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Effects of Water on the Fate of Herbicides in Irrigated Soils

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Citation

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UNIVERSITY OF ARKANSAS
Fayetteville

PROJECT COMPLETION REPORT

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EFFECTS OF WATER ON THE FATE
OF HERBICIDES IN IRRIGATED SOILS

by

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<u>Research Objectives</u>:

1. To determine the significance of herbicide leaching in irrigated soils.

2. To determine the importance of herbicide degradation rate in the field.

3. To determine the effects of soil moisture on the loss of volatile herbicides.

<u>Degree of Completion of Project Objectives</u>:

Leaching aspects of three herbicides was investigated for two locations in Arkansas by burying herbicide treated soils in open 14-cm long sections of 12.7-cm pvc conduit. After 18 months the extent of leaching was determined by comparing soil in the conduit with similarly treated soils in which water was not allowed to pass through the soil (details are presented in pages 22-26 of dissertation I).

Factors affecting herbicide degradation rate was intensively evaluated. Considerable new information has evolved; it is anticipated that this area will produce four papers for publication in refereed scientific journals (details are presented in pages 32-50 of the first dissertation and 26-30, 45-47, and 75-77 of the second dissertation).

The dissipation of pendimethalin, the most volatile of the six herbicides studied, was evaluated using gas chromatography and bioassay detection methods. Both laboratory and field experiments were conducted to further evaluate the disappearance of this volatile herbicide. (A detailed discussion of these studies may be found in pages 18-30 of the second dissertation.)

Research procedures used in these studies are presented in a detailed fashion in the accompanying dissertations.

Listing of Significant Results or Conclusions:

1. A comparison of the mobility of three herbicides revealed that metri-
    buzin would be more likely to leach downward in the soil under
    irrigated conditions than would fluometuron or metolachlor.

2. Leaching is less likely to occur when herbicides are in the top 15 cm
    of the soil profile. Soil at the 45-cm depth is considerably less
    adsorptive.

3. Degradation of herbicides is slower in the winter than in summer
    months.

4. Degradation of pendimethalin was greater in a soil where alternate
    flooding and drying treatments were used as compared to a soil kept
    at field capacity or to a soil kept under continuously flooded condi-
    tions.

5. Oxadiazon appeared to break down relatively fast as measured by a
    fescue bioassay; however, gas chromatographic analyses revealed that
    a considerable amount of the parent herbicide was still present but
    not available to the bioassay plants.

Publications:

The following list represents papers that have been or plan to be
submitted to Weed Science for scientific publication (status is listed in
parentheses).

1. Fate of Metribuzin, Metolachlor, and Fluometuron in Soil. D.C.
    Bouchard, T.L. Lavy, and D.B. Marx (In press).

2. Effects of Soil Water Content on Pendimethalin Dissipation. M.R.
    Barrett and T.L. Lavy (In Departmental Review).

3. Effects of Soil Water Content on Oxadiazon Dissipation. M.R. Barrett
    and T.L. Lavy (Paper being revised).

4. Atrazine Dissipation Rates in Anaerobic and Aerobic Soil Moisture
Regimes. M.R. Barrett and T.L. Lavy (Paper in preparation).

Description of Potential Applications:

All herbicides are somewhat soluble in water. An excess use of water
for irrigation purposes can result in the downward movement of herbicides
in the soil profile. Subsoils are less adsorptive, and a decreased degra-
dation potential exists when herbicides move below the top 15 cm. In
sandy soils, or other areas where extensive irrigation is planned, it is
prudent to attempt to choose a herbicide with high adsorptive capacity
and low water solubility.

If a farmer after-the-fact determines that he has a herbicide carry-
over problem, it is possible to employ a series of wetting-drying cycles to
enhance the dissipation of the herbicide. This practice will be more
beneficial for some herbicide-soil combinations but should be a practical
solution for many.

This research has clarified the fact that water plays a vital role in
increasing the dissipation rate of many of the pesticides which we use to
achieve our high levels of agricultural productivity.

Acknowledgements:

ABSTRACT

EFFECT OF WATER ON THE FATE OF HERBICIDES IN IRRIGATED SOIL

The wide use of soil-applied herbicides necessitates an understanding of
their fate in soil if we are to use them in the most beneficial manner.
All herbicides have some degree of water solubility and the field perfor-
mance of many are dependent on ample, timely availability of soil moisture.
It is important that different aspects of soil-herbicide-water inter-
actions be thoroughly investigated. An excess use of water for irrigation
purposes can result in the downward movement of herbicides in the soil
profile. Subsoils are less adsorptive and a decreased degradation poten-
tial exists when herbicides move below the top 15 cm. In sandy soils, or
other areas where extensive irrigation is planned it is prudent to
attempt to choose a herbicide with high adsorptive capacity and low water
solubility. Leaching of metribuzin, metolachlor, and fluometuron was an
important dissipation process for each of the chemicals over the winter
months when degradation was slow. Pendimethalin dissipation was greater
in alternatively flooded and dried soil than with soil water content at
1/3 bar tension or with a continuous flood. In a laboratory degradation
study, over 59% of the oxadiazon persisted after 20 weeks. In a green-
house study its biological activity was reduced and its persistence in-
creased when applied below the soil surface.

Appendices

Dissertation A: The Adsorption, Mobility, and Degradation
                  of Metribuzin, Metolachlor, and Fluometuron
                  in Two Arkansas Soils.

Dissertation B: Effects of Soil Water Content on the Dis-
                  sipation of Pendimethalin, Oxadiazon, and
                  Atrazine.

Dissertation "A"

THE ADSORPTION, MOBILITY, AND DEGRADATION OF

METRIBUZIN, METOLACHLOR, AND FLUOMETURON

IN TWO ARKANSAS SOILS

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

DERMONT CHARLES BOUCHARD, B.S.
Arizona State University, 1979

August, 1981
The University of Arkansas

ACKNOWLEDGEMENTS

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ABSTRACT

The wide use of soil-applied herbicides necessitates an understanding of their fate in the soil. The adsorption of metribuzin, metolachlor, and fluometuron on a Taloka silt loam and a Roxana silt loam from the 15-cm and 45-cm soil depths was measured using a soil slurry technique. The order of adsorption of the herbicides was fluometuron = metolachlor > metribuzin. Adsorptivity of the soil from 15 cm was greater than the soil from 45 cm. The order of mobility of the herbicides in soil columns was metribuzin > fluometuron > metolachlor. All herbicides were more mobile in the soil from 45 cm than from 15 cm. Degradation of the herbicides in constant temperature chambers at 7, 15, 23, and 37 C was independent of initial herbicide concentration. All herbicides degraded more rapidly with increasing temperature. Metribuzin was most labile followed by fluometuron and metolachlor which were similarly persistent in most treatments. The time required for the initial herbicide concentration to decrease by 50 percent in the Taloka silt loam from 15 cm at 23 C was 2.6, 9.4, and 10.1 weeks for metribuzin, fluometuron, and metolachlor, respectively. A buried herbicide experiment designed to study degradation and leaching of the herbicides under field conditions corroborated the laboratory work. In the buried herbicide experiment, metribuzin degraded rapidly, and metolachlor and fluometuron were moderately persistent. Degradation was slower during the winter and at the 45-cm depth for all herbicides. Leaching was important in the dissipation of all herbicides, especially over winter when degradation was slow.

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INTRODUCTION

Since the inception of primitive agriculture, man's domesticated crops have had to compete with other less desirable plants for the light, water, and nutrients essential for growth. Somewhere in time, man discovered the efficacy of removing this competition from his fields. From that point man has toiled to control the growth of weeds, first with the sweat of his brow and a crude hoe, now with tractor-drawn plows and synthetic organic herbicides.

Modern herbicides may be directly applied to the target weed as a postemergence treatment or to the soil as a preemergence or preplant treatment to control the weed. The interaction of the herbicide with the soil is important in determining the efficacy of weed control and the fate of the chemical in the environment (1,11,25,26,37,39). Therefore, knowledge of the chemical and the soil and their effects on each other is requisite for safe, effective herbicide use. This thesis attempts to add to this knowledge by investigating the adsorption, mobility, and degradation of three soil-applied herbicides--metribuzin (4-amino-6-_tert_-butyl-3-(methylthio)-_as_-triazin-5(4_H_)-one), metolachlor(2-chloro-_N_-(2-ethyl-6-methylphenyl)-_N_-(2-methoxy-1-methylethyl)acetamide), and fluometuron(1,1-dimethyl-3-(α, α, α -trifluoro-_m_-tolyl)urea). The research presented here includes a buried herbicide experiment used to study degradation and leaching of the herbicides at two locations and two soil depths, and laboratory studies to assess the adsorption, mobility, and degradation of the herbicides under controlled conditions.

Fluometuron is a substituted urea herbicide used to control small seeded grasses and broadleaf weeds in cotton (_Gossypium hirsutum_ L.) and sugarcane (_Saccharum officinarum_ L.). Substantial work has been

done to describe the adsorption (16,22,31), mobility (6,17,21), and degradation (5,13,24,28,34) of fluometuron in the soil. However, fluometuron use in Arkansas, the northern limit of cotton's range, poses some special problems. Cotton must be planted in early spring to provide a long enough growing season for maturation. Cold, wet weather and the subsequent loss of cotton stands often require growers to switch for a season to an alternate crop, such as soybeans, that can mature in a shorter time. In some instances, fluometuron residues have been suspected of being the cause of poor stand establishment of the second crop (33).

Metribuzin is an asymmetrical triazine herbicide used to control small seeded grasses and broadleaf weeds in soybeans (Glycine max L.), potatoes (Solanum tuberosum L.), and sugarcane. Most of the research on metribuzin has shown it to be non-persistent in the soil (14,20,30, 41). Adsorption and mobility studies have indicated that metribuzin is weakly adsorbed on many soils and is mobile (15,24,32). Mobile chemicals pose problems in the soil environment when they are leached from the site of application to groundwater or to lower soil depths where degradation is slower (10).

Metolachlor is a relatively new acetanilide herbicide used to control grasses in corn (Zea mays L.). Substantial work has been done with other members of the acetanilide family (3,35,38); however, few papers on metolachlor have been published, and what have been published have dealt primarily with metolachlor's weed control efficacy and persistence in soil (7,35). Additional adsorption, mobility, and persistence research would increase our understanding of this chemical.

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MATERIALS AND METHODS

Adsorption. The adsorption of metribuzin, metolachlor, and fluometuron
on a Taloka silt loam from Fayetteville and a Roxana silt loam from
Alma, Arkansas, was evaluated using a soil slurry technique similar to
that described by Talbert and Fletchall (36). Soils from the 15-cm and
45-cm depths at both locations were air-dried and passed through a
495-μm sieve, and 0.5 g of soil was weighed into a 10-ml screw top cen-
trifuge tube. The water content by weight, θ_w, of the air-dried soil
was 1% ± 0.5%. Technical grade herbicide solutions spiked with the ^{14}C
analogs were made up in .01M $CaCl_2$ so that a 5.0-ml aliquot of solution,
when added to the 0.5 g of soil, would give the following concentrations:
0.12, 0.25, 0.50, 1.00, 2.00, and 4.00 ppmw. Tables 1 and 2 show the
properties of the soils and herbicides used. The herbicide solutions
were added to the soil in the centrifuge tubes, and the tubes were capped
and placed on a rotary shaker at 6 rpm for 24 hours to allow the soil-
herbicide system to reach equilibrium. A kinetics study conducted earlier
had shown that equilibrium was reached by 24 hours. After 24 hours on
the shaker, the centrifuge tubes were spun at 2000 rpm for 5 minutes, and a
1-ml aliquot of the supernatant was taken and counted with a Packard 2650
liquid scintillation spectrometer, utilizing automatic external standard
ratio determination and a quench curve obtained by counting a set of
quenched ^{14}C standards. By comparing the activity (dpm/ml) of the super-
natant with activity of the initial solution, the change in herbicide
concentration of the solution was determined. The change was assumed to
be due to adsorption by the soil. To determine the change in solution
concentration, a standard containing the herbicide solution and no soil
was used to account for adsorption on the centrifuge tube and cap:

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Table 1. Chemical and physical properties of soils used in study.

Soil	Depth	pH	Cation exchange capacity	Sand 2000-50μ	Silt 2-50μ	Clay <2μ	Organic matter
	(cm)		(meq/100g)	--------------(%)--------------			
Taloka silt loam, fine, mixed, thermic, Mollic Alba-	15	5.2	11	23.4	67.5	9.1	1.1
aqalf	45	5.5	13	24.2	62.0	13.8	0.7
Roxana silt loam, coarse-silty, mixed, nonacid, thermic, Typic	15	6.8	19	22.0	62.2	15.8	0.9
Udifluvent	45	7.1	19	30.7	54.7	14.6	0.5

Table 2. Properties of herbicides used in study.

Herbicide	Molecular weight	Purity of technical material	Specific activity of ^{14}C labelled herbicides	Position of label
		(%)		
Metribuzin	214.3	99.6	20.7uCi/mg	carbonyl C
Metolachlor	283.8	97.2	26.3uCi/mg	u-ring
Fluometuron	232.1	99.6	10.3uCi/mg	u-ring

dpm standard - dpm equilibrium solution = dpm adsorbed

The solution activity was converted from dpm/ml to actual herbicide concentration, and the data were expressed as μmoles of herbicide adsorbed/kilogram of soil and μmoles of herbicide/liter of equilibrium solution.

A plot of the amount of herbicide adsorbed versus equilibrium solution concentration at constant temperature (20 C in this experiment) yields an adsorption isotherm. Many researchers have found that over a limited range of concentrations adsorption isotherms can be adequately described by the Freundlich equation (2,4,23,31):

$$x/m = KC^{1/n}$$

In this equation x is the amount of chemical adsorbed per unit weight of adsorbent m, C is the equilibrium solution concentration of the chemical, and K and n are constants. The Freundlich equation is more easily visualized in the linear form by taking the logarithm of both sides of the equation:

$$logx/m = 1/nlogC + logK$$

In a plot of logx/m versus logC, 1/n is the slope of the isotherm and logK is the y intercept. Therefore, the value of K represents the amount of chemical adsorbed at unit concentration of the equilibrium solution. The K values, or distribution coefficients, are useful parameters to compare the adsorption of soil-herbicide systems. The higher the K value, the greater the degree of adsorption. The slope of adsorption isotherms, 1/n, has often been found to be equal to one (8,27). In this experiment the data were tested to see whether they fit the Freundlich equation, 1/n was tested for divergence from unity, and K values were compared using the Newman-Keuls test for significant differences.

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Mobility in soil columns

A soil column study was conducted to compare the mobilities of metribuzin, metolachlor, and fluometuron in a Taloka silt loam from the 15-cm and 45-cm soil depths and a Roxana silt loam from the same depths. Soil columns were constructed from 2.5-cm long sections of 2.5-cm i.d. plexiglass tubing (0.6-cm wall thickness). Lanolin was used to waterproof the joints between sections and seven sections were joined with duct tape to form an 18.0-cm long column. The column base, a 5.0-cm flat section (0.3 cm thick) of plexiglass with three 0.3-cm diameter drilled holes, was permanently bonded to a section of column. A piece of Whatman #1 filter paper was used to cover the base plate holes, and 15 g of air-dried soil (θ_w = 1%) was placed in the bottom section of the column. All soil was air dried and passed through a 0.5-mm sieve before use. The 15 g of soil was treated with a 5.0-ml aliquot of methanolic herbicide solution to give a concentration of 1 ppmw. Technical grade herbicides were used to prepare the solutions which were spiked with the ^{14}C herbicide analogs to give an activity of 20,000 dpm/ml. The methanol was allowed to evaporate for 24 hours before the columns were uniformly filled with 105 g of untreated soil. The average soil bulk densities in the columns for the Taloka silt loam from the 15-cm and 45-cm depths were 1.40 and 1.45 g/cm^3, respectively. For the Roxana soil from the 15-cm and 45-cm depths the average soil bulk densities were 1.34 and 1.38 g/cm^3, respectively. Two replicated columns were prepared for each soil-herbicide combination.

The bases of the columns were immersed 0.5 cm deep in 500 ml of water in 1-liter beakers. The beakers and bottom halves of the columns were then enclosed in polyethylene bags to ensure that all water loss

From the system would be from water that had moved up through the soil and evaporated from the tops of the columns. The columns were placed in a hood with air sweeping lightly across the tops. After 48 hours, the columns were sectioned, and soil in each section was homogenized by manually mixing the soil in a petri dish. Two 2-g samples from each section were added directly to 15 ml of dioxane counting solution (7 g PPO, 50 mg POPOP, 100 g napthalene, 1000 ml dioxane) in a 20-ml glass scintillation vial. The vials were shaken on a rotary shaker at 150 rpm for one hour. The soil particles were allowed to settle for 24 hours, and then the samples were counted with a Packard Tri-Carb 2650 liquid scintillation spectrometer utilizing automatic external standard ratio determination and a soil-acetone quench curve. This method of direct soil counting has been described by Lavy (19).

The dpm per column were normalized so that the sum of activity in the seven column sections equalled one. The normalized values were weighted by multiplying by the numbers one through seven, one for the section that contained the initially treated soil (bottom of the column), two for the adjacent section, and up through seven for the top section of the column. The sum of the weighted values for each herbicide-soil combination may be designated as the mobility factor for that combination as described by Harris who developed this method (9). The range of mobility factors possible in this experiment was one (no movement) to seven (maximum movement).

The effects of soil moisture on the extraction of herbicide from soil using the direct soil counting technique used in the column study were determined. In this experiment, 2 g of air-dried soil was weighed

into scintillation vials, and a 0.5-ml aliquot of ^{14}C spiked methanolic herbicide solution was pipetted onto the soil to give a concentration of 1 ppmw. The methanol was allowed to evaporate for 24 hours, and then water was added to give a θ_w of 1% (no water added), 26% (0.5 ml water added), and 51% (1.0 ml water added). The soil-water-herbicide systems were allowed to equilibrate for 24 hours, then 15 ml of diox-ane counting solution was pipetted into the vials, and the samples were counted as in the column study. The extraction efficiency was deter-mined by dividing final dpm of the sample by initial dpm and multiply-ing by 100.

Degradation at constant temperature

An experiment was set up to study the effects of temperature, autoclaving of soil, and initial herbicide concentration on the degradation rate of metribuzin, metolachlor, and fluometuron. Taloka silt loam from the 15-cm and 45-cm soil depths was passed through a 1.0-cm sieve. Soil aliquots weighing 650 g were placed in doubled polyethylene bags and treated with 10 ml of aqueous herbicide solution to give the following concentrations: metribuzin at 0.3 and 0.6 ppmw; metolachlor at 5.0 and 10.0 ppmw; and fluometuron at 0.5 and 1.0 ppmw. Controls treated with 10 ml of distilled water were also included. The bags containing the soils were then shaken by hand to evenly distribute the herbicides in the soils. After treatment, the Θ_w of the soils was 15%. The polyethylene bags were then sealed with twist ties and placed in constant temperature chambers at 7, 15, 23, and 37 C. A set of soil samples that had been steam autoclaved at 107 C and 20 psi for 2 hours per day over 4 days before treatment with herbicide solution were included in the 23 C treatments.

The soils were checked periodically for changes in θ_w, and water was added when needed to maintain the soils at the initial water content. After 4, 2, or 1 month, the soils were removed and analyzed for herbicide residues. All analyses for herbicide residues were plant bioassays grown for 30 days in a greenhouse. The 650 g of soil was removed from the polyethylene bags and placed in 1-quart plastic pots with individual saucers. The use of individual saucers allowed for alternate subirrigation and top watering of the bioassay plants without cross contamination of treatments. The metribuzin and fluometuron treatments were planted with six cucumber (<u>Cucumis</u> <u>sativas</u> L.)

seeds and thinned to four plants after emergence. The metolachlor

treatments were planted with fifteen pearl millet (_Pennisetum_

typhoides Burm.) seeds and thinned to ten plants after emergence.

Half of the controls were planted to cucumber and half to pearl millet.

Standard curves were prepared by plotting plant dry weight versus herbi-

cide concentration (Figure 1). An index of visual ratings was also pre-

pared by relating type and degree of plant injury to herbicide concentra-

tion (Table 3). Each time that bioassay plants were grown, standards at

zero concentration of herbicide (controls) and at the concentration that

gave GR_{50} were included to monitor any changes in the original standard

curve and visual rating index due to changes in the greenhouse environ-

ment at different times of the year. To determine the concentration of

herbicide in a sample, a composite measurement was obtained using the

visual rating of the plants and plant dry weight. Relating the visual

rating and plant dry weight to the appropriate visual rating index and

standard curve yielded two concentration values which were averaged. The

data were expressed in final form as a plot of herbicide concentration

versus time. The time necessary for the initial herbicide concentration

to decrease by 50 percent was determined graphically and these values

were compared using the Newman-Keuls test for significant differences.
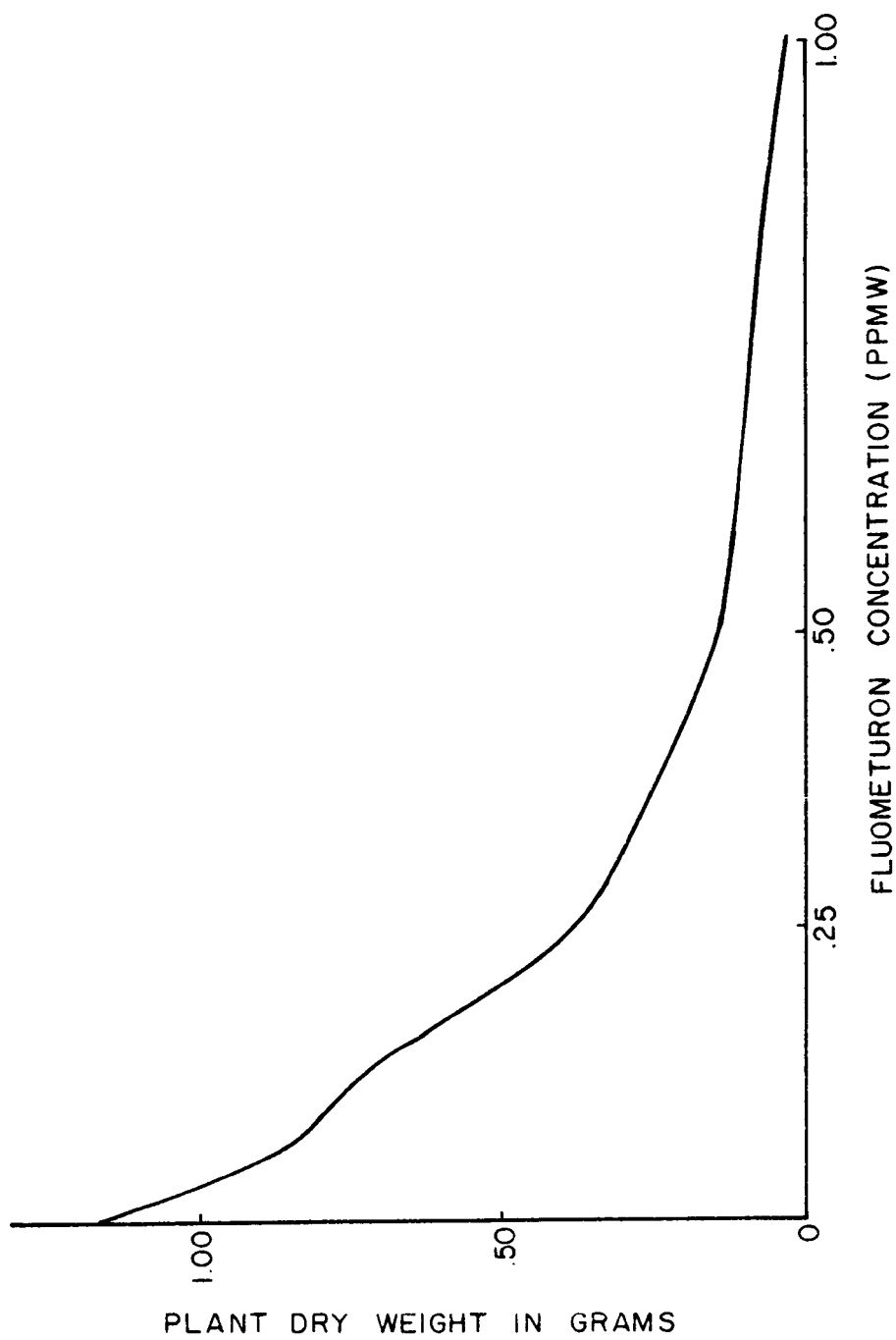
Figure 1. Standard curve relating plant dry weight to fluometuron concentration in Taloka silt loam from the 15-cm soil depth.

Table 3. Visual rating index of fluometuron injury on cucumber in Taloka silt loam from the 15-cm soil depth.

Fluometuron concentration (ppmw)	
0	no effects
0.03	very slight (< 1mm) marginal chlorosis on oldest leaves
0.06	slight (1-2mm) marginal chlorosis on oldest leaves
0.12	moderate (2-3mm) marginal chlorosis on oldest leaves
0.25	moderate marginal chlorosis on oldest leaves, slight chlorosis on youngest leaves
0.50	severe (permeates entire leaf) chlorosis of all leaves, severe stunting of growth
1.00	total kill of plant before first true leaf forms

Buried herbicide study

A buried herbicide study was conducted from October, 1978, to October, 1980, to investigate the effects of geographic location and soil depth on the degradation and leaching of metribuzin, metolachlor, and fluometuron. Taloka silt loam from Fayetteville and Roxana silt loam from Alma, Arkansas, were taken from the 15-cm and 45-cm soil depths and passed through a 1.0-cm sieve. Aliquots of the soils weighing 650 g (o.d. basis) were placed in 13x8x30-cm polyethylene bags and treated with a 10-ml aliquot of herbicide solution to give the following concentrations in the 15-cm and 45-cm soils, respectively—metribuzin at 0.3 and 0.2 ppmw, metolachlor at 10.0 and 6.7 ppmw, and fluometuron at 1.0 and 0.7 ppmw. Under field conditions the concentration of herbicide would usually be lower at the 45-cm soil depth than at the 15-cm depth; therefore, the soil from the 45-cm depth was treated at 2/3 the rate of the soil from 15 cm. Soil not treated with herbicide (controls) was treated with 10 ml of distilled water. The θ_w of the soils after treatment were 12% and 14% for the Taloka soil from 15 cm and 45 cm and 10% and 12% for the Roxana soil from 15 cm and 45 cm. The soils were moist at this water content. After addition of the herbicide solution or distilled water to the soil in the bags, the bags were shaken by hand to distribute evenly the herbicide or water throughout the soil.

The treated soils and controls were placed in quart-size Mason canning jars and situated in a horizontal position in the side of a freshly dug soil pit. The pit was dug 1.5 m deep and 1.5 m wide so that a post hole digger could be used to drill holes in the sides of the pit to accommodate the jars. Each soil treatment was buried at

the same depth from which the soil came, 15 cm or 45 cm. The horizontal orientation of the jars allowed the treated soil to be exposed to the environment of the in situ soil, but would not allow water moving through the in situ soil to leach the treated soil. Thus, these treatments permitted study of herbicide degradation in the field in the absence of leaching.

Treated soil and controls were also placed in 14.0-cm long sections of 12.7-cm diameter pvc conduit sealed at one end with a permeable fiberglass screen. A layer of sand was placed on top of the treated soil in the pvc containers to prevent mixing with the in situ soil. These containers were buried near the Mason jar degradation treatments in a vertical position in 15-cm and 45-cm deep holes dug with a post hole digger. The construction and orientation of the pvc containers allowed the treated soil to be exposed to the environment of the in situ soil and also allowed water moving through the in situ soil to leach the treated soil. Therefore, these treatments permitted study of herbicide dissipation in the field due to both degradation and leaching.

