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To the Graduate Council:

I am submitting herewith a thesis written by Melvin J. Ivey entitled "The Effects of Soil Properties and Applied Water on the Leaching of Atrazine, Simazine, Diuron and DCPA in Soil Columns." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agronomy.

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THE EFFECTS OF SOIL PROPERTIES AND APPLIED WATER ON THE LEACHING OF
ATRAZINE, SIMAZINE, DIURON AND DCPA IN SOIL COLUMNS

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Presented to
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CHAPTER I

INTRODUCTION

Today, there is an increasing demand for information regarding the disappearance of herbicides from soils. Such information is important from at least two standpoints. First, it is essential that a soil-applied herbicide remain in an active state long enough to do the job for which it was intended. Second, its phytotoxicity should become dissipated rapidly enough so that sensitive crops which follow will not be injured. Not only is it possible for frequently applied herbicides to build up to toxic levels even for tolerant crop plants, but often residues from spring-applied herbicides remain in the soil to affect sensitive fall-seeded plants.

Little is known at the present time about what happens to herbicides under a variety of edaphic and climatic conditions. Even when herbicides are applied directly to plants, a substantial amount eventually reaches the soil. The problem of persistence of herbicides in soils is one which faces both farmers and research workers.

Disappearance of herbicides from soils is a complex process which is affected by several interacting variables. These variables include type and rate of application of the herbicide, physical and chemical soil properties, amount of leaching by rainfall, microbiological activity, chemical decomposition, volatilization, photo-decomposition, and plant uptake. The persistence of a herbicide in a given

situation is governed by the prevailing combination of these variables.

This study deals with leaching which is one of the most important factors affecting disappearance of herbicides from soils. In humid agricultural regions particularly, leaching is a major factor influencing the success or failure of preemergence herbicides.

The purpose of this study was to determine the effects of three rates of applied water on movement of four herbicides in columns of four soils.

CHAPTER II

REVIEW OF LITERATURE

I. HISTORY AND IMPORTANCE OF WEED CONTROL

The control of weeds is one of man's oldest agricultural problems, but has been studied scientifically only recently (6).¹ Weed control is a challenge to all farmers because weeds increase production costs, lower yields, and reduce quality of farm products. Losses caused by weeds in the United States are second only to losses from soil erosion and equals combined losses from insects and diseases (34). Agricultural speaking, losses from weeds and costs of controlling them are estimated to be nearly 4 billion dollars annually (34).

Weed control today is carried out on a wider scale than any other pest control operation (6). New herbicides are being introduced so rapidly that it will be several years before their mode of action is understood. Any chemical that blocks a step in any plant process is a potential herbicide (13). The science of weed control has been ranked along with entomology and pathology as factors important to the advancement of agricultural efficiency (6, 51). Herbicides are now helping to provide us with "new land" by reclaiming it from weeds (6). Chemicals have been used to control weeds for centuries, but little

¹Numbers in parentheses refer to literature cited.

practical use was made of them until late in the nineteenth century (51). Finally, with the development of 2,4-dichlorophenoxyacetic acid (2,4-D) and several other effective herbicides, emphasis shifted to increased persistence to obtain full-season weed control. More recently, a host of extremely toxic chemicals with herbicidal value have been developed which may persist beyond the growing season to injure succeeding crops. Present day research efforts have been directed toward an evaluation of the relative importance of each factor affecting persistence or disappearance of herbicides from soils by designing experiments which attempt to control specific variables.

II. FACTORS AFFECTING DISAPPEARANCE OF HERBICIDAL ACTIVITY FROM SOILS

The rate of disappearance of herbicides from soils is a key property which determines their utility for a given use. Both climatic and edaphic conditions influence the effectiveness of preemergence herbicides. The complexities and variations of soil systems complicate the study of the fate of herbicides in soils. There are wide variations among soils in amounts of mineral and organic matter, water, and air. The mineral fraction varies in texture and types and amounts of clay minerals, which also vary in hydration and base saturation (59).

The herbicide itself, including type of compound, solubility, rate applied, method of application, and its vulnerability to a combination of environmental factors must be considered in dissipation studies. The activity of preemergence herbicides may be lost from

soils by several ways including leaching, microbiological decomposition, adsorption, chemical decomposition, vaporization, plant uptake, and photodecomposition. However, according to the majority of research workers, the most important factors involved in the disappearance of herbicidal activity are microbiological decomposition, leaching, adsorption, vaporization and plant uptake (5, 8, 44, 45, 65).

Microbiological Decomposition

Most research workers agree that, in general, microorganisms probably play the leading role in the inactivation of certain herbicides, but other factors frequently become important under certain conditions (5, 11, 29).

Microorganisms generally receive most of the credit for the inactivation of 2,4-D (4, 5, 44, 45, 50), isopropyl N-(3-Chlorophenyl) carbamate (CIPC) (45, 50) isopropyl N-phenylcarbamate (IPC) (43), 2,2-dichloropropionic acid (dalapon) (50), 2-chloro-N, N-diallylacetamide (CDAA), 2-chloroallyl diethyldithiocarbamate (CDEC) (20), 3-(p-chlorophenyl)-1,1-dimethylurea (monuron) (41, 45, 50, 58), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) (50, 58) and 3-amino-2,5-dichlorobenzoic acid (amiben) (48).

Talbert and Fletchall (63), studying inactivation of 2-chloro-4,6-bis(ethylamino)-s- triazine (simazine) and 2-chloro-4-ethylamino-6-isopropylamino-(atrazine) in the field, reported that inactivation occurred only when the environment was favorable for microbial activity. Inactivation was fairly rapid during warm, moist periods but was slow

during dry cool periods. Little inactivation occurred in the fall and little if any during the winter. Sheets and Danielson (59) observed that soil microorganisms metabolize phenylureas and s-triazines but not selectively or preferentially. Behrens (5) suggested that slow microbial decomposition of these formulations help explain why persistence problems have shown up.

Soil microbes have been isolated which can decompose practically any organic compound, including the complex cyclic and short-chained compounds as well as the more vulnerable long-chained formulations (42).

Sheets and Crafts (58) planted oats (Avena sativa L.) periodically in autoclaved and non-autoclaved soils treated with monuron, diuron, 3-phenyl-1,1-dimethylurea (fenuron) and 3-(3,4-dichlorophenyl)-1-methylurea (DMU) to determine the effects of microorganisms on persistence. In each case the phytotoxicity was lost quicker from non-autoclaved soil.

DeRose and Newman (17) discovered that 2,4-D, 2-4,5-trichlorophenoxyacetic (2,4,5-T) and 2-methyl-4-chlorophenoxyacetic acid (MCPA) toxicity to oats disappeared within three to six weeks in non-sterilized soil, but no loss in activity could be detected during six weeks in sterilized soil. In a similar oat bioassay study, Newman et al. (43) noted that IPC persisted more than nine weeks in autoclaved soil.

Inactivation of certain phenoxy herbicides by microbial action has been found to depend less upon the number of halogens than upon their position on the benzene ring. Alexander and Aleem (2), using absorption of ultraviolet light to indicate decomposition, determined

that a chlorine atom in the meta position of the benzene ring retarded microbial decomposition. Whiteside and Alexander, (73) by similar methods, observed that 2,4-D was quickly decomposed when incubated in soil suspension while 2,4,5-T persisted.

Several research workers have reported that herbicides are inactivated quicker under environmental conditions favorable for microbiological activity (26, 45, 63, 59, 32, 48, 8, 54, 55). A warm temperature, an optimum of 20 to 32° C (38, 49), available moisture, 20 to 80 per cent of the water-holding capacity of the soil (43), and food and oxygen are essential for microbial activity. DeRose and Newman (17) found that disappearance of 2,4-D, 2-4,5-T, and MCPA increased with increases in soil moisture from 20 to 100 per cent of the water-holding capacity and doubled as soil temperature increased from 10 to 30° C. Newman et al. (43), noted that there was no difference in the rate of disappearance of IPC from 20 to 80 per cent of the water-holding capacity, but was considerably reduced at 100 per cent and in flooded soil. Sheets and Crafts (58) reported that toxicity to oats disappeared quicker in continuously moist soil than in soil moist or dry during alternate months.

Hernandez and Warren (27) discovered that 2,4-D was still toxic after eight weeks in soil that had been stored at 40° F. The chemical was completely inactivated after four weeks in soil that was stored at 59, 65, and 90° F. They noted that 2,4-D was still toxic in air dried peat after 18 weeks of storage, but in moist and water saturated soil the chemical was inactive after four weeks. 2,4-D was still toxic in

moist, sterilized soil after 12 weeks in storage, but the chemical was inactivated in moist unsterilized soil within four weeks.

In most soils, the available food and oxygen supply for micro-organisms is greater nearer the soil surface, due to higher organic matter levels and adequate aeration. Burnside et al. (8) in field experiments on silty clay loam and loam soils in Nebraska, reported that monuron, simazine, and atrazine are subject to slow microbial breakdown but the rate is dependent upon climatic and edaphic conditions. Burnside et al. (8), along with Crafts and Drever (14), proposed that intensive use of these herbicides in low rainfall areas could result in an accumulation in sub-surface soil horizons where microbial breakdown is slow. Rahn and Baynard (46) noted that additions of manure increased the inactivation of monuron and Kries (39) reported that additions of leaf mold produced the same effect. Holstun and Loomis (32) discovered that large additions of manure or peat temporarily decreased the rate of dalapon decomposition. The rate of inactivation of several herbicides was found by Reid (49) to be increased by increasing aeration.

Both fungi and bacteria are active in herbicide decomposition (23, 65), but generally bacteria are most active at a pH of near neutral (32, 49) while fungal activity steps up at pH values below 5.5 (38).

Leaching

Leaching is such an important factor influencing the success of preemergence herbicides in humid regions that it must be considered

along with microbial action as a major factor involved in the disappearance of herbicides from soils (4, 68). Rainfall can reduce herbicidal effectiveness through leaching, but still, relatively large amounts of rainfall are required to cause most preemergence herbicides to disappear from the upper part of the soil profile. The movement of a herbicide by leaching through the soil causes a reduction in its concentration by dilution and a loss of effectiveness by increasing adsorption by soil colloids (55). There is a definite relationship between climatic and edaphic conditions and the movement, persistence, and activity of herbicides applied to the soil (18).

The susceptibility of a herbicide to leaching is considered by Gantz and Slife (20) to be second in importance to microbial breakdown in persistence evaluation and becomes especially important when the herbicide is toxic to crop plants as well as weeds.

Water solubility and molecular size are indices of herbicide leachability, but are not the only factors involved in leaching differences among various herbicides (48, 59). Leaching and adsorption are closely related because the soil organic matter content and inorganic colloidal fraction greatly inhibits herbicide movement in soils as well as reducing herbicidal activity (32, 48). However, strong adsorption characteristics are essential for preemergence herbicides in order to minimize movement through the soil (40). Leaching is also affected by soil moisture, texture, structure, amount of herbicide applied, and frequency, intensity, and total amount of rainfall (21, 59). According to Hartley (26), leaching of herbicides into the soil is

influenced by the amount of evaporation between rains in addition to solubility, adsorption, and soil moisture level at time of application.

Wiese and Davis (74) found that leaching of soil sterilants by simulated flood irrigation varied with the herbicide, method of herbicide application, and amount of water in the system. Herbicides which tended to leach easily were not affected by method of application and leached as deeply as water penetrated, but relatively insoluble herbicides were affected by method of application.

Upchurch and Pierce (68) proposed that two steps are involved in herbicide leaching. First, the entrance of the herbicide into solution from herbicide particles or from herbicide adsorbed onto soil particles. Second, the adsorption of herbicide from the percolating solution.

