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FLUOMETURON AND 2,4,5-T RESIDUES IN SOIL, SEDIMENT, RUNOFF WATER, AND PERCOLATION WATER

A Dissertation

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

---

by

Glenn Gray Davis

December 1973

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ABSTRACT

The rates of disappearance of 1,1-dimethyl-3-(a,a,a-trifluoro-m-tolyl)urea (fluometuron) and the propylene glycol butyl ether esters and a triethylamine salt of (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) from the application site in field plots and lysimeters were determined. Residual herbicide concentrations were estimated for field plot soil, runoff water collected in the plots after rainfall, and permanently impounded drainage water from the plots. Bioassays, spectrophotometry, and gas-liquid chromatography were utilized to detect residual concentrations of the three compounds. Linear and multicurvilinear equations were developed from known concentrations of the herbicide for prediction of residue amounts in the field plots and lysimeters. The effects of the herbicides on forage sorghum [Sorghum bicolor (L.) Moench, 'Pioneer 931'] plant density and the relationship of stand to forage yield were evaluated.

Preemergence application of fluometuron and 2,4,5-T reduced forage sorghum plant density to 75 and 43 percent of the control, respectively. The annual mean yield of oven-dry forage was 824 g/m^2. There were no differences between forage yields from treated and untreated plots or between weed-free and weedy control plots when means were tested at the 0.05 level of probability.

The herbicides applied to the surface of Etowah silt loam were detected in the 0-1 cm depth of the plot soil within seven days of application. After 60 days no residue could be detected in the 0-1 cm

zone. Fluometuron and 2,4,5-T herbicides present in the 0-15 cm soil zone and fluometuron in the 30-45 cm soil zone 14 days following application were degraded or leached from the sampling area in seven months. Fluometuron was present on day 210 following initial herbicide application but only in plots which were resprayed during the season.

The mean concentration of 2,4,5-T detected in impounded water was 0.04 ppmw. Detectable amounts of 2,4,5-T were not present in fresh runoff water collected in the plots. The ester formulation of 2,4,5-T dissipated more slowly in the impounded water than it did in field plot soil. No 2,4,5-T residues were detected in water seven months following herbicide application.

No detectable quantities of fluometuron residues were found in runoff and impounded water from the field plots 60 days following initial herbicide application. Fluometuron was degraded as rapidly in water as it was in soil.

Residual fluometuron and 2,4,5-T of both formulations were present in lysimeter percolation water 1 to 16 days following application to the soil surface. No detectable residues were present in lysimeter percolation water 90 days following herbicide application.

The data collected in this study indicate that the herbicide treatments did not permanently modify the application site or the nontarget sites to which the compounds migrated. No residual compound from the initial herbicide application could be detected at the end of the crop season.

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CHAPTER I

INTRODUCTION

Herbicides are used extensively in the production of all the major crops of the United States. In the past, agricultural research with herbicides emphasized control of the weed pest with minimal damage to the associated crop plants. Recently the ecological fate of herbicides in the soil-plant environment has been the subject of numerous investigations. Generally, herbicide residue studies deal with persistence at the site of application. Herbicides may be transferred from their site of application to soil or water zones in which conditions may not be conducive to their degradation to innocuous forms. Research is required in order to reassure a concerned public of the safety of current herbicides and to develop a methodology by which the environmental impact of herbicides which may be developed in the future can be estimated reliably before they are released for widespread use. Statistically valid information on the movement of herbicides away from the site of application and the environmental fate of the translocated compounds would contribute to a better understanding of the impact of herbicides on the total ecosystem.

Fox (20) determined that restricting the use of all phenoxy herbicides would increase United States farm production costs about $290 million. Approximately six million additional crop acres and 20 million more hours of labor would be required to keep production

constant. In the same study it was estimated that banning the use of 2,4,5-T on eight million acres of farm and nonfarm land in 1969 would have increased costs to farmers by $32 million. Additional costs would have been involved if substitutes for 2,4,5-T could not include the related phenoxy herbicides.

In the late 1960's, 25 million acres of crop and pasture land were treated with phenoxy herbicides (20). Fluometuron is widely used in Tennessee and in all of the other southern states. Fluometuron is the reference material for all research projects included in the Regional Research Project S-78 on herbicide movement from application sites and effects on nontarget species which was initiated in 1971.

An estimated four billion tons of sediment enter waterways in the United States each year (49). Wadleigh (64) stated "little or no information is available on the role of sediment as a transporting agent for herbicide residues." He considered herbicide movement into major water resources and leaching to depths where degradation mechanisms are relatively ineffective to be potentially the most serious problems associated with the use of herbicides.

The study reported in this paper was designed to gain information concerning the rate of degradation of fluometuron and an amine and ester formulation of 2,4,5-T in the soil within the application site and their distribution to nontarget sites. Therefore, the objectives of the study were:

1. To develop relatively rapid and simple bioassay detection techniques for determining residue levels in field soils;

2. To convert combinations of bioassay ratings and measurements developed from known herbicide concentrations into prediction equations for residues;
3. To determine whether the difference between rates two to four times the normal commercial application rates are detectable in the field environment;
4. To make comparisons among residue concentrations at the site of application, in the soil profile, in runoff and percolation water, and in sediment from the plots; and
5. To observe the effects of these compounds on plant density and forage yield of a semitolerant indicator crop species.

The study was divided into four phases: field plot; glasshouse and plant incubator; lysimeter; and laboratory analyses. Field plots were established for forage growth and soil and water sampling. A lysimeter system which contained a 20-cm soil layer was used to study herbicide residues in percolation water.

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

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

Common Name or Designation	Chemical Name
Atrazine	2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine
Chlorbromuron	3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea
DDE	1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Fluometuron	1,1-dimethyl-3-(a,a,a-trifluoro-m-tolyl)urea
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
Metobromuron	3-(p-bromophenyl)-1-methoxyl-1-methylurea
Monuron	3-(p-chlorophenyl)-1,1-dimethylurea
Neburon	1-butyl-3-(3,4-dichlorophenyl)-1-methylurea
Trifluralin	a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine
2,4-D	(2,4-dichlorophenoxy)acetic acid
2,4,5-T	(2,4,5-trichlorophenoxy)acetic acid

CHAPTER II

REVIEW OF SELECTED LITERATURE

I. HERBICIDE DISSIPATION FROM APPLICATION SITE

Herbicides may be lost from the site of application through physical, biological, and chemical processes (33). The processes involved in herbicide dissipation are generally investigated as separate forces. In a plant-soil-water environment many forces from among the three major categories of processes are involved simultaneously in moving or degrading a given herbicide. Compounds may become biologically inactive and chemically unavailable without being degraded or transported from their site of application (3,8).

Phenoxyacetic Acids

Herbicides of the chlorinated phenoxyacetic acid group are readily decomposed by microorganisms (2). A wide spectrum of microorganisms including bacteria, actinomycetes, and fungi utilize 2,4-D as a carbon source (2). Some microbial species utilize 2,4,5-T as a source of carbon, but the spectrum of organisms which uses 2,4,5-T is not as broad as the spectrum which uses 2,4-D. Root uptake, plant metabolism, and consumption of the plant parts by animals are other means by which the phenoxyacetic acid herbicides disappear from their site of application.

Newman and coworkers (43) made a repeat application of 2,4,5-T triethanolamine at 14 kg/ha to the soil surface of Duffield silty clay loam and measured the rate of disappearance. They concluded that 2,4,5-T disappeared from the soil under field conditions as the result of microbial decomposition, leaching, and adsorption by soil constituents. Adsorption was primarily to the organic matter in the Duffield soil (1.04 percent O.M.). The 2,4,5-T was leached readily by 40 cm of rainfall. Nineteen weeks following application of 14 kg/ha, 1 ppmw of 2,4,5-T was detected by bioassay in the soil plow layer. The herbicide did not disappear more rapidly after retreatment than it did after the initial treatment.

Ultraviolet irradiation significantly reduced the phytotoxicity of 1 ppmw of 2,4,5-T in water (33). MacRae and Alexander (37) demonstrated a pathway of degradation for phenoxyacetic acids. Oxidation and hydrolysis of the 2,4,5-T molecule are feasible under extreme conditions. Losses of 2,4,5-T by volatilization and aerial drift have been documented. Ester formulations are more susceptible than amines to both volatilization and drift (25,32).

Research on the persistence of phenoxyacetic acids in aquatic systems has been limited. Hemmett and Faust (29) used activated sewage sludge as a source of microorganisms for 2,4-D degradation. An aerobic environment was maintained in their aquatic system. Approximately 68 percent of the 2,4-D concentration was used in the microbial respiration process; 32 percent was incorporated into the microbial cells. Biodegradation rate varied directly with microorganism population. Okey

and Bogan (45) found that 2,4-D was degraded in oxygenated aquatic systems but that microbial cultures which were adapted to degrade 2,4-D could not degrade 2,4,5-T. Apparently 2,4-D is not degraded as rapidly in aquatic environments as it is in terrestrial systems.

Substituted Urea Herbicides

Hill and coworkers (30) conducted extensive chemical and biological studies of the fate of monuron and diuron in agricultural soils of the eastern half of the United States. The apparent mode of degradation was determined by sterilizing half of a treated soil sample and comparing the rate of herbicide disappearance in the sterilized and nonsterilized portions. Microbial degradation of monuron was confirmed by measuring the increase in oxygen uptake by bacterium of the Pseudomonas group when three different concentrations of the herbicide were supplied. Oxygen uptake by the bacteria doubled when 0.4×10^{-3} molar monuron was made available to the microorganisms. Oxygen uptake was increased further when yeast extract was included with the monuron.

Among all the soils studied by Hill and coworkers (30) leaching, volatility, and chemical decomposition were considered to be less important means of disappearance than was biological degradation. In Commerce silt loam, leaching accounted for 30 percent of the monuron applied to the surface of a laboratory lysimeter column. These researchers pointed out that the amount of leaching in a soil depends on the water solubility of the compound, distribution and intensity of rainfall, soil characteristics such as texture and structure, and the amount of organic matter present.

Abernathy and Davidson (1) used the Freundlich isotherm relationship to describe fluometuron adsorption results observed with varying levels of $CaCl_2$ in a saturated soil-moisture regime. In an earlier report Davidson and Santelmann (13) summarized the factors which control the rate of movement and distance travelled by a herbicide when it is displaced through soil. The tortuosity of the total path length through the various pore sequences, the flow velocity, and the diffusion coefficient of the molecule involved were described as vital considerations. These researchers varied soil water flux and porosity of glass beads and soil in order to illustrate the importance of flow velocity, molecular diffusion, and adsorption by soil on the amount and distance fluometuron might move through a soil. The adsorbent nature of the column material determined the amount of water required to displace fluometuron from soil. More diuron than fluometuron was adsorbed on a given column of glass beads. In an equilibrium adsorption study Geissbuhler (24) found that metabromuron, chlorbromuron, and trifluralin were adsorbed to soil in increasing amounts from the former to the latter in soil solutions of 0.1 to 10 ng. Mortland (40) reviewed the status of research on interactions between clay and organic compounds. Corey (9) described a method of using nonfluorescent dyes to trace water movement in soil. Bailey and White (3) made a thorough review of adsorption and desorption in soil and discussed adsorption and desorption as they relate to pesticide movement in soil.

Harris (28) developed a relative mobility scale for pesticides based on their movement through Hagerstown silty clay loam and through Lakeland

sandy loam in aluminum tubing. The phenylureas were more mobile than the toluidines but less mobile than the benzoic acid herbicides tested. The assumption was made that pesticide mobility in a subirrigated system approximates movement in percolation water. The mobility factor of each herbicide was divided by the mobility factor of monuron in order to arrive at a relative mobility factor which would relate the herbicides to each other by a single value (27). Upchurch (63) summarized the reports to 1966 on pesticide movement in soil.

II. RESIDUES IN WATER, SEDIMENT, AND SOIL

Phenoxyacetic Acids

In 1965 the U. S. Geological Survey began the collection and analysis for pesticides in water collected from 20 stations on selected streams west of the Mississippi River. Nine insecticides but no 2,4-D nor 2,4,5-T were detected in 1965-1966. Insecticide concentrations ranged from .005 to .090 ppbw (7). During 1966-1967 DDT and 2,4-D were the most commonly found pesticides at the sampling sites (38). The compounds detected most often in 1967-1968 and their frequencies of occurrence are as follows: DDT-72; DDE-37; 2,4-D-36; and 2,4,5-T-24. The highest concentration of either herbicide found was 0.35 ppbw; concentrations exceeded 0.20 ppbw seven times during the year. The highest concentration of DDT detected was 0.12 ppbw. The majority of the residues of all compounds detected fell in the .01 to .09 ppbw range. The Arkansas, Brazos, Canadian, and Sacramento Rivers each contained 2,4,5-T on four or more

of the 12 sampling dates. Detection of the methylated 2,4,5-T was by gas chromatography.

More than 18,000 acres of Nickajack and Guntersville Reservoirs on the Tennessee River were treated with 22 and 44 kg/ha of the diethylamine salt of 2,4-D from April-June 1969 to control Eurasian watermilfoil (Myriophyllum spicatum L.) (66). The average herbicide concentration in water was 4-8 ppmw in samples collected within the treated area eight hours after application. The level dropped to 0.63 and 0.03 ppmw in two weeks and two months, respectively. The maximum concentration in lake-bottom sediment was 0.30 ppmw. The average 2,4-D content in sediment in the three month period following application to overlying water was 0.23 ppmw. Treated water for municipal use which originated in Guntersville Reservoir contained 5.8 and 0.14 ppmw of 2,4-D on April 6 and 11, respectively.

In Guntersville Reservoir, Smith and Isom (57) detected 0.38 ppmw 2,4-D residue in sediment under treated water nine months following application of 44 kg/ha of granular butoxyethanol ester of 2,4-D. Sediment samples were collected with a Petersen dredge and analyzed on a gas chromatograph equipped with an electron capture detector.

Barnett and his coworkers (4) determined the residues of amine and ester formulations of 2,4-D in Cecil sandy loam 120 hours following application of 2.2 and 4.4 kg/ha of the herbicide. High intensity simulated rainfall was applied to the field plots in volumes equal to 1, 20, 80, and 100-year frequency storms for the southeastern United States. Samples were collected 24 hours after the simulated rain.

Residues in three depth zones of 5-7 percent slope soil for the ester and amine formulation are as follows for the 2.2 kg/ha rate in 1964.

Soil Depth (cm)	Ester (ppmw)	Amine (ppmw)
0 - 2.5	5.00	0.92
2.5 - 7.5	1.51	0.85
7.5 - 15.0	0.03	0.72

The amine leached deeper into the soil profile than did the ester. Barnett and his associates attributed movement of the amine to its higher water solubility. More ester than amine was detected in the sediment-water washoff. The herbicide was considered to be adsorbed to the soil particles which eroded into the catchment vessels; therefore, the less soluble ester remained associated with the soil which was washed from the plots.

O'Connor (44) reported that 2,4,5-T adsorption to a calcareous silty clay loam was adequately accounted for by both the Freundlich and Langmuir relationships. Destruction of organic matter resulted in no adsorption of the herbicide. Desorption was enhanced by air drying the soil following adsorption.

