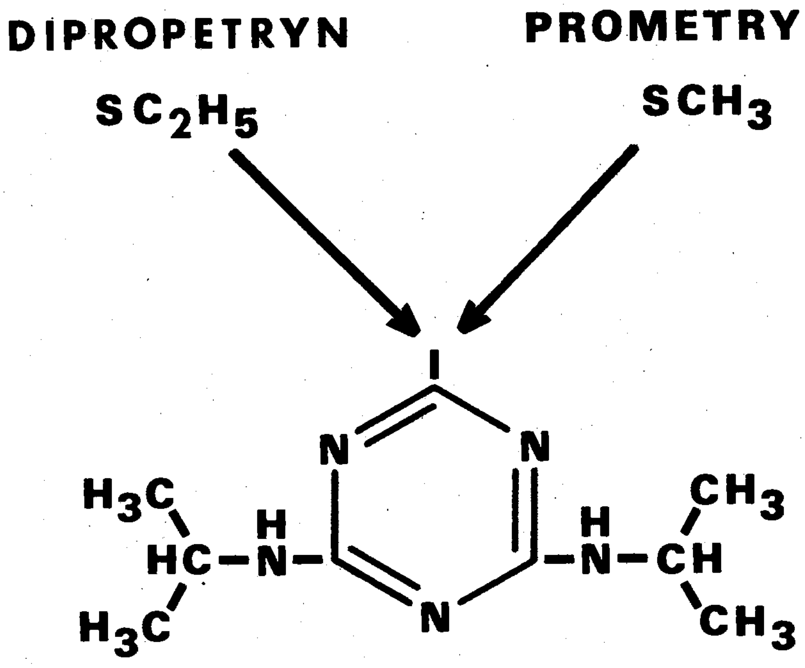

Figure 1. Chemical Structure of Dipropetryn and Prometryn

Differential field activity has been found for these two herbicides. This differential phytotoxicity could be explained under two broad categories--either physiological or edaphic. In practical application there is much overlap and interaction between these categories, and it is therefore sometimes difficult to separate them. Some of the factors more commonly noted to cause differential activity are soil temperature, soil moisture, adsorption by the soil, plant absorption and translocation, plant species susceptibility or resistance, volatility, photodecomposition, and biological and chemical breakdown. At present there has been very little published on the factors affecting dipropetryn phytotoxicity and dissipation; however, much has been published on prometryn and other s-triazines (chemical names for all herbicides reviewed are listed in Table I). Throughout this review most references will discuss the work done with prometryn and other s-triazines.

Triazines are readily absorbed by roots and translocated via the apoplastic system to the shoots. Ashton and Crafts (2)[1] have shown the rate of absorption and translocation was proportional to the amount of water absorbed and/or the transpiration rate. Nishimoto and Warren (27) have shown that root entry of ametryn and diuron by corn (Zea mays L.) and sorghum [Sorghum bicolor (L.) Moench] was important if adventitious roots were present, but less important with adventitious roots absent. Nishimoto et al. (26) have shown different sites of uptake of atrazine by different plant species. Atrazine was more effective on oats (Avena sativa L.) through root exposure and more effective on

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[1] Figures in parentheses refer to Literature Cited.

TABLE I

COMMON AND CHEMICAL NAMES OF HERBICIDES

Common Names	Chemical Names
ametryn	2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine
atrazine	2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine
chloropropham	isopropyl m-chlorocarbanilate
dinoseb	2-sec-butyl-4,6-dinitrophenol
dipropetryn	2-(ethylthio)-4,6-bis(isopropylamino)-s-triazine
diquat	6,7-dihydrodipyrido[1,2-α:2',1'-c]pyrazinediium ion
diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea
fluometuron	1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea
monuron	3-(p-chlorophenyl)-1,1-dimethylurea
picloram	4-amino-3,5,6-trichloropicolinic acid
prometone	2,4-bis(isopropylamino)-6-methoxy-s-triazine
prometryn	2,4-bis(isopropylamino)-6-(methylthio)-s-triazine
propazine	2-chloro-4,6-bis(isopropylamino)-s-triazine
simazine	2-chloro-4,6-bis(ethylamino)-s-triazine

green foxtail [Setaria viridis (L.) Beauv.] through shoot exposure.

Ashton and Crafts (2) have shown that differential phytotoxicity between species can be explained through differential uptake. Differential phytotoxicity of prometryn to cotton and soybeans [Glycine max (L.) Merr.] was due to differential uptake and translocation. Resistance of cotton to prometryn was due to poor translocation, accumulation in lysigenous glands and metabolism. Two days after root treatment, cotton showed 63% of the prometryn in the roots and 37% in the shoots while soybeans showed 23% in the roots and 77% in the shoots. Whitenberg (39) has shown this same accumulation of prometryn by the lysigenous glands of cotton; however, by carbon dioxide collections he showed no ring breakage of prometryn by cotton after a four week period. He suggests that polyphenols may serve as one of the binding or complexing agents for prometryn. Singh et al. (32) has shown that prometryn was more mobile in susceptible species than in resistant plants.

Detoxification of the s-triazines has been shown (8) to occur within both resistant and susceptible plant species. When corn and cucumbers (Cucumis sativa L.) were treated with simazine-C^{14}, it was found that cucumbers produced more carbon^{14} dioxide than did the corn. Since simazine-C^{14} was uniformly labeled in the triazine ring, the evolution of $C^{14}O_2$ must have resulted from splitting the ring, indicating complete decomposition of the basic structure of simazine. The fact that cucumbers metabolize simazine at a more rapid rate than corn illustrates that toxicity is not associated solely with the inability to metabolize the herbicide. Montgomery and Freed (24) have shown that corn metabolizes propazine more rapidly than prometryn. The mechanism in corn responsible for converting chloro-triazines to the hydroxy analog was not active in converting the methylthio-triazines to their hydroxy analog. Corn treated with labeled prometryn did not give off significant amounts of $C^{14}O_2$. Gysin (10) has shown plants that have high peroxidase activity were relatively resistant to simazine and other chloro-triazines. In grasses, such as oats, which do not readily degrade the triazines there is a progressive accumulation of the herbicide from the tip to the base of the blade following root application (2).

Microbiological metabolism or degradation is a significant factor affecting the residual life and toxicity of many pesticides in soils. Soil microorganisms may act upon a pesticide in several ways (21). Gysin (10) has proposed that some soil microorganisms appear to degrade prometryn by oxidation of the methylthio group to a sulfoxide or sulfone. Aspergillus fumigatus has been shown to metabolize simazine (22). A new pathway of metabolism, which does not involve the hydroxy analog reported to occur in higher plants, was proposed for simazine degradation. Murray et al. (25) has shown that A. niger, tamarii and flavus can utilize the methylthio moiety of prometryn as a sulfur nutrient source. They also showed no growth inhibition to fungi cultures at prometryn rates up to 1000 ppm. The methylthio analog of propazine (prometryn) and the methylthio analog of atrazine (ametryn) have a shorter residual activity in general than do the other s-triazines (10). As shown by Gysin (10), the higher solubility of the methylthio triazines cannot be used to explain the rapid breakdown because the methoxy triazines have both higher solubility and persistence.

There has been much research published on triazine interactions with soils. In LeBaron's review (23) the activity and persistence of triazine herbicides in soils were discussed in detail.

The phenomenon of adsorption-desorption directly or indirectly influences the magnitude of the effect, fate and behavior of pesticides in soil systems. Adsorption of s-triazines has been shown to be affected by soil organic matter content (3, 12, 29, 34, 36), soil pH (3, 4, 12, 34, 37), clay content and composition (3, 29, 34, 35, 36, 37), soil temperature (3, 11, 12, 34, 37), herbicide solubility (3, 11, 12, 34), as well as by exchange resins (12, 29, 37) and charcoal (38).

Bailey and White (3) noted reduced phytotoxicity from soils high in organic matter and high in cation exchange capacity. Scott and Weber (29) have shown reduced prometone phytotoxicity to cucumbers when montmorillonite and kaolinite clays and organic matter were added to model soil systems, but no reduced phytotoxicity when an anion-exchange resin was added. Prometryn phytotoxicity was also reduced by additions of montmorillonite clay and soil of high organic matter to growth media (36). Their adsorption isotherms (29, 36) correlated well with phytotoxicity reduction. As shown by Weber (35) the reduction in herbicide concentration resulting from adsorption by soil colloids resulted in less absorption by plant roots. Although the adsorption of the compounds by the soil colloids is in most cases reversible, the decrease in the rate of uptake as a result of the decreased concentration of the free herbicide reduces herbicidal activity of the chemicals.

Harris and Warren (12) have shown that pH, nature of adsorbent and temperature had an effect on adsorption. Other researchers have shown that solubility (3, 11, 12), soil moisture content (3), pore size and pore size distribution (3, 20), and pore-water velocity (20) can affect herbicide adsorption.

Adsorption is an exothermic process while desorption is an endothermic process. An increase in temperature would reduce herbicide adsorption and favor desorption. This phenomenon has been shown by Talbert and Fletchall (34) with prometryn and four other s-triazines, Harris and Warren (12) with atrazine and four other herbicides, Weber et al. (37) with prometone and Harris et al. (11) with prometryn. Harris and Warren (12) have shown that temperature did not affect herbicide adsorption by muck.

The effect of pH on herbicide adsorption has been reviewed extensively (4). Weber et al. (36) showed an increase in prometryn adsorption when the pH was reduced from 6.5 to 4.5. Prometone also showed more adsorption at lower soil pH values (37). The pH will affect the association or dissociation of the herbicide and will therefore affect its adsorption-desorption (3).

There has been disagreement about the effect of solubility on adsorption. Bailey and White (3) have shown that solubility and adsorption were important when comparing closely related herbicides (same family), but were of little use when comparing among different herbicide structural families. Less phytotoxicity was shown (3) in a dry soil than a wet soil when using diuron and cotton. They felt that solubility could be a factor. Harris and Warren (12) also showed no correlation between water solubility and adsorption using five herbicides from different families (chloropropham, diquat, dinoseb, monuron and atrazine). However, Harris et al. (11) showed a lack of relationship between water solubility and adsorption for three similar s-triazines (propazine, atrazine and simazine). Using five s-triazines, Talbert and Fletchall (34) reported that there was greater adsorption of the methoxy- and methylthio- derivatives than there was of the chloro-s-triazine derivatives, indicating there was a direct relationship between water solubility and adsorbability. However, the methylthio- derivatives are also more basic.

The nature of adsorbent has received much research. Bailey and White (3) have shown that aluminum hydroxides and their amorphous precipitates have a positive charge and could act as an exchange site for negative ions. Both atrazine and monuron were adsorbed by anion and cation exchange resins (12). Weber et al. (37) showed prometone adsorption by montmorillonite, but not by kaolinite. X-ray analysis indicated that prometone was located within the clay lattice, but the orientation was uncertain. Prometone was adsorbed by an anion-exchange resin, but to a much lesser extent. In other research Weber et al. (38) showed prometone was adsorbed in small amounts by the Na cation resin and the Cl anion resin and was readily desorbed by deionized water. Talbert and Fletchall (34) showed more adsorption of five s-triazines by organic materials than the clays--illite and montmorillonite. They indicated that even though adsorption by organic material was great the chloro-triazines showed a larger adsorption response to organic materials than did prometone or prometryn. Hayes (13), in a detailed review of adsorption of triazine herbicides by soil organic matter, indicated that soil organic matter is the most active soil component in reducing the phytotoxicity of triazines.

Herbicide mobility in the soil will influence the effectiveness of a herbicide. The extent to which herbicides move in the soil is directly related to the adsorption-desorption characteristics of each herbicide with the soil. Triazine mobility has been shown to correlate well with adsorption (3, 11, 14, 33). As adsorption increases mobility decreases. Adsorption studies have shown prometryn to be the most highly adsorbed s-triazine (9, 11, 34) while mobility studies have shown prometryn to be the least mobile s-triazine (11, 16, 18). Dipropetryn was not included in these studies.

Bailey and White (3) in their review noted less triazine leaching in soils high in organic matter and clay content. Davidson et al. (5) have shown that the non-singularity between herbicide adsorption and desorption relationships were responsible for the concentration distribution in the soil. The non-singularity tends to decrease the maximum herbicide solution concentration as well as increase the length of soil profile over which the distribution occurs. The tailing effect noted for fluometuron, picloram and prometryn in a water-saturated soil was attributed primarily to the non-singularity between the adsorption and desorption processes (6).

CHAPTER III

MATERIALS AND METHODS

Field Study

Field experiments were conducted on the Agronomy Research Station at Perkins, Oklahoma, to evaluate the relative weed control and crop injury potential of dipropetryn. Prometryn was included as a herbicide standard.

Preemergence treatments of 1.12, 2.24 and 3.36 kilograms active ingredient (ai) per hectare (1, 2 and 3 pounds ai per acre, respectively) were applied with an experimental-plot tractor sprayer to the 2.74 by 7.62 meter (9 by 25 feet) plots. A randomized block design was used with three replications per treatment. The soil was a Vanoss sandy loam with a cation exchange capacity of 8.5 meq/100 g, a pH of 5.1 and 1.2% organic matter. The five plant species used were: prickly sida (*Sida spinosa* L.), Texas panicum (*Panicum texanum* Buckl.), soybeans var. Hood, cotton var. Westburn and peanuts var. Spancross. The three crop species were planted in rows 7.62 meters (25 ft) long with 72.6 cm (30 in) centers. The two weed species were planted between the crop species on 76.2 cm centers, giving row spacings of 38.1 cm. On the 29th day after treatment, natural infestations of crabgrass [*Digitaria sanguinalis* (L.) Scop.] and pigweed (*Amaranthus* spp.) were evaluated.

Visual injury ratings were used for evaluation utilizing a scale ranging from 0 (no injury) to 100 (complete plant kill) and expressed as percent injury or percent control. Two ratings were taken, one 15 days and one 29 days after treatment.

Comparative Phytotoxicity

Greenhouse bioassay procedures were used to compare the relative phytotoxicities of dipropetryn and prometryn to eight plant species. Relative phytotoxicities were determined by calculating the GR_{50} for each species (30). The GR_{50} was considered to be the herbicide concentration required to reduce plant growth by 50% as compared to untreated plants. It was derived by plotting the fresh weight of treated plants 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 GR_{50} in ppmw.

Eufaula fine sandy loam soil was used as a growth media. The analysis of this soil is shown in Table II. Various rates of the two herbicides were applied to the soil in plastic bags and thoroughly mixed. To assure a uniform mixture of herbicide and soil and to prevent small "pea sized" clods from containing high herbicide concentrations the soil was then screened through a 2 mm screen and remixed. Styrofoam cups containing 200 grams of treated soil replicated four times in a randomized block design were planted with the following plant species: Italian ryegrass (*Lolium multiflorum*, Lam.), oats var. Cimarron, sorghum var. OK 612, cotton var. Westburn, annual morningglory [*Ipomoea purpurea* (L.) Roth], wheat [*Triticum aestivum* L. (em.

TABLE II

CHEMICAL AND PHYSICAL PROPERTIES OF SOILS AND AMENDED SOILS

	Percent					
Soils and Amendments	Sand	Silt	Clay	OM	CEC*	pH
Quartz sand	100	00	00	0.0	0.4	5.6
Cobb sand	93	4	3	0.6	3.8	7.3
Eufaula fine sandy loam	76	14	10	1.5	5.9	6.4
Teller fine sandy loam	58	23	19	1.3	8.6	5.7
Cobb sand + 2% Muck	93	4	3	2.1	9.0	5.3
Brewer clay loam	27	45	29	2.8	13.5	5.8
Port silty clay	16	42	42	1.8	17.9	6.3
North Carolina Muck	00	00	00	42.3	40.8	3.6

*Meq/100 grams.

