To the Graduate Council:

I am submitting herewith a dissertation written by Jeffrey Eric Herrmann entitled "Influence of Soil and Environmental Factors on the Persistence and Phytotoxicity of Pendimethalin and Flumetralin". I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Plant and Soil Science.

Robert M. Hayes, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor
and Dean of the Graduate School

INFLUENCE OF SOIL AND ENVIRONMENTAL FACTORS ON THE PERSISTENCE AND PHYTOTOXICITY OF PENDIMETHALIN AND FLUMETRALIN

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Jeffrey Eric Herrmann

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DEDICATION

This dissertation is dedicated to my father

Mr. John Edward (Jack) Herrmann (1938 - 1989)

who is my inspiration and role model.

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ABSTRACT

Pendimethalin {*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine} and flumetralin {*N*-ethyl-*N*-(2-chloro-6-fluorobenzyl-2,6-dinitro-α,α,α-trifluoro-*p*-toluidine} are dinitroanilines used for weed and sucker control, respectively, in tobacco. Use of both compounds can cause enhanced injury to crops following tobacco through an interaction. Experiments were conducted to determine if this interaction results from the increased persistence of one or both pesticides. The influence of soil and environmental factors on the persistence of these pesticides and the best model to describe their degradation in soil were evaluated.

Pendimethalin and flumetralin, alone or in combination, were applied to four soils and incubated under four environments for five time intervals. A completely randomized design with a factorial arrangement of treatments was used. Soil concentrations of the pesticides were determined by chemical assay using high performance liquid chromatography. Half-life for each pesticide, alone and in combination, was calculated using the first-order degradation model. The influence of soil properties on pesticide persistence was analyzed by linear correlation with half-lives. Temperature effects on the pesticide degradation rates were determined using activation energies. Effects of soil, soil water content, and temperature on residual phytotoxicity to corn were analyzed. Soil concentration data were fit to

several degradation models and compared for the best fit of the data.

Pendimethalin half-life was shortest in a Decatur clay loam. Flumetralin half-life was shortest in a Dickson silt loam. Flumetralin half-life was longer than the pendimethalin half-life in all soils except the Dickson silt loam. Pendimethalin and flumetralin half-lives, when applied in combination, were not significantly different from half-lives of that pesticide alone, so the interaction is not due to increased persistence. Pesticide half-lives were longer at 15 C than 30 C. No difference in half-lives either pesticide occurred between soil water contents. Soil properties were not highly correlated with persistence. Activation energy was lowest for flumetralin and in the Dickson silt loam soil, indicating possible differences in degradation pathways between pesticides and between soils.

Initially, pendimethalin and flumetralin were equally phytotoxic to corn, with differences over time resulting from temperature and soil effects on pesticide persistence. Observed response of the combination treatment, as the percent of the untreated control, was greater than the calculated expected response although the interaction was not significant. Pesticides were phytotoxic longer in a Sequatchie loam than in the Dickson silt loam.

The biexponential and quadratic models had higher coefficients of determination (r^2) than the first-order model. Little difference was seen between the first-, second, or zero-order models. Higher r^2 values were observed under conditions favoring more rapid degradation.

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CHAPTER I

INTRODUCTION

Agricultural chemicals play a major role in the production of quality tobacco (*Nicotiana tabacum* L.) in Tennessee and other tobacco producing states. Pendimethalin {*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitro-benzenamine}, manufactured by the American Cyanamid Company under the trade name Prowl™, is a popular soil-applied herbicide used for control of most annual grass and some broadleaf weed species in tobacco (Weed Science Society of America, 1989; American Cyanamid Company, 1989). Flumetralin {*N*-ethyl-*N*-(2-chloro-6-fluorobenzyl)-2,6-dinitro-*α*,*α*,*α*-trifluoro-*p*-toluidine}, manufactured by the Ciba-Geigy Corporation under the trade name Prime+™, is a foliar-applied plant growth regulator used for control of axillary buds (suckers) in tobacco (Ciba-Geigy Corporation, 1987). Pendimethalin and flumetralin are dinitroanilines. Their mechanism of action includes inhibition of cell division and elongation (Ashton and Crafts, 1981).

Injury to fall- or spring-planted crops following flumetralin-treated tobacco has been observed and the use of other dinitroanilines, such as pendimethalin, for weed control during the same growing season may result in an interaction causing excessive injury to subsequent crops (Ciba-Geigy

Corporation, 1987; Kittrel et al., 1986; Peedin et al., 1985). A synergistic interaction between pendimethalin and flumetralin, resulting in enhanced injury to wheat (*Triticum aestivum* L.), has been documented (Shelby et al., 1990).

Enhanced crop injury can result from the increased persistence of pesticides applied in combination, particularly where they have the same or similar mechanisms of action. There are many examples where persistence of a pesticide was increased when used in combination with other pesticides (Hurle and Walker, 1980; Kaufman, 1972).

Persistence is not a fixed property of a pesticide, but is influenced by the chemical nature of the pesticides themselves, the physical and chemical properties of the soil, and the environmental conditions (Hamaker, 1972; Hurle and Walker, 1980; Morrill et al., 1982). The influence of these factors on dinitroaniline persistence has been reviewed (Helling, 1976; Weber, 1990), but little is known about their effect on flumetralin behavior in soil or their effect on dinitroanilines in combination.

The detection and quantification of pesticides in soil is routinely done by either chemical or biological assay. Results obtained from each assay on identical soil samples have shown differences in the estimation of pendimethalin concentrations in the soil and the prediction of its persistence (Zimdahl et al., 1984). Determination of the exact nature of a pesticide interaction would necessitate the use of both a biological and chemical

assay (Kaufman, 1972).

Pesticide degradation has often been described using mathematical models, which allow for the estimation of pesticide degradation rates and prediction of future pesticide concentrations. Most pesticide degradation data are fit to a simple exponential equation, corresponding to the first-order degradation model. This model has not always given adequate results for description of the degradation of the dinitroanilines (Zimdahl et al., 1984; Gingerich and Zimdahl, 1976), with some variation in the fit of the data to the model over different soil and environmental conditions (Brewer et al., 1981; Zimdahl and Gwynn, 1977).

The objectives of this research were to determine: 1) if the persistence of pendimethalin and flumetralin applied in combination is different from their persistence applied alone, 2) the influence of soil, soil properties, and environmental factors on the persistence of pendimethalin and flumetralin, 3) the soil concentrations of pendimethalin and flumetralin by chemical and biological assay and compare the assays for accuracy, precision, and sensitivity, and 4) the suitability of several degradation models for describing pendimethalin and flumetralin degradation compared to the first-order degradation model, under a variety of soil and environmental conditions. Objectives 1, 2, and 3 are covered in Chapter II, and objective 4 is covered in Chapter III.

CHAPTER II

INFLUENCE OF SOIL AND ENVIRONMENTAL FACTORS ON THE PERSISTENCE AND PHYTOTOXICITY OF PENDIMETHALIN AND FLUMETRALIN

A. LITERATURE REVIEW

Pesticide Use, Properties, and Mechanism of Action

Pendimethalin is a selective, dinitroaniline herbicide labeled for use in tobacco. It is soil-applied prior to transplanting and incorporated to a depth of 2.5 to 5 cm. Pendimethalin rates for tobacco in Tennessee range from 0.84 to 1.12 kg ai ha^{-1} for coarse-textured soils and 1.12 to 1.68 kg ai ha^{-1} for medium- and fine-textured soils. Higher labeled rates are also recommended when weed pressure is expected to be high or when crop residues, prior to seedbed preparation, are extensive (American Cyanamid Company, 1989).

Selected physical and chemical properties of pendimethalin are in Table 1. Pendimethalin is a highly hydrophobic molecule that is essentially nonpolar and nonionizing. This results in a low water solubility

Table 1. Selected chemical and physical properties of pendimethalin and flumetralin[a].

Property	Pesticide	
	Pendimethalin	Flumetralin
Empirical formula	$C_{13}H_{19}N_3O_4$	$C_{16}H_{12}ClF_4N_3O_4$
Molecular weight (g mol^{-1})	281.3	421.8
Parachor	640	775
Molecular surface area (nm^2)	0.81	0.86
Water solubility (mg L^{-1})	0.275	0.019
Vapor pressure (mm Hg)	30×10^{-6}	$<1 \times 10^{-6}$
Henry's constant	9.1×10^{-4}	---
Soil K_{oc}	24 300	100 000

[a]Source of the values for chemical properties was Weber, J.B. 1990. Behavior of dinitroaniline herbicides in soils. Weed Tech. 4:394-406.

and high lipophilicity. The vapor pressure of pendimethalin is relatively low and makes it only slightly susceptible to volatilization (Helling, 1976; Weber, 1990). Parameters such as parachor (calculated molecular volume), molecular surface area (one molecular side), Henry's constant (expression of distribution between air and water phases), and soil K_{oc} (sorption capacity index for soil organic carbon) are often used to predict pesticide environmental behavior and fate, and are often correlated with soil sorption, bioavailability, and persistence (Weber, 1990).

Pendimethalin's primary mechanism of action is the inhibition of cell division and elongation. Weed control results from the inhibition of roots and shoots growing in the zone of pendimethalin incorporation, causing stunting of the aerial plant portions (Parka and Soper, 1977).

Flumetralin is a dinitroaniline plant growth regulator labeled for control of axillary buds (suckers) following the removal of the terminal inflorescence (a practice called topping) of tobacco (Ciba-Geigy Corporation, 1987). It is applied to the tobacco foliage either by directed spray or hand application to individual plants. The recommended time of application is during the elongated-button stage or early-flower stage. Flumetralin is applied at rates of 0.81 to 1.34 kg ai ha^{-1}, in approximately a 2% solution. The rate of application depends on the number of suckers, type of tobacco, and method of application. Flumetralin has only localized systemic activity, and must contact every leaf axil to be efficacious (Steffens, 1980).

Selected physical and chemical properties of flumetralin are in Table 1. Like pendimethalin, flumetralin is highly hydrophobic and lipophilic, but less water soluble and less likely to volatilize than pendimethalin (Weber, 1990).

The mechanism of action of flumetralin has not been positively determined, but like other dinitroanilines, it is thought that inhibition of cell division and elongation is the primary mechanism (Ciba-Geigy Corporation, 1982) and thus it would have herbicidal activity similar to other dinitroanilines.

Factors Influencing Pesticide Persistence

Persistence is defined as the period of time a pesticide remains intact (in the form of the parent compound) and biologically active in soil (Hiltbold, 1974). Many factors have been shown to affect pesticide persistence in soil. Some of those most commonly studied are: chemical structure and properties of the pesticide in question, initial concentration, temperature, soil water content, time, application, distribution in soil, soil properties, microbial degradation, and possibly previous application of the same, analogous or isomeric compounds (Alexander and Scow, 1989; Hamaker, 1972; Hurle and Walker, 1980; Morrill et al., 1982). Those factors pertaining to this research will be discussed.

Influence of Chemical Structure and Properties

Chemical structure of a pesticide greatly influences molecular stability and degradability (Morrill et al., 1982). Benzene rings substituted with nitro groups, sulfo groups, or chlorine have shown increased stability against degradation in soil (Alexander and Lustigman, 1966). The increased substitution of chlorine on a benzene ring decreased its degradability (Alexander and Lustigman, 1966; Klecka and Gibson, 1980). The position of functional groups on a benzene ring and their position in relation to other groups or side chains greatly influences degradation due to increased or decreased reactivity between pesticide substrate and degrading enzyme (Alexander and Aleem, 1961; Bailey et al., 1970; Bollag, 1974).

In the case of the dinitroanilines, Kennedy and Talbert (1977) stated that the order of persistence of nine dinitroanilines was benefin {*N*-butyl-*N*-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine} > butralin {4-(1,1-dimethylethyl)*N*-(1-methylpropyl)-2,6-dinitrobenzenamine} > oryzalin {4-(dipropylamino)-3,5-dinitrobenzenesulfonamide} > profluralin {*N*-(cyclopropylmethyl)-2,6-dinitro-*N*-propyl-4-(trifluoromethyl)benzenamine} > nitralin {4-(methylsulfonyl)-2,6-dinitro-*N*,*N*-dipropylaniline} > trifluralin {2,6-dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)benzenamine} > penoxalin (pendimethalin) > fluchloralin {*N*-(2-chloroethyl)-2,6-dinitro-*N*-propyl-4-(trifluoromethyl)benzenamine} > dinitramine {N^2,N^3,-diethyl-2,4-dinitro-6-(trifluoromethyl)-1,3-benzenediamine}. Those dinitroanilines with more and

longer hydrocarbon chains were degraded slower than those with fewer and shorter chains. The trifluoromethyl group was the substituent most affected by hydrolysis. Wide structural variation among the dinitroanilines is a result of the many possible functional groups substituted at four positions on the basic dinitroaniline structure (Weber, 1990).

Pesticide properties, such as water solubility, volatility or vapor pressure, molecular weight, parachor, and various partitioning coefficients (K_{ow} and K_{oc}), primarily influence pesticide availability in soil or soil sorption (Shea, 1985). Chemical and physical properties of a pesticide have been correlated with measured rates of degradation of that pesticide in order to predict pesticide persistence (Jury et al., 1983; Jury et al., 1984).