Under conditions of low volume (1.2 cm/ha), low intensity simulated rainfall, Trichell and coworkers (59) found less 2,4,5-T in runoff water than in runoff sediment from field plots with 3-8 percent slope on Irving clay loam soil in the southwestern United States. The unformulated

2,4,5-T was applied at 2.2 kg/ha rate. Residue comparisons for different soil surface types and time periods were as follows:

Soil Surface	24 Hours (ppbw)	4 Months (ppbw)
Sod	3.30	.043
Fallow	2.60	.007

Three to eight percent of the applied compound was recovered in runoff water and sediment.

Soil under 50-190 cm of water in farm ponds which were treated with 1.3 ppmw of the butoxyethanol ester of 2,4-D in granular form contained 4.96 ppmw on day 1 following application, 0.60 on day 12, and none detectable after 55 days (22). The residue level in sediment under water was 10^3 greater than the amount in the water in Frank and Comes' study. Brady (6) determined that the half life of ^{14}C-labeled 2,4,5-T in Louisiana forest soils was eight days.

Substituted Phenylureas

Frank (21) applied 44 kg/ha of monuron and neburon to 15 cm-deep water. During weeks 1-32 following application there was more herbicide in the water than in the underlying soil. After 32 weeks the herbicides were in the upper 10 cm of soil. The concentration of monuron in soil under 15 cm of water did not decrease until the sixteenth week. Neburon concentration in the soil declined after eight weeks but at a slower rate than monuron. Fifteen and thirty-nine percent of the monuron and neburon,

respectively, remained after 128 weeks. Frank concluded that microbial activity was the major factor in the loss of monuron and neburon in an aquatic environment.

In 1969 Geissbuhler (24) stated that no data are available concerning the mode of degradation of fluometuron in soil. He conducted a study on the rate of disappearance of fluometuron in the 0-5 cm layer of a plant-free Swiss clay loam under field conditions. Six ppmw of fluometuron was dissipated to 4 ppmw in 30 days and then disappeared in a linear fashion to < 0.5 ppmw by day 160 following application.

Wiese and coworkers (65) reported that 46 percent of the fluometuron applied to soil was remaining after six months. Residue amounts were determined from visual rating of cotton toxicity symptoms in a greenhouse bioassay. Fluometuron residue was detected 112 days following application to 15 southeastern soils (53). On the basis of data from that study Savage ranked the persistence of atrazine, fluometuron, and linuron in descending order. Net growth of soybeans in a pot bioassay was the measurement by which comparisons were made. Toxicity of three substituted ureas was lost more rapidly from soil maintained in moist condition than from soil which was alternately wet and dry (54). Darding and Freeman (11) found that fluometuron residue in seven soils was significantly correlated (0.85) with soluble phosphorus content when tested at the 5 percent level of probability. Residue concentrations were determined from dry weight of five crops of oats grown for 28 days each and harvested one, three, five, seven, and nine months after 0.3 to 20 ppmw of

fluometuron were mixed into the soils. Phytotoxicity of fluometuron in four of the soils with an organic matter range of 1 percent to 5 percent was not different at any of the five cropping periods. Fluometuron toxicity in the five soils included in the investigation by Darding and Freeman was correlated with organic matter, soluble phosphorus, cation exchange capacity, exchangeable calcium, and total exchangeable bases in two or more of the cropping periods. Phytotoxicity levels did not correlate with the pH values (6.1 - 7.0) of the seven soils studied.

III. DEGRADATION FATE OF PHENOXYALKANOIC ACIDS AND PHENYLUREAS

The side chains of phenoxyalkanoic acids, including 2,4,5-T, generally are considered to be susceptible to beta oxidation when the compounds are exposed to natural ecosystems (2). Beta oxidation involves sequential removal of two carbon fragments from fatty acids until a two-carbon moiety remains. In the case of phenoxyalkanoic formulations with an even number of carbon atoms in the ether-linked fatty acid side chain, the phenoxyacetic acid which remains after beta oxidation is the phytotoxic form of the compound. The universality of the phenoxyacetic acid form in soils treated with a phenoxyalkanoic having an even number of carbon atoms in the side chain is the basis for esterification of the side chain for detection in a gas-liquid chromatograph (58,67). Alexander (2) concluded that several daughter compounds are formed by beta-oxidation, each of which may have a different toxicity and a different persistence.

A soil-derived Flavobacterium cleaved the ether linkage that binds the phenol and the alkanoic moieties of omega-linked 2,4-dichlorophenoxy-alkanoic acids (37). The degradation products were 2,4-dichlorophenol,

4-chlorocatechol, and the free fatty acid corresponding to that bound to the phenoxy compound. Loos and coworkers (34,35) identified phenols as intermediates in the decomposition of 2,4-D by an Arthrobacter species and provided evidence that the conversion did not proceed by way of the corresponding anisoles.

Fluometuron and diuron have the same breakdown pattern in plants (10,50). The process involves stepwise N-demethylation followed by hydrolysis. These steps decrease herbicidal activity (51) and represent detoxification to CO_2, NH_3, and trifluoromethylaniline and dichloroaniline, respectively, for fluometuron and diuron. Geissbuhler (24) stated that no data were available on the degradation in soil but that his preliminary studies indicate that microbial breakdown is similar to that in plants. Hill and his associates (30) showed that other substituted urea herbicides are degraded by microorganisms which are indigenous to soil.

Rubin and Eshel (51) studied the toxicity of fluometuron and three degradation analogs of fluometuron to three plant species. The technical grade chemicals were 1-methyl-3-(a,a,a-trifluoro-m tolyl)urea (DMFM), 3-(a,a,a-trifluoro-m-tolyl)urea (TFMPU), and a,a,a-trifluoro-m-toluidine (TFMA). The compounds were mixed with a 7.4 pH clay soil with 1.5 percent organic matter. In a 30-day greenhouse pot bioassay fluometuron was more toxic than the analogs. The DMFM was 50 percent to 70 percent as toxic as fluometuron, while the other two analogs tested were only 10 percent as toxic as fluometuron. The monomethyl derivative (DMFM) was relatively more toxic to foxtail (Setaria) and redroot pigweed (Amaranthus retroflexus L.) than it was to cotton (Gossypium hirsutum L. Acala 4-42) in Rubin and Eshel's study. Fluometuron degradation rate

was higher in tolerant cotton than in susceptible cucumber (50). Plant species may be differentially susceptible to the monomethyl derivative of fluometuron as well as to the nondegraded herbicide molecule.

IV. METHODS OF ESTIMATING RESIDUE CONCENTRATIONS

Herbicide concentrations in soil, water, and plant extract are commonly estimated by comparing bioassay results or laboratory instrument responses with concentration-response curves derived from known concentrations (4,11,41,46,52). Regression equations which are based on measurements of indicator plants (48) or instrument response such as UV spectrophotometer attenuation readings (12) are used as predictors of unknown concentrations. Logarithmic transformations of concentration (23,48) and probit analysis (19) may enable the researcher to describe relative responses more concisely.

Interference from naturally occurring substances in soil which absorb UV radiation in the same range as the herbicide being tested give rise to apparent residue in control plot samples. Smith (56) corrected fluometuron soil residue data for apparent concentration by subtracting the absorbance of untreated control samples from that of treated samples. In an investigation of monuron and diuron residues in soil by Hill and coworkers (30) alkaline hydrolysis of the control-plot soil samples yielded apparent concentrations of the herbicides. These workers reported the treated soils which analyzed no more concentration than the untreated check as containing one-half the blank rather than as containing zero residue. One-half the apparent concentration

in the untreated soil was considered to be the significant level of detection (0.2 ppmw) in the study. Regression equations with large intercept terms may predict apparent residue concentrations in untreated control samples (16).

V. ENVIRONMENTAL CONSIDERATIONS

Herbicide residue persistence varies with moisture conditions of microclimates (22) and of geographic regions (26). The amount of herbicide removed from the application site in sediment is determined largely by the amount and intensity of the first rainfall following application. The remaining portion of the herbicide may be leached into the profile or degraded in place (18). Twenty-six percent of the ester formulation of 2,4-D was carried off field plots in Georgia by a 100-year frequency (10 cm) rainstorm; 13 percent was carried off by a 1-year frequency (2 cm) rain (4). Residues are more persistent in northern states because the soil remains frozen in the plow layer for several months each year.

Shipman (55) proposed a long-term approach to investigating herbicide residues in the ecosystem. His model was based on Van Dyne's ecosystem concept with climate affecting soils, plants, and animals, including man, but with man as the manipulator of all other constituents of the ecosystem. Pimentel (47) pointed out the complex nature of ecological systems and the basis of some of the problems involved in studying them.

The Federal Water Pollution Control Administration (60) proposed that an application factor which would express toxicity over a long period of exposure be defined and utilized to supplement acute (LD_{50}) and chronic (TL_m) toxicity data. The acute lethal dosage to 50 percent of the test organisms (LD_{50}) is expressed as milligrams of toxicant per kilogram of animal weight. The median tolerance limit (TL_m) is defined as the concentration of toxicant in the test organisms' environment that will cause irreversible damage to 50 percent of the organisms. TL_m is determined in a 48 or 96-hour test. The proposed application factor would be derived by dividing the safe concentration for continuous exposure (determined under controlled conditions) by the TL_m. A separate TL_m would be required for each stream receiving a pollutant. In a given situation the safe concentration in the receiving stream would be determined by multiplying the TL_m for that stream by the application factor of the compound. For compounds such as 2,4-D and 2,4,5-T which are not acutely toxic at less than 1 ppmw it was recommended that an application factor of .01 be used and in the absence of acute toxicity data that environmental levels of not more than 10 ppbw be permitted.

The relationship between rate of disappearance of herbicides from soil and possible accumulation with continued use was expressed as a first order differential equation by Hill and coworkers (30). If a known fraction of the compound disappears in a given time period, then the rate of disappearance is proportional to the amount left in the soil:

$$\frac{dx}{dt} = kx$$

where x = amount present in soil at time (t), and (k) is an experimentally determined constant for a given soil and set of conditions. Under the conditions of their field study, neither monuron nor diuron would accumulate in the soil if 2.2 kg/ha were applied annually.

CHAPTER III

METHODS AND MATERIALS

I. GENERAL INFORMATION

The study reported here was conducted in four major phases. The phases are distinguished from each other by location of the primary operations as listed below: (1) field plots for forage production and residue sampling; (2) lysimeters for water percolation and soil residue; (3) soil bioassay in glasshouse and incubator; and (4) laboratory analyses of herbicide residues in water.

In May 1972 a one-year field study was initiated at Knoxville. Fluometuron and an amine and ester formulation of 2,4,5-T were applied to bordered field plots preemergence to the crop and weeds. The plots were equipped for trapping water and sediment. Forage sorghum was grown on the plots. Phytotoxicity to the crop was estimated, and yields for two harvest dates were recorded. Soil, water, and sediment samples were collected for residue analysis.

Two types of plant bioassays were utilized to detect soil residues. Ultraviolet spectrophotometry (UV) and gas-liquid chromatography (GLC) were used to detect residues in water. Regression equations were derived from known concentrations of each compound in soil and water. Herbicide concentrations in the field samples were predicted by calculations involving the regression equations.

In 1973 an auxiliary study of herbicide in percolation water and residues in soil was conducted in the pit lysimeter installation at Knoxville. Water samples were analyzed for herbicide by UV and GLC methods. Comparisons among soil residues were made from *in situ* bioassay.

II. FIELD PLOTS

Site Description

Field plots were established on the University of Tennessee Plant Science Farm in Knox County, Tennessee. The farm is located three miles north of the boundary between Blount and Knox County and is adjacent to the Fort Loudon Lake reservoir of the main channel of the Tennessee River. The elevation is 253 m.

The plots were on Etowah silt loam. The site was sloping (5-12 percent) and eroded. The pH in the Ap horizon is 5.6-6.0. Organic matter level usually is near 1 percent. The soil formed from mixed alluvial material on old stream terraces. The series is a member of the Ultisols order (17). It is well drained but has a moderately high water holding capacity. The Ap horizon (0-15 cm) is a reddish-brown silt loam with moderate granular structure. The portion of the B horizon from which residue samples were taken in this study (15-45 cm) was a silty clay loam. The plots were positioned on a W-SW facing slope within 200 m of the reservoir.

Winter wheat had been grown on the site in 1970 and 1971. The wheat was mowed and raked off the site two weeks before the experimental

crop was planted. No fertilizer was applied to the site during this experiment or during the previous six months.

Plot Preparation

The soil was prepared for seeding by rototilling the upper 15 cm with a tractor-mounted tiller. A 20 cm high soil border was plowed around each plot.

A detailed differential survey was made of a contiguous land area sufficiently large to accommodate the experiment. The plots were 2 m by 4 m with the long dimension and row direction running north and south. The plots were positioned on the slope so that runoff water drained to one corner. Undisturbed alleys were retained around each plot. Alleys across the primary slope were 1 m wide; alleys up and down the primary slope were 3 m wide. A 60-liter galvanized tub (#2 size) was buried at the low corner of each plot. Three edges of a 1 x 2 m polyethylene sheet were buried in the plot soil and borders. The fourth sheet edge protruded into the buried tub. A liter plastic cup was buried in the plot 1 m from the tub.

Forage Sorghum Establishment

Forage sorghum [Sorghum bicolor (L.) Moench, 'Pioneer 931'] was selected for this experiment because it is partially tolerant to both compounds and would give an indication of injury but neither compound is recommended for this crop in Tennessee. The seeds were drilled in rows 18 cm apart at a rate of 12 kg/ha. When grown in wide (100 cm) row spacing Pioneer 931 is considered to be a full-season ensilage forage with high (40,000 kg/ha, wet weight) yield potential.

Herbicide Treatments and Plot Design

The herbicides used in this experiment with their treatment rates and application dates are listed in Table 2. The field experiment was in a randomized complete block design with three replications. Initial application was preemergence to vegetation. The 2.2 kg/ha respray treatment was applied broadcast seven days after the first forage sorghum harvest. Herbicide treatments were applied in 383 L/ha of water.

Weather Records and Plot Conditions

Soil moisture on the initial spray day and the respray day was ≥ 90 percent of field capacity. Air temperatures 1 m above the surface on the two dates were 21 and 30 C, respectively. Soil temperature at 1 cm was 30 and 33 C on the two days. Wind velocity was estimated at 2 km/h at the time of the initial treatments and at 5 km/h when the respray was applied. Weather data were recorded at the plot site on herbicide application dates.

Precipitation in May-September of 1972 was near normal. Rainfall and temperature records are in Tables A-1 and A-2 in the Appendix. Two high intensity rainstorms occurred on June 6. The first rain was 1.2 cm in 20 minutes and included hail. The second was 4.4 cm in two hours. Impounded water in the tubs measured approximately 4 cm deep after the first storm. There was not sufficient water in the runoff cups for analysis after the first storm. Most tubs were filled to within 10 cm of capacity by the second storm. No plot borders were broken by the water. Several runoff cups were filled with sediment. Some cups were

Table 2. Preemergence Herbicides Applied to Forage Sorghum in Field Plots, Knoxville, 1972

Compound	Treatment[1] kg/ha	Application Date(s)[2]
Fluometuron[3]	2.2	June 1
2,4,5-T,Amine[4]	4.4	June 1
2,4,5-T,Ester[5]	2.2 + 2.2 respray[6]	June 1 & August 2

[1]A weed-free control and a weedy control for each compound was included in each replication.

[2]The same application dates and rates were maintained for the three compounds. Application was by broadcast spray in 383 L/ha of water preemergence to crop and noncrop vegetation.

[3]Provided by Ciba-Geigy Corporation as 'Cotoran.' Concentrations are reported on the basis of active ingredient.