Burnside et al. (8) found leaching to be an important avenue of disappearance of monuron, atrazine, and simazine from loam and silty clay loam soils under field conditions in Nebraska. Although resistant to leaching, the herbicides moved through a 24-inch soil profile. They noted that the amount of herbicide leached varied directly with water solubility, being greatest with monuron, least with simazine, and intermediate with atrazine. Outlining a new concept in the disappearance of herbicides from soils, they proposed that herbicides previously thought to have been broken down had only been removed from upper to lower soil horizons by leaching where extremely toxic levels may accumulate with frequent applications.

Burnside et al. (10) also reported that leaching of simazine

in silt loam under controlled field conditions is not rapid, but is a contributing factor in dispersing the herbicide in the soil.

Hanks (24) reported greater disappearance of 2,4-D by leaching with 16 inches of water than with 10 inches during a six weeks period. Weldon and Timmons (71) stated that disappearance of diuron was more a function of irrigation than of time in Wyoming. The 2 pound per acre rate disappeared within three months when 4 inches of water was applied each month for three months, but 15 months were required for complete disappearance when three 4-inch applications were applied over a 15 month period.

Greater leaching of all herbicides occurs in sandy soils because percolation is high and adsorption is low (5, 48, 57, 52, 47). Rodgers (52) studied leaching of simazine, atrazine, 2-methoxy-4-ethyl-amino-6-isopropylamino-s-triazine (atratone), and 2-chloro-4-diethylamino-6-isopropylamino-s-triazine (ipazine) in Lakeland fine sand and Greeneville fine sand at 2 and 4 pounds per acre and in a muck at 4 and 8 pounds per acre. Leaching was accomplished by the application of 1 or 2-inch increments to totals of 1 to 16 inches of simulated rainfall over a one to four weeks period. The greatest amount of leaching occurred with atrazine as it moved through the 6-inch columns of both sands, but none of the herbicides moved below 1 inch in the muck. In general, the greatest amount of leaching occurred with the higher total amounts of water applied over a short period of time. When 23-inch columns were used, atrazine moved through the entire column in concentrations toxic to oats and cucumbers (Cucumis sativus L.),

particularly at the 4 pound rate with only 4 inches of applied water. Simazine moved to only 4 to 6 inches in killing concentrations and to 12 inches in stunting concentrations.

Rauser and Switzer (48) noted the most rapid loss of amiben activity in sand followed by clay with muck remaining phytotoxic much longer. They explained that these differences are due to the effects of high muck and clay and low sand cation exchange capacities on adsorption of amiben by soil particles. They concluded that leaching is the major factor involved in the disappearance of amiben from sandy soils, leaching and microorganisms are both important in clay, and microorganisms are more important in muck.

Sheets (57) reported that oat bioassays showed that 2 inches of applied water moved the 1 pound per acre rate of monuron and simazine into the 3 to 6-inch depth in sandy loam columns. Ten inches of applied water completely removed the herbicides from the top 6 inches into the lower 10 inches of the columns. Two inches of applied water moved the 20 pound per acre rate into the 0 to 9-inch depth in severely stunting concentrations while 10 inches of applied water resulted in death of oat plants growing in all sections of the columns.

Hill et al. (29), working with substituted ureas on 11 soils, showed that removal from the soils by percolation was not a major factor in disappearance since no herbicide was present below 4 inches after 72 inches of water was applied over a 90 day period.

Adsorption

It is necessary to have a delicate balance between adsorption and persistence of herbicides on one hand and disappearance on the other so that weeds will be controlled throughout the growing season but succeeding sensitive crops will not be damaged (40). Adsorption counteracts the force of leaching, but should not be considered a factor in reducing residues (5) since it contributes to persistence problems under certain soil-herbicide situations. Sheets and Danielson (59) stated that adsorbed herbicides in soil systems are probably gradually desorbed as leaching, chemical and biological decomposition, and plant uptake reduces the concentration in the soil solution.

In laboratory leaching experiments using CDAA and CDEC on silt loam and sand soils, Gantz and Slife (20) found that even though toxic CDAA residues were found in lower soil column layers, toxicity in surface layers was not reduced. They proposed that adsorption does not inhibit activity of these herbicides and tends to prevent leaching from causing a loss of herbicidal effectiveness in medium and heavy textured soils. However, it is generally understood that the phytotoxicity of most herbicides is reduced by soil adsorption requiring different herbicide rates on various soils to achieve the same degree of phytotoxicity. Most of the variation in herbicidal activity in various soils can be attributed to differences in the adsorption capacity of the organic matter and clay fractions. Most workers agree that organic matter is the primary factor affecting adsorption of herbicides (5, 7, 8, 18, 30, 37, 59, 64, 69).

Burnside and Behrens (7) used corn (Zea mays L.) to bioassay simazine phytotoxicity in sand, silt loam, clay, and muck soils. They discovered that toxicity decreased as organic matter and/or clay content increased. Upchurch and Pierce (69) noted that monuron retention in soil leached by simulated rainfall increased from 12 to 40 per cent as organic matter increased from 0.87 to 1.44 per cent. Upchurch and Mason (67) studied the toxicity of 12 soil incorporated herbicides to cotton (Gossypium hirsutum L.). They concluded that regardless of herbicide, approximately five times more herbicide was required with 20 per cent organic matter than with 4 per cent to produce the same degree of toxicity.

Jordan and Day (37), stressing the importance of organic matter on adsorption, reported a positive correlation between soil sand and silt content and ethyl N, N-di-n-propylthiolcarbamate (EPTC) toxicity to oats and nutsedge (Cyperus sp L.) and a negative correlation with organic matter content. Geissbuhler et al. (21) reported strong adsorption of N-(4-chlorophenoxy-phenyl)-NN-dimethylurea (C-1983) which increased from sandy loam to clay loam to humus. Holstun and Loomis (32), working with dalapon on 3 soil types, found that little adsorption occurred after leaching with 1.5 inches of water. Sand additions slightly increased the downward movement of dalapon while manure additions increased dalapon retention in the surface 2 inches.

Harris and Warren (25) revealed a direct relationship between adsorption and soil organic matter content, clay content, and exchange capacity. They added that an inverse relationship exists between

adsorption and pH, solubility, and temperature. Upchurch and Pierce (69) disclosed that adsorption of monuron from a percolating solution in Lakeland sand is affected by soil temperature, organic matter content, herbicide concentration in the percolating solution, and rate of passage of the percolating solution.

Rauser and Switzer (48) reasoned that since amiben is water soluble the amount retained in the soil would be directly related to adsorption. They showed that amiben phytotoxicity remained much longer in muck and clay soils of high exchange capacity than in sands of low exchange capacity. Wiese and Davis (74) observed a general relationship between solubility and depth of herbicide movement in soil tubes. However, they found that completely water soluble amine salt formulations of 2,4,5-T and 2-(2,4,5-trichlorophenoxy) propionic acid (silvex) are leached only one-half as deep as less soluble amine salt formulations of benzoic acid. They concluded that both 2,4,5-T and silvex are highly adsorbed by soil colloids.

Burnside et al. (8) indicated that adsorption of monuron, simazine and atrazine in Nebraska accounts for significant losses of toxicity. They stated that although organic matter content is most important in reducing herbicide toxicity by adsorption, the type of clay is also involved.

Coggins and Crafts (12) reported that additions of clay to nutrient solutions containing substituted urea herbicides reduced the toxicity to barley (Hordeum vulgare L.). An increase in hydrogen ion concentration favored increased adsorption of these herbicides. Davis

and Selman (16) observed that under field conditions a definitely smaller amount of 4,6-dinitro-o-sec-butylphenol (DNBP) was recovered from silty clay loam than from silt loam and sandy loam. They indicated that the chemicals were held in the soil in an unrecoverable form.

Frissel and Bolt (19) studied the adsorption of several herbicides, including 2,4-D, simazine and DNBP on illite, montmorillonite, and kaolinite as a function of pH. They discovered that most of the herbicides are adsorbed in large amounts at low pH, but are only slightly adsorbed at high pH. In a similar experiment with C¹⁴-labeled atrazine and simazine, Talbert and Fletchall (64), noted decreased adsorption with increased pH and temperature. The adsorption of several herbicides, including 2,4-D, 2,4,5-T, monuron, CIPC, and IPC, onto activated charcoal was determined by Leopold et al. (40). At 25° C they noted uniform adsorption at pH values from 2.2 to 8.0, but an increase in temperature to 95° C resulted in the release of 50 per cent of adsorbed 2,4-D in two minutes and near 100 per cent within one hour.

Upchurch (66) showed that organic matter content, cation exchange capacity, and total exchangeable bases were the soil factors most directly correlated with the amount of diuron required to produce a 50 per cent growth reduction in dry shoot weight of cotton and ryegrass (Lolium multiflorum Lam.) plants. He noted that for each 1 per cent increase in organic matter content approximately two p.p.m. additional diuron was required to produce a 50 per cent growth reduction in dry shoot weight in cotton. Ashton and Sheets (3) established

ED 50 values (effective dosage required to reduce growth 50 per cent expressed in p.p.m. concentration) for EPTC injury to oats grown on a wide range of soil types. They showed that 6.5 times as much EPTC was required to reduce the fresh weight of oats 50 per cent in clay soils high in organic matter than in sandy soils low in organic matter.

Sheets and Crafts (58) found that higher concentrations of four phenylurea herbicides were required to reduce growth of oat plants by 50 per cent in clay loam soil than in nutrient solutions. Seventy-two times more DMU, 28 times more diuron, seven times more monuron and two times more fenuron was required.

Chemical Decomposition

Little is known about the chemical reactions that herbicides undergo in soils because of the difficulty of developing a technique by which specific chemical reactions can be isolated. It is known from controlled laboratory experiments that certain herbicides are subject to reactions such as hydrolysis, oxidation, and formation of complexes which result in breakdown of the herbicide accompanied by accumulation of residues (59), but the difficulty lies in accurate determinations of these effects in the field.

There is more information available on photodecomposition than on any other form of chemical decomposition. Weldon and Timmons (72) exposed solutions of 10 p.p.m. monuron and diuron and 95 per cent ethyl alcohol to an 85 watt mercury lamp for 0,2,8, and 28 hour periods. Oat bioassays disclosed a 75 per cent decrease in phytotoxicity of both

herbicides following the 28 hour light period. Hill et al. (29) exposed an aqueous solution of monuron to sunlight in sealed quartz tubes. They discovered an 83 per cent loss of monuron after 48 days. Burnside et al. (8) discovered that monuron can be dissipated from the soil by photodecomposition in Nebraska and suggested that it should be incorporated in the soil. Sheets (54) observed a 50 per cent loss of amiben from an aqueous solution accompanied by a 50 per cent reduction in herbicidal activity after a six hour exposure to sunlight. According to Sheets and Danielson (59), less is known about the direct effect of light on the breakdown of herbicides than any of the factors affecting disappearance, but still, more is known about photodecomposition than any other form of chemical decomposition. They indicated that this factor may be significant in dry, hot, low rainfall areas, but is probably insignificant in humid regions where rains are frequent. Behrens (5) also considers photodecomposition to be of minor importance with most herbicides in the field. Sheets (54) proposed that the greatest losses from photodecomposition would occur in arid regions where herbicides remain exposed on the soil surface for longer periods of time.

Talbert and Fletchall (63) stated that simazine and atrazine are chemically stable but chemical decomposition may be of major importance in losses of triazines from soils under certain conditions. Hill et al. (29) reported that non-biological decomposition of substituted ureas was probably not an important means of disappearance.

Vaporization

All compounds are volatile to a certain degree when applied to the soil surface, but generally, disappearance by vaporization is important only with herbicides having high vapor pressures (59). Rauser and Switzer (48) proposed that loss of herbicidal activity by volatilization is probably only a minor factor with most herbicides but can become important with others. Burnside et al. (8) noted little volatilization of simazine, atrazine, and monuron from Nebraska soils in the field, presumably due to low vapor pressures. Hill et al. (29) indicated that volatilization of substituted urea herbicides from soils is unlikely due to low vapor pressures.

