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I am submitting herewith a dissertation written by Michael B. Akins entitled "The Adsorption, Desorption, and Volatility of Three Dinitroaniline Herbicides in Soil." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Plant and Soil Science.

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THE ADSORPTION, DESORPTION, AND VOLATILITY OF THREE DINITROANILINE HERBICIDES IN SOIL

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Michael B. Akins

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ABSTRACT

The adsorption, desorption, and volatility of dinitramine (N^4,N^4-diethyl-α,α,α-trifluoro-3,5-dinitrotoluene-2,4-diamine), fluchloralin (N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-trifluoromethyl aniline), and profluralin (N-(cyclopropylmethyl)-α,α,α-trifluoro-2,6-dinitro-N-propyl-10-toluidine) were investigated in soil.

Batch adsorption experiments were conducted on four Tennessee soils that had been subjected to various chemical treatments. In one set of extractions soils were sequentially extracted with solvents of increasing polarity. The solvents, the components removed and the change in adsorption relative to nontreated samples of the soils were as follows; ether-waxes and oils-(+22.0%); ethanol-resins-(+34.3%); water-polysaccharides-(+0.8%); 2% HCl-hemicellulose-(+38.2%); and 80% H_2SO_4-cellulose-(+77.2%). In a second set of extractions the following solvents, the components removed and the effect on adsorption relative to the nontreated samples of the soils were as follows; 35% H_2O_2-organic matter-(-21.3%); sodium [citrate-dithionite-bicarbonate]-free iron oxides-(+44.0%); 35% H_2O_2 + sodium [citrate-dithionite-bicarbonate]-organic matter & free iron oxides -(+576.5%). Adsorption was directly related to the soils' organic matter content and the length of the aniline sidechain. The proposed bonding mechanism for adsorption of the three dinitroanilines in soil is a combination of van der Waals-London interactions reinforced by hydrophobic bonding.

Desorption of the three herbicides showed that profluralin was held with a greater force than dinitramine or fluchloralin. The desorption from soils was inversely related to the soil's organic matter content. Average percent of the adsorbed herbicides desorbed by the five rinses was 32.4, 31.0, and 15.1% for dinitramine, fluchloralin, and profluralin.

The effects of herbicidal properties, herbicide rates (12.5 and 25 µg/50 g), soil moisture (25, 50, 75, and 100% of field capacity-FC) and temperature (greenhouse-average maximum daytime temperature 38°C, laboratory-average maximum temperature 25°C) on volatilization of herbicides from soil were investigated. The average loss of herbicides 14 days after application for the 12.5 µg rate was 43.1, 23.9, and 17.4% for dinitramine, fluchloralin, and profluralin, respectively. Slightly lower values (37.7, 21.7, and 16.0%) were observed for the 25 µg rate. Increasing the soil moisture content increased volatilization substantially for all three herbicides. For example, profluralin loss increased from 23.5% at 25% of FC to 56.3% at FC. Generally no statistical difference in loss was recorded between the greenhouse and laboratory samples. This was due to the greenhouse samples being in a dry state for longer periods of time than the laboratory samples. Coefficients of determination (R-Square) obtained from a multiple regression technique were used to estimate the variability of herbicide loss caused by the parameters herbicides, moisture, temperature in the volatility study. The terms in the analysis included the linear, interaction, and square of the linear terms of herbicides (H), moisture (M), and temperature (T). A three variable model (H H2 M2) explained

89% of the variation for the 12.5 µg rate while a four variable model (H HT H2 M2) explained 86% of the variation for the 25 µg rate.

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CHAPTER I

INTRODUCTION

Trifluralin was introduced in the early 1960's and is the most successful member of the dinitroaniline family of herbicides. Since then numerous dinitroaniline type compounds have been introduced, but none of these dinitroaniline compounds have approached the economic success of trifluralin. However, several dinitroaniline type compounds developed in recent years have been able to compete with trifluralin for a portion of the market.

The fate of trifluralin in soil has been studied quite extensively, however little information is available concerning the adsorption-desorption by soil and volatility of the newer compounds. An accumulation of information concerning the fate of the new compounds in soil will help establish their role in modern agriculture.

Profluralin and fluchloralin have been placed on the list of herbicides recommended by the Institute of Agriculture of the University of Tennessee for weed control in cotton and soybeans. Dinitramine, on the other hand, has not been placed on the recommendation list for soybeans because at rates that do not significantly injure soybeans the weed control is erratic. However, states that border Tennessee and which have similar climatic conditions and soils have placed dinitramine on their list of recommended herbicides for soybeans. It is hoped that the information generated from this study will help provide some answers to the erratic behavior of dinitramine in Tennessee.

This study was conducted to gain information on the adsorption, desorption and volatility of three recently introduced dinitroaniline herbicides; dinitramine, fluchloralin, and profluralin. The objectives of this study were:

1. To compare the adsorption of three dinitroaniline herbicides in soil;
2. To determine the soil components that influence adsorption;
3. To determine the desorption process of the three dinitroaniline herbicides;
4. To make the inferences to the bonding mechanisms of the three dinitroaniline herbicides;
5. To determine the effect of soil moisture, temperature, and herbicide rate on the volatility of the three dinitroaniline herbicides from soil;
6. To determine the coefficients of determination (R-Square) for herbicide loss in the volatility studies.

The common and chemical names of compounds referred to in the text are listed in Table 1.

Table 1. Common and Chemical Names of Pesticides Referred to in the Text

Common Name	Chemical Name
An-56477	2,6-dinitro-N,N-di-(2-dichloroethyl)-p-toluidine
BAS-3870-H	N-allyl-N-(2-chloroethyl)-2,6-dinitro-4-trifluoromethyl-aniline
Benefin	N-butyl-N-ethyl-α,α,α-trifluoro-2,6-dinitro-p-toluidine
Butralin	N-sec-butyl-4-tert-butyl-2,6-dinitroaniline
Chlornidine	N,N-(2-chloroethyl)-2,6-dinitro-4-methyl-aniline
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
Dinitramine	N^4,N^4-diethyl-α,α,α-trifluoro-3,5-dinitrotoluene-2,4-diamine
Fluchloralin	N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-trifluoromethyl aniline
GS-38946	N-ethyl-N-tetrahydrofurfuryl-4-trifluoromethyl-2,6-dinitroaniline
GS-39985	N-N-propyl-N-tetrahydrofurfuryl-4-trifluoromethyl-2,6-dinitroaniline
Isopropalin	2,6-dinitro-N,N-dipropylcumidine
Nitralin	4-(methylsulfonyl)-2,6-dinitro-N,N-dipropyl-aniline
Oryzalin	3,5-dinitro-N^4,N^4-dipropylsulfanilamide
Profluralin	N-(cyclopropylmethyl)-α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine
Trifluralin	α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine

CHAPTER II

REVIEW OF SELECTED LITERATURE

I. ADSORPTION-DESORPTION

Seven factors are known to influence the fate and behavior of pesticides in soil systems (4); (1) volatilization, (2) photochemical decomposition, (3) microbial decomposition, (4) plant or organism uptake, (5) chemical decomposition, (6) leaching, (7) adsorption-desorption. All these seven factors are integrally related. The phenomenon of the adsorption-desorption process exerts a great influence on soil-applied pesticides and must be taken into account to determine the rates of soil-applied pesticides.

The chemical nature of the adsorbate and the physio-chemical nature of the adsorbent system determines the adsorption-desorption process. This section of the review will be restricted to those factors that influence dinitroaniline herbicides adsorption-desorption in soil. Information about other organic compounds will be included wherever pertinent for supporting evidence.

Molecular Structure Factors

The adsorption of organic compounds in soil is usually limited to two broad categories of adsorptive forces, physical adsorption and chemisorption (37). Chemisorption is a result of coulombic interactions and formation of chemical bonds between the adsorbent and adsorbate. This sorption is usually an irreversible process. Chemisorption is

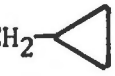
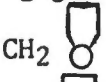
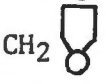
usually not an important bonding mechanism of pesticides in soil. Physical adsorption is a result of electrostatic forces between the adsorbent and adsorbate and is a reversible process. Physical adsorption can be further divided into short-range forces causing nonspecific adsorption and long-range forces causing specific adsorption. Nonspecific adsorption is related to the surface area of the interface and its occurrence is due to the resulting decrease in interfacial free energy. Specific adsorption results from a decrease in free energy at particular charge sites on the surface which exert powerful forces on the herbicide and consequently is a function of the number of sites per unit area. Non-ionic pesticides are likely to be adsorbed nonspecifically while ionic pesticides are more likely to be adsorbed specifically. Nonspecific adsorption results from short-range forces such as van der Waals-London interactions and induced dipole-dipole interactions. On the other hand, specific adsorption results in long-range interactions such as hydrogen bonding and ligand exchange.

The adsorption-desorption of organic compounds in soil is controlled by one or more of the following bonding mechanisms (19): (1) van der Waals-London interactions, (2) hydrophobic bonding, (3) hydrogen bonding, (4) charge transfer, (5) ligand-exchange, (6) ion exchange, (7) direct and induced ion-dipole and dipole-dipole interaction, (8) magnetic interactions, and (9) chemisorption. Several mechanisms or combination of mechanisms may occur simultaneously depending on the chemical and physical nature of the organic compound. The following properties of organic molecules determine the bonding mechanism that occur in soil (4): (1) chemical character, shape, and configuration of molecule, (2) acidity

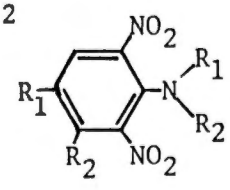
(pK_a), basicity (pK_b) or nonionic nature of the molecule, (3) water solubility, (4) charge distribution, (5) polarity, (6) molecular size, and (7) polarizability. In addition to the molecular properties of the organic pesticide the physiochemical properties of the adsorbing medium influences the type of bonding mechanism. The distribution, magnitude and intensity of the electrical field of the soil colloidal surface along with the colloidal surface area and configuration dictates the molecular bonding interactions (4,19). Molecular bonding is also controlled by the pH and by presence of complexing ions in the soil solution. To review all the factors that affect organic molecular bonding in soil is beyond the scope of this review. The reader is referred to reviews by Bailey and White (2,4), Hanmaker and Thompson (19), Upchurch (58), and Adams (1) for more complete discussions. The remaining portion of this review on bonding mechanisms will be restricted to the possible bonding mechanisms of dinitroanilines in soil.

All the physiologically active dinitroaniline herbicides have nitro group substitution at the 2, 6(ortho) and alkyl substitution at the number 4 (para) positions relative to the amine group on the aniline ring. The amine group is almost always disubstituted with various functional groups besides hydrogen (i.e., ethyl, propyl, chloropropyl, etc.) and can be either symmetrically or asymmetrically substituted. Selected dinitroanilines and their structures presented in Table 2 were obtained from Weber and Monaco (60). Chemical characteristics of the dinitroanilines that affect their adsorption-desorption in soil are the compounds' nonionic character, water solubility, molecular size, and configuration. One of the most important properties governing

Table 2. Chemical Structures of 13 Substituted Dinitroaniline Herbicides[1]

Compound Name	Substituents[2]			
	R_1	R_2	$R_1{}^1$	$R_2{}^1$
Dinitramine	CF_3	NH_2	C_2H_5	C_2H_5
Fluchloralin	CF_3	H	C_3H_7(n)	C_2H_4Cl
Profluralin	CF_3	H		C_3H_7(n)
BAS-3870-H	CF_3	H	$CH_2CH{=}CH_2$	C_2C_4Cl
Trifluralin	CF_3	H	C_3H_7(n)	C_3H_7(n)
Benefin	CF_3	H	C_2H_5	C_4H_9(n)
GS-38946	CF_3	H		C_2H_5
GS-39985	CF_3	H		C_3H_7(n)
An-56477	CH_3	H	C_2H_4Cl	C_2H_4Cl
Butralin	C_4H_9(t)	H	H	C_4H_9(s)
Isopropalin	C_3H_7(i)	H	C_3H_7(n)	C_3H_7(n)
Nitralin	CH_3SO_2	H	C_3H_7(n)	C_3H_7(n)
Oryzalin	NH_2SO_2	H	C_3H_7(n)	C_3H_7(n)

[1]Weber and Monaco (60)

[2] 

adsorption-desorption processes in soil is whether or not an organic compound carries a charge. Basic, acidic, amphoteric, cationic, and anionic organic molecular adsorption are somewhat dependent upon the pH of the soil system. The adsorption of basic and cationic forms is usually enhanced with decreasing pH, while the adsorption of acidic and anionic forms is usually enhanced with increasing pH. For neutral organic compounds the adsorptive capacity is usually not affected by the range of pH values found in agricultural soils. Lambert and coworkers (29,30,31) have postulated that neutral compounds are adsorbed by an "active" organic fraction with an adsorptive capacity which is essentially the same for all neutral organic compounds. Other workers (9,16,17,46) contend that the degree of adsorption is determined by the solubility of the neutral compounds in lipoidal and humic materials.

The low water solubility of the dinitroanilines suggest that the molecules are not readily hydrogen bonded to water molecules, but forms hydrophohic bonds with each other. These hydropohic bonds form cohesive globules within the water medium in the same manner as fat globules. The chemical nature of the organic molecule and the adsorbing media determines the relationship of adsorption to water solubility (3). Bailey et al. (3) concluded that within a chemical family or within an analogue series of basic chemical character, the magnitude of adsorption is related to the degree of water solubility. On the other hand, Leopold et al. (32) found an inverse relationship between water solubility and the extent of adsorption of 17 chlorinated phenoxy herbicides by activated carbon. Increased chlorination of the ring resulted in decreased water solubility and an increase in adsorption.

The adsorption of dinitroanilines as a function of their water solubility was not available in the literature. Table 3 compares the water solubility data compiled by Weber and Monaco (60) to soil solution equilibrium concentrations of twelve dinitroaniline herbicides reported by Harvey (22). With a couple of exceptions Harvey's data indicated an inverse relationship between adsorption and water solubility. The exceptions probably were caused by differences in substitution and changes in configuration.

The relationship between molecular size of organic molecules and adsorption has been investigated quite extensively (3,8,29,30,31,38). Bailey and White (3) found that large organic molecules adsorbed onto montmorillonite are difficult to displace by smaller ions. Lambert and coworkers (29,30,31) developed a relationship of theoretical molecular volume (called the parachor volume) of an analogue series of nitralin to their soil adsorption with the assumption that the adsorbing media was organic matter. They showed that the compounds with larger parachor volumes are adsorbed to a greater extent than ones with smaller parachor volumes. Lambert (30) also compared phenylurea herbicide adsorption data compiled by Hance (16) and found that substituted tertiary amides phenylureas fit his parachor molecular volume theory. The data collected by Harvey (22) was compared to parachor volume in Table 3. A poor relationship existed between the dinitroaniline adsorption and the parachor volume of the dinitroanilines in the study. The poor relationship of molecular size to adsorption was probably due to changes in configuration as suggested by Parfitt and Greenland (38) which overrides the effect of molecular size.

Table 3. Adsorption of Twelve Dinitroaniline Herbicides by Soil as Related to Water Solubility and Parachor Volumes.