[4]Provided by Dow Chemical Company as 'Veon 245,' Lot 8700-42, triethylamine salt. Concentration reported as acid equivalent.

[5]Provided by Dow Chemical Company as 'Esteron 245,' Lot 675481, propylene glycol butyl ether esters. Concentration reported as acid equivalent.

[6]2.2 kg/ha repeated after first forage harvest when regrowth was 10 cm tall.

washed out of the ground by the second storm on June 6. Tubs overflowed on June 28 and 29 following 10 cm of rainfall in two days.

The plots were sprinkler irrigated with 2 cm/day of water from Fort Loudon Lake on June 14 and June 15. No runoff occurred from the irrigations.

Forage Sorghum Stand

The forage sorghum crop stand was rated relative to the control on June 20, 1972. Plant density in the center two square meters of each plot was visually compared with the weed-free control plots of the same replication. The control plot with the highest plant population was assigned a rating of 100. A value from 10 to 100 was recorded for the crop stand in each treated plot.

Forage Sorghum Harvests

Forage was harvested from a square meter quadrat July 26 and October 4, 1972. The plants were clipped 15 cm above the soil surface. The forage sorghum was in the boot stage on the first harvest date and in mid-bloom on the second harvest date. The forage was dried at 70 C to constant weight. Yield was recorded as total dry matter in grams per square meter.

Collection of Samples from Field Plots

Samples of soil, water, and sediment were collected from the field plots for residue analyses. Sampling dates and sources are listed in Table 3. Soil samples were taken from four depths on various dates.

Table 3. Record of Sampling Dates and Other Major Events Related to Field Plots, Knoxville, 1972

Date	Treatments	Event	Media	Residue Sample Sources(s)	Detection
1972					
5/31	All	Plots seeded			
6/1	All	Application			
6/2	All	Collection	Soil	0-1 cm	Bioassay
6/7	All	Collection	Soil	0-1 cm	Bioassay
6/7	All	Collection	Sediment	0-2 cm	Bioassay
6/7	All	Collection	Water	Both[1]	UV; GLC
6/14	All	Collection	Soil	0-45 cm[2]	Bioassay
6/15	All	Stand rating			
7/26	All	Harvest			
8/1	All	Collection	Soil	0-1 cm	Bioassay
8/1	All	Collection	Sediment	0-2 cm	Bioassay
8/1	All	Collection	Water	Both[1]	UV; GLC
8/2	2.2 respray	Application			
8/3	2.2 respray	Collection	Soil	0-1 cm	Bioassay
8/8	2.2 respray	Collection	Water	Runoff	UV; GLC
8/18	2.2 respray	Collection	Water	Impounded	UV; GLC
9/21	Fluometuron	Collection	Water	Both[1]	UV
10/4	All	Harvest			
12/28	All	Collection	Soil	0-45 cm[2]	Bioassay
1973					
2/13	All	Collection	Water	Both[1]	UV; GLC

[1]Water sources were fresh runoff water from a cup buried in each plot and permanently impounded water from a galvanized tub buried at the corner of each plot. Sediment was collected from the surface 2 cm of ooze under the water impounded in the tubs.

[2]Soil cores were taken with a Hoffer soil tube. Cores were separated into three groups by depth (0-15, 15-30, and 30-45 cm).

All depths were not sampled on every sampling day because of labor limitations. All depths, except 0-1 cm, were sampled with a Hoffer soil tube. Six probes per sample were made in a clustered pattern within 1 m of the buried cup and within 2 m of the tub. The sampling cores were divided into three divisions by depth zones, i.e., 0-15, 15-30, 30-45 cm. Soil from each depth zone of six probes was combined for a composite sample on a given sampling day. The probe holes were filled with clean soil taken from control plots. Samples were placed in plastic bags and stored at -10 C until March of 1973.

Water samples were collected from two sources in the plots on various days (Table 3). Samples from the buried cups were runoff water from the most recent rain before sampling date which yielded 100 ml of runoff to the cups. Impounded water from the catchment tubs was dipped from all depths of the tub with minimal disturbance of the sediment under the water. Water samples were stored at -10 C from sampling day to March-May of 1973.

Sediment under the impounded water was dipped with a 4 mm mesh strainer from the upper 2 cm of the bottom ooze. Approximately 200 g (oven-dry basis) was collected on various days (Table 3) and stored in plastic bags at -10 C. The sediment was thawed for analysis in May of 1973.

During June and July of 1972 eight voles were trapped alive in the experimental plots. One female field mouse was maintained in captivity through the last two weeks of gestation. The offspring were observed during a period of two weeks.

III. PREDICTION EQUATION FOR FLUOMETURON IN SOIL

In order to compare fluometuron soil residues on the basis of concentration, regression analysis was used to derive an equation suitable for predicting fluometuron concentrations in field plot soil. Residues of fluometuron in soil were detected by oat (Avena sativa L., 'Blount') seedlings growing in pots in a glasshouse. Concentrations of fluometuron were predicted from various plant measurements by a multiple curvilinear regression equation derived from measurements of oat plants exposed to a series of known concentrations of the herbicide. Concentrations were based on active ingredients of the chemical and oven-dry weight of soil.

Oat Seedling Bioassay

Oat seedlings were grown in wide-mouth 300 ml wax-treated paper containers in the glasshouse during March of 1973. Sufficient Etowah silt loam for the bioassay was removed from the surface 15 cm of the field plot area before the plots were treated. Sixteen concentrations of fluometuron from .01 to 4.0 ppmw plus an untreated control were used to establish the standard curve of plant response to fluometuron. The treatments were replicated three times. Fluometuron suspended in 30 ml of water was mixed with 206 g of air dry (200 g oven-dry equivalents) soil before the medium was placed into the growth containers. Five holes were evenly spaced in a circular pattern within 2 cm of the periphery of the container lids which were fitted on the containers to minimize evaporation. An oat seed was placed through each hole and

pressed into the soil with the radicle end downward. The soil was brought to field capacity as determined by weight. Emergence percentage exceeded 90 and was at a maximum on March 13 (day 4 following seeding). The plants were thinned to the four most uniform seedlings per pot on the fifth day following emergence. The pots were watered with 30 ml of Hoagland #2 nutrient solution (31) initially and at the midpoint of the bioassay. The mean daytime temperature in the glasshouse during the test was approximately 27 C with extremes of 19 and 34 C. Night temperature averaged about 21 C. The average daylight period was 12 hours per day. No artificial illumination was provided.

Measurements

On the fifth day following plant emergence the pots were brought to field capacity as determined by weight, and pot weight was recorded. Water use was determined for the next six 48-hour periods by weighing the pots. If the weight indicated that soil moisture was $\leq$ 50 percent of capacity, sufficient water was added to bring the soil to field capacity. Visual ratings of phytotoxicity symptoms (Table 4) were recorded for six 48-hour periods on the same days that water use was determined. The plants in the control pot were assigned a value of ten. Plant height was recorded on day 6 following emergence. On day 18 following emergence plants were clipped at the lid surface and dried to constant weight at 70 C in a forced-air oven. Dry matter was recorded to 10^{-3} g.

Table 4. Visual Rating Scale for Oat Toxicity Symptoms in the Glasshouse and Lysimeter Bioassays

Rating	Visible Seedling Symptom(s)
10	None (green color) Bronze tips
9	Brown following bronze
8	Flaccid tip Early tip wilt < 1 cm
7	Tip wilt ≥ 1 cm Early tip burn < 5 mm
6	Tip burn, leaf wilt Early leaf burn
5	Leaf burn ≥ 50 percent
4	Pale yellow with white
3	Bleached white
2	Necrotic
1	Dead

Regression Equation

Water use and visual rating for each of the six 48-hour periods, dry matter weight, and plant height plus the square and cube terms of each of these measurements were analyzed by stepwise regression (5,16) with applied concentration as the dependent variable. The analysis was repeated with the natural logarithm of applied concentration as the dependent variable.

The maximum R^2 improvement technique of stepwise regression developed by Goodnight (5) for curvilinear regression was used. Stepwise regression involves the addition of variables to a model in the order of maximum R^2 values and reexamination of the contribution of each previously entered variable by the partial F-test. The R^2 improvement technique yields the model with the highest R^2 at each possible number of independent variables. This technique does not produce a single best model. Each model used to predict concentrations was selected by the investigator on the basis of statistical, biological, and practical considerations.

In the construction of the prediction equation for fluometuron in soil, the last variable entered was required to make a significant contribution to the model at the .01 level of probability. In order to remain in the model a previously entered variable was required to reduce the residual sum of squares significantly when tested at the .01 level. These criteria are conservative but were considered justifiable for the standard curve. No model was accepted which included a quadratic or cubic term of a variable without the corresponding linear term.

The same methods and criteria used for developing a prediction equation for fluometuron residues in soil were used for developing a comparable equation for 2,4,5-T soil residues.

IV. PREDICTION EQUATION FOR 2,4,5-T IN SOIL

In order to compare 2,4,5-T soil residues on the basis of concentration, regression analysis was applied to measurements of root response to known concentrations of 2,4,5-trichlorophenoxyacetic acid. Six replications of 11 concentrations ranging from 0.016 to 4.0 ppmw were included in the standard curve. The equation derived by regression analysis was used to predict residues in field plot soil. Concentrations were expressed as acid equivalents of 2,4,5-T and oven-dry weight of soil.

Soil residues of an amine and ester formulation of 2,4,5-T were detected by cucumber (Cucumis sativa L. 'Straight 8') seedling roots. The petri dish bioassay methods developed by Parker (46) and Ready and Grant (48) were modified (14) for use in this study. The growth medium was Etowah silt loam taken from the field plots before herbicide was applied. Cucumber seeds were pregerminated in moist toweling until the radicles extended to 5 mm before being placed on the treated soil in the petri dish. The test sample consisted of five plants per dish. The samples were placed in an incubator in the dark at 28 C for 24 hours. Root extension during 24-hour and 48-hour incubation periods was measured in millimeters. Average root extension of the four most uniform primary

roots was recorded in mm. Root deformation as compared with the control was rated on a scale of 1-10 (Table 5).

Regression Equation

Root extension and visual rating of root deformation with the square and cubic terms of these two measurements were analyzed by stepwise regression (5,16) with applied concentration as the dependent variable. The analysis was repeated with the natural logarithm of applied concentration as the dependent variable. The regression techniques applied to the 2,4,5-T soil residue standard curve data were the same as those described under "Regression Equation for Fluometuron" in this chapter.

V. DETERMINATION OF FLUOMETURON IN WATER AND SOIL

Fluometuron was extracted from field and lysimeter water samples with n-pentane according to the method of Davidson, Rieck, and Santelmann (12). Pentanes of various qualities were tested to determine their suitability for fluometuron extraction. All grades except spectroquality interfered with the ultraviolet absorbance pattern. Fluometuron concentration relative to known standards was determined on a Perkin-Elmer model 202 ultraviolet-visible spectrophotometer. The sample was scanned in wave lengths of 220-260 nm. Maximum peak height was measured at $240^{\pm 5}$ nm. The spectrophotometer reading was zeroed or nulled by pentane extract of control-plot water.

Concentrations of fluometuron in known standards were regressed on spectrophotometer peak height to develop a prediction equation for

Table 5. Visual Rating Scale for Cucumber Root Toxicity Symptoms in the Petri Dish Bioassay[1]

Rating	Visible Symptom
10	None; equal to control
9	Twisted at one locus
8	Fewer lateral roots than control
7	Proliferation of root hairs
6	Club-shaped lateral roots
5	No lateral roots below level of root extension of preincubated seedling
4	Limited clubbing of primary root
3	Club primary with lateral proliferation
2	Bulbous primary root
1	Club roots

[1]Visible symptoms associated with each successively lower rating were assumed to be inclusive of symptoms of higher ratings unless otherwise specified.

fluometuron in water. The equation was applied to sample data for estimating residue level.

Fluometuron residues in soil and sediment were extracted by spectroquality n-hexane according to the method developed by Smith (56). Extracts were tested in the UV-visible spectrophotometer as discussed above for water. A regression equation was calculated for predicting fluometuron residues in soil.

VI. DETERMINATION OF 2,4,5-T RESIDUES IN WATER

Water samples from the field runoff cups and impoundment tubs were thawed and analyzed by gas-liquid chromatography for residues of 2,4,5-T. The method described by Devine and Zweig (15) was modified slightly for this study. Three hundred ml of acidified water sample were extracted with two 60-ml portions of nanograde benzene. The extract was reduced to near dryness at 60 C using a water-line aspirator. The 2,4,5-T was then esterified with 0.1 molar ethereal alcoholic diazomethane prepared from N-methyl-N-nitroso-p-toluenesulfonamide. The methylated extract was diluted to 1.7 ml in spectroanalyzed acetone for injection into the chromatograph column.

Two µl of acetone solution were injected manually into a Micro Tek model DSS 170 chromatograph equipped with an electron capture detector. Tritium (^{3}H) foil was the ionization source. The inlet, column, and detector temperatures were 170, 160, and 180 C, respectively. A 2.4 m by 3 mm copper column packed with 5 percent SE30 on chromosorb W 60/80 mesh was used. Flow rate of nitrogen carrier gas was approximately

80 ml/min. The optimum operating voltage as determined by background signal profile was 26. Instrument settings for input and output attenuation were 10^2 and 8, respectively.

The concentration of 2,4,5-T was calculated from a prediction equation. The prediction equation was developed by regressing known concentrations of 2,4,5-T on chromatograph peak height. Water from the field plots and lysimeters was analyzed by the same method.

VII. RESIDUE STUDY IN LYSIMETERS

Pit Lysimeter Installation and Soil

An auxiliary study of fluometuron and 2,4,5-T residues was carried out in the pit lysimeter installation located east of Morgan Hall on the agriculture campus of the University of Tennessee, Knoxville. This lysimeter system was discussed in the Twenty-Sixth (61) and Thirty-Ninth (62) Annual Report of the Tennessee Agricultural Experiment Station. It was designed for investigation of percolates from the upper 15-20 cm of a soil profile.

The soil in the lysimeters used in this study was described as belonging to the Cumberland series at the time it was placed into the lysimeter tanks (39). The portion of the Cumberland series from which the soil originated is now part of the Decatur series (42). The distinction is made on base saturation of zones deeper than 125 cm. Both series belong to the Ultisol order. The mechanical analysis for the soil placed in the tanks was 33:48:19 percent for the sand, silt, and clay fractions, respectively. The soil has a loam texture. It was collected

from the Ap horizon of a field on the University of Tennessee's Cherokee Farm in Knox County. The soil was packed into round tanks to a depth of about 15 cm in 1942 (36). The tank surface area is 0.4 m^2.

Experimental Design and Herbicide Treatments

Three replications of treatments in a randomized complete block design were included in the lysimeter experiment. The treatments were 2.2 and 4.4 kg/ha each of fluometuron, 2,4,5-T ester, and 2,4,5-T amine. An untreated control was included in each replication.

The herbicide was sprinkled on the bare soil surface through a 2-mm mesh. The solution was applied at a rate of 200 ml per tank (5000 L/ha). The surface cm of soil was stirred 24 hours after application. The herbicides were applied on February 28, 1973. Air temperature at application time was 14 C. Soil temperature at 2 cm depth was 16 C. Soil moisture was about 90 percent of field capacity. Wind was approximately 5 km/h from the NW.