Four complete sets of degradation and degradation and leaching treatments were buried at each location in October, 1978, and in May, 1979, using a randomized complete block design and four replications. In total, the study included 512 degradation treatments in Mason jars and 512 degradation and leaching treatments in pvc containers. The October treatments were dug up and the soil analyzed for herbicide residues in March, May, and October, 1979, and in October, 1980. These treatments allowed for examination of degradation and leaching of the herbicides over a two-year period. The May treatments were dug up

and analyzed during four successive summer months - June, July, August, and September. These treatments allowed for monthly examination of degradation and leaching of the herbicides over the course of a growing season. All analyses for herbicide residues were by plant bioassay as described in the degradation at constant temperature study. The data were also handled in the same way.

RESULTS AND DISCUSSION

Adsorption

Statistical analysis of the data indicated that the adsorption isotherms were linear and that the slopes of the isotherms did not differ significantly from one. The K values, or distribution coefficients, comparing adsorption of the soil-herbicide systems are contained in Table 4.

For all herbicides adsorption was greatest on the Roxana silt loam from 15 cm followed by adsorption on the Taloka soil from 15 cm. The one exception was metolachlor which was adsorbed equally on the Roxana soil from 45 cm and the Taloka soil from 15 cm. The lower adsorptivity of the soils from the 45 cm depth is consistent with the lower organic matter content at these soil depths. Soil organic matter has been found to be highly correlated with the adsorptive capacity of many soils (8,11). Liu and Cibes-Viade found organic matter to be the most important influence on adsorption of metribuzin and fluometuron followed by cation exchange capacity (22). Ciba-Geigy reports that metolachlor is readily adsorbed by soil organic matter (Ciba-Geigy Corp., Greensboro, N.C.). The higher adsorptivity of the Roxana soil from 15 cm for all herbicides and the Roxana soil from 45 cm for metolachlor was unexpected due to the higher organic matter content of the Taloka soil. However, the difference in organic matter was slight, so that the higher adsorptivity of the Roxana soil might be explained by its higher cation exchange capacity and by differences in the type of clay.

Metribuzin was adsorbed least of the three herbicides and would be expected to be mobile in the Taloka and Roxana soils. The range of

Table 4. Distribution coefficients[a] for metribuzin, metolachlor, and fluometuron in Taloka silt loam and Roxana silt loam from the 15-cm and 45-cm soil depths.[b]

Soils	Depth	metribuzin			metolachlor			fluometuron		
	(cm)	K	N	r^2	K	N	r^2	K	N	r^2
Taloka silt loam	15	0.48 b	0.91	0.97	1.15 e	0.87	0.97	1.42 f	0.90	0.99
	45	0.33 a	0.85	0.91	0.57 c	0.93	0.96	0.74 d	0.89	0.96
Roxana silt loam	15	0.66 cd	0.89	0.98	1.82 g	0.88	0.99	1.69 g	0.92	0.98
	45	0.31 a	0.91	0.93	1.26 ef	0.99	0.99	0.65 cd	0.95	0.98

[a]Distribution coefficient = adsorbed herbicide (μmoles/kg soil) at unit concentration of equilibrium solution (1.0 μmolar solution).

[b]Average of three replications. Values followed by the same letter are not significantly different at the 5% level using the Newman-Keuls test.

K values for metribuzin was consistent with Savage's results in 1976 (29). Metribuzin has been shown to be adsorbed less than atrazine (15). Many of the mechanisms that have been proposed to explain the adsorption of s-triazines on organic and mineral colloids involve protonation of the weakly basic s-triazine molecules (8,40). Metribuzin is a weaker base, pK = 1 (15), than any s-triazine so these mechanisms would not be expected to be as important in the adsorption of metribuzin. Also, metribuzin's relatively high water solubility, 1220 ppm at 20 C (42), means that water will compete strongly with the adsorbent for metribuzin, thus decreasing the amount of metribuzin in the adsorbed phase.

Fluometuron was adsorbed more than metribuzin on all four soils and more than metolachlor on the Taloka soils. However, the relatively low K values for fluometuron indicate that fluometuron would also be mobile in the Taloka and Roxana soils. The range of K values for fluometuron was consistent with the results of other workers (31). The adsorption of fluometuron may be accounted for in part by fluometuron's hydrophobic nature as evidenced by its low water solubility, 90 ppm at 25 C (42). In soil, fluometuron will be present mainly as an unionized molecule; however, nonuniform electron distribution in the molecule will cause it to be mildly polar. It has been proposed that the carbonyl oxygen of fluometuron can form a weak electrostatic bond with an adsorbed cation or a water molecule coordinated with the cation (16). Other weak bonding mechanisms have been proposed (8).

Metolachlor was adsorbed more than metribuzin on all four soils and was adsorbed more than fluometuron on the Roxana soil from 45 cm. Metolachlor was adsorbed to the same degree as fluometuron on the Roxana soil from 15 cm, although at the 10% level of significance

metolachlor was adsorbed to a greater degree. Metolachlor, like fluo-
meturon and metribuzin, would be expected to be mobile in the Taloka and
Roxana soils. These results are consistent with most other research
(7,38).

Mobility in soil columns

This type of column mobility study does not attempt to reproduce field conditions where herbicide movement will occur under both saturated and unsaturated water flow. In the subirrigated columns all water movement is by unsaturated flow and water movement up through the columns is slower than in top-watered columns where saturated flow is occurring. For equal volumes of water, the subirrigated columns are more effective in moving herbicides than top-watered columns operating under saturated flow conditions because the slower movement of water up through the columns allows more time for desorption of the herbicide molecules to occur.

One hour was required for the wetting front to move up to the top of the columns and begin to evaporate. Over the 48-hour period the maximum amount of water evaporated from the top of a column was 12.7 g, which represented 35.2% of the total water content of the wetted column. Because no differences occurred between soils in the amount of water that passed through the columns and evaporated from the top, direct comparisons of the mobilities of metribuzin, metolachlor, and fluometuron could be made without correcting for differences in water movement through the columns.

A general consensus among researchers is that adsorption and desorption are the primary determinates of herbicide mobility. In this study the order of herbicide mobility on all four soils was metribuzin > fluometuron > metolachlor (Table 5). This result is the reverse of the order of adsorption with the exception that metolachlor would have been expected to be more mobile than fluometuron in the Taloka soil on the basis of the adsorption data. The greater mobility of fluometuron on

Table 5. Mobility factors[a] for metribuzin, metolachlor, and fluo-meturon in Taloka silt loam and Roxana silt loam from the 15-cm and 45-cm soil depth.[b]

| Soils | Depth | Herbicides | | |
		metribuzin	metolachlor	fluometuron
	(cm)			
Taloka silt loam	15	4.38 g	2.64 c	2.94 d
	45	4.99 h	3.12 de	3.37 f
Roxana silt loam	15	3.41 f	1.96 a	2.29 b
	45	4.38 g	2.61 c	3.24 ef

[a]Higher mobility factor = greater mobility in soil columns
[b]Average of two replications. Values followed by the same letter are not significantly different at the 5% level using the Newman-Keuls test.

the Taloka soil might be explained by a slower desorption rate for meto-
lachlor than fluometuron. The order of herbicide mobility in the soils
was Taloka silt loam at 45 cm > Roxana silt loam at 45 cm $\geq$ Taloka silt
loam at 15 cm > Roxana silt loam at 15 cm. This order of mobility is
the inverse of the adsorptivity order of the soils.

In summary, the adsorption and column studies showed metribuzin to
be weakly adsorbed and mobile. Therefore, metribuzin would be expected
to be readily moved by rain or irrigation water from the site of applica-
tion to lower soil depths or over the soil surface with run-off water.
Fluometuron was more strongly adsorbed and was less mobile than metri-
buzin in the column study. As a result, fluometuron would be expected
to be less mobile than metribuzin in the soil environment; however,
compared to other herbicides fluometuron would still be classified as
mobile. Metolachlor was adsorbed to the same degree as fluometuron, but
metolachlor was less mobile in the column study. Therefore, metolachlor
would probably be slightly less mobile than fluometuron in the soil en-
vironment, but metolachlor would also be classified as mobile.

Results of the effects of soil moisture on extraction efficiency
are contained in Table 6. At Θ_w = 26% the extraction efficiency was
higher for all chemical-soil combinations than at Θ_w = 1% (air-dried
soil). The increase in extraction efficiency was particularly marked
for fluometuron which showed a fourfold increase in extractability.
No increase in extraction efficiency was realized by increasing the
moisture content to 51%. This was consistent with the results of
Lavy, using atrazine and chloramben, although he found a small increase
in extraction efficiency at Θ_w = 100% (18). The use of moisture con-
tents over 51% was not included in this experiment since the extraction

Table 6. Effects of soil moisture on extraction efficiency of metribuzin, metolachlor, and fluometuron from Taloka silt loam and Roxana silt loam from the 15-cm and 45- soil depths.

| | | Moisture | | |
| | | 1 | 26 | 51 |
Soil-chemical	Depth			
	(cm)		(%)	
Taloka silt loam	15			
metribuzin		55.6	82.2	86.3
metolachlor		62.2	83.1	84.4
fluometuron		28.7	79.2	82.7
Taloka silt loam	45			
metribuzin		63.6	85.3	86.6
metolachlor		73.7	83.3	83.6
fluometuron		18.2	80.7	81.3
Roxana silt loam	15			
metribuzin		61.4	84.9	82.1
metolachlor		69.7	82.9	82.4
fluometuron		20.8	76.9	80.2
Roxana silt loam	45			
metribuzin		64.6	83.5	84.2
metolachlor		76.1	81.9	81.9
fluometuron		17.8	76.5	80.0

efficiency was satisfactorily high at Θ_w = 51%, and inclusion of additional water in the samples increased quenching when liquid scintillation counting was used as the assay technique.

In evaluating the weed control efficacy of a herbicide, its potential for carryover to a subsequent crop, and its potential for impact at points removed from the site of application, the herbicide's adsorption, mobility, and degradation must all be considered. For example, a mobile herbicide that is rapidly degraded in the topsoil may degrade slowly if leached to lower soil depths (10). A persistent herbicide may not pose environmental problems if it remains at the site of application, and adsorption may affect degradation rate by determining the amount of chemical in the soil solution available for microbial attack.

To gather other information needed to evaluate the fate of metribuzin, metolachlor, and fluometuron in soil, degradation of the herbicides at constant temperature was studied. Finally, results of the laboratory adsorption, mobility, and degradation studies were compared to those obtained in a buried herbicide degradation and leaching study set up in an agricultural field.

Degradation at constant temperature

Initial herbicide concentration had no effect on the degradation rate of metribuzin, metolachlor, and fluometuron (Table 7). Since there was no concentration effect, the values reported in Table 7 for the two initial concentrations were averaged and are contained in Table 8. In most treatments the herbicides degraded more rapidly in the 15-cm soil than in the 45-cm soil. An exception was metribuzin, for which no significant differences between the two depths of soil were found at 23 and 37 C. The rapid rate of metribuzin degradation at these temperatures may have masked differences in the degradation rates that a more sensitive experiment may have been able to detect. Roeth, in studying the degradation of atrazine in incubated soils, also found degradation to be slower in soils from lower depths (27).

In soils from both depths metribuzin was most labile. Rapid degradation of metribuzin was expected since other researchers have found metribuzin not to be persistent (20,32). It has been postulated that the non-aromatic ring of metribuzin is more readily degraded than the more stable aromatic ring of the symmetrical triazines (12).

In half of the treatments metolachlor and fluometuron were equally persistent. However, metolachlor was more persistent than fluometuron at 15 C in the two depths of soil and in the 45-cm soil at 23 C. This greater persistence of metolachlor was also reflected in some of the field study treatments. Most researchers have found metolachlor to be more persistent than alachlor (35). Gerber et al. found metolachlor and alachlor to be 50 percent degraded after 26 and 8 days, respectively, of incubation in soil at 22 C. This value for metolachlor is less than half the value reported here for degradation in the 15-cm soil.

Table 7. The time required in weeks for degradation of herbicide to 50 percent of the initial concentration in Taloka silt loam from the 15-cm and 45-cm soil depths at four temperatures and two initial concentrations.[a]

Soil-chemical	Depth (cm)	Initial concentration (ppmw)		Temperature C			
		1X	2X	7	15	23	37
				---------------------------(weeks)---------------------------			
Taloka silt loam	15						
metribuzin		0.3	0.6	16.4 - 13.6	4.5 - 6.3	2.6 - 2.6	2.5 - 2.4
metolachlor		5.0	10.0	--[b]	30.0 - 22.0	10.7 - 9.5	6.5 - 4.0
fluometuron		0.5	1.0	--	22.0 - 20.3	7.8 - 11.0	4.7 - 4.0
Taloka silt loam	45						
metribuzin		0.3	0.6	--	30.0 - 22.0	3.6 - 2.7	3.3 - 2.5
metolachlor		5.0	10.0	--	28.0 - 30.0	17.3 - 11.9	7.1 - 5.7
fluometuron		0.5	1.0	--	27.0 - 22.0	10.8 - 7.4	8.7 - 6.2

[a]Average of three replications
[b]No detectable degradation occurred

Table 8. The time required in weeks for degradation of herbicide to 50 percent of the initial concentration in Taloka silt loam from the 15-cm and 45-cm soil depths at four temperatures.[a]

Soil-chemical	Depth	Temperature C			
		7	15	23	37
	(cm)	---------------(weeks)---------------			
Taloka silt loam	15				
metribuzin		15.0 f	5.4 bc	2.6 a	2.4 a
metolachlor		--[b]	26.0 h	10.1 e	5.2 b
fluometuron		--	21.2 g	9.4 e	4.4 b
Taloka silt loam	45				
metribuzin		--	26.0 h	3.2 a	2.9 a
metolachlor		--	29.0 1	14.6 f	6.4 cd
fluometuron		--	24.5 h	9.1 e	7.4 d

[a]Average of six replications. Values followed by the same letter are not significantly different at the 5% level using the Newman-Keuls test.
[b]No detectable degradation occurred

However, the soil Gerber used had three times more organic matter than the soil used in this experiment, and the larger microbial population that would be expected to accompany the organic matter probably increased the degradation rate. This same effect might explain some of the differences in degradation rates between the soil from the two depths. Little work has been done studying fluometuron degradation in constant temperature chambers. Most of the field work has shown fluometuron to be moderately persistent (24,28). The data presented here indicate that metolachlor and fluometuron should be considered to be moderately persistent since it took 10.1 and 9.4 weeks, respectively, for the initial herbicide concentration to decrease by 50 percent in the Taloka silt loam from 15 cm at 23 C. With the exception of fluometuron degradation at 23 C, all metolachlor and fluometuron treatments degraded more slowly in the soil from the 45-cm depth. Since the adsorption and column mobility studies showed metolachlor and fluometuron to be mobile, their slower degradation rates in soil from lower depths should be considered when evaluating their persistence.

For all chemicals, except metribuzin at 23 and 37 C, degradation occurred more rapidly at the higher temperatures. The degradation rates of metribuzin at 23 and 37 C were not significantly different. Again, the rapid rate of metribuzin degradation at these two temperatures may have masked differences.

After incubation for four months, all autoclaved treatments showed no detectable degradation of metribuzin, metolachlor, or fluometuron. The bioassay plants in the autoclaved controls grew as vigorously as the non-autoclaved controls. Therefore, it appears that microbial degradation is important in the breakdown of all three herbicides.

This degradation at constant temperature experiment completed the laboratory phase of this research. The results obtained in the laboratory indicated that metribuzin is mobile in soil and not persistent, and that metolachlor and fluometuron are mobile and moderately persistent.

It is recognized that a laboratory experiment cannot, and often does not, attempt to mimic field conditions. The results of laboratory work are valuable to compare to work of other researchers and to predict and explain the results of field studies. In the final phase of this study a buried herbicide degradation and leaching experiment was conducted to evaluate the dissipation of metribuzin, metolachlor, and fluometuron under field conditions.

Buried herbicide study

The results of the buried herbicide study indicate that degradation of the herbicides from October, 1978 to March, 1979, took place at a much slower rate than over the May, 1979 to September, 1979, period (Figures 2-13). Due to the dissipation of herbicide residues to undetectable levels in most treatments, and for graphic clarity, the final data points of the two-year treatments (October, 1978 to October, 1980) do not appear in Figures 2-13, but are contained in Table 9. With the exception of metribuzin in the Taloka silt loam at 15 cm and fluometuron in the Roxana silt loam at 15 cm, no detectable degradation occurred in any of the degradation treatments over the October, 1978 to March, 1979, period. By May, 1979, all of the metribuzin degradation treatments and fluometuron degradation treatments in the Roxana silt loam had shown decreases in herbicide concentration. By July, all degradation treatments showed significant decreases in herbicide concentration with the exception of metolachlor at the 45-cm depth in both soils.

The slower degradation rate over winter is not surprising considering the lower soil temperatures and reduced microbial activity occurring during the winter. Both of these conditions were shown to affect degradation rate in the degradation at constant temperature experiment. Though significant reduction in herbicide concentration did not occur in the degradation treatments from October, 1978 to March, 1979, the degradation and leaching treatments showed significant decreases in herbicide concentration indicating that leaching can be an important dissipation mode for these herbicides. This corroborates the laboratory adsorption and column mobility data. The effects of leaching over the May, 1979 to September, 1979, period were not significant for metribuzin in three of the four
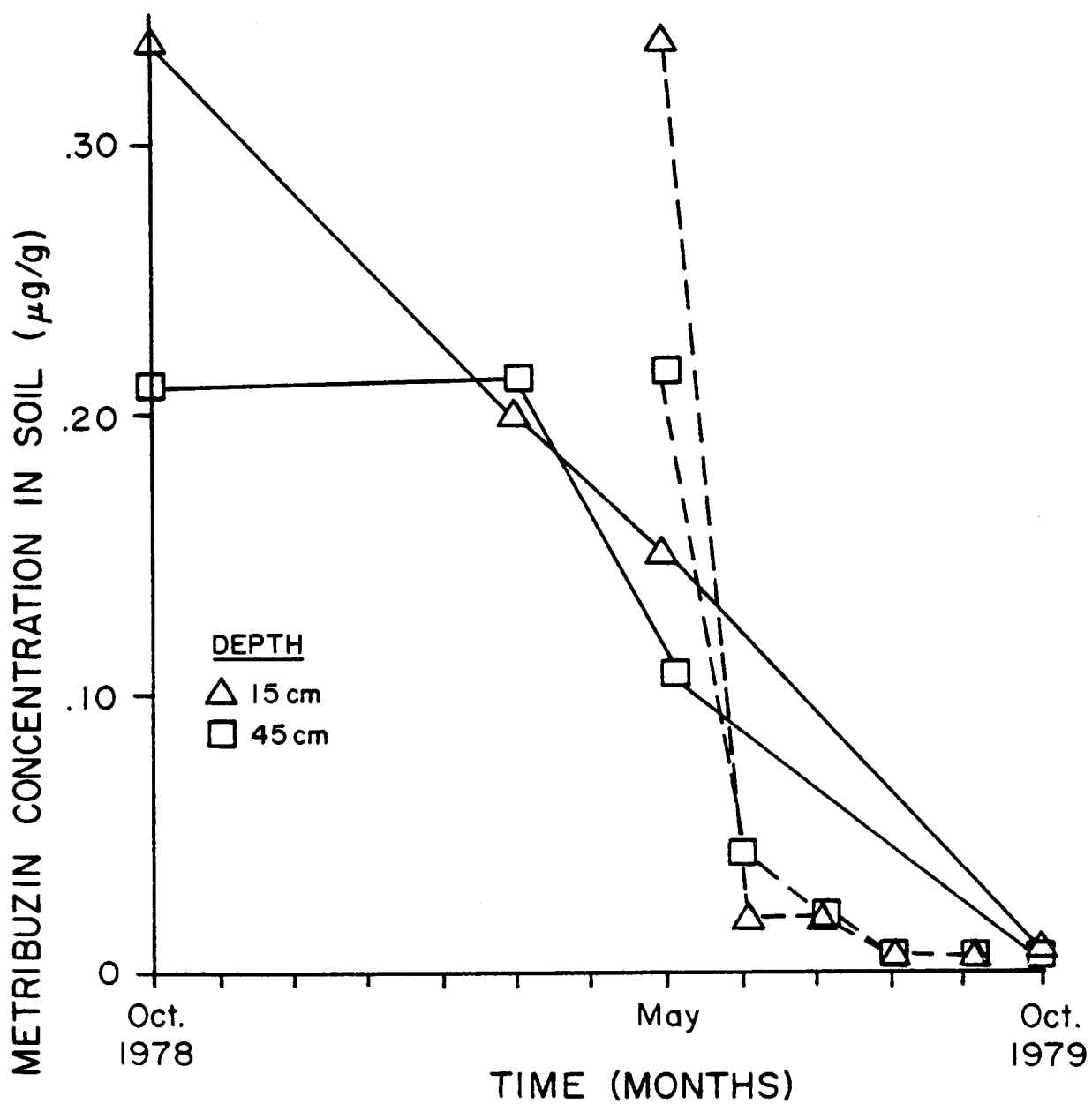
Figure 2. Degradation of metribuzin in Taloka silt loam at the 15-cm
and 45-cm soil depths. Solid lines indicate concentration change over
the course of a year; dashed lines indicate concentration change over
the summer period.

Figure 3. Degradation and leaching of metribuzin in Taloka silt loam at the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.

Figure 4. Degradation of metribuzin in Roxana silt loam at the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.

Figure 5. Degradation and leaching of metribuzin in Roxana silt loam
at the 15-cm and 45-cm soil depths. Solid lines indicate concentratioю
change over the course of a year; dashed lines indicate concentration
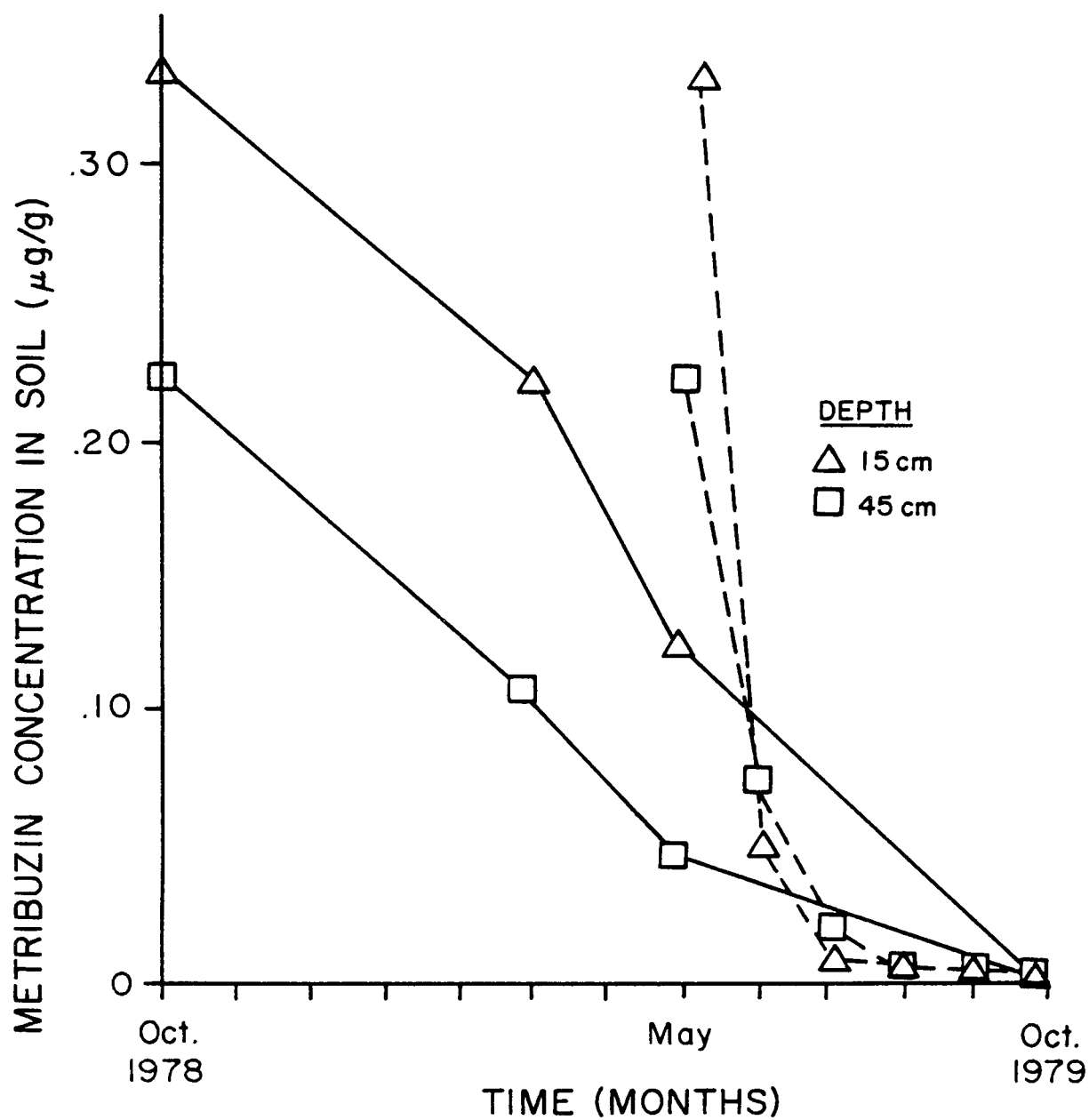change over the summer period.

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Figure 6. Degradation of metolachlor in Taloka silt loam at the 15-cm
and 45-cm soil depths. Solid lines indicate concentration change over
the course of a year; dashed lines indicate concentration change over
the summer period.