Herbicide	Equilibrium Soil-Solution Concentration-μM[1]	Water Solubility[2] ppm	Parachor[2] Volume
Isopropalin	0.02	<0.05	720
Profluralin	0.08	0.1	680
Butralin	0.09	<1	680
Benefin	0.11	0.05	671
Chlornidine	0.11	--	--
Trifluralin	0.12	0.05	671
Dinitramine	0.19	1.1	624
Fluchloralin	0.24	<1	670
Oryzalin	0.30	2.6	761
Nitralin	0.37	0.6	768
GS-39985	0.39	--	743
GS-38946	0.42	1.0	703

[1]Harvey (22).

[2]Weber and Monaco (60).

Soil Factors

Among the factors that have been found to influence the sorption of dinitroanilines by soil are organic matter, clay content, soil moisture conditions, and anion exchange capacity (5,12,22,23,35,36,44,57). Grover (13) investigated the adsorption-desorption of trifluralin by various adsorbents and found that hydrophobic adsorbents adsorbed 20 times more trifluralin than hydrophilic adsorbents. The order of trifluralin adsorption by various adsorbents was; activited charcoal > peat moss > wheat straw ∿ cellulose triacetate > cation exchange resin > anion exchange resin > silica gel ∿ cellulose > kaolinite ∿ montmorillonite. In the same study Grover also found that 57% of adsorbed trifluralin was desorbed from montmorillonite by water, while with the same number of rinses only 10-20% was desorbed from peat moss, cellulose triacetate, and wheat straw.

McCall et al. (33) working with ion exchange resins showed that trifluralin was adsorbed to a much greater extent on nonionic (10 mg/g) resins than on anionic (0.67 mg/g) or cationic (0.17 mg/g) resins. They also determined through desorption studies that trifluralin was adsorbed mainly through physical bonds at sites on the resins where coulombic forces were absent.

The relative strengths of adsorption of 12 dinitroanilines were determined by Harvey (22) in Plano silt loam. Heats of adsorption (ΔH_θ°) calculated from adsorption values at 5° and 25°C ranged from -17.0 to -6.9 kcal/mole. From the calculated ΔH_θ° values the dinitroanilines most strongly adsorbed by the soil were chloronidine, A-820, GS-38946, GS-39985, and benefin. Fluchloralin, isopropalin, and

nitralin were the least strongly adsorbed. Harvey (22) also found that equilibrium concentrations and ΔH_θ° values were not necessarily related. The equilibrium concentrations are primarily dependent upon the extent of adsorption as determined by the number of adsorption sites available in a soil; while ΔH_θ° is primarily dependent upon the mean strength of adsorption at these sites.

Organic matter content of soils is the property most often correlated with dinitroaniline herbicide activity (5,12,23,24,35,36,39 44,57). Bardsley, et al. (5) investigated the toxicity and persistence of surface applied trifluralin (3.42 mg/100 cm^2) as related to organic matter content in soils. They incorporated either alkali-extractions of humic and ulmic acids or activated charcoal with mineral soils of low organic matter content to obtain soil organic matter levels of 1.5, 3.0, 4.5 and 6.0%. The addition of organic material to soils resulted in increased toxicity to barley and cucumber seedlings 41 and 81 days after addition of trifluralin. The increased trifluralin toxicity with increasing organic matter content was attributed to the greater adsorption of the vapor phase of the herbicides. On the other hand, several workers (23,57) have found that increasing the organic matter content in the soil will reduce the phytotoxic effectiveness of some dinitroaniline herbicides. Hollist and Foy (23) found that steamed and nonsteamed organic matter was more effective in reducing trifluralin toxicity to foxtail millet than steamed or nonsteamed montmorillonite and kaolinite. Segraves et al (45) studied the relationship of soil properties of 24 soils to the herbicidal activity of trifluralin and profluralin. Herbicide activity in each soil was assessed by determining the rate of

herbicide required for 50% sorghum root inhibition. The multiple correlation coefficient squared (R^2) indicated that 91 and 84% of the variability in the trifluralin and profluralin additions required to cause a 50% sorghum root inhibition could be accounted for by variation in the total soil carbon content. Talbert and Kennedy (57) studied the effects of activated charcoal on toxicity of trifluralin and nitralin to redroot pigweed. Both trifluralin and nitralin were inactivated when applied to charcoal at 1.8 mg per gram of charcoal.

II. VOLATILITY

The degree to which a herbicide volatilizes directly influences the manner in which it can be used. Herbicides with high vapor pressures require incorporation so that excessive losses and reduced effectiveness are avoided. Dinitroaniline herbicides are a group of herbicides in which some particular compounds require soil incorporation and some do not.

In soil systems, variables that affect herbicide volatility are the vapor pressure of the compounds, soil and air temperature, soil chemical and physical properties, soil water content, herbicide water solubility, and degree of adsorption (53). Review articles by Spencer, et al. (53) and Hartley (21) on pesticide volatilization are recommended by the author to obtain a general background on soil variables that affect volatilization.

The overriding factor that affects herbicide volatility is the compound's vapor pressure. Vapor pressures of dinitroanilines range from 1.0×10^{-6} to 114×10^{-6} mm of Hg at 25°C (60). Dinitroaniline

herbicides with a vapor pressure greater than 14×10^{-6} mm need mechanical incorporation to prevent excessive losses and reduction in effectiveness. Some common dinitroaniline herbicides that have low vapor pressures and do not necessitate incorporation to prevent excessive losses from volatilization are nitralin, oryzalin, and dinitramine (however these herbicides are generally incorporated to obtain uniform weed control). Other dinitroaniline herbicides that have vapor pressures greater than 14×10^{-6} mm Hg and for which soil incorporation is recommended are trifluralin, benefin, isopropalin and fluchloralin.

Parochetti and Hein (40) investigated the volatility of trifluralin, benefin, and nitralin in soil. They varied soil moisture levels, temperature and formulation of herbicides. The study was conducted in a closed glass cylinder in which the air flow could be regulated. They found that increasing soil moisture from air dryness to field capacity increased volatilization approximately 2% during a 3 hour period after being sprayed with trifluralin at a soil temperature of 30°C. The volatility of trifluralin and benefin at a soil temperature of 40°C was greater than at 30°C. At 40°C, significant losses of trifluralin and benefin occurred as soil moisture content increased from air dryness to field capacity, but did not increase significantly from field capacity to saturation. Significantly more trifluralin volatilized than did benefin at all temperatures. No loss of nitralin was recorded under any condition.

A study conducted by Spencer and Cliath (54) investigated the factors affecting trifluralin loss from soil. Trifluralin vapor pressure increased approximately five fold for each 10 degree increase in

temperature between 20-40°C. Vapor density in Gila silt loam increased as trifluralin concentration increased and reached a saturated vapor density equal to that of trifluralin without soil when added at approximately 73 µg/g to soil containing 19% water. Vapor density was markedly less in drier soils and was also inversely related to soil organic matter content.

Bardsley et al. (6) studied trifluralin volatilization as affected by concentration, time, soil moisture content and placement. The two moisture contents were field capacity and maximum retentive capacity. Maximum retentive capacity was defined as the soil moisture content when all the macropores in the soil were filled with water. Vapor losses were greater for the soil at maximum retentive capacity (5.4%) for a 24 hour period than at field capacity (4.5%). Vapor loss of trifluralin from water was found to be proportional to concentration. Subsurface application resulted in much less vapor loss than surface application.

CHAPTER III

METHODS AND MATERIALS

I. HERBICIDES

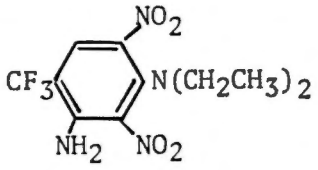
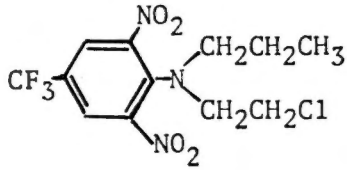
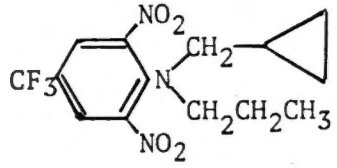
Dinitramine, fluchloralin, and profluralin were the members of the dinitroaniline family used in this study. Some selected chemical and physical properties of each herbicide are listed in Table 4. All three herbicides were of technical grade and were generously supplied by the following companies: Dinitramine—U. S. Borax and Chemical Corporation, fluchloralin—BASF Wyandotte Corporation, profluralin—CIBA-GEIGY Corporation.

II. ADSORPTION

Soils and Soil Treatments

Samples of four Tennessee soils subjected to various chemical treatments were used to determine the extent of adsorption and to delineate factors affecting dinitroaniline adsorption in soil. The four soils were Memphis silt, Iberia silty clay, Maury silt loam, and Decatur silt loam. Selected chemical and physical properties of the soils are presented in Table 5. Various chemical treatments were performed on the soils to remove soil components that may directly or indirectly affect dinitroaniline herbicide adsorption. The chemical treatments were as follows:

Table 4. Selected Chemical Properties of Herbicides in Study[1]

Compound	Structure	Melting Range-C°	Molecular Weight	Water Solubility ppm	Vapor Pressure mm Hg
Dinitramine		98-99	322.2	1.1	3.6×10^{-6} (25°C)
Fluchloralin		42-43	355.7	< 1	6×10^{-6} (20°C)
Profluralin		32-32.5	347.3	0.1	6.9×10^{-5} (25°C)

[1]Obtained from Weber and Monaco (60)

Table 5. Selected Chemical and Physical Properties of Soils[1]

Soil	Texture	Subgroup	pH	Organic Matter Percent	Clay Percent	CEC meq/100 g
Maury	silt loam	Typic Paleudults	6.0	1.6	17.9	10.4
Iberia	silty clay	Vertic Haplaquolls	6.1	3.0	49.0	41.6
Decatur	silt loam	Rhodic Paleudults	6.8	2.5	21.6	11.7
Memphis	silt	Typic Hapludalfs	6.7	1.9	20.0	8.7

[1]Textural analysis, organic matter and clay content were obtained from Department of Plant and Soil Science, University of Tennessee, Knoxville, unpublished data.

1. Organic matter was removed from soils wetted with sodium acetate buffer of pH 5 with hydrogen peroxide by a procedure outlined by Jackson (26).
2. A proximate gross fractionation of organic matter from soils was accomplished by sequential extraction with solvents of increasing polarity from a modified procedure of Waksman and Stevens (59) as outlined by Stevenson (56). Each solvent extracted separate components from the total organic matter composition. The solvents and the fraction extracted are; ether-lipids; ethanol-resins; hot water-polysaccharides; 2% HCl-hemicellulose; 80% H_2SO_4-cellulose. The amount of organic matter extracted by each fraction for each soil is listed in Table 6 as mg/g of soil. The ether and ether + alcohol treated soils were placed under vacuum at 80°C to remove solvents. The remaining treated soils were washed with deionized water and then placed under vacuum at 80°C to remove the solvents.
3. Free iron oxides were removed with a sodium citrate-bicarbonate-dithionite method used by Mehra and Jackson (34). The extracted iron, listed in Table 7, was determined as Fe^{+2} by the colorimetric orthophenathroline method (26). Samples used for cation exchange capacity (CEC) determination were stored under methanol while those used for adsorption studies were washed with deionized water, dried and stored.
4. Organic matter was decomposed with hydrogen peroxide in the pH 5 sodium acetate buffered soil system and was then followed by extraction of free iron oxides by the sodium-citrate-

Table 6. Amount of Organic Matter Removed by the Proximate Analysis Method

Treatment	Soil			
	Maury	Iberia	Decatur	Memphis
	mg/g			
Ether	0.1	0.2	0.1	0.3
Alcohol	0.3	0.8	0.2	0.7
Water	1.1	1.4	1.3	1.1
2% HCl	9.3	13.5	10.8	6.1
80% H_2SO_4	8.5	11.2	9.2	5.4

Table 7. Free Iron Oxide Content of Soils

Soil	Organic Matter Removed	No Pretreatment
	% Fe_2O_3	% Fe_2O_3
Maury	5.0	5.7
Iberia	6.0	6.6
Decatur	6.6	7.1
Memphis	1.5	1.6

bicarbonate-dithionite system. The quantity of extracted iron was determined as previously stated and is listed in Table 7, p. 21.

Cation Exchange Capacity Determination

The cation exchange capacity of the soils and treated soils was determined by the method of weighing the excess salt solution as outlined by Jackson (26). The exchange sites were saturated with Ca^{+2} ions and then replaced by Mg^{+2} ions. The concentration of the exchanged Ca^{+2} was determined with a Perkin Elmer-303 Atomic Adsorption Spectrophotometer. The results are listed in Table 8 as meq/100 g of soil.

Glycerol Retention

The glycerol retention of the soils and treated soils (Table 9) was measured by a modification of a glycerol mono-interlayer sorption method developed by Kinter and Diamond (28) and outlined by Jackson (26). One-half gram samples of each soil treatment (each treatment was replicated six times) were weighed into 2×5 cm aluminum weighing dishes. To each sample, 10 ml of 2% glycerol solution was added. After the samples were allowed to saturate overnight, they were placed in a forced air Precision Scientific Model 825 Oven at 110°C until near dryness. Then the sample dishes were placed in a pan with two additional dishes containing 99% glycerol and arranged as nearly equidistant from the glycerol dishes as possible. The entire pan was covered with a perforated sheet of aluminum foil. The pans were then placed in a Sargent Analytical Oven at 110°C for twenty-four hours. The next day the sample dishes were taken from the oven, allowed to cool for five minutes and then

Table 8. Cation Exchange Capacity of Nontreated and Treated Soils

Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
	meq/100 g			
Nontreated	10.4	41.6	11.7	8.7
Ether	9.0	31.6	11.1	8.7
Ethanol	8.5	30.6	9.9	8.0
Hot Water	8.7	32.6	7.6	5.7
2% HCl	2.6	7.2	2.0	1.6
80% H_2SO_4	1.7	4.4	1.8	1.4
- OM[1]	7.4	14.2	7.7	6.6
- Fe[2]	9.6	39.8	10.0	7.3
- OM & Fe[3]	8.2	17.9	9.3	5.7

[1]Hydrogen peroxide treated soils.

[2]Sodium citrate-bicarbonate-dithionite treated soils.

[3]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils.

Table 9. The Retention of Glycerol by Nontreated and Treated Soils

Soil Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
	mg/g			
Nontreated	20	42	24	11
Ether	25	54	21	10
Alcohol	30	42	24	14
Hot Water	17	25	23	8
2% HCl	11	36	12	8
80% H_2SO_4	12	31	10	8
- OM[1]	14	29	15	9
- Fe[2]	28	24	23	14
- OM & Fe[3]	101	80	91	64

[1]Hydrogen peroxide treated soils.

[2]Sodium citrate-bicarbonate-dithionite treated soils.

