# PERSISTENCE OF PICLORAM, DICAMBA, AND FOUR PHENOXY HERBICIDES IN SOIL AND GRASS

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# CHAPTER I

## INTRODUCTION

There are approximately 7 million acres of post oak and blackjack oak infested land in Oklahoma that could be converted to grassland. Much has been done on brush control practices and good control procedures have been worked out for many of the brush species in Oklahoma.

Over the past years, herbicides have been used widely as one method of brush control and have been shown to give fair to good control of post oak and blackjack oak species. During this period herbicide use was based on control without much regard as to what happened to the herbicide after it had been applied.

The recent trend of looking at all agricultural chemicals from the standpoint of pollution possibilities has caused researchers to investigate not only chemical control practices, but also the herbicides potential for pollution. Some research has been conducted on herbicide residues in other states, but the variation in climate, soil, and other factors has made herbicide residue research necessary in Oklahoma.

The objectives of this study were (1) to determine the actual amount of aerially applied herbicides reaching the understory and forest floor in a post oak-blackjack oak savannah (2) to determine herbicide soil residues in grass and soil due to aerial spraying, and (3) to establish the rate of disappearance of brush control herbicides in soil under controlled conditions.

# CHAPTER II

# REVIEW OF LITERATURE

## Herbicide Disappearance In Soil Under Controlled Conditions

### 2,4-D (2,4-dichlorophenoxy acetic acid)

This herbicide is considered to be the least persistant of the herbicides evaluated in this study. The available research has shown that the length of time required for 2,4-D toxicity to be lost from soil under controlled conditions varies from 14 to 98 days (1, 3, 11, 14, 23, 29, 34, 35, 36, 37, 39, 45, 46, 50).

The presence and length of a lag phase has caused some disagreement among researchers. Audus (3), using a perfusion method with an initial concentration of 10 ppm found that there was a significant decrease in toxicity for the first 3 to 4 days. A lag phase of 7 days followed this period and all toxicity was lost by 14 days. In another perfusion study, it was found that increasing 2,4-D concentration to 200 ppm increased the lag phase to 23 to 28 days with complete degradation in 34 days (46). Another laboratory study indicated that 2,4-D applied to a silty clay loam soil and incubated at 25 C had a 14 day lag phase and complete detoxification occurred in 48 days (34). Different results were obtained by Norris and Greiner (37). No lag phase occurred when 2,4-D amine was applied at 3 pounds per acre and 2,4-D acid had a lag phase of only 3 days.

The length of 2,4-D toxicity is primarily related to environmental conditions but soil type also has an influence (1, 23, 29, 50). A summary of 2,4-D breakdown research stated that 2,4-D is relatively non-toxic to most plants after periods ranging from 14 to 49 days in most soils (29). A large variation was shown by a Hawaiian study which measured 2,4-D toxicity in a silty clay loam and a kaolinitic clay (1). In this study, depending on soil type and environmental factors, the length of time required for 2,4-D toxicity to dissipate from the soils varied from 14 to 98 days. Hanks (23) also found differences in length of persistence of 2,4-D in various soils. In a peat soil, toxicity was gone in 14 days. Toxicity had disappeared from four other soils at the end of 47 days, but remained in a naturally alkaline soil for greater than 47 days. No difference in time required for toxicity to disappear was observed by Warren (50) when a silt loam and a fine sand were observed. In both soils 2,4-D disappeared in 14 days.

The initial rate of application of 2,4-D does not appear to have much effect on persistence (11, 14, 35, 36, 39, 45). A review article by Sheets and Harris (45) stated that 2,4-D applied to soil at rates of 4 to 40 pounds per acre had a residual toxicity of 30 days. The results of a study by DeRose and Newman (14) showed that regardless of rates used 2,4-D persisted for only 67 days. In a greenhouse study 2,4-D was applied to soil at 10 pounds per acre and stored moist for 60 days (11). After 60 days a stand of mustard (Chlorispori sp.) planted in soil treated with 10 pounds per acre showed no appreciable herbicide injury. When 2,4-D was applied at 9 pounds per acre to soils kept moist and in a growth chamber at 35 C, toxicity disappeared in 14 days (39). The toxicity of 2,4-D applied at 2 pounds per acre to

preconditioned forest litter and stored in a growth chamber was lost in 35 to 60 days with only 6% remaining at the end of 35 days (36). A study using a respiration chamber determined that 2,4-D applied at 2 pounds per acre was 89% degraded in 13 days (35).

The formulation may have an effect on persistence. Norris (36) found that 2,4-D acid applied at 3 pounds per acre was 55% degraded in 15 days while 2,4-D amine was only 30% broken down in 15 days.

Dichloroprop [2-(2,4-dichlorophenoxy) propionic acid]

It was expected that dichloroprop breakdown would be slightly slower than 2,4-D. However, an experiment comparing 2,4-D and dichloroprop found large differences in breakdown periods (2). The use of an ultra-violet measuring technique showed that 2,4-D toxicity was lost in 26 days while dichloroprop required 205 days to disappear.

2,4,5-T (2,4,5-trichlorophenoxy acetic acid)

The length of time that 2,4,5-T persisted in the soil is also variable (2, 4, 14, 35, 36, 51). A concentration of 100 ppm was reduced by 2/3 in 210 days with 270 days required for total detoxification (4). These results were obtained using a perfusion method. In three silt loam soils under the same conditions the persistence of 2,4,5-T, as measured by an ultra-violet adsorption technique, was 47 to 124 days in one soil, 124 days in one soil, and 205 days in the other soil (2). A respiration chamber study by Norris determined that only 23% of the 2,4,5-T applied to forest litter had been degraded in 13 days with 53% degraded in 28 days (35).

In another study, 2,4,5-T persisted for 147 days after application,

as measured by soybean [Glycine max (L.) Merrill] bioassay (14). A sorghum (Sorghum bicolor L.) bioassay used by Weise and Rea (51) indicated that 2,4,5-T had disappeared from wet soils in 90 days.

An application of 2,4,5-T at 2 pounds per acre to preconditioned forest floor material persisted for 120 to 180 days (36). In this experiment only 44% of the herbicide was degraded in 20 days.

The disappearance of 2,4,5-T, like 2,4-D, is influenced by soil type (50). In a silt loam soil kept moist and warm, the ester and amine of 2,4,5-T disappeared in 28 days. Under the same conditions in a sandy soil, 2,4,5-T ester still had activity at the end of 56 days, but the amine disappeared in 56 days.

Silvex [2(2,4,5-trichlorophenoxy) propionic acid]

According to two researchers silvex is similar in persistence under controlled conditions to 2,4,5-T (2, 50). A comparison study of the persistence of 2,4,5-T and silvex in three silt loam soils showed that both herbicides persisted from 47 to greater than 205 days (2). The persistence was measured using an ultra-violet adsorption technique and conditions were the same for all three soils. Formulation also influences the residual amount of silvex. In a moist warm sandy soil, silvex ester still had activity at the end of 56 days while the amine form had no activity in 56 days (50).

In a wet soil, silvex was more persistent than 2,4,5-T (51). No residual of 2,4,5-T could be detected at 90 days but residual of silvex could still be detected.

Dicamba (3,6-dichloro-o-anisic acid)

A perfusion type study showed that at the end of 80 days approximately 10% of the original application of dicamba had been broken down indicating that dicamba would be more persistent than the phenoxy herbicides (46). However, Sheets and Harris (45) found that soil persistence of dicamba was similar to 2,4,5-T.

The rate of application of dicamba, in contrast to the phenoxy herbicides, had a definite effect on the length of persistence under controlled conditions (12, 22, 46). Dicamba applied at 1 and 2 ppmw to a silt loam and silty clay loam soil dissipated in 30 days (12). These soils were stored at 35 C and persistence was determined by soybean bioassay. However, by increasing the rate to 4 ppmw Hahn, et al. (22), showed that the time required for dissipation increased to 60 days. The herbicide was applied to a silty clay loam soil and stored at 35 C. Herbicide persistence was measured using cucumber (Cucumis sativis L.) bioassay. Dicamba applied at 8.0 ppmw completely retarded growth of snap beans (Phaseolus vulgaris L.) at the end of 112 days (46). At the same date the application of 0.5 ppmw and 2.0 ppmw had retarded growth of the beans by 4 and 12% respectively.

Dicamba applied at 8 ounces per acre to a moist loam soil and incubated at 55 and 70 F gave almost complete kills of Tartary buckwheat Fagopyrum tataricum (L.) Gaertn. at the end of 84 days (18).

Picloram (4-amino-3,5,6-trichloropicolinic acid)

Picloram, with persistence ranging from greater than 365 days to greater than 423 days, is the most residual herbicide involved in this

experiment (30, 36, 52).

In a sandy loam soil treated with 0.4 ppm, Youngston et al. (52) found that only 6% of the picloram applied had decomposed at the end of 71 days and only 53% at the end of 423 days. In a clay soil decomposition was 5% and 82% at the end of 71 and 423 days, respectively.

In preconditioned forest floor litter picloram applied at 0.5 pounds per acre was 23% inactivated after 120 days and 35% inactivated after 180 days (36).

After 365 days, an average of 15 to 25% of the original application of picloram was detected in three soils (30). The soils used were clay, sandy loam, and a commercial grade of sand. The soils were treated with 0.5 and 2 pounds per acre and kept moist in a growth chamber.

According to Herr et al. (25) several factors influence the residual life of picloram. In a greenhouse study they determined that soil organic matter, precipitation, soil texture, and rate of application effected the length of persistence. In another study it was also determined that soil type, temperature, moisture and light effected the persistence of picloram (30). Picloram was degraded faster at higher temperatures and high moisture content.

## Herbicide Residue in Soil Under Field Conditions

Under controlled conditions the herbicide could not be carried out of the sampling zone by leaching. In the field leaching can occur and should speed the loss of toxicity.

### 2,4-D

The length of breakdown of 2,4-D in the field was similar to

breakdown under controlled conditions (10, 14, 27, 34, 45, 51). The residue of 2,4-D applied at 5 pounds per acre had disappeared in 49 days (14). A review article by Sheets and Harris (45) reported that 2,4-D applied at 5 pounds per acre had an average residual life of 30 days. Klingman (27) stated that 2,4-D applied at 0.5 to 3 pounds per acre to a warm moist soil had a residual life of 7 to 30 days. Another study reported that 2,4-D had essentially disappeared in 35 days (34).

In Puerto Rico a mixture of 2,4-D and 2,4,5-T applied at 24 pounds per acre retarded crop growth for 30 days and in some cases 60 days, but the growth retardation was attributed to 2,4,5-T (10). In a low rainfall area, 18 inches, a residue of 2,4-D remained in a silty clay loam soil for 90 days (51). Sorghum was used as a bioassay plant.

There is a difference between field conditions and controlled conditions in regard to a lag phase. Researchers applied 2,4-D to a silty clay loam soil and reported no observed lag phase (34). None of the literature reviewed reported a lag phase under field conditions.

2,4,5-T

Most researchers agree that 2,4,5-T is more persistant in the field than 2,4-D (27, 34, 45). The review article by Sheets and Harris (45) stated that 2,4,5-T applied at 5 pounds per acre disappeared in 90 days. Under optimum soil and environmental conditions 2,4,5-T applied at 0.5 to 3 pounds per acre has a residual life of 14 to 35 days (27). A study measuring 2,4,5-T residue with cucumber root elongation showed that most of the herbicide had disappeared from a silty clay loam soil in 91 days (34).

The amount of moisture in the soil also has an influence on the

rate of field disappearance. When 2,4,5-T was applied at 5 pounds per acre the amount of residue was closely related to soil moisture content (14). The average residual life in this study was 93 days but as soil moisture levels increased the herbicide disappeared more rapidly. In a low rainfall area, 18 inches, 180 to 300 days was required for the residue of 2,4,5-T to disappear (51).

Dicamba

Dicamba has been shown to be more residual in soils when applied at high rates than the phenoxy herbicides, but it is considered to be less persistant than picloram (13, 16, 17).

A study conducted by Dowler et al. (17) in Puerto Rico found that dicamba applied at 9 pounds per acre had a residue of .001 ppm one year after application. The average rainfall during this study was approximately 26.0 inches. Another study in Puerto Rico concluded that dicamba applied at 3, 9, and 27 pounds per acre was less persistant than picloram applied at the same rates (16).

Dicamba applied at 3, 10, and 20 pounds per acre in May of 1964, showed no residual effect on Great Northern field beans (Phaseoulus vulgaris L.) planted in the dicamba plots in 1966 (13). The soils in this study were two loam soils and a silty clay loam. In this experiment dicamba was rated as less persistant than picloram or 2,3,6-TBA (2,3,6-trichlorobenzoic acid).