The type of formulation and temperature has been shown to affect volatilization (15, 59). Sheets and Danielson (59) found long-chained esters of 2,4-D to be less volatile than short-chained esters. Davis (15) reported a temperature increase of 29 to 36° C to increase DNBP vapor injury of cotton from slight to 70 per cent kill.

Plant Uptake

The adsorption and metabolism of herbicides by plants contribute to the disappearance of herbicidal activity from soils (5, 23, 54, 59, 63). In their study of inactivation of simazine and atrazine in the field, Talbert and Fletchall (63) showed that corn can absorb simazine and metabolize it to nonphytotoxic materials. During the second year of the experiment, the field plots showed longer lasting effects of simazine as compared to atrazine, but more weeds were growing where

last year's corn rows were located. They proposed that the greater density of corn roots in the row area resulted in more absorption of the herbicides by the corn plants. Sheets and Danielson (59) reported that herbicides are absorbed by plant roots and translocated to the serial plant parts where they are subjected to various chemical and physical processes in their breakdown. However, they suggested that plants probably absorb only small amounts of the total amount of a herbicide applied to a soil.

Herbicide and Rate

The disappearance of herbicides from soils is a complex process involving the nature of the compounds, adsorption by soil, soil properties, amount of rainfall and leaching velocity, temperature, and amount of chemical applied (11). The degree of residual toxicity is a factor that must be evaluated before a herbicide can be used most effectively. Herbicide stability is necessary for soil sterilization, rapid disappearance is desired in preplanting treatments, and selective full season activity disappearing by fall is desirable with pre-emergence applications (32).

Herbicide solubility seemed to be an important factor in the downward movement of monuron and diuron in a leaching study by Sheets (56). Monuron (solubility 230 p.p.m.) moved twice as fast as diuron (solubility 42 p.p.m.) through columns of sandy loam and clay loam soils. Burnside et al. (8) suggested that leaching of monuron, simazine, and atrazine in silty clay loam and loam soils in Nebraska

is probably directly related to their water solubilities, being greatest with monuron, intermediate with atrazine and least with simazine. Upchurch and Pierce (68) contended that the general concept that herbicide solubility is the key to leachability needs to be re-evaluated. They maintained that entrance of adsorption herbicide into the soil solution and soil adsorption of herbicide from the percolating soil solution should receive consideration. Leopold et al. (40) measured adsorption and solubility of 17 chlorinated derivatives of phenoxyacetic acid. Three successive chlorine substitutions in the phenyl ring increased adsorption onto activated carbon while decreasing solubility. Both adsorption and solubility affect disappearance of herbicides from soils and these results indicate the existence of an inverse relationship.

Coggins and Crafts (12) studying the electrophoretic behavior of the substituted urea herbicides, discovered that the addition of one or two chlorine atoms increases phytotoxicity. Maximum phytotoxicity resulted from the presence of two chlorine atoms in the aromatic nucleus and two methyl groups on the first nitrogen atom. Aldrich (1) and Warren (70) found chemical formulation to be important in 2,4-D disappearance. They found ester formulations to be more resistant to leaching than amine formulations. Ogle and Warren (45) stated that molecular size, solubility, and the formation of salts in the soil are all criteria for predicting leaching behavior of a herbicide.

The rate of a first order reaction is directly proportional to the concentration of the reacting substance (22). Burschel and Freed

(11) proposed that since most biological processes follow first order kinetics and data presented by Sund (61) indicate that ultimate herbicide breakdown is due to microbial activity, decomposition of herbicides in soils should also follow this pattern. To substantiate this theory, they showed IPC and 3-amino-1,2,4-triazole (amitrole) disappearance to be affected little by rate of application. Audus (4) found microbiological breakdown of 2,4-D to resemble reactions following first order kinetics. Newman et al. (43) found rate of application to have little effect on disappearance of IPC since 50 pounds per acre disappeared almost as quickly as 10 pounds per acre. Sheets (54) found disappearance of simazine during a 13 months period to be practically identical from application rates of 5, 10, and 20 p.p.m. The disappearance of atrazine, simazine, and diuron has been found to decrease at increased rates of application, but not proportionally (31, 41, 53, 62).

Lillie and Aldrich (41), working with monuron in a field study in New Jersey, applied 50 pounds per acre to plots in 1951 and 10 pounds per acre to other plots both in 1951 and 1952. By 1954 more of the chemical had disappeared from the 50 pound per acre plots than from the 10 pound per acre plots. They concluded that climatic differences from 1951 until 1954 influenced disappearance more than rate of application. Other than the effect of climate on microbiological activity, these observations bear out the fact that leaching by rainfall is an important factor in the disappearance of herbicides from soils. Upchurch and Pierce (69), studying the effect of rate of monuron on leaching in

Lakeland sand, reported each two-fold increase in monuron resulted in an increase in monuron content at each soil depth provided that monuron had previously been found at that depth. Rodgers (52) observed that the four pound per acre rate of atrazine, simazine, atratone, and ipazine applied to two fine sands in Florida leached 1 to 2 inches deeper than the two pounds per acre rate. Weldon and Timmons (71) reported the disappearance of diuron from sandy Wyoming soils to be more a function of irrigation than of time. The two pounds per acre rate disappeared in three months under heavy irrigation (three 4-inch water applications during three months), but 15 months were required for complete disappearance under light irrigation (three 4-inch water applications during 15 months). These results would indicate that the role of irrigation in the disappearance of diuron in dry climates may be to provide moisture for microorganisms and maintain a larger amount of herbicide in the soil solution.

III. LEACHING AND SOIL PROPERTIES

The clay and organic matter content of soils largely determines the adsorption capacity. Soil adsorption of herbicides reduces both herbicidal activity and rate of leaching. In order to do the job for which they were intended, preemergence herbicides must be rather strongly adsorbed so that movement through the soil by leaching will be minimized. When the mode of action of a herbicide is dependent upon its entering the plant through the roots, soil properties affecting its movement in the soil become especially important.

Gantz and Slife (20) observed that leaching loss of preemergence weed control is much greater in soils low in clay and organic matter content. Greater movement of both CDAA and CDEC occurred in sandy soil than in silt loam. Rauser and Switzer (48) determined that the most rapid loss of amiben occurred in sand followed by clay with muck retaining phytotoxicity much longer. Sheets (57), using oats in a leaching study to bioassay for the presence of monuron and simazine in soil columns, showed that the herbicides moved downward through the entire column of sandy loam, but moved much less in clay loam columns. Geissbuhler et al. (21) determined that C-1983 was strongly adsorbed and adsorption increased from sandy loam to clay loam to humus allowing little leaching even with 200 ml. of water applied to each column of soil. Ogle and Warren (45) found that 2,4-D leaches rapidly in a sandy soil and readily in silt loam with some being retained in an active form. They reported that 2,4-D is retained in high amounts in muck soil and noted that 16 inches of applied water is necessary to free the surface of all toxicity. Upchurch and Pierce (68) observed that considerably more leaching of monuron occurred in sandy soils than soils high in clay and/or organic matter in the greenhouse. Sheets (56) found that downward movement of monuron and diuron was much less through a clay loam than a sandy loam soil. Rodgers (52) reported that atrazine moved through the entire 23 inches of fine sand columns in concentrations toxic to oats and cucumbers, but remained in the surface 1 inch of muck under similar water and herbicide treatments. Under field conditions, Davis and Selman (16), observed that dinitro weed killers leach more in

sandy soils than in finer textured soils.

Upchurch and Pierce (69) discovered that organic matter is extremely effective in preventing leaching of monuron by simulated rainfall in Lakeland sand. Retention of monuron in the 0-8 inch soil layer varied from 35 to 95 per cent of the amount applied, depending upon organic matter content. Hernandez and Warren (27) found soil organic matter content to be an important factor in determining the rate that 2,4-D is leached into the soil. With 4 inches of applied water, 2,4-D was leached to 5 inches in soils containing 0.25 and 2.2 per cent organic matter, but the chemical penetrated to only 3 inches in soil containing 9 per cent organic matter. Dowler et al. (18) noted that soil type, pH levels, and rainfall affected the distribution and activity of DNBP in soils. A definite inverse relationship between herbicidal effectiveness and soil organic matter content and pH was noted.

In a leaching study using C^{14} -labeled CMU, Sherburne et al. (60) noted that the depth of leaching decreases with an increase in soil moisture content. They also stated that downward movement of CMU decreased as the fraction of smaller size soil particles increased. Hurtt et al. (33) observed that CIPC penetrated to 1-2 inches in dry sandy loam, but moved to only 1/2 inch in moist sandy loam while CIPC moved to 1-2 inches in dry clay and to 3-4 inches in moist clay. In general, CIPC moved deeper in soils at pH 4.2 than at 7.1. Upchurch and Pierce (69) showed that soil moisture content had little or no effect on rate of leaching of monuron in Lakeland sand. In the 0-2 inch

layer, 34 per cent of the monuron applied was retained by the wet soil while 27 per cent was retained by the dry soil. Further studies of leaching of monuron in Lakeland sand showed 79 per cent more monuron to be retained in the 2-8 inch layer at 35° C than at 5° C. Soil temperature had little effect, however, on leaching of monuron from the 0-2 inch soil layer while the 8-12 inch soil layer retained the same amount of monuron regardless of temperature.

IV. LEACHING AND FREQUENCY, INTENSITY, AND TOTAL AMOUNTS OF WATER

Upchurch and Pierce (68) reported results of greenhouse studies in which less frequent applications of simulated rainfall resulted in decreased leaching of monuron in soil columns. They reasoned that prolonged exposure to the atmosphere resulted in more evaporation with less water contributing to the leaching effect. With increased intensities of applied water, more monuron was found in lower soil horizons. They concluded that frequency and intensity of simulated rainfall were secondary in importance to total amount in determining the distribution of monuron in the soil. They proposed that gentle showers would tend to leave herbicides concentrated near the soil surface while heavier rains would cause deeper penetration. Rodgers (52), studying leaching of four triazines in the greenhouse, applied 1 to 16 inches of simulated rainfall in 1 and 2 inch increments over a period of one to four weeks. He observed that a given quantity of simulated rainfall applied in one week was more effective in leaching a given herbicide than the same amount of water applied over a two to

four week period. The higher total amount of water resulted in more rapid and deeper leaching.

Burnside and Lipke (9) determined that weed control results from preemergence applications of amiben on silty clay loam varies from excellent to poor depending upon timeliness and intensity of rains following application of the herbicide. They reported that as the amount of applied water increased up to 2 inches, there was an increase in the amount of amiben moving out of the 0-1 inch soil layer into the 1-3 inch depth. Weldon and Timmons (71), working with diuron on sandy clay loam and loamy sand in Wyoming, showed that frequent irrigation (4 inches of water per month for three months) increased the rapidity of diuron penetration and the rate of diuron disappearance, but did not increase the final depth of movement over infrequent irrigation (4 inches of water every five months for 15 months).

Davis and Selman (16) discovered that the movement of dinitro weed killers in silt loam and silty clay loam soils was related to the rate of movement of water into these soils. Larger concentrations were moved into those soil layers in which percolating water moved at a rate of 0.1 to 0.2 inches per minute. Movement of the herbicides stopped at 4 inches in silt loam and 3 inches in silty clay loam where the rate of water movement dropped to less than 0.1 inch per minute. They concluded that under field conditions a slow drizzle may cause much less leaching of dinitro weed killers into the soil than a short heavy rain having the same total precipitation.

V. LEACHING OF SPECIFIC HERBICIDES

Atrazine and Simazine

Burnside et al. (8), studying leaching of atrazine and simazine in silty clay loam and loam soils, reported movement through the 24-inch depth during 16 months under field conditions in Nebraska. During the first four months, 17.2 inches of rainfall moved simazine to the 3 to 6-inch depth while atrazine moved to the 12 to 18-inch depth. In columns of sandy Florida soils, Rodgers (52) reported movement of atrazine throughout the 23-inch profile while simazine moved no deeper than 12 inches. Both herbicides remained in the surface 1 inch of muck even when the eight pounds per acre rate was leached with 16 inches of water. Burnside et al. (10) revealed that 2 inches of applied water moved a small amount of simazine applied at two pounds per acre into the 3 to 6-inch depth in a silt loam but left a much greater amount in the upper 1 inch.