Thell) var. Triumph], corn and cucumber var. Improved Longgreen. After emergence these species were thinned to 40, 15, 7, 3, 5, 15, 5 and 5 seedlings per pot, respectively. The seedlings were grown under continuous fluorescent light at a light intensity of 10,222 lux (950 foot-candles) at a temperature of 25° C. Sixteen days after planting the above ground plant parts were harvested and weighed.

Phytotoxicity Determination Without Soil

The absolute phytotoxicity of dipropetryn and prometryn was evaluated by two methods, in nutrient solution cultures and in sand cultures. Soybeans were germinated on absorbent paper matting at room temperature. After root formation the seedlings were transferred to aeriated liter beakers containing Hoagland's nutrient solution (19). Two days after transplanting the nutrient solution was treated with either dipropetryn or prometryn at six levels (0, .25, .5, 1, 2 or 3 ppm). The beakers, replicated three times, contained one liter of nutrient solution which was continuously aeriated and grown under continuous fluorescent light at 10,222 lux. Twelve days after transplanting the seedlings were harvested. Phytotoxic symptoms appeared first and were most severe on the first true leaves. Fresh weights were taken on both the first true leaves and on the plant portion above the cotyledons.

Greenhouse bioassay procedures similar to those previously described were used; however, quartz sand was used for a growth media rather than soil in order to reduce the effect of differential adsorption. Adsorption data for quartz sand is shown in Table XIV. Styrofoam cups containing 375 grams of quartz sand were replicated four times. Sorghum was used as a bioassay species. These cups were treated with seven levels of dipropetryn or prometryn (0, .125, .25, .5, 1, 2 or 4 ppmw). Initial watering of the cups was done with 80 ml of full strength Hoagland's nutrient solution. The growing and harvesting procedures after 16 days were as previously described.

Herbicide Uptake and Translocation

Both a resistant species (corn) and a susceptible species (oats) were used to evaluate differential uptake and translocation of dipropetryn and prometryn. Seeds were pre-germinated before treatment. Round plastic cartons containing 300 grams of quartz sand were replicated three times. The pre-germinated seeds were placed on the surface of the sand and were covered with an additional 100 grams of quartz sand. Six seeds of each species were planted in each cup. After planting C^{14} labeled dipropetryn and prometryn were applied in 75 ml of full strength Hoagland's nutrient solution to give herbicide rates of 2 ppmw. These sand cultures were grown at 30° C under continuous fluorescent light. Seven days after treatment the seedlings were harvested. The sand was washed from the roots with tap and distilled water. Fresh root weights and fresh top weights were taken. Three seedlings from each pot were used for liquid scintillation counting while the remaining seedlings were used for autoradiography. Roots and tops were counted separately. Corn tops and roots and oat tops were homogenized in 5 ml of 95% ethanol. Oat roots were homogenized in 15 ml of liquid scintillation counting fluid and the entire root counted. One liter of scintillation counting fluid contained 5 g PPO (p-bis-o-methylstyryl-benzene), 80 g napthalene, 230 ml ethanol, 385 ml p-dioxane and 385 ml xylene. Each counting vial contained 15 ml.

To insure that the C^{14} counted was the parent herbicide and not metabolites, thin-layer chromatography procedures modified from those described by Abbott et al. (1) and Sikka and Davis (31) were used. The modifications consisted of using chloroform:acetone (9:1) as a solvent system and using plates pre-coated (.25 mm thick) with Silica Gel F-254. The lack of florescence was used to locate the herbicide of standard and extracted samples.

Site of Herbicide Uptake

A divided pot technique modified from that described by Parker (28) was used in greenhouse bioassay studies to evaluate the effects of herbicide placement on plant phytotoxicity. Prometryn was included as a herbicide standard. Zones of herbicide placement in the soil which were compared were shoot, root and seed. The same basic technique was used to evaluate all three; however, the seed zone treatments required a slight modification of the procedure.

One pint waxed cylindrical cartons with perforated bottoms were used. The root zone of 4 cm and the shoot zone of 2 cm contained Cobb sand soil (Figure 2). The neutral zone of 1.5 cm contained untreated coarse quartz sand which was retained on a 600 micron screen. The herbicide levels used were 0, 1.5, 3 and 5 ppmw. These treatments were placed either in the root zone or shoot zone, but never both. The quartz sand served as a capillary water movement barrier between the shoot and root zones. The quartz sand had a larger particle size distribution and lower water retention properties than the soil used, and thus capillary movement of water was lowered. Twelve viable oat seeds which had pre-germinated for 36 hours were placed in the middle of the neutral zone. The root zone soil was watered by sub-irrigation while the shoot zone soil was watered from above. The cartons replicated three times were cultured under the same conditions as previously described. Thirteen days after planting the above ground plant parts were harvested and weighed.

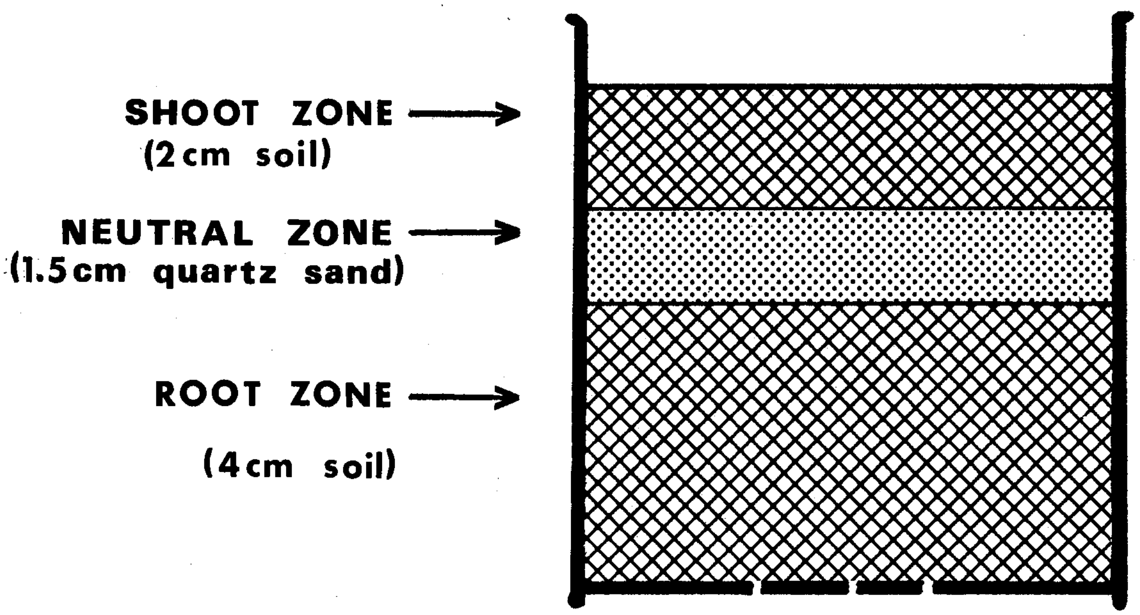


Figure 2. Pot Design Used for Site of Herbicide Uptake Studies

Modification of the procedure was made to determine what effect a treated seed zone would have on the phytotoxicity. The modification consisted of having a treated seed zone of 1 cm above the quartz sand with untreated soil below the sand. No additional soil or sand was above the seed zone. The shoot and root contact in this seed zone appeared to be minimal by examining the seedlings at the end of the experiment. The culturing conditions and harvesting procedures were the same as previously described except these seeds were planted dry and allowed to imbibe soil moisture from the treated area. Also the growth period was 16 days and the treatments were replicated four times.

Effects of Incubation Time, Temperature and Moisture on Dissipation

Greenhouse bioassay procedures were used to determine the persistence of dipropetryn and prometryn in soil samples which had been stored at three temperature levels and two moisture levels. Cobb sand, placed in double plastic bags, was treated with dipropetryn and prometryn and mixed as previously described. Water was added to each bag to bring the soil moisture level to either 5 or 15% by weight. The bags were then stored at incubation temperatures of 10, 25 or 35° C. At specified time intervals after treatment (3, 6, 9, 11, 13 and 15 weeks) samples were removed and bioassayed for residual phytotoxicity. Styrofoam cups (replicated four times) containing 250 g of soil were planted to oats var. Cimarron. Seventeen seeds were planted to each pot with all pots being thinned to 15 seedlings three days after emergence. All growing and harvesting procedures were as previously described. The plants were harvested 18 days after planting and fresh weights taken.

Effects of Soil Moisture on Phytotoxicity

Greenhouse bioassay studies were also used to evaluate the effects of soil moisture levels on dipropetryn phytotoxicity. Cobb sand was treated with dipropetryn as previously described. Varying soil moisture levels were maintained by two methods in two separate studies.

In the first moisture study a watering interval was used to establish different soil moisture levels. The 8 ounce styrofoam cups containing 250 grams of dipropetryn treated soil were replicated four times and planted with oats var. Cimarron. Initially 15 seeds were planted per cup. These cups were thinned to 12 then 10 seedlings per cup on the 5th and 12th day, respectively. On 1, 2 or 3 day intervals the cups were sub-irrigated to field capacity. The culturing and harvesting procedures were the same as previously described. The growth period was 18 days.

The second moisture study used a different method for varying soil moisture. Styrofoam cups containing 250 g of treated soil were replicated four times and planted with oats. Three relative soil moisture levels by weight were obtained by minimum moisture oscillations. After planting all cups were sub-irrigated to field capacity. As the weight of a cup decreased to one of three specified soil moisture levels it was again sub-irrigated to field capacity. The three relative soil moisture levels used were 4, 10 and 16% by weight. The upper and lower soil moisture levels closely approximated the field capacity and permanent wilting point for this soil, respectively. This minimum moisture oscillation was used throughout the bioassay period. The growing and harvesting procedures were the same as previously described. Ten oat seedlings were grown for 16 days to harvest.

Effects of Soil Temperature on Phytotoxicity

Greenhouse bioassay procedures were used to evaluate the effects of soil temperature conditions on dipropetryn phytotoxicity. Cobb sand was treated with dipropetryn as previously described. Round plastic cartons containing 500 g of treated soil were replicated three times and planted with oats. The cups were maintained at one of three soil temperature levels by placing them in thermostatically controlled water baths. Soil temperatures of 12, 24 and 35° C were maintained from two days after emergence of the oat seedlings until harvest. The seedlings were grown for 16 days and harvested as previously described.

Interaction of Soil Temperature and Moisture on Phytotoxicity

Evaluation of soil moisture variables and soil temperature variables on dipropetryn phytotoxicity was determined by bioassay. Double plastic cartons containing 500 g of treated soil, replicated four times and planted with oats, were used. The inner carton had perforated bottoms covered with filter paper to allow for sub-irrigation at specified times. The outer carton was used so that each pot could be placed in a water bath maintained at either 16 or 27° C. The soil moisture levels were 4, 10 and 16% by weight. These relative levels were established and maintained by minimum moisture oscillations as described earlier.

Soil Adsorption-Desorption Isotherms

Differential adsorption-desorption of dipropetryn and prometryn was determined in four naturally occurring Oklahoma soils, in one amended soil and in a quartz sand. The chemical and physical properties of these soils and amendments are shown in Table II.

Adsorption of these herbicides was determined by mixing a solution of C^{14} labeled herbicide with soil in a 1:1 ratio. These isotherms were determined at 26 ± 2^{o} C. Screw cap pyrex tubes (25 by 150 mm) with Teflon seals were used for mixing the herbicide solution and soil. The radioactive herbicide was diluted with unlabeled technical grade herbicide in order to obtain the appropriate counting rates and maintain specified herbicide levels. The herbicide solutions of 1, 2, 4 and 8 ppm were made in .01 Normal $CaCl_2$. Ten grams of soil on an oven dried basis was duplicated for each herbicide rate. Ten ml of appropriate herbicide solution were added to each tube. The tubes containing soil and herbicide solution were shaken for 12 hours on a horizontally set wrist action shaker. Preliminary experiments had shown that 12 hours was sufficient time for soil-herbicide equilibrium to be reached. After shaking, the tubes were centrifuged at 2500 rpm for ten minutes. Duplicate 500 µl samples were transferred from each tube into scintillation vials containing 15 ml of the previously described scintillation fluid. Each vial was then counted for ten minutes in a Beckman liquid scintillation counter.

Desorption was determined on the same samples used for adsorption except that no desorption was determined on the quartz sand. Desorption was done by removing herbicide solution from the centrifuged samples and replacing the removed supernatant with herbicide free .01 Normal $CaCl_2$ solution. Eight successive extractions of herbicide solution and replacement with $CaCl_2$ were made. On the 1st, 2nd, 3rd, 4th, 5th, 6th, 7th and 8th desorption extractions 3, 4, 5, 5, 5, 5, 5 and 5 ml of supernatant, respectively, were removed for a total of 37 ml. Duplicate 500 µl samples of supernatant at each extraction interval were placed in vials and counted. To resuspend the soil after centrifugation a vibrating stirrer (Vortex-Genie) was used. Between each extraction the samples were shaken for 12 hours at 26 ± 2^{o} C.

Herbicide Mobility in Soil

Vertical mobility of dipropetryn was determined by a soil-thin-layer chromatography procedure described by Helling (15, 16, 17) and Helling and Turner (18). Fluometuron was included as a mobile herbicide standard while prometryn was included as a non-mobile herbicide standard. The same natural soils and the one amended soil used for the adsorption-desorption isotherms were used for soil thin-layer chromatography. In addition to these soils, Eufaula fine sandy loam was included. All soils were passed through a 420 micron screen and mixed with distilled water until moderately fluid. Soil thin-layer plates were made by using a conventional thin-layer chromatography-plate-making apparatus. The 20 by 20 cm plates were coated in duplicate with a 1 mm thick layer of each of the natural and amended soils except the Port silty clay which was only .5 mm thick. No binding agents were used with these soils. The plates were air dried at 25^{o} C for six days. Radioactive herbicides, 2 µl (0.02 µC), were spotted in duplicate 1.5 cm from the bottom of each plate. A line was etched 10 cm above the spots to prevent any movement above 10 cm. This was done to facilitate herbicide movement measurements. After spotting, the plates were placed in a conventional thin-layer chromatography tank using water as the solvent system. The lower 0.5 cm of each plate was then immersed in water and chromatographed ascendingly. When the water front reached the 10 cm etched line on the soil plate the plates were removed and air dried for 24 hours. The plates were covered with plastic wrap and placed in contact with X-ray film (Kodak NS2T) for eight days. After exposure the film was developed and herbicide movement measurements taken.