[3]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils.

weighed. After weighing, the samples were returned to the oven for an additional 24 hours and then weighed again. This process was repeated until the dishes obtained near constant weight. The pans were then uncovered and the heating and weighing process continued until constant weight was achieved. Heating the samples in the uncovered condition allows those samples which had adsorbed two interlayers to be adjusted to one layer. If the weight loss of the samples in the uncovered pans was less than 3% than when the samples were covered, the weight before uncovering was accepted. If the weight loss exceeds 3%, the final weight was accepted. In this study only Iberia had a significant weight loss from the covered to the uncovered position.

pH

The pH of each soil and treated soil was measured in a saturated paste by a Beckman Expandomatic pH meter equipped with a glass and a calomel reference electrode. The pH of the ether and alcohol extracted soils was measured after removal of solvents under vacuum at 80°C. The pH of all other remaining treatments was checked after being washed with deionized water and placed under vacuum at 80°C. The readings were recorded to the nearest 0.1 pH unit and are presented in Table 10.

Batch Adsorption

Five ml of a 0.5 ppm solution of the appropriate herbicide were pipetted into 15 ml Corex centrifuge tubes containing 0.5 grams of each soil sample. Each treatment was replicated three times. The tubes were sealed with aluminum foil lined rubber stoppers and masking tape. Each tube was mixed on a vortex mixer and then placed in a reciprocating

Table 10. The pH of Nontreated and Treated Soils

Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
Nontreated	6.0	6.1	6.8	6.7
Ether	6.1	5.9	6.9	6.5
Alcohol	6.1	6.0	6.8	6.6
Water	6.2	6.2	6.6	6.7
2% HCl	2.6	2.3	2.8	3.1
80% H_2SO_4	2.1	2.5	2.1	2.2
- OM[1]	6.9	6.7	6.5	6.6
- Fe[2]	6.9	6.6	6.4	7.5
- OM & Fe[3]	6.9	6.4	6.5	6.2

[1]Hydrogen peroxide treated soils.

[2]Sodium citrate-bicarbonate-dithionite treated soils.

[3]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils.

mechanical shaker (265 cycles per minute). The shaker was set to operate for 7 minute intervals twice each hour for 15 hours. After shaking, the tubes were placed in a super centrifuge for 10 minutes at 12,300 × g.

A 3 ml aliquot was withdrawn from the cleared supernatant and placed in a 10 ml sample vial and sealed with an aluminum foil lined cap. One ml of benzene was added to the vials to extract the herbicide from the aqueous solution. The vials containing the aqueous and benzene layers were shaken for 7 minutes on the reciprocating shaker. A sample was withdrawn from the benzene layer (3 µl for dinitramine and fluchloralin, and 5 µl for profluralin) and injected manually into a gas chromatograph.

A Micro-Tek Model DSS 170 Gas Chromatograph was employed for quantitative determination of the three dinitroaniline herbicides. The instrument was equipped with an electron capture detector which contained a tritium (^{3}H) foil as the ionization source. The inlet, column, and detector temperatures were 225, 175, and 200°C, respectively. A 6 ft by 4 mm OD, 2 mm ID glass column packed with 5% SE 30 on Chromosorb W 110/120 mesh was used. Flow rate of high purity nitrogen was 50 ml/min with 20 ml/min of purge gas. The optimum operating voltage as determined by background signal profile was 18V. The instrument settings for input and output attenuation were 10^{2} and 8, respectively. The retention time for the three compounds at the above settings was; profluralin - 7.0 min., fluchloralin - 6.5 min., dinitramine - 6.0 min.

Stock solutions of the herbicides consisted of 1000 ppm of technical grade herbicide dissolved in methanol. These stock solutions were stored in a refrigerator when not in use. To obtain the 0.5 ppm working

concentration, 1 ml of the stock solution was diluted to 2000 ml with deionized water. The 0.5 ppm solutions were prepared fresh daily. Standards used for determination of sample concentrations were prepared from the 0.5 ppm solution by dilution with deionized water to the desired concentration. Extraction of the standard dinitroanilines from the aqueous solution was identical to that of the unknowns.

Concentration of the dinitroanilines was determined by comparing the peak area of the experimental samples to a standard curve consisting of known concentrations of each herbicide. The area of the peaks was determined by the triangulation method of one-half the product of the peak height times the width of the base at half the peak height. The points on the standard curve were an average of two injections. Standard deviation of the standards were about 5%. A standard curve was prepared with each group of experimental samples to eliminate errors due to day to day instrument fluctations. A typical standard curve for profluralin is presented in the Appendix (Figure 10).

II. DESORPTION

In this study a portion of the three herbicides was desorbed with deionized water from nontreated soil samples from the batch adsorption studies. The samples were rinsed 5 times with each rinse containing 5 ml of deionized water. For each rinse, tubes containing the samples and rinse water were sealed with aluminum foil lined rubber stoppers and masking tape. The samples were then mixed on a vortex mixer and placed in the reciprocating shaker for four hours. The shaker was set to operate twice an hour for 7 minutes for the 4 hours. After each

rinse 3 ml of the cleared supernatant was taken for gas chromatography analysis, while the remaining supernatant was discarded. The procedure for extracting the herbicides from the supernatant and injecting into the gas chromatograph was identical to that described in the adsorption section, except for sample size. Five µl of the first rinse were injected for GLC analysis while 10 µl for the remaining rinses were injected.

III. VOLATILITY

Factors that affect the loss of dinitroaniline herbicide from soil through volatilization were investigated in laboratory and greenhouse experiments. Parameters varied in the study were soil moisture, herbicide concentration, and temperature. The experiment was continued for 14 days and each treatment was replicated three times.

Fifty grams of Memphis silt soil treated with hydrogen bromide gas to eliminate microbiological activity were weighed into 100×15 mm petri dishes. Twenty-five or 12.5 µg of herbicide (equal to 1 and 0.5 lb per acre or 0.89 and 0.45 kg/ha of herbicide on a weight basis) were added to the petri dishes in the volume of water and methanol mixture necessary to obtain the desired soil moisture level. The samples were allowed to equilibrate for two hours and then mixed thoroughly with a spatula. The soil moisture content of the samples was brought up to either field capacity (FC), 75% of FC, 50% of FC, or 25% of FC by the daily addition of water. Field capacity of the Memphis silt soil was determined by a porous plate method (43) and was found to be 20.3%.

To determine the effect of temperature on dinitroaniline volatilization, the study was conducted simultaneously in the laboratory and

greenhouse. Maximum daytime temperatures in the greenhouse for the 14 days averaged 38°C while the minimum nighttime temperatures averaged 20°C. Maximum and minimum average laboratory temperatures were 25 and 23°C, respectively.

Herbicides were extracted from the soil samples by shaking in a 500 ml Erlenmeyer flask with 200 ml methanol for two hours on a shaker. A major portion of the sediment was allowed to settle, then a 50 ml aliquot of the methanol solution was placed in a centrifuge tube. The tubes were centrifuged until the solution had cleared. Twenty-five ml of the cleared solution was flash evaporated to near dryness. Five ml of benzene was used to extract the herbicides from the side of the flask. Five µl of the benzene was then analyzed by gas chromatography. Twenty-five and 12.5 µg standards were prepared in a manner identical to the experimental samples and stored in a freezer until analysis. After thawing, the standards were extracted and analyzed by the same method employed for the experimental samples.

IV. EXPERIMENTAL DESIGNS AND STATISTICAL METHODS

The experimental design of both the adsorption and desorption experiments was a randomized complete block design with a split-split plot arrangement of treatments with herbicides as main treatments and soils as the primary split treatments. The secondary split treatments were soil chemical treatments for the adsorption experiment and number of rinses for the desorption study. The volatility study was treated as a randomized complete block design with a split-split-split plot arrangement with herbicides as main treatments, rates as primary split

treatments, and moisture and temperature as the secondary and tertiary split treatments, respectively. Analysis of variance and F tests were performed on the data by use of IBM Model 360/65 computer with programs written by Barr and Goodnight (7). Linear correlation coefficients were calculated for the association of K_d values and the pH, CEC, and glycerol retention of the soils and treated soils. Separation of treatment means in tables and bar graphs was accomplished by using Duncan's New Multiple Range Test. The level of significance was reported at the $P < 0.05$ level of probability. For the line graphs, Tukey's honestly significant difference test (h.s.d.) at the $P < 0.05$ level of probability was used (55). This test enables one to compare any two means on the line.

The coefficients of determination (R-Square) in the volatility studies were determined by a Stepwise Maximum R-Square multiple regression program developed by Barr and Goodnight (7). This technique looks for the "best" one variable, "best" two variable, "best" three variable models, and etc. until all possibilities have been exhausted. The variables entered into the models were significant at the 0.10 significance level. This program finds the one variable model giving the highest R-Square statistic, then the two variable model that gives the highest R-Square statistic, and so forth. The analysis was terminated when the parameters entered in the models was no longer significant at the 0.10 probability level. The information obtained indicates the relative importance of the prescribed parameters to the overall variation in the data. Included in the analysis were the linear, interaction and

square of linear terms of herbicides (H), moisture (M), and temperatures (T).

CHAPTER IV

RESULTS AND DISCUSSION

I. ADSORPTION

Distribution coefficients (K_d) calculated from measured solution equilibrium concentration values are tabulated in Tables 11, 12, and 13. The K_d values were calculated by substituting the appropriate variables in the formula $x/m = K_d C_{eq}$, where x/m is equal to the amount of herbicide (μg) adsorbed per gram of soil and C_{eq} is equal to the solution concentration (μg/ml). Distribution coefficients represent the ratio of the concentration of the solute on the adsorbent and in the solution. For example, a K_d value of 100 indicates that the concentration of adsorbed herbicide is 100 times greater than the concentration in solution. Soil solution equilibrium herbicide concentrations for each treatment are listed in the Appendix.

Analysis of variance and F tests performed on the distribution coefficients showed differences among herbicides, soils, and chemical treatments at the $P<0.01$ level of probability. Differences in adsorption due to herbicides are illustrated in Figure 1 where the values of K_d for the individual herbicides were obtained by averaging K_d values over nontreated soils for one set of comparisons and over all treatments for the other comparison. The K_d values for the herbicides averaged across nontreated soils was 144.5, 44.9, and 36.5 for profluralin, fluchloralin, and dinitramine respectively. Profluralin adsorption for the nontreated soils was 3.2 times greater than fluchloralin and 4 times greater than

Table 11. Adsorption Distribution Coefficients (K_d) for Dinitramine

Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
None	21.8ab[1]	61.3ik	38.0de	24.7ab
Ether	23.8ab	65.9jk	45.2efg	24.9ab
Alcohol	23.2ab	68.6kl	47.1efg	25.6ab
Water	18.2a	56.0hij	38.6de	24.6ab
2% HCl	33.7cd	76.41m	47.3efg	28.8bc
80% H_2SO_4	56.7hij	83.2m	56.7hij	34.5cd
- OM[2]	18.4a	50.2fgh	33.1cd	19.9ab
- Fe[3]	48.9fgh	101.4n	59.9hijk	42.8df
- OM & Fe[4]	75.71m	155.8p	131.7o	53.8ghi

[1]Means followed by the same letter are not significantly different at the $P < 0.05$ level according to Duncan's New Multiple Range Test.

[2]Hydrogen peroxide treated soils.

[3]Sodium-citrate-bicarbonate-dithionite treated soils.

[4]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils.

Table 12. Adsorption Distribution Coefficients (K_d) for Fluchloralin

Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
None	33.1bcd[1]	66.0jk	45.9efg	34.5cd
Ether	36.8cde	85.0no	51.0ghi	40.4ef
Alcohol	36.8cde	88.7o	55.3hi	37.3cdef
Water	38.6bc	73.6kln	55.5hi	23.1a
2% HCl	39.6ef	103.pq	96.1p	28.6bc
80% H_2SO_4	69.4kl	165.6s	80.0mno	37.0cde
- OM[2]	24.4ab	51.7ghi	45.3efg	19.3a
- Fe[3]	57.1ghi	109.2q	66.1jk	46.8fgh
- OM & Fe[4]	81.3mno	167.7s	128.0r	77.41mn

[1]Means followed by the same letter are not significantly different at the $P < 0.05$ level according to Duncan's New Multiple Range Test.

[2]Hydrogen peroxide treated soils.

[3]Sodium-citrate-bicarbonate-dithionite treated soils.

[4]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils.

Table 13. Adsorption Distribution Coefficients (K_d) for Profluralin

Treatments	Soils			
	Maury	Iberia	Decatur	Memphis
None	94.9b[1]	236.3n	141.4gh	105.3cd
Ether	149.0hi	250.7o	164.6j	165.1j
Alcohol	132.1ef	361.4qr	213.5m	124.1de
Water	102.2bc	252.8o	143.2gh	94.5b
2% HCl	162.6j	355.5q	153.9i	123.0d
80% H_2SO_4	169.3j	366.9r	296.4p	185.4k
- OM[2]	57.2a	201.6l	134.0fg	56.0a
- Fe[3]	165.1j	299.8p	179.1k	125.8e
- OM & Fe[4]	1273.4t	1908.7v	1649.0u	410.1s

[1]Means followed by the same letter are not significantly different at the $P < 0.05$ level according to Duncan's New Multiple Range Test.

[2]Hydrogen peroxide treated soils.

[3]Sodium-citrate-bicarbonate-dithionite treated soils.

[4]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils.