Weather Conditions and Moisture Received

Rainfall, minimum and maximum soil and air temperatures, and relative humidity averages for March, 1973 are listed in Appendix Table A-3. Records for rainfall and moisture received do not agree on March 1 and March 16. Two and one-half cm of tap water were sprinkled on the soil on March 1. The tanks were covered on March 16 to prevent surface water from overflowing.

Samples Collected

Percolation water samples were collected on days 1, 2, 3, 5, 12, 16, and 90 following herbicide application. Collection vessels were emptied after each collection. The samples were stored at 20-25 C until after the 90-day collection date. Extraction and detection methods were the same as those used with field plot water.

Lysimeter Soil Bioassay

The indicator crop for fluometuron residues in the Cumberland loam was 'Blount' oats. The in situ bioassay was conducted in two periods beginning on day 30 and day 50 following herbicide application. The tank was divided into two equal divisions for the split plot arrangement of seeding dates. Twenty-six oat seeds were planted in an evenly spaced pattern on half of the tank on March 27, 1973. The other half of the tank was seeded on April 7. The soil temperature at seeding depth for each date was 11 and 18 C, respectively.

Visual ratings of plant toxicity symptoms were made according to the scale in Table 4, page 30. The first rating was made when the oat seedlings were about 6 cm tall. Statistical analyses were based on the visual rating scores.

Soil residues of the amine and ester formulations of 2,4,5-T in the lysimeter soil were detected by peas (Pisum sativum L. 'Alaska'). Twelve seeds were planted each day. The split plot arrangement and seeding dates were the same as for the oat bioassay discussed above. The number of live plants at each rating date was recorded.

VIII. STATISTICAL METHODS

Stand ratings, yield, standard curve data, soil, water, and sediment residue data, and lysimeter in situ bioassay data were tabulated on computer cards. Analyses of variance were calculated for stand, yield, residue concentrations from the various sampling sources, and lysimeter bioassay ratings. Tests for significant residue differences between treatments and controls are reported in this paper at various levels of probability. Regression tests of significance are reported at or below P = .01. If analyses of variance indicated difference at the .05 level of probability means were separated by Duncan's Multiple Range test at P < .05. The correlation coefficient for stand and yield of forage sorghum was calculated and tested for significance. The term "different" as used in this study in reference to comparison of means denotes significance at a probability level of .05 unless otherwise specified.

Analyses of variance were computed on the residue data for each herbicide compound on each sampling day. Data were analyzed for treatments and compounds across depths for days 14 and 210. In addition, analyses of treatments and formulations within depths and dates by split plot arrangement were considered useful. Forage yields, stand estimates, and phytotoxicity rating data were assumed to be normally distributed; therefore, the data were not transformed for the analyses of variance.

Prediction equations for the estimation of residue concentrations were calculated by regressing concentration applied on observed responses

of indicator plants and of peak heights recorded by the UV spectrophotometer and the GLC. The regression techniques for soil residues of fluometuron and 2,4,5-T were described earlier in this chapter. The prediction equations based on data from the UV and GLC instruments were calculated by least squares estimates using peak height, least squares estimates using logarithmic transformation of peak height, and second order equation-fitting techniques using the linear and quadratic terms of transformed and nontransformed peak height measurements.

Regression methods utilized were according to Draper and Smith (16). Analyses of data were performed on the IBM 360/65 computer at the University of Tennessee, Knoxville. The computer programs used were those included in the Statistical Analysis System (SAS), 1972 edition, developed by Barr and Goodnight (5).

CHAPTER IV

RESULTS AND DISCUSSION

I. FIELD PLOT STUDY

Forage Sorghum Stand

The forage sorghum stand was reduced significantly ($P < .05$) by all treatments of all three compounds applied (Figure 1). The amine and ester formulations of 2,4,5-T reduced the crop stand equally but to a greater extent than fluometuron. When each compound was considered separately, stand was reduced equally by each treatment. Stand reduction was not reflected in forage yield.

Generally, the phenoxy compounds reduced forage sorghum stand by preventing germination or emergence. Epinastic response was observed among seedlings in all plots to which phenoxy compounds were applied, regardless of formulation or rate applied. Sorghum seedling leaves in the fluometuron-treated plots showed symptoms of tip burn and leaf burn. If the necrotic area of the leaf exceeded one-half of the leaf area of the seedling, the plant usually died. Less severe and nonfatal plant symptoms in response to fluometuron included chlorosis of the youngest leaf and height reduction.

No new cases of phytotoxicity were observed between the date of stand rating (June 15) and the first harvest (July 26). Plant survival level was about 90 percent of the June 15 population. Crop height was uniform among all plots on July 1.

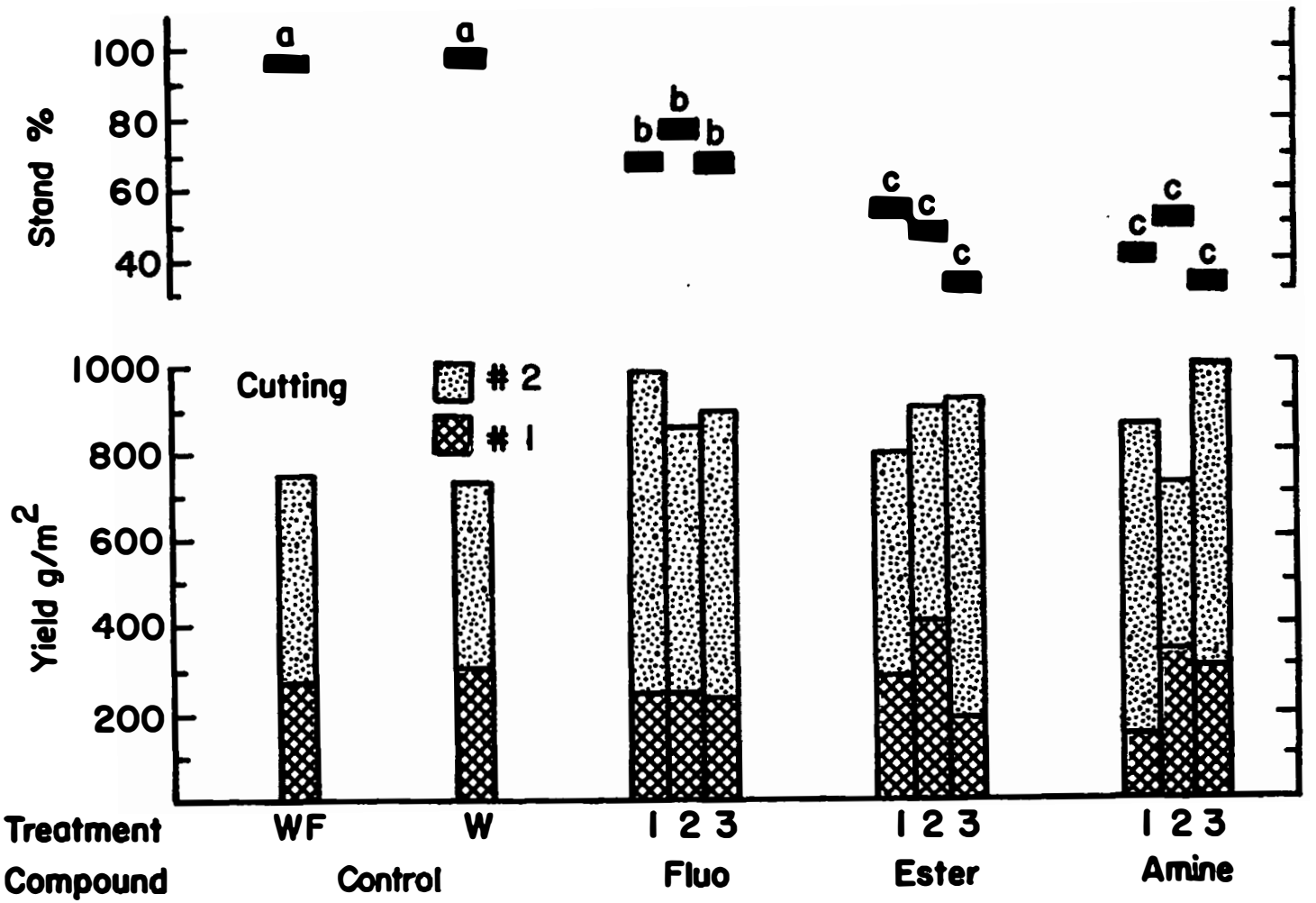

Figure 1. Comparison of forage sorghum stand and yield, 1972. Column means with different letters differ at the .05 level of probability according to Duncan's Multiple Range test. WF = Weedfree; W = Weedy; 1, 2, and 3 = 2.2, 2.2 + 2.2 respray, and 4.4 kg/ha, respectively. Fluo = Fluometuron; amine and ester are formulations of 2,4,5-T.

Weed Control

Control plots. Weedy plants observed in the weedy control plot included the following: large crabgrass [Digitaria sanguinalis (L.) Scop.]; yellow foxtail [Setaria glauca (L.) Beauv.]; goosegrass [Eleusine indica (L.) Gaertn.]; buckhorn plantain (Plantago lanceolate L.); curly dock (Rumex crispus L.); prostrate knotweed (Polygonum aviculare L.); virginia pepperweed (Lepidium virginicum L.); and yellow woodsorrel (Oxalis stricta L.). Less than 10 percent of the ground in the weedy controls was covered by these species. The sorghum plants were taller than the weedy species on all observation dates. There were no broadleaf weeds in the weed-free control at harvest. Crabgrass and goosegrass plants emerged in the weed-free plots in the latter part of each crop growth period. Ground cover was about 25 percent at harvest.

2,4,5-T plots. There were no broadleaf plants nor nonsorghum grasses in the phenoxy-treated plots on July 1. Large crabgrass was the first noncrop species to successfully establish seedlings in the 2,4,5-T-treated plots. Infestation became very heavy after the first forage sorghum harvest. Crabgrass covered about 50 percent of the ground surface of the plots on August 10. Its vigor was reduced during the August 10-31 dry period. The regrowth sorghum in the 4.4 kg/ha plots was chlorotic, probably due to nitrogen deficiency. There were very few broadleaf plants in the 2,4,5-T-treated plots. Buckhorn plantain was the most frequent broadleaf with 1-3 plants per m^2 in 50 percent of the 2,4,5-T plots. Curly dock was the most conspicuous broadleaf weed in

the phenoxy plots, but it was present in only four plots. The 2.2 kg/ha repeat spray 2,4,5-T killed all broadleaf plants and caused the tips of the crabgrass leaves to turn brown but produced no crabgrass control.

Fluometuron plots. Fluometuron controlled the weedy grasses and controlled most of the broadleaf weeds during the first two months following initial application. There were 1-2 buckhorn plantain plants per m^2 in 30 percent of the fluometuron plots. A few curly dock plants grew in the periphery area along the plots, but none invaded the heavily shaded mid-portion of the plots. Weeds did not appear to adversely affect crop growth in the plots treated with fluometuron. No harvest difficulties due to weeds were encountered in the plots.

Forage Sorghum Yield

Yields from the treated plots were not different from yields of weedy or weed-free controls ($P < .05$) for the first or second cutting or for the combined cuttings (Figure 1, page 42). The range of combined yields was from 720 g/m^2 for the weedy control to 990 g/m^2 for the 4.4 kg/ha 2,4,5-T amine-treated plots. The mean yield of combined cuttings of all treatments and controls was 824 g/m^2. The forage yield of the second cutting was significantly greater ($P < .05$) than yield of the first cutting. Two treatment-cutting interactions for forage yield were significant at the 0.1 level. The interactions occurred at the 4.4 kg/ha rate of the ester formulation and at the 2.2 kg/ha rate of the amine. If a cause-effect relationship between herbicide rate and yield account for the difference in yield at the two cutting dates,

it appears that the yield reduction imposed by the high rate at cutting 1 was reversed at cutting 2. This is feasible for several reasons. The 4.4 kg/ha rate of 2,4,5-T ester reduced the crop stand to 30 percent of the control. With stand as a limiting factor, yield on the first harvest date was 170 grams on the square meter harvested. Vigorous tillering occurred after the plants were cut, thus increasing plant density, and any inhibitory level of 2,4,5-T which may have been present early in the first cropping period had dissipated by the time of the second period (days 57-124). As a result, yield from cutting 2 was much higher, and the significant treatment-cutting interaction occurred.

The degree of association between yield and plant density was only 0.12 (not significant at $P < .05$). This indicates that when the stand was reduced growth of the remaining plants compensated for plant numbers to produce yields equal to the stands which were not reduced by phytotoxic herbicide levels. The equality of yields among weedy controls, weed-free controls, and treated plots indicates that neither the mechanical nor chemical weed controls imposed were necessary under the conditions of this study in order to maximize yields. The success of the untreated crop in competing with noncrop species is attributed to the early competitive advantage made possible by the close-planting seeding pattern and to the inherent early growth vigor of the crop cultivar.

Prediction Equation for Fluometuron and 2,4,5-T Residues

Fluometuron in soil. One regression equation was selected from those which met the criteria for an acceptable predictor of fluometuron

in soil. This equation was based on visual ratings (VR) of oat seedlings at the end of the second and fourth observation periods. The equation is referred to as Model I. Model I is shown below with independent variables listed in descending order of their levels of contribution to the equation:

$$\hat{y} = 9.2512 - 0.8086VR4 + 0.0481VR4^2 - 1.4379VR2 + 0.0850VR2^2$$

The square of the multiple correlation coefficient (R^2) was 0.87 indicating that 87 percent of the variability of the independent variables is accounted for by $\hat{y}$. The significance probability of the ratio of the regression mean square to the error mean square was .0001.

Other regression models (II-IV) met the criteria set for a prediction equation for fluometuron in soil but were rejected as inferior to Model I for the purposes of this study. Various characteristics of these models as compared with Model I are listed in Table 6.

Model II had the advantage of simplicity and would require less time for data collection than Models I and IV. The R^2 value was much lower, however, than for any other model. In addition, bioassay oat seedlings did not respond to < 0.5 ppmw of fluometuron at rating period three as distinctly as at later rating periods.

Model III was the best single-variable model developed in this study. Model I was selected over Model III because two observations were considered by the investigator to be less susceptible to human error than one observation. Also, indicator oat seedlings exposed to ≥ 1 ppmw showed distinct phytotoxicity at the second rating period. This rating is included in Model I but not in Model III.

Table 6. Regression Models for Fluometuron in Soil

Model No.	R^2 Value	Variables and Terms
I	0.87	Visual ratings #2 and #4 and their squares
II	0.70	Visual rating #3
III	0.84	Visual rating #4 (log concentration)
IV	0.93	Three visual ratings and two water-use periods with their quadratic and cubic terms.

Model IV had a higher R^2 than any other equation which met the criteria for addition and retention of variables. It had the added advantage of including two types of measurements among its independent variables. Model IV would require more than twice as much data as Model I. Calculations involving Model IV would be prohibitive without a computer. The difference in R^2 values for the models is 6 percent. Model I is more in keeping with the objective of developing simple residue prediction equations; therefore, it was selected in preference to an equation with a higher R^2.

In addition to the prediction equation for fluometuron in soil which was developed from bioassay data, an equation for the same purpose was calculated from ultraviolet absorbance data. Peak height was the independent variable. The square and cube terms of peak height were generated for the calculation; however, the best equation developed included only the linear term of peak height. This linearity of UV absorbance agrees with the findings of Davidson and coworkers (12). The equation produced in this study from spectrophotometer data for predicting fluometuron concentrations in soil was $\hat{y} = 0.225 + 44.57$ peak height with a R^2 value of 0.91.