Figure 7. Degradation and leaching of metolachlor in Taloka silt loam at the 15-cm and 45-soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.
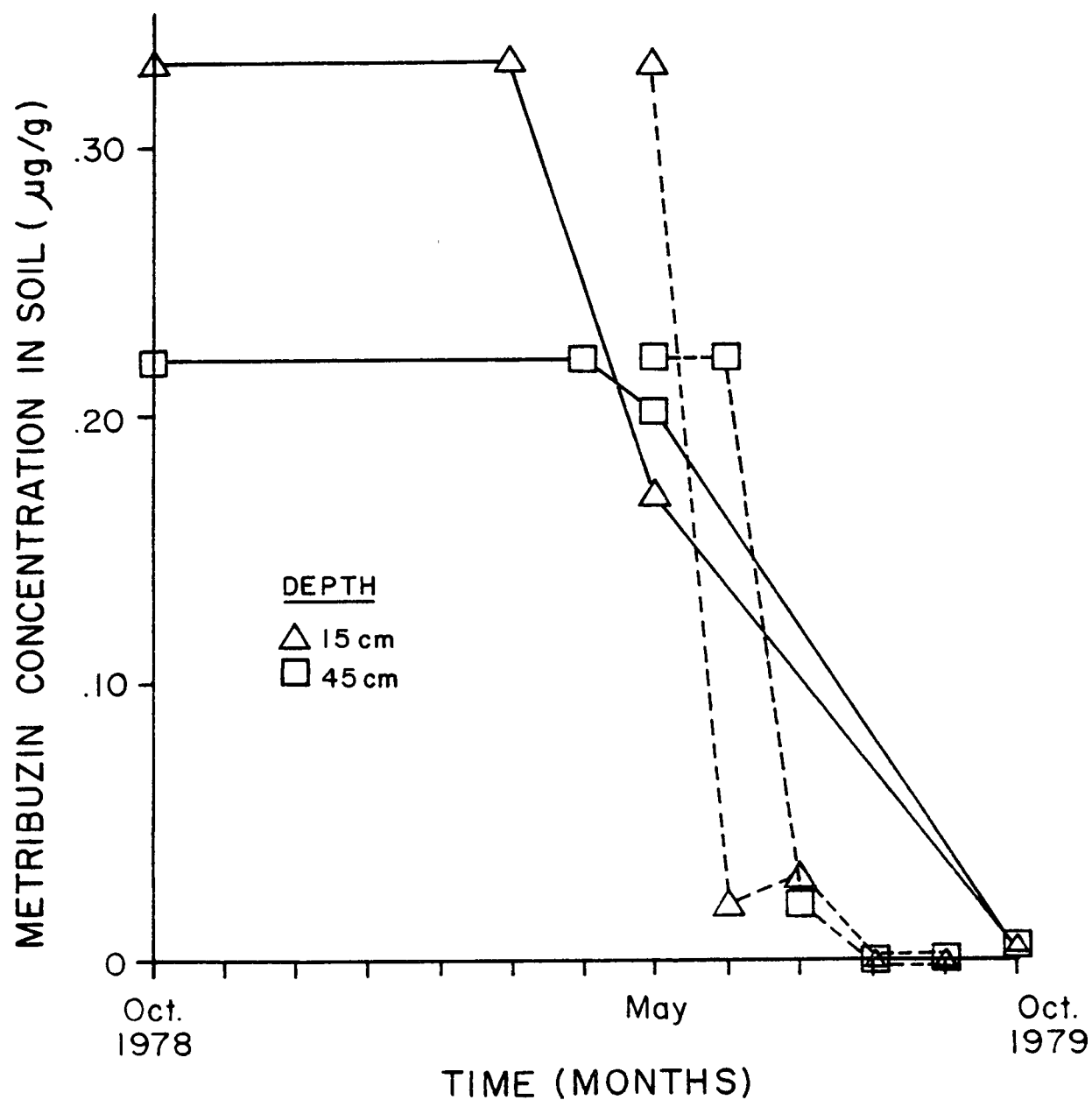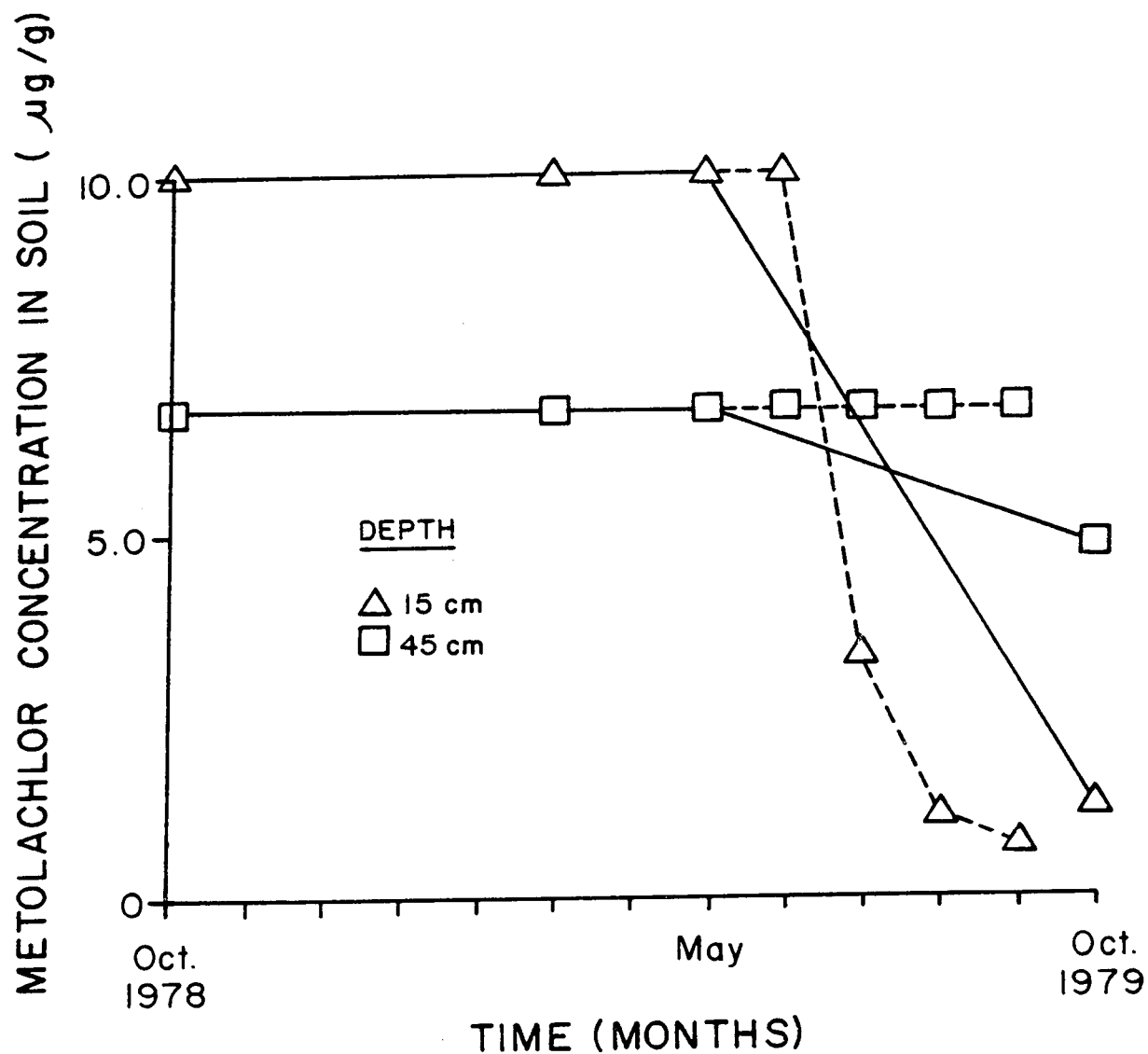
Figure 8. Degradation of metolachlor in Roxana silt loam at the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.
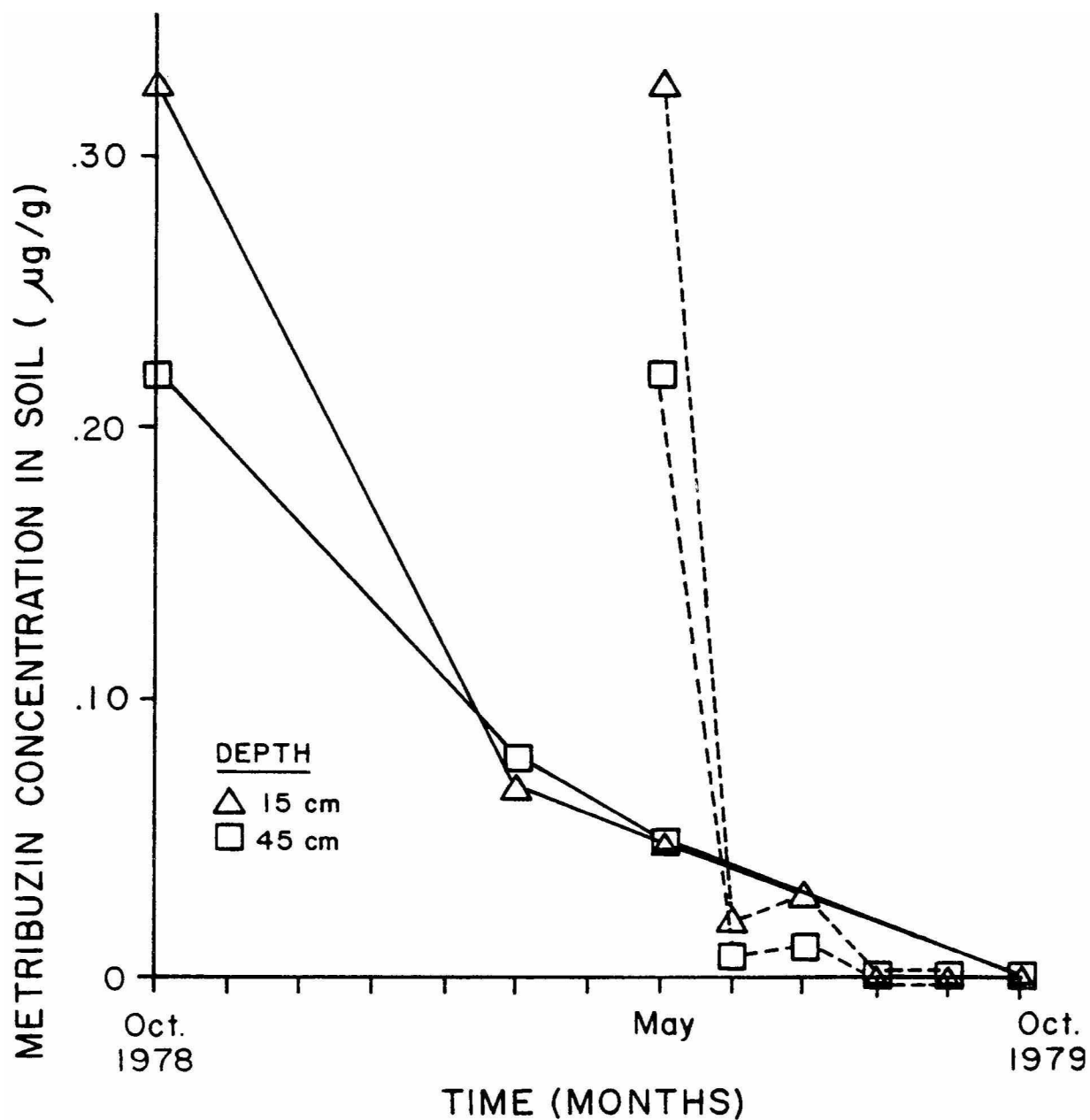
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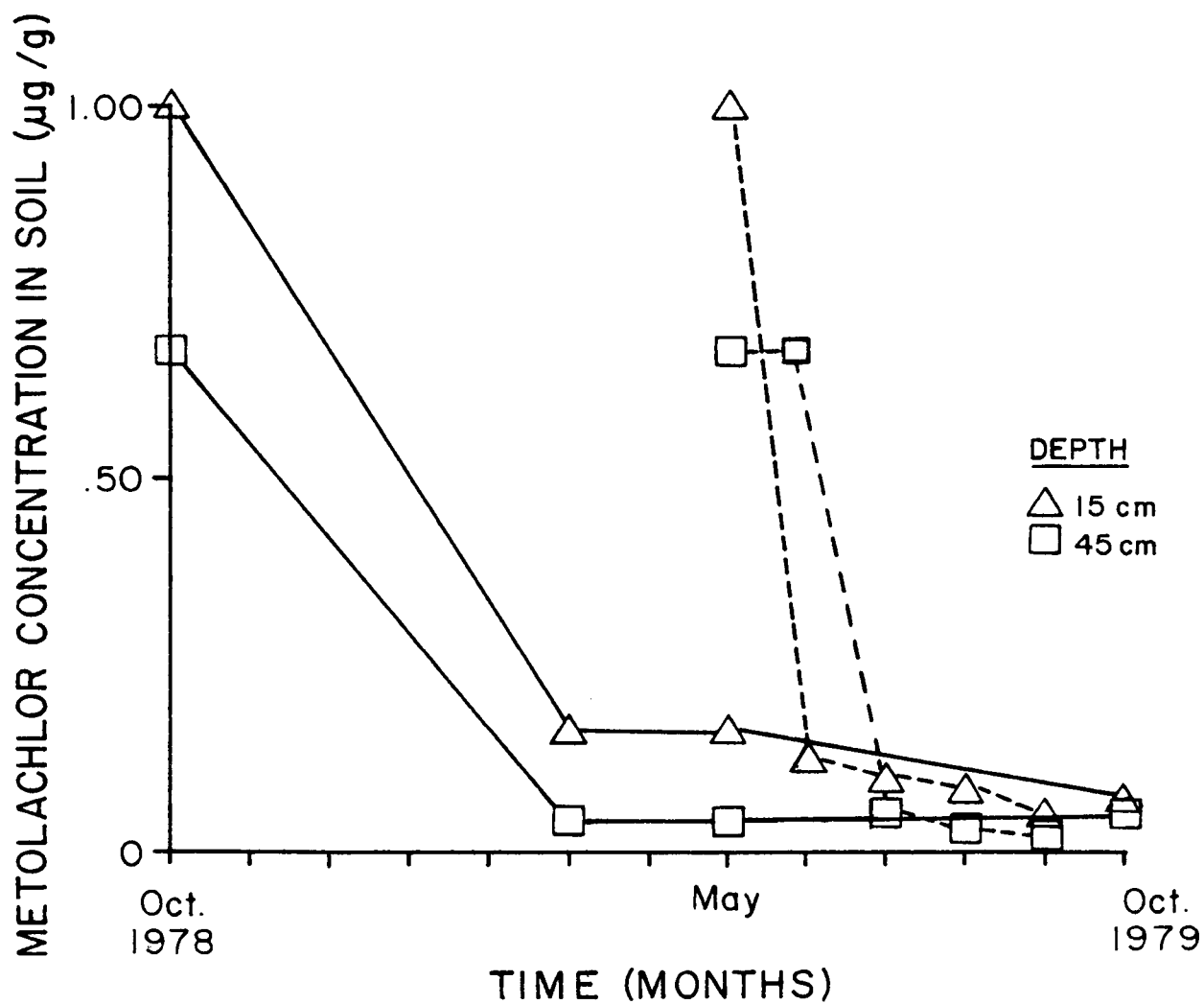
Figure 9. Degradation and leaching of metolachlor in Roxana silt loam at the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.
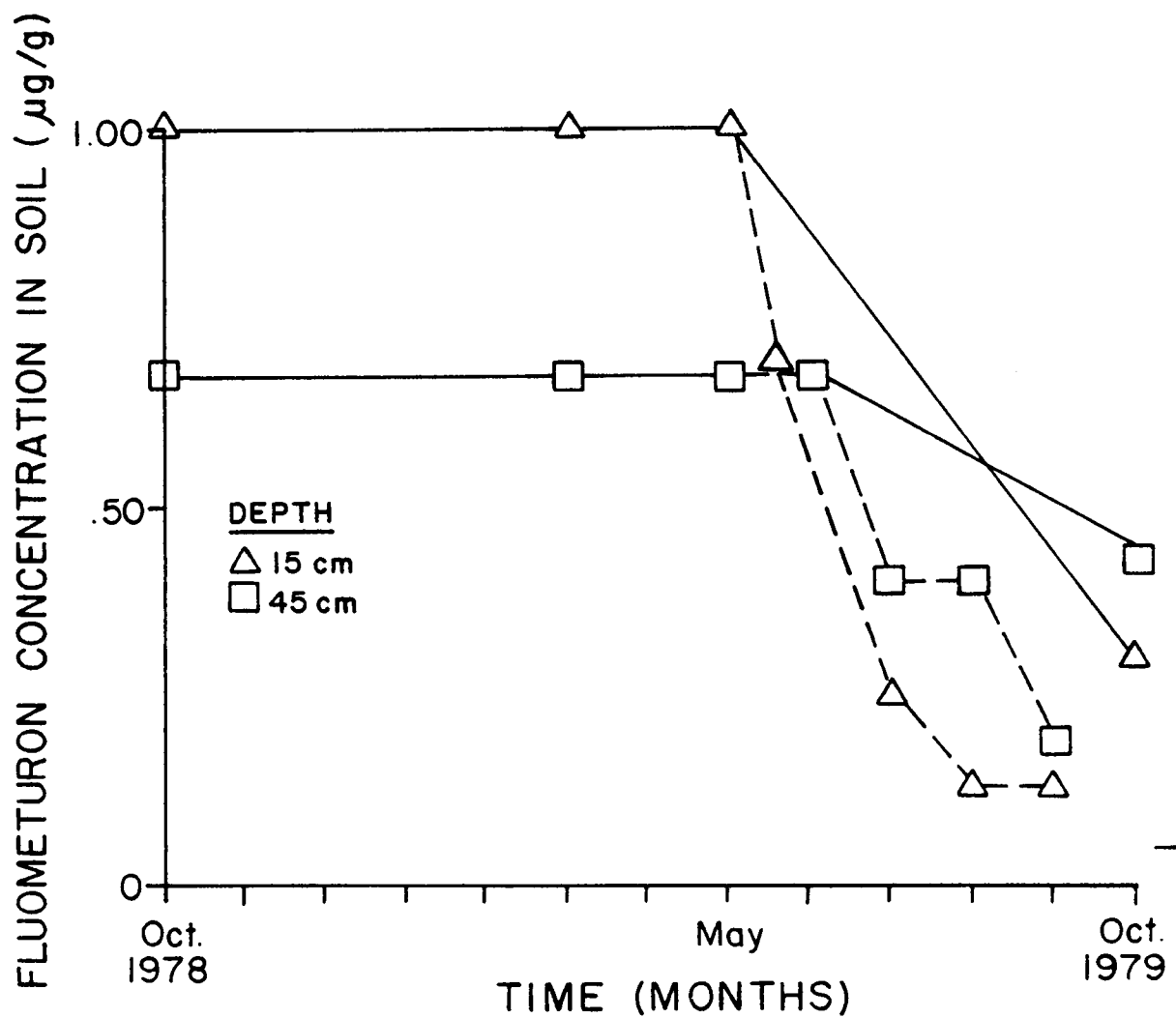
Figure 10. Degradation of fluometuron in Taloka silt loam at the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.
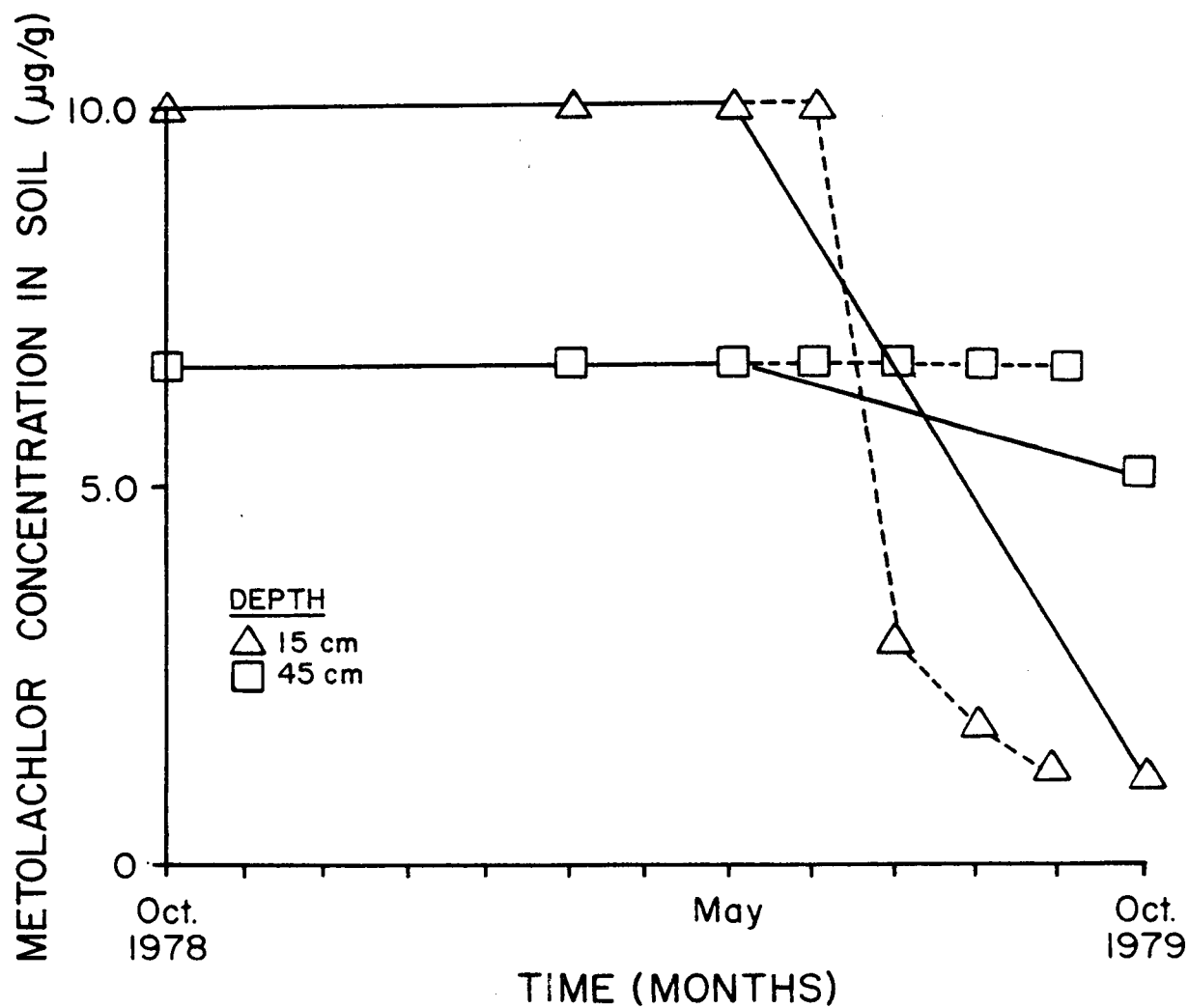
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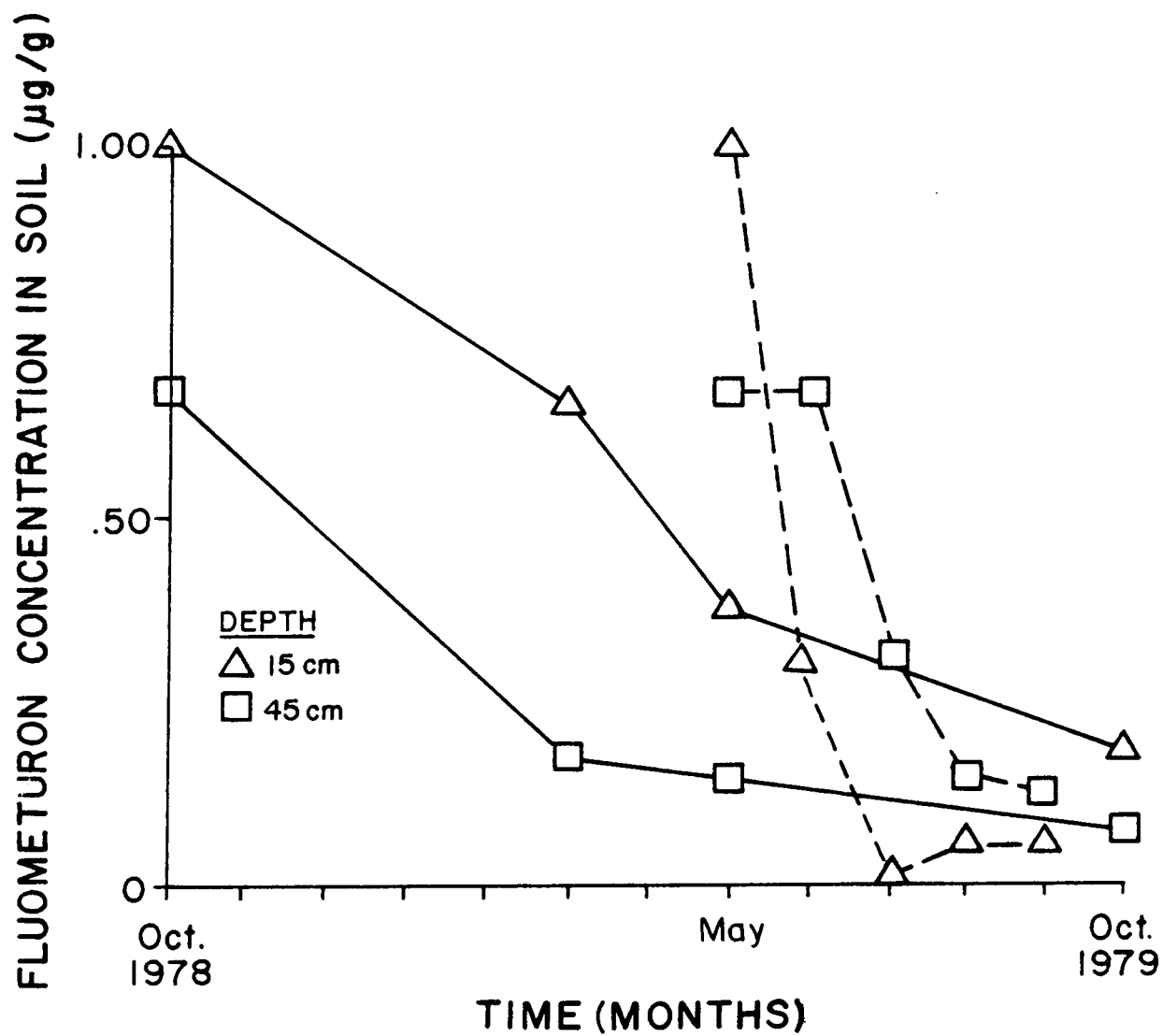
Figure 11. Degradation and leaching of fluometuron in Taloka silt loam from the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.
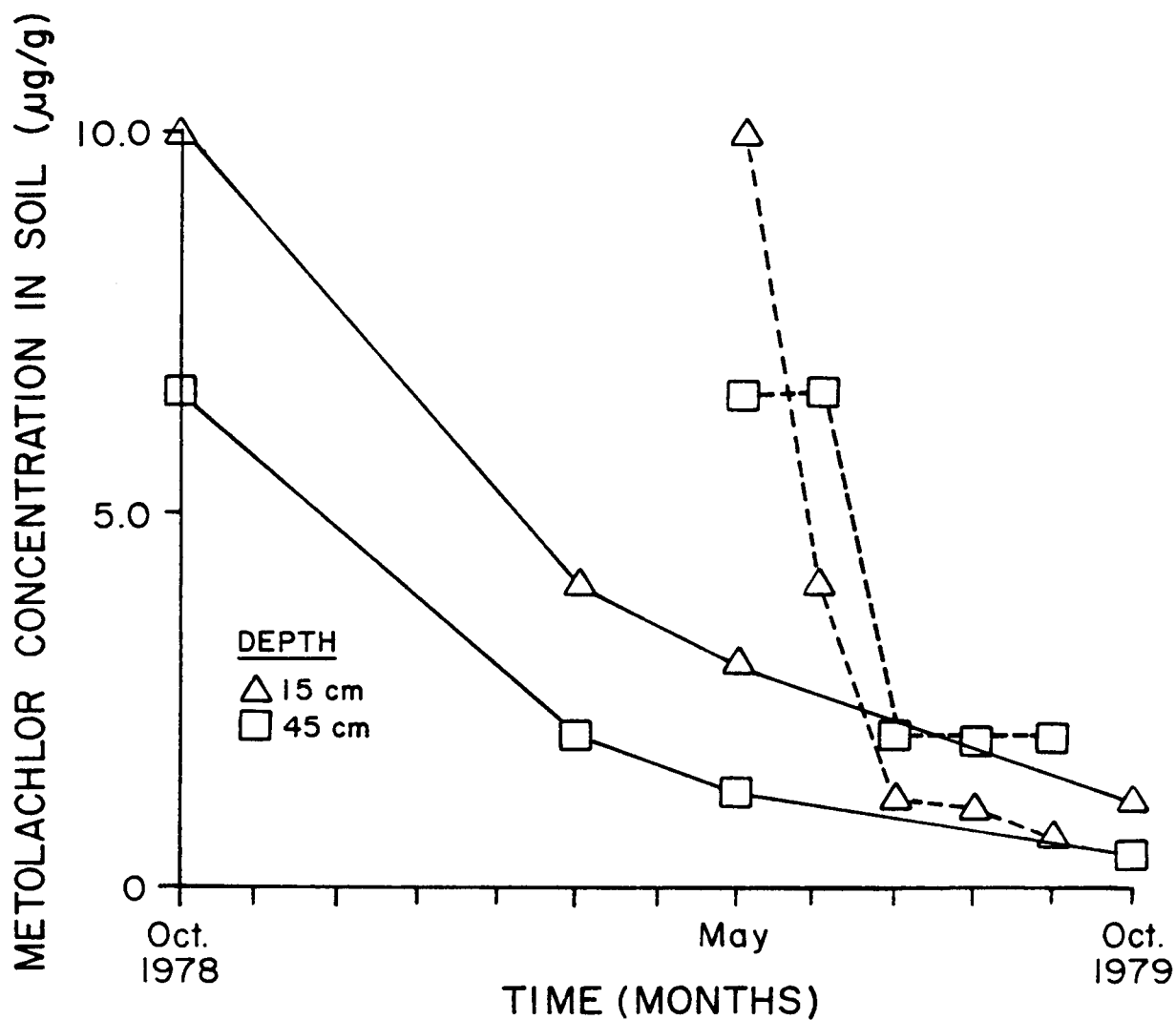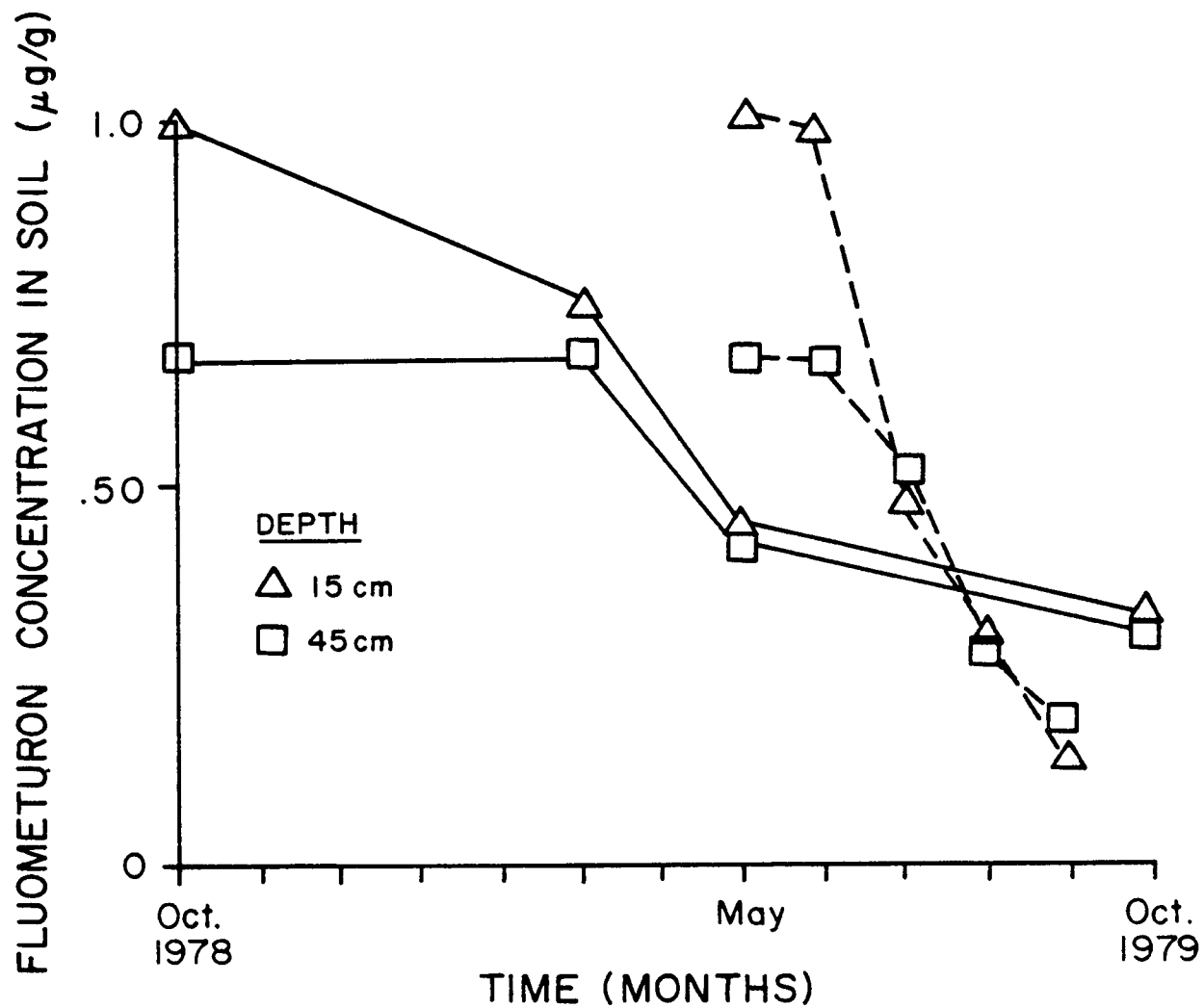
Figure 12. Degradation of fluometuron in Roxana silt loam at the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.
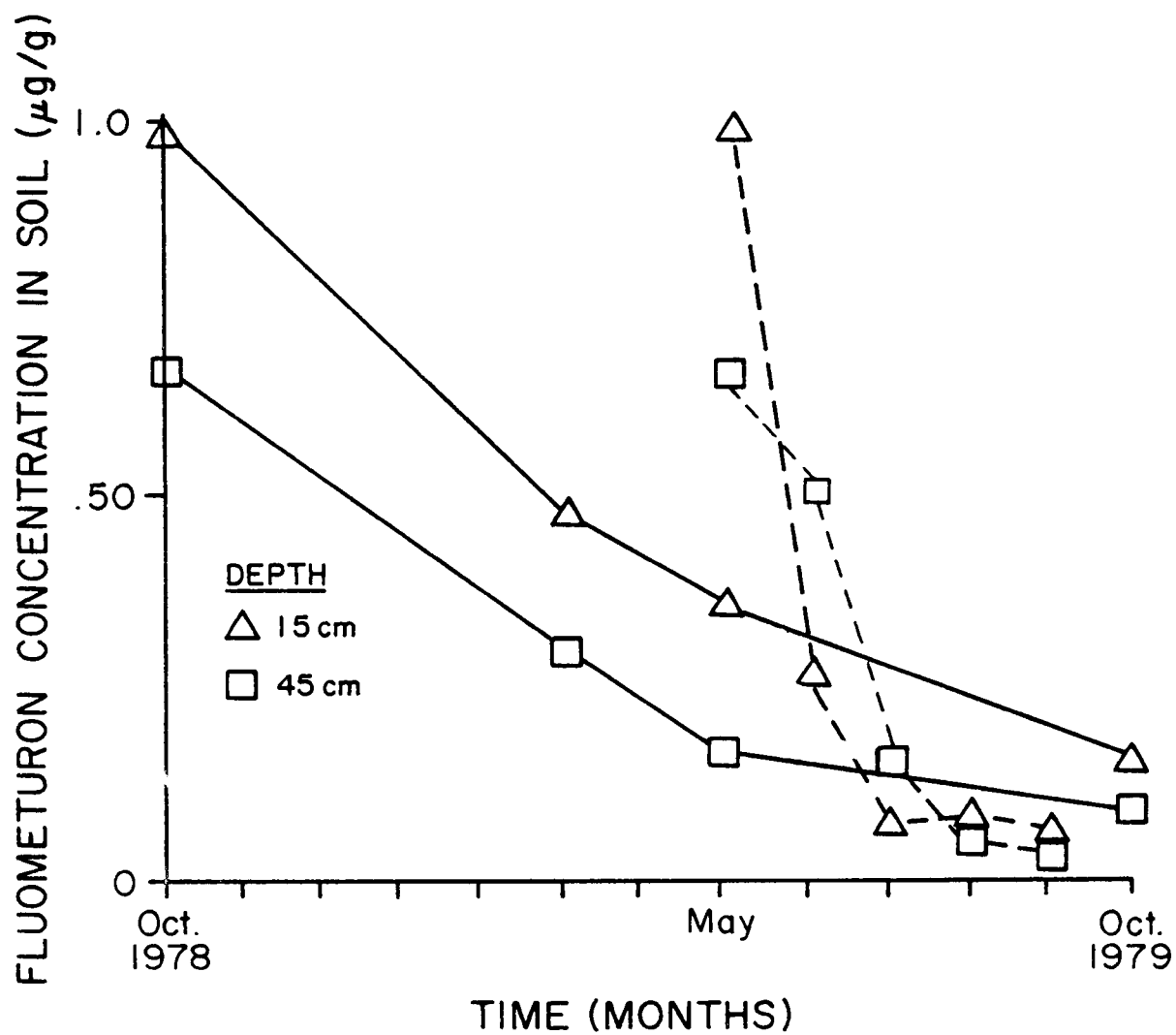
Figure 13. Degradation and leaching of fluometuron in Roxana silt loam at the 15-cm and 45-cm soil depths. Solid lines indicate concentration change over the course of a year; dashed lines indicate concentration change over the summer period.