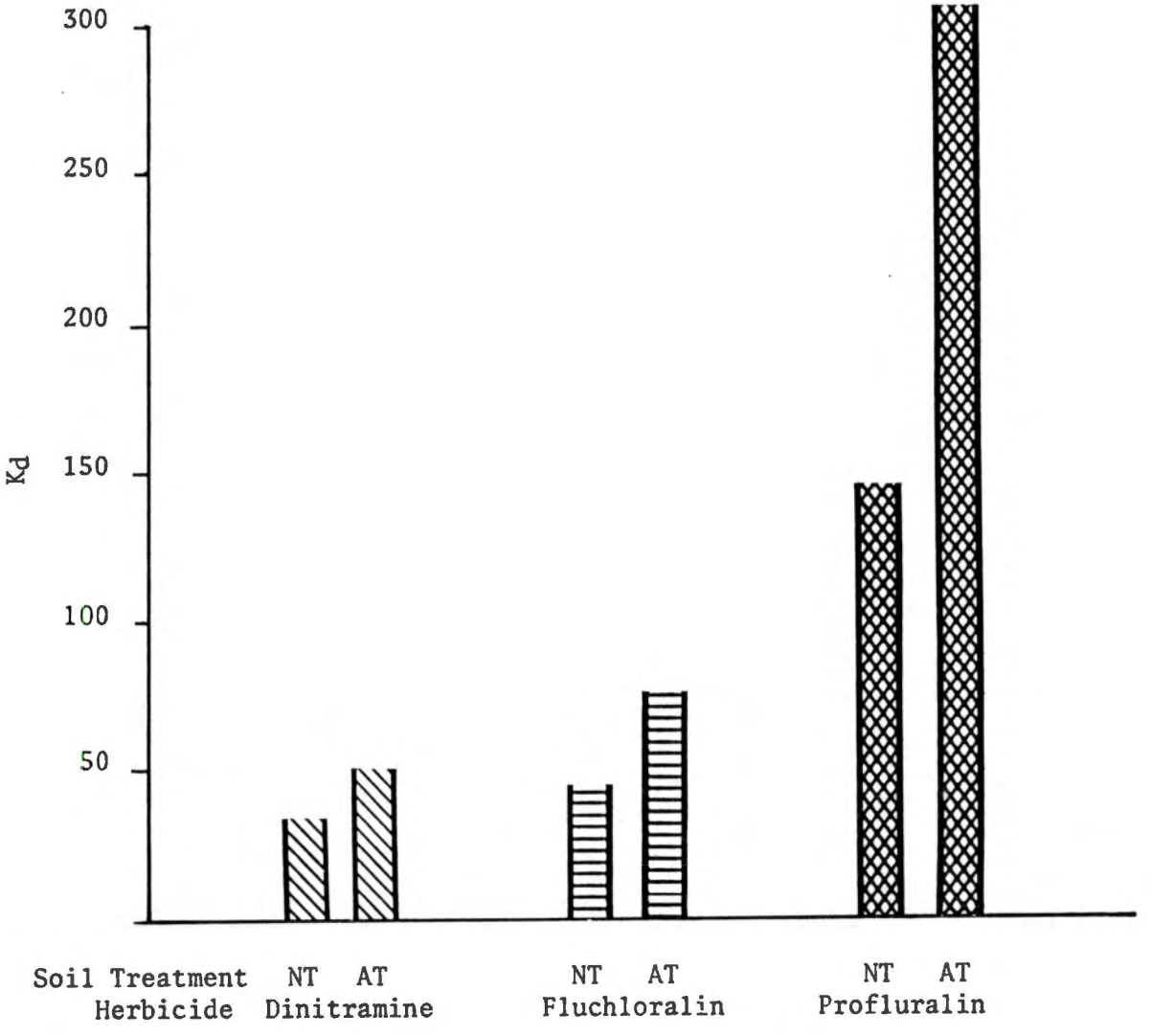


Figure 1. Average Distribution Coefficients (K_d) for the Three Dinitroaniline Herbicides in Soil. NT = Nontreated Soils, AT = All Treatments.

dinitramine. When all treatments were combined profluralin had an average K_d value of 306.7 and was followed by fluchloralin and dinitramine with average K_d values of 63.5 and 50.4, respectively. Averaged over all soils and treated soils, profluralin adsorption was 4.8 times greater than fluchloralin and 6.1 times greater than dinitramine.

The dinitroaniline adsorption by the nontreated soils followed the order of increasing adsorption, Maury ∿ Memphis < Decatur < Iberia for dinitramine and fluchloralin and Maury < Memphis < Decatur < Iberia for profluralin. Adsorption by the nontreated soils was proportional to their organic matter content as shown in Figure 2. This observation is consistent with soil adsorption of other dinitroaniline type herbicides (5,12,23,24,27,36).

Adsorption by the ether and ether + alcohol (hereafter will be called alcohol fraction) extracted soils was increased over the nontreated soils by an average of 22.0 and 34.3%, respectively. Profluralin was the only herbicide whose adsorption was consistently greater ($P<0.05$) for all four ether and alcohol treated soils. The ether and alcohol treatments extracted waxes, oils, and resins, which are lipoidal materials that can block adsorption sites suited for the dinitroaniline herbicides. Although significant increases in adsorption for some soils were observed, the increase in K_d values was not as large as the effect reported by Shin et al. (46) with DDT. They reported a 2-3 fold increase in adsorption. The effect of extracting the lipoidal materials was greatest for Iberia, followed by Decatur, Memphis, and Maury. This order of effect was directly related to the soils' organic matter content.

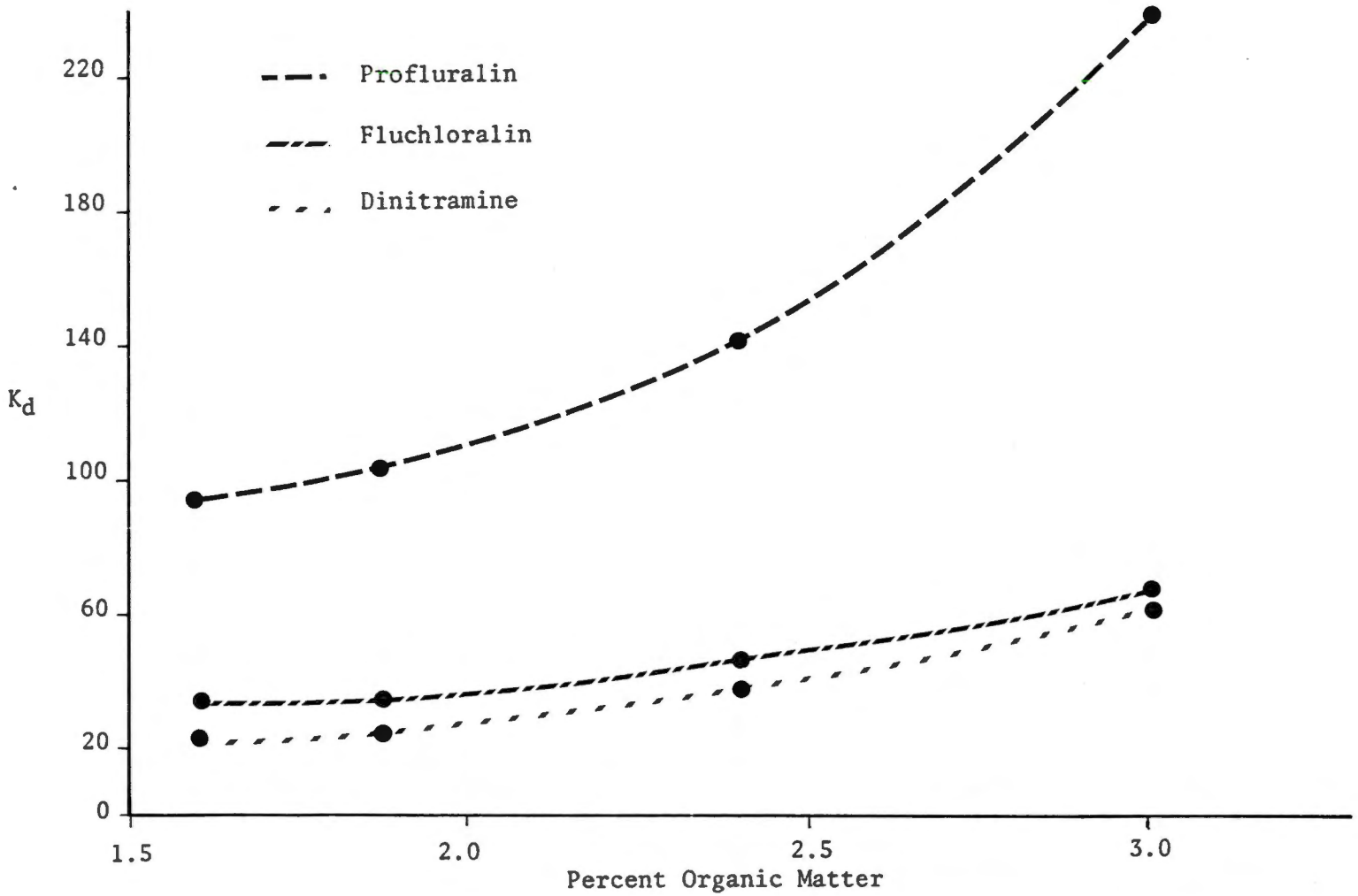


Figure 2. Distribution Coefficients (K_d) versus Organic Matter Content of Nontreated Soils for Three Dinitroaniline Herbicides.

Further extraction with water of the alcohol fraction (hereafter will be called water fraction) decreased dinitroaniline adsorption to equal the adsorption of the nontreated soils. Water removed the polysaccharide fraction of the soils' organic matter. The polysaccharide fraction may have contained the adsorption sites uncovered by the ether and alcohol extractions.

Extractions of the water fraction with 2% HCl (hereafter will be called HCl fraction) increased adsorption by an average of 38.2% over the nontreated soils. Additional extraction of the HCl fraction with 80% H_2SO_4 (hereafter will be called H_2SO_4 fraction) increased herbicide adsorption by an average of 77.2% over the nontreated soils. Several factors caused by extracting the soils with an acid could have resulted in the increase in adsorption. Dinitroanilines are weakly basic compounds ($pKa<0$), therefore the extremely low pH of the soils treated with acid may have caused partial dissociation of the molecules or perhaps even decomposition (2). One would expect an increase in surface area due to the destabilizing effect of removing a portion of the organic matter. The aromatic nature, free radical character, and diversity of surface structure and functional groups provide numerous possibilities for energetic interaction with most classes of organic compounds (11,14).

The increase in adsorption for the acid treated Memphis soil was less prominent than for the other three soils. As shown in Table 7, p. 21, the Memphis soil had less free iron oxide content than did the other soils. Iron oxides at the low pH values would be positively charged. Thus the charge on Memphis soil due to iron would be less than

for any of the other three soils and may account for the difference in adsorption.

The removal of organic matter with hydrogen peroxide decreased the adsorption of the herbicides by an average of 21.3%. The reduction in adsorption by hydrogen peroxide treated soils has been observed by other researchers (17,18,46). When organic matter is destroyed with hydrogen peroxide two important effects on soil adsorption are possible; a reduction in surface area and removal or severe alteration of the adsorption components. Treatment of soils with hydrogen peroxide has been shown to decrease surface area (42). A loss in surface area was reflected in this experiment by reduced glycerol retention (Table 9, p. 24). Destruction of organic matter has decreased soil adsorption for various classes of compounds (9,17,18,46).

The extraction of free iron oxides with sodium citrate-dithionite-bicarbonate from the soils resulted in an increase in herbicide adsorption by an average of 44%. Increased glycerol retention of the soils indicated that at least a portion of the extracted iron oxides was cementing agents for the soil particles. Adsorption of pesticides by iron oxides has been demonstrated by Hance (17), and Hartley (20). However, adsorption of the three dinitroanilines by the free iron oxides in this experiment could not be determined because of the effect of their removal on soil properties.

The removal of both organic matter and free iron oxides resulted in a surprisingly large average increase in herbicide adsorption of 576% over the nontreated soils. Retention of glycerol increased 3.5 fold which indicated a large increase in soil surface area. The large

increase in adsorption shows the mineral fraction is capable of adsorbing appreciable quantities of the herbicides.

Adsorption was directly affected by the chemical and physical properties of the compounds. Profluralin K_d values ranged from 56.0 to 1908.7, while fluchloralin K_d values ranged from 19.3 to 167.7 and dinitramine from 18.2 to 155.8. Harvey (22) reported the same order of adsorption for the same three dinitroanilines. The adsorption of these three compounds are inversely related to their water solubility. Profluralin has the lowest water solubility (0.1 ppm); fluchloralin and dinitramine water solubility values are 1 and 1.1 ppm. respectively. The inverse relationship of adsorption and water solubility is consistent with the finding of other researchers (5). However, Oserby (37) argues that the effect of a compound's water solubility on adsorption is coincidental. He contends that the structure and configuration of the molecule dictates adsorption and that water solubility is a fortuitous property of structure.

The substitution of the aniline side chain of the three herbicides was related to their adsorption. Dinitramine has symmetrical ethyl substitution, while fluchloralin has asymmetrical substitution of a propyl group in one position and a chlorinated ethyl group on the other. Profluralin is substituted asymmetrically with cyclopropylmethyl and propyl groups. Addition of length to side chains has resulted in the increased soil retention in other families of herbicides (16,32). The length and configuration of side chains also affect the size of molecules. One measure of molecular size is the compound's parachor molecular volume (41). Lambert et al. (30,31) found a linear relationship of

adsorption between an analogue series of nitralin based dinitroanilines and their parachor volumes. The parachor volumes of profluralin, fluchloralin, and dinitramine (60) are 680, 670, and 624, respectively. Prediction of adsorption ratios from the parachor volumes, profluralin and fluchloralin adsorption would be close together and both somewhat greater than dinitramine. However, these results were not observed in this study. Fluchloralin adsorption was only slightly larger than dinitramine and both were adsorbed to a lesser extent than profluralin. A weakness of relating a compound's parachor volume to adsorption is that compounds with similar parachor volumes can have different group substitutions. Thus compounds with similar parachor volumes can exhibit differences in properties such as water solubility and vapor pressure.

The association of soil properties such as organic matter content, clay content, sand content, silt content, CEC, pH, calcium content, phosphorus content and specific surface area with pesticide adsorption has been inferred in numerous studies. However in these studies it has not always been appreciated that these individual soil properties are frequently correlated among themselves. In this study correlation coefficients were calculated for K_d values versus pH, CEC, and glycerol retention for the soils and treated soils (Table 14). The analysis showed that cation exchange capacity and pH of the soils and treated soils were not significantly correlated with K_d values. On the other hand, the following significant ($P<0.05$) positive correlation coefficients were obtained for glycerol retention with K_d values; 0.73 for dinitramine; 0.78 for fluchloralin; and 0.88 for profluralin (Table 14). Glycerol retention of the soils and treated soils was used to

Table 14. Linear Correlation Coefficients (r) of Distribution Coefficients (K_d) with Three Properties of Treated Soils

Property	Herbicide		
	Dinitramine	Fluchloralin	Profluralin
	r		
pH	0.04	0.07	0.10
CEC	0.26	0.26	0.25
Glycerol Retention	0.73*	0.78*	0.88*

*Significant at the 5% level

indicate the available soil surface area for dinitroaniline adsorption. The significant correlation coefficients indicate that glycerol retention may be a useful property in predicting dinitroaniline adsorption.

II. DESORPTION

Analysis of variance and F tests performed on the solution equilibrium values revealed that there are differences among herbicides, among soils, and among rinses at the $P<0.01$ level of probability. Solution equilibrium concentration values are tabulated in Tables 15, 16, and 17. Included in the tables are the initial quantity of herbicide in the soils and the total quantity of herbicide extracted by the five rinses.

The desorption of the three dinitroanilines plotted against rinse number for each herbicide is show in Figure 3. The solution equilibrium concentration values for each herbicide were obtained by averaging the four soils. The desorption curves showed different release patterns for each compound. The release of adsorbed herbicide from the soils is determined by the strength of the bonding forces and thus the concentration of herbicide in each rinse is inversely proportional to the strength of the bonding forces. The concentration of rinses one and two for fluchloralin was almost equal to each other which indicates the herbicide in the two rinses was bound to the soil with equal force. The concentration dropped sharply for the third rinse which was followed by a gradual decline in the amount desorbed for the fourth and fifth rinse. The dinitramine concentration in the first rinse was not significantly

Table 15. The Desorption of Dinitramine from Nontreated Soils by Five Successive Rinses of Water

Rinse Number	Soils			
	Maury	Iberia	Decatur	Memphis
	------Solution Equilibrium Concentration-µg/ml-------			
1	0.067i[1]	0.033h	0.021def	0.064i
2	0.035h	0.014bc	0.023efg	0.025fg
3	0.026fg	0.014bc	0.024fg	0.027g
4	0.018cde	0.010b	0.013bc	0.024fg
5	0.012b	0.003a	0.009b	0.017cd
	----------Quantity of Herbicide-µg----------			
Total[2]	0.790	0.365	0.450	0.785
Initial[3]	1.714	2.149	1.979	1.780

[1]Means followed by the same letter are not significantly different at the $P < 0.05$ level of probability according to Duncan's New Multiple Range Test.