Influence of Environmental Factors

Environmental factors such as soil water content and temperature play an important role in determining pesticide persistence in soil. Persistence of most pesticides in soil, including the dinitroanilines, increases as the soil water content decreases (Hollist and Foy, 1971; Horowitz et al., 1974; Hurle and Walker, 1980; Poku and Zimdahl, 1980; Zimdahl and Gwynn, 1977). Walker and Bond (1977) concluded that pendimethalin has the potential for carryover under dry soil conditions. As soil water content increased from 12.5% to 75% of field capacity in a sandy loam soil, half-life of pendimethalin decreased from 563 d to 122 d. Similar results were

obtained by Barrett and Lavy (1983), where pendimethalin half-life was 56 d in a silt loam soil measured at a 30 kPa soil water content. No significant degradation of pendimethalin occurred in air-dry soil after 56 d. Zimdahl et al. (1984) found that pendimethalin half-lives at 30 C in a clay loam soil at 100 and 75% of field capacity were 56 and 54 d respectively, while at 50% field capacity, pendimethalin half-life increased to 73 d. Savage (1978) found a pendimethalin half-life of 99 d in a clay soil at field capacity, while half-lives of fluchloralin, trifluralin, profluralin, butralin, and dinitramine were 52, 48, 44, 36, and 31 d, respectively, under identical conditions. Persistence of all six dinitroanilines was reduced in flooded soil, indicating dinitroaniline persistence is shorter under anaerobic conditions.

As with most reactions, increased temperature results in increased reaction rates (Atkins, 1986). Temperature effects on pesticide degradation are a result of increased abiotic and biotic reaction rates (Morrill et al., 1982). Dinitroaniline persistence is increased as temperature is decreased (Gingerich and Zimdahl, 1976; Horowitz et al., 1974; Poku and Zimdahl, 1980; Probst et al., 1967). Walker and Bond (1977) found pendimethalin half-lives of 98 and 409 d, in a sandy loam soil at 75% field capacity, and temperatures of 30 C and 10 C, respectively. Zimdahl et al. (1984) found that pendimethalin half-lives, in a clay loam soil at 75% field capacity were 54 d at 30 C and 101 d at 10 C.

Temperature dependence of a reaction rate for a specific chemical or

biological reaction, adhering to first-order kinetics, is often expressed by the Arrhenius equation. This expression allows calculation of an activation energy for that reaction. It is interpreted as the amount of energy required by molecules to react (Atkins, 1986; Meikle et al., 1973; Zimdahl et al., 1970).

Activation energies calculated for degradation reactions of pesticides can be used to make some inferences and predictions about the degradation mechanism or pathway for a pesticide or family of pesticides. Activation energies for microbial processes are normally at or below 20 kJ mol^{-1}, while those for chemical processes are greater than 75 kJ mol^{-1}. This wide difference in activation energies between biotic and abiotic processes could be a basis for determining the predominant process responsible for degradation of a particular pesticide or pesticide family (Meikle et al., 1973). Pesticides with the same basic chemical structure, such as pendimethalin and flumetralin, that have similar activation energies should follow similar initial steps in their degradation pathways (Zimdahl et al., 1970). Gingerich and Zimdahl (1976) determined that the activation energies for isopropalin {4-(1-methylethyl)-2,6-dinitro-*N*,*N*-dipropylbenzenamine} under aerobic and anaerobic conditions, were 15.5 (64.8) and 15.8 (66.1) kcal mol^{-1} (kJ mol^{-1}), respectively. They concluded that the aerobic and anaerobic degradation pathways of this pesticide were similar, and primarily non-enzymatic.

Rate of pesticide degradation is dependent on soil and environmental

factors, however relative activation energies within a family of pesticides should remain constant and independent of the soil environment (Zimdahl et al., 1970).

Influence of Soil and Soil Properties

The persistence of dinitroanilines has been shown to vary depending on the soil series used (Savage, 1978; Savage and Jordan, 1980; Zimdahl and Gwynn, 1977). The influence of soil on pesticide persistence is not well understood due to the wide range of values for soil properties within the many classified soil series, and the interaction of these soil properties.

Increases in soil organic matter content generally result in increased adsorption of pesticides and thus increased pesticide persistence (Carringer et al., 1975; Bardsley et al., 1967; Weed and Weber, 1974). However, soil microbial populations are generally positively correlated with soil organic matter content, which could result in increased degradation in high organic matter soils (Hamaker, 1972; Hurle and Walker, 1980). Also, soil organic matter can promote abiotic degradation of many herbicides (Stevenson, 1972). Walker and Bond (1977) found increased persistence of pendimethalin in seven soils, as organic matter increased, with half-lives ranging from 72 to 172 d. Bregger (1985) noticed slower dissipation of flumetralin in soils with a higher percent humic matter compared to those with a lower percent humic matter.

Trifluralin and nitralin have a negative correlation with pH, indicating that higher soil concentrations were associated with lower pH soils (Savage, 1973). However, Corbin and Upchurch (1967) found no pH effect for trifluralin applied to two high organic matter soils, adjusted to four pH levels. Since most dinitroanilines are nonpolar and nonionizable (Weber, 1990), increased persistence at low soil pH should be due to decreased microbial activity, and not increased soil adsorption (Corbin and Upchurch, 1967; Hurle and Walker, 1980).

Persistence of several dinitroanilines was shown to increase as clay content increased, however organic matter content also increased (Savage, 1978; Savage and Jordan, 1980). Clay content and cation exchange capacity were positively correlated with soil concentrations of nitralin, but negatively correlated with trifluralin soil concentrations. Organic matter, clay content, and cation exchange capacity all exhibited high, positive intercorrelations (Savage, 1973). Assessing the influence of a single soil property on persistence is difficult due to the many interrelationships among soil factors (Hamaker, 1972).

Influence of Pesticide Combinations

The presence of two or more pesticides in soil resulting from successive or simultaneous applications of different pesticides (due to the use of tank mixtures or complex spray programs) is a common occurrence.

This has resulted in several instances of deviations from the normal behavior of a particular pesticide applied in combination with another pesticide. Possible causes of these deviations include increased or decreased persistence, altered toxicity, complex residue formation, or altered mode or path of degradation (Kaufman, 1972; Kaufman, 1977).

Increased persistence of a pesticide in the presence of another pesticide could be caused by decreased soil microbial populations or activity and the associated effects on enzymes, competition of the pesticides for degradation sites, or other physicochemical interactions of the pesticides in soil that would disrupt normal degradation processes (Cervelli et al., 1978; Kaufman 1972). Examples of increased persistence have been cited for several pesticide combinations (Kaufman, 1966; Kaufman et al., 1970; Kaufman et al., 1971; Walker, 1970). No evidence of increased persistence has been documented for the dinitroanilines, although some research has been conducted. Fluchloralin persistence in field studies was not found to be affected by the insecticide DBCP {1,2-dibromo-3-chloropropane} (Brewer et al., 1981), and trifluralin persistence was not affected by the herbicides triallate {*S*-(2,3,3-trichloro-2-propenyl) bis(1-methylethyl)carbamothioate} (Smith, 1979) or chloramben {3-amino-2,5-dichlorobenzoic acid} (Smith and Hayden, 1982).

Interaction of Pendimethalin and Flumetralin

Flumetralin has the potential to reach the soil surface due to application of excessive volumes to tobacco (Ciba-Geigy Corporation, 1987). Injury to rotational crops, such as fall-planted small grains or spring-planted corn (*Zea mays* L.) following flumetralin-treated tobacco has been documented (Bregger, 1985; Kittrell et al., 1986; Rawls, 1986). Application of 1.3 kg ai ha^{-1} of flumetralin to the soil surface resulted in corn injury 285 d after application. Flumetralin soil concentrations remaining from the initial application varied among soils with variable organic matter content (Bregger, 1985). Pendimethalin can temporarily reduce tobacco development under adverse weather conditions for plant growth, such as cold/wet or hot/dry conditions (American Cyanamid Company, 1989).

Tobacco production using flumetralin for sucker control in conjunction with a soil-applied dinitroaniline for weed control creates the possibility of an interaction (Ciba-Geigy Corporation, 1987; Peedin et al., 1985; Rawls, 1986). Shelby et al. (1990) detected a synergistic interaction of pendimethalin and flumetralin on wheat, following tobacco treated with pendimethalin and flumetralin. Wheat injury was less than or equal to 17% with pendimethalin alone, applied at 1.7 kg ai ha^{-1}, and 14% and 48% with flumetralin alone, applied at rates of 29 and 86 mg ai per plant, respectively. The combination of pendimethalin and flumetralin produced injury of 58%

and greater than 75% for the low and high rates of flumetralin, respectively. The observed wheat injury due to the combination treatment was greater than the expected injury, indicating a synergistic interaction. The expected injury was calculated according to Colby's method, which uses the percent injury (or percent of an untreated control) due to each pesticide applied alone to calculate the expected injury (or response) for the pesticides applied in combination (Colby, 1967). Colby states that when observed injury is less than expected injury, the interaction is called antagonistic, and when observed injury equals expected injury, the interaction is called additive. Synergistic interactions are often a result of greater or enhanced sensitivity to a given pesticide in the presence of a second pesticide (Kaufman, 1972).

Pesticide Quantification Techniques

Determination of pesticide concentrations in soil is usually done by biological or chemical-physical assays (Jacques and Harvey, 1979). A soil biological assay measures the bioavailable or phytotoxic fraction of a pesticide in soil (Lavy and Santelmann, 1986). A chemical-physical assay usually involves the extraction or removal of the pesticide from the soil and quantification by chromatographic techniques. This assay attempts to account for the majority of the total pesticide remaining in soil. The ideal extraction procedure must therefore be able to remove bound pesticide

molecules (Weete, 1986). Chemical and biological assays both give valid results, although they may not necessarily be similar results. The half-life of pendimethalin was 47 d as determined by chemical assay, and 78 to 111 d, according to biological assay (Zimdahl et al., 1984).

Determination of the exact nature of a pesticide interaction would require both types of assays. A chemical assay can measure the pesticide concentration at one time or the change in pesticide concentration over time to determine if the interaction was due to increased persistence of one or both pesticides. This could not be done by a biological assay. However a biological assay could determine if the interaction was due to increased or altered toxicity, which can not be done by a chemical assay (Kaufman, 1972).

B. MATERIALS AND METHODS

Experimental Treatments

To accomplish the objectives of this research, pendimethalin and flumetralin persistence was determined by monitoring soil concentrations of each pesticide over time under various experimental conditions. The treatments used were four soils, three pesticide treatments, two soil water contents, two temperatures, and five time intervals.

Soils

Soils used in this study were selected based on their frequent use in tobacco production in Tennessee and the southeast and on their wide variation in physical and chemical properties[1]. Soils used were Decatur clay loam (clayey, kaolinitic, thermic Rhodic Paleudult), Dickson silt loam (fine-silty, siliceous, thermic Glossic Fragiudult), Norfolk loamy sand (fine-loamy, siliceous, thermic Typic Paleudult), and Sequatchie loam (fine-loamy, siliceous, thermic Humic Hapludult).

Decatur and Sequatchie soil samples were collected from representative sites in Grainger County, Tennessee. Dickson soil samples were collected from a representative site in Dickson County, Tennessee. Norfolk soil samples were collected from the Central Crops Research Station near Clayton, North Carolina. Previous pesticide use at these sites did not include pendimethalin or flumetralin.

Bulk samples of each soil were collected from the upper 15 cm of the soil profile, using either a bucket auger or shovel. Samples were sieved to pass a 2 mm (10 mesh) sieve and stored in plastic bags in boxes at the field soil water content and room temperature until characterization analysis and experimental use. Additional sample collection was required for all soils and collections were taken at the same sites as initially.

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[1]Fowlkes, D.J. and J.R. Jared. 1988. Personal communication. Ext. Plant and Soil Sci., Univ. of Tennessee, Knoxville, TN 37901-1071.

Standard characterization analyses were conducted to determine the values for those physical and chemical properties of soil that influence pesticide persistence. Percent total carbon was determined by dry combustion at 2200 C (Leco CR12 carbon analyzer, model 781-700) (Nelson and Sommers, 1982). Percent organic matter was determined by the Walkley-Black method using chromic and sulfuric acids. For this procedure, organic carbon content was determined and then multiplied by a factor of 1.72 to obtain the percent organic matter (Nelson and Sommers, 1982). Percent sand, silt, and clay were determined by particle-size analysis using the pipette method (Gee and Bauder, 1986). Soil water contents were determined by calculating the amount of water retention per g of soil (w,w) at -33 and -100 kPa using the pressure plate method (Klute, 1986). Soil pH was determined with a glass electrode pH meter (Orion Research Inc., model no. 611) using a 1:1 (v/v) soil:water mixture (McLean, 1982). Cation exchange capacity was determined by the ammonium acetate (pH 7) method (Chapman, 1965). Data for chemical and physical properties for each soil are in Table 2.