2,4,5-T in soil. Regression equations for predicting concentrations of 2,4,5-T in soil were calculated for the amine and the ester formulation separately for both the 24-hour and 48-hour incubation periods. These calculations were repeated for the formulations combined for each incubation period. An equation which met the criteria for entrance and

retention of independent variables into the equation was calculated for each formulation-incubation time combination. Because of the tendency of different formulations of 2,4,5-T which are released in the soil environment to undergo beta oxidation and become a common moiety (2), a prediction equation for both formulations was selected for use in this study. The R^2 values of equations based on data from 24-hour and 48-hour incubation periods varied only 5 percent; therefore, a prediction equation based on 24-hour incubation data was selected.

The regression equation selected for prediction of concentrations of 2,4,5-T in soil was based on the independent variable root extension (RE). The R^2 was 0.70. The equation included the linear, quadratic, and cubic terms of the independent variable as follows:

$$\hat{y} = 4.8149 - 0.5076RE + 0.0178RE^2 - 0.0002RE^3$$

One model which met the specified criteria was developed from the linear term of root extension. Another acceptable model included the linear and quadratic terms of root extension. The respective R^2 values were 0.51 and 0.67. When the common logarithm of concentration was regressed on root extension and on percentage of roots deformed the R^2 values were 0.64 and 0.67, respectively.

The correlation coefficient for root extension and root deformation was -0.87 and was significant at $P < .0001$. Because of the high correlation between the two independent variables and the high degree of association between each independent variable and the dependent variable, root deformation did not contribute significantly ($P < .01$) to a

prediction equation which included root extension. The converse was also true (i.e., root extension did not contribute to an equation which included deformation).

Fluometuron in water. The regression equation calculated for predicting fluometuron concentration in water was based on UV absorbance at $240^{\pm}$ 5 nm. The equation follows: $\hat{y} = 0.080 + 29.548$ peak height. The associated R^2 value was 0.91. This equation was utilized in predicting fluometuron concentrations in water from the field plots and percolation water from the lysimeters.

2,4,5-T in water. Peak height (PHT) from chromatography of a series of 2,4,5-T standards was the independent variable in the regression equation. The quadratic and cubic terms were generated. The R^2 of the equation selected for predicting concentrations of the ester and amine formulations was 0.95. The equation was $\hat{y} = -21.008 + 3.694PHT + .005\ PHT^2$. The R^2 of the linear equation for peak height was 0.94, but the intercept term was -175.9. One of the disadvantages of using prediction equations rather than rating systems or visual reading from a standard curve is prediction of nonzero values for the control by a regression equation with a large intercept term.

Herbicide Residues in Field Soils

Concentrations of phytotoxic materials in the soil varied among herbicide compounds, concentrations applied, sampling depths, and days elapsed since herbicide application. Fluometuron residues were generally present in higher concentrations than 2,4,5-T residues.

Fluometuron Detected by Bioassay

In the surface centimeter of soil on the second and seventh days following fluometuron application an average of 6.9 ppmw of fluometuron was detected by an oat bioassay. The treatments were significantly different from the control on days 2 and 7 but not different on day 60 (Table 7). The 2.2 + 2.2 kg/ha plots had less residue on day 7 than on day 2. For all treatments combined, fluometuron residue in the 0-1 cm soil level was approximately 20 times greater on day 7 than on day 60.

Fluometuron residues varied among the three depths tested on day 14 following application (Table 8). There were no differences among application rates. When residues were averaged across depths, all rates were significantly different from the control. On day 210 (Table 8) there were no differences among treatments or depths when tested at the .05 level of probability. When tested at $P < 0.1$ there was more fluometuron at 30-45 cm in the 2.2 + 2.2 kg/ha respray plots than in any other combination of depths and treatments on day 210.

On day 14 and on day 210 fluometuron residues in the 0-15 and 30-45 cm depths were equal, but the amount in each zone was greater than the amount in the 15-30 cm zone. Much of the difference can be accounted for in terms of organic matter and clay content of the soil at the three depths when the data are separated by days. On day 14 residue concentrations for each application treatment followed the same pattern as the combined data (Table 8). There was more compound in the upper and lower depth zones than in the intermediate zone

Table 7. Fluometuron Residues in Etowah Silt Loam (0-1 cm) on Three Dates Following Herbicide Application

Application Rate	Sampling Day		
	2	7	60[1]
kg/ha	ppmw		
2.2	6.74a[2]	6.74a	.32c
2.2 + 2.2[3]	7.14a	5.91b	.29c
4.4	7.14a	7.14a	.41c
Control	.06c	.08c	.09c

[1]When residue data were analyzed for day 60 alone the treatments were different from the control at the 0.3 level of probability.

[2]Values followed by the same letter do not differ at the .05 level of probability using Duncan's Multiple Range test. Residue detected by bioassay.

[3]Split applications of 2.2 kg/ha applied on day 0 and repeated on day 61.

Table 8. Fluometuron Residues in Three Depth Zones of Etowah Silt Loam on Two Dates Following Application

Application Rate	Depths (cm) 0-15	15-30	30-45	Means
kg/ha	ppmw			
	Day 14			
2.2	1.18a[1]	.02b	.65a	.61y
2.2 + 2.2[2]	.75a	.02b	.76a	.51y
4.4	.85a	.20b	.64a	.57y
Control	.05b	.09b	.09b	.09z
$\bar{x}$ of rates (w/o control)	.93p	.07q	.68p	
	Day 210			
2.2	.09a	.09a	.14a[3]	.11y
2.2 + 2.2[2]	.06a	.09a	.29a[3]	.15y
4.4	.09a	.09a	.09a	.09y
Control	.09a	.09a	.09a	.09y
$\bar{x}$ of rates (w/o control)	.08p	.09p	.17p	
	Combined Days			
Overall means	.51p	.08q	.43p	

[1]Values within a day or within a set of means followed by the same letter are not different ($P < .05$). Tested by Duncan's Multiple Range test. Residue detected by bioassay.

[2]Split applications of 2.2 kg/ha applied on day 0 and repeated on day 61.

[3]This value is different from all others in day 210 when tested at $P < 0.1$.

(15-30 cm). These differences cannot be adequately explained with the information gained in this study; however, some observations can be made. The herbicide was applied to the soil surface and the plots received three inches of moisture before day 14. Thus, the upper zone had more direct exposure to the herbicide than did the other depths. The organic matter level of the 0-15 cm zone would be expected to be greater than in either of the other two zones. Darding and Freeman (11) considered organic matter to be the major factor which accounts for retention of phenylurea herbicides in a given soil. The presence of organic matter may account for the higher concentration of compound in the 0-15 cm zone than in the 15-30 cm zone, but it would have a negative influence on the rate of residue migration to the 30-45 cm zone. Increasing concentration at greater depths is a function of the amount available for migration, the depth to which the moisture wetting front penetrates (13), and degradation forces (30).

On day 210 the residue concentration for the 2.2 + 2.2 respray treatments in the 30-45 cm zone was statistically different from the two zones above it at the 0.1 level of probability but not at the .05 level (Table 8). Because the concentration detected in the lower zone was observed to be distinctly more phytotoxic to oat seedlings in the bioassay than the concentration in the other two zones, the difference is biologically significant and therefore will be discussed. There were no differences among depths for the 2.2 or 4.4 kg/ha application rates on day 210.

The second application of 2.2 kg/ha of fluometuron was made to the predesignated plots 60 days following the initial application. Samples taken on day 210 contained herbicidal material which had been exposed to the soil-crop environment for 150 and 210 days. No phytotoxic residues were detected in the 0-15 or 15-30 cm zones. The residues present in the 30-45 cm zone may be a function of the average moisture wetting front during the season. If as much or more herbicide was retained in the 15-30 cm depth zone as at 30-45 cm, the lesser amount present on day 210 may indicate a differential in microbial and/or chemical detoxification rates in the two zones. Harris (27) obtained similar depth differential results with triazines and fenac.

When data from days 14 and 210 are compared by depths (Table 9), it is apparent that compound retained at the earlier date in the 0-15 and 30-45 cm zone plus that added on day 61 was detoxified or otherwise dissipated before day 210.

Comparison of fluometuron soil residues detected by UV and bioassay. Fluometuron residues were detected by the UV spectrophotometer method in soil samples collected from the 0-1 cm depth on days 2, 7, and 62. There were no statistical differences among UV peak heights or among fluometuron concentrations predicted by the regression equation in plot soils sampled from 0-1 cm on day 60 and from three depths on day 14 and day 210. The treatments were not different from the controls. This is in contrast to the results of the oat bioassay on the same samples.

Fluometuron concentrations as low as 0.75 ppmw were detected by the UV method from concentrations of fluometuron in soil. The UV method

Table 9. Comparison of Fluometuron Residues in Three Depth Zones of Etowah Silt Loam[1]

Days Following Application	Depth	Fluometuron Residue Amount
	cm	ppmw
14	0-15	.94a[2]
210	0-15	.08b
14	15-30	.07b
210	15-30	.09b
14	30-45	.68a
210	30-45	.17b

[1]Treatments are as shown in Table 8, page 53. Residue detected by bioassay.

[2]Values followed by the same letter are not statistically different, $P < .05$. Duncan's Multiple Range test. Average of three replications of three treatments. Control excluded.

is valid for fluometuron concentrations as low as those detected by oat bioassay in field soils collected from the 0-15 cm depth on day 14 (Table 8, page 53). Two possible explanations for the discrepancy between fluometuron concentrations detected by UV and bioassay are: (1) the UV spectrophotometer method is not consistently sensitive at $\leq$ 1 ppmw; or (2) the fluometuron in the field plot soils had been sufficiently modified in structure by day 14 to be nonabsorbent at $240^{\pm}$ 5 nm wave lengths although still biologically active.

2,4,5-T residues in field soil--bioassay. Residues of amine and ester formulations of 2,4,5-T were detected in the 0-1 cm depth of Etowah silt loam on days 2 and 7 following application. There were no differences among residue levels of 2,4,5-T, regardless of formulation (amine or ester) or application rate (2.2 or 4.4 kg/ha) (Table 10). Residue levels of each application rate within each formulation and of both formulations were statistically different from the control on days 2 and 7.

There were no residues of the amine or ester of 2,4,5-T in the 0-1 cm soil depth 60 days after herbicide application (Table 10). The dissipation of the large amounts present on day 6 can be attributed to the interaction of all the chemical, physical, and biological forces which are known to transport and detoxify 2,4,5-T. Downward movement into the soil profile, movement in runoff water, movement in association with soil particles such as occurs in sheet erosion, and microbial degradation are some of the major forces which could feasibly have acted on the 2,4,5-T

Table 10. Residues of Two Formulations of 2,4,5-T in Etowah Silt Loam (0-1 cm) on Three Dates Following Herbicide Application

Sampling Day	Application Rate (kg/ha) 2.2	4.4	Control
	ppmw		
	Amine		
2	2.73a[1]	3.62a	.17b
7	3.40a	3.28a	.22b
60	.17b	.25b	.22b
	Ester		
2	3.07a	3.43a	.21b
7	3.25a	3.65a	.19b
60	.24b	.18b	.24b

[1]Values within the amine or ester followed by the same letter do not differ at the .05 level of probability. Duncan's Multiple Range test. Residue detected by bioassay.

present on day 7 (2,33). The first three factors are discussed in this paper.

In soil samples collected from the 0-15, 15-30 and 30-45 cm depths on day 14 there was more 2,4,5-T residue of the ester formulation in the 0-15 cm zone of the 4.4 kg/ha rate plots than in any other treatment level or soil depth for either formulation (Table 11). No other residue concentrations were different from the control on day 14. A residue level of 1.64 ppmw was predicted by the curvilinear regression equation for the ester 4.4 kg/ha treatment in the 0-15 cm zone as compared with .07 ppmw predicted for the control. This rather substantial level (1.64 ppmw) had dissipated by day 210. On day 210 there were no residues of 2,4,5-T detected at any of the three depths under any treatment.

Due to the ionic nature and resultant high water solubility of the amine and the converse for the ester, more ester than amine was expected to be retained near the application site. The solubility factor could also account for more ester in the upper soil zone than in the deeper zones. The solubility differential between the amine and ester formulations should be reflected in the relative amounts of the two formulations in runoff water. These comparisons are discussed in the field water section of this paper.

Field soil residues: all compounds. When soil residues of fluometuron, 2,4,5-T amine, and 2,4,5-T ester were compared, fluometuron was generally present in greater amounts than either of the other

Table 11. Residues of Two Formulations of 2,4,5-T in Three Depths of Etowah Silt Loam 14 Days After Application to the Soil Surface

Sampling Depth	Application Rate (kg/ha)		
	2.2	4.4	Control
cm	ppmw		
	Amine		
0-15	.25a[1]	.23a	.18a
15-30	.16a	.18a	.09a
30-45	.20a	.13a	.16a
	Ester		
0-15	.24a	1.64b	.07a
15-30	.21a	.12a	.15a
30-45	.17a	.25a	.17a

[1]Within a formulation values followed by the same letter do not differ at the .05 level of probability. Duncan's Multiple Range test. Residues detected by bioassay.

compounds (Figure 2). The exception occurred on day 14. Ester residue in the 0-15 cm soil zone was equal to fluometuron concentration in depths 0-15 and 30-45 cm and greater than fluometuron in the 15-30 cm zone (Table 12). As discussed in the section on 2,4,5-T in the soil, the ester residue exceeded the amine on day 14. On this date the concentration of fluometuron in the 15-30 cm zone and amine in all depth zones was like the control.

On days 2 and 7 fluometuron residue levels were greater than either phenoxy at the .05 level of probability (Figure 2 and Table 13). Concentration means across all treatments ranged from 3.00 ppmw for 2,4,5-T amine to 7.01 ppmw for fluometuron. There were no differences among treatments. Residue levels were not different from the control on day 60 (Table 13). No phenoxy residues were detected in soil sampled on day 210. Fluometuron residue values for the 2.2 + 2.2 kg/ha respray application in the 30-45 cm soil zone exceeded the control on day 210 when tested at the $P < 0.1$ level of probability.

Toxicity Symptoms in Voles

No toxicity symptoms were detected in voles which were live-trapped in the treated plots.