[2]Sum of rinses.

[3]Initial quantity of herbicide in soils.

Table 16. The Desorption of Fluchloralin from Nontreated Soils by Five Successive Rinses of Water

Rinse Number	Soils			
	Maury	Iberia	Decatur	Memphis
	------Solution Equilibrium Concentration-µg/ml-------			
1	0.062k[1]	0.034g	0.042h	0.057jk
2	0.054j	0.036g	0.038gh	0.048i
3	0.023f	0.005abc	0.015de	0.020ef
4	0.008abc	0.004ab	0.009bc	0.015de
5	0.004ab	0.003a	0.007abc	0.010cd
	----------Quantity of Herbicide-µg----------			
Total[2]	0.755	0.415	0.555	0.745
Initial[3]	1.917	2.170	2.050	1.938

[1]Means followed by the same letter are not significantly different at the $P < 0.05$ level of probability according to Duncan's New Multiple Range Test.

[2]Sum of Rinses.

[3]Initial quantity of herbicide in soils.

Table 17. The Desorption of Profluralin from Nontreated Soils by Five Successive Rinses of Water

Rinse Number	Soils			
	Maury	Iberia	Decatur	Memphis
	------Solution Equilibrium Concentration-µg/ml-------			
1	0.027f[1]	0.014cd	0.019de	0.023ef
2	0.020e	0.011abc	0.012bc	0.019de
3	0.019de	0.010abc	0.010abc	0.018de
4	0.010abc	0.010abc	0.010abc	0.013bc
5	0.009ab	0.006a	0.008ab	0.010abc
	----------Quantity of Herbicide-µg----------			
Total[2]	0.425	0.260	0.300	0.415
Initial[3]	2.261	2.400	2.335	2.283

[1]Means followed by the same letter are not significantly different at the $P < 0.05$ level of probability according to Duncan's New Multiple Range Test.

[2]Sum of rinses.

[3]Initial quantity of herbicides in soils.

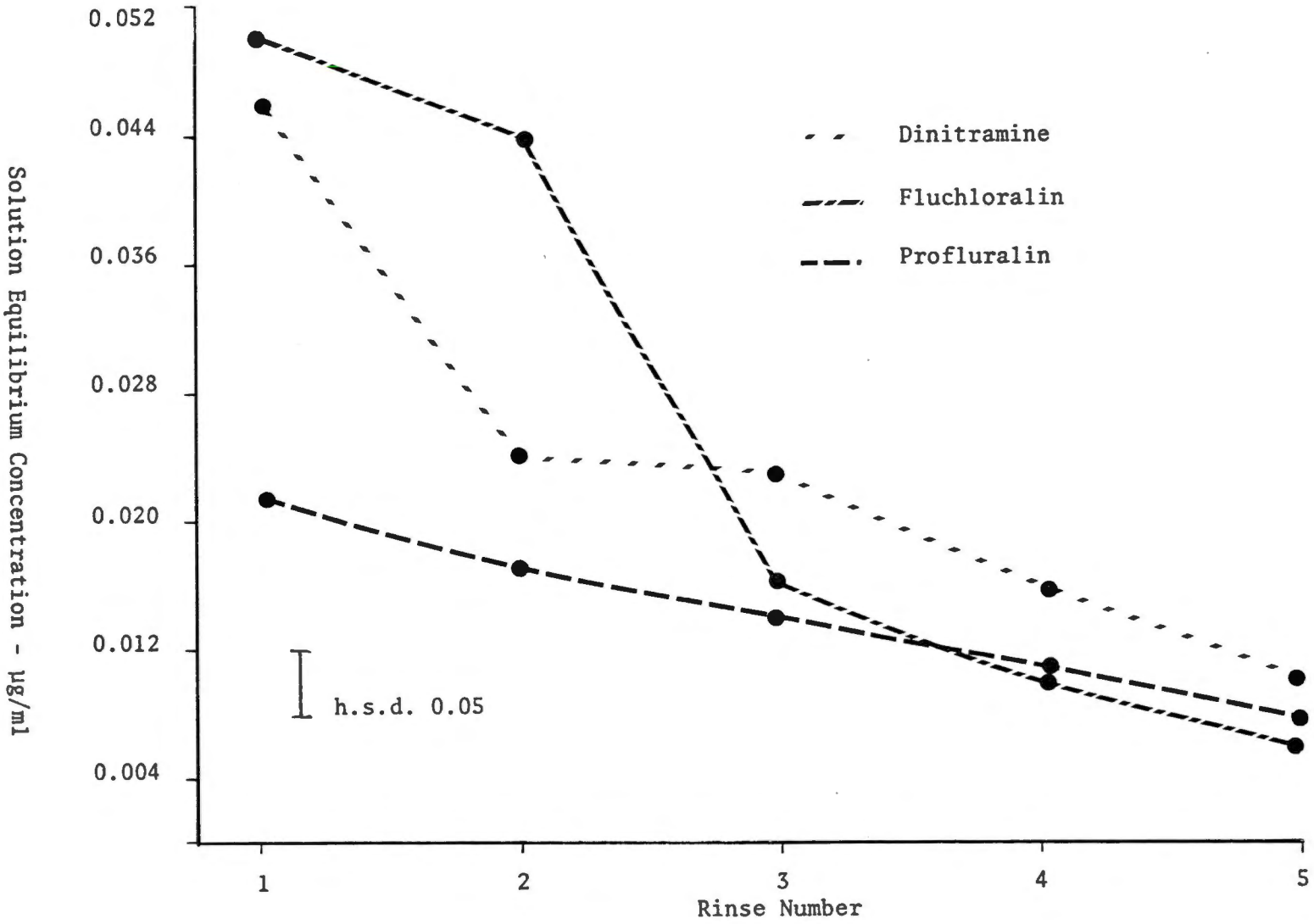


Figure 3. The Desorption of Three Dinitroaniline Herbicides from the Nontreated Soils by Five Successive Rinses of Water. The Values Plotted Were Averaged Across Soils.

different from the first rinse of fluchloralin, however a sharp decline occurred in the concentration of the second rinse. The second and third rinses of dinitramine were essentially equal to each other and then displayed the pattern of gradual decline from rinses 3 to 5. Profluralin exhibited a gradual decline in the concentration extracted with each successive rinse. The amount of profluralin desorbed with rinses 1 and 2 was significantly lower than for the other two compounds. By the fourth rinse the concentration of each herbicide in the rinses was essentially equal to each other. These release patterns indicate that the bonding forces of dinitramine and fluchloralin to soil are weaker than for profluralin.

In Figure 4 the solution concentration rinse number was plotted against rinse number for the four soils. The solution concentration values were obtained by averaging the three herbicides. All four soils exhibited a similar desorption pattern, i.e. in each subsequent rinse herbicide concentration decreased. Equivalent quantities and percentages of the adsorbed dinitramine and fluchloralin were desorbed from the soils when all five rinses were combined. Dinitramine desorption from Maury, Iberia, Decatur, and Memphis was 46.1, 17.0, 22.7, and 44.1%, respectively. Fluchloralin desorption for Maury, Iberia, Decatur, and Memphis was 39.4, 19.1, 27.0, and 38.4%, respectively. Profluralin desorption was lower than dinitramine or fluchloralin with values of 18.8, 10.8, 12.8, and 18.2% (released from Muary, Iberia, Decatur, and Memphis, respectively). The desorption of the three dinitroanilines was inversely related to the soils' organic matter content.

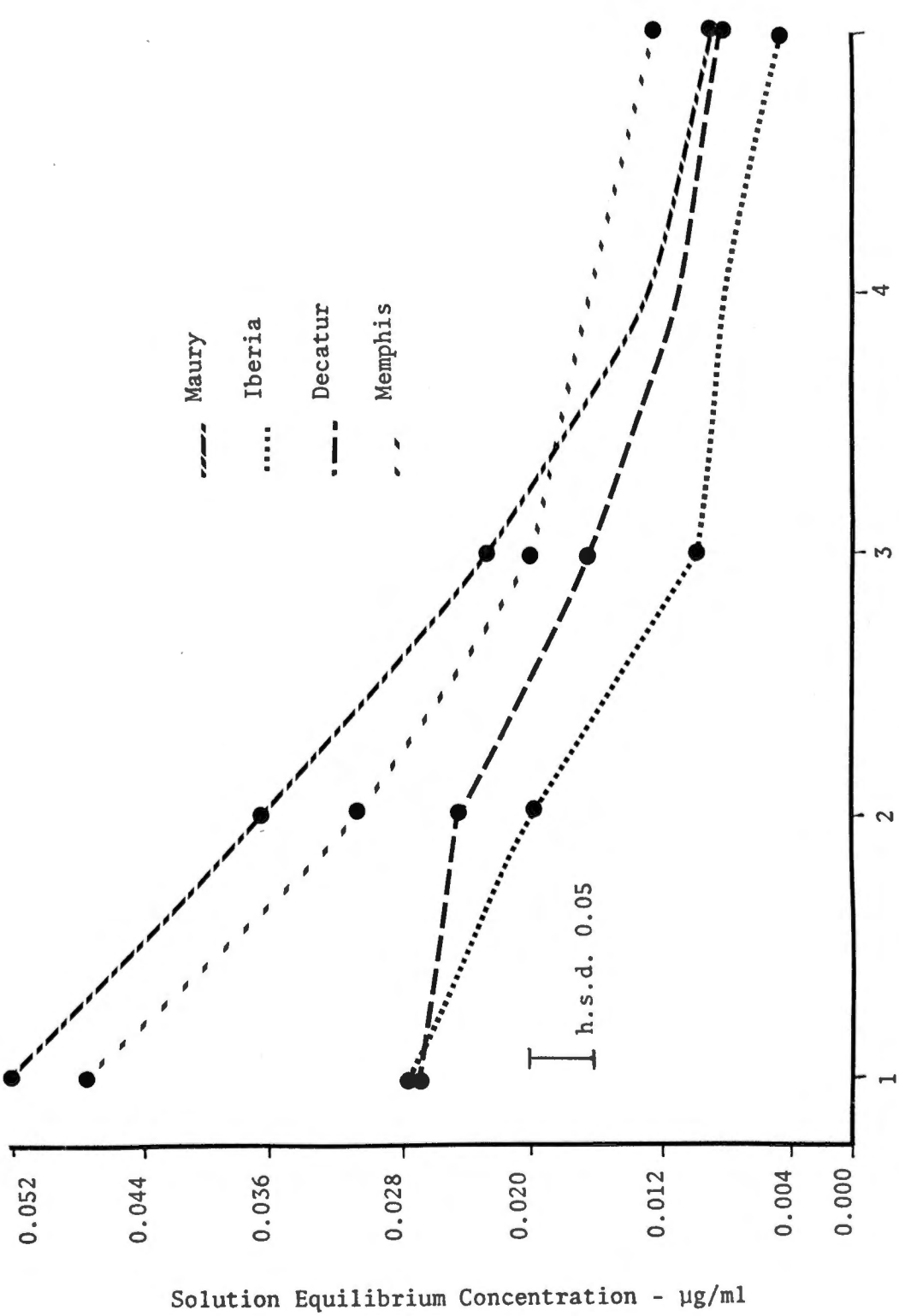


Figure 4. The Desorption of the Three Dinitroaniline Herbicides from Nontreated Soils by Five Successive Rinses of Water. The Values Plotted Were Averaged Across Herbicides.

The adsorptive forces holding the three dinitroanilines are quite strong and once adsorbed the process is not readily reversible for at least a portion of the adsorbed herbicide. The observation that profluralin is held more tightly than either dinitramine or fluchloralin is in conflict with Harvey's (22) conclusions. He measured heats of adsorption (ΔH_θ°) values for the adsorption of the three dinitroanilines and determined that profluralin (-12.2) and dinitramine (-13.5) would be held more tightly than fluchloralin (-6.9). The more negative the ΔH_θ° values the greater the bond strength.

III. BONDING FORCES

The adsorption in soil of the three herbicides in this study can be classified as nonspecific physical adsorption, consisting of short-range forces. The adsorption is nonspecific since the adsorption of the three herbicides has been shown to be a function of surface area. Excluding the hydrogen peroxide plus sodium-citrate-dithionite-bicarbonate treated soils, relatively little change (<2 fold) in adsorption was observed for the chemically treated soils which greatly altered the composition of the adsorption components. The hydrogen peroxide plus sodium citrate-dithionite-bicarbonate treated soils exhibited a large increase in adsorption along with a large increase in glycerol retention. The nonspecific physical adsorption of the three dinitroaniline herbicides results from a combination of van der Waals-London forces reinforced by hydrophobic bonding. The van der Waals-London bonding forces are the major bonding mechanisms of nonionic compounds, while hydrophobic bonding is caused by the repulsion of nonpolar molecules from a structured water

system. The bonding combination of van der Waals-London forces reinforced by hydrophobic bonding has resulted in very strong bonding of some organochlorine insecticides (19).

IV. VOLATILITY

The quantity of herbicide extracted from the Memphis soil 14 days after application of either 12.5 or 25 µg of herbicide per 50 g of soil is tabulated in Tables 18 and 19, respectively. Analysis of variance and F tests performed on the extracted herbicide values revealed that there were differences at the $P<0.01$ level of probability among herbicides, soil moisture levels, and temperatures. To facilitate discussion, the amount of extracted herbicides is summarized as percent loss in Table 20, but all statistical inferences are to Tables 18 and 19.

The loss of herbicides at both rates in percent of the total applied is presented in Figure 5. The values for the individual herbicides were obtained by averaging means across moisture and temperature levels for each rate. For both rates the order of loss from the Memphis soil was profluralin > fluchloralin > dinitramine and was significant at the $P<0.05$ level of probability. The average percent loss of profluralin, fluchloralin, and dinitramine from Figure 5 for the 12.5 µg rate was 43.1, 23.9, and 17.4%, respectively. Slightly lower values (37.7, 21.7, and 16.0%) were observed for the 25 µg rate. This order of dinitroaniline loss is not surprising since the vapor pressure of profluralin is approximately 10 times greater than that of fluchloralin and 20 times greater than dinitramine (see Table 4, p. 17).

Table 18. Micrograms of Dinitroaniline Herbicides Remaining in Memphis Silt 14 Days after Application of 12.5 µg/50 g of Soil at Different Moisture Levels and Temperature Regimes

Moisture	Herbicides					
	Dinitramine		Fluchloralin		Profluralin	
	L[1]	G[2]	L	G	L	G
	µg Recovered					
FC[3]	8.70cde[4]	8.40cd	8.36cd	9.10cde	5.21a	5.71a
75% FC	10.64gh	10.23fgh	9.11cdef	9.15cdef	5.71a	6.10ab
50% FC	10.94ghi	10.77gh	9.33cdef	9.49def	7.98c	7.01b
25% FC	12.23i	11.12ghi	11.35hi	10.30fgh	9.90efg	9.23cdef

[1]Laboratory samples.