Diuron

Hill et al. (29) disclosed that 72 inches of water applied over a 90 day period failed to move diuron deeper than 4 inches in 11 soils. Sheets (56) showed that large amounts of applied water were necessary to move low rates of diuron measurable distances downward through sandy loam columns. When high herbicide rates were used, leaching occurred much more readily. Hill and McGahen (28) noted that diuron applied at one and two pounds per acre for two years did not leach below 4 inches in sand, loamy sand, and silt loam soils during 28 months. Weldon and

Timmons (71) reported that diuron applied at two and four pounds per acre to sandy clay loam and loamy sand in Wyoming was not carried below 4 inches by 12 inches of irrigation water. The highest concentration of diuron remained in the 0 to 1/2-inch horizon with less remaining in the 1/2 to 2-inch horizon. Hollingsworth (31) found that diuron at rates up to four pounds per acre was not leached below 1 inch in sandy clay loam by 9 inches of rainfall during a 5 1/2 months field study in Mississippi.

DCPA

No literature concerning the leaching of 2,3,5,6-tetrachloroterephthalic acid (DCPA) was found.

CHAPTER III

MATERIALS AND PROCEDURES

I. DESIGN

A leaching study involving four preemergence herbicides, four soils, and three water treatments was carried out in the greenhouse at Knoxville from June through October, 1964.

The leaching procedure involved applying measured amounts of water to the surface of soil columns which had been treated with herbicides. After leaching, the columns composed of soil-filled plastic sewer pipe 3 inches in diameter and 28 inches tall were sawed into uniform 2-inch sections and planted to oats.

The aerial portions of the plants were harvested 28 days after planting, dried for 24 hours at 70° C, and weighed.

The experiment was carried out in triplicate using a randomized complete block design. Leaching, planting, and harvest dates were staggered to space the work load.

II. SOILS

Four agriculturally important soils with varying properties were selected from different locations within the state (Table 1). Approximately 1/2 ton of each of the four soils was taken from the Ap horizon, mixed, run through a 5.5 mm. sieve, and air dried. Laboratory determinations of physical and chemical properties were

TABLE 1. Source and grams per 3 x 28-inch column of four soils used to study leaching of herbicides by applied water

Soil	Source	Grams/column
Cumberland loam	U. T. Blount County Farm	4200
Sequatchie fine sandy loam	U. T. Plant Science Farm--Knox County	4500
Collins silt loam	West Tenn. Exp. Sta. Jackson, Tenn.	4200
Bowdre clay loam	Mississippi River Bottom State Prison Farm Fort Pillow, Tenn.	4100

made (Table 2). Sections of black plastic sewer pipe 3 inches in diameter and 30 inches tall were filled to within 2 inches of the top with the proper weight of each air dry soil.

Nylon netting held in place by rubber bands was used to cover the bottom end of each pipe. This held the soil in place and also allowed the soil to be saturated and drained.

Saturation of the soil columns was accomplished by sub-irrigation and was complete within 48 hours. They were then placed in a vertical position and allowed to drain four days.

III. HERBICIDES

Three of the four herbicides used were selected because they were found to be persistent in a three year study by Jones and Andrews (35). They are atrazine, simazine, and diuron. The fourth herbicide, DCPA, was selected because little is known about its behavior in soils at the present time. Two rates of herbicides, the recommended rate (1X) and two and one half times the recommended rate (2.5X), were used (Table 3).

Aqueous suspensions of the herbicides were made up immediately before they were applied to the surface of the soil columns. Herbicides were applied with a pipette as a suspension in 20 ml. of water.

Immediately after the herbicides were applied, 100 grams of sand was poured onto the surface of the soil to form a layer approximately 1 inch thick. Preliminary studies showed this to be necessary to prevent puddling of the soil surface and to aid infiltration during

TABLE 2. Selected properties of four soils used to study leaching of herbicides by applied water in soil columns

Soil	Percentage organic matter	pH	Cation exchange capacity me./100 grams	Percentage		
				Sand	Silt	Clay
Cumberland loam	2.2	7.1	7.9	32.0	43.0	25.0
Sequatchie fine sandy loam	1.6	5.6	4.0	80.0	14.9	5.1
Collins silt loam	1.1	6.3	4.7	23.3	68.6	8.1
Bowdre clay loam	3.0	5.5	20.9	38.6	21.2	40.2

TABLE 3. Solubility and rates of application of herbicides applied to surfaces of soil columns and leached with applied water

Herbicide	Solubility in p.p.m.	Rates in pounds of active ingredient per acre	
		1X ^a	2.5X
Atrazine	70	2	5
Simazine	5	2	5
Diuron	42	1	2.5
DCPA	0.5	4	10

^a X = recommended rate of application.

the leaching phase. The sand was saturated with 25 ml. of water so that all applied water would contribute to leaching. Three total amounts of water, equivalent to 3, 9, and 18 inches, were applied to leach the herbicides into the soil.

IV. LEACHING

Leaching was started one hour after herbicides were applied. The equivalent of 3 inches of demineralized water was applied daily to each column during the leaching periods. Eighty-seven ml. of water (equivalent to $3/4$ inch) was applied four times each day at three hour intervals.

Columns receiving an equivalent of 18 inches of water were leached six days while columns receiving an equivalent of 9 inches of water were leached three days and those receiving an equivalent of 3 inches of water were leached one day. Columns were kept covered with inverted plastic petri dishes for 14 days from the beginning of the leaching period until planting date to minimize evaporation. Herbicides were in contact with the soil 14 days before oats were planted (Table 4).

Twenty-seven columns of each of the four soils, making a total of 108 columns, were required for each replication. The 108 columns represented four soils, four herbicides at two rates each, and three water treatments. A total of 324 soil columns were required for the experiment.

TABLE 4. Schedule of leaching and bioassay procedures used in studying movement of herbicides in soil columns by applied water

Replication	Water treatments in inches	Date of herbicide application	Planting date	Harvest date
1	18	Aug. 3	Aug. 17	Sept. 14
1	9	6	20	17
1	3	8	22	19
2	18	Aug. 24	Sept. 7	Oct. 5
2	9	27	10	8
2	3	29	12	10
3	18	Sept. 14	Sept. 28	Oct. 26
3	9	17	Oct. 1	29
3	3	19	3	31

V. BIOASSAY

A radial arm saw was used to saw each 28-inch soil column into fourteen 2-inch sections. Four oat seeds were planted in each of ten sections. Four sections, taken from depths of 12-14, 16-18, 20-22, and 24-26 inches in the columns were discarded to reduce the size of the experiment. The sections were placed in petri dishes on tables in the greenhouse and watered once daily with demineralized water. Twenty-eight days after planting, all living aerial portions of the plants were clipped at the soil surface and oven dried for 24 hours at 70° C. The dried plant tissue was weighed and the weight recorded to the nearest milligram. All dead plants were given a weight of zero.

Each replication provided 1,080 separate soil column sections in which plants were grown. The entire experiment of three replications yielded a total of 3,240 separate weight determinations.

CHAPTER IV

RESULTS AND DISCUSSION

I. GENERAL OBSERVATIONS

Oats showed both stunting and killing in treatments of atrazine, simazine, and diuron, but were unaffected by DCPA (Tables 5-20, Appendix). No herbicidal effect on germination could be detected. Atrazine was the most toxic to oat plants of the four herbicides tested with simazine second and diuron third. Atrazine and simazine data are in accord with results of Rodgers (52). Differences in toxicity between atrazine and simazine could be attributed to solubility differences (Table 3, page 34), but the low toxicity of diuron at the rates used could be due to the fact that diuron is more readily adsorbed by soil colloids than either atrazine or simazine. The solubility of DCPA is lowest of the four herbicides studied (Table 3, page 34) and apparently, oats are not sensitive to the chemical at the rates used. This is in agreement with results of Jones (36) who could detect no injury to oats in the field by the 1X and 2.5X rates of DCPA.

In general, oven dry weights increased gradually with horizon depth in the columns (Tables 5-20, Appendix). This effect was more noticeable in DCPA columns since there was no herbicide toxicity (Tables 17-20, Appendix). This also occurred in control columns which received no herbicide. Possibly this could have been due to leaching of plant nutrients, especially nitrogen, by applied water.

In practically all cases, 18 inches of applied water, the highest amount used, resulted in the deepest penetration of herbicides in all soil columns. This is in agreement with the findings of Rodgers (52). Less leaching and/or toxicity to oat plants occurred in the soils higher in clay and organic matter (Table 2, page 33) than in lighter textured soils high in sand and silt and low in organic matter content. Results of several workers (16, 20, 21, 45, 48, 52, 57, 69) bear out this observation. No definite correlation between pH and leaching of the herbicides could be detected. Cation exchange capacity is associated directly with clay and organic matter content.

In general, the 2.5X rate of herbicides was leached 2 to 4 inches deeper than the 1X rate. Also, quicker, more complete kills and more severe stunting of plants were obtained with the higher rate. Results of work by Rodgers (52) were similar.

Plants which were completely killed or weighed less than 10 per cent of the weight of control plants were given a weight of zero. Plants weighing between 10 and 90 per cent of the weight of control plants were judged to be stunted and plants weighing from 90 to 100 per cent or more of the weight of control plants were considered to be unaffected by the herbicides. All weights are averages of three replications.

II. ATRAZINE

Bowdre Clay Loam

With 3 inches of applied water, the 1X rate of atrazine killed

plants growing in the surface 2 inches of Bowdre clay loam and severely stunted plants growing in the 2 to 4-inch section (Figure 1). When 9 inches of water was applied, plants were killed through the 4-inch depth and stunted to a depth of 6 inches. When 18 inches of water was applied, plants growing in the surface 4 inches were killed and considerable stunting occurred to the 10-inch depth. Killing concentrations of atrazine applied at the 2.5X rate (Figure 2) leached 2 inches deeper than the 1X rate and stunting concentrations were leached 2 to 4 inches deeper than the 1X rate.

Cumberland Loam

Plants growing in sections of Cumberland loam columns which had been treated with the 1X rate of atrazine (Figure 1) and leached with the equivalent of 3 inches of water were killed to the 4-inch depth and stunted to 8 inches. Nine inches of applied water resulted in the leaching of killing concentrations throughout the upper 8 inches of the columns while stunting concentrations were leached to 12 inches. With the application of 18 inches of water, stunting concentrations remained in the 0 to 2-inch sections and killing concentrations appeared in the 2 to 12-inch segment of the columns. Stunting concentrations were also present at the 12 to 16-inch depth.