Pesticide Treatments

Pesticide treatments used in this study were pendimethalin alone, flumetralin alone, and a combination of pendimethalin and flumetralin. All pesticides were applied at a rate of 4 μg ai g^{-1} of soil. The combination

Table 2. Soil characterization data for selected chemical and physical properties of experimental soil samples.

Soil Properties[a]	Soils			
	Decatur clay loam	Dickson silt loam	Norfolk loamy sand	Sequatchie loam
% Total carbon	0.8	1.8	0.4	1.1
% Organic matter	1.1	2.9	0.6	1.4
CEC[b] (cmol+ kg^{-1})	8.7	6.8	1.8	4.4
pH	6.9	4.9	5.8	5.5
% Sand	25.2	6.5	85.3	44.2
% Silt	41.1	80.2	8.5	44.7
% Clay	33.7	13.3	6.2	11.1
% Soil water (@ -33 kPa)	20.2	28.3	5.2	17.1
% Soil water (@ -100 kPa)	16.3	18.4	3.8	12.8

[a]Standard methods for soil characterization analyses were used and are given in text.

[b]CEC is the abbreviation for cation exchange capacity.

treatment of pendimethalin and flumetralin was used in order to determine if the persistence of either pesticide was altered due to the presence of the other pesticide in the soil, compared to their persistence applied alone.

Application rates of pendimethalin and flumetralin used in this study were approximately 4 to 6 times higher than the labeled rates of these pesticides, on a soil weight basis. This was done to ensure detectable concentrations of the pesticides at the final sampling time. Use of pesticide application rates higher than the normal use rate is a common practice in soil dissipation studies, including those for the dintiroanilines (Zimdahl and Gwynn, 1977; Zimdahl et al., 1984).

Environmental Treatments

Environmental treatments included two soil water contents and two temperatures. Soil water content treatments were the percent soil moistures of each soil determined at tensions of -33 and -100 kPa, with the former value approximating field capacity. Incubation temperatures were 15 and 30 C.

Experimental Design

A completely randomized design with a factorial arrangement of treatments was used. The total number of treatment combinations was 48

(four soils by three pesticide treatments by two soil water contents by two temperatures). Each treatment combination was replicated four times and pesticide concentration determined after five time intervals. Total number of experimental samples was 960. A summary of experimental treatments is in Table 3.

Application of Treatments

Subsamples from each bulk soil sample were air-dried, their gravimetric water content determined, and then separated into 2000 g (oven dry weight basis) subsamples. Pesticide treatments were applied to soil subsamples to obtain a final soil concentration for each pesticide of 4 $\mu g\ g^{-1}$ of soil. Technical grade pendimethalin and flumetralin, at 90.1 and 96.4% purity, respectively, were formulated at 200 μg ai ml^{-1} in acetone. Pesticide solutions were applied with a pipette in 40 ml aliquots to the surface of the soil samples under a fume hood in the laboratory. After evaporation of the acetone from the soil, samples were placed in large plastic bags and thoroughly mixed for approximately 5 min to obtain even distribution of the pesticides within each sample.

Soil water content treatments were imposed on treated soil samples by dividing each 2000 g subsample into four 500 g subsamples and adding appropriate volumes of water to bring each subsample to the specific soil

Table 3. Summary of experimental treatments and their levels.

Treatments[1]	Levels
Soil (4)	Decatur clay loam
	Dickson silt loam
	Norfolk loamy sand
	Sequatchie loam
Pesticide treatment (3)	Pendimethalin alone @ 4 μg ai g^{-1}
	Flumetralin alone @ 4 μg ai g^{-1}
	Pendimethalin @ 4 μg ai g^{-1} + Flumetralin @ 4 μg ai g^{-1}
Soil water content (2)	-33 kPa
	-100 kPa
Temperature (2)	15 C
	30 C
Time (5)	0
	30
	60
	120
	180

[1]Number of levels of experimental factors is in parenthesis. Total number of samples, with four replications of each factorial treatment combination, was 960.

water content for that sample. Samples were placed in 1000 ml glass jars and were allowed to equilibrate at room temperature for 2 d prior to the start the of incubation.

Temperature treatments were imposed on soil samples by placing the sample jars in dark incubators (Precision Scientific, model 815) either at 15 C or 30 C. Samples were incubated for times of 0, 30, 60, 120, and 180 d. Foil-lined caps were placed on the sample jars, but only slightly turned in order to maintain air contact with the outside environment and to prevent rapid loss of soil water. Distilled water was added to samples weekly to maintain the appropriate soil water content.

After incubation, samples were air-dried for approximately 24 hrs and then the soil water content of the air-dried samples was determined. This was done to compute an oven-dry weight for the subsample to be assayed and thus correct for inherent differences in air-dry soil water content between the soils. Samples were stored at -20 C until analysis.

Due to the large number of samples (960), all samples could not be incubated at together. Two separate incubation events were required. For the first incubation event, only one replication of each of the 48 treatment combinations was incubated over the five time intervals (240 samples). This was done to determine the feasibility and practicality of the study. Samples were incubated at staggered times, so all samples could be removed at the same time. Upon analysis of these results, it was determined that the study

was valid. For the second incubation event, three replications of all 48 treatment combinations were applied to another set of samples and incubated over the five time periods (720 samples).

Chemical Assay of Samples

Pesticide Extraction Procedure

Extraction of pendimethalin and flumetralin from soil was conducted according to a modified version of that used by Bregger (1985). Approximately 50 g (oven dry weight basis) of soil was taken from each of the 960 samples, and mixed with 200 ml of reagent grade acetone. Each sample was then placed in a 500 ml plastic bottle and shaken for 10 min to remove the pesticides from soil constituents. Mixtures were filtered into a 500 ml side-arm filtering flask under vacuum using a Buchner funnel apparatus and glass fiber filter paper (Baxter Scientific, grade 391). Each sample bottle was rinsed with three 25 ml aliquots of acetone. Filtered solutions were transferred to 250 or 500 ml evaporating flasks and connected to a rotary evaporator (Buchi model EL131) equipped with a heated water bath (Buchi model no. 461) set at 35 C in which the evaporating flasks were immersed. After evaporation of the sample solution to dryness, an additional 10 ml aliquot of acetone was added and the sample was again evaporated to dryness.

Dried pesticides were resuspended in 10 ml of spectrophotometric grade methanol and transferred to a 10 ml disposable syringe attached to a 25 mm filter holder (Gelman Sciences, product no. 4320) containing a 0.2 μm nylon membrane filter (Gelman Sciences, Nylaflo). Pesticide solutions were filtered into 11 ml clear glass sample vials and stored in a freezer maintained at -20 C, until analyzed, to prevent degradation of the pesticides in solution.

High Performance Liquid Chromatography Analysis

Extracted pesticides were separated, identified, and quantified by reverse-phase high performance liquid chromatography (HPLC). The two HPLC units used for analysis were equipped with essentially identical components. These components included sample injector ports (Waters model U6K), pumps (Waters model 501), and spectrophotometric detectors (Waters model 484 or Waters model 481).

The HPLC method was adapted from the method outlined for dinitroanilines by Supelco, Inc. (1989). Parameters for HPLC analysis included a mobile phase flow rate of 1 ml min^{-1}, a detector wavelength of 254 nm (UV), a pressure of approximately 17.23 MPa, a sensitivity of 1 AUFS, and an injection volume of 25 μl (Hamilton Microliter syringe).

The analytical column (Waters Novapak™ C_{18}) used was packed with 4 μm, C_{18} media in a 15 cm steel column. This type of column is commonly

used for reverse-phase liquid chromatography for analysis of nonpolar compounds. A guard column (Alltech Direct Connect™), packed with C_{18} pellicular media, was connected in-line, preceding the analytical column, to protect the analytical column from contaminant particles in the pesticide solution samples and the mobil phase.

The mobile phase employed was a three part mixture of tetrahydrofuran, water, and methanol (50:40:10; v,v,v,). All mobile phase reagents were spectrophotometric grade except the water, which was distilled and deionized. Reagents were filtered under vacuum through a 0.5 μm membrane filter (Millipore Co.) contained in a filter apparatus attached to a side-arm flask. Dissolved gases were removed under vacuum.

Retention times, under these conditions, were approximately 4 and 7 min for pendimethalin and flumetralin, respectively.

Pesticide Standards

Standard solutions of pendimethalin and flumetralin were prepared using analytical grade flumetralin and pendimethalin, with purities of 99.6 and 99.1%, respectively. Stock solutions containing 1 mg ai L^{-1} of each pesticide were prepared in acetone. Serial dilutions were made to obtain concentrations 0.05, 0.1, 0.5, 1, 10, 20, and 100 μg ai ml^{-1} of both pendimethalin and flumetralin. Standards contained both pesticides in order to reduce the number of HPLC injections used for calibration.

Pesticide standards were injected into the HPLC prior to sample analyses to determine the practicality of the method, the upper and lower concentration limits of detection, the relationship between peak response (peak height or area) with pesticide concentration for calibration purposes, and the compatibility of pesticides in solution. Lower limits of detection were 0.05 μg ml^{-1} (1.25 ng) for both pendimethalin and flumetralin, with an injection volume of 25 μl. Signal-to-noise ratios were too low below this concentration to allow accurate determination of pesticide peak height or area.

Peak height and area for pendimethalin and flumetralin gave linear responses to increasing concentrations of pendimethalin and flumetralin ($r^2 > 0.95$). However, peak height was chosen for calibration with pesticide concentration because peak areas were subject to variation in measurement due to interference from sample impurities. Concentrations of pendimethalin and flumetralin measured alone were not different from those concentrations measured in combination. Therefore, extracted solutions containing both pendimethalin and flumetralin could be analyzed at one time.

Calibration of samples

Pesticide standards were external (not present in the sample solution). Pesticide concentrations of 1, 10, and 20 μg ai ml^{-1} were injected before each sample analysis session to verify acceptable instrument operation and

for construction of an initial standard calibration curve. Due to the high r^2 values obtained for the range of pesticide standards used, samples could be calibrated using only one standard. A standard was injected for every three to five sample injections for calibration purposes. This frequent calibration was necessary to account for variations in peak response that occur.

Chemical Assay Data Transformation

The concentration of both pendimethalin and flumetralin could be determined with the HPLC analysis within each sample containing both pendimethalin and flumetralin. Thus, two measurements (pendimethalin concentration and flumetralin concentration) were recorded for each of the 320 samples containing both pendimethalin and flumetralin, while one measurement (pendimethalin concentration) was recorded in each of the 320 samples containing only pendimethalin, and one measurement (flumetralin concentration) was recorded in each of the 320 samples containing only flumetralin. From the 960 samples, 1280 measurements were recorded. These measurements are differentiated by pesticide (pendimethalin or flumetralin) and by the status of the pesticides (alone or in combination with the other pesticide). These differentiations, pesticide and pesticide status, were specified as separate classification variables. The treatment factors and their levels are now specified as soils (4), pesticides (2), pesticide status

(2), soil water content (2), temperature (2), and time (5).

Upon determination of pendimethalin or flumetralin solution concentration in each sample, the soil concentration of each pesticide was calculated. The soil concentration data were corrected for any pesticide loss that may have occurred during the periods between the pesticide applications and the start of the sample incubation and from the end of incubation to sample analysis. This would account for any pesticide lost during pesticide application and mixing, the equilibration period before incubation, treated soil sample drying, pesticide extraction, solvent evaporation, filtration, and also that portion of pesticide remaining in the soil sample after extraction. This correction factor was calculated for each soil by pesticide by pesticide status combination by dividing the measured soil concentration of each pesticide by pesticide status combination at time 0 by 4 (the initial application rate for each pesticide in $\mu g\ g^{-1}$ of soil). The identical procedures were used for each sample so pesticide loss is assumed to be equal for all samples within a soil by pesticide by pesticide status combination. The percent recovery correction factors are in Table 4.

Soil concentration data, averaged across four replications, for each pesticide by pesticide status by soil water content by temperature combination over the five time intervals for the Decatur, Dickson, Norfolk, and Sequatchie soils are in the appendix in Tables A1, A2, A3, and A4, respectively.

Table 4. Percent recovery correction factors for pendimethalin and flumetralin, alone and in combination, in each soil[a].

Soil	Pendimethalin		Flumetralin	
	Alone	Combination	Alone	Combination
	(% Recovery)			
Decatur clay loam	81.7 ± 6.0	80.0 ± 7.1	81.3 ± 3.6	80.1 ± 5.8
Dickson silt loam	97.6 ± 2.0	96.3 ± 4.6	92.4 ± 4.1	97.3 ± 5.9
Norfolk loamy sand	91.2 ± 8.0	94.1 ± 8.0	89.0 ± 9.2	95.3 ± 6.7
Sequatchie loam	96.1 ± 3.0	92.1 ± 10.4	95.1 ± 9.0	91.5 ± 8.9

[a]Values for percent recovery include the standard error of the mean and were averaged over eight replications.