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Table 9. Concentration of metolachlor and fluometuron in buried herbicide treatments after two years as determined by plant bioassay.[a]

Soil	Depth	Herbicide concentration			
		metolachlor		fluometuron	
		t_o	$t_{2 \text{ years}}$	t_o	$t_{2 \text{ years}}$
	(cm)		(ppmw)		
Taloka silt loam	15	10.0	nd[b]	1.0	0.03
	45	6.7	0.81	0.67	0.08
Roxana silt loam	15	10.0	nd	1.0	0.05
	45	6.7	nd	0.67	0.04

[a]Average of three replications
[b]Not detectable

soils, the Roxana soil at 45 cm being the exception (Table 10). Rainfall of 43.8 cm and 57.9 cm fell at Fayetteville and Alma, respectively, during this period so that the potential for leaching existed. However, the effects of leaching may have been masked by metribuzin's rapid rate of degradation over this period.

Location did not affect the dissipation rate of the three herbicides over the May, 1979 to September, 1979, period. It was expected that in the warmer, wetter Alma climate, degradation and leaching would occur more rapidly than at Fayetteville. Tables 11 and 12 contain climatological data and soil temperature data, respectively. The temperature differences between Alma and Fayetteville were not great. The major difference was in the amount of precipitation received. Location did affect leaching of the herbicides from October, 1978 to May, 1979. During this period, dissipation of the herbicides in the degradation and leaching treatments occurred more rapidly at Alma than at Fayetteville. These effects may be attributed to the greater amount of precipitation at Alma over this period. At Fayetteville and Alma the water leaching through the soil profile did not affect the θ_w of the soil in the Mason jars, i.e. the degradation treatments. The θ_w of the jars varied ± 3% from that at the time of initial treatment and burial.

As in the degradation at constant temperature experiment, metribuzin degraded faster than metolachlor or fluometuron. No detectable residues of metribuzin were present at either soil depth at Alma or Fayetteville at the end of the summer period. As would be expected, all residues in the degradation and leaching treatments were also dissipated to undetectable levels over this period. Even though metribuzin is probably mobile in the soil, its rapid rate of degradation

Table 10. The time required in weeks for dissipation of buried herbi-
cide to 50 percent of the initial concentration under degra-
dation and degradation and leaching conditions.[a]

| Soil-chemical | Depth | Degradation | | Degradation and leaching | |
		Oct. 78- Oct. 79	May 79- Sept. 79	Oct.78- Oct. 79	May 79- Sept. 79
	(cm)		(weeks)		
Taloka silt loam	15				
metribuzin		28.0 kl	3.0 ab	25.5 k	3.0 ab
metolachlor		40.0 mn	7.5 de	17.0 ij	3.5 ab
fluometuron		42.5 n	5.0 bc	24.5 k	3.0 ab
Taloka silt loam	45				
metribuzin		28.5 kl	2.5 a	19.5 j	3.0 ab
metolachlor		68.0 p	--[b]	15.0 hi	7.5 de
fluometuron		60.0 o	13.5 gh	14.0 gh	8.5 e
Roxana silt loam	15				
metribuzin		30.1 l	2.5 a	13.5 gh	2.5 a
metolachlor		39.5 mn	7.5 de	12.0 fg	2.5 a
fluometuron		26.5 k	8.5 e	19.5 j	3.0 ab
Roxana silt loam	45				
metribuzin		37.0 m	6.0 cd	16.0 i	2.0 a
metolachlor		62.0 o	--	11.0 f	7.0 cde
fluometuron		44.0 n	12.0 fg	19.0 j	7.0 cde

[a]Average of four replications. Values followed by the same letter are
not significantly different at the 5% level using the Newman-Keuls
test.
[b]No detectable degradation occurred.

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Table 11. Climatological data from Alma and Fayetteville, Arkansas.

	Average temperature		Total precipitation	
	Fayetteville	Alma	Fayetteville	Alma
	----------(C)--------		--------(cm)---------	
Oct.78-Oct.79	12.7	14.6	97.5	131.5
Oct.79-Oct.80	14.5	16.2	72.4	78.0
May79-Sept.79	22.2	24.6	43.8	57.9

Table 12. Soil temperatures at Alma and Fayetteville, Arkansas.

Date	Fayetteville		Alma	
	15-cm	45-cm	15-cm	45-cm
	------(C)-------		----(C)------	
1979				
May	17.8	11.7	18.3	12.8
June	27.2	22.2	29.4	23.9
July	31.3	26.7	34.4	28.9
August	25.0	23.9	25.6	25.6
September	25.0	22.2	23.9	23.9
October	18.3	19.4	21.1	21.1
1980				
October	18.3	20.6	16.7	19.4

at the 15-cm and 45-cm soil depths make the persistence of residues
unlikely.

From May, 1979 to September, 1979, metolachlor and fluometuron both
degraded more slowly than metribuzin in all soils except the Taloka soil
at 15 cm where the difference between the degradation rate of metribuzin
and fluometuron was significant only at the 10% level. Residues of
metolachlor and fluometuron were still detectable in some degradation
treatments after two years (Table 9), while metribuzin had degraded to
undetectable levels over this period. Also, in the degradation and
leaching treatments at 45 cm in both soils, metolachlor and fluometuron
were more persistent than metribuzin. Metolachlor and fluometuron varied
little in their degradation rates at the 15-cm depth; however, metola-
chlor showed greater persistence at the 45-cm depth. Metolachlor and
fluometuron both degraded more slowly at the lower soil depth. Even at
the end of the summer period no detectable change in the initial metola-
chlor concentration at the 45-cm depth occurred. The slower degradation
rate of metolachlor and fluometuron at the lower soil depth was probably
due to the lower soil temperature and decreased microbial activity at
the lower soil depths. Roeth found that microbial activity and degra-
dation of atrazine both decreased with increasing soil depth (27).
Harris et al. also found degradation rate to decrease with increasing
soil depth at twelve locations in the U.S. and Puerto Rico (10).

SUMMARY AND CONCLUSIONS

The degradation of metribuzin, metolachlor, and fluometuron was slow over the winter period, and leaching was important in the dissipation of these herbicides over this period. Although metribuzin was mobile in soil, it degraded rapidly during the summer and should not cause adverse environmental effects when properly used. Both metolachlor and fluometuron appear to be mobile and moderately persistent in soil. Metolachlor and fluometuron did not degrade as rapidly as metribuzin, especially at the 45-cm depth, and residues of these chemicals could persist beyond the desired time needed for effective weed control. Although residues of metolachlor and fluometuron were still detectable in some degradation treatments after two years, the concentration of these chemicals under actual field conditions would not be high enough to affect any but the most sensitive bioassay crop.

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Dissertation "B"

EFFECTS OF SOIL WATER CONTENT ON THE DISSIPATION OF

PENDIMETHALIN, OXADIAZON, AND ATRAZINE

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

By

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GENERAL INTRODUCTION

In the early years of commercial pesticide use many environ-
mental effects were largely unknown. That has changed now, and
factors influencing the effectiveness and the environmental
impact of pesticides has been the subject of intense scientific
research for many years.

Herbicides are pesticides which are used for weed control.
Many of these compounds are soil-applied and their persistence
in soil is determined by their chemical nature, the soil type,
temperature, soil microbial populations, the method of applica-
tion, and soil moisture among other factors.

Soil moisture has been found to have a significant effect on
the activity on weeds and the persistence of herbicides. In
flooded soils the mechanisms of herbicide dissipation may be quite
different than those occurring in soils where aerobic conditions
predominate. In rice production, weed control with herbicides has
become an increasingly significant factor in improved yields in
many areas of the world. Since in many rice production systems
the soil will be temporarily or continuously flooded, it is
important to know how the dissipation rates of herbicides used for
weed control in rice will be affected by both aerobic and anaerobic
soil moisture regimes. This information would also be useful for
determining the carry-over potential of herbicides used in crops
grown in rotation with rice.

These investigations were carried out to determine the effects of soil moisture in interaction with various other physical, chemical, and biological factors on the dissipation rates of three herbicides from soil. Two of these herbicides, oxadiazon and pendimethalin, are used for weed control in rice. The third herbicide, atrazine, is used in crops which may be grown in rotation with rice. The three chapters of this dissertation present the results and discuss the significance of investigations carried out with these three herbicides.

Chapter I

Effects of Soil Water Content on Pendimethalin Dissipation

ABSTRACT

Pendimethalin [N-(1-ethylpropyl)-3,4 dimethyl-2,6-dinitrobenzene-amine] is used for residual weed control in a variety of crops. Laboratory and field studies were conducted to evaluate pendimethalin dissipation over time in a Crowley silt loam. One laboratory study revealed that dissipation rates approximately followed pseudo first-order kinetics over an eight week period. Persistence was very high in soil at air-dry moisture (93% remaining after eight weeks). Half-lives for 1/3 bar (29% soil water content), continuous flood, and alternately flooded and dried treatments averaged 59, 63, and 30 days, respectively. Application rate, over the range of 0.5 to 2 μg incorporated per gram of soil did not have a significant influence on the half-lives. Measurements of pendimethalin residues with gas-liquid chromatography and a root bioassay with grain sorghum [Sorghum bicolor (L.) Moench] gave similar results except that the bioassay tended to detect lower concentrations of pendimethalin than gas-liquid chromatography with increasing time after application. Autoclaving was found to reduce pendimethalin dissipation at 2/3 bar (22% soil water content) but not in flooded soil. Fertilizer amendments did not have an effect. An edaphic chlorophycean alga, Uronema trentonense Lee increased soil pH and redox potential but did not affect the amount of pendimethalin lost over 12 weeks. Dissipation in the field in each of two years was studied with lowland rice (flush irrigated then flooded about two weeks after application), upland rice (flush irrigated throughout the season), and soybean (furrow irrigated as needed) management systems. Soil water content had a

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strong influence on the amount of pendimethalin which dissipated, especially for about the first two weeks after herbicide application. "Half-lives" in the field were much shorter during the initial two weeks, being from 3 to 6 days for lowland rice, 4 to 7 days for up-land rice, and 5 to 28 days for the soybean management system. Incorporation of pendimethalin and reduced irrigation in soybeans appeared to be responsible for greater persistence of pendimethalin, which has the potential to carry over in this system at high application rates.

INTRODUCTION

Pendimethalin is a soil-applied herbicide used for residual weed control in a variety of crops, including soybeans and rice. Dinitroaniline herbicides, including pendimethalin, have been shown to, in general, have persistence inversely related to soil water content (5, 8, 11, 17, 19, 20, 23). Most studies show degradation of dinitroaniline herbicides to occur more rapidly in anaerobic than in aerobic soil (8, 11, 19), although Camper et al. (5) found more rapid degradation of two dinitroaniline herbicides in aerobic soil.

Studies on herbicide dissipation which isolate one or two environmental effects at various levels fail to provide needed information on the interaction of effects. The effects of some constant moisture levels on pendimethalin dissipation have been documented (23) but results of such studies are not directly applicable to the highly variable conditions in the field.

The extent of some modes of dissipation, such as microbial degradation or volatilization could be related to the rate of change of soil water content as well as soil water content itself. Populations of soil microorganisms are dependent on the soil water content, with the greatest number of aerobic microorganisms predominating at moisture approaching field capacity (1). Flooding soil changes the composition and metabolic activity of the soil microbial flora (25). The relationship between soil water content and the volatility of the dinitroaniline herbicide trifluralin (α,α,α-trifluoro-2,6-dinitro-$\underline{N}$,$\underline{N}$-dipropyl-p-toluidine) has been investigated and for the

most part increased with increasing soil water content up to at least field capacity (4, 10).

Traditionally, herbicide residues analyses have been performed using chemical or biological assays. Walker and Bond (23) found that a gas-liquid chromatography (GLC) and a root bioassay method for pendimethalin soil residues resulted in similar measurements at various times after treatment. Such close correspondence does not always occur between such analytical methods (2, 9). Information is needed on how changes in soil water content affect herbicide adsorption, ease of chemical extraction, and biological activity of the herbicide on assay plants. Growth characteristics of the bioassay plant are also important.

One or two-phase first-order events have been used to describe dissipation of various dinitroaniline herbicides (4, 16, 26). La-Fleur (12) has used data on herbicide soil adsorption and leaching to predict herbicide dissipation based on the theory of a two-phase first-order event occurring. It is desirable to be able to predict herbicide dissipation in field situations with collection of a minimal amount of data such as soil moisture and temperature (22). However, environmental conditions affecting the soil which has received a herbicide can be extremely variable. Therefore, it is necessary to obtain an understanding of the relationship of environmental factors with the extent to which herbicide dissipation occurs by various modes. In particular, soil water content might strongly affect dissipation rates. How dissipation by volatilization, decomposition, leaching, adsorption, or other modes interacts with

soil water content to affect pendimethalin dissipation rate should be a subject of more study.

The objectives of this research were to (1) examine the effect of soil moisture on pendimethalin dissipation over time including aerobic, anaerobic, and alternately anaerobic and aerobic soil conditions; (2) determine the effects of application rate and method of analysis (chemical or bioassay) on measured herbicide concentration; (3) characterize the interaction, if any, between the above factors; (4) test the effect of soil fertility and auto-claving on pendimethalin anaerobic and aerobic dissipation; (5) examine pendimethalin dissipation in the field under different irrigation and crop management systems.

MATERIALS AND METHODS

Residue Analysis. Crowley silt loam (5% sand, 21% clay, 74% silt, 1.7% organic-matter, and pH 5.5) was used for all experiments. Soil water tension of 1/3 bar occurred with a 29% weight/weight soil water content.[1] Two methods were used to determine levels of pendimethalin remaining in the soil over various time intervals: extraction of pendimethalin from soil and subsequent analysis by gas-liquid chromatography (GLC) and a bioassay with grain sorghum.

Extraction and analysis with GLC were based on methods used for other dinitroaniline herbicides (4). Soil extractions were carried out by adding 50 or 100 ml of 75:25 hexane:acetone to 25 or 50 g of air-dried 2mm sieved soil, respectively. The soil-solvent mixture was agitated at 260 rpm on an orbital shaker for one hour and vacuum filtered, the solution was passed through anhydrous sodium sulfate, and collected. Dinitramine (N^4, N^4-diethyl- α, α, α-trifluoro-3,5-dinitrotoluene-2,4-diamine) was added as an internal standard. Aliquots were analyzed with a gas-liquid chromatograph equipped with a ^{63}Ni electron capture detector and a glass column packed with 3% OV-17 on Gas-Chrom Q. Temperatures were 200, 180 and 325 C for the inlet, oven, and detector, respectively, and the carrier gas was 95:5 argon:methane. Recovery of pendimethalin from Crowley silt loam samples spiked in the range from .05 to 4 µg/g averaged 83%.

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[1] P.K. Jung 1979 . Effects of Drought on Forrest Soybeans. M.S. Thesis, University of Arkansas, 131 pages.

Bioassays were done using grain sorghum root elongation as the response variable similar to the technique of Parker (14). Twelve pregerminated grain sorghum seeds were planted in 150 g of soil at 24% moisture and incubated at 32 C for 44 hours. Pendimethalin concentration was determined by calculation of the percent inhibition of root growth (using the length of the roots in mm) and interpolating this with a standard curve developed from the responses of the roots to known soil concentrations of the herbicide.

The standard curves were obtained by fitting the data to a three-parameter exponential model of the form

$$Y = B_0 - B_1 e^{-B_2 C}$$

where Y = percent inhibition

B_0 = the maximum inhibition occurring

B_1 and B_2 = Constants associated with the herbicide concentration effect on inhibition

C = herbicide concentration, ppmw

$B_0 - B_1$ = inhibition when the herbicide conc. = 0.

This model fitted the data well at concentrations up to 2 µg/g. Pendimethalin concentrations greater than 2 µg/g were estimated by linear interpolation between data points. Curve fitting was done using the NLIN procedure of the SAS 79.5 computer statistical package.

Laboratory Studies. The first study was carried out with the soil at 25 C in the dark. All treatments were replicated three times for both GLC and bioassay analyses. Application rates were

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0, 0.5, 1.0, and 2.0 ppmw. Pendimethalin for this and the follow-

ing experiments was applied in 1 ml of hexane solution per 50 g

of soil to give the desired initial concentration of herbicide in

the soil. At least 12 hours after treatment was allowed for the

solvent to evaporate before beginning the experiment. The water

treatments were (1) air dried, (2) 1/3 bar (29% moisture),

(3) continuous flood (60% moisture) and (4) alternate flooding,

maintained at 60% moisture on alternate weeks, then left uncovered

in the containers the other weeks, the moisture level declining

to 16±6% over the seven day period. Bioassays and GLC analyses

were made from whole samples 0, 2, 4, and 8 weeks after treatment,

150 g of soil for bioassays, and 50 g for GLC.

Data was analyzed by a factorial analysis of covariance (ANCOVA)

with time and initial concentration as the covariates. Additionally,

to model the data for each treatment, regressions over time on the

natural logarithms were performed.

The second laboratory study examined the effects of fertilizer

amendments and autoclaving on pendimethalin persistence with a 2/3 bar

moisture and a flooded regime. The experimental design was an 8

(soil treatments) x 2 (soil moisture treatments) x 2 (herbicide

rates) x 4 replications factorial. The soil treatments were as

follows:

   a. No fertilizer without autoclaving

   b. No fertilizer + autoclaving

   c. 22.5 mg Micracle-Gro® (18-18-21) fertilizer = 27 µg/g N

       in soil + no autoclaving

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d. Same as (c) but with autoclaving

e. 90 mg Miracle-Gro® fertilizer + no autoclaving

f. Same as (e) but with autoclaving

g. 9 mg urea = 27 µg/g N without autoclaving

h. 36 mg urea = 108 µg/g N without autoclaving

Fertilizer treatments were incorporated throughout the soil samples before autoclaving. All samples consisted of 150 g of soil which was incubated for 10 days at 28 C in 250 ml beakers. Autoclaved treatments were moistened to 2/3 bar in 250 ml cotton-plugged beakers, autoclaved at 121 C and 1.3 kg/cm^2 pressure for one hour on two consecutive days and also two days after the second auto-claving.

All bioassay residue analyses included a control with no herbi-cide added to check for variability in growth potential. Pendi-methalin was added to the soil by pipetting onto the soil surface 3 ml of filter sterilized solution of 100 µg/ml of the herbicide in hexane. For all treatments control samples were treated with 3 ml of pure hexane. At the end of the 10 day incubation the soil was prepared for bioassay by uncovering the beakers and drying it to approximately 15% soil water content over four days before the sorghum seeds were planted. Before this drying period all auto-claved, and selected other, treatments were tested for contamina-tion by adding approximately 1 g of wet soil to three culture tubes containing sterilized nutrient broth. Visual observations for the presence of microorganisms were made after one and three days at 25 C.

A third laboratory study examined the effects of autoclaving, two edaphic chlorophycean algae (3, 13), and light intensity on pendimethalin dissipation in anaerobic soil. For all treatments 150 g of soil was added to 500 ml Erlenmeyer flasks and 90 mg of Miracle-Gro® 18-18-20 was incorporated into the soil. Autoclaved treatments were then prepared as in the second laboratory study. Pendimethalin was added to the soil surface from a filter-sterilized solution in hexane to give a concentration of 4 µg/g of soil. The next day, soil was flooded with 300 ml of sterile distilled water. All flasks were placed in a growth chamber with a 16:8 LD cycle at 31 C in the light and 25 C in the dark cycle. The light intensity was 575 µwatts/cm^2 for red and 430 µwatts/cm^2 for blue wavelengths. The soil was incubated for 12 weeks and subjected to the following treatments:

a. dark (flask wrapped in aluminum foil) without autoclaving

b. dark + autoclaving

c. light without autoclaving

d. light + autoclaving

e. light + autoclaving then inoculated with a unialgal culture of Bracteacoccus minor.

f. light + autoclaving then inoculated with a unialgal culture of Uronema trentonense.