[2]Greenhouse samples.

[3]Field Capacity.

[4]Means followed by the same letter are not significantly different at the $P < 0.05$ level of probability according to Duncan's New Multiple Range Test.

Table 19. Micrograms of Dinitroaniline Herbicides Remaining in Memphis Silt 14 Days after Application of 25 µg/50 g of Soil at Different Moisture Levels and Temperature Regimes

Moisture	Herbicides					
	Dinitramine		Fluchloralin		Profluralin	
	L[1]	G[2]	L	G	L	G
	µg Recovered					
FC[3]	20.35fg[4]	19.17ef	17.53d	17.72d	11.91a	12.71a
75% FC	22.64hi	19.34ef	19.48ef	18.57de	14.64bc	14.48b
50% FC	22.61hi	20.35fg	20.37fg	19.38ef	15.85c	14.53b
25% FC	23.06i	20.44fg	22.34hi	21.37gh	20.50fg	19.88ef

[1]Laboratory samples.

[2]Greenhouse samples.

[3]Field Capacity.

[4]Means followed by the same letter are not significantly different at the $P < 0.05$ level of probability according to Duncan's New Multiple Range Test.

Table 20. The Loss of Dinitroaniline Herbicides from Memphis Silt after Volatilization for 14 Days at Different Moisture Levels and Temperature Regimes

Moisture	Herbicides					
	Dinitramine		Fluchloralin		Profluralin	
	L[1]	G[2]	L	G	L	G
	Percent loss of 12.5 µg Rate					
FC[3]	30.4	32.8	33.1	27.9	58.3	54.3
75% FC	14.9	18.2	27.1	26.8	54.3	51.2
50% FC	12.5	13.8	25.4	24.1	36.2	43.9
25% FC	2.2	11.0	9.2	17.6	20.8	26.2
	Percent loss of 25 µg Rate					
FC	18.6	23.3	29.9	29.2	52.4	49.2
75% FC	9.4	22.6	22.1	25.7	41.4	42.1
50% FC	9.6	18.6	18.5	22.5	36.3	41.9
25% FC	7.8	18.2	10.6	14.5	18.0	20.5

[1]Laboratory samples.

[2]Greenhouse samples.

[3]Field Capacity.

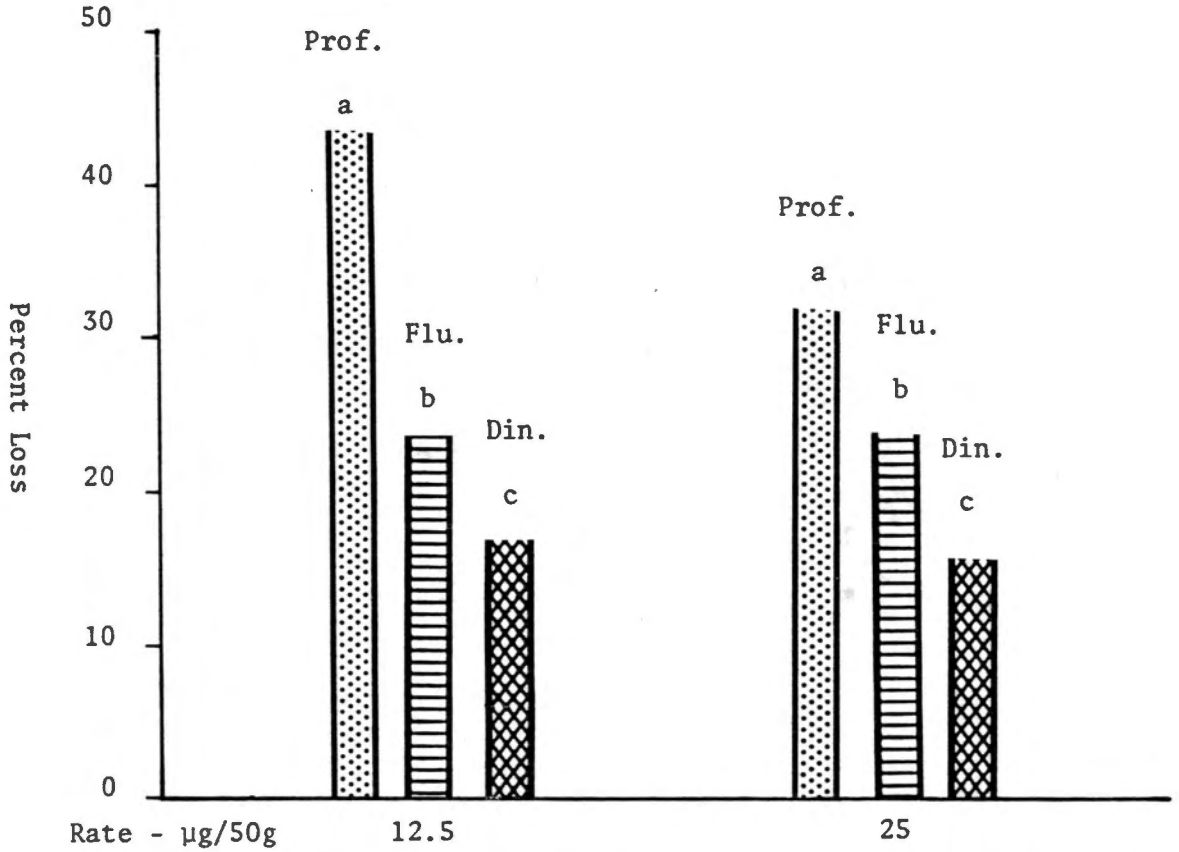


Figure 5. The Percent Loss from Memphis Silt of the Three Dinitroaniline Herbicides at Two Rates. Bars with the Same Letter Within a Rate Are Not Significantly Different at the $P < 0.05$ Level of Probability According to Duncan's New Multiple Range Test. Prof. = Profluralin, Flu. = Fluchloralin, Din. = Dinitramine.

Substantially more loss of herbicides occurred from the 25 µg samples that from the 12.5 µg samples. However, on a percentage basis the loss from the 25 µg samples was less that from the 12.5 µg samples (Figure 5). These results are similar to those of other investigators (6,10,48,54). Since dinitroanilines have limited solubility in water their concentrations in aqueous solution is very small. A greater portion of the 25 µg rate would have remained adsorbed or in the crystalline state as compared to the 12.5 µg rate.

The moisture content of the samples greatly influenced the loss of all three herbicides. The relationship of moisture to the amount of herbicide remaining in the soil is illustrated in Figures 6 and 7. The means for the points were obtained by averaging the values across replications and temperatures. A substantial increase in dinitroaniline volatilization was observed with increased soil moisture content. The largest increment of loss for profluralin and fluchloralin was from 25 to 50% of FC, while for dinitramine the largest increment of loss occurred from 75% of FC to FC. The presence of water in the soil apparently enhanced profluralin volatilization more than it did the other two herbicides. For example, profluralin loss from the 12.5 µg samples ranged from a low of 23.5% at 25% of FC to 56.3% at FC. Over the same soil moisture range fluchloralin and dinitramine loss increased from 13.4 to 27.6% and from 6.6 to 31.6%, respectively. A similar order of loss was recorded for the 25 µg samples. The enhancement of pesticide volatilization with increasing soil moisture has been observed by other investigators (6,15,25,47,48,49,50,51,52,54).

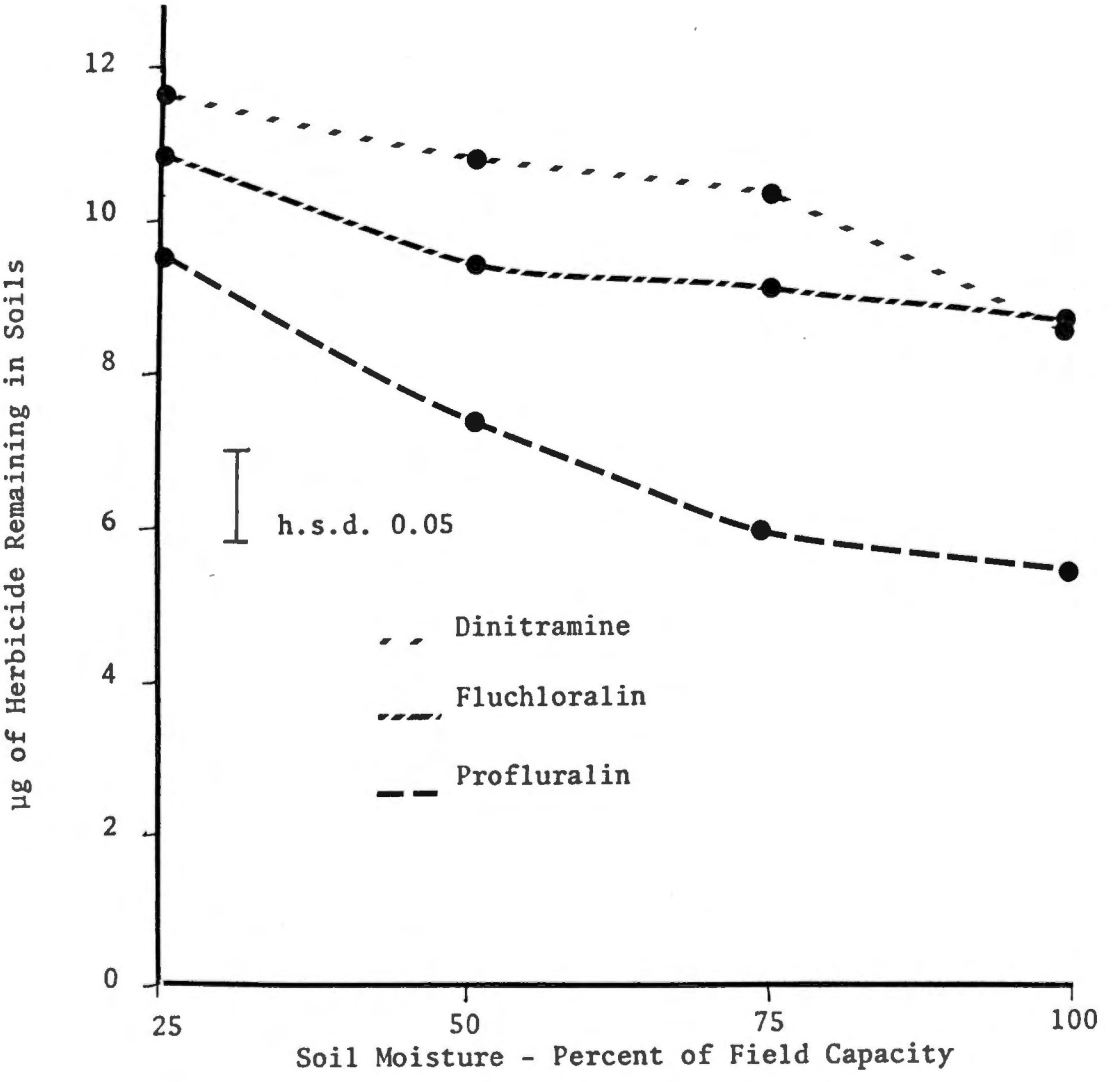


Figure 6. The Effect of Soil Moisture on the Amount of Dinitroaniline Herbicides Remaining in Memphis Silt 14 Days after Application of 12.5 µg/50 g Soil. The Values Plotted Were Averaged Across Temperature Regimes.

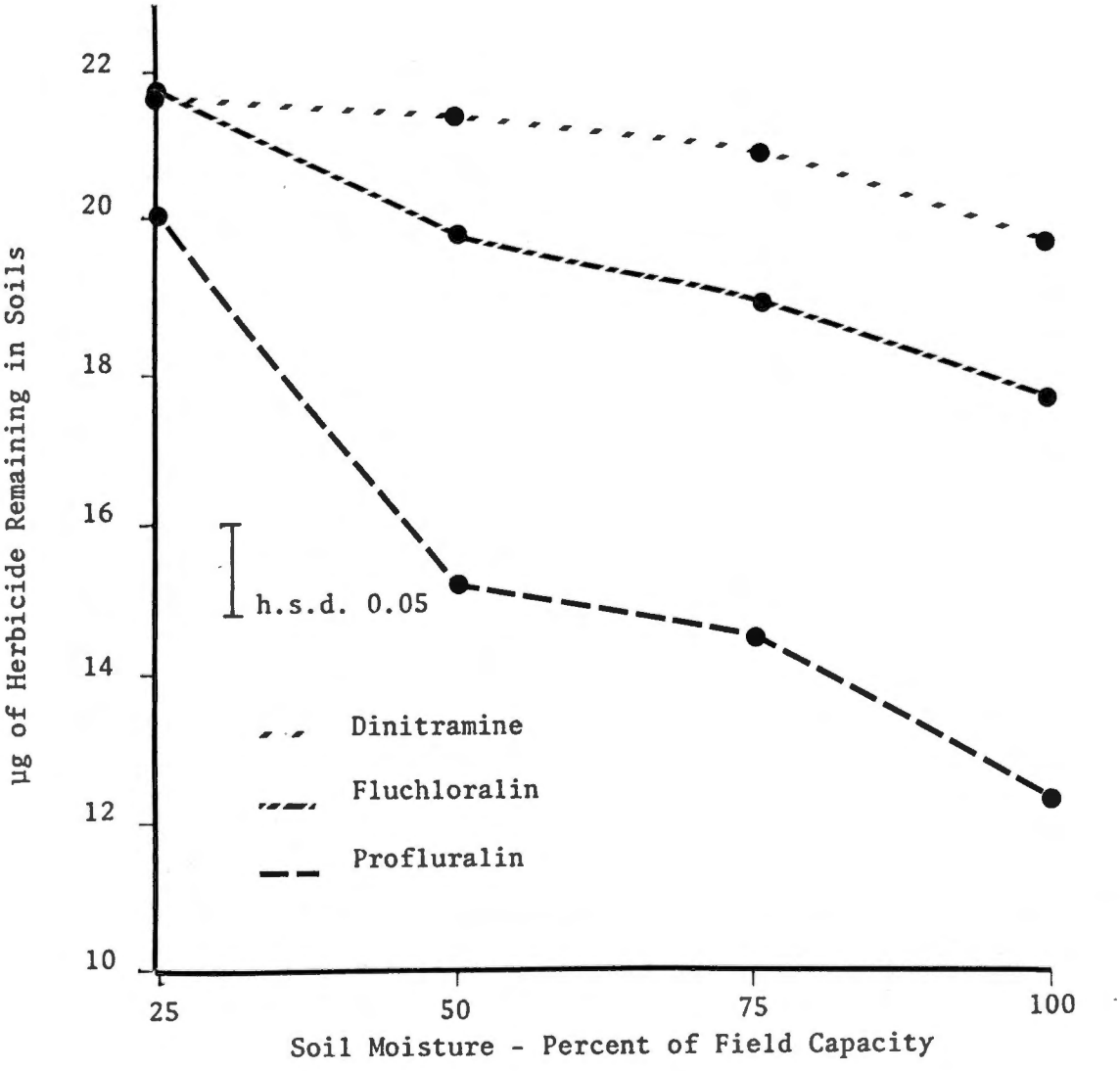


Figure 7. The Effect of Soil Moisture on the Amount of Dinitroaniline Herbicide Remaining in Memphis Silt 14 Days after Application of 25 µg/50 g Soil. The Values Plotted Were Averaged Across Temperature Regimes.