CHAPTER IV

RESULTS AND DISCUSSION

Field Studies

The field studies indicated that dipropetryn treatments resulted in less crop injury than did prometryn treatments (Table III). Cotton and soybeans were the most resistant while peanuts showed the greatest susceptibility to both herbicides. There was little difference in crop injury between the first and second ratings, indicating that permanent injury to the crop occurred. Dipropetryn treatments resulted in less weed control to all four weed species than did prometryn. Texas panicum, the most resistant weed, was not adequately controlled by either herbicide; however, prometryn provided better control than dipropetryn at the 2.24 and 3.36 kg/ha rates. Prickly sida, crabgrass and pigweed were also controlled better by prometryn. Again there was little difference noted in Texas panicum and prickly sida control between the first and second ratings. This differential weed control and crop injury appeared to be rate dependent. When the dipropetryn rates were increased to obtain the same degree of weed control as obtained with prometryn (i.e., crabgrass control with prometryn at 2.24 kg/ha and dipropetryn at 3.36 kg/ha), the amount of crop injury from dipropetryn treatments was equal to or less than that obtained with prometryn treatments (i.e., cotton 10 and 10, peanut 40 and 17 and

TABLE III

THE COMPARATIVE EFFECTS OF DIPROPETRYN AND PROMETRYN ON SEVEN PLANT SPECIES BY FIELD EVALUATION

Herbicide	Rate kg/ha	Species Evaluated													
		Cotton		Peanut		Soybean		Texas panicum		Prickly sida		Crabgrass		Pigweed	
		Days After Treatment													
		15	29	15	29	15	29	15	29	15	29	15	29	15	29
Dipropetryn	1.12	0*	0	20	43	0	0	10	7	10	10	--	20	--	43
Prometryn	1.12	0	3	23	33	3	23	10	10	33	50	--	43	--	73
Dipropetryn	2.24	0	0	23	30	0	10	3	3	20	20	--	43	--	70
Prometryn	2.24	7	10	20	40	3	30	20	23	50	43	--	53	--	93
Dipropetryn	3.36	7	10	20	17	0	7	13	13	20	25	--	53	--	80
Prometryn	3.36	10	27	37	57	33	47	26	27	77	73	--	57	--	87

*Figures represent average percent control of three replications.

soybean 30 and 7 for prometryn at 2.24 kg/ha and dipropetryn at 3.36 ka/ha respectively). This same trend was apparent when making similar comparisons with other weed species. Cotton showed good selectivity with both herbicides, but selectivity to peanuts and soybeans was best with dipropetryn.

Comparative Phytotoxicity

From greenhouse bioassay comparisons as shown in Tables IV and IX, prometryn gave the lowest GR_{50} values for all plant species evaluated except ryegrass, indicating prometryn was more phytotoxic than dipropetryn to these selected species. There was a rather wide range of susceptibility noted among these species. Ryegrass was the most susceptible to both herbicides while cotton was the most resistant. As shown in Tables IV and VIII, the correlation coefficients were .83 or higher and the coefficient of variation ranged from 9.6 to 26.3. The increase in morningglory and cotton growth after herbicide treatment was in agreement with what Ashton and Crafts (2) have reported. At subtoxic concentrations certain triazine treatments have resulted in an increase in chlorophyll content and growth stimulation.

Phytotoxicity Determination Without Soil

The results of absolute phytotoxicity evaluations determined without soil-herbicide influences are shown in Table V and Figure 3. Phytotoxicity of dipropetryn and prometryn to soybeans grown in herbicide treated nutrient solution cultures is shown in Table V. From measurements taken on the whole plant top, dipropetryn was significantly less phytotoxic than prometryn at the .25 and .5 ppm levels.

Dipropetryn gave more plant growth than prometryn at the 1 ppm level, but the difference was not significant. Dipropetryn treatments of .25, .5 and 1 ppm also gave more growth of the first true leaves than prometryn treatments of the same rates; however, only the .25 ppm level resulted in leaf weights which were significantly different.

TABLE IV

COMPARATIVE GR_{50} VALUES OF DIPROPETRYN AND PROMETRYN TO EIGHT PLANT SPECIES

	Herbicide				
	Prometryn			Dipropetryn	
Plant Species	GR_{50}[1/] ppmw	Corr. Coeff.	Diff. in GR_{50}'s ppmw	GR_{50} ppmw	Corr. Coeff.
Ryegrass	.67	.98	.20	.47	.94
Cucumber	.77	.88	2.20	2.97	.77
Sorghum	.80	.92	1.35	2.15	.90
Oats	1.03	.91	.11	1.14	.98
Morningglory	1.25	.87	.90	2.15	.83
Wheat	1.25	.86	4.54	5.79	.89
Corn	9.64	.92	5.76	15.40	.99
Cotton	15.00	.85	17.00+	32.00+	.84

[1/] Herbicide concentration in ppmw required to reduce plant growth by 50% when compared to untreated check plants.

TABLE V

ABSOLUTE PHYTOTOXICITY OF DIPROPETRYN AND PROMETRYN TO SOYBEANS

Herbicide	Herbicide Rate (ppm) 0	.25	.5	1	2	3
			Whole Plant Top[*]			
Dipropetryn	5.4 a[**]	4.0 b	3.8 b	2.2 c	1.8 c	1.5 c
Prometryn	5.4 a	2.1 c	2.2 c	1.5 c	1.7 c	1.8 c
			First True Leaves[*]			
Dipropetryn	1.91 a	1.50 ab	1.23 bc	.74 cd	.79 cd	.72 d
Prometryn	1.91 a	.72 d	.93 cd	.69 d	.86 cd	1.07 b-d

[*] Average fresh weight (grams) of three replications.

[**] Numbers followed by the same letter within each plant portion evaluated are not significantly different at the 5 percent level according to Duncan's New Multiple Range Test.

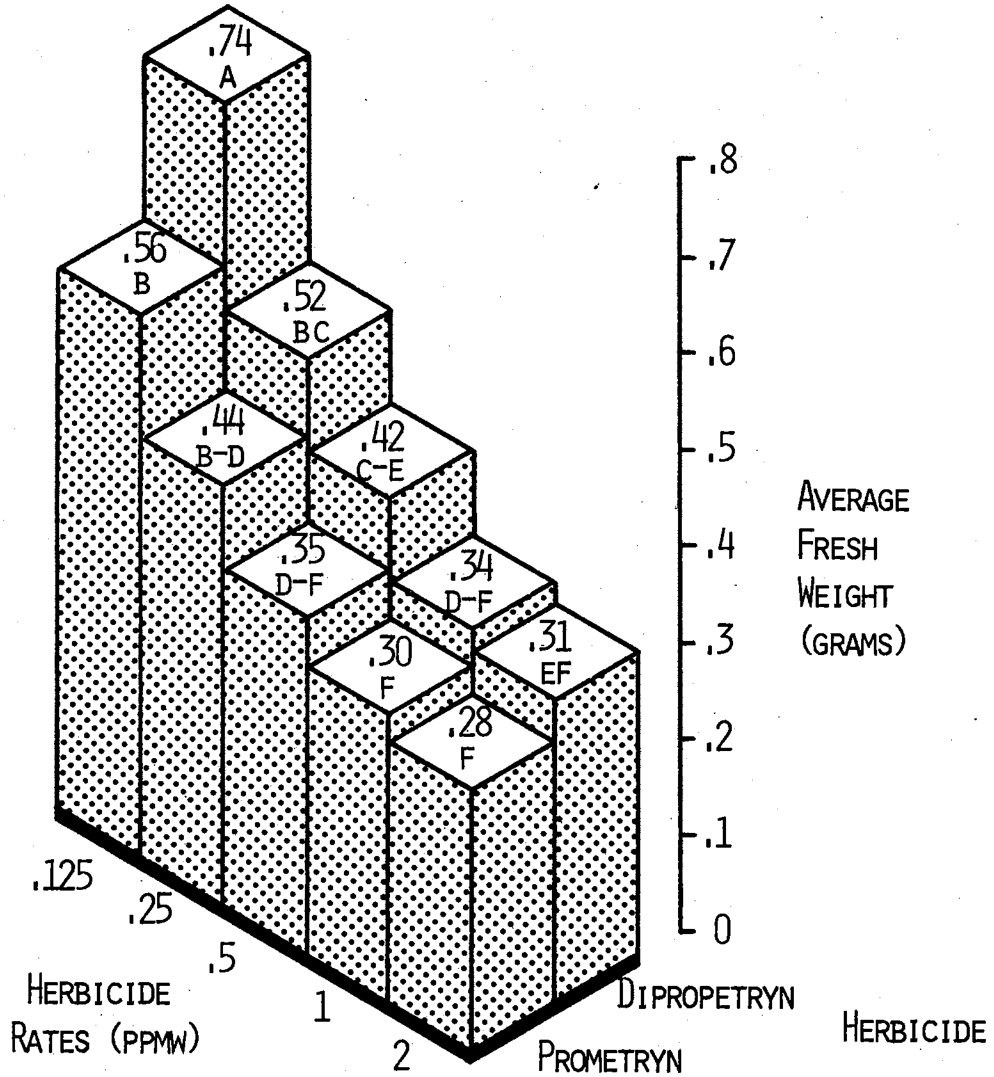


Figure 3. Phytotoxicity of Dipropetryn and Prometryn to Grain Sorghum

Quartz sand cultures of grain sorghum treated with dipropetryn and prometryn were also used for phytotoxicity determinations. As shown in Table XIV, quartz sand adsorbed very little of either dipropetryn or prometryn and was therefore considered to have little or no differential influence on the bioassay study. As shown in Figure 3, dipropetryn allowed more plant growth than prometryn at all five herbicide rates; however, only the lowest herbicide rate resulted in plant growth which was significantly increased.

From these two studies it appears that at the lower herbicide rates dipropetryn was less phytotoxic than prometryn; however, at the higher herbicide levels there was no significant difference between dipropetryn or prometryn. At sub-lethal concentrations, prometryn caused more growth reduction than dipropetryn. The narrow margin of differential phytotoxicity as shown in these last two studies does not explain the wide margin of differential phytotoxicity as shown in the comparative phytotoxicity study.

Herbicide Uptake and Translocation

Thin-layer chromatographic analysis of the ethanol extracts of corn tops and roots and oat tops showed no major metabolites of either herbicide. No spots were apparent on the thin-layer plates except those of the parent herbicides identified by comparing the Rf values (.85 and .91 for dipropetryn and prometryn, respectively) of herbicide standards with plant extracts.

Dipropetryn and prometryn uptake by corn and oats is shown in Figures 4, 5 and 6. The more susceptible oats showed more dipropetryn and prometryn in the tops when compared to corn. There was also more

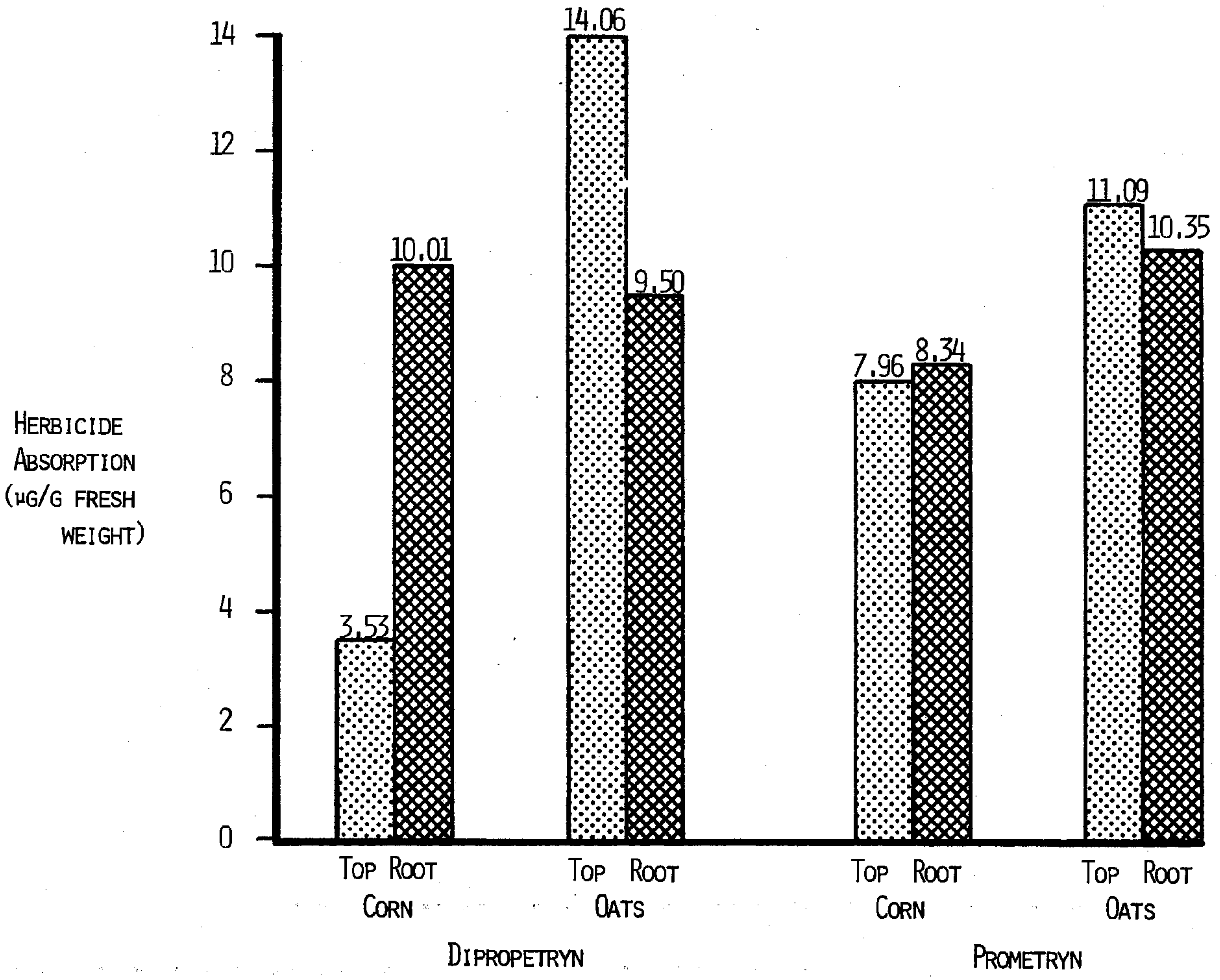


Figure 4. Uptake and Translocation of Dipropetryn and Prometryn

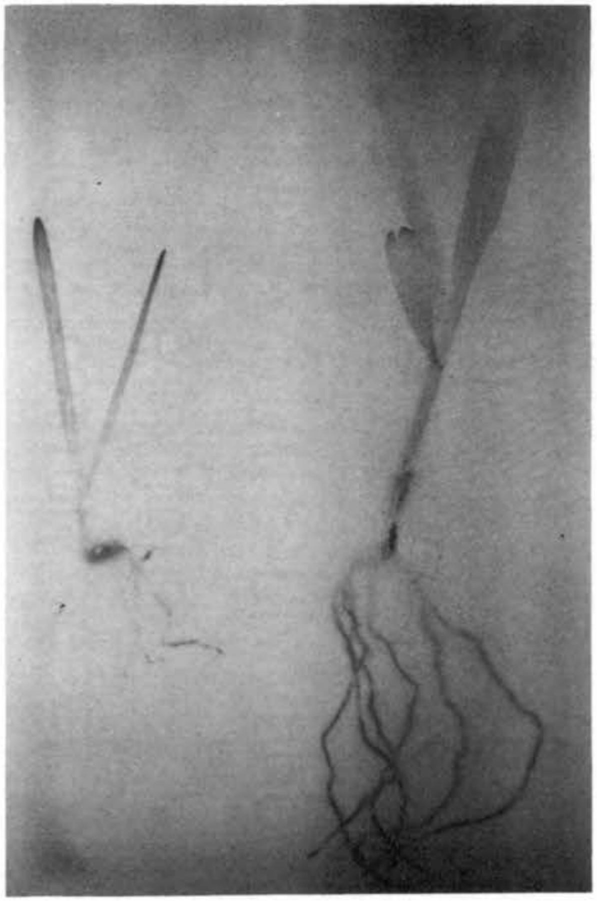


Figure 5. Autoradiograph of Dipropetryn Uptake and Translocation by Corn and Oats