After incubation, both soil and floodwater of autoclaved treatments were checked for presence of microorganisms as in the second laboratory study. Redox potential (Eh) and pH of the soil and water

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were measured with an Orion ion analyzer. Soil measurements were made
by placing the tip of the electrodes to one half the depth of the
soil, without disturbing it and waiting three minutes before taking
a reading. To prepare for GLC analysis excess water was drained
from the soil which was subsequently dried by flowing air over the
surface for twelve hours. All soil samples were analyzed by gas-
liquid chromatography.

Field Studies. All field studies were conducted in Crowley silt
loam at the Rice Branch Experiment Station of the University of
Arkansas at Stuttgart. Pendimethalin dissipation over time was
evaluated with GLC and duplicate bioassay analyses for each observa-
tion in three management systems in both 1980 and 1981. These in-
cluded a flush irrigated and subsequently flooded system (lowland
rice), a frequently flush irrigated but never flooded system (upland
rice), and a system with furrow irrigation (soybeans). Dates of the
herbicide applications are given in Table 1, dates of irrigation
are indicated in Figure 3, and related climatological data in Table 2.

Each field study was subjected to analysis of covariance (ANCOVA)
with time after herbicide application as the covariate. Regression
was performed on the natural logarithm of the data for each treat-
ment, assuming one or two-phase pseudo first-order kinetics.

1. Lowland rice. Starbonnet rice was dry seeded and pendi-
methalin was applied in a tank-mix with propanil (3',4'-dichloro-
propionanilide) at 0.84 kg/ha at the two-leaf stage of barnyardgrass
(Echinochloa crusgrali) or at 1.2 kg/ha at the four-leaf stage.

Table 1.1 Dates of pendimethalin application for field experiments.

Management system	Application rate	Date of application	
		1980	1981
	kg/ha		
Lowland rice	0.84	5-19	5-12
	1.12	5-23	5-21
Upland rice	1.12	5-7	5-12
Soybeans	0.84	6-27	6-12
	1.68	6-27	6-12

Table 1.2 Climatological data for field experiments.

Month	1980 Soil temp. °C High	Low	Avg.	Precip. Total, mm	1981 Soil temp. °C High	Low	Avg.	Precip. Total, mm
May	28	11	19.0	156	28	16	21.4	197
June	34	19	25.1	38	35	24	28.2	116
July	36	22	29.6	8	37	24	31.5	38
August	34	22	28.8	5	36	23	29.6	54
Sept.	33	13	25.4	139	31	19	26.2	21
Oct.	22	4	14.6	77	29	11	19.5	113

Daily precipitation totals over 5 mm, May - July, 1980 and 1981

1980 Date	Precip., mm	1981 Date	Precip., mm
5-13	51	5-9, 10	28
5-14	49	5-14	16
5-15	9	5-17	80
5-16	24	5-25	17
5-22	10	5-26	43
5-23	6	6-3	22
6-20	27	6-4	23
6-24, 25	11	6-6	55
7-21, 22	7	7-5, 6	11
		7-29, 30	20

Soil samples of at least 1000 g were taken with a trowel from the upper 7.5 cm by combining samples from at least five places in each plot. The soil was stored at -10 C until ready for analysis. Sampling was done immediately before herbicide application and at approximately 0, 4, 10, 20, 50, 80, and 225 days after. A permanent flood until harvest was applied June 5 in 1980 and June 3 in 1981, being interrupted for only 6 days at midseason for straighthead control. The field design was a randomized complete block with three replications per treatment.

2. Upland rice. Management differed from the flooded rice in that the field area was never flooded, but was flush-irrigated as needed to maintain adequate soil moisture for continued growth of the rice. Pendimethalin was applied with propanil at 1.2 kg/ha at the 4-leaf stage of barnyardgrass. Sampling was from three sub-plots of the single treatment, using the same procedure as with the flooded rice.

3. Soybeans. The soybeans were grown under a furrow irrigated system and planted later than the rice experiments (Table 1). Pendimethalin was applied preplant incorporated to a depth of 5 cm at 0, 0.84, or 1.68 kg/ha. The field design was a randomized complete block with three replications. Soil sampling and statistical analyses were done as described above.

RESULTS AND DISCUSSION

Laboratory studies. For most moisture treatments pseudo first-order kinetics described dissipation reasonably well over the eight-week period of the first laboratory study (Table 3). Persistence was too great for the air-dry treatments to detect any significant dissipation over time, therefore, these are not included. The average amount remaining in the air-dry treatments was 93% of the original concentration. There was no significant difference between dissipation rates for the 1/3 bar and continuous flood treatments which had, respectively, average half-lives of 59 and 63 days and both averaged 52% of the pendimethalin remaining after eight weeks (Table 3). This suggests there is probably not a substantial change in the dissipation rate occurring by varying soil water content from 1/3 bar tension to flooded conditions. Parr and Smith (15) found that dissipation of trifluralin in Crowley silt laom was faster at 1/3 bar soil moisture than in flooded soil, and that volatilization did not account for this difference.

Dissipation was most rapid with the alternate flood treatment, the average half life being 30 days, and an average of 28% remained after 56 days (Table 3). The significant increase in pendimethalin dissipation rates when soil water content fluctuated between approximately 16% soil water content and saturated conditions indicates that one or more modes of dissipation must be profoundly accelerated by the wetting and drying of the soil. This is consistenf with the results of Brewer and Lavy (4) obtained with three other dinitroaniline herbicides subjected to the same moisture treatments.

Table 1.3. Predicted first-order half-lives and actual amounts of

pendimethalin in soil after eight weeks at 25 C.

Treatment					
Moisture regime	Application rate µg/g	Method of analysis	r^2 [a]	Half-life w/std.error limits (days)	% remaining at 56 days
1/3 Bar	0.5	GLC	.770**	61<72<88	59
		bioassay	.390*	34<48<82	49
	1.0	GLC	.573**	59<75<103	58
		bioassay	.529**	43<56<80	46
	2.0	GLC	.562**	49<63<88	56
		bioassay	.776**	35<41<49	42
Contin-uous flood	0.5	GLC	.592**	81<104<148	63
		bioassay	.597**	42<54<76	55
	1.0	GLC	.522**	58<76<113	60
		bioassay	ND [b]	46 [b]	43
	2.0	GLC	.568**	46<60<84	55
		bioassay	ND [b]	40 [b]	38
Alter-nate flood	0.5	GLC	.853**	22<25<29	22
		bioassay	.605**	29<37<52	35
	1.0	GLC	.704**	21<25<33	25
		bioassay	ND [b]	29 [b]	29
	2.0	GLC	.585**	29<37<52	33
		bioassay	.636**	21<26<31	22

a r^2 = squared correlation coefficient

** = highly significant, p < .01,

* = significant, p < .05

[b] Due to variability in data and/or missing data the error in
predicting initial and final concentratons by a first order
model was > 15%. Therefore, no r^2 is presented and the
half-life was determined by interpolation from the data.

Savage (19) found that, with flooded and field capacity soil moisture treatments which were dried for 20 day periods before each of several sampling times, the pendimethalin dissipation rate was greater with the flooded treatment. Possible explanations for an acceleration of dissipation with alternate flooding are that wide fluctuations in soil moisture increases losses by (1) volatilization, (2) microbial degradation, (3) chemical decomposition or (4) formation of bound residues not extractable by mixing with an organic solvent and/or unavailable for plant uptake.

1. Volatilization losses from soil can be significant, for some dinitroaniline herbicides (4, 9, 11, 24). The rate of volatilization of trifluralin has been shown to be highly variable, being positively correlated to surface soil water content which often varies significantly diurnally, the increase of radiation intensity during the day causing movement of trifluralin to the surface along a moisture gradient (7). Thus, repeated wetting and drying of the soil might bring more of the applied herbicide to the soil surface and allow for a significant increase in volatilization. However, pendimethalin volatility is relatively low compared to trifluralin (8) and whether significant loss by this mechanism occurs would have to be verified. In the laboratory studies surface fluctuation in soil moisture would not have been caused by diurnal variations in soil moisture, since the soil was covered and the temperature was constant. The increased loss by volatilization, if it occurred, should be directly related to the number of times the soil was physically wetted and dried.

2. Findings on the importance of microbial degradation of dinitroaniline herbicides vary (8). Camper et al. (5) found that sterilization of three soils totally inhibited the degradation of the dinitroaniline herbicides profluralin ($\underline{N}$-(cyclopropylmethyl)-α, α, α, -trifluoro-2,6-dinitro-$\underline{N}$-propyl-$\underline{p}$-toluidine) and trifluralin under both anaerobic and aerobic conditions. In one study, pendimethalin did not have a significantly different degradation rate in non-autoclaved from autoclaved soil under a flood or at field capacity (19), however, no mention is made of any efforts to maintain sterile conditions during the course of the experiment. In the second laboratory study, only under aerobic conditions at 2/3 bar soil water tension did autoclaving significantly increase pendimethalin persistence (Table 4). This occurred even though tests for the presence of microorganisms with nutrient growth cultures were positive for about 50% of the autoclaved samples. Possibly during the transformation in soil from anaerobic to predominately aerobic conditions the activation of metabolic activity by aerobic soil microorganisms includes an increase in utilization of complex organic molecules such as pendimethalin.

If the increased persistence of the autoclaved, moist aerobic treatments in the second laboratory study is due to elimination or reduction of soil microorganisms, then microbial degradation is probably the primary mode of dissipation for incorporated applications of pendimethalin in aerobic soil. The properties of soil are changed by autoclaving (9), however, and this could also affect dissipation. An increase in dissipation with fertilization of the

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Table 1.4. Effects of soil fertility and microbial levels on pendimethalin dissipation after two weeks at 25 C and at two moisture levels.

Moisture[a]	Auto-claving[b]	Fertilizer[c] treatment	Pend. conc., μg/g[c]
22	+	0	2.16 a
22	+	1C	1.92 a
22	+	4C	1.78 ab
22	−	1U	1.22 bc
60	−	4C	1.19 c
60	−	4U	1.17 c
60	−	1C	1.14 c
60	+	1C	1.11 c
60	−	0	1.10 c
60	+	4C	1.07 c
60	+	0	0.98 c
22	−	4C	0.96 c
22	−	0	0.93 c
22	−	4U	0.87 c
22	−	1C	0.86 c
60	−	1U	0.83 c

[a] 22% moisture = 2/3 bar soil water tension

[b] "+" = autoclaved before herbicide treatment
"−" = no autoclaving

[c] 0 = no fertilizer applied; 1C and 4C = low and high levels of a complete fertilizer, respectively as described in text; 1U and 4U = low and high levels of urea, respectively. Means followed by the same letter are not significantly different by the LSD at p < .05. All data listed is from soil with an initial concentration of 2 μg/g pendimethalin.

soil might have occurred if inorganic nutrients were limiting microbial degradation, but this did not occur for any of the treatments. Analysis for inorganic nutrients of the soil before treatment was not done, but the soil was obtained from an area that had not been fertilized in recent years. Greenhouse experiments carried out previously with a number of plants resulted in poor growth unless the soil was fertilized. Further study is needed to verify a significant role of microorganisms in aerobic pendimethalin degradation. The effects of additions of carbon sources, fertilizers, and different sterilization methods in combination should be examined.

In anaerobic flooded soil in the third laboratory study pendimethalin dissipated at similar rates in autoclaved and nonautoclaved soil. Presence of microorganisms was not detected in autoclaved non-inoculated samples. No growth of Bracteacoccus minor was detected in any flasks inoculated with it. Growth of B. minor was probably inhibited by pendimethalin since it was observed growing in a similarly composed medium without pendimethalin present. Uronema trentonense grew quite profusely in the flasks inoculated with it, and significantly (by Duncan's multiple range p < .01) raised the pH: from 6.1 - 6.5 to 7.1 and from 6.5 - 6.7 to 7.7, respectively, in soil and in water flooded for 12 weeks. Redox potential did not vary significantly between any of the treatments, except that the Eh was higher in the water of U. trentonense inoculated flasks (+ 122 mV) than all other treatments (+ 32 to + 50 mV). Uronema trentonense grew on the surface of soil particles but it or other

microorganisms did not appear to be significantly involved in pendimethalin metabolism since the loss of pendimethalin from the soil was not significantly affected by any of the treatments. Algae, however, might affect anaerobic herbicide degradation in submerged soils by their influence on the solution chemistry.

3. Consistent with the hypothesis of increased chemical decomposition is that the rate of decomposition of soil organic matter has been shown to be greater with alternation between anaerobic and aerobic conditions than with continuous anaerobic conditions (18). Movement of pendimethalin to "active sites" in soil organic matter or clay particles during a wetting/drying cycle might occur thereby increasing the amount of herbicide available for decomposition. The depletion of soil-nitrogen which occurs with alternation of anaerobic and aerobic conditions (18) might favor microbial metabolism of aniline compounds as a minor nitrogen source. Further studies on the effect of wetting and drying on pendimethalin decompositon should examine the amounts and chemical nature of metabolites formed under these conditions.

Changes in the redox potential as the soil is flooded and dried may result in differences in the types of reactions predominating with decomposition of organic molecules. The pesticide carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-$\underline{N}$-methyl carbamate) underwent more extensive degradation when exposed alternately to anaerobic and aerobic conditions in soil, although no significant difference in dissipation of the parent compound was found (21). Degradation of trifluralin is initially primarily

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by nitro reduction under anaerobic or by dealklylation under aerobic conditions (6) and it is possible that alternation of these conditions could have a synergistic effect on dinitroaniline degradation.

4. The relationship between bioactivity and extractibility in organic solvents of several dinitroaniline herbicides has been discussed by Helling and Krivonak (9). They demonstrated that exhaustive extraction of the herbicides left "bound" residues in the soil which were only slowly released or degraded and appeared to still be partially available for plant uptake. It is, however, difficult to prove the extent of soil bound residues of the parent compound which remain after application of a pesticide. It is plausible that wetting and drying of soil causes an accumulation of bound residues, but there may also be a concomitant increase in chemical degradation as described above, compensating for the increase in bound parent compound.

Data from the first laboratory study showed after eight weeks there might be a significant difference in the measurements of pendimethalin soil residues obtained with a gas-liquid chromatography analysis and a bioassay (Figure 1). Results from the first laboratory experiment, but not from most of the field experiments, seem to indicate that the proportion of the extractable residues available for plant uptake (by the GLC method) decreases over time. Our observations with field samples collected several months after application were that quite often residues which by GLC analyses were found to be near, but above bioassay detection limits, did not in fact have observable effects on sorghum when bioassays were performed.

The percent pendimethalin remaining after eight weeks in the
first laboratory study decreased from averages of 47 to 44 to 41
with the 0.5, 1.0, and 2.0 µg/g application, respectively (Table 3,
Figure 2). This difference was not significant but indicates that
while a pseudo first-order type equation may describe pendimethalin
dissipation adequately, it may not provide a full explanation of
the mechanism of dissipation. This assumption may be adequate for
characterization of dissipation for agricultural rates since the
range of initial concentrations used is relatively narrow. The
1/3 bar and continuous flood treatments had similar pendimethalin
concentrations throughout all sample times (Figure 2). Alternate
flood treatments varied in the time at which they began to have
lower pendimethalin concentrations than the other moist treatments
(Figure 2), but had considerably shorter half lives at all applica-
tion rates (Table 3).

Field studies. Dissipation of pendimethalin was most rapid
with the lowland rice, intermediate with the upland rice, and
slowest with irrigated soybeans in both 1980 and 1981 (Figure 3,
Table 5). In many cases the dissipation appeared to follow a two-
phase pseudo first-order rate, with the first rate more rapid.
With lowland rice data appear to confirm a slower second-phase
dissipation rate in 1980, but only one sampling time had residues
within the range of detection and quantitation for this second
phase. With upland rice, the loss of pendimethalin from the soil
on a percentage basis consistently occurred at a more rapid rate
in the first 15 to 20 days after application in both years.

Table 1.5. Initial phase half-lives for pendimethalin dissipation in the field.

Mgmt. system[a]	Rate (kg/ha)	Anal. method	1980		1981	
			r^2 [b]	half-life days	r^2	half-life days
IS	0.84	GLC	.815	18.2[c]	.817	5.3
		bioassay	.843	12.9[c]	.853	4.7
	1.68	GLC	.517	28.3[c]	.711	7.1
		bioassay	.967	15.7[c]	.765	6.5
UR	1.12	GLC	.882	5.8	.851	3.9
		bioassay	.858	5.0	.710	6.5
LR	0.84	GLC	.821	4.7	.945	3.5
		bioassay	.890	3.1	.905	3.5
	1.12	GLC	.716	6.0	.623	3.4
		bioassay	.726	3.2	.918	2.9

[a] IS = irrigated soybeans, UR = upland rice, LR = lowland rice.

[b] r^2 = squared correlation coefficient, All coefficients are highly significant (p < .01).

[c] Due to a smaller number of sampling times it was necessary to base these half-lives on a longer period after application. This may have resulted in an overestimation of the half-lives for the initial period after application.

In 1980 with the irrigated soybeans pendimethalin dissipation was much slower than for the other management systems while in 1981 the difference was less until about 15 days after treatment, by which time it was much slower. Only with the soybean system were potentially phytotoxic levels of pendimethalin remaining at the end of the growing season. Winter samples taken from both the irrigated soybeans and upland rice plots after the 1980 applications indicated that dissipation was extremely slow during the winter months (Figure 3).

Initial phase half-lives were calculated for the field experiments and were generally similar for each application rate and method of analysis within each management system used (Table 5). The half-lives are based on only three or four sampling periods because the half-life became much longer or residues declined below detectable levels after this time (Figure 3). Half-lives after this initial phase, where detectable, were longer for all management systems. Two-phase pseudo first-order kinetics with the first phase having a shorter half-life has been used to describe dissipation of dinitroaniline herbicides by other researchers (4, 26).

Dissipation was usually much more rapid in the field than in the laboratory for about two weeks after application (Figures 2, 3). Even in the alternate flood laboratory treatment less rapid pendimethalin disappearence resulted than in the field experiments with the exception of the irrigated soybeans treatment in 1980. There are at least three variables which could have a sufficient

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effect on the dissipation rate of pendimethalin or other dinitroaniline herbicides to account for these differences: (1) moisture, (2) temperature - the rate increases with increasing temperature (23), (3) application method - the rate decreases with increasing depth of incorporation (11). In the present studies, differences with moisture favored more rapid loss of pendimethalin in the field. Soil temperatures in the initial period after application were lower in the field than the laboratory for the rice management systems, favoring less rapid loss, and were about the same for the soybeans (Table 2). Alternation of wetting from rain and irrigation and drying occurred with both upland and lowland rice each year at intervals more frequent than one week (Figure 3). Given the acceleration of dissipation caused by the alternation of flooded and drying conditions for one week each in the laboratory, it might be that more frequent and more intense wetting and drying causes even more rapid dissipation. The method of application is an important difference - pendimethalin applications were surface applied with the rice management unlike the laboratory and irrigated soybean treatments. This could substantially increase losses by volatilization, photodecomposition, or dispersal accounting for much of the loss in persistence. Incorporation can greatly reduce losses of dinitroaniline herbicides from soil during the first few days after application (11). For all of the pendimethalin applications in rice except the 1.12 kg/ha rate with lowland rice in 1980, several significant rainfall events occurred during the first 15 days after application

of the herbicides (Tables 1, 2). With the irrigated soybeans, incorporation of pendimethalin and a lower frequency of irrigation (Figure 3) would tend to favor less rapid loss, whereas the higher temperatures after application would favor more rapid loss. Therefore, the differences in pendimethalin persistence between the various field and laboratory experiments are reasonable given the findings of the present and previous studies concerning the effects of soil moisture, temperature, concentration, time in the soil, and the placement of application on dissipation.

General Discussion. These experiments illustrate that the dissipation rate of a herbicide from soil can be greatly altered within the range of environmental conditions it is likely to be exposed to. The effects of many parameters must be understood in detail before herbicide persistence in the field can be predicted with confidence.

Results of the present studies indicate that, in situations where pendimethalin soil applications are not incorporated, the degree of activity achieved will be highly dependent on the changes in soil water content over the first several days after application. In situations where soil water content may reach levels near saturation and subsequently decline near the surface, activity may be sharply reduced. This often occurs with dry-seeded rice in Arkansas. Consistent with this are the reports of rice farmers near the site of the field experiments in 1981 that pendimethalin failed to provide residual weed control when two or more rainfalls occurred totalling several centimeters within a few days after application.

Soil water content appears to be a critical variable affecting pendimethalin dissipation rates and its effects are often indirect, possibly through affecting soil microbial populations involved in pendimethalin degradation, altering volatilization rates, or formation of bound residues. The present studies indicated that examination of the effect of changes in environmental conditions over time on herbicide persistence may be necessary for an understanding of the mechanisms of dissipation of herbicides such as pendimethalin and to effectively use laboratory studies to interpret or predict field dissipation.