First-order Degradation Model

To simplify statistical analyses, data were transformed using the first-order degradation model to convert the soil concentration data of each pesticide over time from a nonlinear to a linear expression. The first-order model is described by the linear equation

$$\ln\left(\frac{C}{C_0}\right) = -kt$$

where C is the observed sample concentration at time t, C_0 is the original concentration at time 0, k is the first-order rate constant, and t is time (Nash, 1988; Hamaker, 1972). Rate constants were estimated by regression analysis by plotting $\ln(C/C_0)$ as a function of time. The slope of the regression line is equal to the first order rate constant.

Data were grouped into each soil by pesticide by pesticide status by soil water content by temperature treatment combination and regressed over the five time intervals. This resulted in 64 treatment combinations each with 20 observations.

The test for a significant linear relationship between the transformed dependent variable, $\ln(C/C_0)$, and the independent variable, time, was with the F-statistic, $P \leq 0.05$. The F-statistic tests the null hypothesis

$$H_0: \beta = 0$$

where the β is the slope of the regression line. Rejection of the null hypothesis for values of $P \leq 0.05$ indicates that the slope of the regression

line is not zero. This test is equal to the test for a significant correlation coefficient, r, between the dependent and independent variables (SAS Institute Inc., 1985b).

Half-life Calculation

The first-order half-life values for each treatment combination were calculated using the equation

$$T_{½} = \frac{-0.693}{k}$$

where $T_{½}$ is the pesticide half-life and k is the slope of the regression line or degradation rate constant (Atkins, 1986; Hamaker, 1972).

Data Analysis

Influence of Soil and Environmental Factors on Pesticide Half-lives

Statistical analysis of pesticide half-life data for significant effects due to treatments (soil, pesticide, pesticide status, soil water content, and temperature) and two-way interactions of the treatments was by analysis of variance. The effects of soil and environmental factors on pesticide half-life were analyzed by mean separation of the treatment means using Fisher's least significant difference (LSD) at $P \leq 0.05$. Significant differences between pesticides were detected by contrasts.

Influence of Soil Properties on Pesticide Half-lives

The influence of soil properties on pesticide persistence was analyzed by correlation analysis. Half-life values for each pesticide by pesticide status treatment were correlated with measured values of each soil property. These included organic matter, total carbon, cation exchange capacity, pH, percent clay, soil water content, and temperature. Sample correlation coefficients were determined using the statistic Pearson product-moment correlation (SAS Institute Inc., 1985a).

Significant correlations were determined according to the null hypothesis

$$H_0: r = 0$$

or that the correlation coefficient (r) equals zero. Rejection of the null hypothesis for $P \leq 0.05$ indicated a significant correlation between a soil property and a pesticide by pesticide interaction half-life (SAS Institute Inc., 1985a). Correlation coefficients between soil properties were also determined.

Influence of Temperature on Pesticide Degradation Rates

The influence of temperature on pesticide degradation rates was analyzed by calculation of the activation energy for each soil by pesticide by

pesticide interaction by soil water content combination using the equation

$$E_a = \frac{2.303R*T_1*T_2}{\Delta T} * \log\left(\frac{k_1}{k_2}\right)$$

where E_a is the energy of activation, R is the ideal gas constant, T_1 is the absolute temperature at 15 C, T_2 is the absolute temperature at 30 C, ΔT is the difference in absolute temperatures, k_1 is the degradation rate at T_1 , and k_2 is the degradation rate at T_2 (Gingerich and Zimdahl, 1976). Statistical analysis of significant treatment effects and two-way interactions of treatments was by analysis of variance.

Biological Assay of Samples

Biological assays were conducted to determine the influence of soil and environmental factors on the persistence and phytotoxicity of pendimethalin and flumetralin, applied alone and in combination. The same experimental samples used in the chemical assay were used for the biological assay so a comparison of the two assays could be done.

Sample preparation

The samples from each soil were assayed at one time for operational considerations. This necessitated the construction of only one standard concentration curve for each soil by pesticide treatment combination.

Samples were removed from cold storage and thawed. Approximately 350 g of soil was placed in 500 cc plastic pots. Standard concentrations of pendimethalin and flumetralin were formulated in acetone. Treatments for standard concentrations were pendimethalin alone, flumetralin alone, and a pendimethalin plus flumetralin combination. Standard concentrations were applied to soil to give final soil concentrations of 0.05, 0.1, 0.5, 1, 2, and 4 μg ai g^{-1} of soil (oven-dry weight basis) for each pesticide. Four replications of each pesticide treatment standard were used.

Corn (var. Pioneer 3369A) was used as the indicator species. Seeds were germinated on moistened cheese cloth and those seedlings with approximately 5 mm radical lengths were selected and placed in each sample and standard pot. Two seedlings were transplanted per pot. Seedlings were placed on top on the treated soil sample and covered with approximately 2 cm of washed sand.

Environmental conditions within the greenhouse between soils was quite variable due to the differences in time of assays. Assays for two soils, Decatur and Norfolk, were unsuccessful due to unavoidable loss, and no measurements were taken on these soils. Results of the biological assay for the Sequatchie and Dickson samples will be presented.

Biological Assay Data analysis

Variables measured included shoot height, fresh root weight, and dry root weight. Measurements were taken on each of two plants per pot, and the mean of each measurement per pot were analyzed for each sample. Only shoot height measurements indicated any treatment differences, and only these results will be presented.

Residual Phytotoxicity of Pesticides

Shoot height data for each sample were converted to the percent of the untreated control by dividing sample shoot height by the mean shoot height of the untreated control samples. Analysis for significant effects due to pesticide, soil water content, temperature on corn response (percent of untreated control) over time were analyzed by analysis of variance with mean separation of treatment means by Fisher's least significant difference (LSD) at $P \leq 0.05$.

Interaction of Pesticides

Analysis of the interaction effect due to the combination of pendimethalin and flumetralin was determined by calculation of the expected response of the combination treatment using Colby's equation

$$E = \frac{A*B}{100}$$

where E is the expected response of the pendimethalin and flumetralin combination (as percent of untreated control), A is the observed response with pendimethalin alone, and B is the observed response with flumetralin alone. The difference between the expected response and the observed response indicate the type of interaction, where a positive number signifies an antagonistic interaction, a negative number signifies a synergistic interaction, and zero indicates an additive effect (Colby, 1967).

C. RESULTS AND DISCUSSION

Influence of Soil and Environmental Factors on the Persistence of Pendimethalin and Flumetralin

Analysis of variance of half-life data indicated significant differences in half-lives due to soils, pesticides, and temperatures. No significant differences were detected due to pesticide status or soil water contents. The significant effect of pesticides on half-life indicated that pendimethalin and flumetralin half-lives were different and would respond differently to each treatment factor. This necessitated the separation of the half-life data into two groups, pendimethalin half-lives and flumetralin half-lives, to

determine the influence of soil and environmental factors on the half-lives of each pesticide. Separate analyses of variance were done on each pesticide half-life data. Difference between pendimethalin and flumetralin half-lives in each soil, soil water content, and temperature were analyzed by construction of contrasts in the combined half-life analysis for each two-way interaction involving pesticide. These results will be presented with the results for each pesticide analysis.

Within each pesticide analysis, significant differences existed due to soil and temperature, but not due to pesticide status or soil water content. Since there was no effect due to pesticide status, half-life data were averaged across this factor for each pesticide. The influence of soil, soil water content, and temperature on pendimethalin and flumetralin half-life will be discussed. Data will be also presented on the differences in pendimethalin and flumetralin half-lives, alone and in combination (pesticide status effect) within each soil, soil water content, and temperature. Differences were detected using contrasts for each soil, soil water content, and temperature interaction with pesticide status, within each pesticide.

Influence of Soil on Pendimethalin and Flumetralin Half-lives

Significant differences in half-lives were detected between pendimethalin and flumetralin in each soil (Table 5). In the Decatur, Norfolk, and Sequatchie soils, pendimethalin half-life was much shorter than the

Table 5. Influence of soil on pendimethalin and flumetralin half-lives[a].

Soil	Pesticide		Contrast[b]
	Pendimethalin	Flumetralin	
	----------(d)----------		
Decatur clay loam	87	330	**
Dickson silt loam	298	230	NS
Norfolk loamy sand	266	516	**
Sequatchie loam	262	491	**
LSD[c]	45	90	

[a]Half-life means are for each soil by pesticide combination, averaged across pesticide status, soil water content, and temperature.

[b]Contrast indicates the difference between pesticides in each soil. No significance is indicated by NS, and significance at $P \leq 0.01$ is indicated by **.

[c]Pairwise comparisons between soils within each pesticide are by Fisher's least significant difference (LSD) at $P \leq 0.05$.

flumetralin half-life. The differences between pesticide half-lives was 250 d in the Norfolk soil, 243 d in the Decatur soil, and 229 d in the Sequatchie soil. However in the Dickson soil, the flumetralin half-life was shorter, but not different from the pendimethalin half-life. The difference in half-lives in Dickson soil was 68 d.

Significant differences in both the pendimethalin and flumetralin half-lives were detected between soils (Table 5). For pendimethalin, the half-life was shortest in the Decatur soil, followed by the Sequatchie, Norfolk, and Dickson soils. Pendimethalin half-life in the Decatur soil was significantly shorter than the half-lives for the other three soils. Different results were found for flumetralin, where the shortest half-life was in the Dickson soil, followed by the Decatur, Sequatchie, and Norfolk soils. Flumetralin half-life in the Dickson soil was significantly shorter than that in the other three soils, and half-life in the Decatur soil was significantly less than that in the other two soils.

A significant interaction effect for soil by pesticide was detected in the combined analysis of variance of the half-life data. This interaction is a result of the shorter half-life for flumetralin in the Dickson soil. The reason for this interaction is not clear. The organic matter content of the Dickson soil was 2.9% (Table 2), two times higher than in the Sequatchie and Decatur soils, and nearly five times higher than in the Norfolk soil. The dinitroanilines are strongly adsorbed in soil, primarily to the organic matter

fraction. This is indicated by the high soil organic carbon partitioning coefficients (K_{oc}) for the dinitroanilines (Weber, 1990). Values for pendimethalin and flumetralin are 24 300 and 100 000, respectively (Table 1). Increased organic matter content normally results in increased adsorption and thus lower concentrations in soil solution. This subsequently results in decreased pesticide degradation since adsorption is thought to protect pesticides from degradation (Hurle and Walker, 1980). This agrees with the results of Bregger (1985), who found flumetralin dissipated to 35% of its initial application rate in a soil with 0.1% humic matter, and to 60% of its initial application in soils with 1 and 1.9% humic matter. The higher K_{oc} value for flumetralin indicates that it should persist longer than pendimethalin because of its expected greater adsorption. Flumetralin did persist longer than pendimethalin in the Decatur, Norfolk, and Sequatchie soils, but not in the Dickson soil. Increased persistence of pendimethalin was observed in the Dickson soil, and it is logical to assume that flumetralin persistence should have been longer in the Dickson soil. However, this was not the case.

A possible explanation for decreased persistence of flumetralin in the more organic Dickson soil is increased microbial activity. Soil degradation of the dinitroanilines is primarily by soil microorganisms (Weber, 1990). The activity of soil microorganisms is normally higher in more organic soils (Hurle and Walker, 1980). Degradation of flumetralin could have been increased in

the more organic Dickson soil compared to other soils with less organic matter. It is not clear at this point why a similar increase in degradation did not occur with pendimethalin. It is possible that flumetralin is degraded by soil microorganisms to a greater extent than pendimethalin.

Influence of Soil Water Content on Pendimethalin and Flumetralin Half-lives

Significant differences were detected between pendimethalin and flumetralin at each soil water content (Table 6). At -33 kPa, pendimethalin half-life was 217 d, significantly shorter than the flumetralin half-life of 377 d. At -100 kPa, the half-life of pendimethalin was 237 d, significantly shorter than the flumetralin half-life of 406 d.

No difference between half-lives was observed between soil water content for pendimethalin or flumetralin (Table 6). Pesticide half-lives were slightly shorter at the higher soil water content, which agrees with results documented in previous research on the dinitroanilines (Hollist and Foy, 1971; Horowitz et al., 1974; Poku and Zimdahl, 1980; Zimdahl and Gwynn, 1977). However these decreases in half-life with increased soil water content were only 7 to 8%. Pendimethalin half-life at field capacity (-33 kPa) in this study was approximately two to four times higher than those reported by other researchers (Barrett and Lavy, 1983; Savage, 1978; Walker and Bond, 1977; Zimdahl et al., 1984). This is likely a result of differences in temperature, soil series, soil properties, and environmental

Table 6. Influence of soil water content on pendimethalin and flumetralin half-lives[a].

Soil Water Content	Pesticide		Contrast[b]
	Pendimethalin	Flumetralin	
(kPa)	----------(d)----------		
-33	217	377	**
-100	237	406	**
LSD[c]	NS	NS	

[a]Half-life means are for each soil water content by pesticide combination, averaged across soil, pesticide status, and temperature.

[b]Contrast indicates the difference between pesticides at each soil water content. Significance at $P \leq 0.01$ is indicated by **.