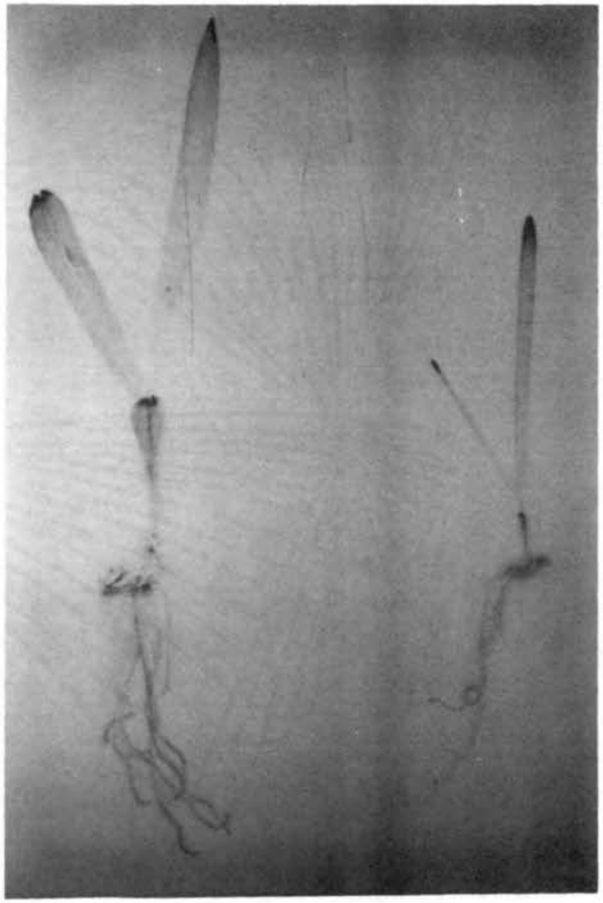


Figure 6. Autoradiograph of Prometryn Uptake and Translocation by Corn and Oats

total dipropetryn and prometryn in the oat seedlings. However, more prometryn than dipropetryn was apparent in the corn tops. There was also more total prometryn than dipropetryn apparent in the treated corn plants. Oats have been shown to be more susceptible to prometryn than dipropetryn (Tables IV, IX, X and XI); however, oats appeared to show more dipropetryn in tops and the total seedling than prometryn.

The autoradiographs (Figures 5 and 6) show less apparent herbicide in the corn tops with dipropetryn treatment than with the prometryn treatment. With both herbicides and crop species there was more herbicide accumulation in the leaf and coleoptile tips than in the whole leaf. The root tips also show more accumulation of dipropetryn and prometryn.

Site of Herbicide Uptake

Both shoot uptake and root uptake of dipropetryn and prometryn resulted in decreased growth or increased phytotoxicity when compared to untreated check plants as shown in Tables X and XI and Figure 7. No one particular site of uptake was apparent with these two s-triazines as no significant difference was shown between the two zones of herbicide placement. Again prometryn was more phytotoxic than dipropetryn regardless of the zone of herbicide placement. There was earlier chlorosis of the oat seedlings with the shoot zone treatments. The chlorosis appeared 2 or 3 days before chlorosis was apparent in the root zone treatments.

Both dipropetryn and prometryn appeared to be more phytotoxic when applied to the seed zone as compared to the root or shoot zone treatments; however, with the modification in the culturing technique the

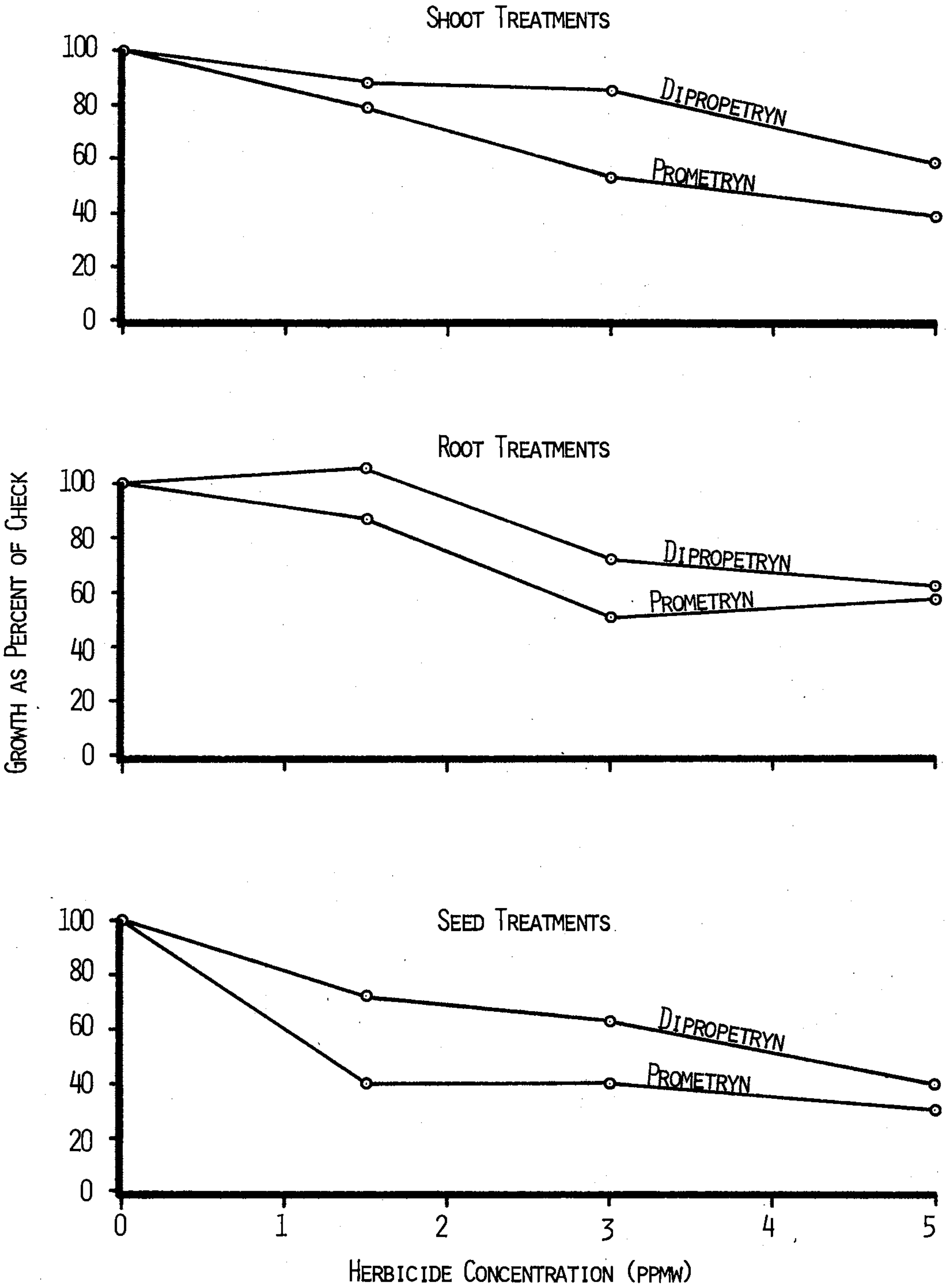


Figure 7. Effects of Herbicide Placement on Dipropetryn and Prometryn Phytotoxicity

actual value of the comparison is not known. Nishimoto et al. (25) also showed proximity to the seed increased the effectiveness of atrazine to oats and green foxtail. Again prometryn was more phytotoxic than dipropetryn.

Effects of Incubation Time, Temperature and Moisture on Dissipation

To illustrate the more important factors affecting dissipation of dipropetryn, three dimensional graphs were used (Figures 8, 9, 10 and 11). The data is in Table XII. There was no statistical difference noted between the dissipation of dipropetryn and prometryn; therefore, only graphs of dipropetryn data will be shown. Throughout this section, dissipation will not necessarily mean complete disappearance of the chemical, but the inactivation or unavailability of dipropetryn and prometryn as indicated by bioassay species.

As incubation time increased phytotoxicity decreased (Figure 8), indicating reduced activity or increasing dissipation with an increase in time. After the 15th week no residual phytotoxicity was apparent from the lowest herbicide rate. As the incubation storage temperature was reduced from 35 to 10° C there was an increase in phytotoxicity (Figure 9), indicating a reduced dissipation rate with a reduction in incubation temperature. There was essentially no dissipation of dipropetryn at the 10° C incubation temperature. As the incubation time increased there was less phytotoxicity noted at the two higher temperatures, indicating increased dissipation as time passed. With the highest incubation temperature no residual phytotoxicity was noted after nine weeks of incubation.

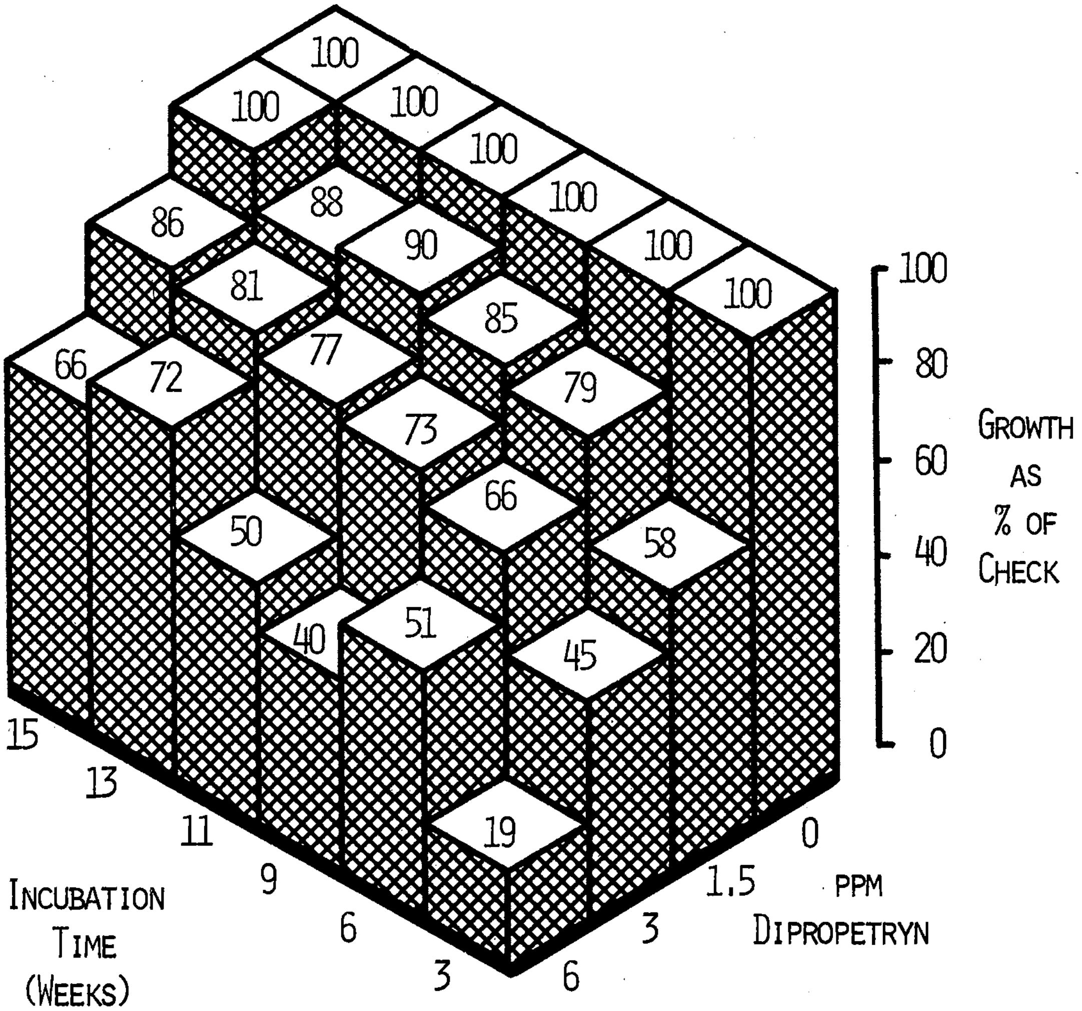


Figure 8. Effect of Incubation Time on Dipropetryn Dissipation

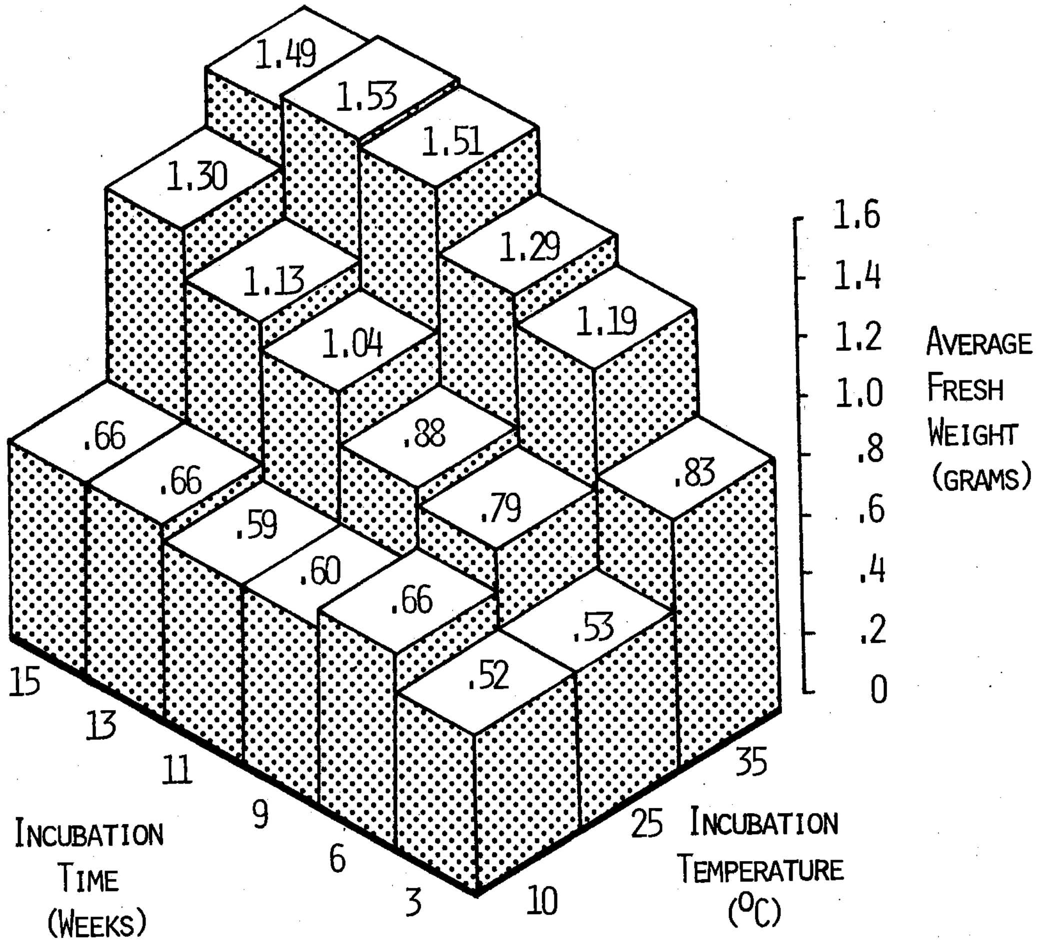


Figure 9. Effect of Incubation Time and Incubation Temperature on Dipropetryn Dissipation