Picloram

Picloram is a promising residual herbicide for use in brush control (9, 10, 16, 17, 20, 24, 26, 30, 32, 42, 48). Picloram applied at 9 and

27 pounds per acre in Puerto Rico had a residual concentration of .005 ppmw in the 0 to 6 inch zone after 3 months (16). The application of 27 pounds per acre had a concentration of .025 ppmw in the same zone at the end of 365 days. Picloram applied at 9 pounds per acre in another area of Puerto Rico had a residual of .002 ppmw in the 0 to 6 inch zone 365 days after application (17). In New Zealand picloram was applied to bare silt loam soil at 1 pound per acre and white clover (Trifolium repens) was used for residue analysis (32). A rating scale in which 0 equaled no clover establishment and 1 equaled 20% establishment with severe foliage damage was used. The clover rating at the end of 84 days was 0.6 and 0.9 at the end of 147 days.

The soil type has a large influence on the length of picloram's residual life in the soil (9, 10, 20, 24, 26, 30, 42, 48). The amount of rainfall received after application of picloram is also important, but these two factors are too interconnected to choose one as the most important factor in predicting picloram residues in the soil.

In a high rainfall area, 41.72 inches during the study, the persistence of picloram was evaluated and compared in a silty clay loam soil (24). Picloram applied to the silty clay at 8 ounces per acre had a residue of .030 and .019 ppmw at the end of 101 and 280 days, respectively. The application of 4 ounces per acre to the silt loam soil resulted in a residue of .105 ppmw at the end of 97 days and .004 at the end of 245 days. In another high rainfall area, 58 inches, the growth of sorghum, wheat (Triticum vulgara Vill.) or rice (Oryza sativa L.) was not affected 90 days after the application of 6 pounds per acre of picloram (10). In a semiarid region, rainfall often less than 20 inches per year, picloram applied at 0.25 pounds per acre had a

detectable residue in the 0 to 6 inch zone for 60 to 235 days in a sandy loam soil (42). Under the same conditions picloram disappeared from a loamy sand in 71 to 150 days.

A review article by Hoffman (26) reported that 100 days after the application of 1 gallon per acre of Tordon 225 (1 pound acid equivalent of triethylamine salt of picloram plus 1 pound acid equivalent of triethylamine salt of 2,4,5-T) to a clay loam soil there was no detectable residue. The rainfall received during this period was 13.9 inches. The application of 0.75 pounds per acre of picloram to a deep clay soil under the same rainfall amount resulted in a detectable residue 360 days after application in the 0 to 6 inch zone.

A pasture area in Nebraska treated with 1.94 pounds per acre had a residue of .031 ppm in the 0 to 12 inch zone after 365 days and 16 inches of rain (48).

After the application of 1.68 pounds per acre to a silty clay loam soil Goring (20) found that 96% of the picloram had disappeared in 150 days. The study area received 19 inches of rain during the experiment.

A soil type comparison study showed that picloram applied at 1 pound per acre to a bare clay loam and a sandy soil would persist in the clay soil for 90 to 180 days and in the sandy soil for less than 90 days (9). The residue measurements were taken in the 0 to 6 inch zone. A similar study evaluated a fine sandy loam and a gravelly sandy loam soil (30). There was no detectable residue in the surface soil of the fine sandy loam after 84 days, but a detectable residue remained in the gravelly sandy loam for greater than 182 days. Picloram was applied at 2 and 8 pounds per acre.

## Herbicide Distribution to Various Levels

A limited number of studies has been conducted on the amount of herbicide that reaches the various canopy levels and soil surface in a multi-storied type vegetation with aerial application.

A study by Bouse and Lehman (8) was conducted in Texas to measure the penetration of aerial sprays through a dense postoak (Quercus stellata Wangenh.) canopy and a yaupon (Ilex vomitora Ait.) understory canopy. The results showed that penetration through the post oak canopy ranged from 19 to 22% with only 4 to 7% penetrating both canopies and reaching the forest floor. An earlier study in Texas was conducted under canopies of McCartney Rose (Rosa bracteata Wendl), mesquite [Prosopis juliflora (Swartz.) DC.] and dense stands of live oak (Quercus virginiana Mill.) (7). In this study, 8% of a water spray reached the soil under the McCartney Rose, 60% under mesquite, and 12% under dense live oak canopies. A higher percentage of herbicide reaching the soil surface was obtained using a helicopter to spray pure stands of scrub oak (Quercus dumosa Nutt.) (49). The measurements taken 10 feet on both sides of the spray swath showed that 30% of the herbicide reached ground level. The helicopter was flying at slow speeds and using the rotor downdraft to obtain greater foliage penetration.

There is some additional information on spray penetration using ground equipment (30, 43). More spray should be expected to reach ground level with ground applications than with aerial application since the height of the boom is lower. Research using a ground spray boom 10 to 12 feet above ground level and spraying 4 to 6 foot tall honey mesquite [ Prosopis juliflora (Swartz) DC. var. glandulosa, (Torr.)

Cockerell] trees showed that half of the herbicide applied reached the soil surface (43). In another study Merkle, et al. (30) using a boom 15 feet above the ground found that 25% of the spray reached the ground in mixed brush with only 10% reaching the soil surface in an area covered with live oak.

## Herbicide Persistence in Grass

The grass vegetation serves as another interceptor of the herbicides before they reach the soil during application. This initial herbicide coverage plus any additional root uptake represents the potential herbicide residue in the plants.

### 2,4-D

The breakdown of 2,4-D in living plants appears to be rapid (28, 33). A pasture sprayed with an acid of 2,4-D at 2 pounds per acre had a residue of 58.3 ppm immediately after spraying, but only 5 ppm 7 days later (28). The grass sprayed with the same rate of 2,4-D ester had 26.6 ppm residue immediately after spraying and 13.7 ppm later.

A study by Morton et al. (33) found that 2,4-D had a half-life of about 14 days in the green tissue of silver beardgrass (Andropogon saccharoides Sw.), little bluestem, (Andropogon scoparius Michx.), and dallisgrass (Paspalum dilatatum Poiret). At the end of 105 days the concentration was 1 to 2 ppm in the green tissue. In litter tissue that was kept moist by frequent rainfall the half-life of 2,4-D was 20 days.

## 2,4,5-T and Dicamba

The study by Morton et al. (33) found that 2,4,5-T and dicamba applied to little bluestem, silver beardgrass, and dallisgrass had a half-life of 14 days in the green tissue. The concentration at the end of 105 days was 1 to 2 ppm. In moist litter tissue the average half-life of 2,4,5-T and dicamba was 19 and 18 days, respectively. It was found that important reductions of herbicide did not occur in the litter tissue when no rainfall occurred.

A residue of 2890 ppb was obtained immediately after spraying 2 pounds per acre of 2,4,5-T ester on little bluestem, brown seed paspalum (Paspalum plicatulum Michx.), and Indiangrass [ Sorghastrum nutans (L.) Nash ] while the acid applied at the same rate had a residue of 4060 ppb (5). The ester was down to 170 ppb and the acid down to 60 ppb at the end of 180 days.

## Picloram

Picloram applied as the amine salt at .28 kg. per hectare on windmillgrass (Chloris verticillata Nutt.) and threeawn (Aristida sp.) had an initial concentration of 80.0 ppm (44). The concentration in the grasses was .130 ppm 130 days after application. The initial concentration of 24 ppm at another collection site had dropped to .12 ppm 72 days later.

Getzendamer (19) determined that liquid formulations of picloram deposit up to 200 ppm on grass for each pound per acre applied. He reported that under Oklahoma conditions an application rate of 0.75 pounds per acre had a residue of 50 ppm immediately after spraying and

10 ppm after 14 days. After 14 days the concentration declined steadily with no detectable residue remaining at the end of 112 days.

The concentration of picloram applied at 1 pound per acre 30 days after application was 2.65 ppm of fresh weight in a Texas experiment (5). The concentration at the end of 180 days was reduced to .01 ppm.

A review article by Hoffman (26) stated that 79 days after the application of 1 pound per acre a residue of 1.5 ppm was detected in grass. No residue was detectable 170 days after the application of 0.5 pounds per acre.

# CHAPTER III

# METHODS AND MATERIALS

## Field Studies

The herbicides in the field studies were aerially applied with a mono-winged airplane with a 40 foot spray swath. The conditions during spraying were an air temperature of 70 to 76 F and a wind speed of 5 to 10 mph.

The herbicide treatments used were 2,4,5-T triethylamine salt at 2 pounds per acre plus 1 pound per acre of dicamba, 2,4,5-T triethylamine salt at 2 pounds per acre plus 1 pound per acre of triethylamine salt of picloram, 2,4,5-T propylene glycol butyl ether ester at 2 pounds per acre, and 1.5 pounds per acre of 2,4-D butoxyethanol ester plus 1.5 pounds per acre of dicloroprop butoxyethanol ester.

Each treatment was applied to four 320 ft. by 1320 ft. plots of blackjack-postoak savannah, for a total of 16 plots. All treatments except the 2,4,5-T plus picloram were applied June 8 and 9, 1970. Rain delayed the application of this treatment until June 16 and 17, 1970.

### Herbicide Distribution to Various Levels

Collection Technique. Six of the sixteen plots were sampled in order to determine the amount of herbicide reaching the various levels in the forest canopy. Two of the plots sampled received the 2,4,5-T

plus dicamba treatment and the other plot was sprayed with the 2,4,5-T plus picloram treatment.

The collection system consisted of 3 petri dishes glued to a small board. These boards were then placed either on the forest floor, above the understory species but below the overstory species, or above the overstory trees. The average height of the overstory oak trees was 40 feet with the understory species averaging 4 to 6 feet. The sampling boards were placed on a stand and the stand tied to trees to obtain the necessary height for understory and overstory measurements. Within each plot, three collection areas (subplots) were sampled. These were located along the center line of the plot and were spaced approximately 200 feet apart.

After the entire plot was sprayed the petri dishes were collected, taped shut, and placed in a box so no light could reach them. The petri dishes were stored in the laboratory until analysis.

Extraction. The extraction procedure for 2,4,5-T plus dicamba was an acid extraction procedure. A 2% solution of HCl was prepared by placing 2 milliliter (ml) of concentrated HCl in 100 ml of distilled water. Ten ml of the HCl solution was pipeted into the petri dishes and the solution allowed to stand for 15 minutes. The HCl solution was poured directly into a 125 ml seperatory funnel. The petri dish was rewashed with an additional 10 and 5 ml of HCl solution which was poured into the funnel to make a total of 25 ml in the seperatory funnel. The solution was extracted with 25 ml of diethyl ether twice and once with 15 ml of ether. With each extraction the funnel was shaken 15 seconds. After the liquids seperated the HCl solution was

drained off and the ether transferred to a 100 ml beaker. The combined ether extract of 65 ml was evaporated to 5 ml using a steam bath at 50 C. The 5 ml portion was placed in a 18 by 155 mm culture tube with a 10 ml mark and esterified using the Schlenck-Gellerman micro technique described later under esterification procedure.

An acid extraction procedure was used to extract 2,4,5-T plus picloram from the petri dishes. A 0.5 solution of $H_2PO_4$ was prepared by adding 0.5 ml of concentrated $H_2PO_4$ to 100 ml of distilled water. Ten ml of the $H_2PO_4$ solution was pipeted into the petri dish and allowed to stand for 30 minutes. The 10 ml of solution was poured directly into a 25 ml volumetric flask. The petri dish was rewashed with 10 ml and 5 ml of $H_2PO_4$ solution and added to the volumetric to make a total volume of exactly 25 ml. The 25 ml of solution was divided into 2 equal portions with one sample extracted with benzene and the other sample extracted with chloroform.

The 2,4,5-T sample was extracted twice with 25 ml of nanograde benzene and once with 15 ml. A 60 ml seperatory funnel was used. During each extraction the funnel was shaken 15 seconds. After the liquids seperated the $H_2PO_4$ solution was drained off and the benzene was evaporated to 10 ml using a steam bath at 50 C and placed in a culture tube.

The 10 ml portion was esterified using the procedure described later under esterification procedure.

For picloram extraction the other 12.5 ml aliquot was extracted twice with 25 ml of reagent grade chloroform using a 60 ml seperatory funnel. After extraction 5 grams of $Na_2SO_4$ was added to the 50 ml total of chloroform and allowed to stand for 2 to 3 hours. The mixture

was then filtered into a 100 ml beaker using Schleicher and Schleicher (S&S) #597 filter paper. The $Na_2SO_4$ remaining in the beaker was washed 3 times with 5 ml of chloroform which was added to the 50 ml in the beaker. The total of 65 ml of chloroform was evaporated to dryness using a steam bath at 50 C. The picloram was then taken up in 5 ml of diethyl ether and placed in a 18 by 150 mm culture tube with a 10 ml mark. This sample was esterified using the Schlenck-Gellerman micro technique described below.