Several factors have been found to contribute to the increased volatilization caused by the presence of water in soil. The vapor pressure of pesticides in aqueous solution is higher than that of crystals which can be present in dry soils. The loss of the compounds is then controlled to some extent by the amount of pesticide in solution. When the pesticide in solution is depleted by volatilization the water displaces some of the herbicide from the soil surface by competition of the water for the adsorption sites. Thus, as long as water is present in soil a constant displacement of adsorbed herbicide from soil interfacial surfaces occurs and volatilization is enhanced.

Water also influences pesticide volatilization by controlling the rate of movement of the pesticide from within the soil to the surface. This rate of movement is influenced by; (1) movement of herbicide away from the evaporation surface; (2) water loss; (3) rate of diffusion and mass flow of herbicide from within the soil to the evaporation surface. In this study the soil in the dishes was not maintained at a constant soil mositure level, but rather enough water was added each day to achieve the desired moisture content. When the samples were checked for loss the next day, they were found to be very dry in both the greenhouse and laboratory. For all practical purposes, most of the added water evaporated between applications. Adequate circulation of air occurred above the samples in both the greenhouse and laboratory so that the samples became almost air dry between applications of water. The suction gradient caused by the water evaporation resulted in an appreciable upward movement of water to the evaporating surface carrying with it by mass flow any herbicide in the soil solution. In a system such as the

one used in this experiment, the water loss acts as a pump and continuously carries the dinitroanilines to the soil surface. The air movement above the samples would also enhance the loss of herbicides by sweeping away the herbicides in the air layer just above the soil surface, therefore maintaining a concentration gradient from the soil surface to the air layers above the soil. Even after the soils had dried, small amounts of the herbicides would continue to move to the soil surface via diffusion. When the soil was rewetted the quantity of herbicide collected at the soil surface was lost almost immediately.

Temperature is usually an important factor influencing volatility of pesticides. The effect of temperature on dinitroaniline volatilization in this study was not as easily determined as the effect of moisture, because of the manner in which the study was conducted. The percent loss for the three herbicides at two temperatures is shown in Figure 8. The plotted values were obtained by averaging means across moisture levels. The 25 µg greenhouse samples of dinitramine were the only samples exhibiting significant ($P<0.05$) increments of loss over comparable samples in the laboratory. For all other comparisons, although no statistical differences were present, loss was greater from the greenhouse samples than the laboratory samples.

When the loss of the three herbicides at two temperatures and four moisture levels are compared as in Figure 9 the observed temperature effect in this experiment can be explained. As the water content decreased from FC to 25% of FC the differences in volatilization due to higher temperatures between the greenhouse samples and laboratory samples became larger. Increasing temperature usually enhances pesticide

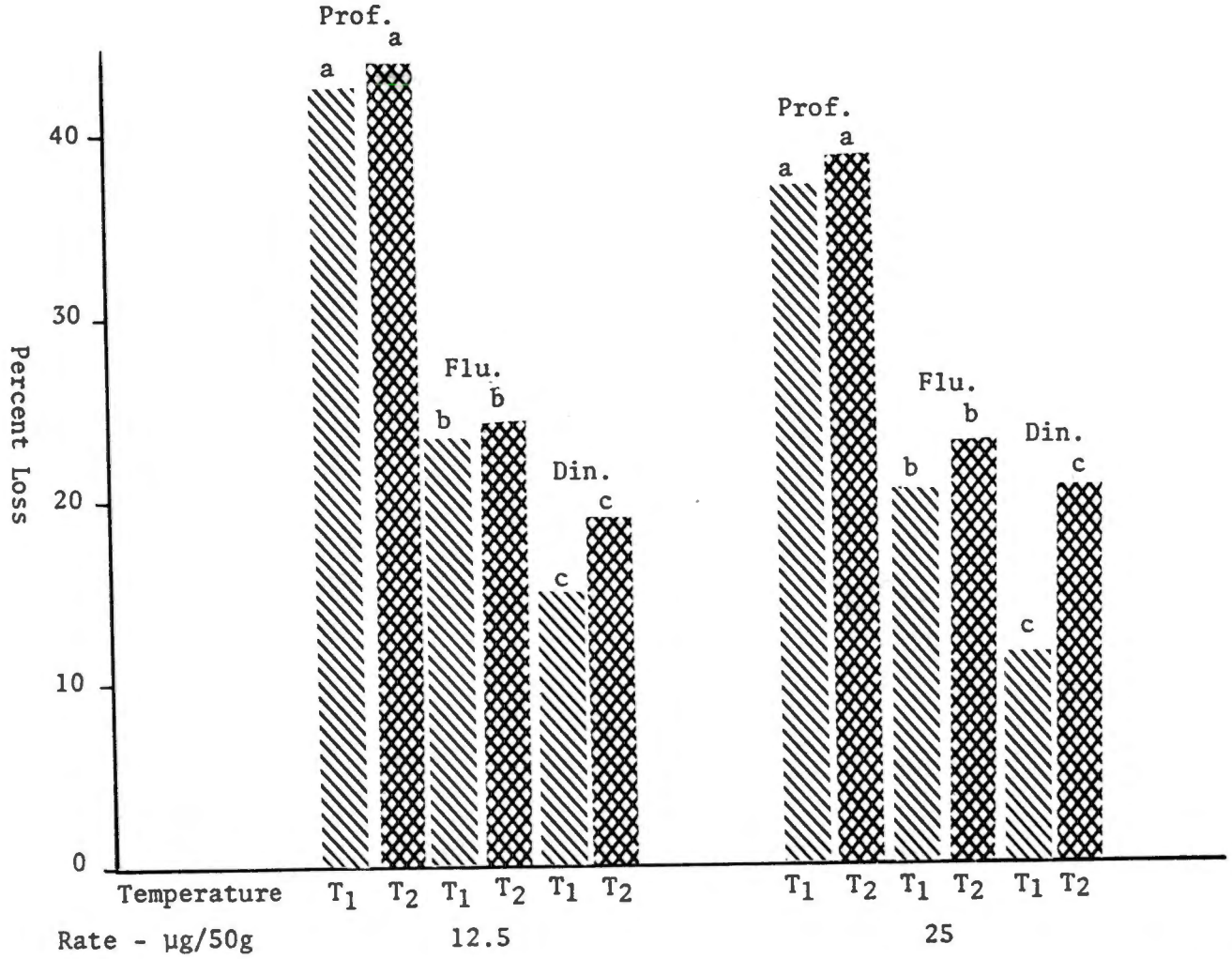


Figure 8. The Percent Loss of Three Dinitroaniline Herbicides from Memphis Silt at Two Rates and Two Temperature Regimes. The Values Plotted Were Averaged across Moisture Levels. Bars with the Same Letter within a Rate Are Not Significantly Different at the $P < 0.05$ Level of Probability According to Duncan's New Multiple Range Test. Prof.= Profluralin, Flu.=Fluchloralin, Din.=Dinitramine. T_1=Laboratory, T_2=Greenhouse.

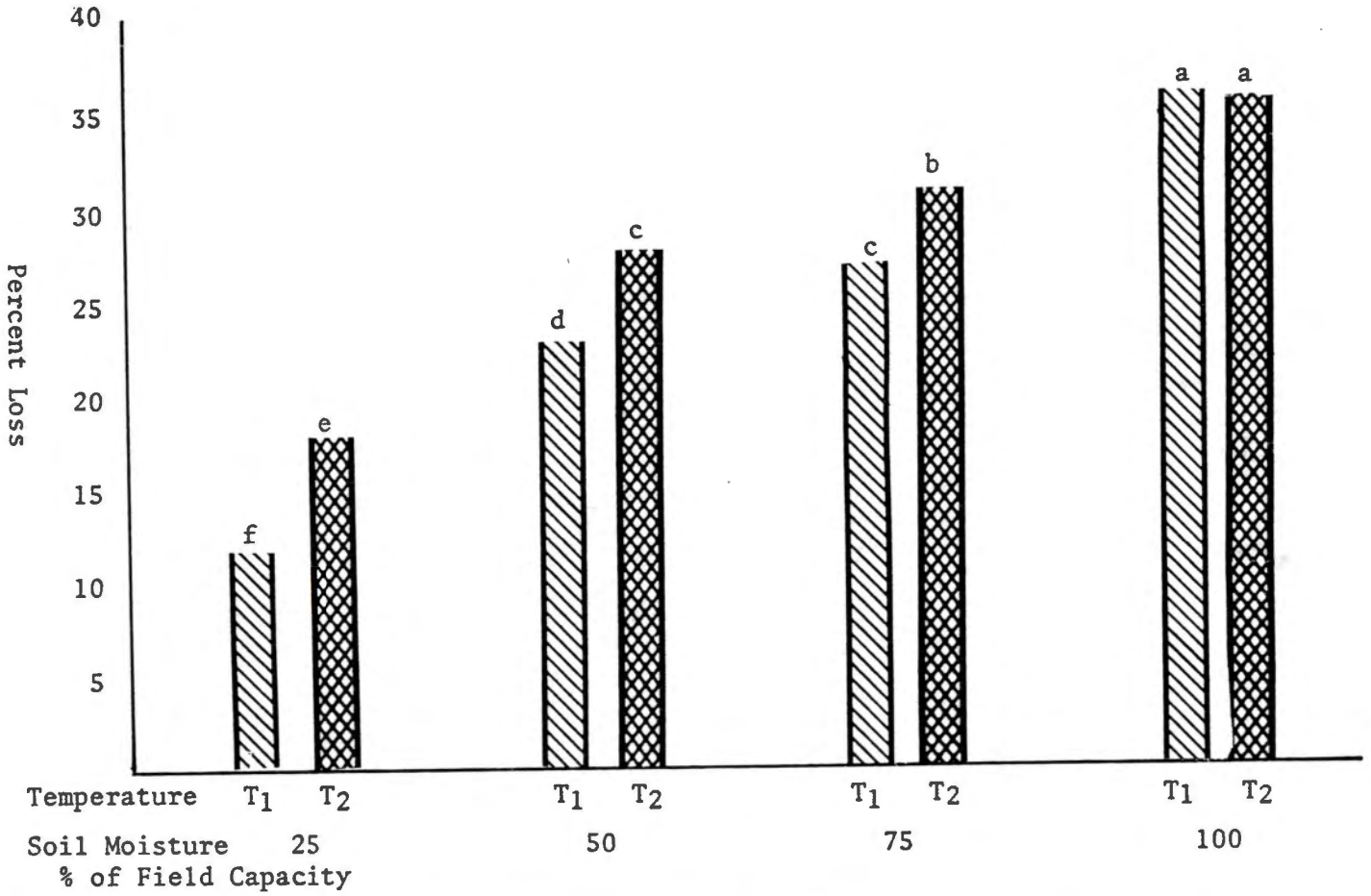


Figure 9. The Percent Loss of Three Dinitroanilines from Memphis Silt at Four Moisture Levels and Two Temperature Regimes. The Values Plotted Were Averaged across Rates. Bars with the Same Letter Are not Significantly Different at the $P < 0.05$ Level of Probability According to Duncan's New Multiple Range Test. T_1 = Laboratory, T_2 = Greenhouse.

volatilization by increasing the vapor pressure of the compounds. Increasing temperature also affects the volatility of soil incorporated pesticides by accelerating soil water loss and pesticide diffusion. However, as seen in this experiment the water loss from the soil can be affected in such a way as to cancel the higher temperature effect on volatilization. A rapid loss of water from the greenhouse samples resulted in those samples remaining in a dry condition for longer periods of time than the laboratory samples. Therefore, the enhancement of volatilization due to water in the soil would terminate sooner for the greenhouse samples than for the laboratory samples. The higher drying rate of the greenhouse samples appeared to have equalized dinitroaniline loss at FC and decreased the temperature effect for the other moisture treatments. The difference in time between the greenhouse and laboratory samples to become dry declined with decreasing soil moisture content. The effect of temperature on herbicide loss for the 25, 50, and 75% of FC samples was not masked as effectively as for the 100% of FC samples and significant differences of loss between the two temperatures appeared.

An estimation of the variability of herbicide loss caused by the parameters, herbicides, soil moisture, and temperature and the combinations of those parameters was obtained by the multiple regression technique as previously described in Chapter III. Included in the analysis with the linear terms of herbicides (H), moisture (M), and temperature (T), were the interaction of the linear terms (HM,HT,MT,HMT) and the squares of the linear terms (H2, M2, T2). The analysis was performed separately on each rate. A portion of the analysis is

presented in Table 21 and contains the number of terms in the models, R-Square values and the variables in the models.

All the models presented in Table 21 had at least one square term which shows that the loss of herbicides from the soil was nonlinear. The square of the soil moisture term (M2) was the single most important term in the analysis and accounted for 36 and 28% of the variation for the 12.5 and 25 µg samples, respectively. The linear and square terms (H H2) of herbicides were found to be the best two variable model for both applications and explained 53 and 54% of the total variation for the 12.5 and 25 µg samples, respectively. For both applications the best three variable model (H H2 M2) explained 89% of the variation for the 12.5 µg samples and 82% for the 25 µg samples. Models that contained four or more variable did not significantly increase the R-Square statistic for the 12.5 µg samples. A four variable model (H HT H2 M2) was obtained for the 25 µg samples with the addition of the herbicide × temperature interaction term (HT). The interaction term HT contributed 4% to the variation explained by the four variable model. Models with five or more variables did not significantly increase the amount of variation for the 25 µg samples.

The analysis reveals that the properties of herbicides caused the greatest amount of variation in the loss of the herbicides from soil. Soil moisture was the second most important source of variation, while the effect of temperature on the loss of herbicides was not very important. The results of the effect of herbicide properties and soil moisture on volatilization were predictable. The vapor pressure of a compound is the most important factor controlling the loss of herbicides

Table 21. Multiple Regression Maximum R-Square Improvement Analysis for Coefficients of Determination (R-Square) for the Variation in the Volatility Study

Number in Model	R-Square	Variables in Model
	12.5 µg Rate	
1	0.36	M2[1]
2	0.53	H H2[2]
3	0.89	H H2 M2
	25 µg Rate	
1	0.28	M2
2	0.54	H H2
3	0.82	H H2 M2
4	0.86	H HT H2 M2[3]

[1]The square of the linear term (M) for moisture

[2]The linear (H) and square term (H2), for herbicides, respectively

[3]HT is the interaction term of Herbicides and Temperature

from soil by volatilization. Soil moisture content has been shown to have a substantial effect on volatilization in this study and in the studies of other investigators (6,25,48,52) for similar experiments. The small amount of variation caused by temperature was probably due to the manner in which the study was conducted. The expected increase in loss of herbicides due to higher vapor pressures resulting from higher temperatures was nullified because the samples in the greenhouse remained dry for longer periods of time than the samples in the laboratory.