[c]Pairwise comparisons between soil water contents within each pesticide were not significant (NS) according to by Fisher's least significant difference (LSD) at $P \leq 0.05$.

conditions between this study and their studies. Also these half-life valuesfor pendimethalin are averaged over soils and temperatures.

Influence of Temperature on Pendimethalin and Flumetralin Half-lives

Pendimethalin half-life was significantly shorter than the flumetralin half-life at 15 C and at 30 C (Table 7). The difference between pendimethalin and flumetralin half-lives increased as temperature increased. The pendimethalin half-life was 38% shorter than the flumetralin half-life at 15 C and 50% shorter at 30 C.

Significant differences in half-lives were obtained between temperatures for pendimethalin and flumetralin (Table 7). For pendimethalin, the half-life at 15 C was 190 d longer than the half-life at 30 C. This difference was 258 d for flumetralin.

The pendimethalin half-life at 30 C was longer than those reported for pendimethalin in the literature at 30 C (Walker and Bond, 1977; Zimdahl et al., 1984). This discrepancy is probably a result of averaging the pendimethalin half-lives over soils and soil water contents, as well as differences in experimental conditions.

A significant interaction effect was observed for soil by temperature with both the pendimethalin and flumetralin half-life analyses of variance. Means for each soil by pesticide by temperature combination are in Table 8. In the Decatur, Norfolk, and Sequatchie soils, pendimethalin half-life

Table 7. Influence of temperature on pendimethalin and flumetralin half-lives[a].

Temperature	Pesticide		Contrast[b]
	Pendimethalin	Flumetralin	
(C)	----------(d)----------		
15	322	521	**
30	132	263	**
LSD[c]	32	64	

[a]Half-life means are for each temperature by pesticide combination, averaged across soil, pesticide status, soil water content, and temperature.

[b]Contrast indicates the difference between pesticides at each temperature. Significance at $P \leq 0.01$ is indicated by **.

[c]Pairwise comparisons between temperatures within each pesticide are by Fisher's least significant difference (LSD) at $P \leq 0.05$.

Table 8. Mean half-lives for pendimethalin and flumetralin at 15 and 30 C in the Decatur, Dickson, Norfolk, and Sequatchie soils[a].

Soil	Temperature	Pesticide	
		Pendimethalin	Flumetralin
	(C)	----------(d)----------	
Decatur clay loam	15	129 ± 11	477 ± 42
	30	45 ± 2	183 ± 3
Dickson silt loam	15	396 ± 23	252 ± 31
	30	199 ± 23	209 ± 27
Norfolk loamy sand	15	373 ± 33	691 ± 75
	30	148 ± 8	341 ± 11
Sequatchie loam	15	389 ± 40	663 ± 63
	30	134 ± 8	318 ± 25

[a]Mean values for half-lives are averaged over pesticide status and soil water content and are followed by their standard error.

decreased 60 to 65% and flumetralin half-life decreased 50 to 60%, as temperature increased from 15 to 30 C. In the Dickson soil, this decreasewas 50% for pendimethalin and only 17% for flumetralin. Thus, the smaller change in pesticide half-life in response to temperature in the Dickson soil resulted in this interaction effect.

Decreased half-lives of these pesticides as temperature increased could be a result of increased volatilization, as well as increased pesticide degradation rates. Vapor pressures of both pesticides are below 50×10^{-6} mm Hg. Pesticides with vapor pressures above this level are believed to be subject to greater volatilization losses than those pesticides with vapor pressures below this limit (Weber, 1990).

Influence of Soil and Environmental Factors on Interaction of Pendimethalin and Flumetralin

Analysis of variance of the combined half-life data indicated no significant effect of pesticide status. This means there was no difference in pesticide half-life whether it was applied alone or in combination with the other pesticide. There were also no significant two-way interaction effects with pesticide status for soil, soil water content, or temperature. Separation of the data by pesticide revealed no significant effects due to pesticide status for either pendimethalin or flumetralin. Differences in pendimethalin and flumetralin half-life due to pesticide status for each soil, soil water

content, and temperature will be discussed.

There was no significant soil by pesticide status interaction for any of the four soils (Table 9). The half-life of pendimethalin applied alone was not different from the pendimethalin half-life when applied in combination with flumetralin. This was also true for flumetralin, where the half-life applied alone was similar to the half-life when applied in combination with pendimethalin. Differences in half-life were larger for flumetralin than for pendimethalin, but results were variable. In the Dickson soil, the half-life of flumetralin, applied in combination with pendimethalin, was 94 d shorter than the half-life of flumetralin applied alone, with similar results for the Norfolk and Sequatchie soils. However, in the Decatur soil, the half-life of flumetralin applied in combination with pendimethalin was 60 d longer than the half-life of flumetralin applied alone. The half-life for pendimethalin applied in combination with flumetralin was shorter than the half-life for pendimethalin applied alone in the Dickson and Norfolk soils. The half-life of pendimethalin applied alone was shorter than the half-life of pendimethalin in combination with flumetralin in the Decatur and Sequatchie soils.

There was a significant soil water content by pesticide status interaction. At the -100 kPa soil water content, the half-life for pendimethalin applied alone was 48 d shorter than the half-life for pendimethalin applied in combination with flumetralin (Table 10). No other significant differences were detected, although at the -100 kPa soil water

Table 9. Difference in half-life of pendimethalin and flumetralin, applied in combination, as compared to their half-life when applied alone in each soil[a].

Soil	$\Delta T_{½}$[b]	
	Pendimethalin	Flumetralin
	----------(d)----------	
Decatur clay loam	+16	+66
Dickson silt loam	-14	-94
Norfolk loamy sand	-10	-80
Sequatchie loam	+51	-75

[a]Pendimethalin and flumetralin were applied to soil, alone and in combination, at a rate of 4 $\mu g\ g^{-1}$ of soil each.

[b]Differences were calculated by subtracting the half-life of each pesticide applied alone from the half-life of each applied in combination, within each soil by pesticide combination. Differences were analyzed by contrasts within each pesticide and were not significant at $P \leq 0.05$.

Table 10. Difference in half-life of pendimethalin and flumetralin in combination, as compared to their half-lives when applied alone at -33 and -100 kPa[a].

	$\Delta T_{½}$[b]			
Soil Water Content	Pendimethalin		Flumetralin	
(kPa)	----------(d)----------			
-33	-28	NS	-21	NS
-100	+48	*	-70	NS

[a]Pendimethalin and flumetralin were applied to soil, alone and in combination, at a rate of 4 $\mu g\ g^{-1}$ of soil each.

[b]Differences were calculated by subtracting the half-life of each pesticide applied alone from the half-life of each applied in combination, within each soil water content by pesticide combination. Differences were analyzed by contrasts and are either not significant (NS) or significant at $P \leq 0.05$ (*).

content, the flumetralin half-life when applied in combination with pendimethalin was 70 d shorter than the flumetralin half-life when appliedalone.

There was no significant temperature by pesticide status interaction (Table 11). The half-life of pendimethalin when applied in combination was not different from the half-life applied alone. This is also true for flumetralin. However, at both temperatures, flumetralin half-life in combination was shorter than the half-life for flumetralin applied alone.

These data generally agree with that of others who have studied dinitroaniline persistence in the presence of other pesticides. The presence of the insecticide DBCP did not influence fluchloralin persistence (Brewer et al., 1981), and trifluralin persistence was not affected by the presence of triallate (Smith, 1979) or chloramben (Smith and Hayden, 1982). The significant difference in pendimethalin half-lives at the -100 kPa soil water content was not understood because differences in flumetralin half-lives at this same soil water content were greater. Although there were no significant differences due to pesticide status for flumetralin, there was a trend towards shorter persistence of flumetralin, when applied in combination with pendimethalin, than when applied alone.

Table 11. Difference in half-life of pendimethalin and flumetralin in combination, as compared to their half-lives when applied alone at 15 and 30 C[a].

	$\Delta T_{½}$[b]	
Temperature	Pendimethalin	Flumetralin
(C)	----------(d)----------	
15	+26	-21
30	-6	-70

[a]Pendimethalin and flumetralin were applied to soil, alone and in combination, at a rate of 4 $\mu g\ g^{-1}$ of soil each.

[b]Differences were calculated by subtracting the half-life of each pesticide applied alone from the half-life of each applied in combination, within each temperature by pesticide combination. Differences were analyzed by contrasts and are not significant at $P \leq 0.05$.

Influence of Soil Properties on Pendimethalin and Flumetralin Half-lives

Soil has a great influence on persistence of pendimethalin and flumetralin as indicated by its significant effect on half-lives in the previous section. A specific soil, as presented in that section, is a unitless entity, with only relative comparison value to other soils. Assignment of values or units to a soil via analysis of certain soil properties is necessary to quantify its effect on persistence.

The correlation coefficient (r) for each soil property with the half-life of each pesticide, alone and in combination, are in Table 12. The soil water contents and temperatures where half-lives were measured are also included in the correlation analysis to illustrate the influence of these environmental factors on persistence. The only soil properties significantly correlated with pendimethalin half-lives were pH and % clay. Temperature was the only environmental factor significantly correlated with pendimethalin half-life. Both pendimethalin treatments had low correlation coefficients with soil water content, with r values of -0.04 and -0.12 for pendimethalin and pendimethalin in combination with flumetralin, respectively.

Cation exchange capacity (CEC), pH, % clay, temperature, and soil water content were negatively correlated with pendimethalin half-life. Positive r values were obtained for % total carbon and % organic matter with pendimethalin half-life.

For flumetralin alone, CEC was the only soil property significantly

Table 12. Correlation coefficients between soil property values and environmental conditions with the half-lives of pendimethalin and flumetralin, applied alone and in combination[a].

Property	Pesticide			
	Alone		Combination	
	Pendimethalin	Flumetralin	Pendimethalin	Flumetralin
	(r)			
% Total Carbon	0.26	-0.37	0.23	-0.54 *
% Organic Matter	0.29	-0.39	0.23	-0.57 *
CEC[b]	-0.39	-0.56 *	-0.35	-0.39
pH	-0.62 **	-0.07	-0.54 *	0.25
% Clay	-0.60 *	-0.42	-0.53 *	-0.14
Soil Water Content	-0.04	-0.52 *	-0.12	-0.47
Temperature	-0.67 **	-0.67 **	-0.73 **	-0.63 **

[a]Correlation coefficients (r) are different from zero at $P \leq 0.05$ and $P \leq 0.01$ when indicated by (*) and (**), respectively.

[b]Abbreviation for cation exchange capacity.

correlated with half-life, while for flumetralin in combination with pendimethalin, % total carbon and % percent organic matter were significantly correlated with half-life. Negative correlation coefficients were properties for flumetralin alone and for all but pH for flumetralin inobtained for all soil combination with pendimethalin. As with pendimethalin, temperature was significantly correlated with both flumetralin treatments. Soil water content was also significantly correlated with the half-life for flumetralin applied alone.

For this study, a positive correlation coefficient for a soil property indicates that as the value for a soil property increases, half-life also increases. Positive correlations of pendimethalin half-life with % organic matter and % total carbon were expected, however r values were low, which was not expected. Previous research has shown highly significant positive correlations of dinitroaniline persistence with % organic matter (Bardsley et al., 1967; Carringer et al., 1975; Savage, 1973; Weed and Weber, 1974).

Negative correlation of a soil property with half-life indicates that as values for a soil property increase, half-life decreases. Negative correlation of pH with pendimethalin half-life agrees with results obtained by Savage (1973), where soil concentrations for the dinitroanilines nitralin and trifluralin were negatively correlated with pH. Soil pH can directly influence persistence of herbicides by altering molecular stability, or by affecting

herbicide adsorption or soil microbial populations (Hurle and Walker, 1980). Since dinitroanilines are nonpolar and nonionizable (Weber, 1990), pH would not be expected to influence molecular stability or adsorption, so any pH effect would likely be through its influence on microbial populations and activity.

Negative correlations of CEC and % clay with pendimethalin and flumetralin half-lives were not expected. As percent clay and CEC increase, adsorption usually increases, leading to increased persistence and half-lives. A positive correlation was observed between % clay and CEC, but not between % clay and % organic matter or between CEC and % organic matter (Table 13). CEC, % clay, and % organic matter are usually positively correlated with each other (Savage, 1973).

Negative correlations of organic matter and total carbon with flumetralin half-life were not expected initially. However after calculation of the flumetralin half-life in Dickson soil, where flumetralin half-life was shortest in the soil with the higher % organic matter and % total carbon, this result was expected. It has been suggested that for pesticides that are primarily degraded by soil microorganisms, increased microbial activity associated with soils high in organic matter content could result in increased degradation of these pesticides (Hurle and Walker, 1980). Dinitroanilines are thought to be degraded primarily by soil microorganisms (Weber, 1990). No literature is available as to what extent flumetralin degradation is controlled

Table 13. Correlation coefficients among soil property values determined for the Decatur clay loam, Dickson silt loam, Norfolk loamy sand, and Sequatchie loam[a].