Esterification Procedure. The 2,4,5-T plus dicamba and the picloram samples were esterified using the Schlenck-Gellerman micro technique described by Smith, et al. (47). In this procedure a diazomethane precursor, N'N' dinitroso-N'N dimethyl terephthalamide, was used instead of pre-prepared diazomethane. Esterification was accomplished by using three 18 by 145 mm test tubes set up in a gas train. Ten ml of ether was placed in the first tube to saturate a nitrogen stream passing into the second tube. Then 2 ml of 60% aqueous KOH, 1.5 ml carbitol, and 1.5 ml diethyl ether was added to the second tube. The third tube in the system was the one containing the sample to be esterified.

Ten milligrams of N'N' dinitroso-N'N dimethyl terephthalamide was added to the second tube just before passing $N_2$ through the train at 60 ml per minute. The second tube was stoppered quickly and the $N_2$ diazomethane allowed to bubble through the sample in the third tube for 60 seconds.

After esterification the sample was evaporated to 2 ml using a water bath at 45 C. Then 5 ml of 1% acetic acid was placed in the culture tube to destroy the excess methylating agent. The sample was

made to 10 ml volume by adding the appropriate amount of ether. The herbicide was contained in the top 5 ml portion and 1 microliter of this solution was injected into the chromatograph.

The 2,4,5-T sample was esterified by placing 0.5 ml of methanolic HCl[1] in the culture tube that contained the sample. The sample containing the HCl was heated for 4 hours on a hot plate at 60 C. The tubes were heated by placing them in a 1000 ml beaker and covering them with 3 layers of paper towels. After heating, the sample was made to 10 ml volume with the addition of benzene and 1 microliter of this solution was injected into the chromatograph.

Chromatographic Analysis. For analysis 1 microliter of the esterified solution was injected into a Hewlett-Packard Model 5750 gas chromatograph equipped with an electron capture detector. Ni 63 was the ionization source. The injector, column, and detector temperatures were 180, 170, and 180 C, respectively for 2,4,5-T plus dicamba analysis and 290, 200, and 250 C, respectively for 2,4,5-T plus picloram analysis. A glass column was used that was 1/4 inch by 6 feet. It was packed with 80 to 100 mesh Chromosorb WAWDMCS coated with 3% silicone gum rubber, SE 30. The flow rate of the 5% methane-agron carrier gas was approximately 40 ml per minute through the column with an additional purge flow of 80 ml per minute.

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[1]Instant Methanolic Kit, available from Applied Science Laboratories, Inc., P. O. Box 444, State College, Pennsylvania.

Herbicide Residue in Field Soil and Grass

Collection Technique. Sampling of soil was started on June 12, 1970, in the plots that received phenoxy herbicides and dicamba. Soil samples from the picloram plots and all grass samples were collected June 17, 1970. All soil and grass samples were then again collected on July 10, 1970 and at 4 week intervals through October 2, 1970. The plots that received picloram and dicamba were also sampled May through September of 1971.

The grass samples were collected in the same area as the soil samples with 15 subsamples combined to make a composite sample. The top growth that would be available for grazing was collected and this was seperated into green and dead tissue in the laboratory and analyzed seperately. The primary grass species in the sample were little bluestem, broomsedge bluestem, (Andropogon virginicus), and beaked panic, (Panicum anseps).

The soil and grass samples were frozen after collection and kept frozen until ready for analysis. Prior to analysis the soil samples were allowed to air dry. A random sample of 10 grams was taken and used for analysis. The grass samples were air dried, ground in a Wiley mill, and a random 10 gram sample taken for analysis.

Soil Residue Extraction and Analysis. The phenoxy herbicide extraction procedure was basically the same as the procedure described by Norris and Greiner (37). Ten grams of the soil sample was placed in a 4 ounce jar and 40 ml of 1 N NaOH was added to the sample. The sample was shaken by hand and digested for 4 hours in a 75 to 85 C water bath. The samples were then removed from the bath and centrif-

uged while hot for 5 minutes at 1300 rpm. The supernatant was decanted into a 100 ml beaker. The residue was resuspended by adding 40 ml of hot NaOH and shaking by hand. The sample was centrifuged for 5 minutes at 1300 rpm and the supernatant added to the previous supernatant. The NaOH solution was acidified by adding 8 ml of concentrated HCl to the solution. The solution was evaporated to 40 ml using a hot plate at 50 to 60 C. The herbicide was extracted from the solution by shaking the solution twice with 50 ml of nanograde benzene and once with 25 ml of benzene in a 125 ml seperatory funnel. The combined benzene extract was evaporated to 10 ml using a steam bath at 50 C and this portion poured into a culture tube containing a molecular sieve material. The sieve material was used to absorb moisture in the sample. The samples were esterified using the esterification technique described for 2,4,5-T previously.

The analysis of the phenoxy herbicides was the same as that described for 2,4,5-T plus picloram analysis. Dichloroprop and 2,4-D could not be analyzed seperately because their peaks could not be seperated.

The dicamba extraction procedure used was a slightly modified version of the analytical method published by the Velsicol Chemical Corporation[2]. Ten grams of soil was placed in a 1 pint jar with 2 ml of 10% $H_2SO_4$ and 100 ml diethyl ether. The jar was stoppered with a foil-lined screw cap and shook for 60 minutes on a mechanical shaker. After shaking, the soilds were allowed to settle and the ether filitered

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[2]Determination of Residue of Dicamba and 5-hydroxy Dicamba. Analytical Method of Velsicol Chemical Corporation. Chicago, Ill.

into a 250 ml beaker using S&S #597 filter paper. The total filtrate was evaporated to 10 ml using a water bath at 50 C. This 10 ml extract was used in the chromatographic clean-up.

The reagents needed for column preparation were buffer solution, Celite buffer mixture, and equilibrated ether. The buffer solution was prepared by mixing equal volumes of 2M $NaH_2PO_4 \cdot H_2O$ and 2M $K_2HPO_4 \cdot 3H_2O$. The Celite buffer mixture was prepared by adding 40 ml of the buffer solution to 100 grams of Celite 545 in small portions and stirring thoroughly. The ether was equilibrated by shaking 1.5 liter residue grade ether with 100 ml of buffer solution for 1 minute in a 2 liter seperatory funnel. The lower layer, which was the buffer solution, was discarded after each equilibration.

The column used for sample clean-up was prepared using a 100 ml biuret tube with a glass stopcock. The tube was filled 3/4 full with buffer equilibrated ether. Fifteen grams of Celite buffer packing was added to the tube in small portions with periodic draining and addition of equilibrated ether to keep the packing covered. The column packing was completed by applying gentle air pressure 2 or 3 times and adding the ether required to keep the packing covered. The column was filled with fresh equilibrated ether and allowed to drain until the solvent reached the top of the packing. This completed column preparation and the column was ready for sample clean-up.

The 10 ml extract of ether obtained from the extraction procedure was quantitatively transferred to the column after a few ml of equilibrated ether was added to the sample. After the sample was poured into the tube 50 ml of equilibrated ether was also added to the tube. The stopcock was opened and the solvent allowed to drain until the solvent

just reached the top of the packing. The eluate collected was discarded, the tip of the tube rinsed, and a clean 250 ml beaker placed under the tube. The column was developed by passing 265 ml of equilibrated ether through the column which eluted dicamba. The 265 ml of ether collected was evaporated to 5 ml using a water bath at 50 C.

The 5 ml portion was poured into a culture tube and esterified using the micro esterification technique previously described. Chromatographic analysis was the same as that described for the dicamba plus 2,4,5-T analysis.

The picloram extraction method was essentially the procedure reported by Saha and Gadallah (40). Ten ml of 0.5% $H_2PO_4$ solution and 50 ml of ACS grade acetone was added to 10 grams of soil and shook for 1 hour on a mechanical shaker. After shaking, the mixture was filtered through S&S #597 filter paper and the residue was washed 3 times with 20 ml of acetone. The total filtrate of 110 ml was transferred to a seperatory funnel and diluted with 100 ml of distilled water. The solution was extracted once with 75 ml chloroform and the aqueous layer re-extracted twice with 25 ml of chloroform. Fifteen to 20 grams of anhydrous $Na_2SO_4$ was added to the combined chloroform extract and allowed to stand for 2 to 3 hours. The mixture was filtered into a round bottom boiling flask and the $Na_2SO_4$ washed 3 times with 5 ml of chloroform. The filtrate was evaporated to dryness and taken up in 5 ml of diethyl ether. The ether was transferred to a culture tube and esterified using the micro esterification technique previously described. The only change in chromatographic analysis from previous procedures was that the injector column, and detector temperatures were 285, 210, and 240 C, respectively.

Grass Residue Extraction and Analysis. The extraction method used for the phenoxy herbicides was a modified version of the procedure described by Hagin and Linscott (21). Ten grams of the ground sample was placed in a 250 ml beaker. Thirty ml of boiling water was poured over the sample and the sample heated on a hot plate until the water just boiled. The sample was removed from the heat and swirled to obtain adequate coverage. The sample was allowed to cool and then transferred quantatively to a 150 ml glass blending cup. The beaker was rinsed 2 times with 20 ml of 2-propanol and once with 15 ml of 2-propanol with each rinse added to the blending cup. The sample was mixed for 5 minutes with a Virtis blender at medium speed. After blending the homogenate was filtered into a 250 ml flask using S&S #597 filter paper moistened with distilled water. The plant residue was rinsed from the blenders mixing head into the cup with 10 ml of 2-propanol and the cup was rinsed twice with 20 ml 2-propanol with each rinse filtered through the funnel. The 2-propanol extract was transferred to a 250 ml volumetric and made to volume with 2-propanol.

For sample clean-up three 60 ml seperatory funnels with a teflon stopcock were used. Twenty-five ml of 2-propanol extract was pipeted into the first 60 ml seperatory funnel and the sample was extracted with 10 ml of petroleum ether by shaking for 30 seconds. Ten ml of 0.03N HCl was then added to the mixture in the first funnel and the mixture was again shaken for 30 seconds. The lower aqueous layer was drawn into a second 60 ml funnel and 10 ml of petroleum ether was added. This funnel was shaken for 30 seconds. The lower aqueous layer was drawn into a third 60 ml seperatory funnel and 1 drop of concentrated HCl and 10 ml of a 1 to 1 volume of petroleum ether and

diethyl ether was added. This mixture was shaken for 20 seconds and the lower layer discarded after seperation. Then 5 ml of deionized water was added to the ether extracts in all three funnels. Each funnel was shaken for 20 seconds and after seperation the lower layer was discarded. The ether extracts in the second and third funnel were added to the extract in the first funnel. The second and third funnel were rinsed with 5 ml of ether and the ether was added to the first funnel. Ten ml of deionized water was added to the combined ether extract in the first funnel and the mixture was shaken for 20 seconds. After seperation the lower layer was discarded, the ether extract was transferred to a 250 ml boiling flask, and the seperatory funnel rinsed 2 times with 3 ml of diethyl ether. The rinses were added to the boiling flask and the ether evaporated to 5 ml using a 45 C water bath and a evaporator.

The 5 ml sample was esterified using the micro esterification technique previously described. There was an interferring peak in the 2,4,5-T region so the oven temperature was lowered to 175 C to obtain peak seperation.

The extraction method used for dicamba is the same as the procedure described by the Velsicol Chemical Corporation. Ten grams of the ground grass sample was placed in a Waring blender with 250 ml of ether and 5 ml 10% $H_2SO_4$. The cup was capped and blended at a high speed for 10 minutes. The supernatant was filtered through S&S #597 filter paper into a 250 ml beaker. The ether was evaporated to 10 ml with a 50 C water bath and the 10 ml sample used in the chromatographic clean-up. All the procedures used in grass sample clean-up, esterification, and analysis were the same as those previously described for dicamba in

soil.

The method used for the extraction of picloram from grass was essentially the method described by Bjerke, et al. (6). A 10 gram sample of ground grass placed in a 1 pint jar was extracted by shaking the sample with 100 ml of aqueous 0.1N KOH solution for 30 minutes on a mechanical shaker. After shaking, the mixture was filtered through a Buchner funnel packed with a 1 centimeter (cm) pad of Celite 545 into a 250 ml flask. The filter cake was washed with a sufficient amount of solvent to bring the volume close to 200 ml. The volume was then adjusted to exactly 250 ml by transferring the filtrate to a 250 ml glass-stoppered graduate cylinder and adding a sufficient amount of distilled water. The graduate cylinder was stoppered and was shaken by hand. After shaking an aliquot of 25 ml was taken from the graduate cylinder and diluted with 10 ml of distilled water. The diluted extract was acidified by adding 5 to 6 drops of 6N $H_2SO_4$ to the extract. Then approximately 3 grams of NaCl was added to the extract. After stirring to dissolve the NaCl, the solution was extracted with 40 ml and 20 ml of ethyl ether. A 60 ml seperatory funnel was used and the solution was shaken lightly for 15 seconds. The two ether extracts were combined in a 50 ml beaker and evaporated to 2 ml in a water bath at 50 C. A small amount of $Na_2SO_4$ was added to absorb any water present before evaporation was started. After evaporation the 2 ml of ether was transferred to a culture tube and the $Na_2SO_4$ rinsed with 3 ml of ether. The rinse was added to the culture tube for a total volume of 5 ml of ether. The 5 ml was esterified using the micro esterification technique previously described and chromatographic analysis was the same as that

described for picloram in soil.