The 2.5X rate of atrazine (Figure 2) penetrated deeper in Cumberland loam columns and caused more severe stunting of oat plants than did the 1X rate. Three inches of water leached killing concentrations into the 0 to 8-inch section and stunting concentrations to

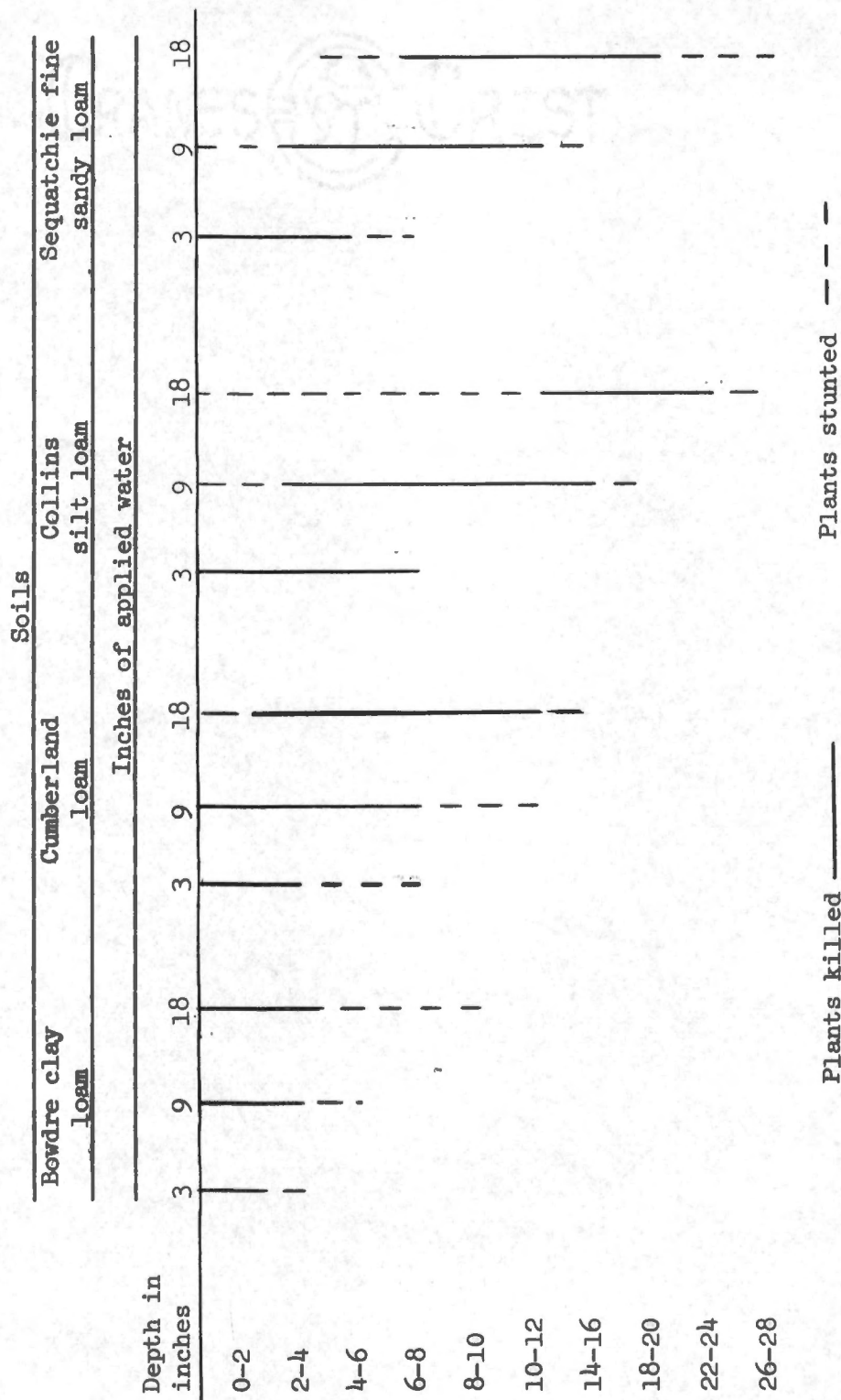


Figure 1. Depth of leaching of the 1X (recommended) rate of atrazine in concentrations toxic to oat plants in columns of four soils by three rates of applied water.

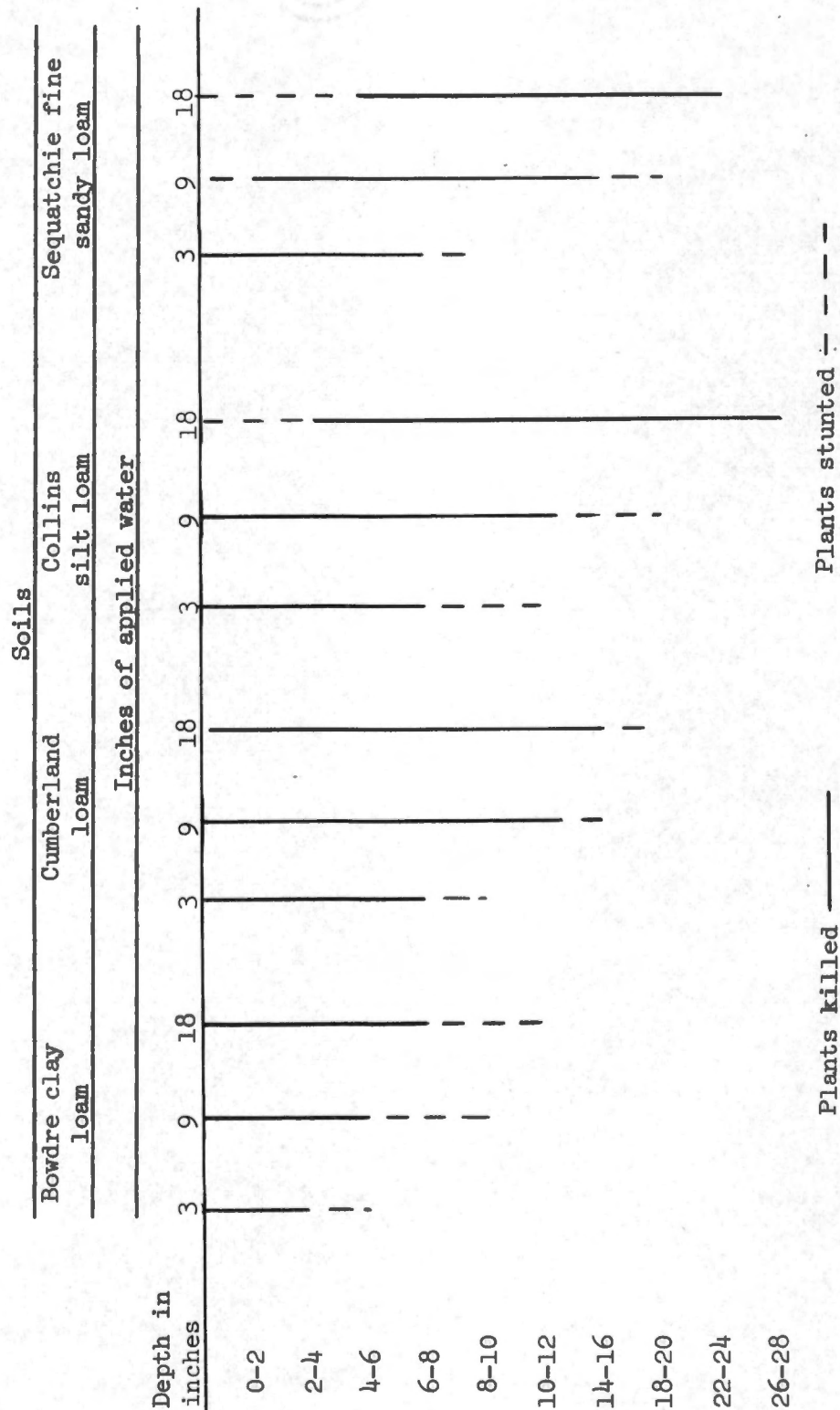


Figure 2. Depth of leaching of the 2.5X (2 1/2 times recommended) rate of atrazine in concentrations toxic to oat plants in columns of four soils by three rates of applied water.

10 inches. The equivalent of 9 inches of applied water moved killing concentrations of atrazine through the 0 to 12-inch section of the columns while stunting concentrations appeared at the 12 to 16-inch depth. The 18-inch water treatment distributed killing concentrations throughout the upper 16 inches of the columns and stunting concentrations into the 16 to 20-inch depth.

Collins Silt Loam

In Collins silt loam, 3 inches of water leached the 1X rate of atrazine (Figure 1, page 41) through the 8-inch depth in killing concentrations. At the 2.5X rate (Figure 2, page 42) plants were killed to the same depth and stunted to 12 inches. With the equivalent of 9 inches of applied water the 1X rate of atrazine remained in the top 4 inches in stunting concentrations, but killing concentrations were present in the 4 to 16-inch sections. Plants growing in the 16 to 20-inch sections were severely stunted. The 2.5X rate caused killing of plants through the 12-inch depth and stunting to 20 inches. Eighteen inches of water carried killing concentrations of the 1X rate of atrazine to the 12 to 24-inch depth in Collins silt loam. In addition, stunting concentrations remained in the surface 12 inches. The 2.5X rate of atrazine remained in the surface 4 inches in stunting concentrations and killed plants throughout the 4 to 28-inch depth.

Sequatchie Fine Sandy Loam

Three inches of water leached killing concentrations of the 1X rate of atrazine (Figure 1, page 41) to the 6 inch depth in Sequatchie

fine sandy loam and to 8 inches in stunting concentrations. Nine inches of applied water resulted in slight stunting of the indicator plants growing in the surface 4 inches while those growing in the 4 to 12-inch sections were killed. Stunted plants again appeared at the 12 to 16-inch level. Eighteen inches of water leached killing concentrations into the 8 to 20-inch section of the columns. Stunting of oat plants occurred at the 4 to 8-inch level and again at the 20 to 28-inch depth. Plants growing in the 2 to 4-inch sections were unaffected.

Killing concentrations of atrazine applied at the 2.5X rate (Figure 2, page 42) were distributed throughout the upper 8 inches of the columns by 3 inches of applied water. Plants growing in the 8 to 10-inch section were stunted. Nine inches of applied water resulted in stunting of plants growing in the 0 to 2-inch and 16 to 20-inch sections and the death of plants grown in the 2 to 16-inch sections. Eighteen inches of applied water distributed stunting concentrations of atrazine throughout the surface 6 inches of the columns and killing concentrations were leached into the 6 to 24-inch segment.

III. SIMAZINE

Results obtained with simazine were similar to those obtained with atrazine, but in general, plants grown in atrazine-treated columns showed more complete killing and more severe stunting than those grown in simazine treated columns.

Bowdre Clay Loam

The 1X rate of simazine remained in the surface 2 inches of the columns in killing concentrations when 3 inches of water was applied (Figure 3). With the application of 9 inches of water, killing concentrations remained in the surface 2 inches and stunting concentrations were distributed throughout the 2 to 6-inch depth. Eighteen inches of applied water resulted in no killing of plants, but plants grown in the upper 6 inches of the columns were stunted.

The 2.5X rate of simazine (Figure 4) killed plants grown in the surface 2 inches of Bowdre clay loam columns after leaching with 3 inches of water and stunted plants grown in the 2 to 6-inch section. Results with the 9-inch water treatment were similar to the 3-inch water treatment. Eighteen inches of applied water distributed killing concentrations into the surface 4 inches and stunting concentrations into the 4 to 8-inch section.