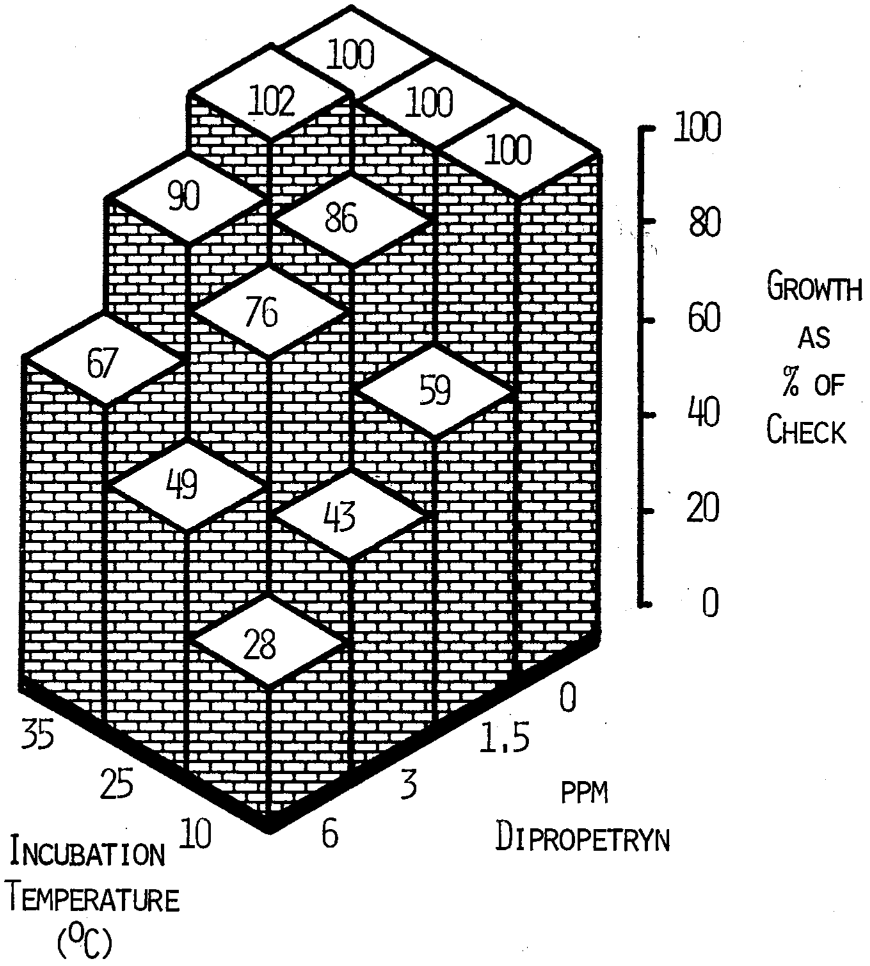


Figure 10. Effect of Incubation Temperature on Dipropetryn Dissipation

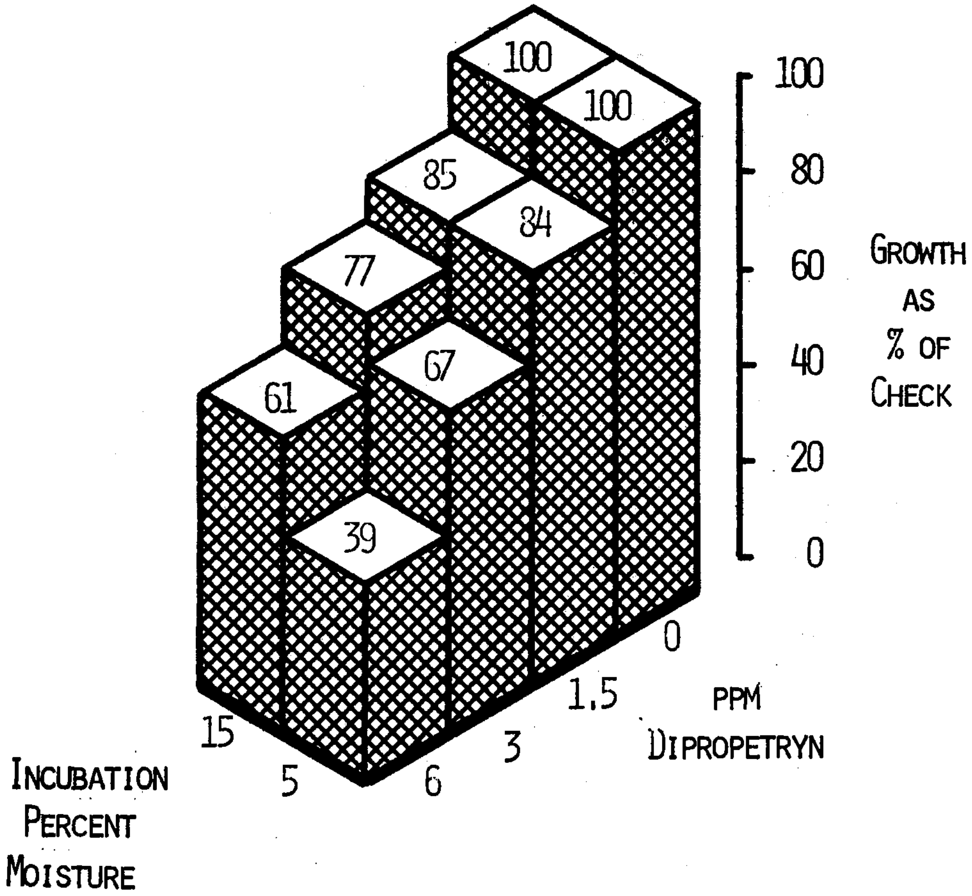


Figure 11. Effect of Incubation Moisture on Dipropetryn Dissipation

The effect of incubation temperature on dipropetryn activity is shown in Figure 10. As the herbicide rates increased, decreased plant growth (increased phytotoxicity) was noted. The higher incubation temperatures resulted in less phytotoxicity at the end of the incubation period than the lower temperatures. The highest temperature and lowest herbicide rate resulted in complete inactivation.

As shown in Figure 11, higher incubation soil moisture reduced residual phytotoxicity or resulted in increased dissipation when compared to the lower incubation soil moisture. The dissipation response to soil moisture content was not as dramatic as soil temperature, but the response to increasing soil moisture content showed a significant increase in herbicide dissipation.

Effects of Soil Moisture on Phytotoxicity

When using watering intervals to establish relative soil moisture levels there was a slight, but statistically significant difference between watering intervals (Figure 12). The watering interval of 1 day (which gave a higher relative soil moisture content) showed less phytotoxicity than the watering intervals of 2 and 3 days.

As shown in Figure 13, an effect of dipropetryn on water usage by oat seedlings was noted. Six days after planting, the water usage of the treated oat seedlings did not increase while the water usage of the check plants increased until the 12th day. This differential water usage was apparent long before any phytotoxic symptoms were noted. Phytotoxic symptoms or chlorosis were noted on the 12th and 13th day after planting.

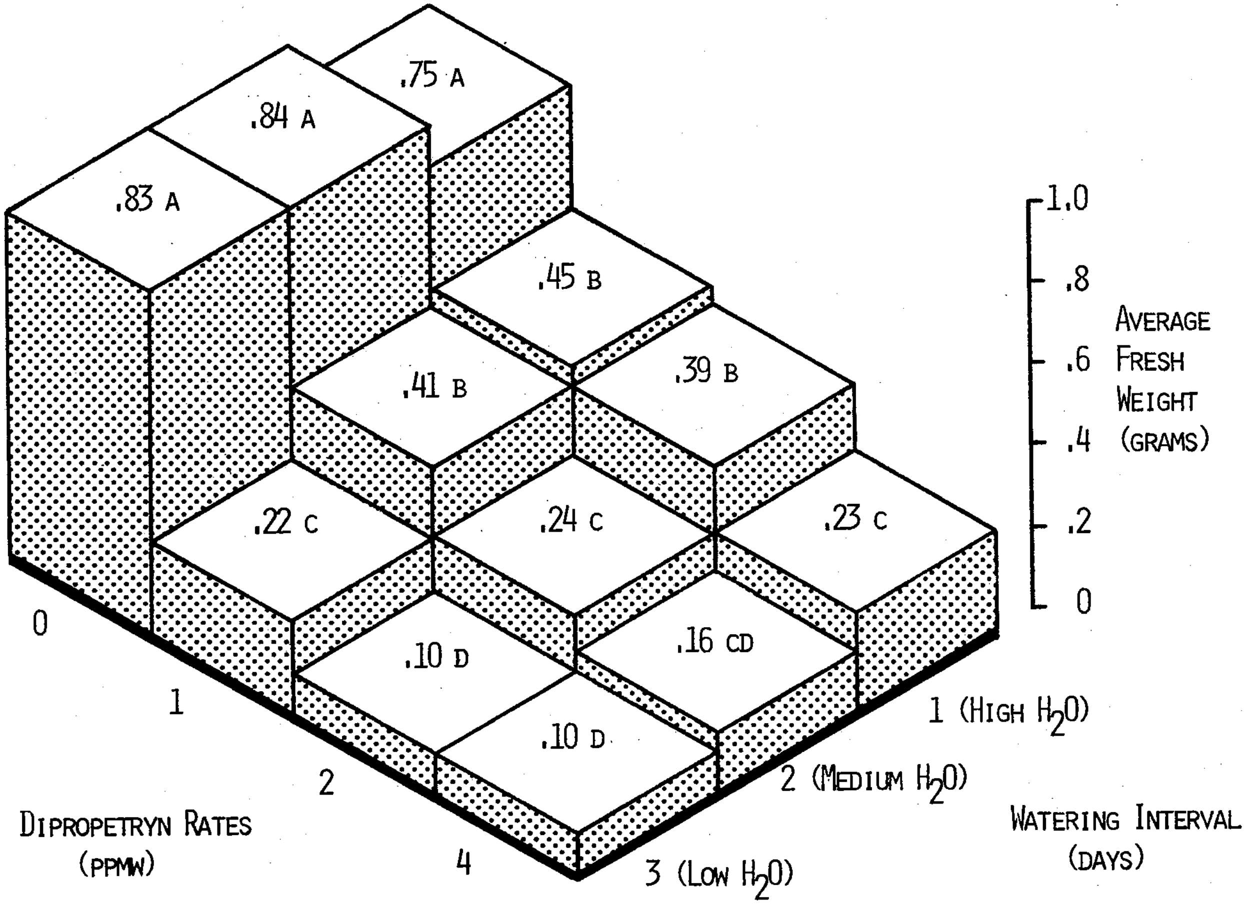


Figure 12. Effect of Watering Intervals on Dipropetryn Phytotoxicity

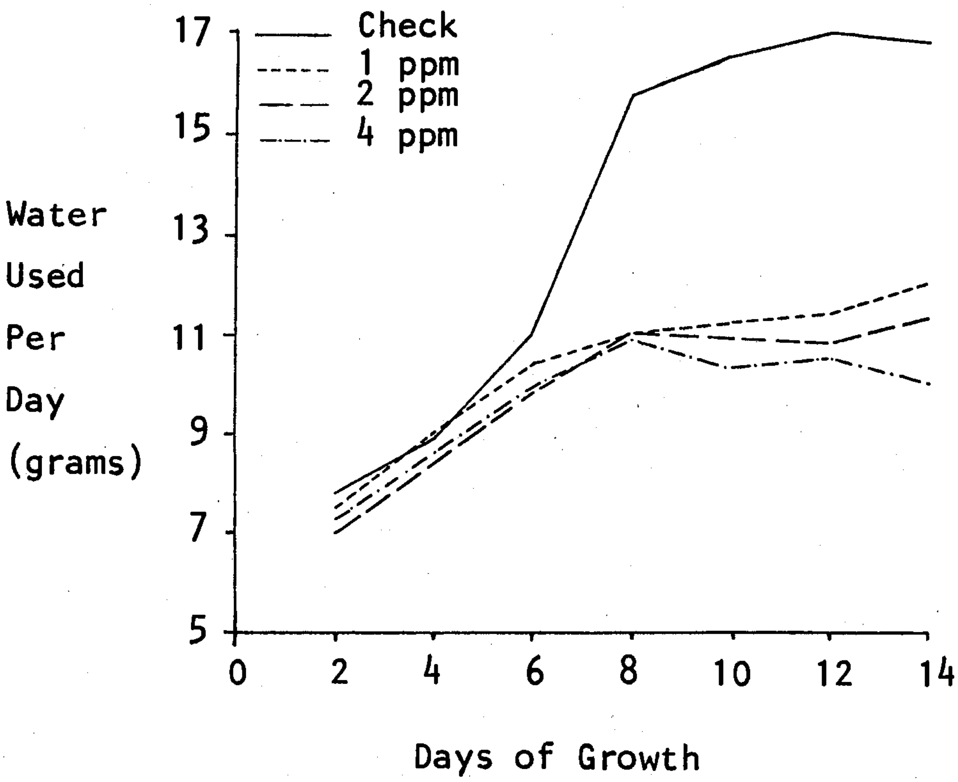


Figure 13. Effect of Dipropetryn on Water Usage by Oat Seedlings

When minimum moisture oscillations were used to establish relative soil moisture levels there was no effect on dipropetryn phytotoxicity (Figure 14). There was increased phytotoxicity with increasing herbicide rates as indicated by reduced plant growth.

Effects of Soil Temperature on Phytotoxicity

As shown in Table XIII and Figure 15, increased soil temperatures resulted in increased dipropetryn phytotoxicity of oat seedlings. There was much less phytotoxicity apparent at the 12° C temperature than at the 24 or 25° C temperatures. Plant growth also decreased with increasing herbicide rates indicating more phytotoxicity. Ashton and Crafts (2) have shown increased root temperatures and herbicide concentration caused an increase in absorption of triazines.

Interaction of Temperature and Moisture

Table VI shows the results of soil temperature and soil moisture interactions on dipropetryn phytotoxicity. As before, soil moisture levels established by watering oscillations did not affect dipropetryn phytotoxicity while soil temperature showed an effect. Dipropetryn phytotoxicity was higher at the 27° C temperature as compared to the 16° C temperature. There was no interaction between relative soil moisture levels and soil temperature as shown in Table VI.