Soil Property	Soil Property				
	% Clay	pH	CEC	% Total Carbon	% Organic Matter
	----------(r)----------				
% Organic Matter	-0.04	-0.67	+0.44	+0.99	-----
% Total Carbon	-0.01	-0.65	+0.48	-----	+0.99
CEC	+0.87	+0.36	-----	+0.47	+0.45
pH	+0.77	-----	+0.36	-0.65	-0.67
% Clay	-----	+0.77	+0.87	-0.01	-0.04

[a]Correlation coefficients measure closeness of linear relationship between two variables and lie between 1 and -1.

by soil microorganisms.

In general, soil properties have been poorly correlated with herbicide persistence data in laboratory tests (Meikle et al., 1973). Usually, soil water content and temperature have a greater effect on persistence, when varied over a wide range, than soil properties (Nash, 1988). This was indicated in this experiment by the significant correlation with temperature for all pesticide treatments. It is also very difficult to determine the influence of a single soil property on pesticide persistence because many soil factors are interrelated, such as % clay, CEC, and % organic matter.

Influence of Temperature on Pesticide Degradation Rates

Analysis of variance of activation energy data indicated significant differences due to soils and pesticides, but not pesticide status or soil water content. Therefore, activation energies were averaged over pesticide status and soil water content. However, analysis of variance of activation energy data within each soil or each pesticide did not result in a significant F-test for the model, indicating that the amount of variance accounted for by the model was too low. Therefore, no statistical analysis of the data could be performed.

Activation energy means for each soil by pesticide combination are given in Table 14. The activation energy for flumetralin was lower than that for pendimethalin in all soils. The greatest difference between pendimethalin

Table 14. Mean activation energies for pendimethalin and flumetralin in a Decatur clay loam, a Dickson silt loam, a Norfolk loamy sand, and a Sequatchie loam[a].

Soil	Pesticide	
	Pendimethalin	Flumetralin
	----------(kJ mol^{-1})----------	
Decatur clay loam	49.3 ± 1.5	40.5 ± 4.0
Dickson silt loam	28.7 ± 7.1	9.7 ± 3.1
Norfolk loamy sand	45.5 ± 5.0	40.0 ± 6.0
Sequatchie loam	46.4 ± 2.8	39.4 ± 4.9

[a]Activation energy means (± standard error of the mean) are for each pesticide and soil combination and are averaged over pesticide status and soil water content.

and flumetralin was observed in the Dickson soil, where the activation energy of flumetralin was almost three times lower than that of pendimethalin. Differences between the activation energies of flumetralin and pendimethalin were not as great in the other soils.

Activation energies for each pesticide appeared to differ between soils. Pendimethalin activation energies in the Decatur, Norfolk, and Dickson soils were similar, as were the activation energies for flumetralin in these soils. In the Dickson soil, activation energy for each pesticide was decreased.

Differences in activation energies between soils could be caused by differences in soil microbial populations or activity. Reactions catalyzed by microbial enzymes would have lower activation energies (near 21 kJ mol^{-1}) than those for non-catalyzed chemical reactions (above 75 kJ mol^{-1}). The lowest activation energies were found in Dickson soil, which had the highest organic matter content. Higher soil microbial activities are normally found in soils with higher organic matter contents (Hurle and Walker 1980). Higher microbial populations or activity could have resulted in greater microbial degradation of these pesticides in the Dickson soil than in the other, less organic soils.

Lower activation energies for flumetralin compared to pendimethalin could be an indication that the degradation pathways for the two pesticides are slightly different, at least in more organic soils. It may also mean that

flumetralin is degraded by soil microorganisms to a greater extent than pendimethalin.

These data do not confirm real differences in degradation mechanisms or pathways between pesticides or within soils. They are only an indication of potential differences under these conditions, in these specific soils.

Residual Phytotoxicity of Pendimethalin and Flumetralin

Soil bioassay analyses of Dickson and Sequatchie soil samples did not allow determination of soil pesticide concentrations due to the poor response of corn shoot height to increasing pesticide concentrations. Regression analysis of pendimethalin concentration as a function of corn shoot height did not produce a straight line, indicating that reduction in corn shoot height with increasing concentrations of pendimethalin or flumetralin was not a linear function. Logarithmic data transformation also failed to produce a satisfactory standard response curve. Analysis of variance of corn shoot height data did reveal differences between treatments.

Influence of Pesticide Treatments on the Residual Phytotoxicity

At all times, a greater corn response (higher percent of untreated control) was measured for pendimethalin alone than with pendimethalin and flumetralin (Fig. 1). At 0, 60, and 120 d, the measured corn response in the

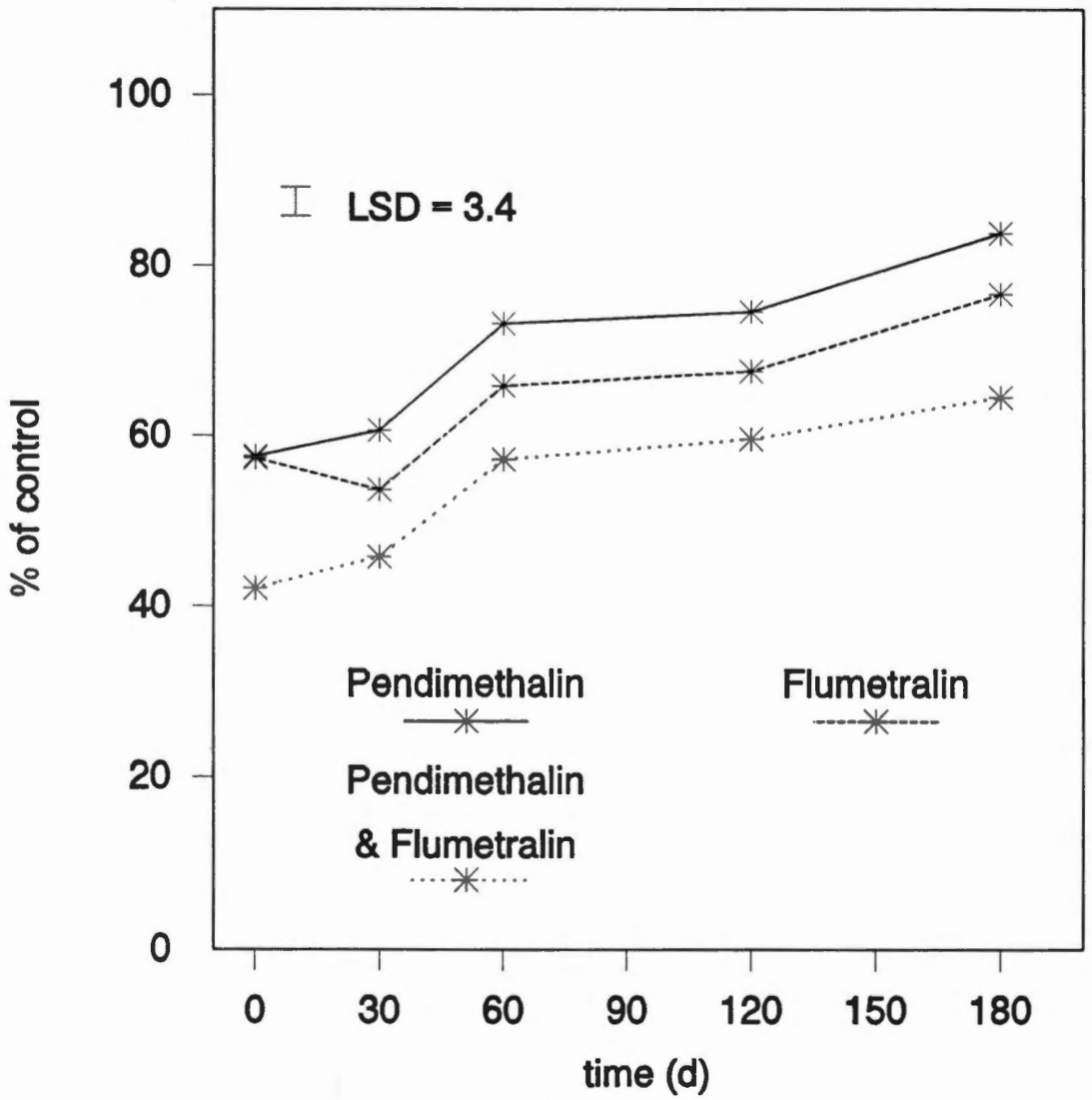

Figure 1. Effect of pesticide treatments on pesticide phytotoxicity over time, as indicated by corn height response (% of untreated control), in a Dickson silt loam. Comparison of pesticide treatment means within a time are compared with Fisher's least significant difference (LSD) at $P \leq 0.05$.

flumetralin alone treatment was greater than that for the combination treatment. However, at 30 and 180 d, no difference in response was detected between these treatments. At 60 and 120 d, corn response in the pendimethalin alone treatment was greater than that for the flumetralin alone treatment. No difference in response occurred between pendimethalin alone and flumetralin alone at 0 or 180 d.

In the Sequatchie soil, significant differences were detected between treatments at 0, 30, and 60 d, but not at 120 or 180 d (Fig. 2). At 0, 30, and 60 d, response for pendimethalin alone was greater than response for pendimethalin and flumetralin. Only at 60 d was there a significant difference between the response in the flumetralin alone treatment and the response in the pendimethalin and flumetralin combination treatment. A significant difference between pendimethalin alone and flumetralin alone was detected at 30 d.

Initially, response in the pendimethalin alone treatment was essentially equal to the response for the flumetralin alone treatment in the Dickson soil, while in the Sequatchie soil, corn response in the pendimethalin alone treatment was greater but not statistically different from the response with flumetralin alone. Therefore, differences detected between these treatments over time are probably not due to differences in phytotoxicity between pendimethalin and flumetralin. Results reported in Chapter II indicated a definite difference in soil half-life between pendimethalin and flumetralin in

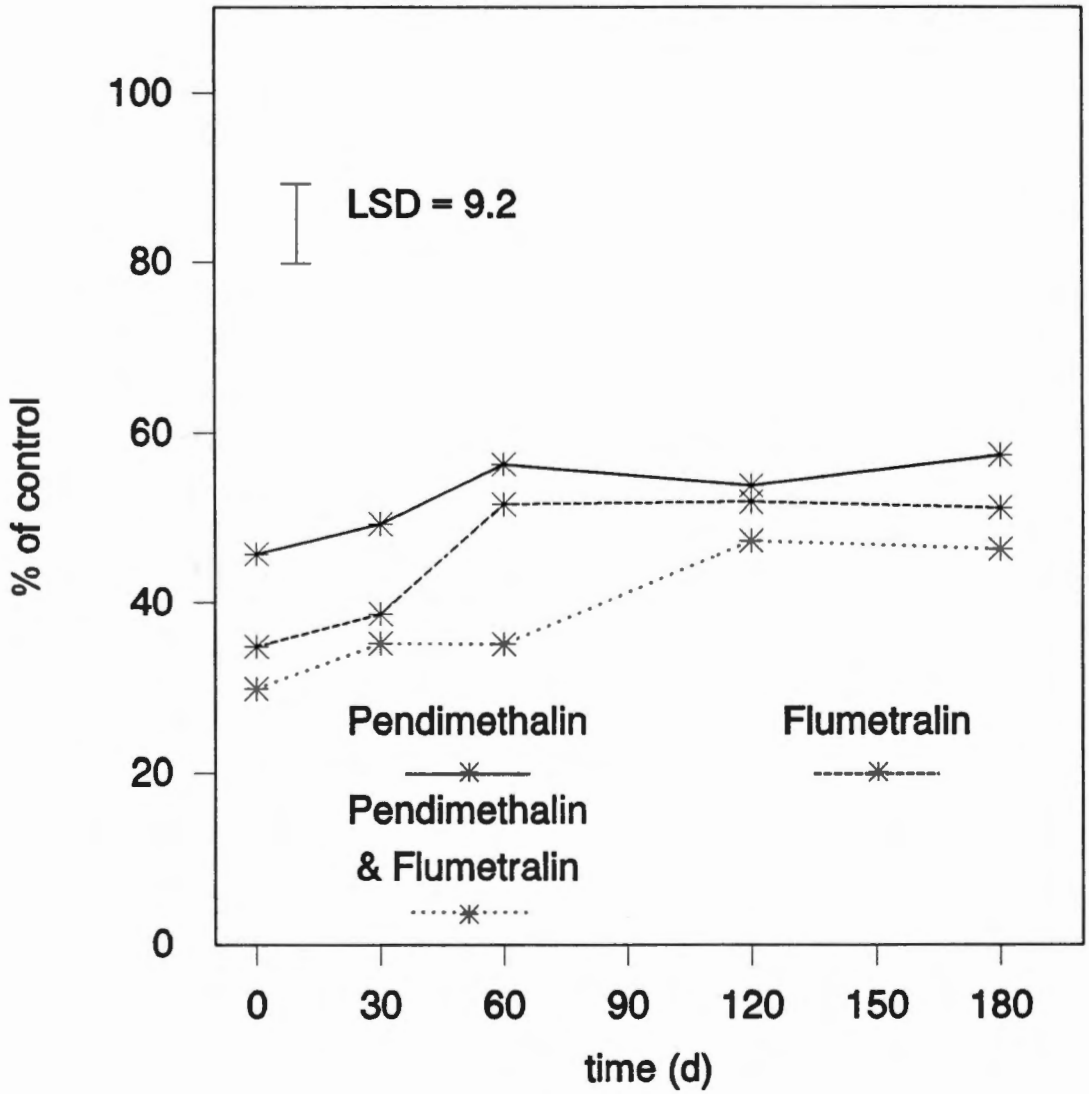

Figure 2. Effect of pesticide treatments on pesticide phytotoxicity over time, as indicated by corn height response (% of untreated control), in a Sequatchie loam. Comparison of pesticide treatment means within a time are compared with Fisher's least significant difference (LSD) at $P \leq 0.05$.

the Sequatchie soil, but not in the Dickson soil. Thus in the Sequatchie soil, pesticide treatment differences can be attributed to differences in soil concentration of these pesticides over time. In the Dickson soil this cannot be stated. Half-life data reported in Chapter II were based on the total soil concentration of these pesticides, while bioassay response only measures the phytotoxic portion of the total soil concentration of a pesticide. It is possible that pendimethalin and flumetralin are different in their bioavailability within the Dickson soil.