Cumberland Loam

Three inches of applied water moved killing concentrations of simazine applied at the 1X rate into the surface 4 inches of Cumberland loam columns and stunting concentrations to the 6-inch depth (Figure 3, page 46). The 9-inch water treatment resulted in the death of plants grown in sections taken from the upper 6 inches of the columns. Plants grown at the 6 to 10-inch depth were stunted. Eighteen inches of applied water left stunting concentrations of simazine in the surface 4 inches of the columns, but leached killing concentrations into the

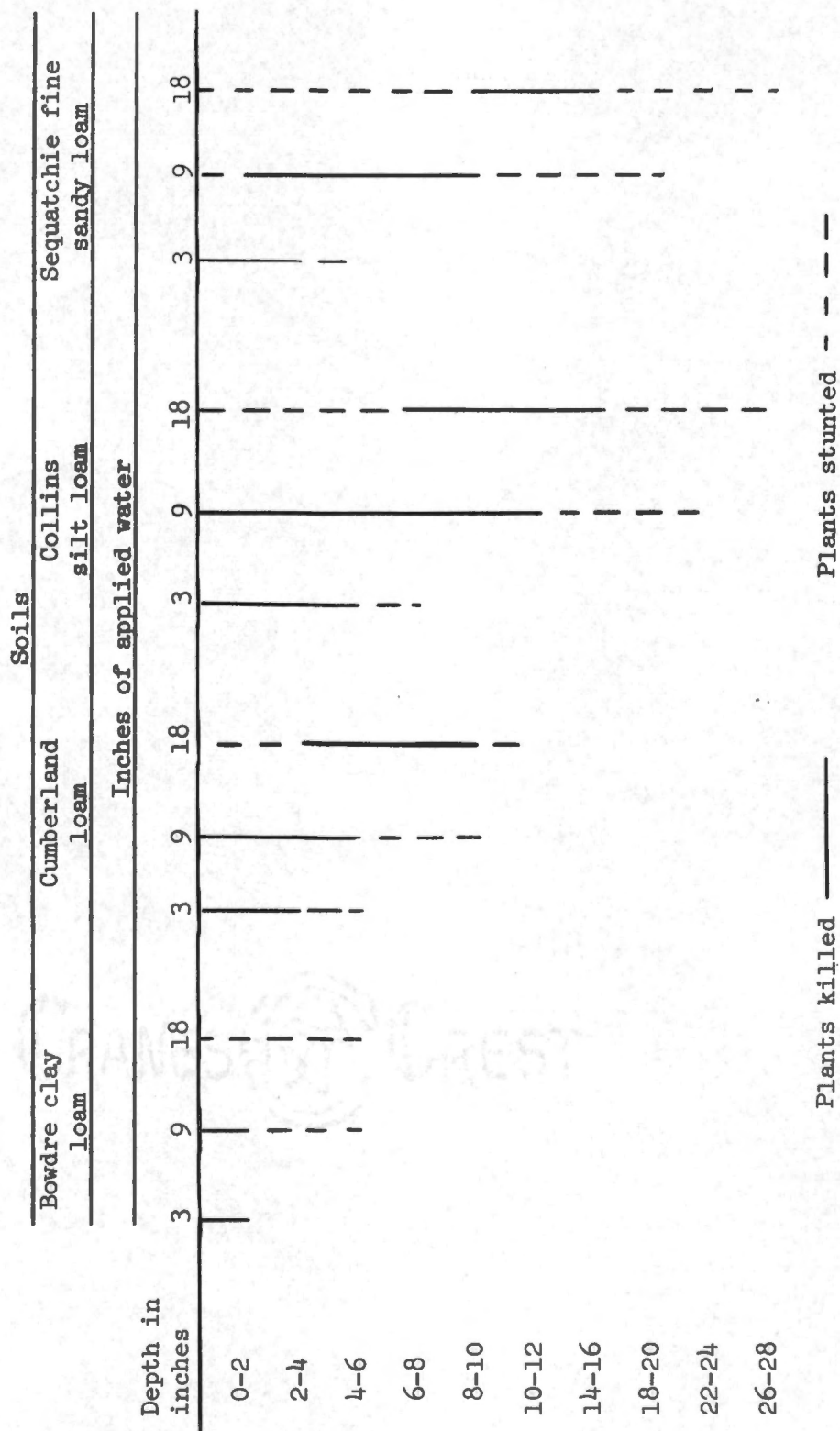


Figure 3. Depth of leaching of the 1X (recommended) rate of simazine in concentrations toxic to oat plants in columns of four soils by three rates of applied water.

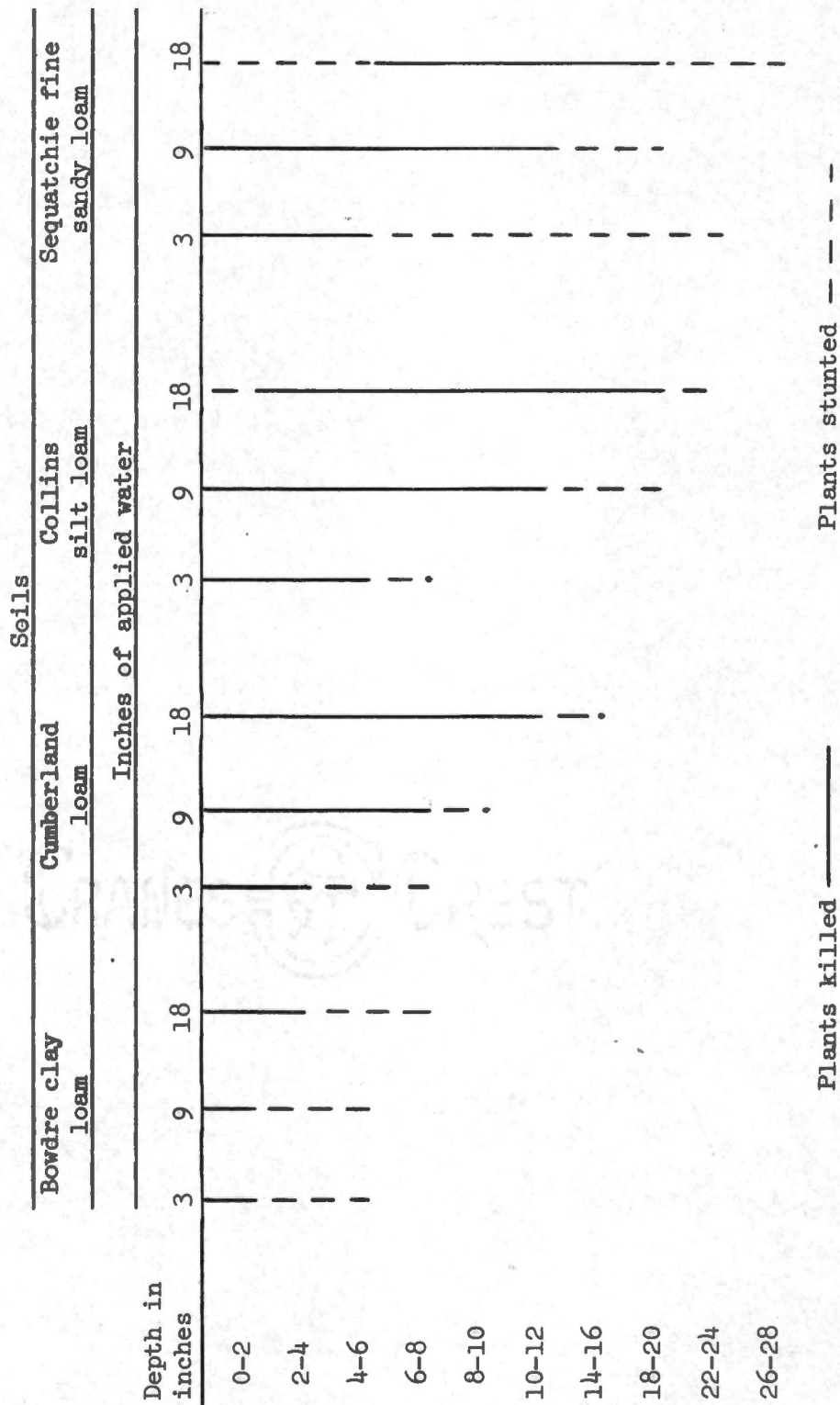


Figure 4. Depth of leaching of the 2.5X (2 1/2 times recommended) rate of simazine in concentrations toxic to oat plants in columns of four soils by three rates of applied water.

4 to 10-inch segment of the columns. Stunting of plants also appeared at the 10 to 12-inch depth.

Three inches of water distributed killing concentrations of simazine applied at the 2.5X rate (Figure 4, page 47) through the upper 4 inches of Cumberland loam columns. In addition, stunting concentrations accumulated within the 4 to 8-inch section. The application of 9 inches of water resulted in killing of plants throughout the upper 8 inches of the columns. Stunting occurred 2 inches deeper. Eighteen inches of water moved killing concentrations into the 0 to 12-inch portion of the columns and stunting concentrations into the 12 to 16-inch section.

Collins Silt Loam

Plants growing in the upper 6 inches of Collins silt loam columns were killed after the 1X rate of simazine (Figure 3, page 46) was applied to the surface and leached with 3 inches of water. Stunting of oat plants occurred among plants growing in the 6 to 8-inch section. Nine inches of applied water distributed killing concentrations throughout the 0 to 12-inch segment of the columns. Stunting concentrations moved into the 12 to 24-inch section. Eighteen inches of applied water left stunting concentrations of simazine within the 0 to 8-inch sections of the columns and deposited killing concentrations throughout the 8 to 16-inch levels. Also stunting concentrations appeared at the 16 to 28-inch level.

The 2.5X rate of simazine (Figure 4, page 47) was leached through

the 0 to 6-inch sections of Collins silt loam in killing concentrations by 3 inches of applied water. Plants growing in the 6 to 8-inch sections were stunted. Death of oat plants occurred in sections taken from the 0 to 12-inch portion of the columns after leaching with 9 inches of water. Stunting occurred in the 12 to 20-inch sections. Eighteen inches of water left stunting concentrations in the 0 to 2-inch section while killing concentrations were present throughout the 2 to 20-inch levels. Stunting occurred in the 20 to 24-inch sections also.

Sequatchie Fine Sandy Loam

With the application of 3 inches of water the 1X rate of simazine (Figure 3, page 46) resulted in death of plants grown in the surface 4 inches of Sequatchie fine sandy loam. Plants growing in the 4 to 6-inch section were stunted. Nine inches of water resulted in stunting of plants growing in the 0 to 2-inch section and killing of plants growing in the 2 to 10-inch sections. Stunting also occurred in the 10 to 20-inch sections. After leaching with 18 inches of water, stunting concentrations were present in the 0 to 10-inch sections and again in the 16 to 28-inch sections while plants growing in the 10 to 16-inch sections were killed.

Killing concentrations of the 2.5X rate of simazine (Figure 4, page 47) were present in the 0 to 6-inch sections of Sequatchie fine sandy loam columns after leaching with 3 inches of water. Stunting concentrations appeared in the 6 to 24-inch sections. Plants grown in the 0 to 12-inch sections were killed when the columns were leached

with 9 inches of water. Stunting of plants occurred in the 12 to 20-inch sections. Eighteen inches of water resulted in stunting of plants grown in the 0 to 6-inch sections and again in the lower 4 inches of the columns while killing of plants occurred in the 6 to 20-inch sections.

IV. DIURON

Bowdre Clay Loam

In columns leached with 3 inches of water, the 1X rate of diuron (Figure 5) caused stunting of oat plants grown in sections taken from the surface 6 inches. Stunting concentrations remained in the surface 4 inches of diuron treated columns leached with 9 inches of water. When 18 inches of water was applied stunting concentrations appeared only in the surface 2 inches of the columns.

The 2.5X rate of diuron (Figure 6) caused stunting of plants grown in the surface 2-inch section of Bowdre clay loam columns which were leached with 3 inches of water. Plants growing in the surface 2-inch sections were killed after the columns had been leached with 9 inches of water. Results with the 18-inch water treatment showed killing of plants grown in the upper 2-inch section and stunting of plants grown in the 2 to 4-inch section of the columns.