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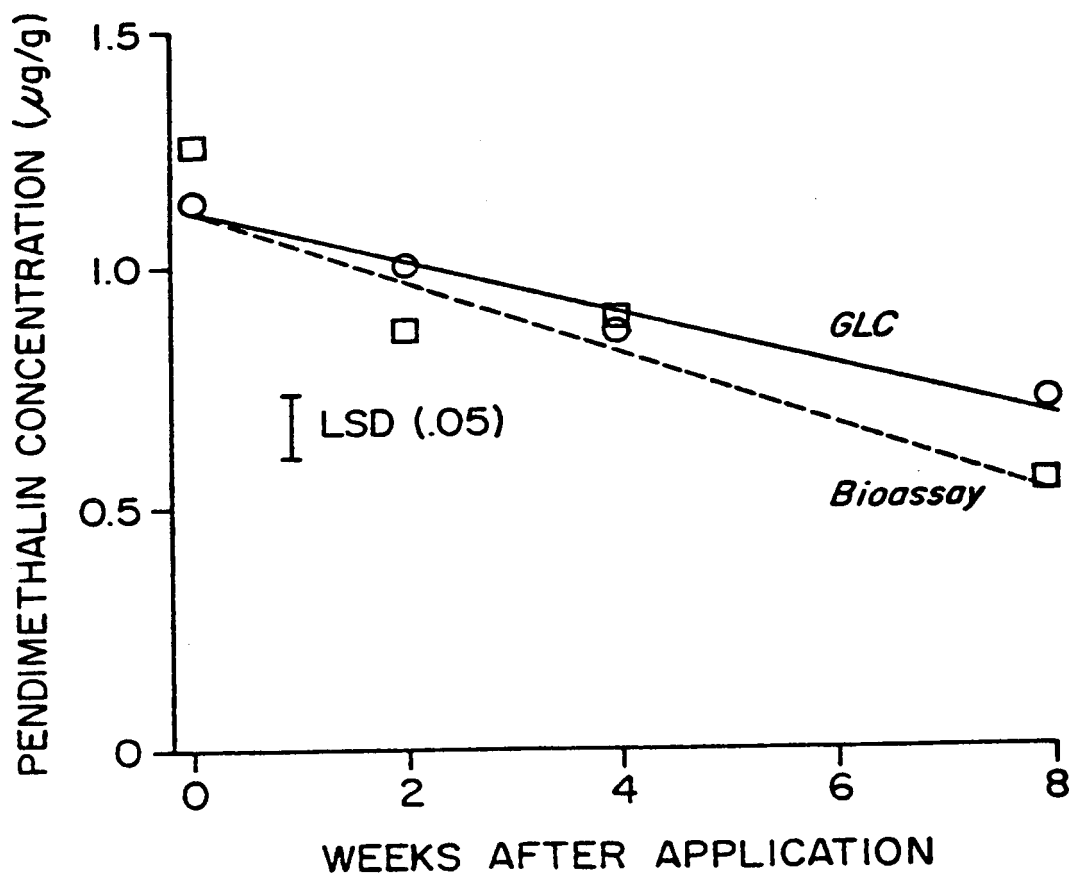
Figure 1.1   Pendimethalin dissipation over time by gas-liquid
chromatography and bioassay. All values represent
means over three initial concentrations and four
moisture treatments.
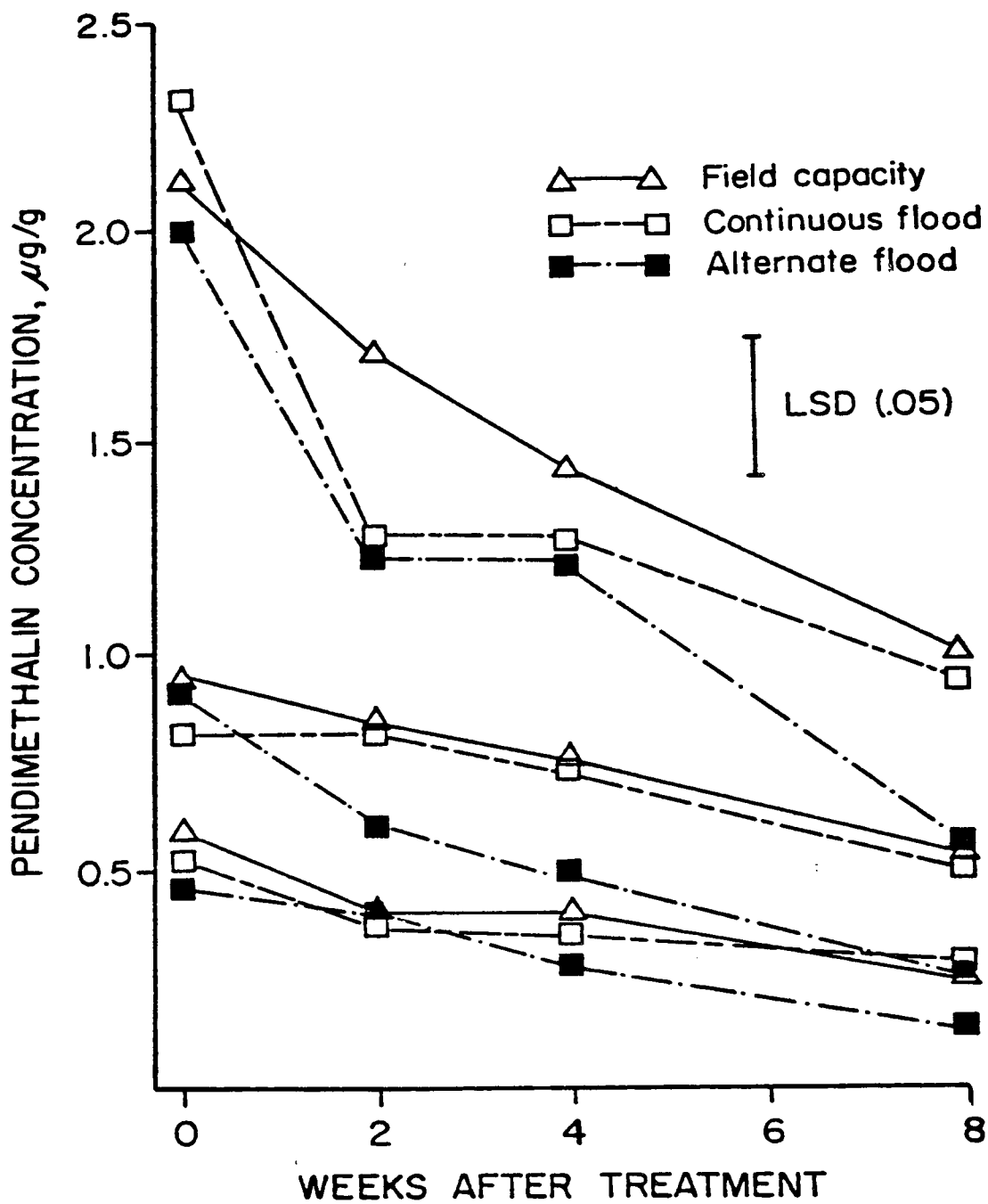
Figure 1.2. Dissipation of pendimethalin at three application rates and three moisture regimes. All values represent means over both methods of analysis.
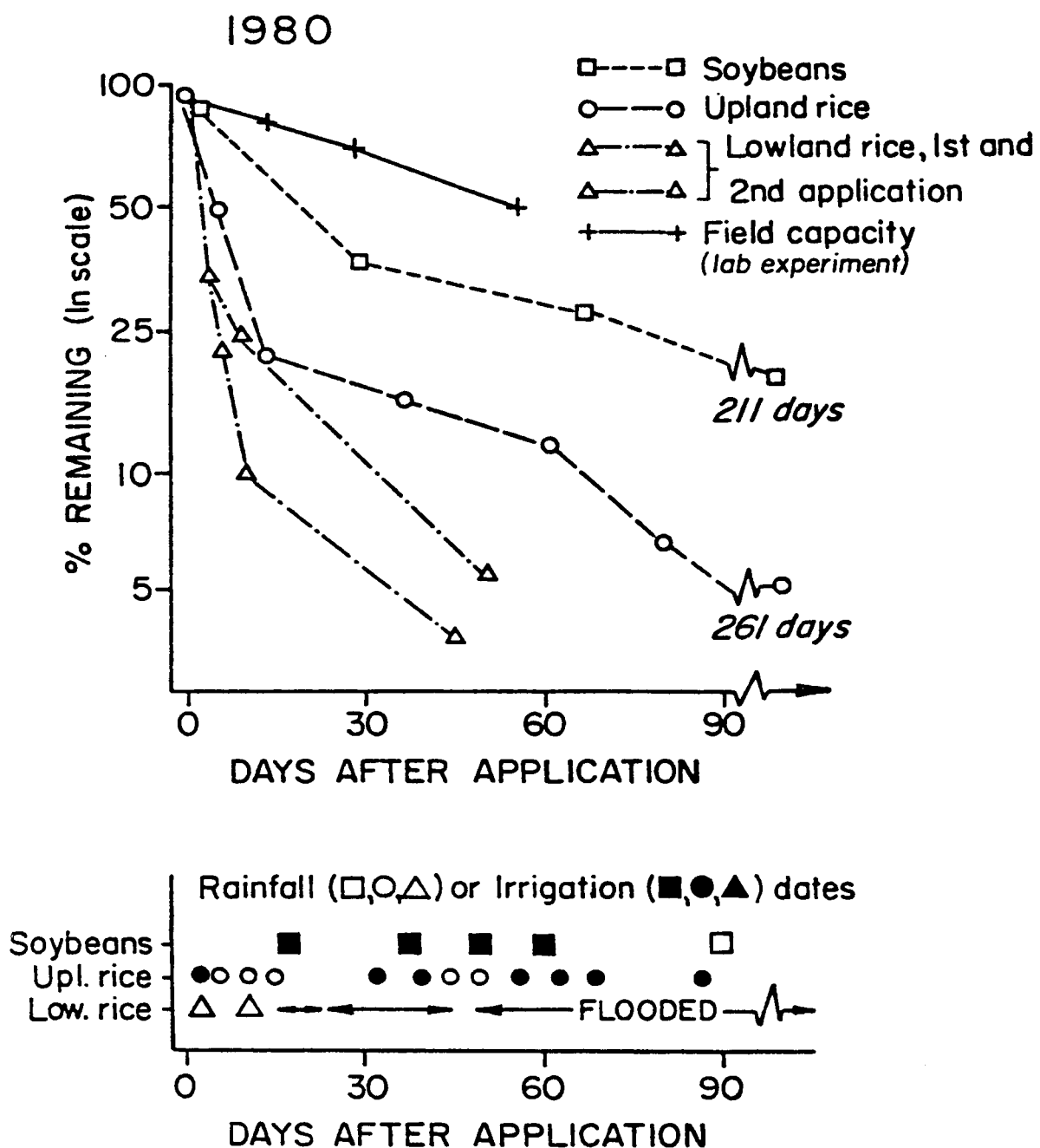
Figure 1.3. Dissipation of pendimethalin in the field with three crop management systems in 1980 and 1981. All values represent means over both methods of analysis.
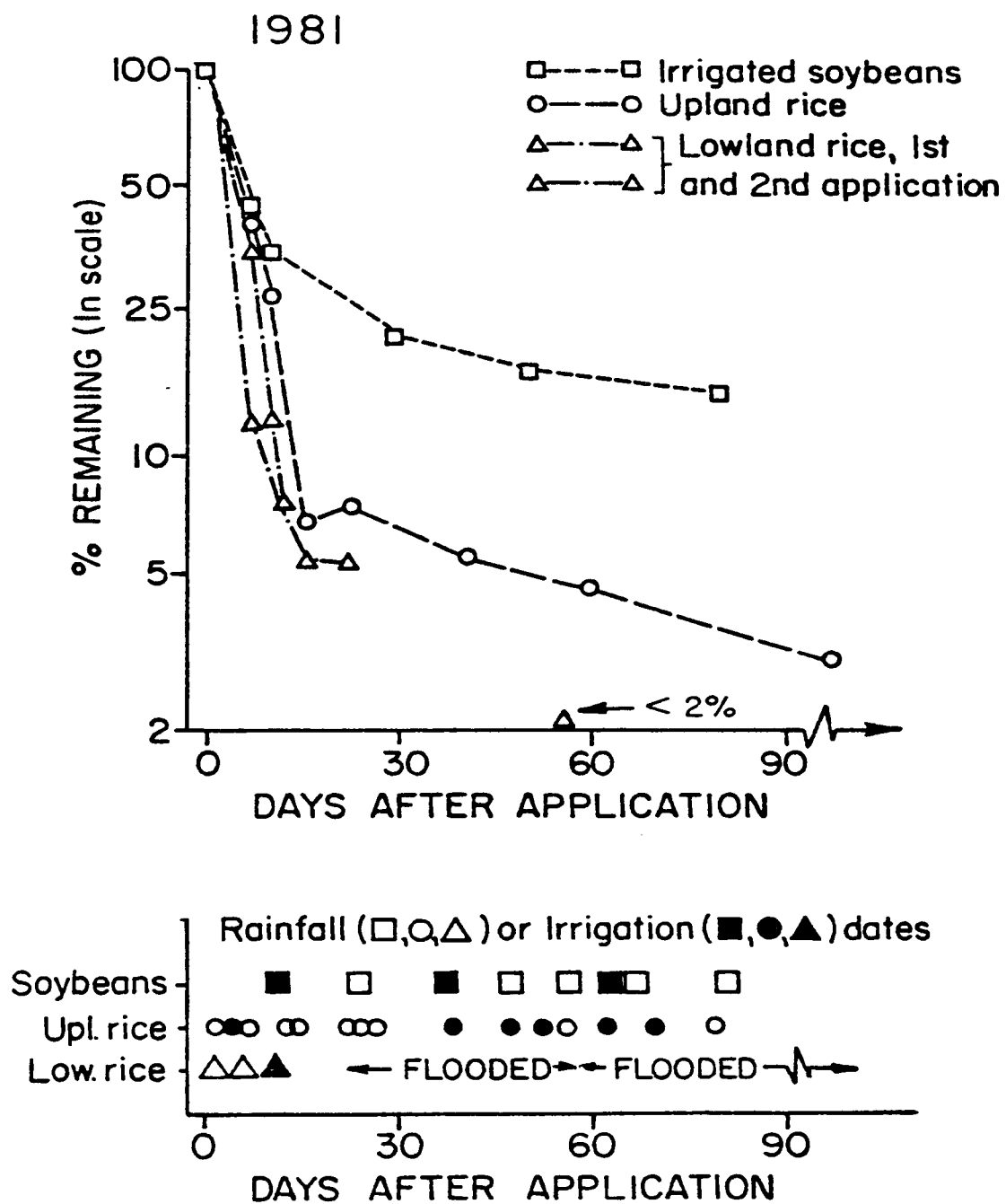
Figure 1.3 (continued).

Chapter II

Effects of Soil Water Content on Oxadiazon Dissipation

ABSTRACT

Oxadiazon [2-tert-butyl-4(2,4-dichloro-5-isopropoxyphenyl)-Δ^2 1,3,4-oxadiazolin-5-one] is used for weed control in rice in a variety of water management systems. Laboratory, greenhouse, and field experiments were conducted to evaluate soil water influences on oxadiazon dissipation in a Crowley silt loam. Comparison of a chemical method with analysis by gas-liquid chromatography and a bioassay with tall fescue (Festuca arundinacea Schreb.) indicated that by eight weeks after oxadiazon was applied an average of 45% of the oxadiazon remaining in soil exposed to different soil water regimes was biologically inactive. Oxadiazon dissipation was negligible over 20 weeks in air-dry soil. Between 1/3 bar, continuous flood, and alternate flood laboratory treatments at 25 C oxadiazon dissipation varied very little, with an average of 59% remaining after 20 weeks. Increasing the application rate fourfold increased oxadiazon persistence slightly. In a greenhouse study subsurface application of oxadiazon reduced its biological activity but increased its persistence as much as four times compared to surface-applied oxadiazon. In field studies surface-applied oxadiazon initially had a half-life of four to 11 days with flooded and 15 to 33 days with irrigated, non-flooded rice (Oryza sativa L.) management systems. Oxadiazon dissipation in the field was much slower in the field beginning 10 to 40 days after application, but did not exhibit any phytotoxicity after this time. These studies indicate that oxadiazon carry over potential is greatest when the herbicide is incorporated following application.

INTRODUCTION

Oxadiazon is a soil applied herbicide which is recommended for use in rice, orchards, ornamentals, and turf (15). Use of oxadiazon for weed control in rice has been initiated in numerous countries throughout Africa, Asia, Europe, North America, and South America (1, 9, 13, 14, 17).

Ambrosi et al. [5] found less than 25% of oxadiazon was degraded after 175 days in soil under both moist (75% field capacity) and flooded conditions. Another study found 73-96% of the applied oxadiazon remaining after 144 days in three soils which were exposed to saturated or flooded moisture levels (13). Rhône-Poulenc indicates that oxadiazon has a half-life of two to six months in soil (17).

Evidence for the persistence of oxadiazon is also provided by its residual weed control. Ghobrial (9) found that oxadiazon gave good residual control of weeds for six to seven weeks at 0.5 or 1.0 kg/ha in irrigated dry seeded rice. Mermoud et al. (14) achieved good weed control in sprinkler irrigated rice 11 weeks after application with oxadiazon. Excellent residual control of broadleaf and sedge weeds in dry-seeded rice was obtained with oxadiazon at 1.5 kg/ha in a poorly leveled field which was irrigated periodically (1).

Other data in the literature on oxadiazon consistently indicate it has properties which should cause it to be one of the more persistent herbicides in use today. Oxadiazon is low in water solubility; about 0.7 mg/liter, and strongly adsorbed by soil organic matter (8).

In most soils leaching of oxadiazon is negligible (4). Volatilization losses at 75% field capacity and in flooded soil are reported to be an insignificant mode of dissipation (5).

Information is needed on the dissipation over time of oxadiazon as affected by climatic conditions to evaluate conditions for effective residual control and potential carry over problems when oxadiazon is used. This herbicide is used, or being evaluated for use, in a wide variety of water management systems with rice in many countries. Due to the potential for persistence of oxadiazon, it is important to evaluate how different soil moisture conditions affect dissipation of this herbicide.

This research was carried out to determine the effects of soil water content and application rate on oxadiazon dissipation over time, and to compare a chemical assay and a bioassay method for oxadiazon soil residues. Additionally, influence of depth of application in soil on the phytotoxicity and persistence of oxadiazon was examined. Lastly, oxadiazon dissipation over time in the field was studied with different water management systems.

MATERIALS AND METHODS

Residue Analysis. For the laboratory, greenhouse, and field

experiments oxadiazon residues in a Crowley silt loam (5% sand,

21% clay, 74% silt, 1.7% organic matter and pH 5.5) were examined

by both a chemical determination and a bioassay.

Soil extractions were carried out by adding 50 or 100 ml of

75:25 hexane:acetone to 25 or 50 g of air-dried 2 mm sieved soil,

respectively. The soil-solvent mixture was agitated at 260 rpm on

an orbital shaker for one hour before vacuum filtering. To the

filtered solution was added 1 g anhydrous sodium sulfate per 10 ml

of solution and the mixture was agitated three times for a minute

at five minute intervals to remove any water present. Pendimethalin

(N-1-ethylpropyl)-3,4 dimethyl-2,6-dinitrobenzeneamine) was added

as an internal standard, using 0.5 or 1.0 ml of 100 μg/g solution

in hexane for 50 or 100 ml of extraction solvent, respectively.

Aliquots were analyzed with a gas-liquid chromatograph equipped with

a ^{63}Ni electron capture detector and a glass column packed with 3%

OV-17 on Gas-chrom Q or 3% OV-225 on 80/100 Chromosorb W-HP. Tempera-

tures were 250, 210 to 225, and 350 C for the inlet, oven, and detector,

respectively, and the carrier gas was 95:5 argon:methane. Recovery

of oxadiazon from spiked Crowley silt loam ranged from 89±3% at 0.1

μg/g to 95±3% at 4.0 μg/g.

Two bioassay plants were used: Kentucky 31 tall fescue (Festuca

arundinacea Schreb.) and red sprangletop [Leptochloa filiformis (Lam.)

Beauv.] Tall fescue was used for all bioassays in a laboratory and

a greenhouse study while both tall fescue and red sprangletop were used in the field study. For all bioassays 600 g of spiked soil or soil to be analyzed for residues was added to 12 by 12 cm plastic pots with drainage holes. For field sample bioassays, approximately 25 tall fescue seeds were planted in one side of the pots and about 50 sprangletop seeds on the other side with a border zone of soil 2.5 cm wide in the center with no seeds planted. All bioassays were conducted in a greenhouse. Sprangletop was rated for injury on the basis of extent of chlorosis and percent germination. Tall fescue was rated by the amount of twisting of stems as well as the extent of chlorosis. Injury ratings were taken approximately 30 days after planting.

Standard curves for determination of oxadiazon residues were obtained by linear interpolation between percent plant injury obtained with various levels of herbicide spikes between 0 and 8 µg/g of soil. Tall fescue could be used to quantitate oxadiazon residues between 0.5 and 8 µg/g of soil whereas red sprangletop could be used for oxadiazon quantitation between 0.3 and 1.25 µg/g of soil.

Laboratory study. Crowley silt loam was incubated in the dark at 25 C. The effect of application rate, moisture, time, and analytical method on oxadiazon persistence was investigated. Application rates were 0, 1, 2, and 4 µg/g for GLC analysis and 0, 2, 4, and 8 µg/g for bioassay. Oxadiazon was applied in 1 ml of hexane solution per 50 g of soil to give the desired initial concentration

of herbicide in the soil. At least 12 hours after treatment was allowed for the solvent to evaporate before initiating moisture treatments. Water treatments used were: 1/3 bar (29% moisture), continuous flood (60% moisture), and alternate flood, (maintained at 60% moisture in loosely covered containers for one week periods, then left uncovered in the containers on alternate weeks). All treatment combinations were replicated five times each for GLC and bioassay determinations. Sample sizes were 50 g for GLC analysis (in loosely stoppered 250 ml Erlenmeyer flasks) and 600 g for bioassay (in plastic pots covered with aluminum foil). A total of 400 flasks and 400 pots allowed GLC analyses and bioassays to be made from whole samples 0, 2, 4, 8, and 20 weeks after treatment. For each time, moist soil treatments were prepared for bioassay by drying the soil intact in the pots in a greenhouse for up to seven days. Soil for bioassays using standard concentrations of oxadiazon were also placed in the greenhouse at the same time. After drying, bioassays were conducted in the same pots they were previously incubated in. Data were analyzed by: (1) a factorial analysis of variance (ANOVA) of the effects of moisture regime, application rate, time, and method of analysis excluding the 1 µg/g rate measured by gas-liquid chromatography and the 8 µg/g rate measured by bioassay; (2) analysis of covariance (ANCOVA) with time as the covariate with the same data set; (3) ANCOVA with GLC data only, and; (4) ANCOVA with bioassay data only, all with the zero application rate of oxadiazon excluded. Natural logarithms

of the data for each treatment were subjected to regression analysis over time to determine the suitability of first-order kinetics in describing oxadiazon dissipation.

Greenhouse study. Oxadiazon persistence and activity was examined in applications at differing depths of soil in 12 by 12 cm plastic pots. The total weight of soil in each pot was 800 g. The total soil depth was 11.5 cm.

The following treatments were used:

1. Control - 4 ml hexane added to 800 g soil.

2. 1.6 mg oxadiazon added from 4 ml of 400 ug/g of oxadiazon in hexane to the upper 1.2 cm of soil.

3. 1.6 mg oxadiazon added to soil from 1.2 to 3.2 cm deep.

4. 1.6 mg oxadiazon added to soil from 3.2 to 11.5 cm deep.

5. 1.6 mg oxadiazon incorporated throughout the soil.

6. 0.2 mg oxadiazon added to the upper 1.2 cm of soil.

7. 0.4 mg oxadiazon added to soil from 1.2 to 3.2 cm deep.

All treatments were replicated six times. Tall fescue seed was planted and percent injury was evaluated after 30 days. At 45 days after planting, soil cores were taken from the 11.5 cm deep soil. Three replicates of treatments 1, 2, 3, 4, and 5 were taken with a soil sampling tube and divided into four equal parts by depth. All samples were analyzed for oxadiazon residues by gas-liquid chromatography.

Field studies. All field studies were conducted in Crowley silt loam at the Rice Branch Experiment Station of the University

of Arkansas at Stuttgart. Oxadiazon dissipation over time was evaluated in two rice management systems in both 1980 and 1981: (1) a flush irrigated and subsequently flooded system (lowland rice), and (2) a frequently flush irrigated but never flooded system (upland rice). Dates of oxadiazon application were May 19 and 23 (lowland rice) and May 7 (upland rice) in 1980 and May 12 and 21 (lowland rice) and May 12 (upland rice) in 1981. A flood was applied June 5 in 1980 and June 4 in 1981. Related climatological data and timing of irrigations have been presented previously (6). Soil samples of at least 1400 g were taken with a trowel from the upper 7.5 cm of soil by combining samples from at least five places in each plot. The soil was stored at -10 C until ready for analysis.

Each field study was subjected to analysis of covariance (ANCOVA) with time after herbicide application as the covariate. Regressin was performed on the natural logarithm of the data for each treatment over an initial time interval of 10 to 40 days to test for the applicability of pseudo first-order kinetics.

RESULTS AND DISCUSSION

Laboratory study. Oxadiazon dissipation was significantly
affected by the application rate and soil water content (Table 1).
Measurements of oxadiazon residues varied with the method of
analysis (Figure 1).

The proportion of residues detected by bioassay compared to
the residues detected by GLC analysis declined from an average of
1.00 to 0.96 to 0.84 to 0.55 to 0.56 at 0, 2, 4, 8, and 20 weeks
(Figures 1). Residues detected by bioassay became especially lower
over time than those detected by GLC analysis with the air-dry
moisture treatment (Figures 2-5). The air-dry treatment averaged
47% of the original oxadiazon remaining after 20 weeks as measured
by bioassay, compared to 37% on the average for the other moisture
regimes (Table 1). Corresponding averages for the GLC measurements
were 96% for the air-dry and 59% for the remaining moisture regimes.
Thus, it appears that there is a portion of adsorbed oxadiazon in
the soil which is unavailable for plant uptake but which is extract-
able by methods such as used in this study for GLC analysis. This
reversibly adsorbed portion could be increasing up to an equilibrium
point, which as this study suggests is about eight weeks, since the
ratio of residues detected by GLC to those detected by bioassay did
not change after this time.

Persistence of oxadiazon as measured by initial half lives
with different application rates was similar (Table 1). After
four to eight weeks, however, the dissipation rate slowed with
the moist soil regimes for both GLC and bioassay detectable

Table 2.1 Initial phase first-order half-lives and actual amounts

of oxadiazon in soil after 20 weeks at 25 C.

Method of analysis	Applic. rate μg/g	Moisture regime[a]	r^2[b]	Initial half-life w/std. error limits (weeks)	% remaining at 20 wks
GLC	1.0	AD	ND	ND	94[d]
		FC	.903**	16<17<18	43
		CF	.655**	15<17<20	46
		AF	.367**[c]	26[c]	68
	2.0	AD	ND	ND	94
		FC	.662**	17<20<24	51
		CF	.867**	15<17<18	45
		AF	.460**[c]	12[c]	65
	4.0	AD	ND	ND	99
		FC	.649**[c]	16[c]	68
		CF	.336**[c]	26[c]	70
		AF	.725**[c]	13[c]	73
Bioassay	2.0	AD	.335**	15<22<44	48
		FC	.347**	10<13<17	32
		CF	.255**	12<16<21	30
		AF	.155*	16<22<40	44
	4.0	AD	.211*	20<28<47	49
		FC	.531**	9<11<14	34
		CF	.580**	9<11<13	31
		AF	.556**	9<11<14	31
	8.0	AD	.618**	12<14<17	43
		FC	.477**	12<15<19	48
		CF	.591**	10<12<15	39
		AF	.382**	12<15<21	41

[a]AD = air-dry, FC = field capacity (1/3 bar soil water tension),

　　　CF = continuous flood, AF = alternately flooded.

[b]Squared correlation coefficient　　** = highly significant,

　　　p < .01; * = significant, p < .05, ND = no data.

[c]Indicates values based on regressions over the first eight weeks. All
　　other regressions were over the entire 20 week period.

[d]Percent remaining at eight weeks (more than 100% was found at
　　20 weeks, indicating the amount remaining was probably
　　overestimated).

oxadiazon (Figures 2-5). The change to a slower dissipation rate or longer half-life was more pronounced at higher application rates (Figures 2-4).

Adsorption of oxadiazon is likely an important factor in the treatment effects discussed heretofore. A substantial portion of a herbicide which is strongly adsorbed to soil clay and organic matter is often retained in the soil in a form unavailable to plants (16, 18). Since oxadiazon is strongly adsorbed to soil colloids (8), this favors the retention of it in a biologically unavailable soil fraction. In the present study noninstantaneous formation of bound residues resistent to chemical extraction may have been small as evidenced by the fact that the oxadiazon concentration determined by GLC declined only 4% over 20 weeks with the air-dry soil treatment. However, there could have been formation of bound residues with the moist treatments which did not occur with the air-dry treatment.

With the exception of the air-dry treatment analyzed by GLC, there was very little difference in dissipation rates with the moisture regimes used. This is consistent with the findings of Ambrosi et al. (5) that dissipation of ^{14}C phenyl-labelled oxadiazon occurred at similar rates with 75% field capacity and flooded soil treatments.

Greenhouse study. Application depth had a strong influence on both the bioactivity and soil persistence of oxadiazon. Activity of oxadiazon on tall fescue planted after application was observed for all three application zones used, but was greatest when present

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in the top 1.2 cm and least when applied at 3.2-11.5 cm depth

(Figure 6). In treatments not shown, when the total amount of herbi-

cide applied was reduced to 12.5% of that in the treatments in

Figure 6 in the upper 1.2 cm, tall fescue injury was only 14%.

When the amount of herbicide applied was reduced to 25%

of the treatments in Figure 6 and applied in the 1.2-3.2 cm layer

injury was 47%. These results seem to verify that oxadiazon

activity on tall fescue is greater in the upper 3 cm of soil. Per-

sistence of oxadiazon 45 days after planting was the same for the

top two application zones but activity on tall fescue was signifi-

cantly greater when oxadiazon was applied to the top 1.2 cm. Per-

sistence of oxadiazon applied more than three cm below the surface

was much greater with only 13% being lost from the soil compared

to 54 and 55% for the application to the top and second layer,

respectively, and 34% from the application which was incorporated

throughout.

Distribution of oxadiazon through different sampling zones

was concentrated in the treated zones, indicating very little

leaching had occurred. Increased disappearance rates of oxadiazon

with soil at or near the surface might be due to photodecomposition,

which was shown to occur by Ambrosi and Desmoras (2), and more

recently found to be a significant mode of dissipation in flooded

soils but not in saturated soils (13). Volatilization was found

to account for 1% or less of oxadiazon lost from moist or flooded

soil after 25 weeks (5). Plant uptake of oxadiazon might be more

efficient in the upper 3.2 cm layer of soil, causing higher activity

when the herbicide application is concentrated near the surface.
Bingham et al. (7) reported that uptake of oxadiazon by peanuts
(Arachis hypogaea L.) increased when increased moisture caused
more root growth near the surface. In the present study, however,
roots of tall fescue were found to be distributed throughout all
depths, although they were more dense near the surface. The higher
activity in soil near the surface might also be explained by a
greater susceptibility of tall fescue to phytotoxic effects of
oxadiazon when the plants are young and the roots shallow. Indica-
tion of the potential for plant uptake is given by the works of
Ishuzuka et al. (10) who found that about 5% of oxadiazon applied
to a nutrient solution was absorbed by roots of rice seedlings
within 10 days, and Ambrosi and Desmoras (3) who found 1 to 5%
of oxadiazon applied to three soils was taken up by rice and
soybeans [Glycine max (L.) Merr.].

Field studies. Persistence of oxadiazon in the field in both
1980 and 1981 was much less than in the laboratory study. However,
after an initial period of rapid dissipation lasting about 10-40
days, there was a sharp drop in the rate at which oxadiazon was
being lost from the soil. In this second phase, the rate of loss
was comparable to that observed in the laboratory study (Figures
7, 8). This second phase was not observed with residue determina-
tions by bioassay since at that point oxadiazon concentrations had
declined to levels below bioassay detection limits.

Half-lives in the field during the first phase ranged from four
to 17 days except for upland rice management in 1981 (33 days)

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(Table 2) as compared to half-lives ranging from 78 to 179 days for the moist treatments in the laboratory study (Table 1). The persistence of oxadiazon was initially greater in the upland rice than the lowland rice water management system, average half-lives being six and 16 days in 1980 and six and 15 days in 1981 for lowland and upland rice, respectively, excluding regressions which were not highly significant. Soil moisture, in the laboratory study, did not have much effect on oxadiazon dissipation rate over a range of moisture levels encompassing conditions likely to occur in the field. It might be that with the surface applications of the field experiments in the present study, soil moisture effects on oxadiazon dissipation rates are magnified.

General discussion. Extrapolation of data from the greenhouse study shows that incorporation of oxadiazon in Crowley silt loam appears to increase several fold the time for 50% disappearance. Incorporation might be largely responsible for the more than 10-fold increase in the half-life of oxadiazon in moist soil in the laboratory over the half-life in the field.

Adsorption of oxadiazon by soil colloids might be a major factor restricting its decomposition after non-adsorbed herbicide on the soil surface is dissipated and the remaining herbicide becomes more evenly distributed in the soil. LaFleur (12) has postulated that a two-phase first-order event described pesticide dissipation because dissipation during the initial phase is dominated by free non-adsorbed pesticide. In the second phase,

Table 2.2 Initial phase first-order half-lives for oxadiazon

dissipation in the field.

Year	Management system	GLC r^{2a}	GLC half-life days	Bioassay r^{2a}	Bioassay half-life days
1980	Lowland rice #1	.874**	6.2	.940**	6.3
	Lowland rice #2	.432**	7.2	.392NS	10.7
	Upland rice	.831**	15.8	.696**	16.5
1981	Lowland rice #1	.743**	6.4	.653**	8.6
	Lowland rice #2	.935**	4.0	.676**	4.7
	Upland rice	.856**	15.1	.357*	33.0

[a]Squared correlation coefficient, ** = highly significant,
p < .01, * = significant, p < .05, NS = not significant.

free pesticide concentration is relatively low and stable and this rate of loss of pesticide is significantly slower. Related experiments (11) indicated that sometimes several weeks are required for pesticide adsorption to reach dynamic equilibrium with soil organic matter. In the field experiments of the present study there may have been two types of processes dominating oxadiazon dissipation in sequential phases after application. Strong circumstantial evidence for this is provided by the much slower dissipation rate of oxadiazon which occurred beginning 10 to 40 days after application (Figures 7, 8). Several researchers have shown that adsorbents often decrease herbicide dissipation rates, depending on the chemical nature of the adsorbent and the herbicide (15, 16, 18).