## Herbicide Disappearance Under Controlled Conditions

For this study the top 1 inch of soil and partially decomposed vegetative residue was collected from a postoak and blackjack oak area in the Cross Timbers region near Stillwater and from the Ouichita Highlands of eastern Oklahoma. These soils were used to determine if a difference in breakdown would exist between two forest soils from different locations in Oklahoma or if breakdown would vary from soils under a grassland and forest type cover. The top 1 inch of soil and litter was also collected from a grass covered area in the open spots of the Ouichita Highlands forest area. These soils were taken from areas that had received no herbicides. Table 1 gives the characteristics of the soils used in this experiment.

These soils were thoroughly mixed and 130 grams placed in each styrofoam cup. The cups were kept moist in a growth chamber for 2 weeks prior to the herbicide application in order to allow maximum microbial activity at the time of herbicide application. The growth chamber was set for a 16 hour day at 24 C and an 8 hour night at 18 C. The cups were arranged in a completely randomized design.

The herbicides used were diethanol amine salt formulations of 2,4-D, dichloroporp, 2,4,5-T, silvex, and potassium salt of picloram, applied at 4.79 micrograms per gram of soil which is equivalent to 2 pounds per acre. Dicamba (dimethyl amine salt) was applied at 2.47 micrograms per gram of soil or 1 pound per acre. All herbicides were topically applied in a water mixture. The phenoxy herbicides were sampled at 0, 5, 10, 20, and 40 days with picloram and dicamba being

TABLE I

CHARACTERISTICS OF SOILS USED IN THE HERBICIDE DISAPPEARANCE UNDER CONTROLLED CONDITIONS EXPERIMENT

| Vegetative Area | Textural Class | Percent Sand | Silt | Clay | CEC (meg/100 gm) | Percent Organic Matter |
|---|---|---|---|---|---|---|
| Ouichita Highlands | | | | | | |
| Forest | Loam | 54.5 | 29.0 | 15.5 | 11.0 | 3.3 |
| Grasslands | Loam | 55.0 | 28.5 | 16.5 | 8.5 | 2.8 |
| Cross Timbers Forest | Loam | 50.0 | 31.5 | 18.5 | 12.0 | 3.8 |

sampled at 0, 20, 40, 60, and 100 days. All herbicide treatments as well as non-treated checks were replicated three times.

The cups were frozen immediately after sampling and kept frozen until ready for analysis. Prior to analysis the soil samples were air dried and a random composite sample of 10 grams taken for analysis. All herbicides were extracted, esterified, and analyzed using the same procedure previously described for the field soil. Dichloroprop and silvex were extracted, esterified, and analyzed using the phenoxy procedure previously described.

# CHAPTER IV

## RESULTS AND DISCUSSION

### Herbicide Disappearance From Soil Under Controlled Conditions

#### 2,4-D

There was no observable lag phase with a rapid disappearance for the first 20 days (Figure 1). However, the first measurement was taken 5 days after application and a short lag phase, such as the one observed by Norris and Greiner (37), would not have been detected.

The soil used had no effect on the amount of residual herbicide at any given time after application. For example, approximately 5% still remained in all 3 soils after 20 days. This time period is within the range revealed by the literature required for 2,4-D toxicity to disappear. The percent of herbicide remaining in the soil from 20 to 40 days was fairly constant and it is possible that the extraction procedure was able to remove some herbicide from the soil that was bound in some form and was unavailable to soil microorganisms.

For all soil samples the percentage given was based on the amount recovered at 0 days. This helped adjust for the herbicide that was in the sample but was not detected due to losses during extraction and esterification.

The phenoxy soil extraction procedure used gave a recovery of 84% with 85% esterification. The lowest concentration of 2,4-D that could

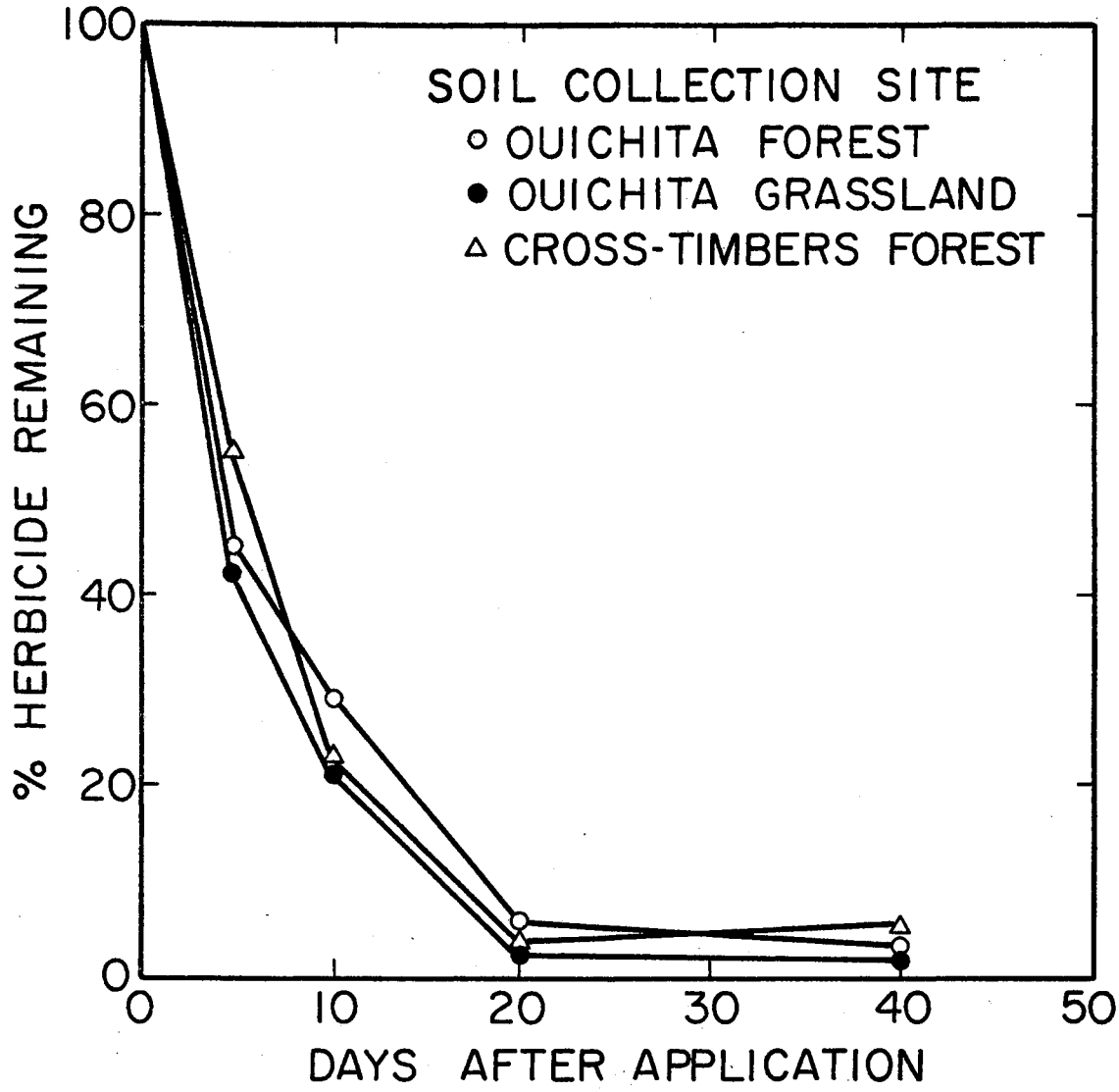


Figure 1. The Disappearance of 2,4-D From 3 Soils Under Controlled Conditions

be detected by this method was 5 ppb. The recovery figures were obtained from soils spiked with known concentrations of herbicides.

Dichloroprop

The disappearance pattern of dichloroprop was similar to 2,4-D as shown by Figure 2. There was no observable lag phase and disappearance was rapid for the first 20 days. However, some difference was noted. At the end of 20 days the amount of dichloroprop that had disappeared was less than the amount of 2,4-D that had disappeared. Also type of vegetative cover had some influence on disappearance rate. The two forest soils contained 21% of the original application at the end of 20 days while the grassland soil contained only 6%. The percent of dichloroprop that had not disappeared at the end of 40 days ranged from 3% in the grassland soil to 12% in the forest soils.

The time period for disappearance observed in this study for dichloroprop appeared to be much faster than the 205 days reported by Alexander and Aleem (2).

The extraction procedure gave 50% recovery of dichloroprop. There were no esters of dichloroprop available so no measurements of percent esterification could be made. The lowest concentration of dichloroprop that could be detected by this method was 8.0 ppb.

2,4,5-T

There was a slight lag phase of 5 days in the two forest soils and then a rapid disappearance during the next 5 days (Figure 3). After the first 10 days the disappearance rate leveled off and declined at a steady rate.

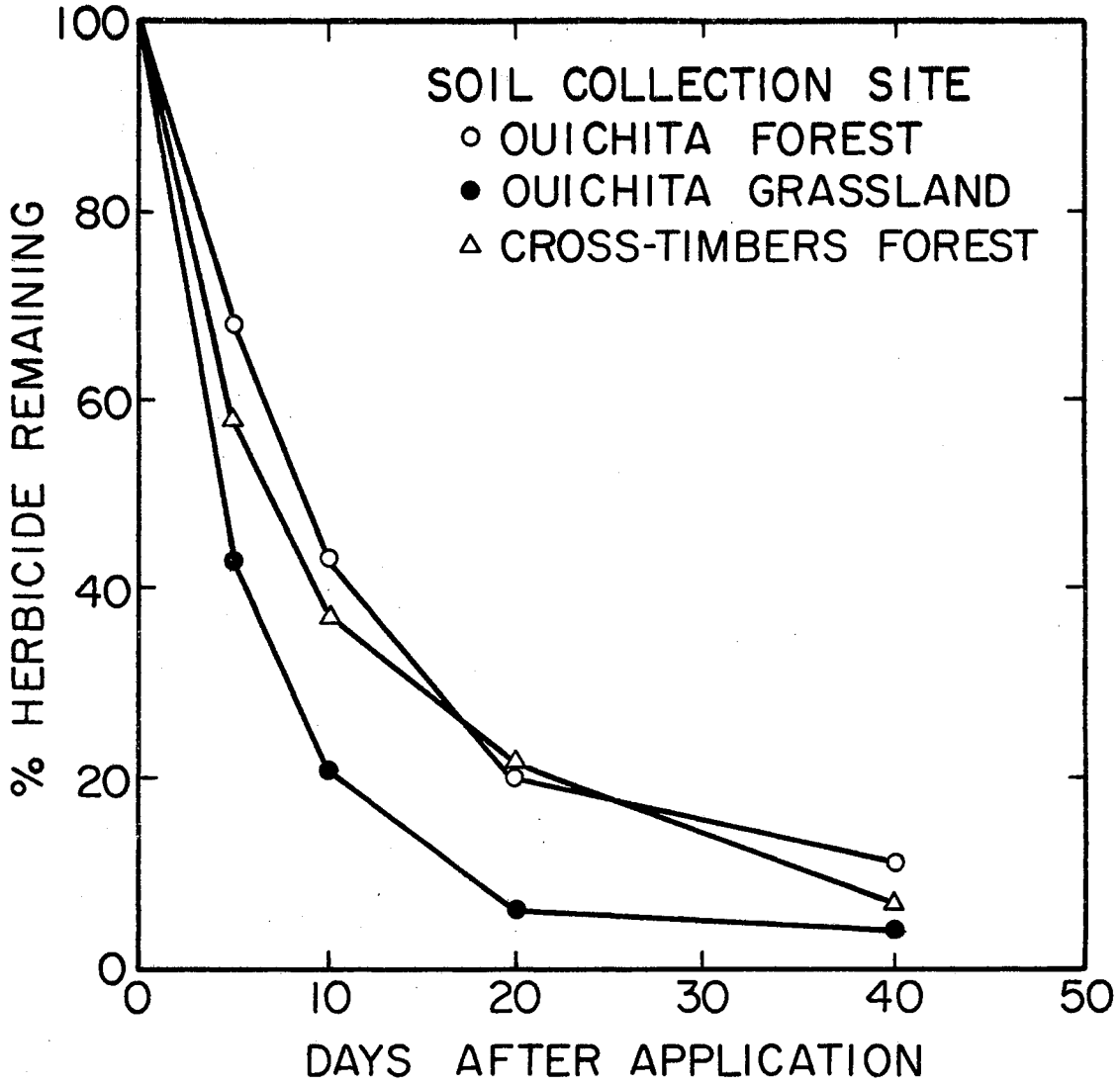


Figure 2. The Disappearance of Dichloroprop From 3 Soils Under Controlled Conditions