V. APPLICATION OF THESE RESULTS TO PRACTICAL PROBLEMS

Information gathered in this study may help explain the soybean injury problem encountered with dinitramine in Tennessee. The adsorption experiments using four Tennessee soils revealed that dinitramine was not adsorbed to as great extent as was fluchloralin or profluralin. Adsorption by soil of all three compounds was proportional to the soil organic matter content. The desorption experiments showed that over 30% of adsorbed dinitramine and fluchloralin was desorbed with five rinses of water while profluralin desorption was about 15%. Thus substantial amounts of dinitramine and fluchloralin could be brought into solution during periods of heavy rainfall. The volatility study revealed that a smaller percentage of dinitramine was volatilized from Memphis silt than was either fluchloralin or profluralin.

From the evidence gathered in this study the possibility exists that if the three herbicides are applied at equal rates a larger portion of dinitramine would be available in the soil to injure developing soybeans

than would be either fluchloralin or profluralin. The low organic matter content of Tennessee's soils and subsequent low adsorptive capacity provides less resistance to the movement of dinitramine through the soil. Dinitramine is applied at rates that range from 0.33 to 0.50 lb/A in the top 2-3 inches of soil so that the soybean roots will develop underneath the herbicides layer. When moderate or heavy rainfall occurs a portion of the dinitramine will dissolve into solution and leach into the soybean root zone and may cause injury. Another ramification of this leaching process is that the concentration of herbicides in the surface layer is diluted and thus erratic weed control may occur.

CHAPTER V

SUMMARY AND CONCLUSIONS

I. ADSORPTION

Distribution coefficients were determined from batch adsorption studies that were conducted on four soils subjected to nine chemical treatments as previously described. The order of increasing dinitroaniline soil adsorption was dinitramine < fluchloralin < profluralin. Averaged over all the soil treatments profluralin, fluchloralin, and dinitramine distribution coefficients were 306.5, 64.6, and 50.4, respectively. The order of dinitroaniline adsorption by the nontreated soils was Maury < Memphis < Decatur < Iberia. The order of adsorption of the three herbicides by the soils was related to the soils' organic matter content.

The order of adsorption of the three dinitroanilines was proportional to the length of their aniline sidechain; profluralin > fluchloralin > dinitramine. Lengthening the aniline sidechain of the compounds resulted in an increase of the molecules lipoidal properties. Increasing the lipoidal properties of herbicides has been shown to increase their soil adsorption in other studies (9,32).

II. SOIL COMPONENTS

A sequential extraction of the soils with solvents of increasing polarity was performed to remove selected components of the soils' organic

matter that may affect adsorption. Dinitroaniline adsorption by the ether and alcohol extracted soils was enhanced by an average of 27 and 31%, respectively. The increase in adsorption was due to the removal of lipoidal materials that blocked adsorption sites. Further extraction with hot water which removed the polysacchride fraction of the soils' organic matter decreased adsorption to that of the orginal nontreated soils. The polysacchride fraction must have contained those additional adsorption sites exposed in the ether and alcohol extracted soils. Extraction of the hot water treated soils with 2% HCl increased dinitroaniline adsorption by an average of 38.2% over the nontreated soils. Further digestion with 80% H_2SO_4 increased adsorption to an even greater extent of 77.2%. The pH of the acid treated soils was lowered to values between 2 and 3. The extreme surface acidity of the soils may cause partial dissociation of the molecules or perhaps even decomposition (2). The two acid extractions did not affect adsorption by the Memphis soil to as great extent as the other soils. The free iron oxide content of the Memphis soil was half that of the other soils and at the extremely low pH's the positive charge for the Memphis soil would be less than the other three soils.

The destruction of organic matter with hydrogen peroxide decreased dinitroaniline adsorption by an average of 21.3%. This removal of organic matter decreased both available adsorption sites and surface area of the soils. Soils treated with sodium-citrate-dithionite-bicarbonate caused an increase in dinitroaniline adsorption for all four soils. The iron oxides were acting as cemeting agents for the soil particles as evidenced by an observed increase in glycerol retention. Treatment of

soils with hydrogen peroxide followed by extractions of free iron oxides caused a 6.8 fold increase in adsorption over the nontreated soils and a 3.5 fold increase in glycerol retention. This is a strong indication that the mineral fraction of soils have a strong affinity for dinitroanilines.

Linear correlation coefficients (r) were calculated for the association of K_d values with pH, CEC, and glycerol retention of the soils and treated soils. The r values obtained for the correlation of K_d with pH and CEC were not significantly correlated at the $P<0.05$ level of probability. Positive significant correlation coefficients ($P< 0.05$) were obtained for the association of K_d with glycerol retention. The r values of dinitramine, fluchloralin, and profluralin for the association of K_d with glycerol retention were 0.73, 0.78, and 0.88, respectively, which indicates that dinitroaniline adsorption increased with increasing surface area.

III. DESORPTION

The nontreated soils from the batch adsorption experiment were subjected to five rinses of distilled water. The percentage of adsorbed herbicides desorbed by the five rinses was 32.4, 31.0, and 15.2% for dinitramine, fluchloralin, and profluralin, respectively.

The dinitroaniline release curves shows that profluralin is held with a greater force than are either dinitramine or fluchloralin. Release curves of the soils revealed that desorption was inversely related to soil organic matter.

IV. BONDING MECHANISMS

The adsorptive forces involved in the adsorption of the three dinitroanilines were nonspecific physical adsorption. The bonding mechanisms are a combination of van der Waals-London forces reinforced by hydrophobic bonding. Van der Waals-London interactions are the main bonding forces of nonionic compounds while hydrophobic bonding arises from the repulsion of nonpolar molecules from structured water. Relatively little change in adsorption (<2 fold) due to the soil chemical treatments occurred except for the hydrogen peroxide + sodium citrate-dithionite-bicarbonate treated soils which experienced a large increase in adsorption (6.8 fold). All the soil chemical treatments except for the hydrogen peroxide + sodium-citrate-dithionite-bicarbonate treatment produced relatively little change in the soil glycerol retention values, while the latter treated soils showed a large increase in glycerol retention.

V. VOLATILITY

The loss of profluralin by volatilization from the Memphis soil for all treatments was significantly higher than the other two herbicides. Generally, fluchloralin losses were greater than dinitramine. The order of herbicide loss was proportional to the compounds vapor pressure. A greater loss of herbicides occurred from the 25 µg rate samples, than from the 12.5 µg rate samples. However, less percentage of herbicide was lost from the 25 µg samples than from the 12.5 µg samples. Since the compounds are practically water insoluble a greater proportion of

the herbicides in the 12.5 µg samples would be in solution than the 25 µg samples.

A direct relationship was observed between herbicide volatilization and soil moisture. Averaged across temperature levels profluralin loss increased from 23.5% at 25% of FC to 56.3% at FC for the 12.5 µg rate. Over the same moisture range fluchloralin and dinitramine loss increased from 13.4 to 27.6%, and 6.6 to 31.6% respectively. Similar results were observed for the 25 µg rate. A combination of the following factors induced by the presence of water in soil could have increased herbicide volatilization; (1) The vapor pressure of herbicides was higher in aqueous solution than in the crystalline form; (2) Competition of water with the adsorbed herbicides for adsorption sites continuously replaces the herbicides in solution lost by volatilization; (3) Water accelerates the movement of herbicides from within the soil to the evaporation surface.

The effect of temperature on volatilization for the 100% of FC samples was confounded because the samples in the greenhouse were in a dry condition for longer periods of time than those in the laboratory. Significant differences between the laboratory and greenhouse samples were observed for the 75, 50, and 25% of FC.

VI. COEFFICIENTS OF DETERMINATION

Results from the Stepwise R-Square multiple regression analysis showed that a combination of two parameters (herbicides and moisture) accounted for nearly all of the observed variation in the volatility data. A three variable model (H H2 M2) was sufficient to explain the

variation (89%) for the 12.5 µg samples. A four variable model (H HT H2 M2) accounted for 86% of the total variation for the 25 µg samples.

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APPENDIX

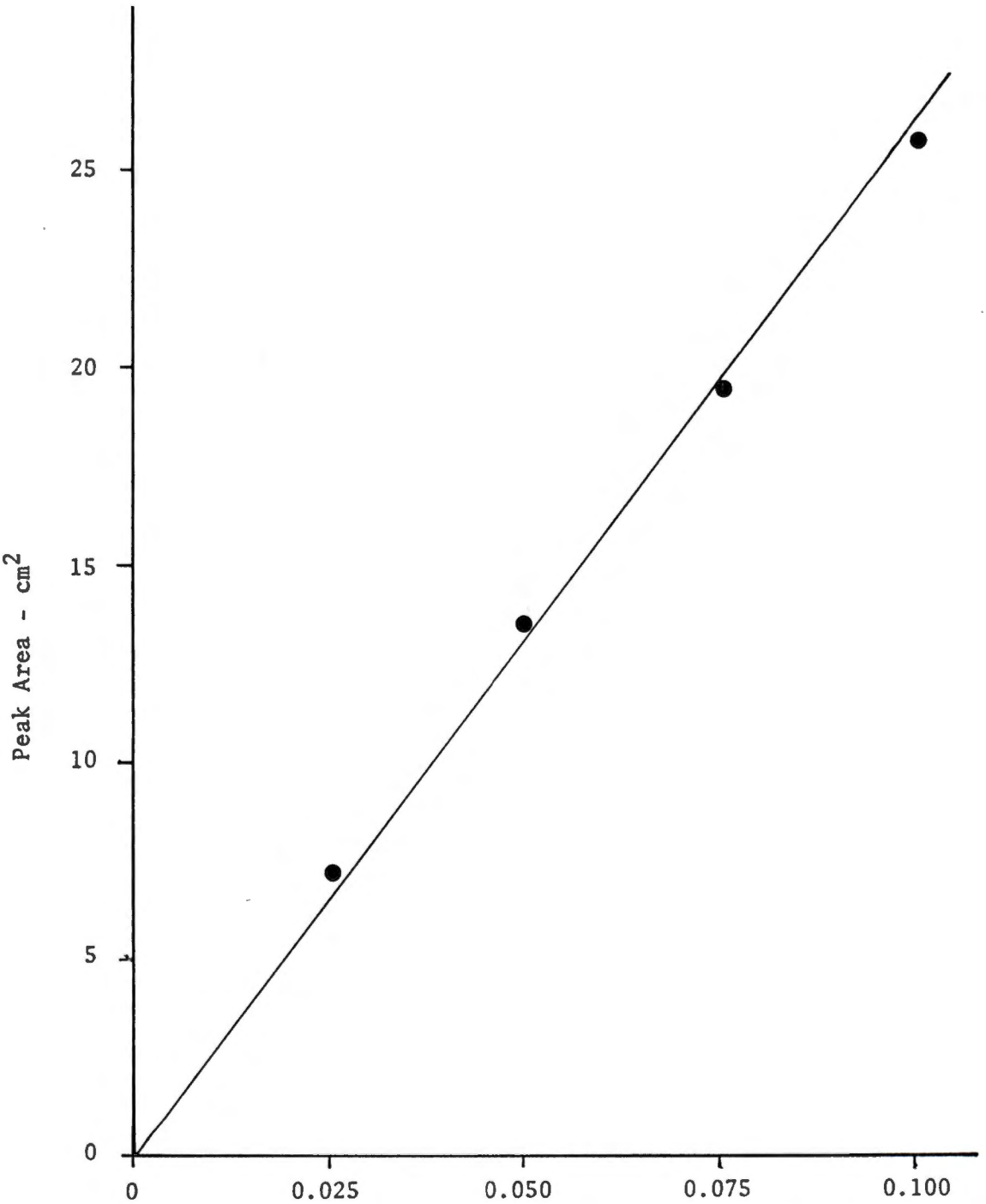

Figure 10. A Typical Standard Curve for Profluralin Where Peak Area Is Plotted Against Concentration of Standards.

Table A-1. Solution Equilibrium Concentration Values of Dinitramine from the Batch Adsorption Studies with Four Soils after Different Treatments

Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
	µg-ml			
Nontreated	0.157	0.070	0.104	0.144
Ether	0.148	0.068	0.091	0.143
Alcohol	0.151	0.071	0.088	0.141
Water	0.177	0.048	0.103	0.154
2% HCl	0.115	0.058	0.087	0.167
80% H_2SO_4	0.075	0.056	0.075	0.152
- OM[1]	0.176	0.083	0.116	0.167
- Fe[2]	0.107	0.045	0.072	0.079
-OM & Fe[3]	0.060	0.029	0.038	0.094

[1]Hydrogen peroxide treated soils

[2]Sodium-citrate-bicarbonate-dithionite treated soils

[3]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils

Table A-2. Solution Equilibrium Concentration Values of Fluchloralin from the Batch Adsorption Studies with Four Soils after Different Treatments

Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
	µg-ml			
Nontreated	0.117	0.066	0.090	0.105
Ether	0.107	0.054	0.081	0.103
Alcohol	0.107	0.052	0.077	0.104
Water	0.130	0.060	0.076	0.152
2% HCl	0.101	0.043	0.046	0.130
80% H_2SO_4	0.063	0.029	0.055	0.106
- OM[1]	0.145	0.081	0.091	0.171
- Fe[2]	0.072	0.042	0.069	0.079
- OM & Fe[3]	0.057	0.029	0.037	0.056

[1]Hydrogen peroxide treated soils

[2]Sodium-citrate-bicarbonate-dithionite treated soils

[3]Hydrogen peroxide followed by sodium citrate-bicarbonate-dithionite soils

Table A-3. Solution Equilibrium Concentration Values of Profluralin from the Batch Adsorption Studies with Four Soils after Different Treatments

Treatment	Soils			
	Maury	Iberia	Decatur	Memphis
	μg-ml			
Nontreated	0.048	0.020	0.033	0.043
Ether	0.032	0.020	0.028	0.030
Alcohol	0.036	0.014	0.022	0.036
Water	0.045	0.019	0.041	0.055
2% HCl	0.031	0.015	0.031	0.057
80% H_2SO_4	0.035	0.014	0.017	0.045
- OM[1]	0.074	0.023	0.035	0.076
- Fe[2]	0.030	0.016	0.026	0.035
- OM & Fe[3]	0.004	0.001	0.003	0.009

[1]Hydrogen peroxide treated soils

[2]Sodium-citrate-bicarbonate-dithionite treated soils

[3]Hydrogen peroxide followed by sodium-citrate-bicarbonate-dithionite treated soils

VITA

Michael Boyd Akins was born in Monroe County, Tennessee, July 11, 1949. His parents are Arnold and Ruby Akins. He attended public schools in Monroe County, Tennessee, and was graduated from Vonore High School in 1967. He attended Hiwassee Junior College for two years and then enrolled in the University of Tennessee, Knoxville. He received a Bachelor of Science Degree in Chemistry in June of 1972 and immediately began study toward the Master of Science degree in Agriculture at the University of Tennessee, Knoxville which he received in December 1973. In the fall of 1973 he began additional graduate study at the University of Tennessee, Knoxville and received a Doctor of Philosphy degree with a major in Plant and Soil Science in March 1977.

He is married to the former Teresa Ann DeLorenzo of Knoxville, Tennessee. They currently do not have any children.