Differences in response between pendimethalin and flumetralin in combination were expected since total initial pesticide concentration in the combination treatment was twice that in the pendimethalin alone or flumetralin alone treatments.

Influence of Soil Water Content on the Residual Phytotoxicity

No significant differences in corn responses were detected at any time between soil water content treatments in either the Dickson (Fig. 3) or the Sequatchie (Fig. 4) soils. At 30, 60, 120, and 180 d, corn response was greater for the -33 kPa treatments than the -100 kPa treatments, with somewhat greater differences in the Sequatchie soil than in the Dickson soil. These results are similar to those reported in Chapter II, where soil water content did not result in significant differences in pesticide half-lives in the Dickson or Sequatchie soils.

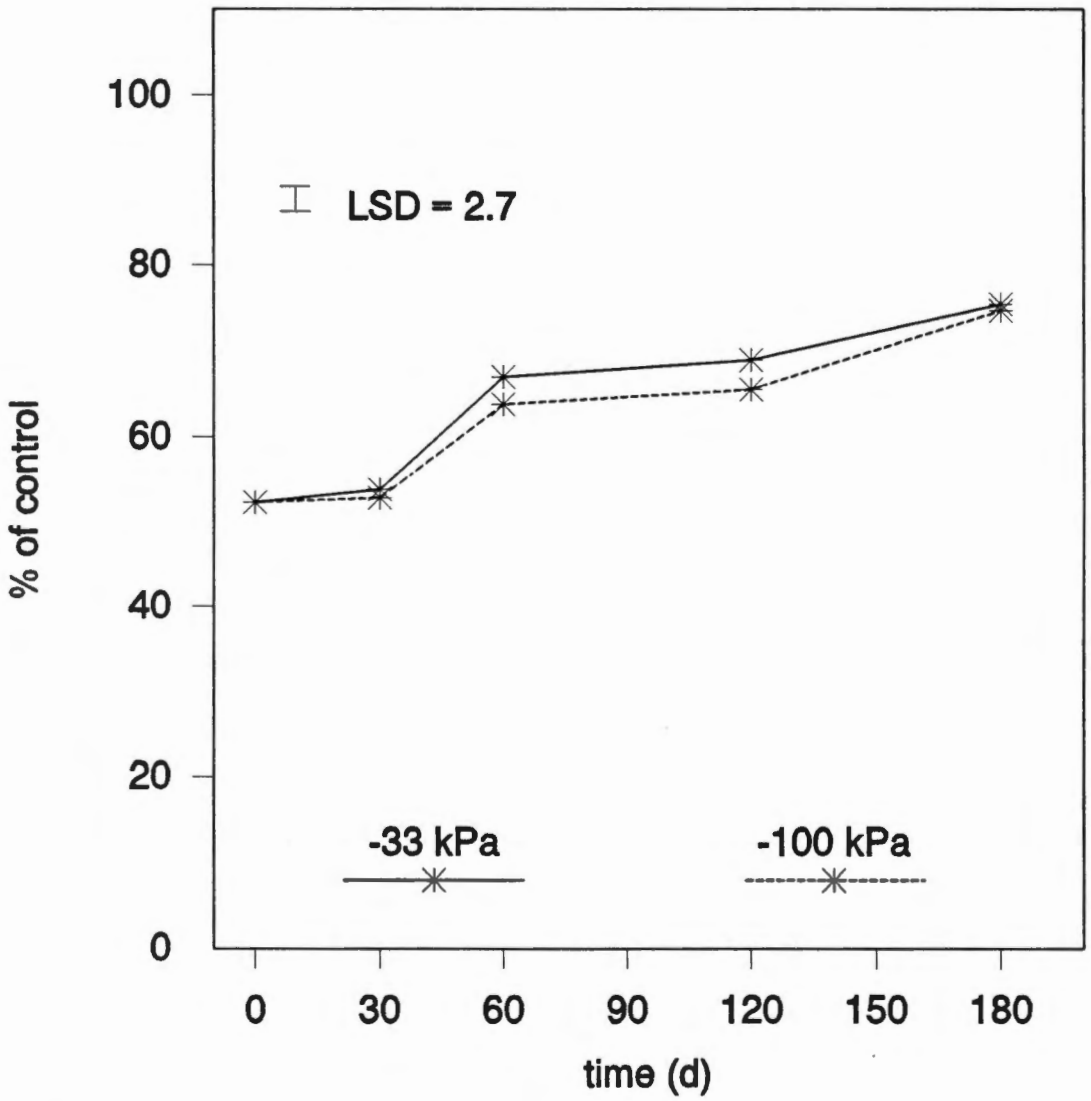

Figure 3. Effect of soil water content on pesticide phytotoxicity over time, as indicated by corn height response (% of untreated control), in a Dickson silt loam. Soil water content means within a time are not different according to Fisher's least significant difference (LSD) at $P \leq 0.05$.

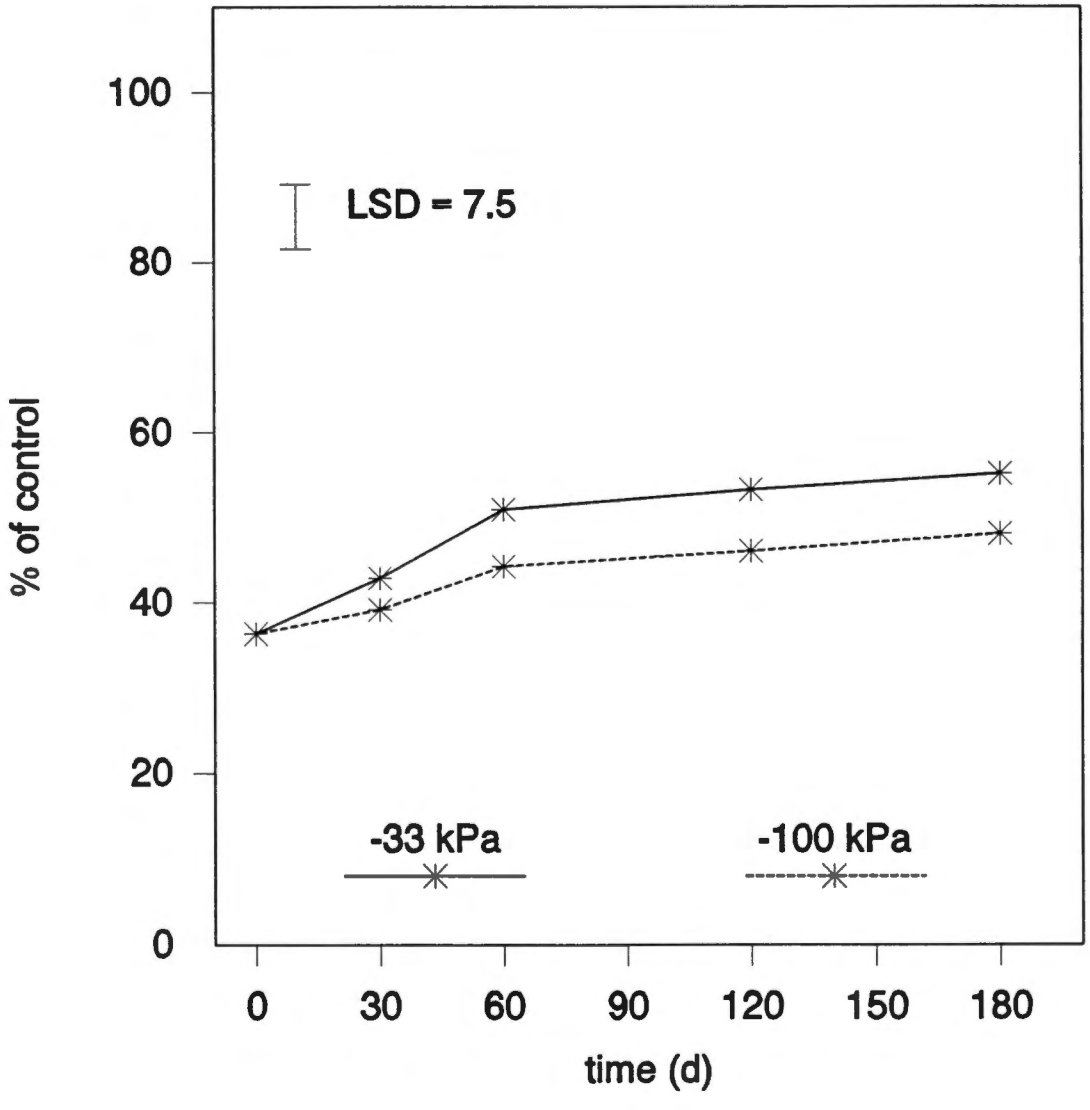

Figure 4. Effect of soil water content on pesticide phytotoxicity over time, as indicated by corn height response (% of untreated control), in a Sequatchie loam. Soil water content means within a time are not different according to Fisher's least significant difference (LSD) at $P \leq 0.05$.

Influence of Temperature on the Residual Phytotoxicity

Temperature influenced the pesticide remaining in the soil as evidenced by the significant differences in corn response in the Dickson(Fig. 5) and Sequatchie (Fig. 6) soils. For the Dickson soil, corn response with the 30 C treatment was greater than that in the 15 C treatment at 30, 60, 120, and 180 d. For the Sequatchie soil, response was greater for the 30 C compared to 15 C treatment at only 30 d. The differences in corn response between temperatures are a result of more pesticide remaining at 15 C than at 30 C. The greater variability in the Sequatchie bioassay data compared to the Dickson data may have resulted in the failure of the analysis to detect apparent differences in corn responses to temperature effects on the remaining pesticide in the Sequatchie soil.

Comparison of the responses between soils for pesticide treatment, soil water content, and temperature indicates greater phytotoxicity, as indicated by a lower percent of control in the Sequatchie soil compared to the Dickson soil.

Analysis of the Interaction of Pendimethalin and Flumetralin in Combination

Expected response of the combination treatment of pendimethalin and flumetralin was compared to the observed response for each soil water content by temperature combination, for the Dickson and Sequatchie soils (Table 15). No general pattern was observed for this interaction over