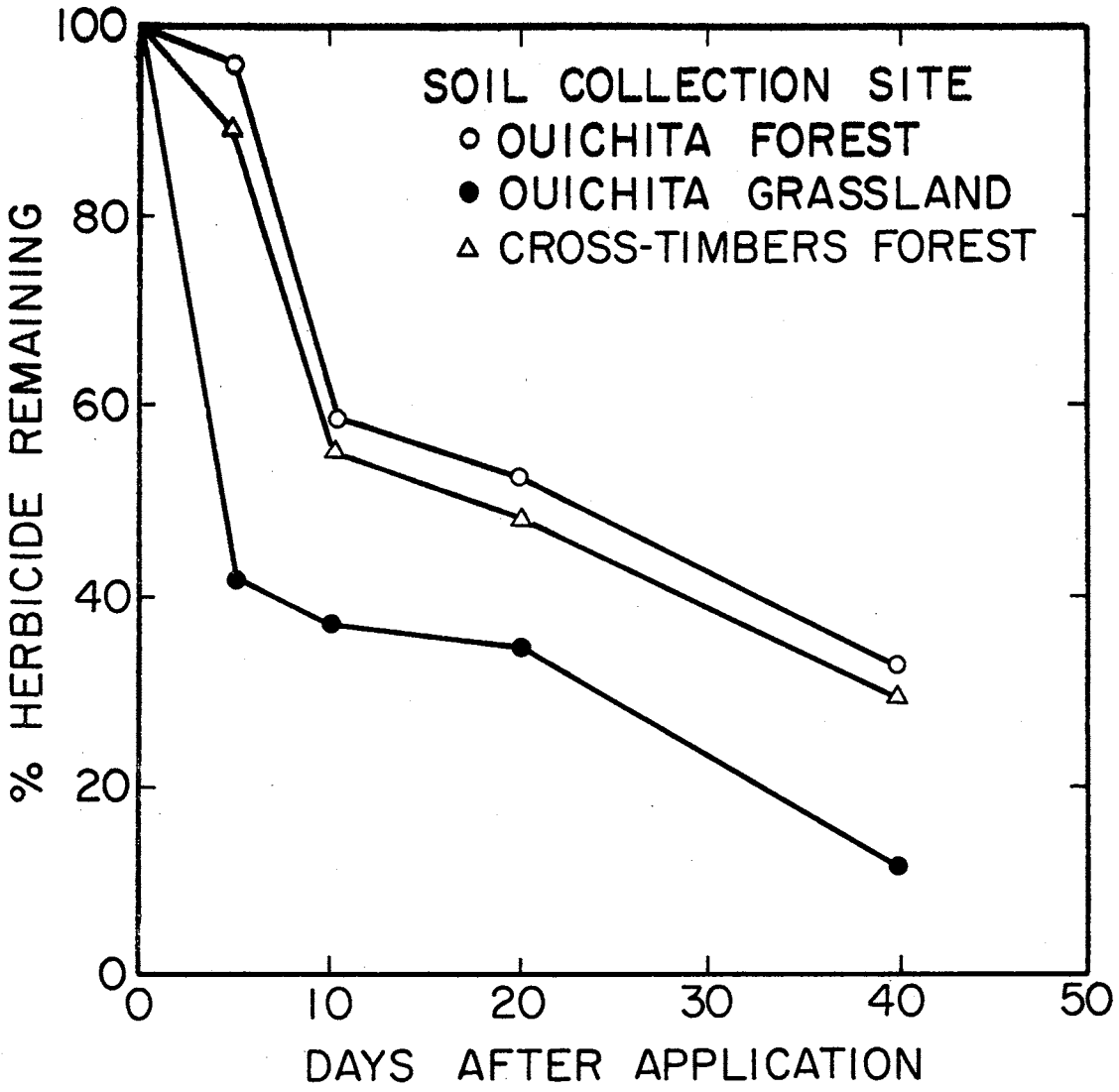


Figure 3. The Disappearance of 2,4,5-T From 3 Soils Under Controlled Conditions

In the grassland soil no lag phase was observed with disappearance rapid for only the first 5 days. An average of 51% of the herbicide remained in the forest soils at the end of 20 days with only 33% remaining in the grassland soil. At the end of 40 days the forest soils contained an average of 33% and the grassland soil had 10% of the original application remaining.

All of the herbicides evaluated in this study tended to disappear faster in the grassland soil than in the forest soils, but 2,4,5-T was the only herbicide where the difference at the end of 40 days was significant at the .05 level.

The phenoxy extraction procedure gave 73% recovery of 2,4,5-T with 91% esterification. The lowest detectable concentration in soil was 1.5 ppb.

Silvex

The disappearance of silvex was similar to 2,4,5-T (Figure 4). The similarity of silvex and 2,4,5-T disappearance observed in this study agrees with the literature (2, 50). There was a short lag phase in the Ouichita forest soil. There was a rapid disappearance period for the first 10 days with the rate of disappearance remaining fairly constant through 40 days. At the end of 20 days an average of 36% still remained in the forest soils with 27% present in the grassland soil. At the end of 40 days an average of 15% of the herbicide was present in the Ouichita grassland and Cross Timbers forest soil while the Ouichita forest soil contained about 29% of the original application.

Recovery of silvex was 67% with 97% esterification. The lowest detectable concentration was 1.8 ppb.

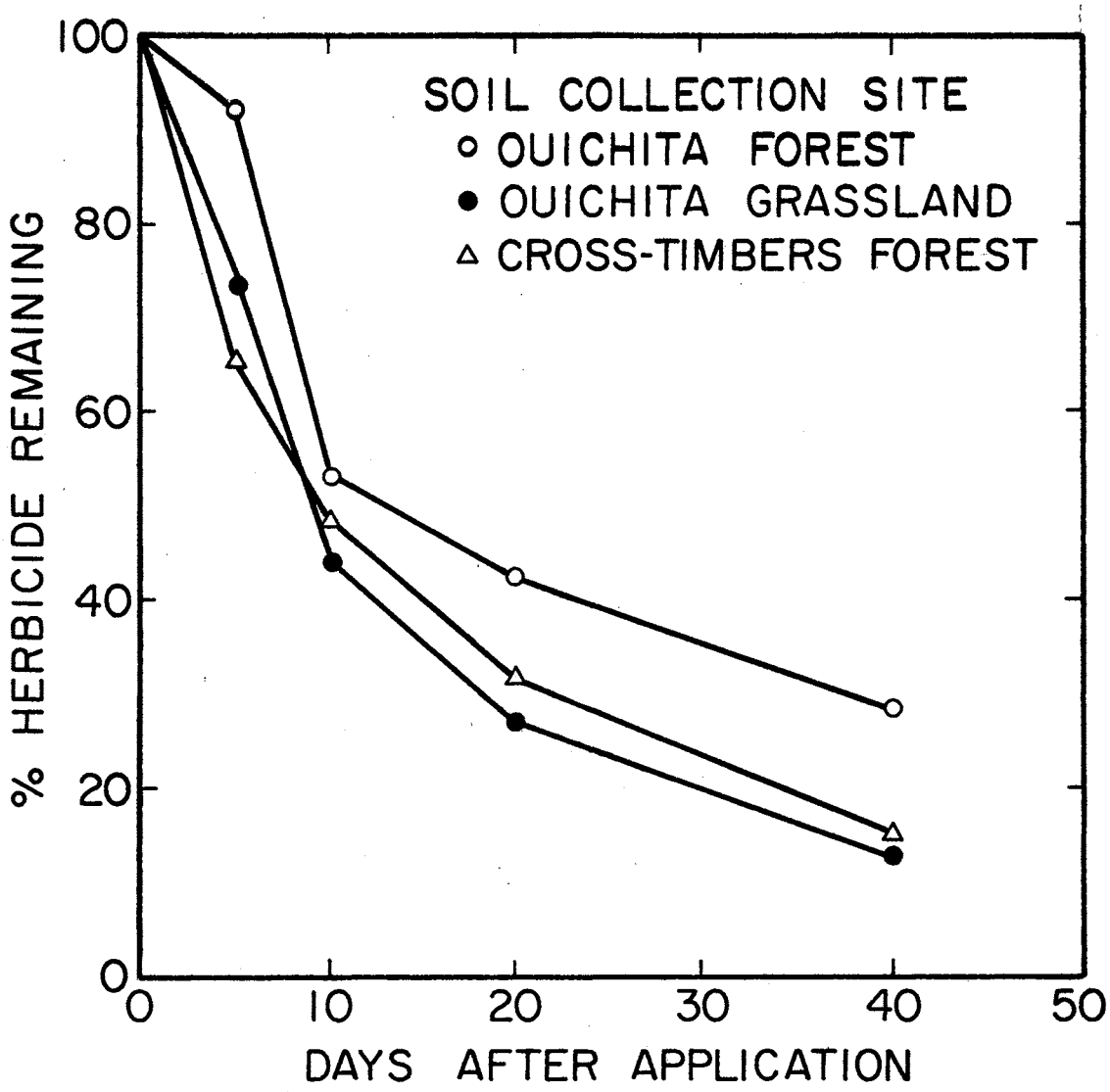


Figure 4. The Disappearance of Silvex From 3 Soils Under Controlled Conditions

Dicamba

In this study there was a rapid disappearance of dicamba for the first 20 days in all soils (Figure 5). After the first 20 days disappearance was gradual in the forest soils for the next 80 days with approximately 5% of the herbicide remaining at the end of 100 days. In the grassland soil the rapid disappearance period continued through 40 days and then leveled off. At the end of 100 days the grassland soil contained about 2% of the original application.

With one exception, the literature revealed that dicamba and 2,4,5-T were comparable in length of time required for disappearance. The studies by Burnside and Lavy (12) indicate that dicamba is less persistant than 2,4,5-T with disappearance occurring in 30 days. At the end of 40 days the two forest soils in this study contained an average of 24% which is lower than the amount of 2,4,5-T not degraded at this point, which agrees with the study cited previously.

The extraction procedure gave 81% recovery and the esterification technique gave 70% esterification. The lowest detectable concentration from soils spiked with known concentrations was 1.6 ppb.

Picloram

Picloram was the most persistant herbicide in this study (Figure 6). There was an average of 84% of the herbicide remaining at 40 days with only a small amount of disappearance during the next 40 days. At the end of 100 days 63% of the original application remained in the grassland and Cross Timbers forest soil while 77% remained in the Ouichita forest soil.