Soil Adsorption-Desorption Isotherms

For equilibrium conditions, several investigators (4, 6) have reported that the relationship between the solution and adsorbed phases of an organic pesticide can be described with the Freundlich equation:

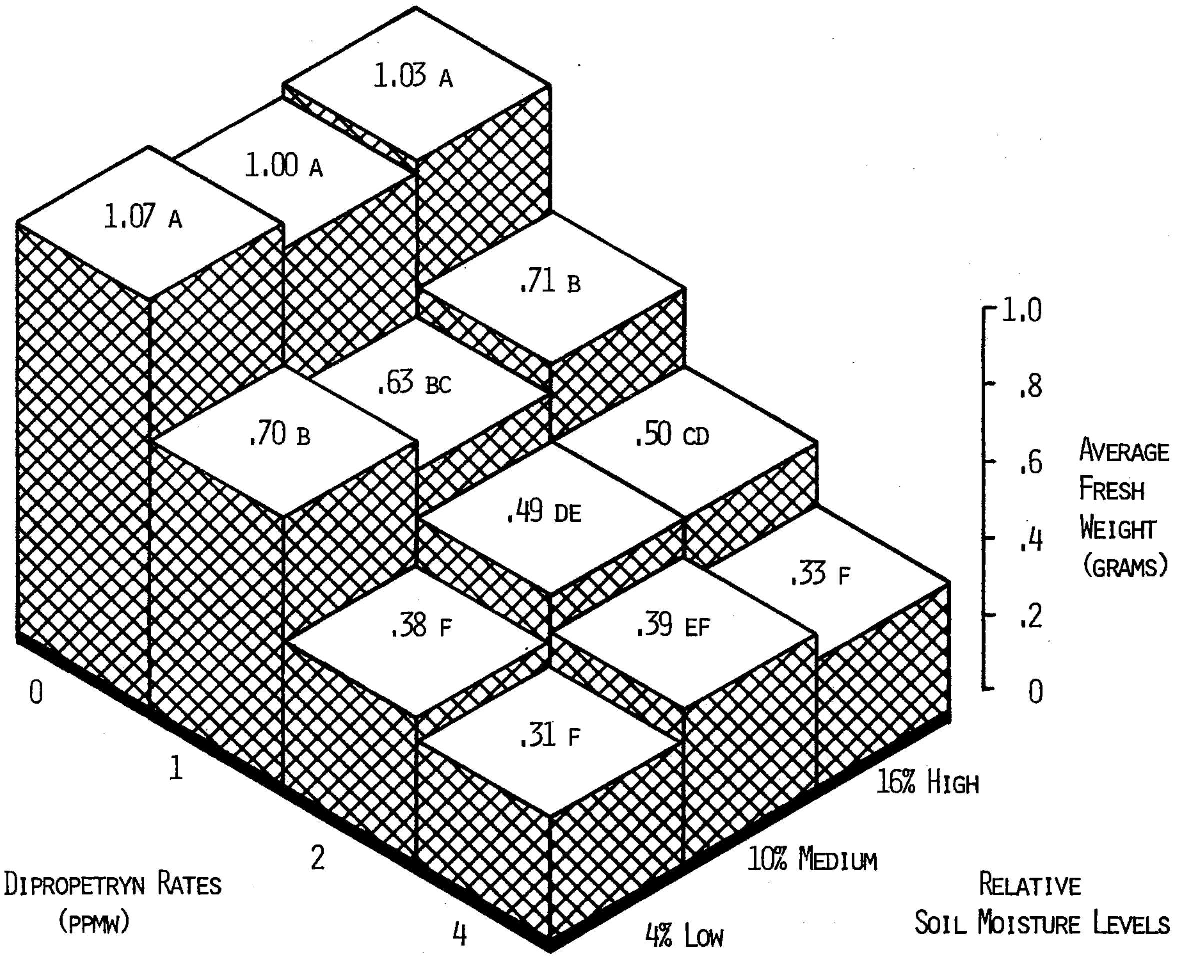


Figure 14. Effect of Relative Soil Moisture on Dipropetryn Phytotoxicity

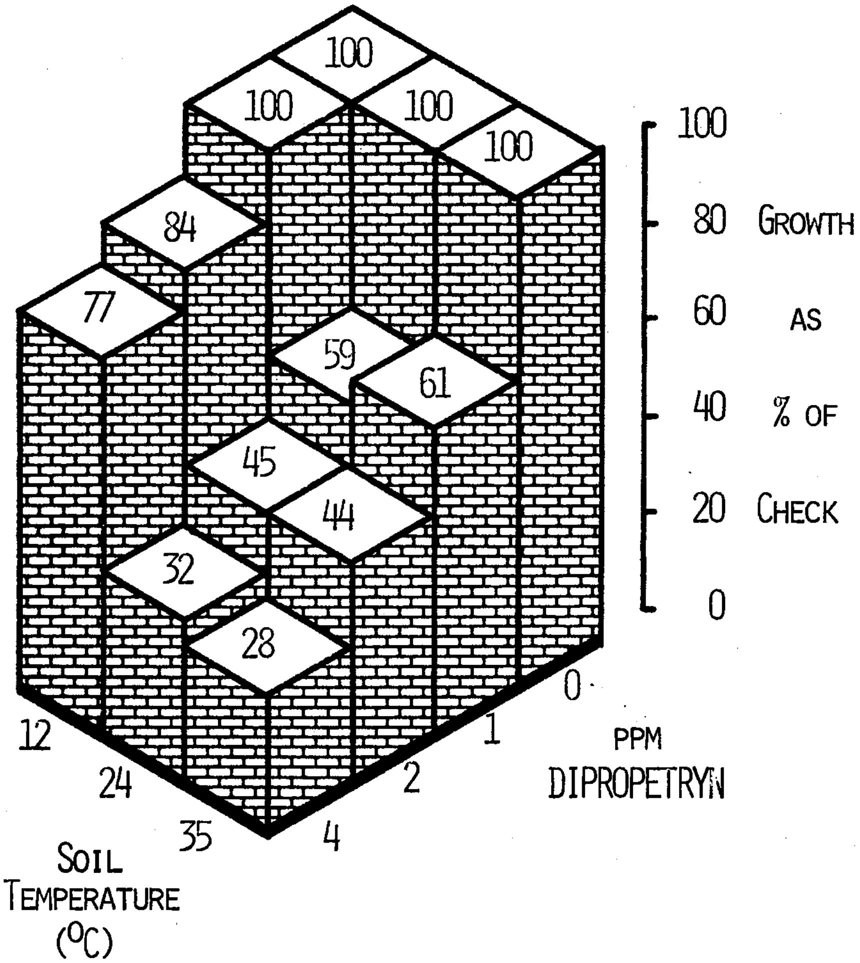


Figure 15. Effect of Soil Temperature on Dipropetryn Phytotoxicity

TABLE VI

EFFECT OF SOIL MOISTURE AND SOIL TEMPERATURE ON DIPROPETRYN PHYTOTOXICITY

Soil Treatment		Dipropetryn Rates (ppmw)			
Percent Moisture	Soil Temperature	0	1	2	4
	°C		*Avena sativa* Growth*		
4	16	1.289 ab**	1.306 ab	1.152 a-d	1.013 de
4	27	1.210 a-c	1.002 de	.725 fg	.506 h
10	16	1.264 a-c	1.086 cd	1.022 de	.986 de
10	27	1.335 a	.867 ef	.585 gh	.470 h
16	16	1.322 a	1.122 b-d	.971 de	.980 de
16	27	1.241 a-c	1.050 de	.653 gh	.597 gh

*Values represent the average fresh weight (grams) of four replications.

**Numbers followed by the same letter are not significantly different at the 5 percent level according to Duncan's New Multiple Range Test. Treatment f = 17.81 (sign. at .05), Temperature f = 150.46 (sign. at .05), Moisture f = 3.66 (non-sign.) and Moisture X Temperature f = 2.28 (non-sign.), C.V. = 12.96.

$$S = KC^{1/N}$$

where S is the adsorbed concentration (μg/g), C is the solution concentration (μg/cm^3), K is the distribution coefficient and N is a constant that varies with the chemical and adsorbent. Equilibrium adsorption and desorption isotherms for dipropetryn and prometryn were described reasonably well by the Freundlich equation. The Freundlich equation values for adsorption are shown in Table XIV and for desorption in Table XV.

Adsorption of dipropetryn by six adsorbents is shown in Figure 16. Cobb sand + 2% muck showed the greatest amount of adsorption with quartz sand showing the least adsorption. This same trend was apparent with prometryn; however, the amount of adsorption was consistently less than dipropetryn as shown in Tables VII and XIV. In general the soils with higher cation exchange capacities and organic matter contents showed more adsorption. Adsorption of dipropetryn by these adsorbents is shown in Figure 16 as being nearly linear with concentration.

When comparing the adsorption of dipropetryn and prometryn to these adsorbents (Soil Characteristics, Table II), dipropetryn was more highly adsorbed than prometryn except with quartz sand which showed little if any adsorption. When looking at the K values or distribution coefficients (Table XIV) the K values for dipropetryn are generally twice as large as the K values for prometryn, except with Cobb sand + 2% muck and quartz sand, indicating more adsorption of dipropetryn than prometryn. Table VII shows the actual amounts of herbicide adsorbed from the four rates used.

When comparing the adsorbents (Tables VII and XIV) the general trend was more adsorption of both herbicides with increasing cation

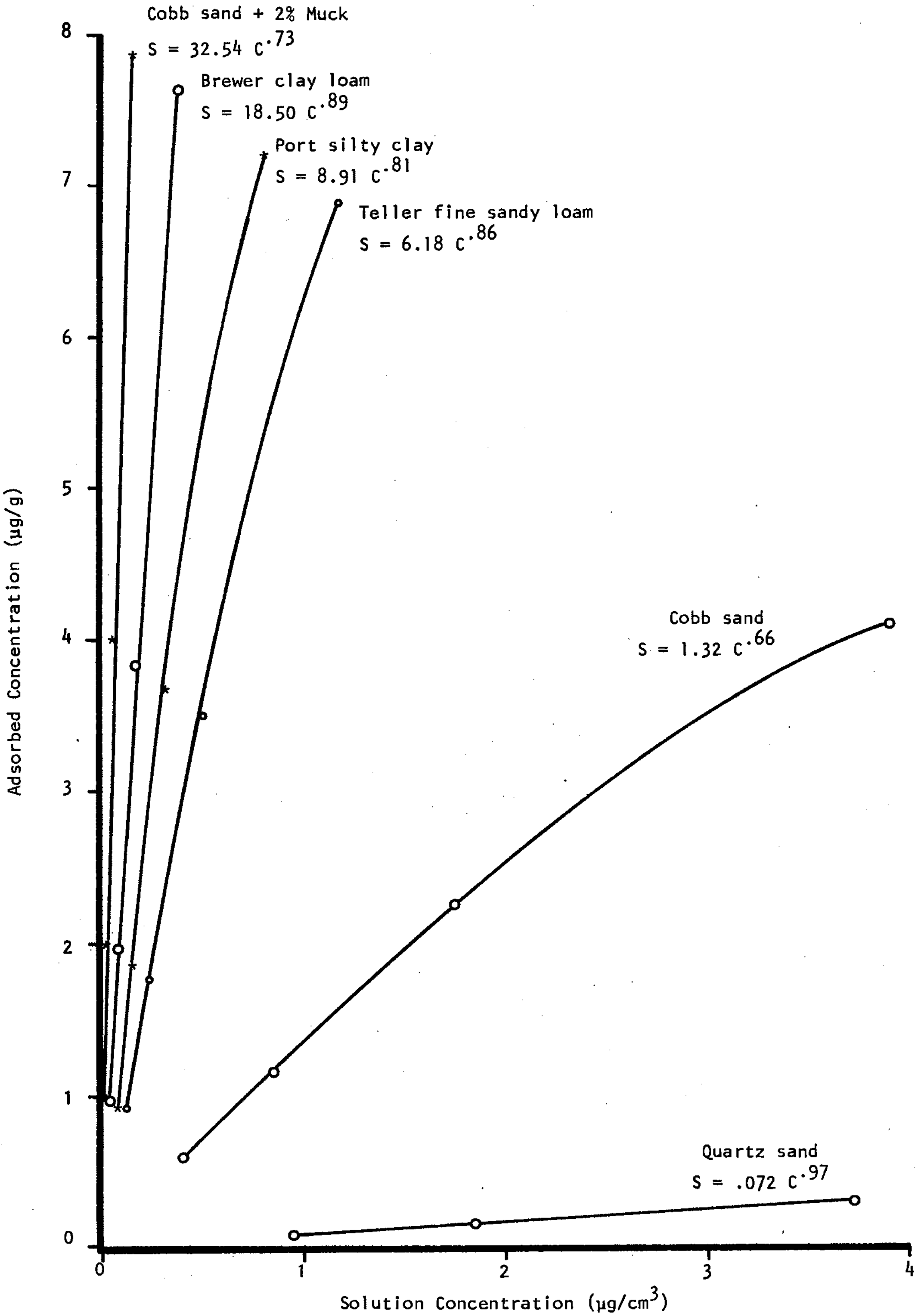


Figure 16. Adsorption of Dipropetryn by Six Adsorbents.

TABLE VII

ADSORPTION-DESORPTION OF DIPROPETRYN AND PROMETRYN BY FIVE SOILS

	Herbicide							
	Dipropetryn				Prometryn			
	Initial Herbicide Concentration (µg/g)							
Soil Type	1	2	4	8	1	2	4	8
Cobb sand + 2% Muck								
Initial Ads.	.99	1.98	3.94	7.87	.99	1.97	3.92	7.80
Solution Conc.	.01*	.02	.06	.13	.01	.03	.08	.20
Ads. after 8 Ext.	.95	1.90	3.78	7.51	.94	1.87	3.69	7.29
Total Des.	.04	.08	.16	.36	.05	.10	.23	.51
% Des.	3.90	3.90	4.10	4.50	4.20	5.00	5.90	6.50
Brewer clay loam								
Initial Ads.	.96	1.93	3.84	7.62	.94	1.87	3.69	7.31
Solution Conc.	.04	.07	.16	.38	.06	.13	.31	.69
Ads. after 8 Ext.	.87	1.72	3.40	6.64	.79	1.51	2.94	5.66
Total Des.	.09	.21	.44	.98	.15	.36	.75	1.65
% Des.	9.90	10.90	11.50	12.90	16.50	19.20	20.40	22.60
Port silty clay								
Initial Ads.	.94	1.86	3.68	7.22	.89	1.73	3.40	6.53
Solution Conc.	.06	.14	.32	.78	.11	.27	.60	1.47
Ads. after 8 Ext.	.79	1.50	2.92	5.56	.66	1.25	2.33	4.38
Total Des.	.15	.36	.76	1.66	.23	.48	1.07	2.15
% Des.	16.00	19.20	20.50	22.90	26.10	27.90	31.50	32.80
Teller fine sandy loam								
Initial Ads.	.89	1.77	3.50	6.84	.84	1.61	3.09	6.08
Solution Conc.	.11	.23	.50	1.16	.16	.39	.91	1.92
Ads. after 8 Ext.	.66	1.27	2.45	4.55	.52	.89	1.64	3.10
Total Des.	.23	.50	1.05	2.29	.32	.72	1.45	2.98
% Des.	26.30	28.40	30.00	33.50	38.20	44.90	46.80	49.00
Cobb sand								
Initial Ads.	.60	1.15	2.25	4.09	.45	.74	1.30	2.60
Solution Conc.	.40	.85	1.75	3.91	.55	1.26	2.70	5.40
Ads. after 8 Ext.	.20	.39	.76	1.31	.13	.13	.19	.38
Total Des.	.40	.76	1.49	2.78	.32	.61	1.11	2.22
% Des.	67.10	66.50	66.20	68.10	70.80	83.00	85.50	85.30

*Concentration is µg/cm^3.

exchange capacity or organic matter levels and decreasing soil pH. Table II shows the chemical and physical properties of soils and amended soils used in this study. Port silty clay had a higher cation exchange capacity than Brewer clay loam, but showed less adsorption of both dipropetryn and prometryn. An explanation of this could be due to the pH of the soil, Port silty clay had a pH of 6.3 while Brewer clay loam had a pH of 5.8. This would be consistent with what Weber (36) reported in that decreased soil pH resulted in increased triazine adsorption. Another explanation would be that Port silty clay had 1% less organic matter than the Brewer clay loam. This would be consistent with what Hayes (13) reported. Cobb sand + 2% muck showed the greatest amount of adsorption of both herbicides while it had only 2.1% organic matter and a cation exchange capacity of 9.0. It should be noted that Cobb sand + 2% muck had the lowest pH and it was an amended soil rather than a naturally weathered soil. The North Carolina muck which was added had a very low pH (3.6) and a very high cation exchange capacity (40.8 meq/100 g). The adsorption of dipropetryn and prometryn by these adsorbents, with their varied cation exchange capacities, pH's and organic matter contents requires that all three factors be considered. It appeared that all three factors resulted in an adsorption response; however, none of the factors alone was held constant. Regardless of the responsible factor, dipropetryn was more highly adsorbed than prometryn.