2,4,5-T and Fluometuron in Sediment

Sediment under water was assayed for phenoxyacetic acid residues on days 7, 60, 70, and 80 following herbicide application. Statistical analysis of root measurement showed that root extension was inhibited [compared with the control ($P < .05$)] by residue in sediment collected

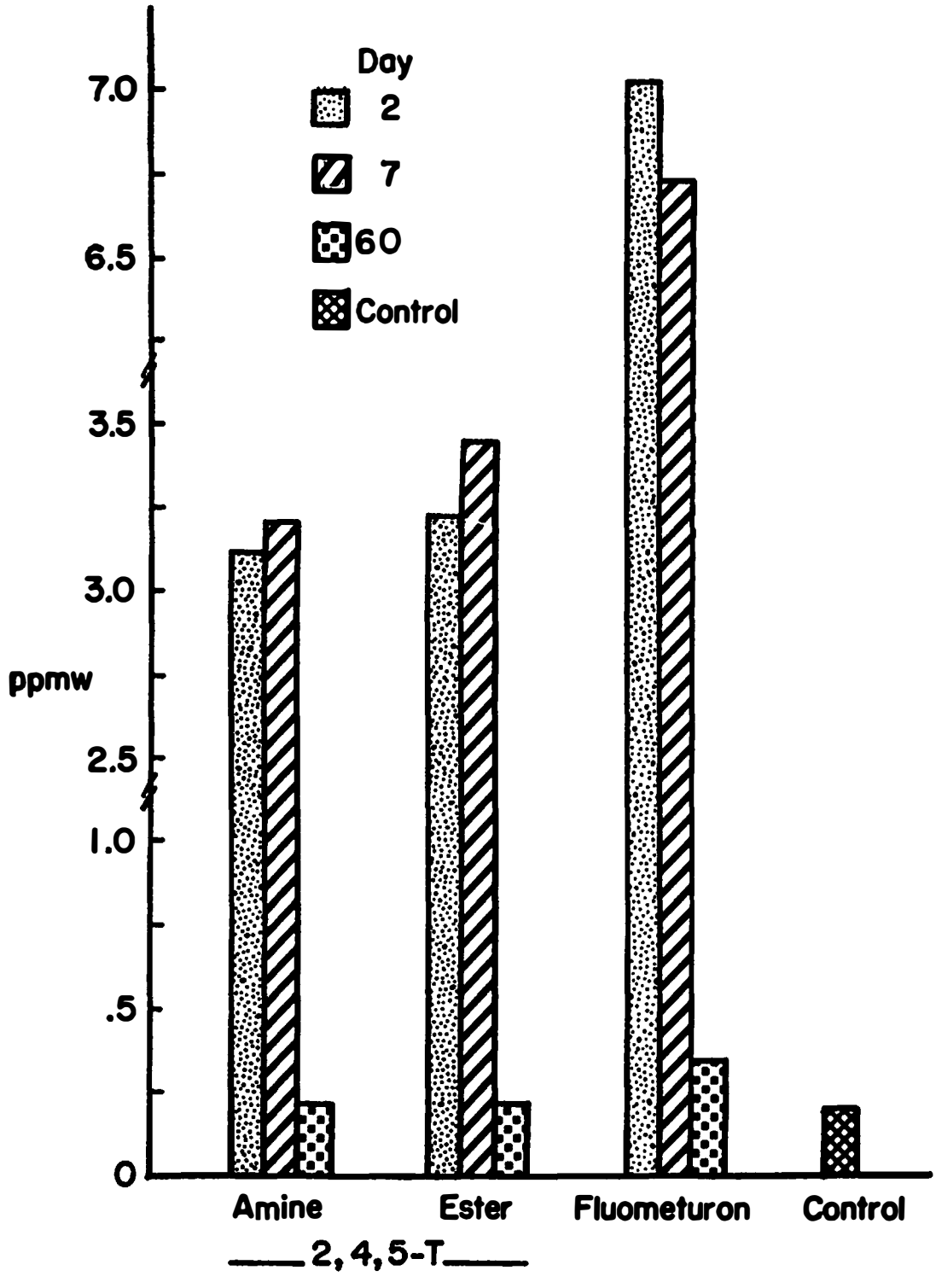

Figure 2. Herbicide residues in 0-1 cm depth of Etowah silt loam on three dates following surface application. Average of three rates. Concentrations were predicted from the regression equation from the respective bioassay data sets.

Table 12. Residues of Three Compounds in Three Depth Zones of Etowah Silt Loam 14 Days Following Herbicide Application to the Soil Surface

Herbicide Compound	Sampling Depths (cm)		
	0-15	15-30	30-45
	ppmw		
Fluometuron	.93a[1]	.08b	.68ab
2,4,5-T, Ester	.70ab	.20b	.17b
2,4,5-T, Amine	.24b	.17b	.17b
Control	.18b	.16b	.13b

[1]Each concentration is the mean of three replications. Values followed by the same letter are not different, $P < .05$. Tested by Duncan's Multiple Range. Residues detected by bioassays.

Table 13. Residue Concentrations of Three Compounds in Etowah Silt Loam (0-1 cm) on Three Different Days Following Application

Herbicide Compound	Sampling Day 2	7	60
	ppmw		
Fluometuron	7.01a[1]	6.60a	.34c
2,4,5-T, Ester	3.15b	3.39b	.23c
2,4,5-T, Amine	3.00b	3.18b	.21c
Controls $\bar{x}$	.16c	.12c	.14c

[1]Each concentration is the mean of three replications of three treatments. Values followed by the same letter are not different at the .05 level of probability as tested by Duncan's Multiple Range. Residue detected by bioassay.

from all treated plots on day 7 and in sediment collected on day 70 from the 2.2 + 2.2 kg/ha respray plots. When the prediction equation which was developed for 2,4,5-T concentrations in soil was applied to the root extension measurements for sediment, the concentrations predicted by the regression equation did not differ from the control (Figures 3 and 4). The ester and amine formulations inhibited root extension equally in the sediment study. There were no differences between treatments and controls either by root extension measurements or predicted residue concentration in sediment collected on days 60 and 80. In references to the discrepancies between root inhibition and predicted residue concentrations on days 7 and 70, it appears that the prediction equation which was developed on normal field soil was not valid for use with sediment. Residue concentrations of the 2,4,5-T formulations in sediment under impounded water are compared with concentrations in the 0-1 cm soil zone in graph form in Figures 3 and 4. There was a low degree of association between the amount of residue in the 0-1 cm soil zone and the amount in the sediment trapped in the catchment tank for the given plot one to three weeks later.

No fluometuron was detected by UV absorbance or bioassay in sediment washed from the field plots.

2,4,5-T and Fluometuron in Field Plot Water

Residues of 2,4,5-T in field plot water varied between collection sources and between formulations. On days 7 and 60 there was more 2,4,5-T in the permanently impounded water than in the recent runoff

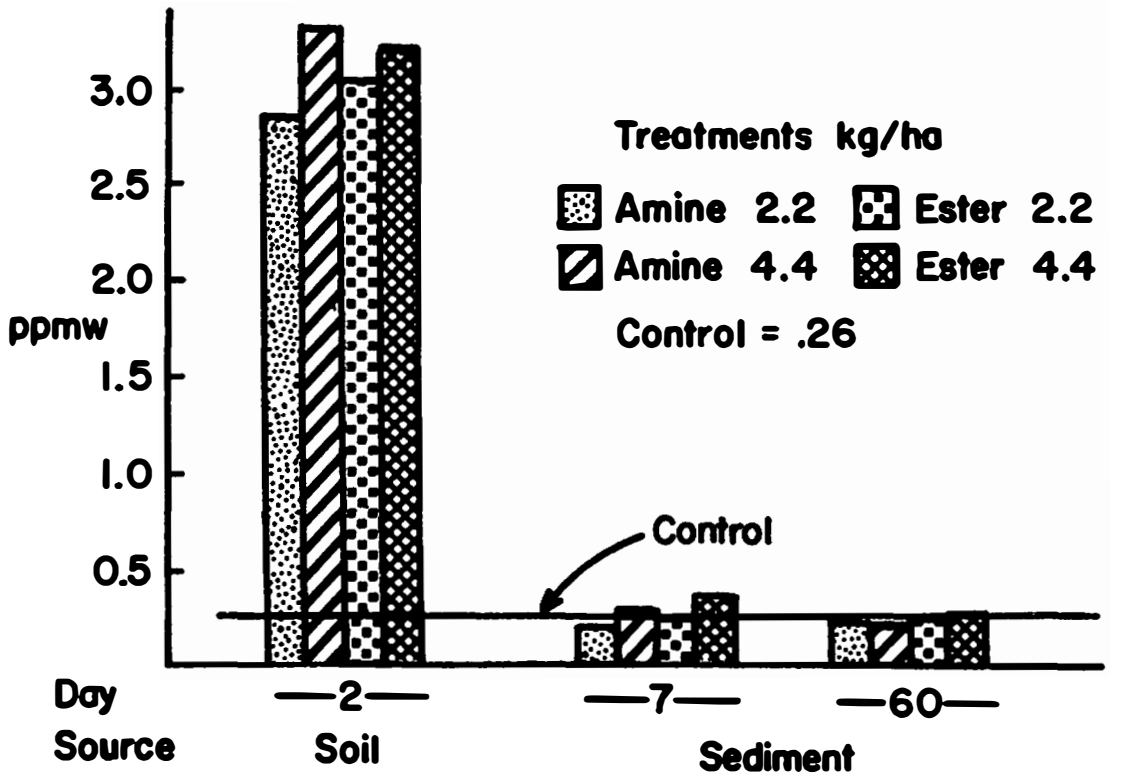

Figure 3. 2,4,5-T in 0-1 cm soil and in sediment under impounded water. Concentrations were predicted by regression equation developed from cucumber root bioassay data.

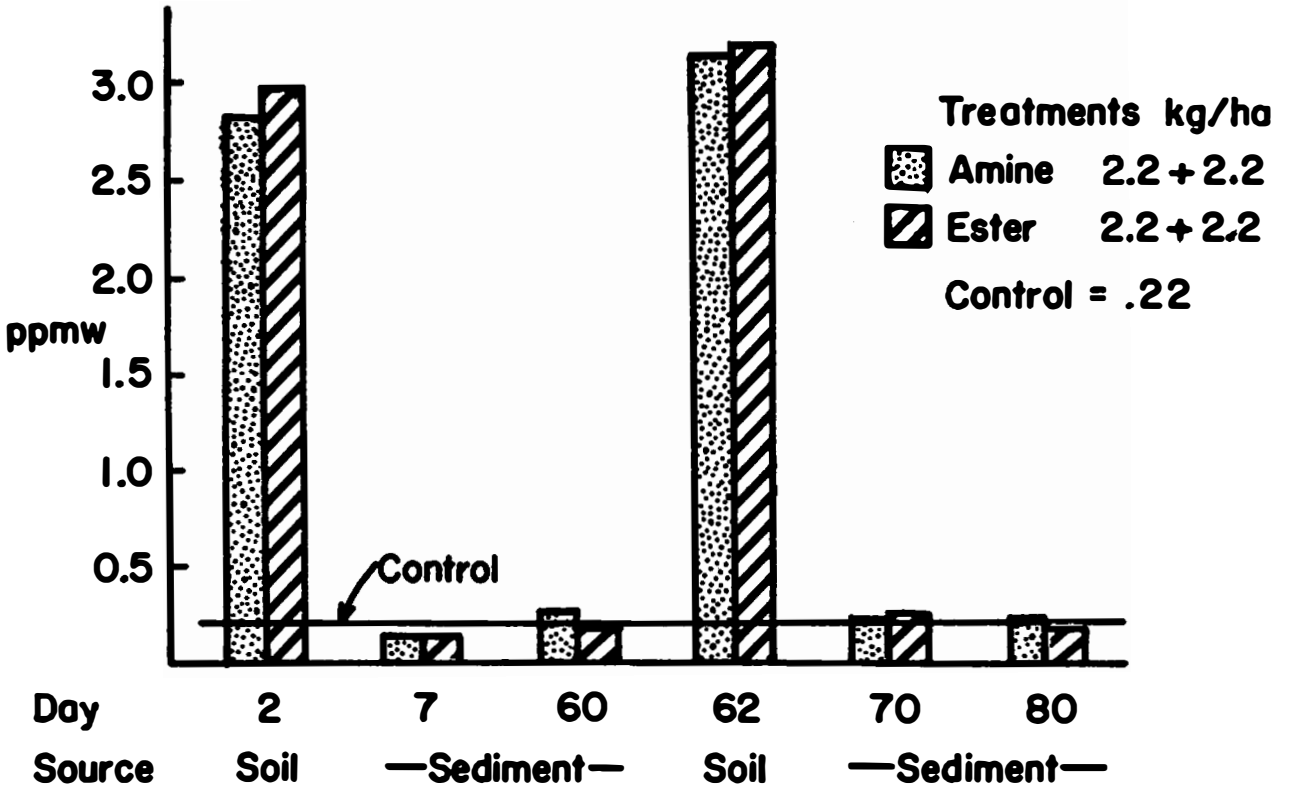

Figure 4. 2,4,5-T in 0-1 cm of respray plots and in sediment under impounded runoff water. Residues detected by cucumber root bioassay. Concentrations predicted by regression equation developed from bioassay standard curve.

water (Table 14). The mean residue level for all treatments was higher in impounded water on day 7 than in impounded water on day 60 (Table 15). The range of concentrations on the two days ranged from a high of .083 ppmw in the 4.4 kg/ha ester treatment on day 7 to .010 ppmw in the 2.2 kg/ha amine treatment on day 60. Many differences were identified among samples of impounded water for the two days (Table 15); however, very few trends were established with the limited number of replications involved. Probably the most important trend observed over time was the relatively increased amount of ester as compared with amine in the impounded water on day 60. The formula by day interaction was significant at the 0.1 level of probability (Figure 5). The increase in ester residue in water over time relative to the amine was influenced by rate of runoff from the plots and the difference in rate of loss from the impounded water. The water soluble amine may have been lost from the impoundment more readily than the less soluble ester because of water overflow from the tubs during high intensity rain storms which occurred in June of 1972.

When all sampling dates were considered together within or across days, there were no differences among treatment rates. There were differences between days 7 and 60 for all treatments of both formulas (Table 16). Residue levels in water from the respray plots distinctly increased within ten days after treatment with the second 2.2 kg/ha of 2,4,5-T (Table 17). There was more 2,4,5-T in the fresh runoff source on day 70 than in the permanent impoundment. The level of amine in runoff exceeded the level of ester in the same source. There was more

Table 14. Comparison of Water Collection Sources on Concentration of 2,4,5-T Where Each Mean in the Table Represents Three Replications of Three Treatments of Two Formulations

Source[1]	Collection Day[2]	2,4,5-T Concentration ppmw
Runoff	7	.005a[3]
Impounded	7	.048b
Runoff	60	.006a
Impounded	60	.026c
Control		0a

[1]"Runoff" was collected in cups buried in the plots. "Impounded" refers to water collected in galvanized tubs buried at the lowest corner of each bordered plot.

[2]Number of days following herbicide application.

[3]Means followed by the same letter are not different at the .05 level of probability as tested by Duncan's Multiple Range. Residue detected by gas chromatography.

Table 15. Residues of Amines and Esters of 2,4,5-T in Permanently Impounded Water from Etowah Silt Loam Field Plots

Treatments Applied	Sampling Days 7	Sampling Days 60	Formulation Means[1]
kg/ha	ppmw	ppmw	ppmw
	Amine		
2.2	.073b[2]	.010j	
2.2 + 2.2	.022gh	.016i	
4.4	.045d	.017h	.031p
	Ester		
2.2	.042e	.030f	
2.2 + 2.2	.022h	.054c	
4.4	.080a	.028g	.043q
Means by days[1]	.048y	.026z	

[1]Independent comparisons were made for each set of two means. Differences between values in a set are indicated by the convention in footnote 2. Residue detected by gas chromatography.

[2]Values, except means, which are followed by the same letter do not differ at the .05 level of probability as determined by Duncan's Multiple Range test.