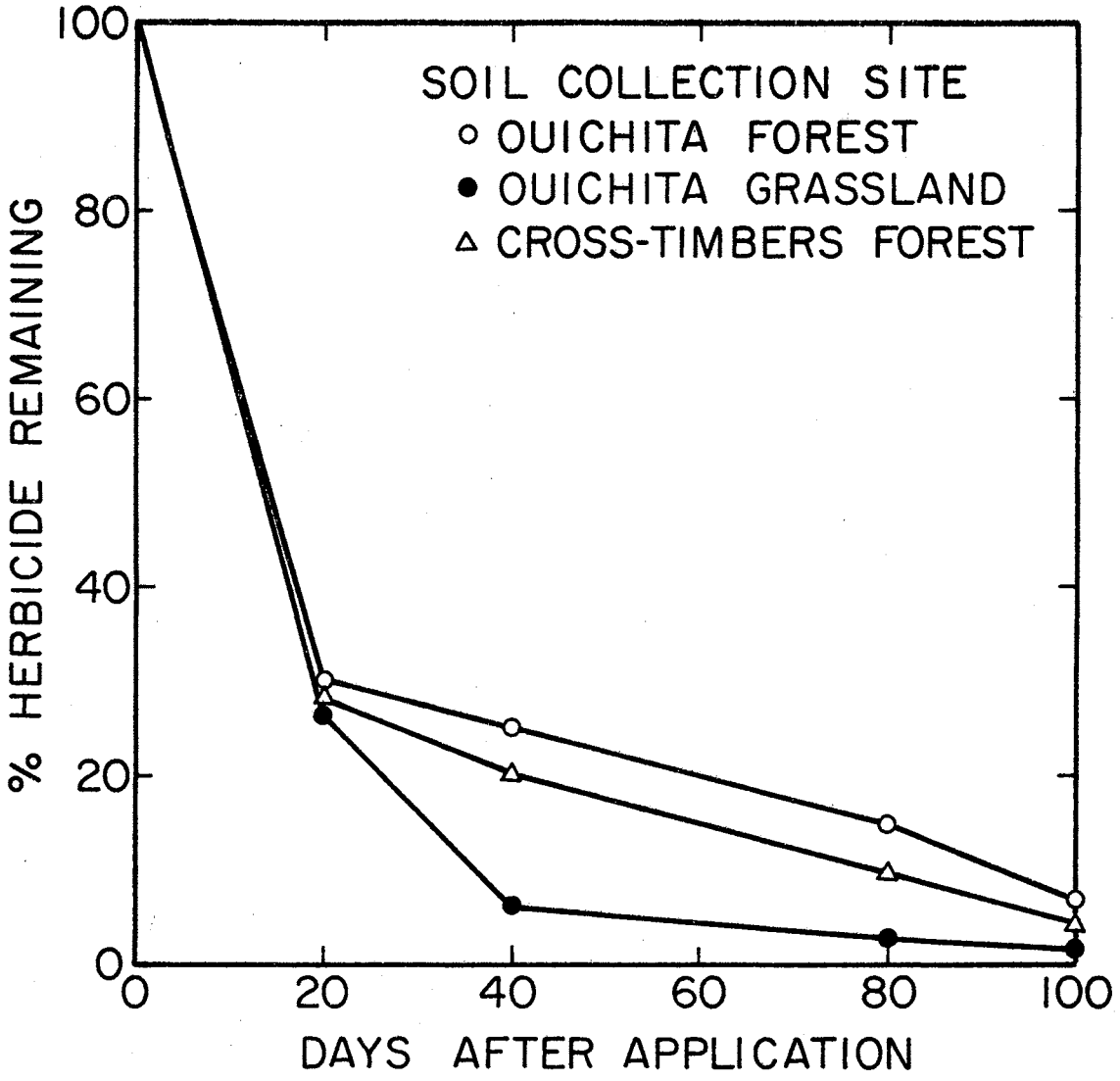


Figure 5. The Disappearance of Dicamba From 3 Soils Under Controlled Conditions

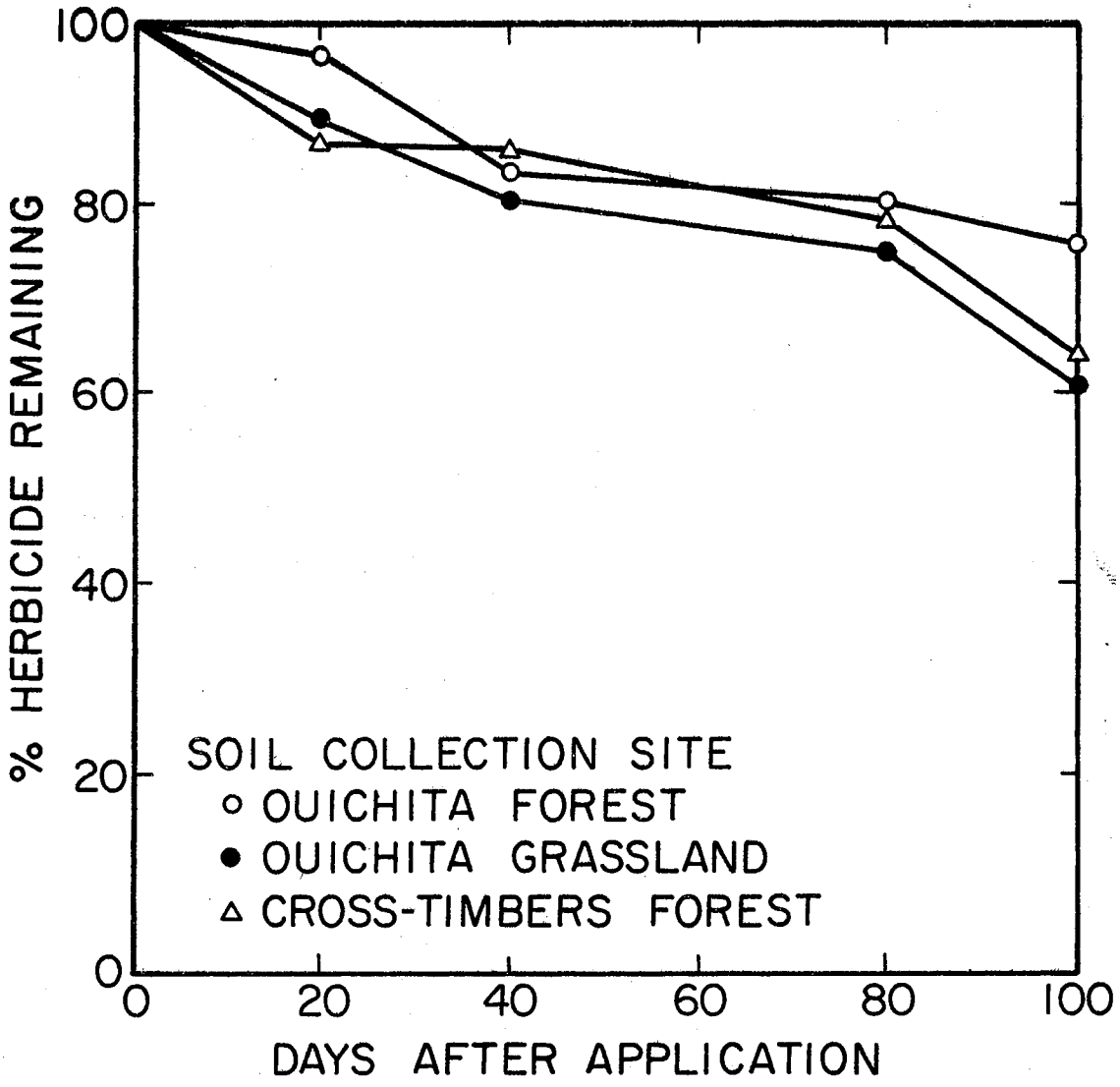


Figure 6. The Disappearance of Picloram From 3 Soils Under Controlled Conditions

The literature reviewed indicated that picloram was persistant in soils (30, 36, 52). This study also showed that picloram was residual in soils since only 23 to 34% of the original application disappeared in 100 days.

The procedure used for picloram extraction gave 79% recovery with an esterification of 72%. The lowest detectable concentration was 1.5 ppb.

## Herbicide Disappearance From Soil Under Field Conditions

### 2,4,5-T

The 2,4,5-T plots were sprayed June 9 and received a rain on June 11 (Table II). It was June 12 before the plots could be sampled so the June reading of .28 pounds per acre represents the amount deposited during spraying plus the amount washed from the foliage by rain minus any amount that was broken down or leached out of the sampled zone (Figure 7). After the June reading the disappearance rate was fairly rapid for 4 weeks and then slowed down during the next 4 week period. The September sample contained no detectable residue so 2,4,5-T had disappeared in 90 days. The time required for 2,4,5-T to disappear under field conditions agreed closely with the literature. There was sufficient rainfall early in the study to move the herbicide into the soil where it was subject to microbial degradation. Leaching probably does not play a major role in 2,4,5-T disappearance since 2,4,5-T disappeared under controlled conditions in approximately 100 days.

The lowest detectable concentration in field soil with the extration procedure used was 2.8 ppb. This is based on soil samples treated

TABLE II

RAINFALL DATA AT SARKEY FOUNDATION
AREA NEAR HOLDENVILLE, OKLAHOMA
JUNE THROUGH OCTOBER, 1970

| Month | Date Received | Amount Received in Inches |
|---|---|---|
| June | 1 | 1.70 |
| | 2 | .40 |
| | 4 | .50 |
| | 11 | 1.15 |
| | 21 | .62 |
| | | Total 4.37 |
| July | 8 | .08 |
| | 10 | .20 |
| | 11 | .26 |
| | | Total .54 |
| August | 1 | .50 |
| | 19 | .62 |
| | | Total 1.12 |
| September | 1 | .94 |
| | 13 | 1.35 |
| | 18 | 1.75 |
| | 22 | 2.55 |
| | | Total 6.59 |
| October | 7 | 3.80 |
| | 22 | .70 |
| | 24 | 3.70 |
| | | Total 8.20 |

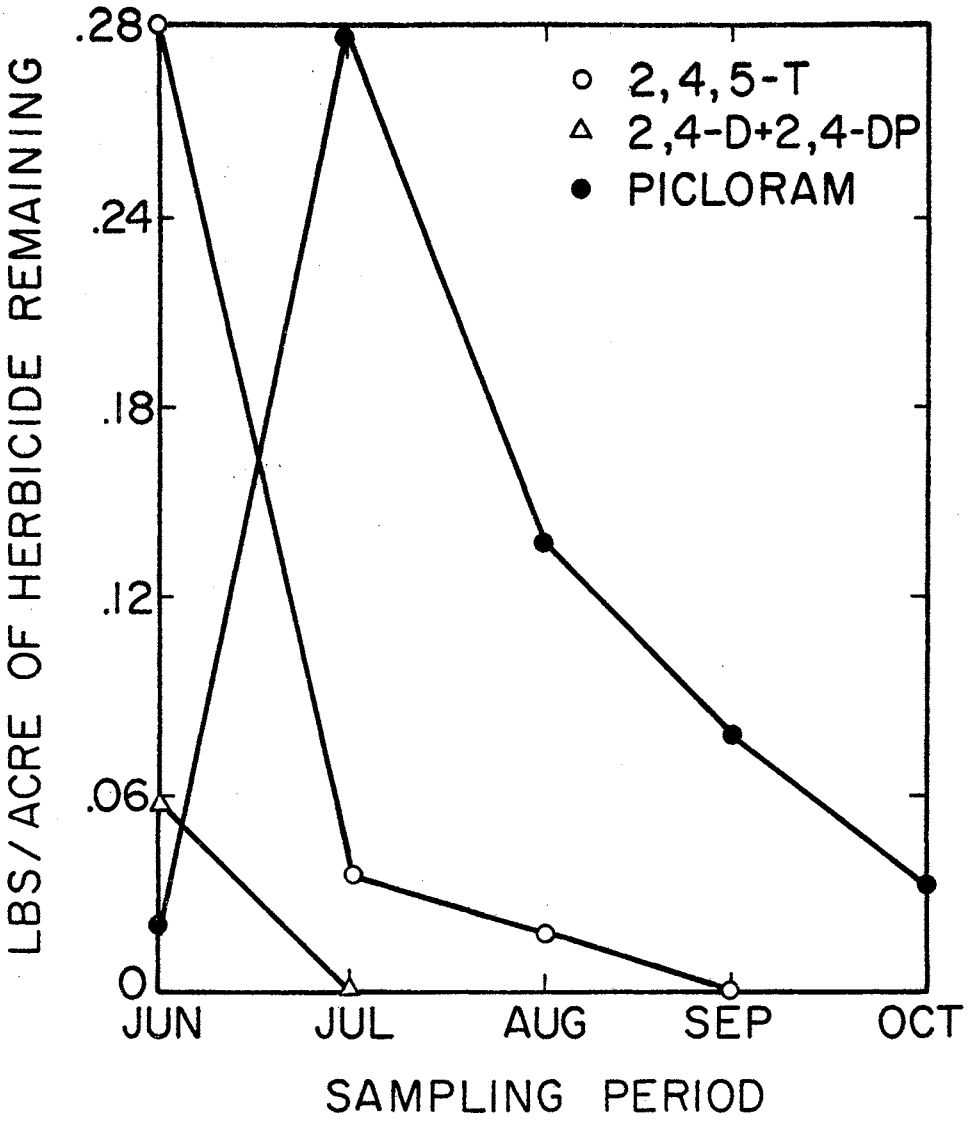


Figure 7. The Disappearance of Aerially Applied Herbicides From Soil Under Field Conditions

with a known concentration and ran through the extraction procedure.

2,4-D Plus Dichloroprop

Only .06 pounds per acre of herbicide residue (2,4-D plus dichloroprop) was detected in June and no residue was detected 4 weeks later (Figure 7). The June reading for these plots also represents the initial amount deposited plus the herbicide washed from the foliage minus any disappearance or leaching. According to the studies on disappearance under controlled conditions the amount of time between spraying and sampling, 4 days, was long enough to allow for some of the herbicides to be microbially broken down. The rain received one day after application was enough to move the herbicide into the soil. This should account for part of the difference in the June reading of the 2,4,5-T plots and the 2,4-D plus dichloroprop plots. The comparison of the field disappearance and disappearance under controlled conditions showed that the two are similar in length of time required for herbicide disappearance.