Cumberland Loam

Death of plants growing in the surface 2-inch section of Cumberland loam columns occurred when the 1X rate of diuron (Figure 5)

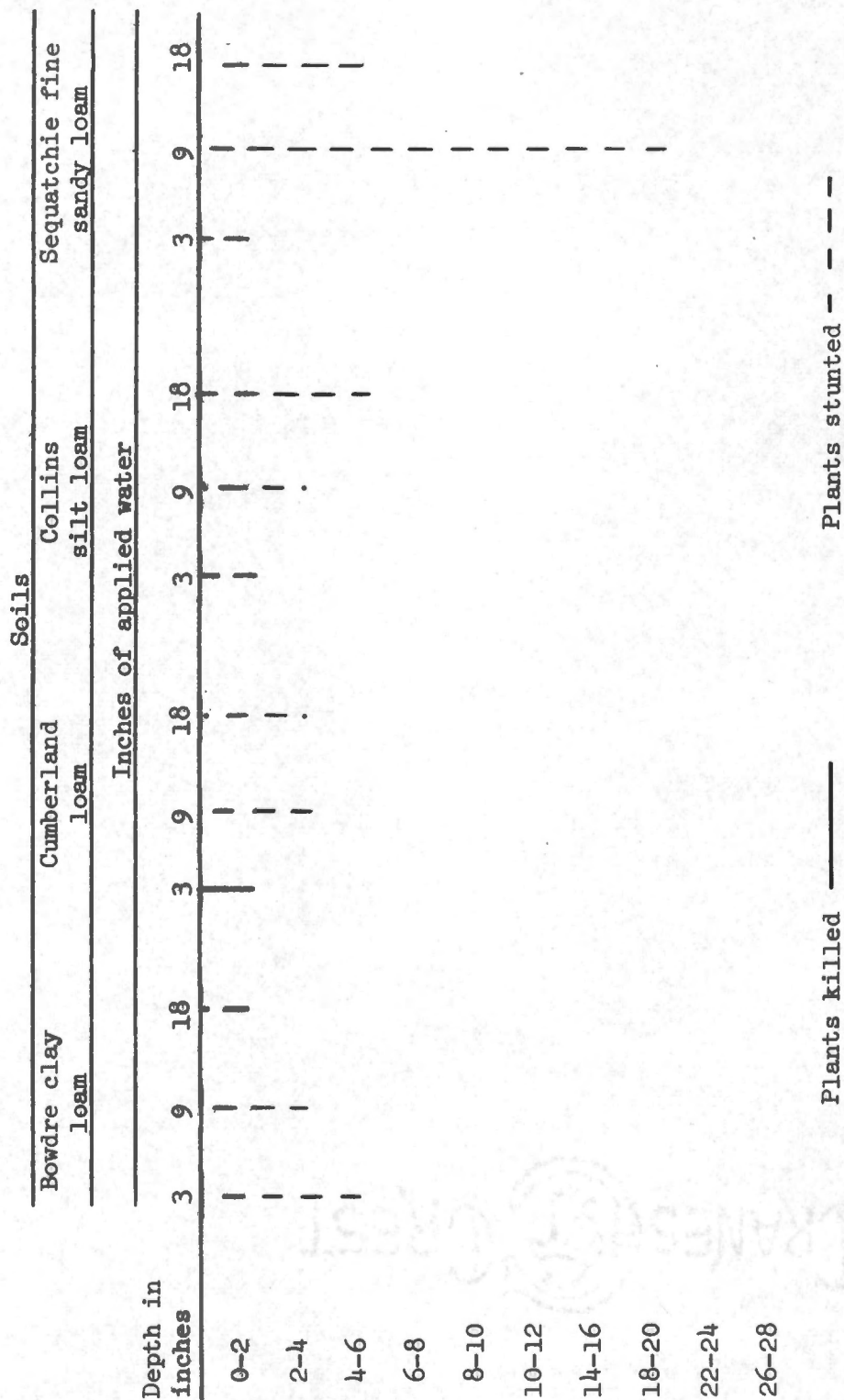


Figure 5. Depth of leaching of the 1X (recommended) rate of diuron in concentrations toxic to oat plants in columns of four soils by three rates of applied water.

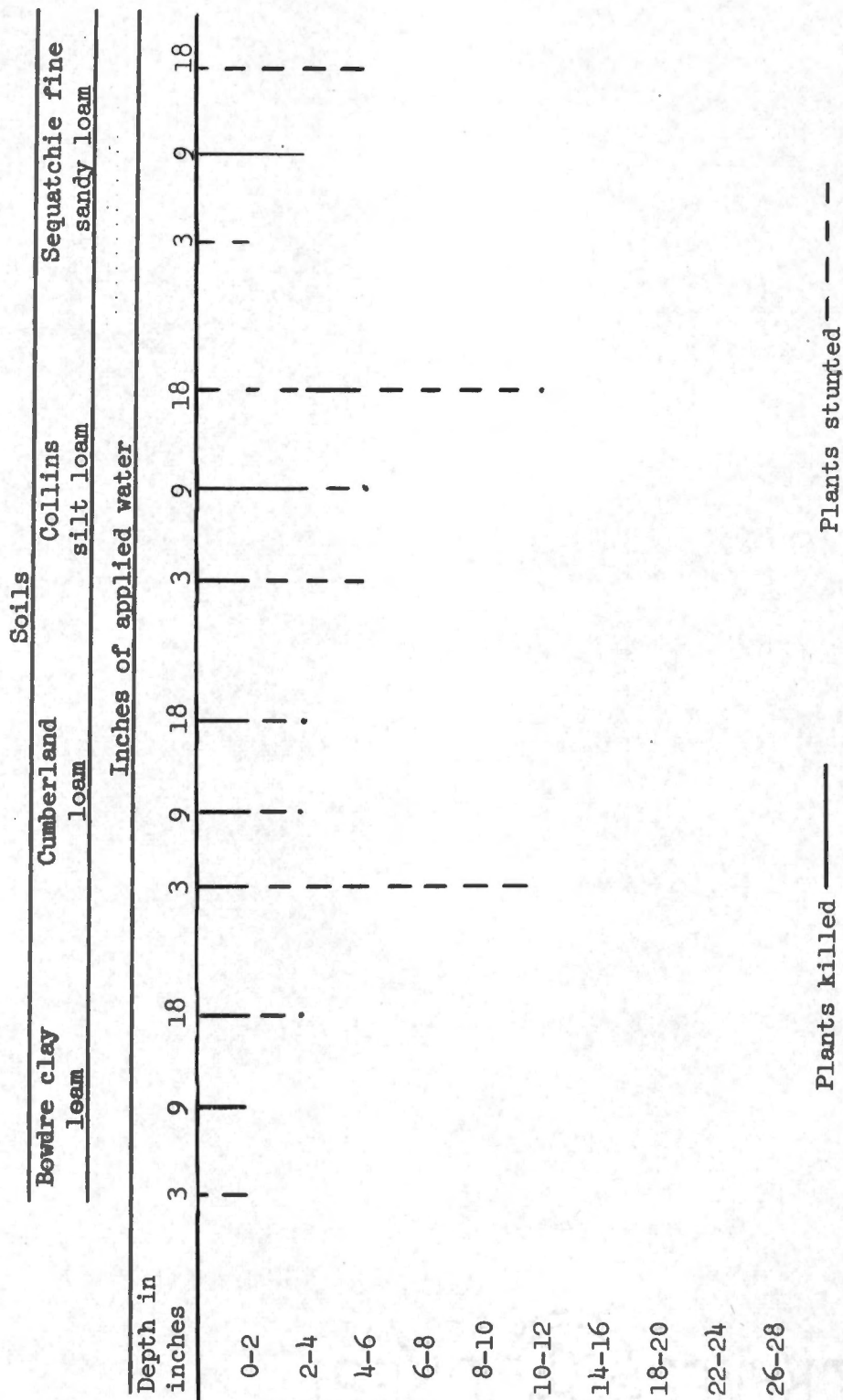


Figure 6. Depth of leaching of the 2.5X (2 1/2 times recommended) rate of diuron in concentrations toxic to oat plants in columns of four soils by three rates of applied water.

was leached with 3 inches of water. Leaching with 9 and 18 inches of water resulted in stunting of plants grown in sections taken from the 0 to 4-inch sections of the columns.

Death of plants grown in the 0 to 2-inch section and stunting of plants grown in sections taken from the 2 to 12-inch portion of the columns occurred when the 2.5X rate of diuron (Figure 6, page 52) was leached with 3 inches of water. When leached with 9 and 18 inches of water killing concentrations remained in the surface 2-inch section and stunting concentrations appeared in the 2 to 4-inch section.

Collins Silt Loam

The 1X rate of diuron (Figure 5, page 51) did not cause the death of any plants grown in sections taken from Collins silt loam columns, but stunting did occur. Stunting occurred to depths of 2, 4 and 6 inches in columns leached with 3, 9, and 18 inches of water respectively.

The 2.5X rate of diuron (Figure 6, page 52) affected oat plants more severely than the 1X rate. With 3 inches of applied water diuron remained in the surface 2-inch section in killing concentrations and penetrated the 2 to 6-inch sections in stunting concentrations. After leaching with 9 inches of water, plants grown in the 0 to 4-inch sections were killed, and plants grown at the 4 to 6-inch depth were stunted. The 18-inch water treatment resulted in stunting of plants at the 0 to 4-inch and the 6 to 12-inch levels of the columns while plants growing at the 4 to 6-inch level were killed.

Sequatchie Fine Sandy Loam

The 1X rate of diuron (Figure 5, page 51) did not cause killing of plants grown in Sequatchie fine sandy loam, but stunting occurred with all three treatments. Stunting concentrations remained in the surface 2-inch section after leaching with 3 inches of water, but the 9-inch water treatment resulted in stunting of plants grown in sections taken from the 0 to 20-inch portion of the columns. The 18-inch water treatment leached stunting concentrations to the 6-inch depth.

Three inches of applied water left stunting concentrations of the 2.5X rate of diuron (Figure 6, page 52) in the surface 2-inch section of Sequatchie fine sandy loam columns. Plants grown in sections taken from the surface 4 inches of columns which had been leached with 9 inches of water were killed. Stunting of plants grown in the 0 to 8-inch sections occurred after the columns were leached with 18 inches of water.

V. DCPA

DCPA did not adversely affect oat plants grown in any soil column section. Presumably oats were tolerant to DCPA at the rates used.

CHAPTER V

SUMMARY AND CONCLUSIONS

In order to evaluate the leaching behavior of suspected persistent herbicides by controlled amounts of water in agriculturally important soils, a leaching study involving four herbicides at two rates, four soils, and three water treatments was initiated. The effects of water and soil properties on the movement of atrazine, simazine, diuron and DCPA in soil columns was studied.

Herbicides were applied at the 1X (recommended) and 2.5X (2 1/2 times recommended) rates to the surface of samples of Bowdre clay loam, Collins silt loam, Cumberland loam, and Sequatchie fine sandy loam in 3 inch by 30 inch plastic pipe columns, and leached with equivalents of 3, 9, and 18 inches of applied water.

Oats were used as the indicator plant to bioassay ten 2-inch sections of the columns for the presence of herbicides.

Data were collected by harvesting all living aerial portions of 28 day old plants and recording oven dry weights.

In most cases, herbicides applied at the 2.5X rate moved 2 to 4 inches deeper than at the 1X rate. In most cases the depth of herbicide movement in the columns varied directly with the rate of applied water.

Atrazine and simazine were more toxic to oat plants and moved deeper in the columns than diuron, but DCPA was not toxic to oat plants

at the rates used. Leaching of atrazine, simazine, and diuron was more pronounced in Sequatchie fine sandy loam and Collins silt loam than in Bowdre clay loam and Cumberland loam. In addition to deeper herbicide penetration, more severe stunting occurred among oat plants growing in sections of Sequatchie and Collins. These soils contain a high percentage of sand and silt and are low in clay, organic matter and cation exchange capacity.

Of the four soils used, less leaching of atrazine, simazine, and diuron occurred in Bowdre clay loam than in the other three. This soil was much higher in montmorillonitic clay and organic matter content and had a higher cation exchange capacity than the other three soils.

An intermediate amount of leaching of atrazine, simazine, and diuron occurred in Cumberland loam columns. Atrazine and simazine penetrated deeper than in Bowdre clay loam, but not as deeply as in Collins silt loam and Sequatchie fine sandy loam. Diuron penetrated both Cumberland loam and Bowdre clay loam columns to approximately the same depth, but toxicity to oat plants was more severe in Cumberland loam.

Solubility of herbicides is indicative of their leaching behavior, but soil adsorptive characteristics are also a factor. More leaching occurred with atrazine, the most soluble of the herbicides used than with others. Diuron is several times more soluble than simazine, but was leached considerably less. It is known that diuron is more readily adsorbed by soil colloids than either atrazine or simazine.