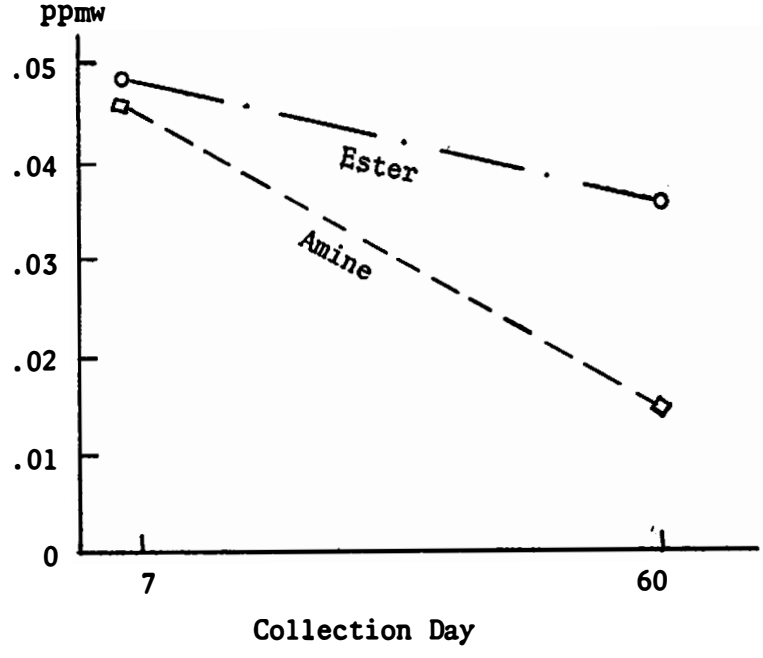

Figure 5. Residue differentials of two formulations of 2,4,5-T in permanently impounded water. The formulation-day interaction is significant at $P < 0.1$, by analysis of variance. Residue detected by gas chromatography.

Table 16. Residues of Amines and Esters of 2,4,5-T in Runoff Water Collected in Buried Cups in Field Plots on Etowah Silt Loam

Treatments Applied	Sampling Days		Sampling Days	
	7	60	7	60
kg/ha	ppmw			
	Amine		Ester	
2.2	.006a[1]	.014a	.002a	.001a
2.2 + 2.2	.005a	.001a	.002a	.003a
4.4	.006a	.001a	.011a	.017a
Control	0a	0a	0a	0a

[1]Values which are followed by the same letter do not differ at the .05 level of probability as determined by Duncan's Multiple Range test. Residue detected by gas chromatography.

Table 17. 2,4,5-T Residues in Runoff Water and Permanently Impounded Water on Day 70[1]

Treatment kg/ha	Formulation	Source	Concentration ppmw
2.2 + 2.2	Amine	Runoff	.131a[2]
	Ester	Runoff	.081b
	Ester	Impounded	.039c
	Amine	Impounded	.031d
Control			0e

[1]Plots were resprayed on day 61 following initial application.

[2]Values followed by the same letter are not statistically different, $P < .05$. Tested by Duncan's Multiple Range test. Residue detected by gas chromatography.

ester than amine in the impounded water source on day 70. No meaningful increase in 2,4,5-T residues in water could be detected 50 days after the second application of 2.2 kg/ha of each formulation to the 2.2 + 2.2 respray plots. The concentrations detected in the respray plots on day 50 were .002 and .003 ppmw, respectively, for amine and ester in impounded water and 0 and .001 ppmw in fresh runoff water. None of these values were statistically different from the control (Table 16).

No 2,4,5-T residues were detected in runoff water or impounded water 250 days following the initial herbicide application. This was 190 days following the respray application.

Fluometuron in Field Water

Due to interference by pentene and perhaps other impurities in the pentane used for extracting fluometuron from water samples, only three collection dates were successfully extracted and scanned in an ultra-violet light source. Permanently impounded water but not fresh runoff water was analyzed from collection day 60. Water samples from both sources and for all treatments for day 110 were analyzed. Water from the 2.2 + 2.2 kg/ha respray plots was analyzed for day 70. Concentrations presented were predicted by a linear regression equation developed from known amounts of fluometuron in glass-distilled water. The equation is:

$$\hat{y} = .0802 + (29.5484) \text{ (Peak Height)}$$

The fluometuron concentrations predicted for day 60 were not different from the control. On day 110 there were differences among treatments for impounded water but not for runoff water (Table 18).

Table 18. Fluometuron Residues in Water from Two Collection Sources in Field Plots on Day 110[1]

Treatment Applied	Sampling Source: Runoff Water Concentration Predicted	Sampling Source: Impounded Water Concentration Predicted
kg/ha	ppmw	ppmw
2.2	2.61a	3.80a
2.2 + 2.2	2.40a	9.08b
4.4	1.82a	3.70a
Control	1.62a	3.46a

[1]The respray application was on day 61.

[2]Values followed by the same letter are not different as tested by Duncan's Multiple Range at P < .05. Residue detected by UV.

Residue levels in the resprayed plots exceeded those in other treatments. Runoff water on day 110 did not vary from the control. Interference from the extracting solvent, decaying organic matter, or both resulted in high predicted values for the controls of both water sources. Variability among replications was higher for runoff water than for impounded water. The concentration predicted for impounded water was greater than the concentration predicted for runoff water when tested at the 0.1 level of probability. The respective concentrations were 5.53 and 2.27 ppmw.

On day 70 samples from both the runoff and impounded water in the 2.2 + 2.2 kg/ha respray treatment contained more fluometuron ($P < .05$) than the control (Table 19). Residues in the impounded water were greater than residues in the runoff water. All values for the treatment exceeded those for the control. No residual fluometuron was detected in field plot water seven months following initial application.

II. LYSIMETER STUDY

Herbicide Residues in Lysimeter Percolation Water

Residues of one or more of the compounds applied to the lysimeter soil were detected in percolation water on six of the seven sampling dates. Fluometuron was present on three of the sampling dates, amine on five, and ester on two (Figure 6). Day 16 following application was the only sampling day on which all compounds were detected on one date. The concentration of fluometuron was greater than the concentration of either formulation of 2,4,5-T on each date.

Table 19. Fluometuron Residues in Runoff Water and Permanently Impounded Water on Day 70 After Initial Application[1]

Treatment Applied	Source	Fluometuron Concentration
kg/ha		ppmw
2.2 + 2.2	Runoff	3.81a[2]
2.2 + 2.2	Impounded	1.46b
Control		0c

[1]The respray application was on day 61.

[2]Values followed by the same letter are not different at the .05 level of probability according to Duncan's Multiple Range test. Residue detected by UV.

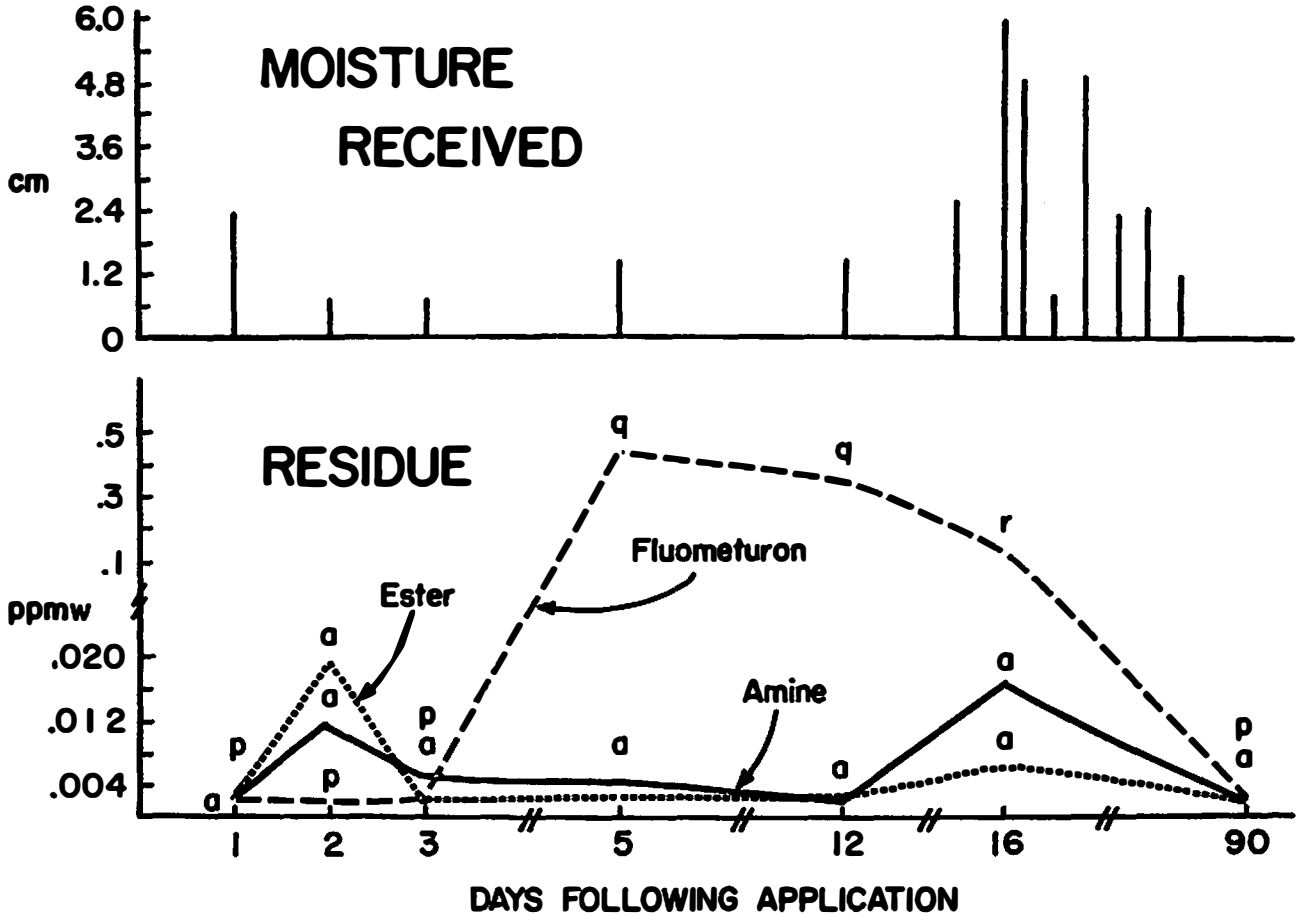

Figure 6. Herbicide concentration in lysimeter percolation water. Cumberland silt loam Ap horizon. Fluometuron detected by UV; 2,4,5-T by GLC. Concentrations predicted by respective regression equations. 2.2 and 4.4 kg/ha rates are combined. Points on a line associated with the same letter are not different ($P < 0.05$). No points on the amine and ester line differ ($P < 0.05$).

Fluometuron. The average concentrations of fluometuron for both treatment rates (2.2 and 4.4 kg/ha) were 0.42, 0.34, and 0.16 ppmw for sampling days 5, 12, and 16, respectively (Figure 6). The concentrations on days 5 and 12 were not different from each other but were significantly greater than the residue concentration on day 16. Fluometuron residues on all three dates were greater than the control ($P < .05$). On day 12 percolation water from the 4.4 kg/ha treatment contained higher residue concentration than the 2.2 kg/ha treatment ($P < .05$). The interaction of application rate and sampling date was significant at the 0.1 level of probability, indicating that the rates did not respond uniformly in relation to each other across dates. The residue from the 2.2 kg/ha treatment numerically exceeded the concentration from the 4.4 kg/ha treatment on day 5. The order was reversed on the other two dates on which fluometuron was present in the lysimeter percolation water.

The "F" value for replications exceeded the "F" value for application rates on each date fluometuron was detected, indicating high variability among lysimeter tanks. This is one of the disadvantages of testing residue movement by percolation in a soil which has been disturbed. Both sources of variance were tested by the replication times application-rate error term. The correlation between UV peak height and the concentration of fluometuron predicted by the regression equation was 0.97 (significant at $P < .001$). These statistics indicate that the regression equation was a highly consistent predictor of fluometuron concentration.

2,4,5-T. There were no differences in concentration between the residues from the amine and ester formulations of 2,4,5-T in the lysimeter percolation water on any of the seven sampling dates. The two treatment levels (2.2 and 4.4 kg/ha) for each formulation were not different ($P < 0.1$). On day 2 both treatments for each formulation were different ($P < 0.1$) from the control (Figure 6, page 78). On sampling day 16 the treatments in the amine and ester were each different from the control when tested at the 0.1 level of probability. The regression equation was a consistent predictor of concentration. The differences among replications were not significant ($P < 0.1$) in data from any sampling date.

Herbicide Residues in Lysimeter Tank Soil

Emergence counts of peas 30 days following application of 2,4,5-T amine were not different from the counts on day 50. When both days were considered, the 2.2 kg/ha rate tanks had significantly more plants ($P < .05$) than the 4.4 kg/ha tanks. Both application rates had fewer plants than the control on day 30 and on day 50.

There was no difference in emergence between the 2.2 and 4.4 kg/ha rates of the ester of 2,4,5-T. The higher rate was different from the control on day 30 ($P < .05$). Significantly less residual phytotoxicity of the ester existed on day 50 than on day 30. Plant emergence counts were not statistically different for the amine and ester formulations of 2,4,5-T.

Visual ratings of oat seedlings were lower for the 4.4 kg/ha rate of fluometuron on day 30 than for the 2.2 kg/ha rate on day 30 or day 50. The rating for the 2.2 kg/ha treatment was not different from the control on day 30. Residues from the 2.2 and 4.4 kg/ha rates were greater than the control on day 50 ($P < .05$). There were no rate-day interactions among herbicide compounds in the lysimeter *in situ* bioassay study.

CHAPTER V

SUMMARY AND CONCLUSIONS

I. APPROACH TO THE HERBICIDE RESIDUE STUDY

This research was conducted in four major phases: field plots; lysimeter; bioassay; and chemical and physical analyses. Fluometuron and an amine and ester formulation of 2,4,5-T were applied to field plots. Phytotoxicity to forage sorghum was estimated, and forage yields were compared with crop stand in the various treatments. Water, soil, and sediment samples were collected for residue analysis. Two types of bioassays were utilized for detecting soil residues. Ultraviolet spectrophotometry and gas-liquid chromatography were used to detect residues in water. Prediction equations were derived from known concentrations of the herbicides. Concentrations in field samples were estimated by applying the prediction equations to residue data.

The herbicides which were applied to field plots were also applied to lysimeter soils. Percolation water was collected from the lysimeters and analyzed in the same way as field-plot water. Residues in the lysimeter soils were compared by toxicity ratings and plant survival in an *in situ* bioassay.

II. PREDICTION EQUATIONS FOR RESIDUAL HERBICIDE CONCENTRATIONS

The prediction equation for fluometuron in soil included visual ratings from two 48-hour growth periods of oat seedlings in a pot bioassay.

Eighty-seven percent of the variability in concentration in the standards was accounted for by these two ratings. Cucumber root extension during a 24-hour exposure to known concentrations of 2,4,5-T in a petri dish bioassay was the only independent variable included in the prediction equation for 2,4,5-T in soil. The R^2 value of the regression equation was 0.70. A linear equation was derived for the regression of fluometuron concentration in water on ultraviolet absorbance. The linear and quadratic terms were included in the regression equation selected for predicting 2,4,5-T in water. The R^2 values for the fluometuron and 2,4,5-T water residue prediction equations were 0.91 and 0.95, respectively.