Dicamba

In the plots treated with dicamba the June reading was only .007 pounds per acre with no detectable residue in the July sample, so it had disappeared in less than 30 days. Dicamba is not shown in Figure 7 since the initial concentration in June was so low.

According to Burnside and Lavy (12) a low rate of dicamba can be degraded in 30 days under controlled conditions. In this study dicamba was applied at 1 pound per acre under field conditions, so leaching could speed dicamba disappearance.

The lowest concentration detectable from field soil was 3.2 ppb.

Picloram

In the plots treated with picloram .04 pounds per acre was received from spraying alone (Figure 7). No rain was received after spraying or before the soil samples were collected. Rain was received before the next sampling date so the reading of .28 pounds per acre represents the initial deposit plus washoff minus any disappearance or leaching that may have occurred. This shows that a substantial amount of herbicide that is deposited on the foliage is washed to the soil by rainfall. The disappearance of picloram was fairly steady throughout the remaining sampling in that season. The October sample still contained .04 pounds per acre or 16% of the maximum reading on July 10. A soil sample taken in early May of 1971, contained no detectable residue so picloram had disappeared during the October, 1970 to May, 1971 interval. Picloram did persist in the field soil for greater than 120 days.

Under field conditions approximately 84% of the herbicide measured in July had disappeared in 90 days while only 37 to 23% had disappeared after 100 days under controlled conditions. From this it can be seen that disappearance of picloram from the top 4 inches of the soil, unlike the phenoxy herbicides and dicamba, is probably related to the amount of leaching that occurs.

The disappearance of picloram in greater than 120 days with a total of 20.8 inches of rainfall is approximately the same as the results obtained by studies carried out under similar conditions (41, 26).

The extraction procedure for picloram had a lower detection limit of 1.2 ppb.

## Herbicide Disappearance From Grass Under Field Conditions

### 2,4-D Plus Dichloroprop

The amounts of herbicide residue in grass from the application of 2,4-D plus dichloroprop are shown in Figure 8. The June reading of 41.9 ppm in the dead tissues and 30.8 in the green tissues represented the amount deposited on the grass during spraying plus the herbicide washed off the tree foliage minus any breakdown that may have occurred during the 8 days between spraying and sample collection. The breakdown of 2,4-D and dichloroprop was rapid from June to July in both dead and green tissue. By the July sampling the green tissue contained 6.3 ppm and the dead tissue 11.0 ppm. By the August sampling the herbicide concentration in green and dead tissue was 2.4 and 4.3 ppm respectively. Only .035 ppm could be detected in the green tissue and 3.72 ppm in the dead tissue of the September sample.

It is assumed that actual breakdown in the green tissue and dilution or leaching by rainfall in the dead tissue caused the concentration to decline in the grasses. The large decrease from June to July could also be caused by a simple dilution. Between the June and July samples 4.37 inches of rain occurred which would cause a flush of grass growth. In the case of 2,4-D if the herbicide was being broken down rapidly in the soil less herbicide would be available for root uptake to replenish the herbicide being diluted in the top growth. The gradual decline in concentration from July to September would have to be attributed to continued dilution by plant growth. It is thought that both breakdown and dilution caused the decline in 2,4-D and dichloroprop concentration.

The lowest detectable concentration of 2,4-D and dichloroprop in

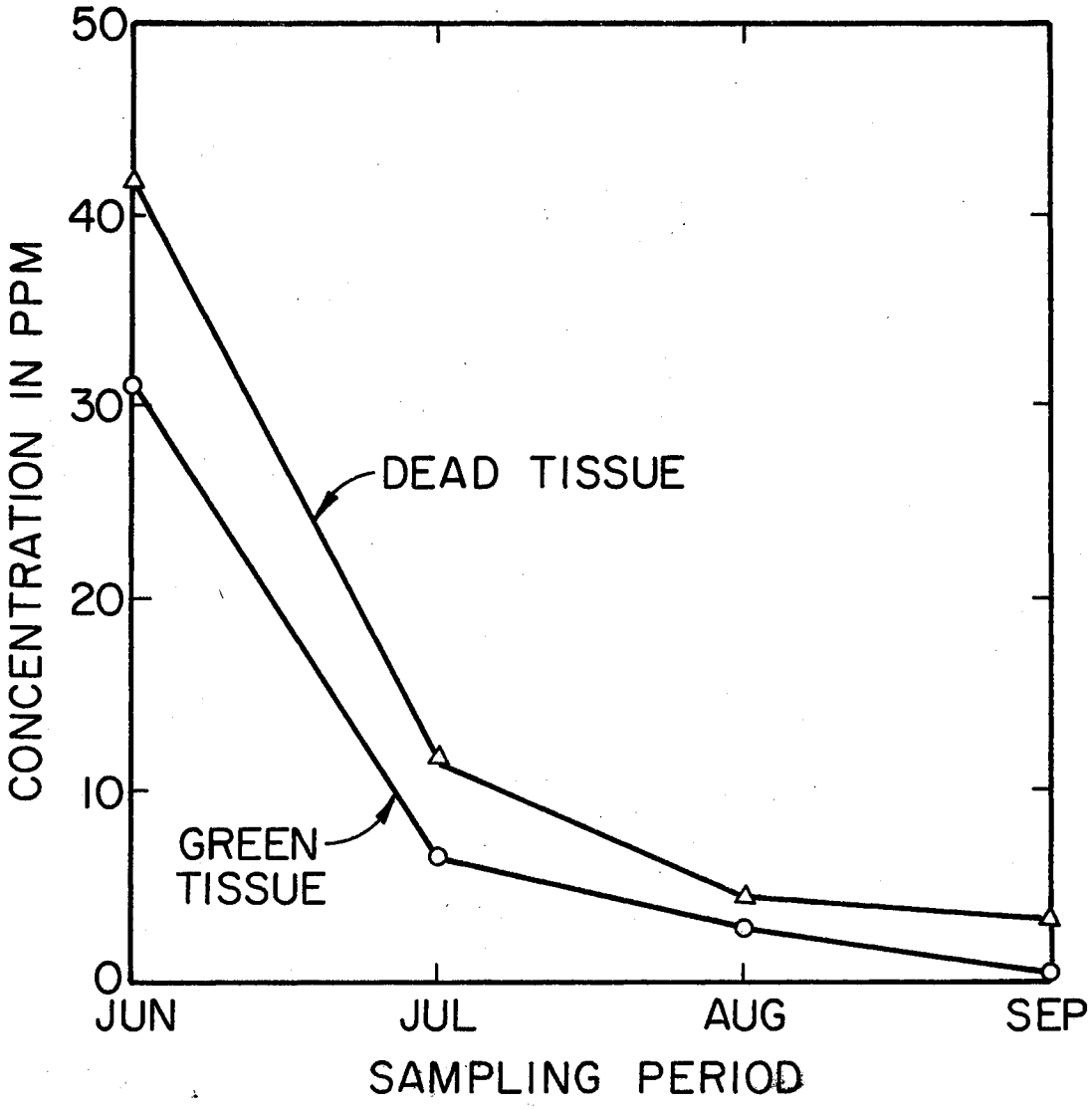


Figure 8. The Disappearance of 2,4-D Plus Dichloroprop From Grass Under Field Conditions

grass was 1.8 ppb.

2,4,5-T

The disappearance of 2,4,5-T is similar to 2,4-D, but does not have a rapid breakdown period (Figure 9). The herbicide concentration in the June sample was 40.8 and 41.3 ppm for green and dead tissue, respectively. Herbicide concentration in both tissues declined gradually, with less herbicide being in the green tissue. The concentration in the dead tissue in September was 2.89 ppm and 2.49 ppm in the green tissue.

The gradual decline in herbicide concentration in the green tissue suggests that either breakdown in the plant was slow or herbicide uptake by the roots was occurring. The field persistence study shows that 2,4,5-T will persist in the top 4 inches of the soil for at least 90 days, so herbicide is available to the roots for at least 90 days. As was the case with 2,4-D it is expected that rainfall decreases the herbicide concentration in the dead tissues through leaching. The lowest detectable concentration was 1.7 ppb.

Picloram

The concentration of picloram in the green and dead tissue immediately after spraying was 35 and 26 ppm, respectively (Figure 10). The concentration in the dead tissue declined rapidly from June to July and then leveled off. The concentration in the September sample was 10 ppm.

The concentration in the green tissue declined slightly from June to July and then began a steady drop to the September sample. At the end of 90 days the concentration in the green tissue was 5.0 ppm.