These studies indicate oxadiazon persistence is only slightly affected by variations in soil water content, except that it is greatly increased in dry soil. Due to the substantial adsorption of oxadiazon by organic matter and clay, a significant reservoir of biologically inactive oxadiazon may remain in the soil long after herbicidal activity is lost. This is of potential significance in that buildup of residues, especially in soils with high adsorptive capacity, could possibly occur when oxadiazon applications are repeated in the same field in successive years.

Further research is needed to examine the mechanisms for oxadiazon dissipation in soils especially at the soil-water interface. Also useful would be more information on the specific effects of different clays and types of organic matter.

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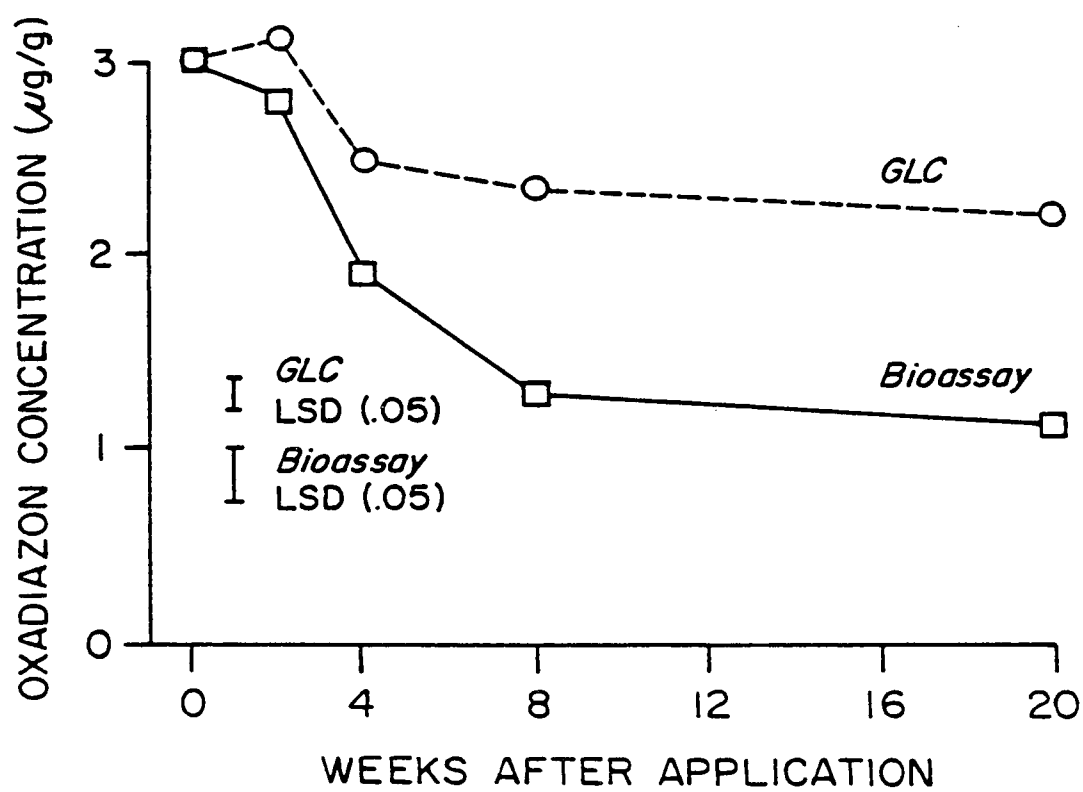
Figure 2.1.   Oxadiazon dissipation over time by gas-liquid chromatography
            and bioassay. All values are averages over all moisture
            regimes and the 2 and 4 ug/g application rates for each
            method.

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Figure 2.2. Oxadiazon dissipation over time with four soil moisture regimes as determined by gas-liquid chromatography: 1 µg/g application rate.

Figure 2.3. Oxadiazon dissipation over time with four soil moisture
regimes as determined by gas-liquid chromatography:
2 µg/g application rate.
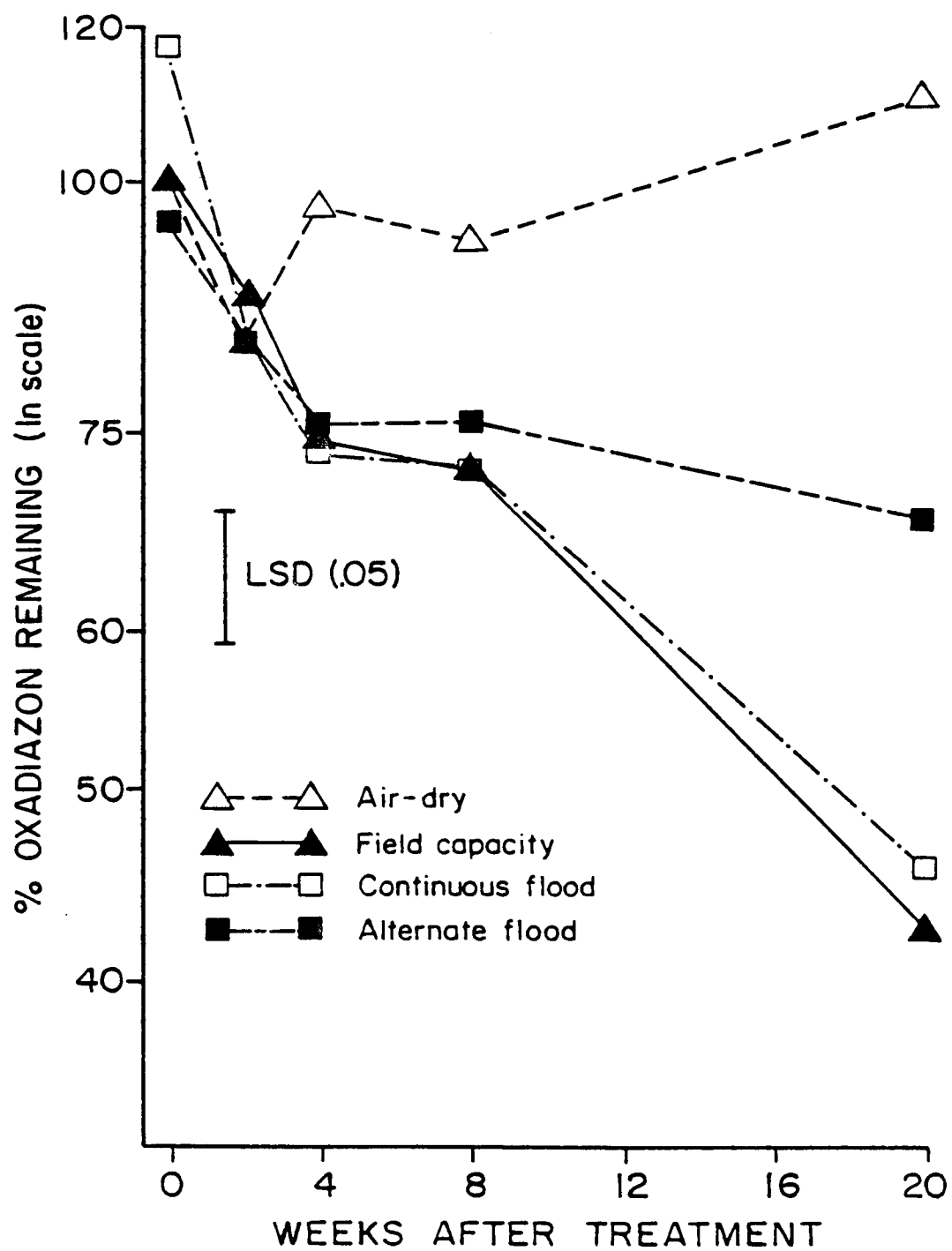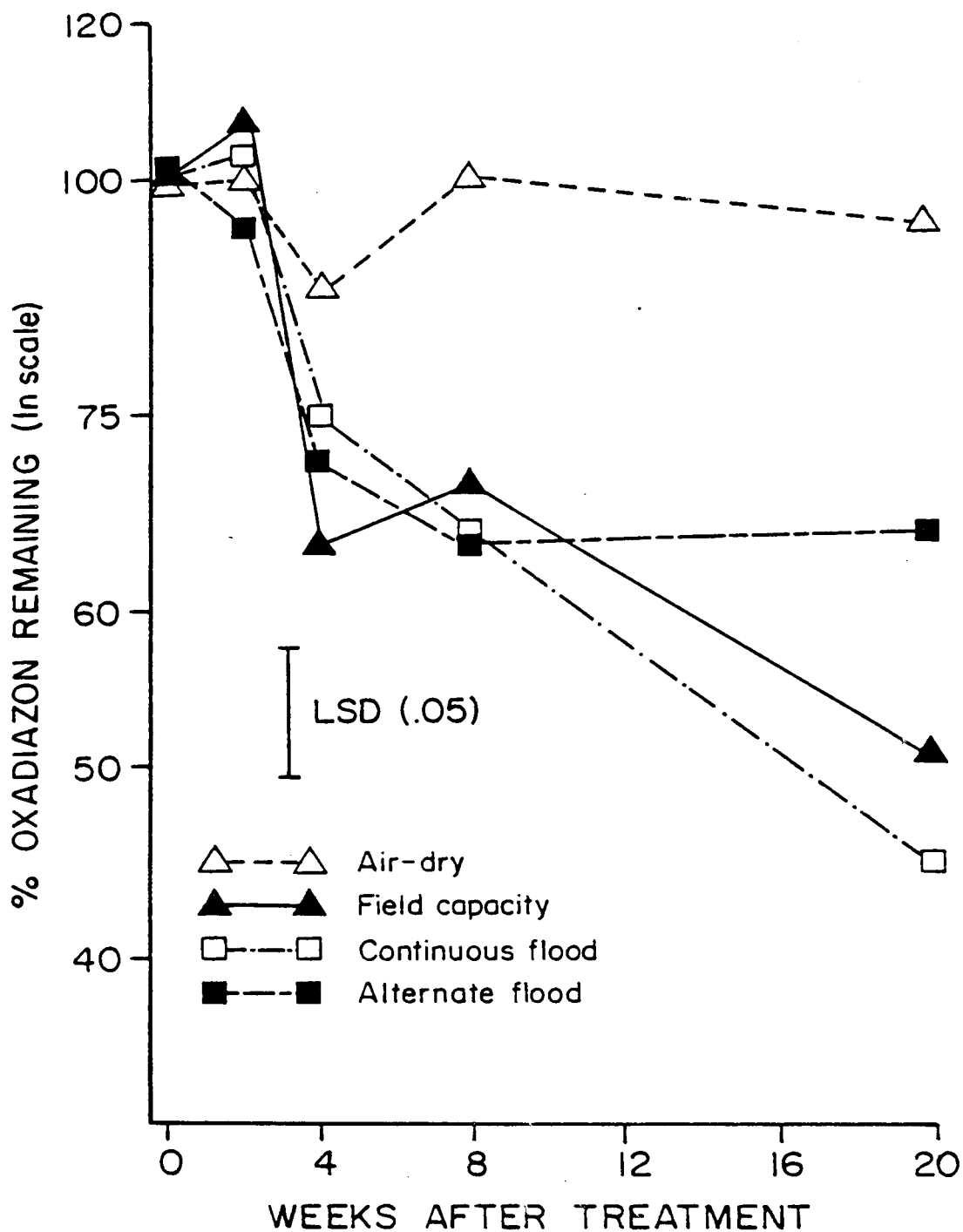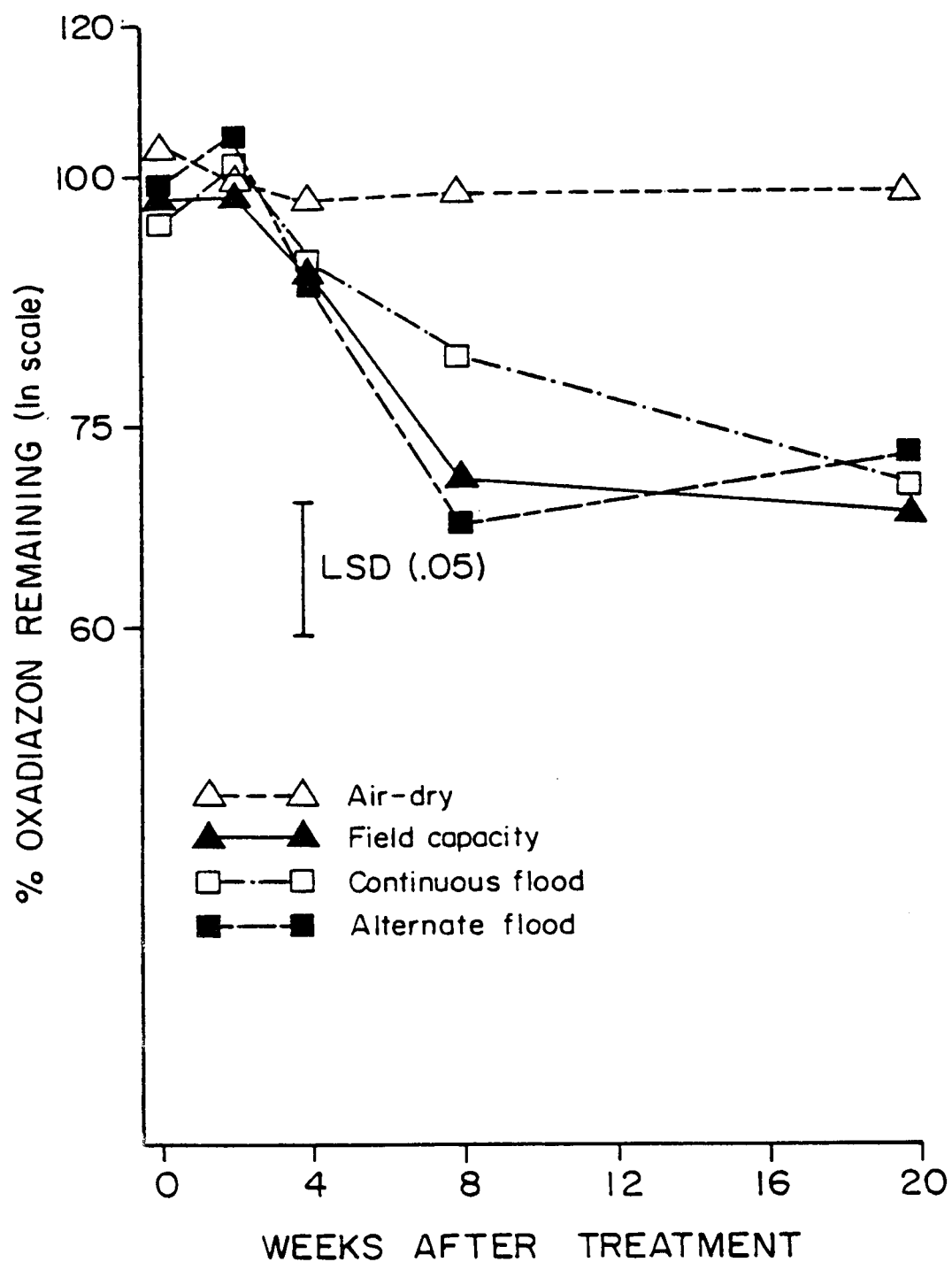
Figure 2.4. Oxadiazon dissipation over time with four moisture regimes as determined by gas-liquid chromatography: 4 µg/g application rate.
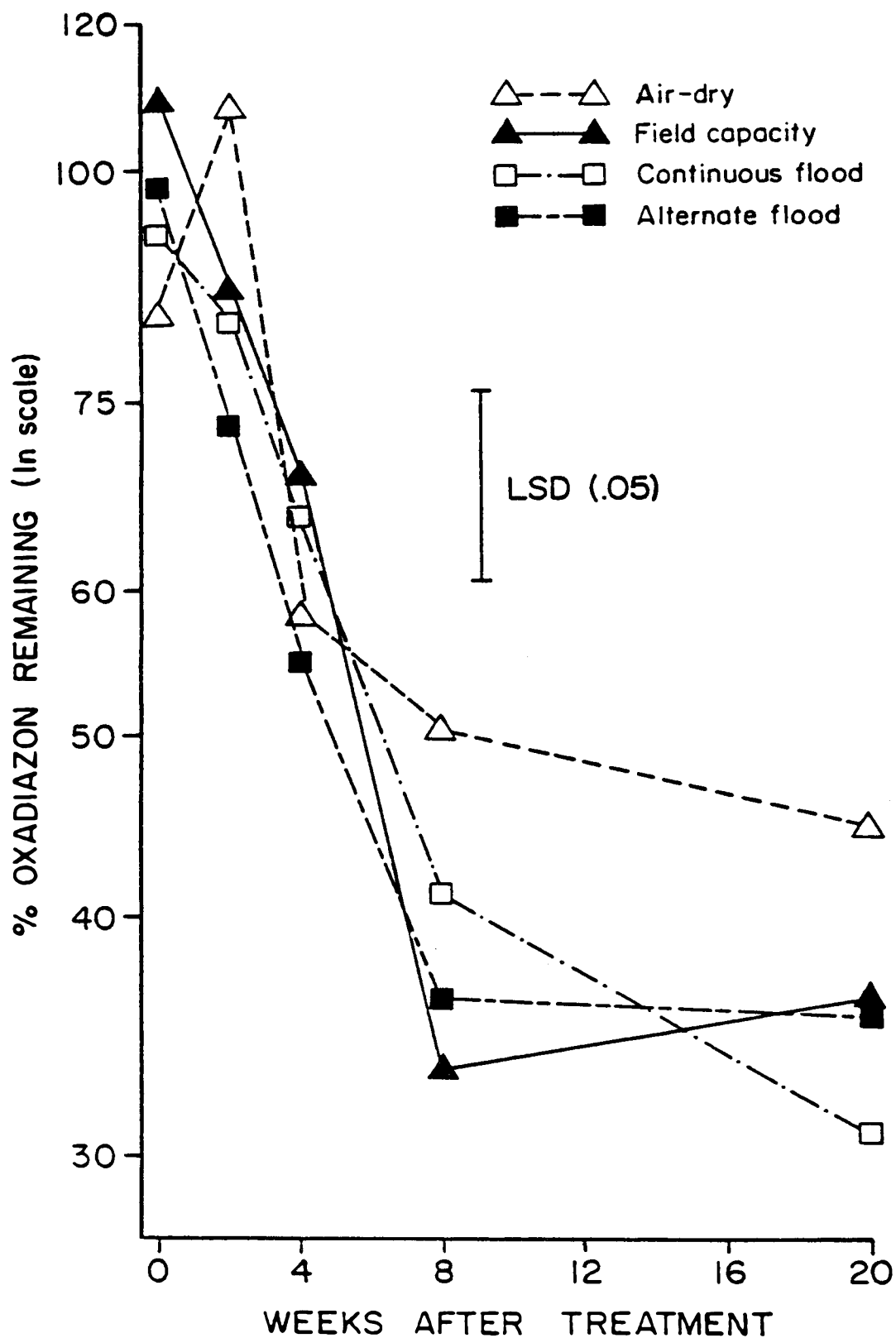
Figure 2.5.   Oxadiazon dissipation over time with four soil
moisture regimes as determined by a tall fescue
bioassay. All data are averages over three
application rates.

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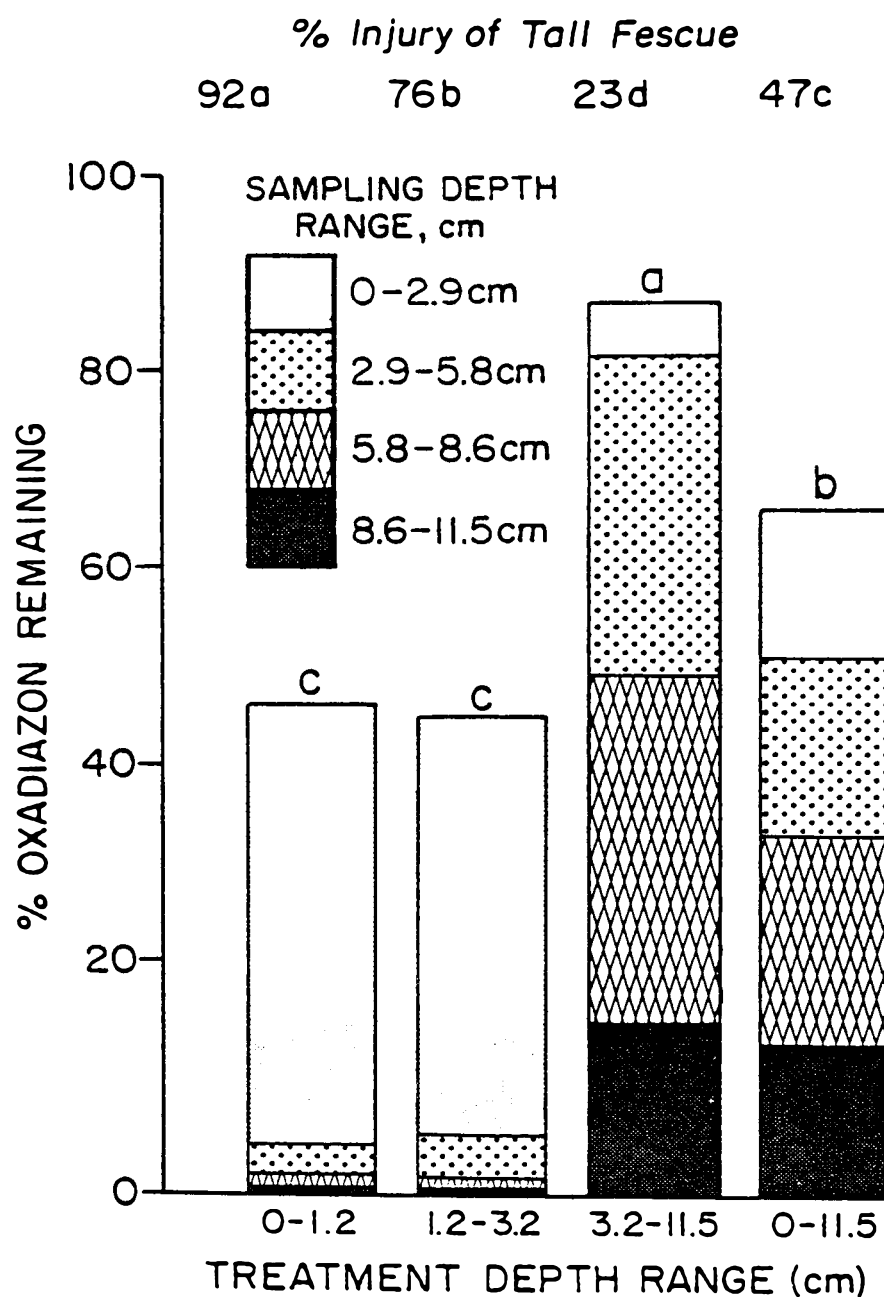
Figure 2.6. Effect of oxadiazon soil application depth on percent injury to tall fescue planted after application and oxadiazon concentration in soil 45 days later. Percentage of the total volume of the soil for the four sampling depths declined from 28% at the top to 21% at the bottom.
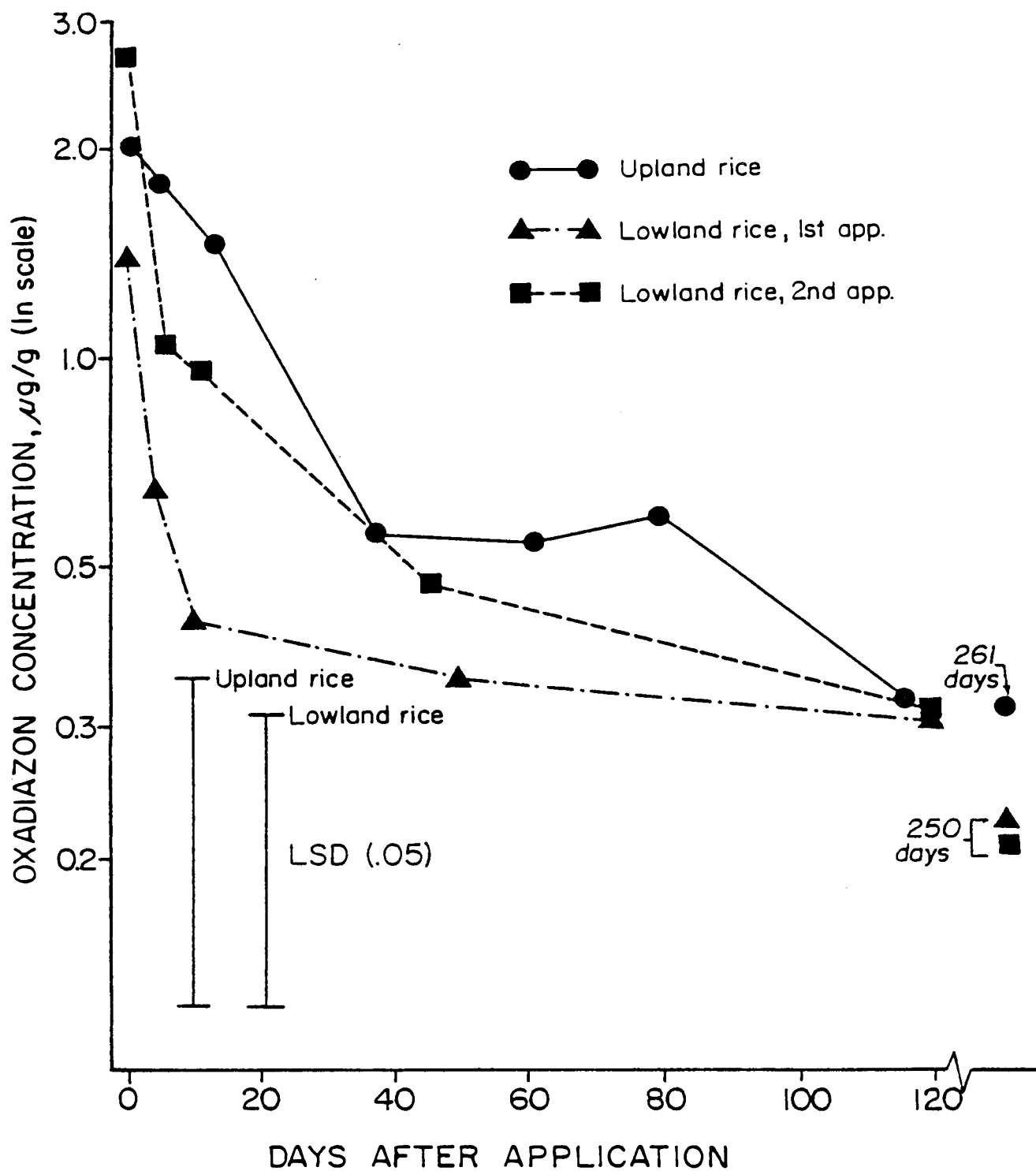
Figure 2.7. Oxadiazon dissipation in the field with two water
management systems as measured by gas-liquid chroma-
tography. 1980.