As shown in Tables VII and XV, less dipropetryn than prometryn was desorbed. The adsorbents showing the greatest amounts of adsorption also showed the least amounts of desorption. Cobb sand + 2% muck desorbed approximately 4% of the dipropetryn adsorbed, while Cobb sand desorbed approximately 65% of the adsorbed dipropetryn. An increase in the percent of dipropetryn and prometryn desorbed as the herbicide rates increased was also noted.

Herbicide Mobility in Soil

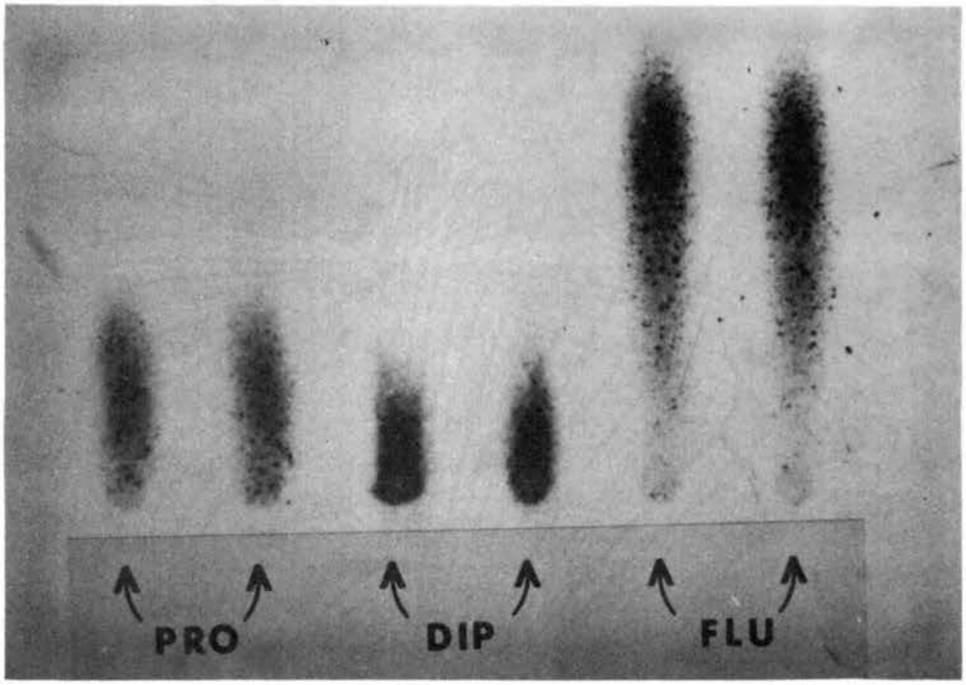
Vertical soil mobility of dipropetryn, prometryn and fluometuron, as determined by soil thin-layer chromatography, is shown in Table VIII. In this study fluometuron was also included as a standard. Differential mobility of these herbicides with the various soils was apparent in that dipropetryn showed the least movement while fluometuron showed the greatest. In general, as the cation exchange capacity, organic matter, and clay levels decreased the mobility of all three herbicides increased. There was good correlation between the adsorption-desorption isotherms and herbicide mobility. Soils showing the highest amounts of adsorption showed the least amounts of herbicide mobility. The Rf values for prometryn from these soil thin-layer plates were similar to the Rf values for prometryn which Hellin (16) and Helling and Turner (18) reported.

TABLE VIII

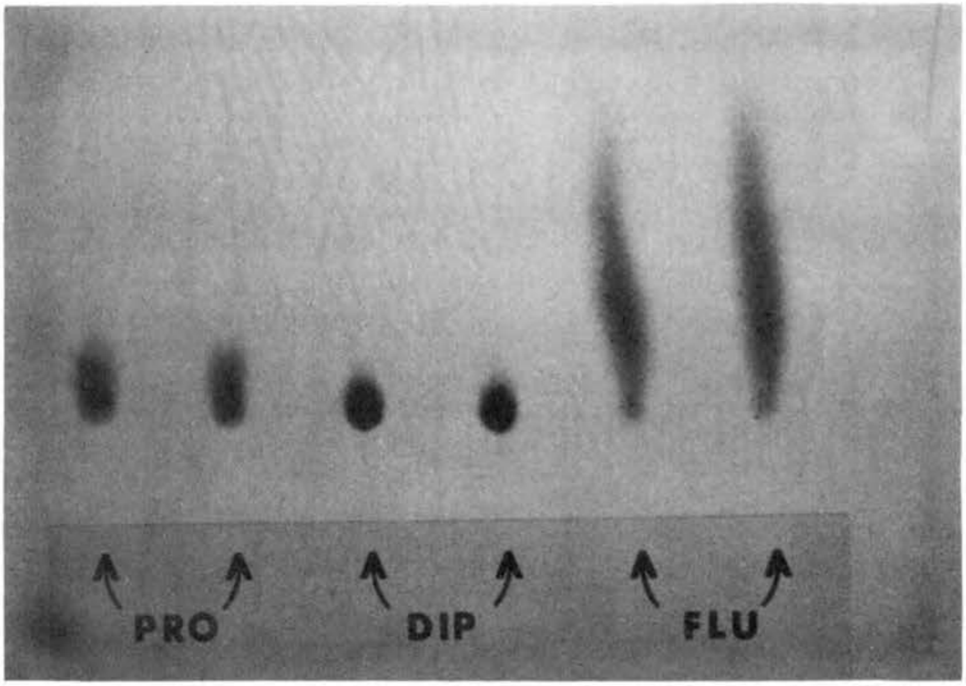
HERBICIDE MOVEMENT IN SOIL USING SOIL THIN-LAYER CHROMATOGRAPHY

	Herbicide		
Soil Type	Dipropetryn	Prometryn	Fluometuron
		Rf Value	
Brewer clay loam	.03 i*	.08 i	.41 e
Cobb sand + 2% Muck	.07 i	.12 h	.46 de
Port silty clay	.14 h	.20 g	.50 d
Teller fine sandy loam	.16 gh	.26 f	.80 b
Eufaula fine sandy loam	.17 gh	.27 f	.62 c
Cobb sand	.45 de	.63 c	.95 a

*Numbers followed by the same letter are not significantly different at the 5% level according to Duncan's New Multiple Range Test. C.V. = 9.58.

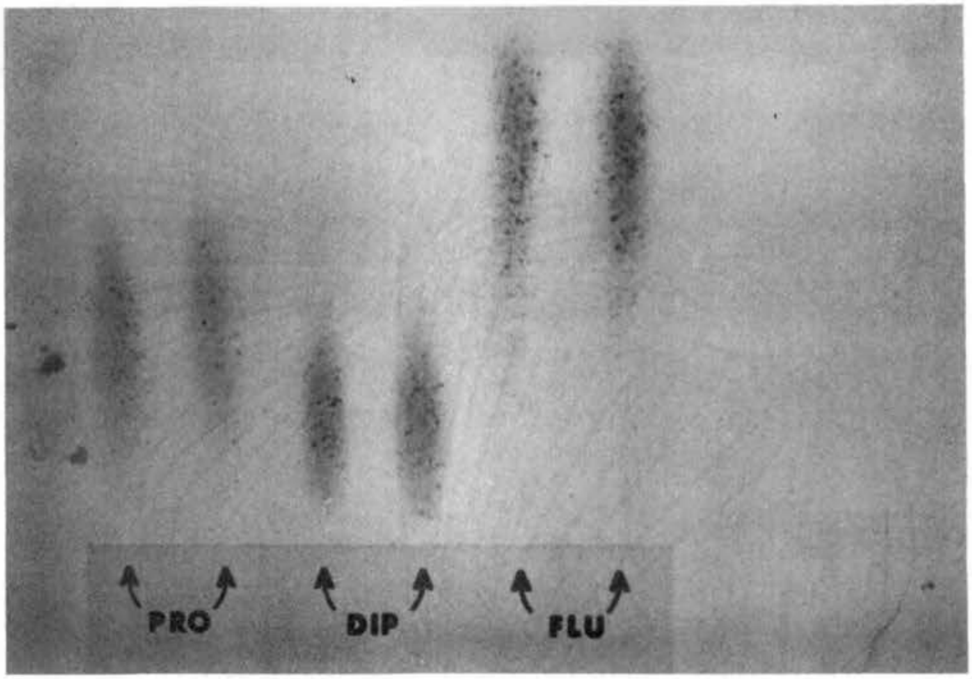


Eufaula fine sandy loam

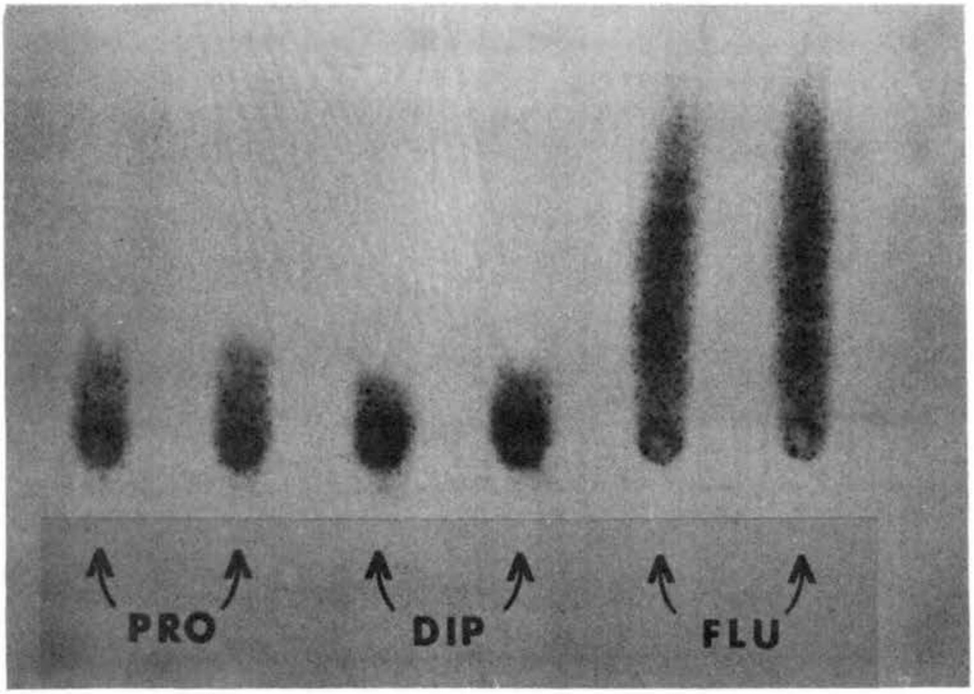


Brewer clay loam

Figure 17. Herbicide Mobility in Two Natural Oklahoma Soils



Cobb sand



Cobb sand + 2% Muck

Figure 18. Herbicide Mobility in One Natural Soil and One Amended Soil

Discussion

In all field and greenhouse studies prometryn showed greater phytotoxicity than equivalent rates of dipropetryn. Absolute phytotoxicity values obtained from solution-herbicide and sand-herbicide studies showed no significant differential phytotoxicity between dipropetryn and prometryn except at the lower herbicide rates where dipropetryn was less phytotoxic. With soil studies the margin of differential phytotoxicity between dipropetryn and prometryn was much wider for most species than with solution or sand studies, indicating the soil-herbicide interaction apparently was responsible for some of the differential phytotoxicity noted.

Differential uptake and translocation could partially explain the difference in susceptibility between plant species and the difference in phytotoxicity between dipropetryn and prometryn. Ashton and Crafts (2) showed that cotton resistance to prometryn was due to differential uptake and translocation--less prometryn appeared in cotton tops as compared to cotton roots or soybean tops. Corn was more susceptible to prometryn than dipropetryn and more prometryn than dipropetryn was found in corn tops. Oats were more susceptible than corn to both herbicides, more of both herbicides appeared in oat seedlings than corn seedlings. Herbicide-soil placement experiments showed no difference between shoot and root uptake of dipropetryn or prometryn by oat seedlings; however, prometryn was more phytotoxic than dipropetryn. Seed zone treatments caused the greatest amount of phytotoxicity with both herbicides. Nishimoto et al. (25) showed that proximity to the seed increased atrazine phytotoxicity.

Dipropetryn and prometryn showed increased disappearance from the soil with increased incubation temperature, incubation soil moisture levels and incubation time. This would be expected with biological and chemical breakdown. Soil adsorption-desorption would not have been expected to respond in this manner. More adsorption would have occurred at the lower temperatures and lower soil moisture levels. Of the factors evaluated, incubation soil temperature appeared to be the most important single environmental factor causing dissipation.

Relative soil moisture levels established by two methods caused different effects on dipropetryn phytotoxicity. Watering intervals resulted in differential dipropetryn phytotoxicity while minimum moisture oscillations did not. With both watering methods and with the soil used, a true water stress to the bioassay species (oats) was not obtained. The check plants showed no significant differential response to relative soil moisture levels. The moisture present in this sandy soil (Cobb sand) appeared to be readily available to the plant species. Minimum moisture oscillations appeared to be the better method of the two for establishing soil moisture variables, especially near the end of the experiment when water usage was affected by the herbicide treatments.

Increased soil temperature resulted in increased dipropetryn phytotoxicity. As the temperature increased herbicide adsorption decreased allowing more herbicide to be available for bioassay species. Also the increased soil temperature could result in a higher plant respiration rate and probably more herbicide uptake. No soil temperature by soil moisture interaction was apparent, probably because there was no apparent moisture stress.

Differential plant availability of dipropetryn and prometryn as a result of differential soil adsorption-desorption appeared to be a source for differential phytotoxicity in the soil-herbicide studies. Differential translocation to plant type was also shown with both herbicides. With all adsorbents evaluated, dipropetryn showed more adsorption and less desorption than prometryn. It was difficult to determine which soil factor was most responsible for adsorption-desorption of these two herbicides. It appeared that pH, percent organic matter, clay content and cation exchange capacity affect the adsorption-desorption processes of these herbicides. Cation exchange capacity might be the best single indicies for adsorption since both clay content and percent organic matter generally increase the cation exchange capacity; however, the other factors should also be considered. The largest adsorption response was caused by amending soil with muck where only 2% muck resulted in the greatest adsorption; however, the pH was also reduced. More research in this area is needed to further evaluate these factors.

Mobility of dipropetryn and prometryn correlated well with adsorption isotherms. Soils which caused high adsorption and low desorption showed the least amount of herbicide mobility. Prometryn was previously reported (11, 16, 18) as being the least mobile methylthio-s-triazine; however, these data have shown that dipropetryn, an ethylthio-s-triazine, was less mobile than prometryn.