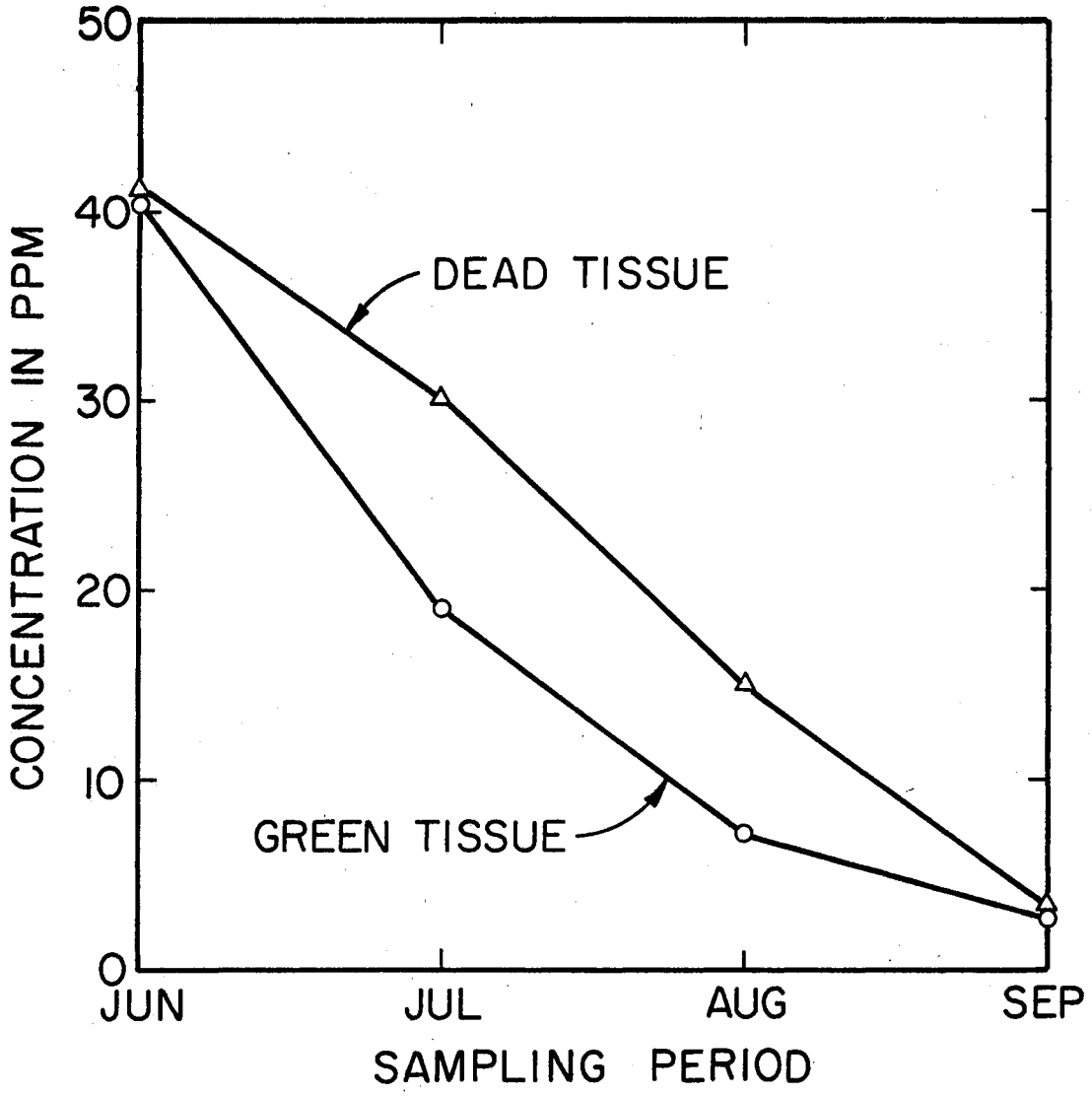


Figure 9. The Disappearance of 2,4,5-T From Grass Under Field Conditions

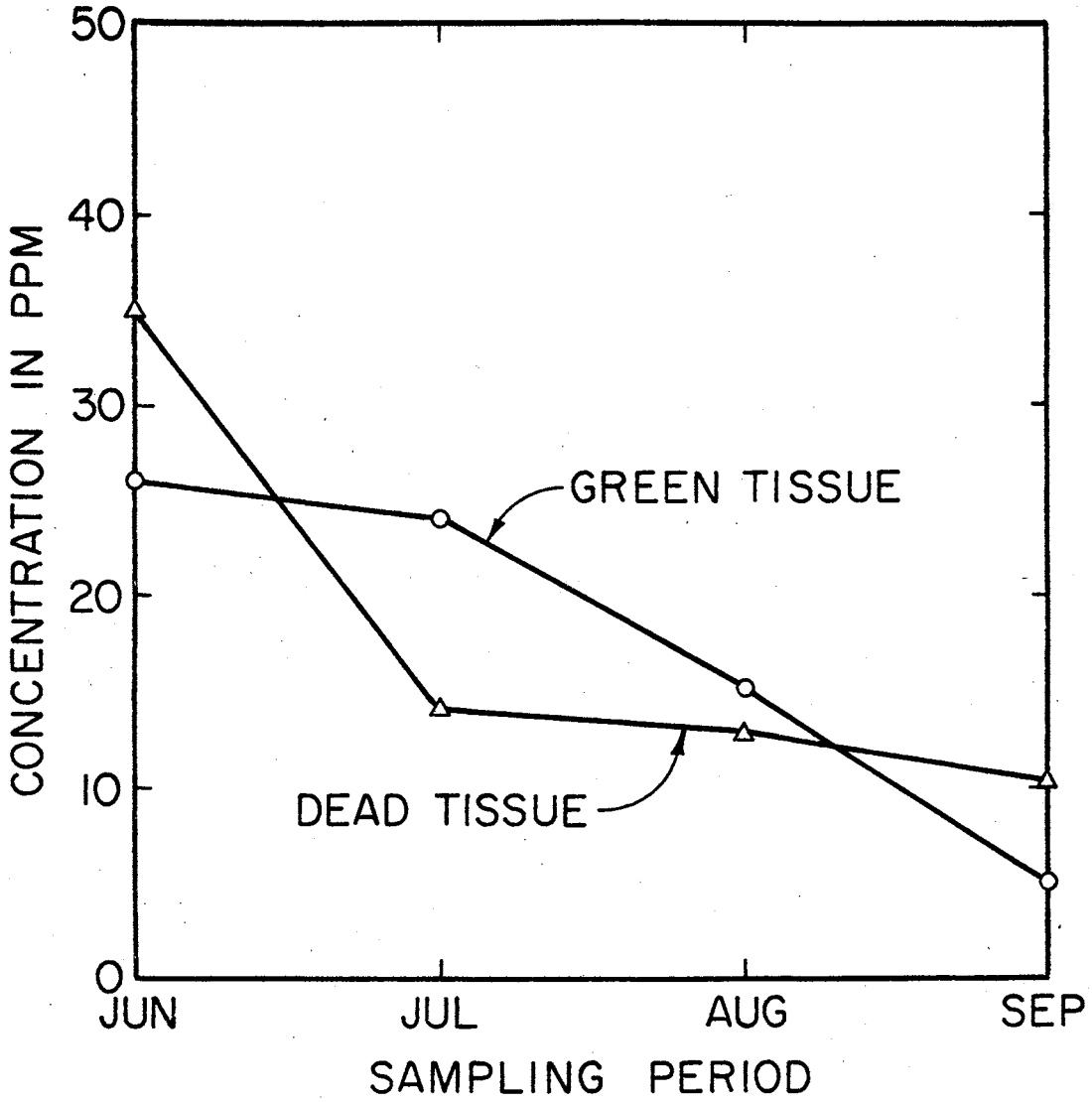


Figure 10. The Disappearance of Picloram From Grass Under Field Conditions

The drop in concentration in the dead tissue and only a slight drop in the green tissue could be attributed to the rainfall received during this period. The 4.37 inches of rainfall received would be enough to lower the concentration in the dead tissue by leaching. This would also cause a flush of growth and the herbicide could be taken up by the roots. During July and August a total of 1.76 inches of rain was received as small showers. This allowed some leaching from the dead tissues and since uptake by roots was limited, disappearance of the herbicide by the plant exceeded uptake which resulted in a decreased residue. The lowest detectable concentration of picloram with the procedure used was 53.0 ppb in grass.

Dicamba

The green tissue only was analyzed for dicamba residue. Dicamba had a low concentration of 7.7 ppm in the June sample with a steady decline through August (Figure 11). There was no detectable residue in the September sample so dicamba disappeared from the grass in 60 to 90 days.

There was a low amount of dicamba in both the field soil and grass tissue. Also the persistence was shorter in both the soil and grass than expected. This may be due to the amount of rain received after spraying plus the soil texture (Table I).

## Herbicide Distribution to Various Canopy Levels

In the herbicide distribution study the amount of herbicide reaching the petri dishes placed above the overstory was considered to be 100 percent and the percentage reaching the other levels was calculated

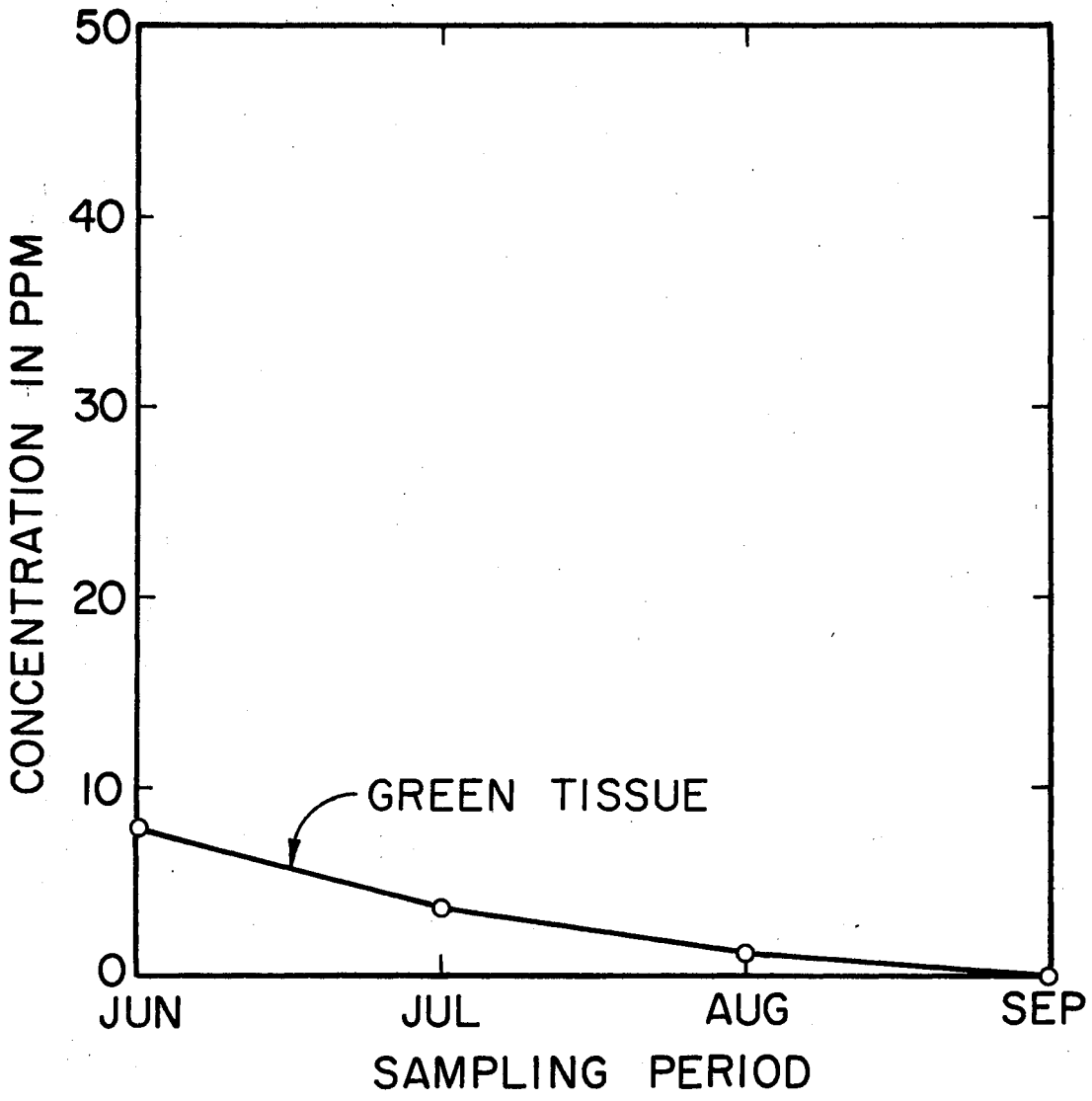


Figure 11. The Disappearance of Dicamba From Grass Under Field Conditions

from this value. This was done to eliminate some of the variation from plot to plot. The results show that an average of 33% of the herbicide reached the understory species and only 13% reached the forest floor (Table III). The results are highly variable with the amount reaching the understory ranging from 23 to 51% and 3 to 30% reaching the forest floor. These figures are an average of the three herbicides sampled. These variations were attributed to differences in the thickness of the forest canopy, wind speed and direction, speed of the airplane, and sampling position in the spray swath.

TABLE III

HERBICIDE DISTRIBUTION DURING AERIAL APPLICATION TO VARIOUS LEVELS IN A MULTI-STORIED-TYPE VEGETATION

| Herbicide | Plot # | Percent compared to Overstory | |
|---|---|---|---|
| | | Understory | Ground |
| 2,4,5-T | 10 | 47 | 13 |
| 2,4,5-T | 3 | 40 | 10 |
| 2,4,5-T | 9 | 51 | 30 |
| Dicamba | 3 | 36 | 12 |
| Dicamba | 9 | 38 | 21 |
| Picloram | 10 | 23 | 3 |

# CHAPTER V

## SUMMARY

Studies were conducted to determine the herbicides residue in soil and grass that resulted from aerial applications and to determine residues in soils under controlled conditions. In the experiment under controlled conditions three similar soils were collected from a Cross Timbers area, Ouichita Highlands forest area, and a Ouichita Highlands grassland area. These soils were selected to see if herbicide disappearance would vary between similar soils from different areas of Oklahoma or if herbicide disappearance would vary between a soil covered by forest and a soil covered by grass. A measure of the amount of aerially applied herbicide that reached the various canopy levels in a multistoried type vegetation was also made in the field study.

In summarizing the results of the experiment on herbicide disappearance under controlled conditions the 6 herbicides can be ranked from rapid to slow by comparing the amount of herbicide remaining at 40 days. The disappearance of 2,4-D was the most rapid with only 3% of the original application remaining at the end of 40 days. Dichloroprop was next with an average of 10% remaining. Dicamba, silvex, and 2,4,5-T were intermediate as to rate of disappearance and had 17, 19, and 24%, respectively, remaining at the end of 40 days. Picloram was the least degradable herbicide with 84% remaining at 40 days and 70% left at the end of 100 days.

A comparison of the three soils used showed that herbicide disappearance was not drastically effected by soils from different areas and soils having different vegetative cover. The only difference in the amount that disappeared after 40 days that was significant at the 5% level was the faster disappearance of 2,4,5-T in the grassland soil.

In the field study of herbicide disappearance in soil no herbicide could be detected in the 2,4-D plus dichloroprop or dicamba plots 30 days after application. Residues of 2,4,5-T persisted from 60 to 90 days and picloram residues were still detectable at the end of 120 days. Picloram was not detectable at 300 days.

By comparing the amount of time required for field disappearance to disappearance under controlled conditions it can be seen that field disappearance of herbicides is faster than disappearance from cups and some of this is attributed to leaching. This was especially true with picloram.

In the grass residue study, picloram and 2,4,5-T persisted for greater than 90 days while 2,4-D plus dichloroprop and dicamba persisted for less than 90 days. Picloram was considered more persistant than 2,4,5-T since picloram had a larger concentration at the end of 90 days. All of the herbicides had a larger concentration in the dead tissue at the end of 90 days than the green tissue. The concentration in the green tissue varied from no detectable residue with 2,4-D plus dichloroprop and dicamba to 5 ppm with picloram at the end of 90 days. The concentration of 2,4,5-T in the green tissue was approximately 2 ppm at 90 days. In grass, herbicide persistence or residue is determined by the amount of growth, actual breakdown, and the length of time the herbicide remains available for root uptake.

In the herbicide distribution study the amount of herbicide that reached the various levels of the forest canopy was very variable within each plot. Based on the amount of herbicide collected above the overstory trees, only 33% of the herbicide penetrated the overstory trees and reached the understory species. Only 13% of the herbicide penetrated both canopies and reached the forest floor.

This experiment indicated the amount of herbicide that would reach the forest floor during spraying. Also, a general idea of the amount of herbicide that was washed from the tree foliage to the soil by rainfall was obtained. The total amount of herbicide that reaches the forest floor during spraying plus the amount washed from the tree foliage represents the amount of herbicide that may cause residue problems in the soil and grass.

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