III. FORAGE SORGHUM CROP STAND AND YIELD

The forage sorghum stand was reduced by all treatments of fluometuron, 2,4,5-T amine, and 2,4,5-T ester. Fluometuron reduced the sorghum stand to 70-80 percent of the control. The 2,4,5-T formulations reduced stand to 30-55 percent of the control. Stand reduction in the treated plots did not lower forage yields as compared with the weedy and weed-free control plots. The mean yield for both cutting dates in all treatments and controls was 824 g/m^2. The lack of correlation between stand and yield in the treatments in which plant population was reduced and the similarity in yield between the treated plots and weedy control indicate that neither chemical nor mechanical weed control was necessary for maximizing forage yield in this study. The success of the weedy control (untreated) in competing with noncrop species is attributed to

the early competitive advantage of the evenly distributed high population and inherent rapid growth rate of the forage sorghum cultivar.

IV. FIELD SOIL RESIDUES

Concentrations of fluometuron and the amine and ester formulations of 2,4,5-T decreased with time from the application dates. Fluometuron was generally present in higher concentrations than either formulation of 2,4,5-T at each depth and date. An average of 3.4 ppmw of the amine and ester of 2,4,5-T was present in the 0-1 cm soil zone on the seventh day following application. Residues of the ester formulation of 2,4,5-T were detected on the fourteenth day in the 0-15 cm soil depth. No 2,4,5-T remained in the 0-1 cm zone on day 60 nor at any depth of the soil profile from 0-45 cm after seven months.

Fluometuron in the 0-1 cm depth decreased from 6.0 ppmw on day 7 following application to a level not different from the control on day 60. Fluometuron varied among depths but not among treatments on day 14. More fluometuron was present in the 30-45 cm zone than in the 15-30 cm zone. As would be expected, within 14 days of application there was more residue in the 0-15 cm depth zone than in the deeper zones. The herbicide concentration in the 30-45 cm zone indicates the depth to which the compound had leached in percolating water in the 14 days after application to the soil surface. The concentration in the 0-15 cm depth as compared with deeper zones can be explained on the basis of the higher organic matter content in the surface soil. Greater fluometuron persistence in soil was usually associated with the soil zone with highest organic matter content.

On day 210 the fluometuron concentration in the 30-45 cm zone of the 2.2 kg/ha respray treatment was higher than the concentration in the 0-15 and 15-30 cm zones. The additional herbicide carried to the deeper zone following respray apparently was not degraded to a nontoxic form within 150 days. This soil zone is below the area of maximum microbial activity, thus disappearance would be due primarily to percolating water.

Fluometuron residue levels in field plot soil as determined by UV methods coincided with the concentrations estimated from bioassay detection methods on days 2 and 7 following herbicide application. No fluometuron residue was detected by UV absorbance from day 14 samples. Two possible explanations for the discrepancy between methods on day 14 are: (1) the UV method is not consistently sensitive at < 1 ppmw; or (2) the fluometuron in the field plot soils had been modified in structure by day 14 to the extent that it was nonabsorbent at 240 nm wavelength although still biologically active.

V. RESIDUAL HERBICIDE IN SEDIMENT

The equation developed for estimating 2,4,5-T in soil was not valid when applied to cucumber root response to 2,4,5-T residue in sediment under water. Sediment washed from the treated plots within ten days of 2,4,5-T application contained residues which inhibited cucumber root extension. The phytotoxicity had dissipated within two weeks following its detection. No fluometuron residue was detected in sediment by UV absorbance or oat bioassay.

VI. HERBICIDE IN FIELD PLOT WATER

The average concentrations of amine and ester formulations of 2,4,5-T in fresh runoff water and permanently impounded water were 0.005 and 0.037 ppmw, respectively. There were no residue differences ($P < .05$) between the treatments and the control when runoff water from individual rains was tested for 2,4,5-T. Residues of the amine formulation in impounded water decreased from day 7 to day 60 following application to the plot surfaces. Residues of the ester in impounded water increased during the same period of time. Two opposing forces of input and outgo operate to determine residual levels of biodegradable compounds. The ester formulation of 2,4,5-T which was carried to the water trap in the time period between seven and sixty days following herbicide application exceeded the amount which was degraded by chemical and biological forces acting on the compound carried into the water trap before day 6. The converse was true for the amine. More herbicide disappeared from the impounded water than entered during the same time period.

More amine than ester may have been lost in overflow from the catchment tubs during the time period between day 7 and day 60. This possibility is consistent with the difference in water solubility of the two formulations. The less soluble ester would remain adsorbed to the sediment carried into the catchment tub and thus tend to settle to the bottom with the sediment rather than being carried out in the overflow water. No comparisons can be made in this study between

residue concentration in water and sediment under the water because of the difficulty encountered in quantifying the residue amount in sediment. A very small amount of the herbicide detected in the field plot moved into the impounded water and sediment. The ester formulation of 2,4,5-T disappeared more slowly from the sediment than from the 0-1 cm of soil.

The concentrations of fluometuron in water samples collected following the initial application were not determined due to interference from impurities in the extraction solvent. No fluometuron was detected in impounded water 60 days following application to the soil plots. Runoff and impounded water collected from the 2.2 + 2.2 kg/ha treatment ten days following respray contained 3.8 and 1.5 ppmw of fluometuron. On day 110 impounded water contained more fluometuron than did fresh runoff water. Fresh runoff water in treated plots on day 110 was not different from water in the control plots. No residual fluometuron was detected in field plot water seven months following initial application. Fluometuron was degraded as rapidly in water as it was in soil or in sediment under water.

VII. HERBICIDE RESIDUES IN LYSIMETER PERCOLATION WATER AND SOIL

Residual 2,4,5-T occurred in lysimeter percolation water over a longer number of days than fluometuron. Fluometuron concentrations in water were greater than 2,4,5-T concentrations. The amine and ester formulations and treatment rates of 2,4,5-T responded alike in percolation water. Five to sixteen days following application fluometuron was

leached from the 20-cm deep lysimeter soil layer by percolating water. No 2,4,5-T or fluometuron were detected in lysimeter percolation water 90 days following herbicide application to the soil surface.

Variability among lysimeter tanks was greater than variability among herbicide treatments on some sampling days, but the lysimeter system in which the soil had not been disturbed for 30 years was considered to be more nearly like a field soil profile than a newly packed laboratory percolation column would have been.

Bioassay plants grown in the lysimeter tanks indicated that toxic material was present 30 and 50 days following herbicide application. These residues would be expected to dissipate at the same rate as the residue in the field plots. No residual phytotoxicity would be expected after seven months.

VIII. GENERALIZATION

Generally there were no differences in residual herbicide concentrations among application treatments. Phytotoxic levels of all three compounds within two weeks of application dates were indicated by crop stand reduction, response of indicator plants, and by chromatographic and spectrophotometric methods. Phytotoxic levels of the herbicide applied at the beginning of the crop season did not persist in the field plots beyond the growing season. On the basis of the rate of disappearance of the initial application, fluometuron residues from the respray treatment would be expected to dissipate before the next crop season. The herbicides did migrate from the application site in runoff water,

percolation water, and sediment washed from the soil surface; however, these residues in nontarget regions disappeared as rapidly as the residues on the original test plots. This study indicates that the field environmental characteristics measured were not permanently modified by the fluometuron and 2,4,5-T treatments which were applied.

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APPENDIX

APPENDIX

Table A-1. Climatic Data Pertaining to Plant Science Farm, University of Tennessee, Knoxville, 1972[1]

Date	Rainfall[2]	Temperature[3]		Evaporation[4]
		Max.	Min.	
	in.	-------F--------		in.
May 1		79	55	.18
2		81	62	.22
3	.98	79	59	.11
4	1.03	68	52	.20
5		67	48	.13
6		75	48	.22
7		80	54	.19
8	.27	80	59	.20
9	.13	67	59	.07
10		69	48	.23
11		68	49	.28
12		74	50	.20
13	.29	80	57	.16
14	1.19	63	58	.23
15	.50	78	59	.13
16		78	55	.12
17		78	56	.28
18		77	55	.23
19		79	55	.17
20	.09	74	57	.14
21	.47	73	58	.01
22		76	63	.11
23	1.04	81	58	.01
24		80	57	.33
25		81	58	.29
26		85	61	.29
27		76	57	.06
28		76	62	.18
29		80	61	.21
30		80	60	.11
31	.18	79	61	.18
June 1		69	45	.11
2		73	48	.38
3		80	54	.26
4		86	59	.24
5		85	64	.16

Table A-1. (continued)

Date	Rainfall[2]	Temperature[3] Max.	Temperature[3] Min.	Evaporation[4]
	in.	-------F--------		in.
June 6		92	66	.24
7	2.00	87	63	.32
8		83	58	.26
9		86	68	.27
10	.29	81	64	.17
11		76	49	.19
12		76	51	.23
13		82	68	.23
14		86	63	.24
15		89	67	.27
16		90	69	.28
17	.22	82	69	.12
18		81	65	.07
19	.13	86	67	.25
20	.45	82	65	.23
21		80	68	.22
22		80	60	.23
23		73	55	.30
24		77	57	.31
25		84	57	.10
26		85	74	.07
27		85	63	.27
28	3.05	87	64	---
29	1.40	74	64	---
30	.14	84	61	.14
July 1		84	63	.20
2		87	68	.21
3	.34	83	68	.39
4		83	68	.15
5	2.03	79	63	.26
6		73	57	.15
7		75	55	.26
8		81	58	.13
9		84	63	.38
10	.80	84	64	.10
11		85	65	.26
12		87	67	.37
13		89	69	.32
14		89	66	.31
15		87	72	.40

Table A-1. (continued)

Date	Rainfall[2]	Temperature[3] Max.	Temperature[3] Min.	Evaporation[4]
	in.	-------F--------		in.
July 16	.15	88	71	.25
17	.34	82	71	.03
18	.39	84	67	.17
19		88	70	.21
20	.15	90	67	.15
21		90	72	.24
22		91	75	.20
23		93	73	.26
24		93	72	.19
25	.06	93	70	.29
26	.35	87	69	.19
27		89	70	.19
28	.74	86	69	.26
29	1.00	78	69	.09
30	.46	80	69	.18
31	.22	83	68	.11
Aug. 1	.03	84	66	.19
2	.02	84	69	.12
3	1.47	85	67	.45
4		88	74	.22
5		89	70	.21
6		83	67	.16
7	.05	85	70	.19
8	.05	87	65	.16
9	.16	83	66	.13
10	.52	79	67	.30
11	.02	80	67	.09
12		85	69	.19
13		84	69	.19
14		86	67	.18
15		88	68	.23
16		87	67	.32
17		91	71	.21
18		87	72	.33
19		90	71	.24
20		92	71	.14
21		91	69	.15
22		88	68	.19
23		88	67	.25
24		80	67	.23

Table A-1. (continued)

Date	Rainfall[2]	Temperature[3] Max.	Temperature[3] Min.	Evaporation[4]
	in.	F	F	in.
Aug. 25		88	69	.19
26		88	72	.17
27		90	74	.23
28		86	64	.30
29		83	63	.19
30		86	63	.23
31		87	66	.19
Sept. 1		83	63	.19
2	.21	84	60	.19
3		86	61	.06
4		79	66	.18
5	.43	73	61	.20
6		78	58	.10
7		81	60	.19
8		80	58	.21
9		82	66	.20
10		84	59	.32
11		83	63	.26
12		84	61	.17
13		86	57	.19
14		90	64	.19
15		86	63	.17
16		86	67	.20
17	.23	73	68	.14
18	.67	80	67	.07
19		86	66	.19
20		86	63	.05
21		80	61	.19
22		80	64	.14
23		82	64	.10
24	.06	82	64	.07
25		80	60	.15
26		81	65	.22
27	.99	73	68	.06
28	.63	80	67	.07
29	.60	79	67	.26
30	1.35	67	45	.12

[1]Data Source: Environmental Data Service, National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

Table A-1. (continued)

[2]Data collected at Plant Science Farm, University of Tennessee.

[3]Data collected at McGhee-Tyson Airport.

[4]Measured in standard Weather Service-type pan of 4-foot diameter, Plant Science Farm, University of Tennessee.

Table A-2. Monthly Climatic Data for May-December, 1972 Knoxville, Tennessee[1]

Data	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Temperature (F)[2]								
Average	64.9	70.8	75.5	75.9	71.9	56.8	47.7	44.8
Departure from normal	-2.8	-4.9	-2.9	-1.5	-.3	-4.1	-1.2	3.2
Rainfall[3] (in.)	6.17	7.73	7.03	2.32	5.17	6.80	4.05	8.94
Evaporation[4] (total in.)	5.47	6.60	6.90	6.57	4.85	---	---	---
Soil temperature[5] at 4 inches (F)								
Maximum	84	93	98	92	89	72	66	53
Minimum	51	54	59	68	61	38	32	29
Average	66	74	78	79	74	57	46	41
Percentage of possible sunshine[2]	56	64	56	66	54	52	37	25
Average relative humidity (percent)[2]								
7:00 A.M.	81	80	92	94	96	91	81	84
1:00 P.M.	59	52	66	63	65	67	63	74

[1]Data Source: Environmental Data Service, National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

[2]Data collected at McGhee-Tyson Airport.

[3]Data collected at Plant Science Farm, University of Tennessee.

[4]Measured in standard Weather Service-type pan of 4-foot diameter, Plant Science Farm, University of Tennessee.

[5]Under bare ground, Cumberland silty clay loam, 6 percent slope to east, Plant Science Farm, University of Tennessee.

Table A-3. Climatic Data Pertinent to Lysimeter Study March, 1973 Knoxville[1]

March 1973	Rainfall[2]	Air Temperature[2]	
		Max.	Min.
	in.	----------F----------	
1	---	56	33
2	T	62	38
3	.49	60	49
4	---	64	47
5	.56	71	52
6	T	75	50
7	.11	74	55
8	---	65	55
9	---	76	57
10	---	75	52
11	---	76	52
12	.73	67	53
13	---	77	44
14	---	78	43
15	1.07	82	60
16	3.30	69	57
17	1.90	60	38
18	.01	45	35
19	---	56	33
20	.01	64	36
21	.61	53	37
22	.10	42	31
23	---	52	33
24	---	58	40
25	.11	67	46
26	.04	69	49
27	.14	57	48
28	---	60	45
29	.17	69	49
30	.11	59	48
31	.52	71	54
Total	9.99	65	46

Percent of possible sunshine for month of March - 40

[1]Data Source: Environmental Data Service, National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

[2]Data collected at University of Tennessee Main Campus Station.

VITA

Glenn Gray Davis was born in Jackson County, Arkansas, August 23, 1936. His parents are M. Henry and Nola Gray Davis. He attended a rural elementary school in Randolph County, Arkansas, and was graduated from Pocahontas High School in 1954. He pursued a preagriculture education program at Harding College in 1954-1955 and at Abilene Christian College from 1955 to 1957. He completed the requirements for the Bachelor of Science degree in Agricultural Education at Texas Technological College in 1959. He taught vocational agriculture in the Happy, Texas, Public Schools in 1959-60 and taught science courses in the Abilene Public Schools in 1960-62.

In 1962 he accepted a position as Instructor in Agriculture at Lubbock Christian College and served in that capacity until 1970. During this period he enrolled in the Graduate School of Texas Technological College and received the Master of Science degree with a major in Agronomy and a minor in Entomology in 1965. In the fall of 1970 he began a three-year leave of absence from Lubbock Christian College for graduate study at the University of Tennessee. He received the Doctor of Philosophy degree with a major in Plant and Soil Science and a minor in Ecology in December 1973. He is a member of the Weed Science Society, Sigma Xi, Phi Sigma, Gamma Sigma Delta, and Phi Kappa Phi.

He is married to the former Freda Sue Paxson of Monroe, Oklahoma. They have two children, Suzanne and Lanette.