CHAPTER V

SUMMARY

Field, greenhouse and laboratory studies were conducted to gain a better understanding of dipropetryn: its phytotoxicity, persistence, adsorption-desorption characteristics and soil mobility. Prometryn was included in many studies as a herbicide standard.

Field studies indicated that prometryn was more phytotoxic than dipropetryn when comparing crop injury and weed control percentages. The differential phytotoxicity appeared to be rate dependent; when dipropetryn rates were increased to obtain the same weed control as obtained with prometryn the amount of crop injury from dipropetryn treatments was less or equal to that obtained with prometryn treatments.

Greenhouse bioassay studies showed that prometryn was more phytotoxic than dipropetryn to seven of eight species evaluated. Ryegrass was shown to be the most susceptible to both herbicides while cotton was the most resistant.

Nutrient solution cultures with soybeans and sand cultures with sorghum showed no difference in absolute phytotoxicity values between dipropetryn and prometryn except at the lowest herbicide rates where dipropetryn was shown to be less phytotoxic than prometryn.

Differential uptake and translocation was shown by oats and corn. More dipropetryn and prometryn was apparent in the oat tops as compared to the corn tops. There was also more total dipropetryn and prometryn in oat seedlings than in corn seedlings. More prometryn than dipropetryn was apparent in the corn tops. With both herbicides and crop species there was more accumulation of herbicides in the leaf, coleoptile and root tips. After seven days no metabolites of either herbicide were apparent in either plants species.

Site of uptake studies showed both shoot and root uptake of dipropetryn and prometryn was important with neither being the primary site of uptake. Both herbicides appeared to be more phytotoxic when applied to the seed zone; however, with the modification in the culturing technique the actual value of the comparison is not known.

Dissipation of dipropetryn and prometryn was greater at higher soil incubation temperatures and higher soil moisture levels. Dissipation was also shown to increase with increasing incubation time. This would be expected if biological degradation was the reason for dissipation. No significant difference was shown between the dissipation rates of dipropetryn or prometryn.

Relative soil moisture levels established by watering intervals resulted in differential dipropetryn phytotoxicity. More phytotoxicity was noted in the drier soil than with the wetter soil. Water usage by oat seedlings with dipropetryn treatments was affected. Water usage of dipropetryn treated oat seedlings did not increase after 6 days while the water usage of the check plants increased until the 12th day. Soil moisture levels established by watering oscillations resulted in no differential dipropetryn phytotoxicity.

Increased soil temperature resulted in increased dipropetryn phytotoxicity when compared to low soil temperature levels. No interaction between soil temperature levels and soil moisture levels was shown.

Soil adsorption-desorption processes of dipropetryn and prometryn appeared to be affected by pH, clay content, organic matter levels and cation exchange capacity of the adsorbents. Adsorption increased with increasing clay content, cation exchange capacity and organic matter levels, and decreasing pH values. With all adsorbents, dipropetryn was more highly adsorbed than prometryn. Cobb sand + 2% muck showed the most adsorption while quartz sand showed the least adsorption with both herbicides. After eight successive extractions more dipropetryn was shown to remain adsorbed as compared to prometryn.

Differential mobility of dipropetryn, prometryn and fluometuron determined by soil thin-layer chromatography with six adsorbent materials was shown. Mobility of dipropetryn and prometryn correlated well with adsorption-desorption isotherms. Soils showing the highest adsorption values and the least desorption values allowed the least herbicide mobility. With all adsorbents evaluated, dipropetryn showed the least mobility with fluometuron showing the most mobility.

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APPENDIX

TABLE IX

EFFECTS OF DIPROPETRYN AND PROMETRYN TO EIGHT PLANT SPECIES

Species		0**	Herbicide Rate (ppmw)										GR$_{50}$ ppmw	Corr. Coeff.	C.V.
			0	.1	.5	1	2	4	5	8	16	32			
			Growth as Percent of Check*												
Corn	Dipropetryn	6.43	100	--	--	95	80	72	--	58	52	--	15.4	.99	9.6
	Prometryn	6.52	100	--	--	80	70	73	--	48	46	--	9.6	.92	11.4
Cotton	Dipropetryn	4.97	100	--	--	101	103	92	--	97	93	88	32.0	.84	12.1
	Prometryn	4.79	100	--	--	93	109	101	--	88	59	22	15.0	.85	16.5
Cucumber	Dipropetryn	3.08	100	88	90	85	81	--	37	--	--	--	3.0	.77	15.2
	Prometryn	3.66	100	85	89	39	5	--	5	--	--	--	.8	.88	20.9
Morning-glory	Dipropetryn	1.67	100	122	143	114	76	--	9	--	--	--	2.2	.83	13.8
	Prometryn	1.21	100	118	130	80	12	--	7	--	--	--	1.3	.87	22.8
Oats	Dipropetryn	1.91	100	83	67	58	41	--	23	--	--	--	1.1	.98	14.0
	Prometryn	2.18	100	86	87	58	29	--	11	--	--	--	1.0	.91	16.6
Ryegrass	Dipropetryn	2.08	100	62	59	43	28	--	19	--	--	--	.5	.94	21.2
	Prometryn	1.96	100	85	63	29	19	--	13	--	--	--	.7	.98	13.5
Sorghum	Dipropetryn	2.11	100	81	78	68	58	--	32	--	--	--	2.2	.90	13.6
	Prometryn	2.11	100	83	78	52	16	--	9	--	--	--	.8	.92	26.3
Wheat	Dipropetryn	2.51	100	--	--	102	76	49	--	25	29	--	5.8	.89	11.2
	Prometryn	2.45	100	--	--	53	38	40	--	28	32	--	1.3	.86	21.3

*Values represent the average growth as percent of check of four replications.

**Values represent average fresh weight (grams) of untreated check plants.

TABLE X

PHYTOTOXIC EFFECTS OF SHOOT AND ROOT ZONE HERBICIDE PLACEMENTS

Zone of Treatment	Herbicide	Herbicide Concentration (ppmw)			
		0	1.5	3	5
		Avena sativa growth*			
Shoot	Dipropetryn	.68a	.60a-c	.58b-e	.40e-h
Shoot	Prometryn	.68a	.54c-f	.36g-i	.26i
Root	Dipropetryn	.68a	.73a	.49c-g	.43d-h
Root	Prometryn	.68a	.59b-d	.35h-i	.39f-h

Treatment F=13.03 (Significant at .05). C.V.=13.28.

*Average fresh weight (grams) of three replications. Numbers followed by the same letter are not significantly different at the 5% level according to Duncan's New Multiple Range Test.

TABLE XI

PHYTOTOXIC EFFECTS OF SEED ZONE HERBICIDE PLACEMENT

Herbicide	Herbicide Concentration (ppmw)			
	0	1.5	3	5
	Avena sativa growth*			
Dipropetryn	1.22a	.75b	.65b	.49c
Prometryn	1.22a	.49c	.49c	.37d

Treatment F=63.35 (Significant at .05). C.V.=11.89.

*Average fresh weight (grams) of four replications. Numbers followed by the same letter are not significantly different at the 5% level according to Duncan's New Multiple Range Test.

TABLE XII

EFFECTS OF TIME, TEMPERATURE AND SOIL MOISTURE ON DIPROPETRYN AND PROMETRYN DISSIPATION

Treatments		Weeks of Incubation					
ppm Dipropetryn	Soil Variable	3	6	9	11	13	15
				Avena sativa Growth*			
0	A-10°, B-5%	1.109	1.141	.982	1.084	.944	1.007
1.5		.249	.758	.537	.744	.831	.868
3		.340	.503	.482	.399	.649	.527
6		.125	.492	.229	.284	.451	.336
0	A-25°, B-5%	1.025	1.140	1.207	1.258	1.267	1.356
1.5		.594	.998	1.054	1.101	1.022	1.337
3		.299	.586	.759	1.012	1.065	1.159
6		.150	.439	.187	.574	.765	.934
0	A-35°, B-5%	1.234	1.290	1.388	1.549	1.560	1.497
1.5		1.119	1.175	1.469	1.590	1.403	1.640
3		.556	.978	1.065	1.428	1.415	1.540
6		.196	.613	.438	.920	1.038	.542
0	A-10°, B-15%	1.154	1.041	1.108	1.042	1.080	1.057
1.5		.455	.642	.568	.625	.668	.643
3		.518	.439	.451	.349	.226	.633
6		.202	.245	.422	.204	.381	.209
0	A-25°, B-15%	1.079	1.102	1.229	1.350	1.281	1.309
1.5		.613	.671	1.166	1.254	1.203	1.508
3		.315	.930	1.083	1.316	1.182	1.350
6		.201	.484	.355	.447	1.242	1.449
0	A-35°, B-15%	1.177	1.435	1.505	1.658	1.592	1.610
1.5		.935	1.420	1.537	1.841	1.742	1.891
3		1.007	1.273	1.592	1.589	1.776	1.526
6		.385	1.348	1.358	1.511	1.729	1.684
Prometryn							
0	A-10°, B-5%	1.109	1.141	.982	1.084	.994	1.007
1.5		.437	.492	.575	.658	.628	.531
3		.146	.302	.225	.267	.234	.351
6		.242	.175	.157	.231	.172	.280
0	A-25°, B-5%	1.025	1.140	1.207	1.258	1.267	1.356
1.5		.431	.990	1.035	1.117	1.538	1.250
3		.236	.823	.883	1.149	1.022	1.210
6		.234	.322	.204	.531	.662	.915
0	A-35°, B-5%	1.234	1.290	1.388	1.549	1.560	1.497
1.5		1.212	1.103	1.357	1.583	1.577	1.593
3		.271	1.246	1.455	1.392	1.311	1.526
6		.164	.666	.943	1.389	.739	1.352
0	A-10°, B-15%	1.154	1.041	1.108	1.042	1.080	1.057
1.5		.389	.865	.397	.802	1.089	.626
3		.199	.486	.269	.266	.155	.266
6		.365	.384	.292	.225	.086	.170
0	A-25°, B-15%	1.079	1.102	1.229	1.350	1.281	1.309
1.5		.994	1.291	1.361	1.299	1.307	1.486
3		.155	.757	1.206	1.270	1.274	1.474
6		.230	.694	.472	.736	1.005	1.209
0	A-35°, B-15%	1.177	1.435	1.505	1.658	1.592	1.610
1.5		1.238	1.578	1.318	1.738	1.709	1.576
3		.670	1.374	1.510	1.541	1.407	1.611
6		.307	1.230	1.469	1.495	1.526	1.706

A=Temperature, B=Percent soil moisture, C=Time, D=Herbicide levels and E=Herbicide. F values: A=3616.25**, B=361.63**, C=471.10**, D=1414.46**, E=N.S., A x B=95.16**, A x D=108.76**, B x D=42.79**, A x B x D=24.57**, A x C=96.20**, A x B x C=5.01**, C x D=26.64**, B x C x D=4.67**, A x C x D=14.13**, A x B x C x D=5.44**, A x E=21.34**, A x B x E=20.20**, D x E=9.60**, B x D x E=7.77**, A x D x E=8.50**, B x C x E=4.94** and C x D x E=10.27**.

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*Average of four replications; fresh weight in grams.

**Significant at .05.

TABLE XIII

EFFECT OF SOIL TEMPERATURE ON DIPROPETRYN PHYTOTOXICITY

Soil Temperature (°C)	Dipropetryn Rates (ppmw)			
	0	1	2	4
		Avena sativa Growth[*]		
12	.806 b[**]	.803 b	.675 d	.623 d
24	1.091 a	.644 d	.492 e	.344 f
35	.733 c	.451 e	.326 f	.209 g

[*] Average fresh weight (grams) of three replications. C.V. = 6.55.

[**] Numbers followed by the same letter are not significantly different at the 5 percent level according to Duncan's New Multiple Range Test.

TABLE XIV

FREUDLICH EQUATION VALUES FOR ADSORPTION OF DIPROPETRYN AND PROMETRYN

	Soil Type											
	Cobb Sand + 2% Muck		Brewer Clay Loam		Port Silty Clay		Teller Fine Sandy Loam		Cobb Sand		Quartz Sand	
Herbicide	K	1/N	K	1/N	K	1/N	K	1/N	K	1/N	K	1/N
Dipropetryn	32.54	.73	18.50	.89	8.91	.81	6.18	.86	1.32	.86	.07	.97
Prometryn	28.95	.79	9.95	.83	4.90	.76	3.49	.80	.66	.77	.07	-.54

Correlation coefficients were .99 with all adsorption isotherms except prometryn on quartz sand which was .72.

TABLE XV

FREUNDLICH EQUATION VALUES FOR DESORPTION OF DIPROPETRYN AND PROMETRYN

		Herbicide							
		Dipropetryn Rates (µg/g)				Prometryn Rates (µg/g)			
Soil Type	Values	1	2	4	8	1	2	4	8
Cobb sand + 2% Muck	K	.88	2.10	5.65	11.04	.84	1.63	4.25	11.20
	1/N	-.02	.02	.12	.16	-.03	-.05	.04	.21
	Corr. Coeff.	.40	.20	.62	.93	.69	.36	.35	.69
Brewer clay loam	K	1.48	4.04	6.78	10.90	3.02	4.02	5.70	8.74
	1/N	.14	.29	.31	.35	.39	.39	.38	.45
	Corr. Coeff.	.82	.97	.89	.94	.79	.92	.90	.97
Port silty clay	K	3.42	4.40	6.97	8.57	2.57	4.29	4.98	6.20
	1/N	.45	.44	.51	.46	.46	.58	.54	.49
	Corr. Coeff.	.91	.96	.96	.97	.92	.93	.96	.97
Teller fine sandy loam	K	2.94	4.85	5.43	6.67	2.16	3.09	3.51	4.24
	1/N	.51	.63	.56	.58	.53	.66	.63	.61
	Corr. Coeff.	.94	.97	.99	.98	.99	.99	.99	.99
Cobb sand	K	1.11	1.30	1.67	2.01	.60	.66	.69	.86
	1/N	.65	.59	.57	.59	.51	.68	.70	.69
	Corr. Coeff.	.99	.99	.99	.99	.99	.99	.99	.99

VITA

Donald Scott Murray

Candidate for the Degree of

Doctor of Philosophy

Thesis: ENVIRONMENTAL AND SOIL FACTORS AFFECTING THE DISSIPATION, PHYTOTOXICITY AND MOBILITY OF DIPROPETRYN

Major Field: Crop Science

Biographical:

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Education: Graduated from Pauls Valley High School, Pauls Valley, Oklahoma, in May, 1962; received the Bachelor of Science degree from Oklahoma State University with a major in Agronomy in July, 1966; received the Master of Science degree from Oklahoma State University with a major in Agronomy in May, 1968; completed the requirements for the Doctor of Philosophy degree in July, 1974, with a major in Crop Science.

Experience: Employed by G-Wiz Fertilizer, Inc., as laborer during summers and vacations, 1961 to 1963; part-time laboratory technician April, 1964, to September, 1966; Graduate Research Assistant, Oklahoma State University, September, 1966, to February, 1968; Research Assistant, Oklahoma State University, February, 1968, to June, 1968; active duty in the United States Army, June, 1968, to April, 1971; Graduate Research Assistant, Oklahoma State University, April, 1971, to August, 1974.

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