In view of the fact that some herbicides are easily moved down through the soil by percolating water there is a real possibility, as hypothesized by Burnside et al. (8), of an appreciable accumulation at deeper soil levels where deactivation is slow.

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APPENDIX
BIOASSAY WEIGHTS

TABLE 5. Milligrams of oven dried oat plants grown in sections of atrazine treated columns of Bowdre clay loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	<u>0 lbs. per acre</u>			<u>2 lbs. per acre</u>			<u>5 lbs. per acre</u>		
	<u>Inches of Applied Water</u>								
	3	9	18	3	9	18	3	9	18
0-2	182	190	208	0	0	3	0	0	2
2-4	212	201	200	92	2	6	0	0	0
4-6	255	204	205	254	57	41	109	7	0
6-8	284	171	230	320	165	127	248	80	4
8-10	303	176	188	318	200	154	289	153	67
10-12	296	195	208	309	203	249	275	177	73
14-16	317	193	252	307	230	327	280	214	242
18-20	286	264	313	329	250	337	319	291	322
22-24	283	294	305	329	299	332	296	336	338
26-28	270	399	304	329	373	334	315	389	268

TABLE 6. Milligrams of oven dried oat plants grown in sections of atrazine treated columns of Cumberland loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			2 lbs. per acre			5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	156	130	139	0	2	65	0	0	8
2-4	151	147	137	0	0	11	0	0	0
4-6	165	117	135	28	0	3	0	0	0
6-8	164	134	119	89	7	0	7	0	0
8-10	154	137	145	135	15	0	109	0	0
10-12	158	124	144	147	47	0	172	0	0
14-16	143	131	136	177	127	37	165	116	0
18-20	156	153	146	191	142	135	151	136	26
22-24	176	138	135	191	146	161	169	131	153
26-28	164	166	196	170	156	134	169	141	164

TABLE 7. Milligrams of oven dried oat plants grown in sections of atrazine treated columns of Collins silt loam leached with three rates of water, average of three replication

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			2 lbs. per acre			5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	154	146	128	0	72	125	0	0	78
2-4	156	143	143	0	25	108	0	0	50
4-6	233	143	147	0	1	68	0	0	11
6-8	216	141	132	0	0	25	0	0	4
8-10	190	120	145	198	0	20	52	0	0
10-12	233	169	135	239	0	15	191	0	0
14-16	204	168	137	226	14	0	210	63	0
18-20	190	226	136	199	164	0	192	117	0
22-24	197	243	167	208	213	0	188	232	0
26-28	228	178	177	237	187	137	143	191	5

TABLE 8. Milligrams of oven dried oat plants grown in sections of atrazine treated columns of Sequatchie fine sandy loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			2 lbs. per acre			5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	207	153	149	0	122	130	0	39	117
2-4	161	122	134	0	27	139	0	4	67
4-6	153	153	157	0	1	88	0	0	22
6-8	169	148	143	72	0	58	14	0	9
8-10	222	144	160	187	0	4	114	0	0
10-12	223	153	146	189	0	0	225	0	0
14-16	257	161	114	214	80	0	233	14	0
18-20	249	206	165	204	165	0	192	149	0
22-24	211	193	227	188	169	72	194	215	4
26-28	212	193	225	192	221	176	187	237	201

TABLE 9. Milligrams of oven dried oat plants grown in sections of simazine treated columns of Bowdre clay loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			2 lbs. per acre			5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	182	190	208	0	0	16	0	0	0
2-4	212	201	200	208	157	66	122	54	11
4-6	255	204	205	253	174	182	228	140	118
6-8	284	171	230	325	192	201	277	171	127
8-10	303	176	188	306	192	215	314	213	187
10-12	296	195	208	308	183	219	365	193	181
14-16	317	193	252	352	211	258	346	234	240
18-20	286	264	313	331	250	347	312	312	330
22-24	283	294	305	324	318	378	305	323	332
26-28	270	399	304	327	347	318	319	318	313

TABLE 10. Milligrams of oven dried oat plants grown in sections of simazine treated columns of Cumberland loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	<u>0 lbs. per acre</u>			<u>2 lbs. per acre</u>			<u>5 lbs. per acre</u>		
	<u>Inches of Applied Water</u>								
	3	9	18	3	9	18	3	9	18
0-2	156	130	139	0	6	66	0	0	5
2-4	151	147	137	4	0	15	0	1	0
4-6	165	117	135	121	3	7	73	0	0
6-8	164	134	119	166	40	6	135	0	0
8-10	154	137	145	133	80	7	168	18	0
10-12	158	124	144	152	141	18	160	134	0
14-16	143	131	136	155	138	129	153	133	77
18-20	156	153	146	169	152	133	149	151	145
22-24	176	138	135	180	145	140	147	161	143
26-28	164	166	196	174	149	157	148	167	180

TABLE 11. Milligrams of oven dried oat plants grown in sections of simazine treated columns of Collins silt loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			2 lbs. per acre			5 lbs. per acre.		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	154	146	128	0	8	81	0	4	25
2-4	156	143	143	0	0	44	0	0	14
4-6	233	143	147	0	0	25	0	0	1
6-8	216	141	132	121	0	17	153	0	1
8-10	190	120	145	231	0	7	271	0	1
10-12	233	169	135	231	6	7	239	0	1
14-16	204	168	137	208	117	8	206	86	0
18-20	190	226	136	211	150	24	184	182	0
22-24	197	243	167	188	196	119	186	232	100
26-28	228	178	177	177	240	151	168	191	205

Table 12. Milligrams of oven-dried oat plants grown in sections of simazine treated columns of Sequatchie fine sandy loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			2 lbs. per acre			5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	207	153	149	0	69	103	0	0	59
2-4	161	122	134	0	10	87	0	0	24
4-6	153	153	157	50	4	64	11	0	16
6-8	169	148	143	157	2	37	151	0	3
8-10	222	144	160	204	0	27	172	0	1
10-12	223	153	146	213	22	8	196	0	0
14-16	257	161	114	200	127	3	184	141	0
18-20	249	206	165	210	164	60	193	172	3
22-24	211	193	227	188	182	127	173	180	165
26-28	212	193	225	206	197	163	235	204	158

TABLE 13. Milligrams of oven dried oat plants grown in sections of diuron treated columns of Bowdre clay loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			1 lb. per acre			2.5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	182	190	208	132	57	89	23	0	0
2-4	212	201	200	187	169	200	204	212	148
4-6	255	204	205	181	191	181	225	176	202
6-8	284	171	230	304	180	215	324	186	197
8-10	303	176	188	351	165	210	312	173	229
10-12	296	195	208	305	181	235	342	193	220
14-16	317	193	252	294	223	252	335	218	248
18-20	286	264	313	329	258	325	353	285	280
22-24	283	293	305	313	346	348	282	327	345
26-28	270	399	304	278	302	321	281	325	311

TABLE 14. Milligrams of oven dried oat plants grown in sections of diuron treated columns of Cumberland loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			1 lb. per acre			2.5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	156	130	139	0	51	66	0	1	0
2-4	151	147	137	138	110	123	127	84	60
4-6	165	117	135	158	118	132	145	121	144
6-8	164	134	119	151	135	139	145	147	162
8-10	154	137	145	156	146	147	131	123	140
10-12	158	124	144	150	149	148	132	140	118
14-16	143	131	136	139	152	136	146	145	134
18-20	156	153	146	142	161	146	138	130	145
22-24	176	138	135	144	149	139	155	125	133
26-28	164	166	196	183	157	164	145	126	158

TABLE 15. Milligrams of oven dried oat plants grown in sections of diuron treated columns of Collins silt loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			1 lb. per acre			2.5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	154	146	128	53	71	90	0	3	67
2-4	156	143	143	164	70	88	40	6	35
4-6	233	143	147	186	129	96	201	81	6
6-8	216	141	132	222	147	123	229	136	107
8-10	190	120	145	247	134	131	241	152	113
10-12	233	169	135	261	134	116	177	137	121
14-16	204	168	137	203	133	141	182	132	138
18-20	190	226	136	212	183	143	242	215	147
22-24	197	243	167	189	164	152	245	210	171
26-28	228	178	177	188	224	163	183	213	203

TABLE 16. Milligrams of oven dried oat plants grown in sections of diuron treated columns of Sequatchie fine sandy loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			1 lb. per acre			2.5 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	207	153	149	4	63	124	28	0	87
2-4	161	122	134	162	70	99	156	0	12
4-6	153	153	157	157	124	122	174	144	23
6-8	169	148	143	155	126	137	157	143	127
8-10	222	144	160	152	129	145	187	146	148
10-12	223	153	146	211	118	141	205	149	147
14-16	257	161	114	238	142	136	245	157	144
18-20	249	206	165	158	145	138	268	135	147
22-24	211	193	227	200	187	196	200	191	190
26-28	212	193	225	228	243	182	198	227	232

TABLE 17. Milligrams of oven dried oat plants grown in sections of DCPA treated columns of Bowdre clay loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			4 lbs. per acre			10 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	182	190	208	179	197	217	189	208	201
2-4	212	201	200	202	187	244	203	182	200
4-6	255	204	205	262	167	192	273	185	184
6-8	284	171	230	325	175	217	326	170	209
8-10	303	176	188	355	167	201	315	190	204
10-12	296	195	208	345	202	223	331	199	207
14-16	317	193	252	316	190	261	313	249	265
18-20	286	264	313	308	253	350	336	265	331
22-24	283	294	305	278	287	349	331	287	342
26-28	270	399	304	300	348	353	349	303	292

TABLE 18. Milligrams of oven dried oat plants grown in sections of DCPA treated columns of Cumberland loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			4 lbs. per acre			10 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	156	130	139	152	147	202	139	175	135
2-4	151	147	137	179	127	143	141	142	129
4-6	165	117	135	143	151	145	137	142	138
6-8	164	134	119	158	154	122	149	127	138
8-10	154	137	145	173	138	133	156	145	140
10-12	158	124	144	131	140	156	154	124	140
14-16	143	131	136	166	121	141	147	130	153
18-20	156	153	146	180	138	139	146	128	131
22-24	176	138	135	177	152	157	166	149	145
26-28	164	166	196	184	144	184	156	151	145

TABLE 19. Milligrams of oven dried oat plants grown in sections of DCPA treated columns of Collins silt loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			4 lbs. per acre			10 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	154	146	128	157	152	150	164	144	132
2-4	156	143	143	166	140	143	166	144	136
4-6	233	143	147	194	144	141	224	140	139
6-8	216	141	132	213	136	131	206	133	143
8-10	190	120	145	220	131	135	227	135	135
10-12	233	169	135	228	138	141	204	131	131
14-16	204	168	137	216	136	162	194	155	129
18-20	190	226	136	226	147	160	163	167	188
22-24	197	143	167	203	250	158	174	200	190
26-28	228	178	177	228	195	174	187	184	216

TABLE 20. Milligrams of oven dried oat plants grown in sections of DCPA treated columns of Sequatchie fine sandy loam leached with three rates of water, average of three replications

Depth in inches	Rate of Herbicide--Active Ingredient								
	0 lbs. per acre			4 lbs. per acre			10 lbs. per acre		
	Inches of Applied Water								
	3	9	18	3	9	18	3	9	18
0-2	207	153	149	197	137	146	203	151	139
2-4	161	122	134	150	125	132	156	132	131
4-6	153	153	157	151	136	142	161	144	140
6-8	169	153	143	155	101	134	147	131	155
8-10	222	148	160	177	131	144	190	135	146
10-12	223	144	146	203	116	152	221	135	138
14-16	257	153	114	189	120	131	249	160	129
18-20	249	161	165	182	110	153	246	155	160
22-24	211	206	227	178	157	215	191	192	194
26-28	212	193	225	189	243	194	207	188	207