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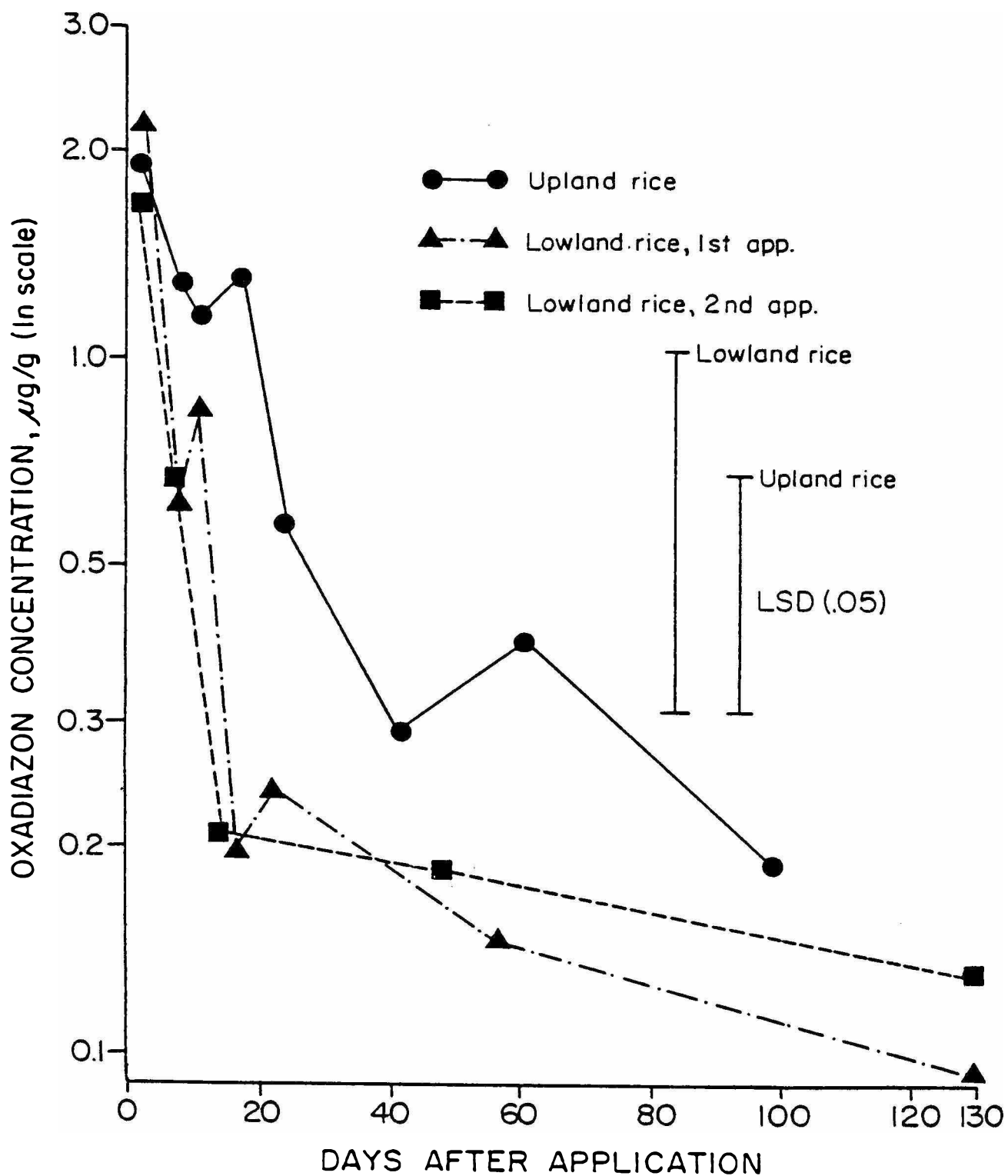
Figure 2.8. Oxadiazon dissipation in the field with two water manage-
ment systems as measured by gas-liquid chromatography. 1981.

Chapter III

Atrazine Dissipation Rates
in Anaerobic and Aerobic Soil Moisture Regimes

ABSTRACT

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-$\underline{s}$-triazine]
is a herbicide with carry-over potential that is used for weed con-
trol in crops which may be grown in rotation with rice. Dissipa-
tion rates determined by high pressure liquid chromatography (HPLC)
in four moisture regimes at 25 C in a Crowley silt loam followed
pseudo first-order kinetics. The half-lives were increased, how-
ever, from an average of 47 to 56 days for 1/3 bar, flooded, and
alternately flooded moisture regimes as the application rate was
increased from 1 to 4 μg/g. Average half-lives for air-dry, field
capacity, flooded, and alternately flooded moisture regimes were
>> 165, 52, 49, and 52 days, respectively, indicating that atrazine
persistence is similar in anaerobic or alternately anaerobic con-
ditions to that in moist, predominately aerobic soil. Both HPLC
and bioassays with soybeans [Glycine max (L.) Merr.] were used to
determine atrazine residues in soil planted to grain sorghum
[Sorghum bicolor (L.) Moench] in each of two years. Half-lives
ranged from 18 to 25 and 20 to 32 days with preemergence and pre-
plant incorporated treatments, respectively. Atrazine half-lives
determined by bioassay averaged 28 and 23 days for the two years
compared to 23 and 21 days with HPLC analyses. The soybean bioassay
had a sensitivity range for concentrations of atrazine in soil that
was comparable to the HPLC method when the soil was diluted as
necessary to achieve a herbicide concentration in the most sensi-
tive range of the bioassay. When high dilutions of 10 to 20-fold
were made the bioassay method underestimated atrazine concentration.

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INTRODUCTION

Dissipation rates of atrazine in soil have been the subject
of a number of studies (4,9, 10, 15, 16, 17, 18, 19, 20, 23). Some
variables which have been shown to influence atrazine dissipation
rate in soil include temperature (15, 16, 17, 20, 23), moisture
(10, 19, 20), concentration (4, 9, 18), and depth of incorporation
(4). In most studies pseudo first-order kinetics have adequately
described atrazine dissipation in the laboratory (10, 18, 19, 20,
23) but others have found dissipation to deviate significantly from
a first-order rate (9). In the field factors affecting atrazine
persistence are dynamic, and first-order kinetics may not be
adequate to describe atrazine dissipation without accounting for
the effect of change in conditions over time such as temperature
and moisture (20).

Atrazine persistence in soils is sufficient to result in
carry over of phytotoxic residues in some field conditions (17).
The dissipation rate of atrazine in general is more rapid with in-
creasing soil water content below field capacity (19, 20). Rates
of atrazine chemical and microbial degradation may decline somewhat
when the water content is sufficient to flood the soil (6). De-
gradation of atrazine to a hydroxy derivative has been shown to be
an important dissipation mode in flooded (21) and aerobic (1) soil.

Specific information is lacking on how anaerobic conditions
might alter atrazine dissipation rates. Atrazine is used for weed
control in situations where anaerobic conditions are unlikely to
predominate in soil. However, atrazine sometimes is applied with

crops that are followed in rotation by rice, where anaerobic conditions often do predominate.

This research was carried out to determine the effect of continuous and alternate anaerobic conditions on atrazine dissipation rates at three initial concentrations in Crowley silt loam. This soil is commonly used for rice production in rotation with other crops in Arkansas and Louisiana. Field experiments were also conducted in irrigated grain sorghum to determine the potential for atrazine carry over when surface applied or preplant incorporated in Crowley silt loam.

MATERIALS AND METHODS

Residue analysis. A C rowley silt loam (5% sand, 21% clay, 74%

silt, 1.7% organic matter, and pH 5.5) was used for all experiments.

Atrazine was chemically extracted from soil and then analyzed by

high pressure liquid chromatography (HPLC) in both the laboratory

and field experiments. For the field study analyses a bioassay

using soybeans was also used as an analytical tool.

The chemical extraction was based on an established method

for gas-liquid chromatographic analysis (14). Soil extractions

were carried out by adding 50 g of soil with known moisture con-

tent to a 250 ml round bottom flask along with 100 ml of 90%

acetonitrile. The soil-solvent mixture was refluxed for one hour,

then immediately cooled in an ice bath. The mixture was filtered

and 60 ml of the filtrate was added to a 500 ml separatory funnel.

To the filtrate was added 300 ml of water plus 20 ml of saturated

aqueous NaCl. Two extractions were carried out in the separatory

funnel with 25 ml of dichloromethane. The combined fractions of

dichloromethane were evaporated to dryness in test tubes in an

Organomation N-Evap®. To the residue in the test tubes was added

2 ml dichloromethane.

A Silica Sep-Pack® (Waters Associates, Inc) was flushed in

sequence with 3 ml 5% diethyl ether in dichloromethane, and twice

with 2 ml of 100% dichloromethane before adding the 2 ml of dichloro-

methane containing the atrazine residue. Subsequently, 6 ml of 3%

diethyl ether in dichloromethane was flushed through the Sep-pak®and

discarded along with all previous fractions. A final rinse of the

Sep-Pak® with 13 ml of 5% ether in dichloromethane was used to elute the atrazine from the Sep-Pak®. To this solution was added 3 ml of 2 µg/ml linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea)] in dichloromethane which was used as an internal standard.

Analysis for atrazine was performed with a liquid chromatograph equipped with a fixed 254-nm UV detector, and a 5 mm i.d. Radial-Pak 10 µm C_8 column. The mobile phase was 30% acetonitrile – 70% water at a flow rate of 2 ml/min. Recovery of atrazine from Crowley silt loam spiked in the range from 0.05 to 8.00 µg/g averaged 84%.

Soybean bioassays were performed in a greenhouse for all field experiments. A standard curve was obtained for the bioassays from ratings of soybean injury due to known concentrations of atrazine. Ratings were based on the extent of chlorosis and loss of foliage 28 days after planting. Standard curves were determined with each bioassay. Atrazine concentration was determined by linear regression of the injury rating for atrazine concentrations from 0.1 to 0.5 µg/g of soil. For soil containing atrazine residues in excess of 0.5 µg/g the treated soil was bioassayed again using a dilution technique. The soil was passed through a 2 mm sieve and thoroughly mixed with untreated 2 mm sieved soil in proportions to manipulate the residue level to the range of greatest sensitivity of the bioassay.

Laboratory study. This study was carried out in an incubator at 25 C in the dark. Effects of the following factors on atrazine dissipation rate were studied in a factorial design: (1) the application rate at 0, 1, 2, and 4 µg/g; (2) soil moisture using

air-dry, 29% moisture (1/3 bar), 60% moisture (continuous flood), and an alternately flooded and dried (to 21±5% soil moisture) regime over a seven day period. Entire 50 g samples were extracted for HPLC analysis 0, 30, 50, and 165 days after treatment.

Data converted to percent original concentration remaining and log-transformed were analyzed by a factorial analysis of variance and analysis of covariance (ANCOVA) with time as the covariate. Regressions over time for each treatment combination was performed to test the applicability of pseudo first-order kinetics.

Field study. Atrazine dissipation rates in Crowley silt loam were evaluated at the Rice Branch Experiment Station of the University of Arkansas at Stuttgart. Atrazine was applied pre-emergence or preplant incorporated to a depth of 5 cm at 2.24 kg/ha in plots which were subsequently planted to grain sorghum. Application dates were May 28 in 1980 and May 14 in 1981. The field design was a randomized complete block with three replications per treatment.

Atrazine dissipation over time was evaluated using both HPLC analyses and bioassays. Soil sampling for residue analysis was done prior to and immediately after atrazine applications, and at various time intervals thereafter, as shown in Figure 2. Soil samples of at least 1000 g were taken with a trowel from the upper 7.5 cm by combining samples from at least five places in each plot. The soil was stored at -10 C until ready for analysis. Plots were

furrow irrigated 46, 64, and 88 days after treatment in 1980, and 34 and 62 days after treatment in 1981. Relevant climatological data have been presented earlier (2).

The field study was subjected to analysis of covariance (ANCOVA) with time after herbicide application as the covariate. Regression was performed on the natural logarithm of the data collected for each treatment from 0 to 100 days after application to test for the applicability of pseudo first-order kinetics in describing atrazine dissipation.

RESULTS AND DISCUSSION

Laboratory study. Atrazine dissipation was significantly affected by the moisture regime and by the application rate, and was adequately described by pseudo first-order kinetics for all moisture regimes except the air-dry regime (Table 1). The half-life of atrazine for the moist soil treatments increased from an average of 47 to 50 to 56 days as the application rate was increased from 1 to 2 to 4 μg/g. Similar effects of initial concentration on atrazine dissipation have been reported in other studies at constant moisture levels in aerobic soil (9, 18). The assumption made, for a first-order type rate of loss, that the half-life is independent of the starting concentration is, therefore, not strictly true for atrazine dissipation.

There was significant loss of atrazine in the air-dry moisture regime over 165 days as revealed by analysis of variance. The air-dry atrazine dissipation rate was, however, much slower than with the other moisture regimes and was not significantly related to a first-order model (Table 1 and Figure 1). There was significantly more atrazine persistence in the 1/3 bar than the continuous flood or alternate flood moisture regimes. This difference is small, however, and did not exceed the variability in half-lives with these treatments.

Hurle and Kibler (10) have demonstrated that the relationship between soil moisture and atrazine dissipation rate can be altered by previous wetting and drying. In four soils with a wide range

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Table 3.1. Effect of moisture regime and application rate on the half-life of atrazine in soil at 25 C. Values in parenthesis are the corresponding squared correlation coefficients which are all highly significant at $p < .01$, except for air-dry treatments.

Moisture reg.	Application rate, $\mu g/g$						Mean half-life	Mean % Remaining[a]
	1		2		4			
	--------(half-life, days)-----------------							
Air-dry	448	(.25)	275	(.22)	400	(.25)	-	92 a
Field cap.	51	(.91)	44	(.91)	61	(.88)	52	56 b
Cont. flood	43	(.94)	53	(.87)	51	(.87)	49	49 c
Altern. flood	48	(.88)	53	(.92)	55	(.95)	52	49 c
Mean half-l.[b]	47		50		56			
Mean % rem.[a]	58 b		61 ab		64 a			

[a] I.E., average percent atrazine remaining over all four sampling times. Means followed by the same letter are not significantly different at $p < .05$ by Duncan's Multiple Range Test.

[b] Omitting the air-dry treatment, which has non-significant correlation coefficients.

of adsorptive capacities Fusi and Franci (5) found that alternate
wetting and drying resulted in atrazine persistence intermediate
between persistence in soil kept at air-dry or at 100% field
capacity. Lavy et al. (12) found degradation of atrazine to occur
at similar rates in aerobic soil and anaerobic soil (in sealed
containers) kept at the same moisture content. The present study
indicates that the dissipation rate of atrazine in a flooded soil
is not greatly altered from the rate in moist aerobic soil. Varia-
tions in soil water content above some minimum level (in this study
about 70% field capacity) did not affect the dissipation rate sub-
stantially. However, evidence from another study (10) indicates
that drying the soil to very low moisture levels can have a signi-
ficant effect.

Field study. Atrazine dissipation was described adequately
by pseudo first-order kinetics in spite of the more variable con-
ditions in the field (Table 2). Half-lives were slightly longer
for the preplant incorporated than the preemergence applications
in both 1980 and 1981, but the persistence was significantly
greater for preplant incorporated applications only in 1980
(at $p < .05$, as revealed by analysis of covariance). The slight
increase in persistence of atrazine with incorporation is typical
for this compound (13). Results of the present study indicate
that modes of dissipation specifically associated with the sur-
face, such as volatilization and photodecomposition, probably
accounted for only a small proportion of the atrazine dissipated.

Table 3.2. Half-lives calculated for up to 100 days after treatment for preplant incorporated and preemergence applications of atrazine in the field. Values in parenthesis are the corresponding squared correlation coefficients (all values are highly significant at p $<$ .01).

Application type	------(Year)------------------				
	1980		1981		
	Bioassay	HPLC	Bioassay	HPLC	Mean
	----------(half life, days)---------------------				
Preemergence	25 (.97)	18 (.85)	21 (.80)	18 (.81)	21
Preplant incorp.	32 (.85)	20 (.87)	24 (.80)	24 (.89)	25
Mean	28	19	23	21	

Analysis of covariance of the data indicated that in 1980, but not in 1981, there was a significant difference in atrazine residues as determined by bioassay and HPLC analysis. Bioassay determinations of atrazine levels in 1980 were lower than HPLC dterminations up to 10 days and greater after 30 days, which is reflected by the longer half-lives estimated by bioassay than HPLC analysis in 1980 (Table 2). Although application rates were planned to be the same both years the initial concentrations found by HPLC analysis were more than two times greater in 1980 than 1981. For the samples taken soon after application, to achieve an atrazine concentration in the soil in the range of sensitivity of the soybean bioassay it was necessary to dilute the soil 10 to 20 times with untreated soil. Even with thorough mixing of the soil, there may not be as uniform a distribution of atrazine in the soil in the diluted samples as the non-diluted samples. Therefore, atrazine may not be available for uptake by as much of the root system in the diluted soil, resulting in lower estimates of atrazine concentration.

Winter samples taken in 1980 indicate that atrazine dissipation was much slower in this period, presumably due to the temperature decline. Potential carry over of atrazine probably is best determined by the dissipation rate during the summer and the fall, when most loss of atrazine is likely to occur.

General discussion. In the atrazine field studies, the half-life of atrazine averaged 23 days over all treatments (Table 2) compared to an average of 51 days over all moist soil treatments in the laboratory study (Table 1). Possible reasons for this

include differences in (1) temperature, (2) leaching, (3) pH, or (4) moisture, all of which can significantly affect the dissipation rate of atrazine from soil.

1. Increasing temperature increases the rate of atrazine dissipation (19). Temperatures were not higher in the field at least in the initial weeks after application (2), and it seems unlikely that temperature accounted for differences between field and laboratory dissipation rates.

2. Recent studies have examined atrazine leaching in detail (9, 22) and indicate that the percentage of field applications of atrazine dissipated by leaching more than a few centimeters in depth is small in several soils of widely different texture and organic moisture content. However, extensive movement of atrazine in the upper 30 cm occurred near the bottom of a watershed where soil moisture was presumed to be high (22). In the present study, significant rainfall occurred 0, 3, 11, 12, 20, 21, and 22 days after the atrazine applications in 1981 but only occurred twice within a month after applications in 1980. Leaching seems a possible explanation for much of the increased dissipation in the field in 1981 but not in 1980.

3. The chemical degradation rate of atrazine has been shown to be, in many cases, increased significantly as soil pH decreases below neutrality (3, 11) although this is not always the case (8). In dissipation studies with another herbicide, the pH of flooded Crowley silt loam after 12 weeks had risen to from 6.1 to 7.1, depending on the microbial population present (2). However, if pH

differences in flooded and moist aerobic Crowley silt loam were controlling the rate of hydrolysis of atrazine, then the moist treatments in our laboratory study would be expected to exhibit more pronounced differences in dissipation rate than occurred.

4. Soil water content in the upper 7.5 cm from which atrazine residues were determined would have been lower than the 1/3 bar, flooded, or alternately floded laboratory treatments most of the time. This might have resulted in more favorable conditions for certain modes of dissipation, such as degradation by aerobic soil micro-organisms.

This research demonstrates that atrazine persistence in Crowley silt loam is not affected substantially by variations in soil water from 1/3 bar tension to flooded conditions. Soil incorporation of the chemical only slightly increased the dissipation rate of atrazine in irrigated grain sorghum averaging 23 days compared to an average of 51 days when incubated in the laboratory at 25 C in the same soil subjected to 1/3 bar, flooded, or alternately flooded moisture regimes. Atrazine carry over from standard application rates in Crowley silt loam would not be expected to be a problem under irrigated conditions, in flooded fields, or in areas receiving good summer rainfall.

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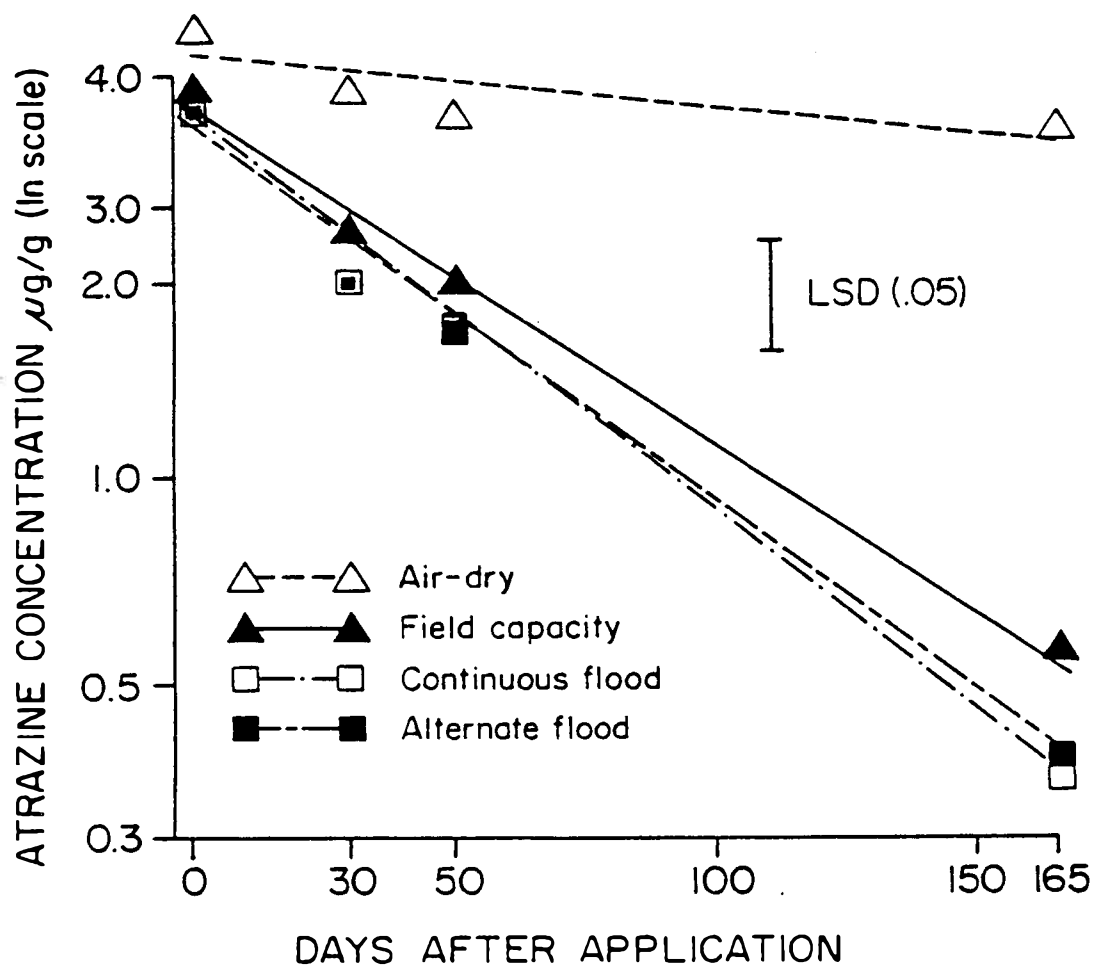
Figure 3.1. Atrazine dissipation over time from a 4 μg/g application rate with four soil moisture regimes.
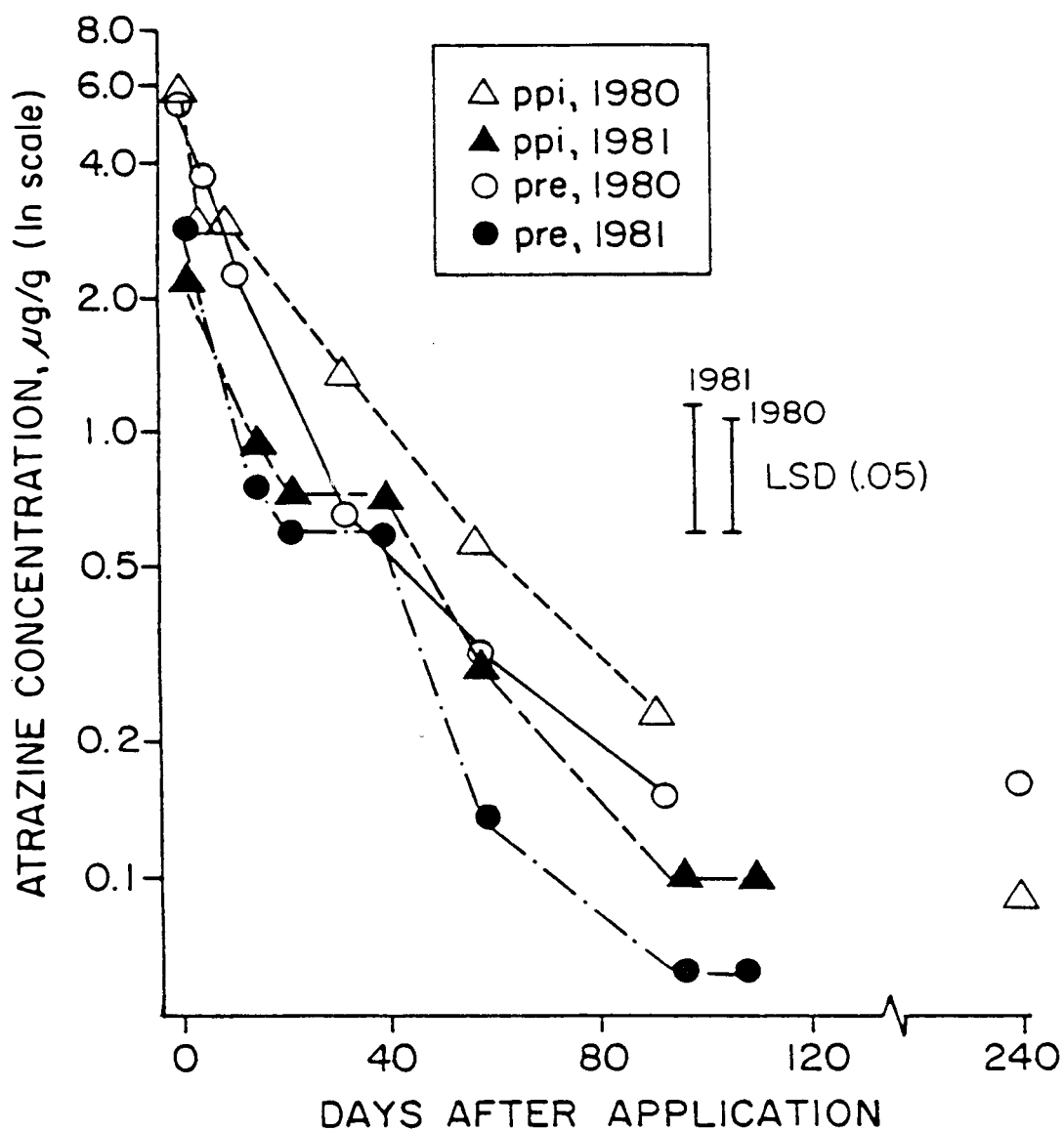
Figure 3.2. Atrazine dissipation from preemergence and preplant incorporated applications in an irrigated field in 1980 and 1981.

ABSTRACT

The effects of aerobic and anaerobic soil moisture regimes
on the dissipation rates of three herbicides were examined in a
Crowley silt loam. The dissipation rate of pendimethalin
[N-(1-ethylpropyl)-3,4 dimethyl-2,6-dinitrobenzeneamine] was
greater in alternately flooded and dried soil than with soil
water content at 1/3 bar tension or with a continuous flood, these
treatments having half-lives averaging 30, 59, and 63 days respec-
tively, at 25 C. Autoclaving was found to reduce pendimethalin
dissipation at 2/3 bar soil water tension but not in flooded soil.
In field studies, the "half-life" of pendimethalin was much
shorter during the initial two weeks after application than after
this time. The initial period half-lives with three water manage-
ment systems ranged from 3 to 6 days for a lowland rice (Oryza
sativa L.), 4 to 7 days for an upland rice, and 5 to 28 days for an
irrigated soybeans [Glycine max (L.) Merr.] system. The dissipation
of oxadiazon [2-tert-butyl-4(2,4-dichloro-5-isopropoxyphenyl)-Δ^2-1,
3,4-oxadiazolin-5-one] did not vary significantly between 1/3 bar,
continuous flood, and alternate flood treatments, with an average of
59% remaining after 20 weeks. Comparison of residue determinations
with gas-liquid chromatography and a bioassay with tall fescue
(Festuca arundinacea Schreb.) indicated that by eight weeks after
oxadiazon was applied an average of 45% of the oxadiazon remaining
in soil exposed to different soil water regimes was biologically
inactive. In a greenhouse study subsurface application of oxadiazon

reduced its biological activity but increased its persistence as much as four times compared to surface-applied oxadiazon. In field studies, surface-applied oxadiazon initially had a half-life of 4 to 11 days with lowland rice and 15 to 33 days with upland rice. Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino-s-triazine] had average half-lives of 52, 49, and 52 days with field capacity, flooded, and alternately flooded moisture regimes, respectively. Atrazine half-lives ranged from 18 to 25 and 20 to 32 days with preemergence and preplant incorporated treatments, respectively, in an irrigated field planted to grain sorghum [Sorghum bicolor (L.) Moench].