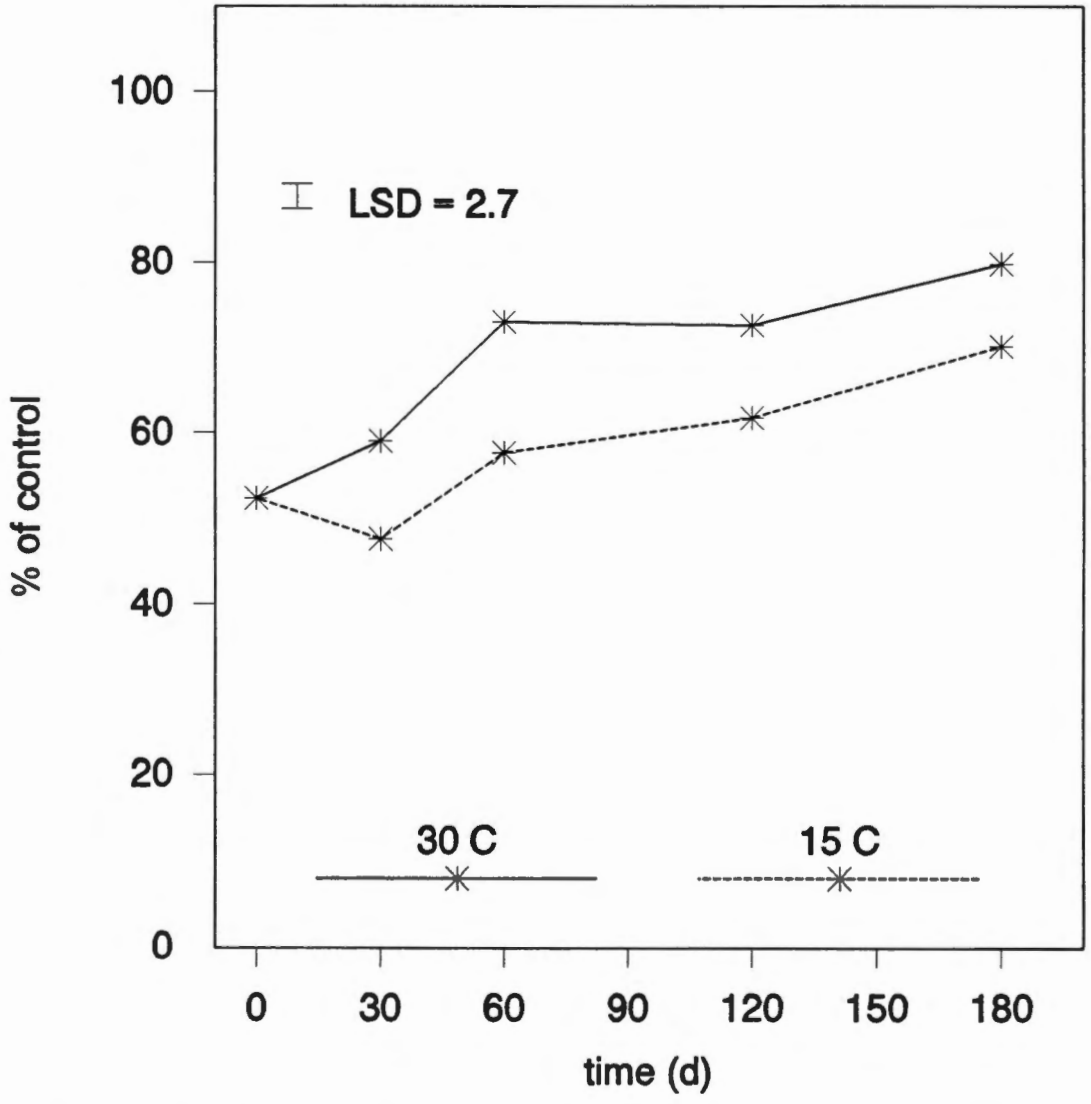

Figure 5. Effect of temperature on pesticide phytotoxicity over time, as indicated by corn height response (% of untreated control), in a Dickson silt loam. Comparison of temperature means within a time are compared with Fisher's least significant difference (LSD) at $P \leq 0.05$.

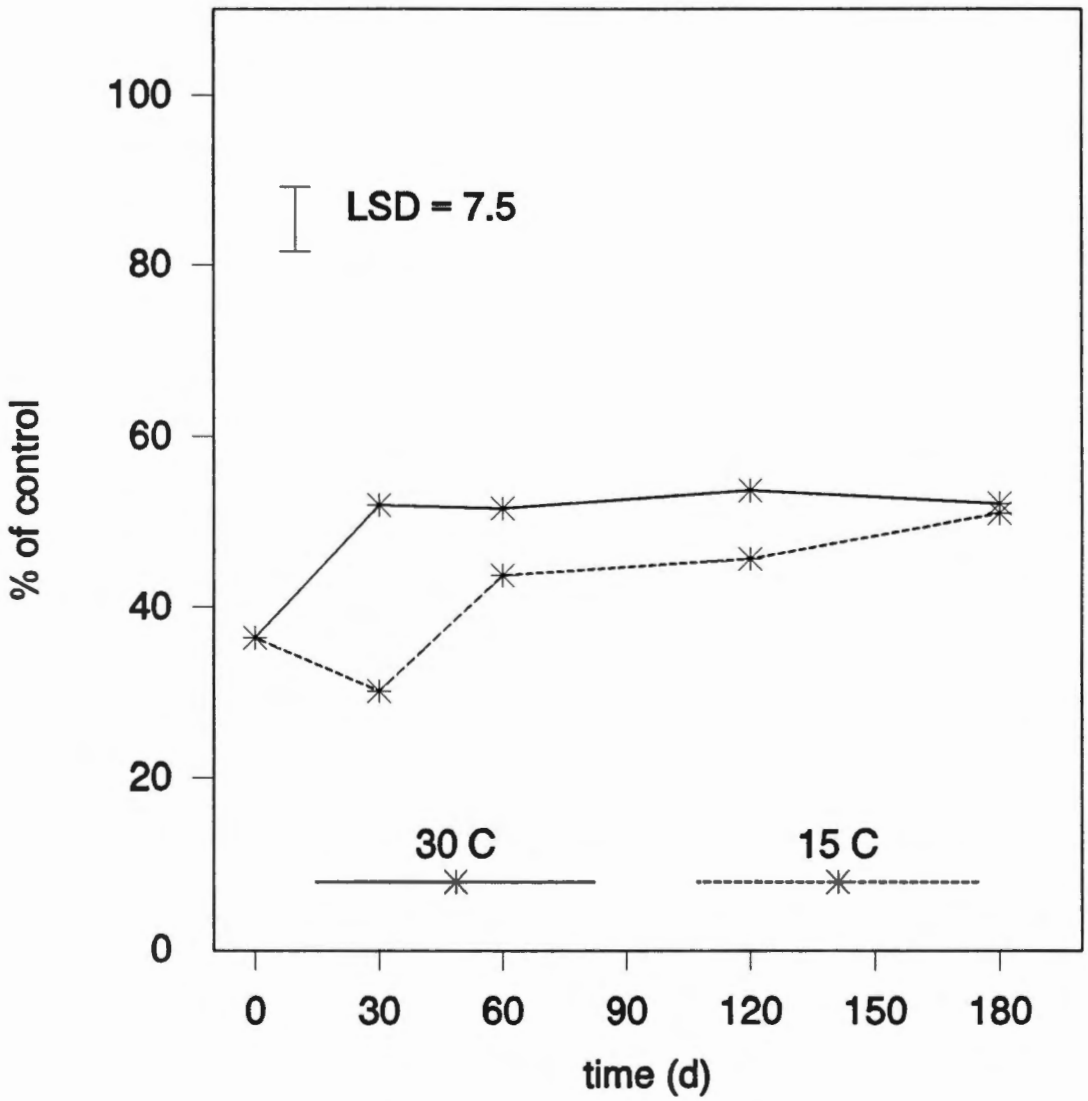

Figure 6. Effect of temperature on pesticide phytotoxicity over time, as indicated by corn height response (% of untreated control), in a Sequatchie loam. Comparison of temperature means within a time are compared with Fisher's least significant difference (LSD) at $P \leq 0.05$.

Table 15. Observed and expected responses of pendimethalin and flumetralin in combination and their interaction effect, in two soils and under four environments[a].

Soil	Environment[b]	Response		Interaction[c]
		Observed	Expected	
		(% of untreated control)		
Dickson silt loam	-33 kPa, 15 C	48	43	5
	-33 kPa, 30 C	64	56	8
	-100 kPa, 15 C	52	40	12
	-100 kPa, 30 C	64	56	8
Sequatchie loam	-33 kPa, 15 C	39	18	21
	-33 kPa, 30 C	42	26	16
	-100 kPa, 15 C	23	20	3
	-100 kPa, 30 C	33	25	8

[a]Observed response is the actual measured plant response for the pendimethalin and flumetralin combination treatment. Expected response is calculated by Colby's equation using the response for each pesticide applied alone.

[b]Environment indicates each soil water content by temperature treatment combination, within each soil, averaged over time and replications (n = 20).

[c]Interaction refers to difference between observed and expected responses. A positive value indicates an antagonistic effect, a negative value indicates a synergistic effect, and no difference indicates an additive effect.

time, indicated by a lower percent of control, in the Sequatchie soil than in the Dickson soil. so results were averaged across all five times. No trends were apparent within soil water content or temperature treatments. For each soil water content by temperature combination in both soils, observed response was greater than expected response. For these data, using percent of untreated control as the method of corn shoot height data transformation, the interaction number was positive. Thus, for these data, the interaction response was antagonistic. This means that the observed or actual phytotoxicity to corn from the pendimethalin and flumetralin combination was less than the expected phytotoxicity. There was a difference in response between soils, where the interaction effect was greater in Sequatchie soil compared to Dickson soil.

These results are somewhat conflicting to those reported by Shelby et al. (1990) where a synergistic interaction was observed with pendimethalin and flumetralin on wheat injury. However, different methods of experimentation were used in each study.

Comparison of the chemical assay with the biological assay for accuracy, precision, and sensitivity are not possible since the determination of soil concentrations by the biological assay were not determined. However, due to the poor response of corn shoot height to pesticide concentration, it can be stated that the sensitivity of the chemical assay was higher than that of the biological assay.

CHAPTER III

MODELING PENDIMETHALIN AND FLUMETRALIN DEGRADATION IN SOIL

A. LITERATURE REVIEW

Models of Pesticide Degradation

Rate of pesticide degradation is of primary importance in evaluation of pesticide persistence. Mathematical models are used to estimate rates of degradation, which can then be used for quantification of pesticide concentrations at any time and for prediction of future pesticide concentrations. This information is needed for proper assessment of risk to susceptible species through exposure to persistent pesticides (Alexander and Scow, 1989; Hurle and Walker, 1980; Hamaker, 1972).

First-order Model

Pesticide degradation has often been described by the first-order kinetic model (Bouchard et al., 1985; Hamaker, 1972; Hyzak and Zimdahl, 1974; Meikle et al., 1973; Zimdahl et al., 1970). The first-order differential

rate equation is

$$\frac{dC}{dt} = -kt^n$$

where dC/dt is the rate of reaction rate, k is the first-order rate constant, C is the pesticide concentration, and n is the order of reaction, which is 1 for the first-order model (Alexander and Scow, 1989; Atkins, 1986; Hamaker, 1972).

For the first-order model, degradation rate, k, is directly proportional to concentration and reactant concentration decreases exponentially with time, at a rate determined by the rate constant. First-order rate constants are independent of initial concentration, but dependent on temperature, (Atkins, 1986). Integration of the first-order differential rate equation from an initial time 0 to a later time t gives an exponential equation

$$C = C_0 e^{-kt}$$

where C is the pesticide concentration at some time t, C_0 is the pesticide concentration at time 0 or initial concentration, k is first-order rate constant, and t is time (Atkins, 1986; Nash, 1988). Graphical representation of this equation yields a nonlinear plot that shows an initial rapid decline in concentration followed by a subsequent slower decline in concentration.

In order to simplify analysis, data are transformed to fit a linear equation by plotting $\ln[C/C_0]$ as a function of time. For degradation reactions conforming to first-order kinetics, the resulting line will be straight

with a negative slope. The first-order degradation constant will be equal to k (Alexander and Scow, 1989; Atkins, 1986; Hamaker, 1972; Hurle and Walker, 1980).

First-order kinetics are often referred to as half-life kinetics because if half of a pesticide remains at time t, then half of that which remains will be left at time 2t, and half again at time 3t (Alexander and Scow, 1989). Half-life ($T_{½}$) is defined as the time it takes for the concentration of a substance to decrease to one-half its initial value (Atkins, 1986), and it is easily calculated for first-order kinetics using the first-order degradation constant. Half-life is independent of the initial pesticide concentration, meaning that the same half-life will be obtained regardless of the initial concentration (Hamaker, 1972; Hurle and Walker, 1980). This statement obviously has some limitations as far as pesticide degradation in the soil is concerned, but for a reaction to be classified as first-order, this assumption must be obeyed. The half-life concept has been used frequently to compare rates of herbicide degradation and therefore persistence (Hurle and Walker, 1980).

The advantages of using the first-order model for describing pesticide degradation are; mathematical simplicity, ease in extrapolating to zero concentration, provides a basis for comparison of different curves or rates of degradation, and ease in analysis and presentation of data (Alexander and Scow, 1989; Bazin et al., 1976; Zimdahl and Gwynn, 1977).

Some disadvantages of using the first-order model to describe

pesticide degradation are that it is often empirically based. Use of the first-order model is often a result of its goodness of fit with pesticide degradation data. In this situation, no insight into mechanisms of degradation are obtained (Alexander and Scow, 1989; Hamaker, 1972). Also, due to the chemical and biological complexity of soil as a medium for degradation, the first-order model can oversimplify in many situations. Variations in soil microbial activity with time, competing reactions or sequences within degradation mechanisms, and the influence of adsorption and desorption kinetics on the availability of pesticides for degradation all contribute to the complex nature of pesticide degradation in soil, and the first-order model cannot account for these. These variation can therefore result in the failure of the first-order model to adequately describe degradation in many cases (Hurle and Walker, 1980).

Several researchers have used first-order kinetics to describe dinitroaniline degradation in soil under a wide range of soil and environmental conditions (Gingerich and Zimdahl, 1976; Hayden and Smith, 1980; Jensen and Kimball, 1980; LaFleur, 1979; LaFleur et al., 1978; Poku and Zimdahl, 1976; Pritchard and Stobbe, 1980; Savage, 1973; Zimdahl and Gwynn, 1977). For pendimethalin, Walker and Bond (1977) found the rate of degradation to conform to first-order kinetics in seven soils varying widely in percent carbon, percent clay, and pH. Barrett and Lavy (1983) used the first-order model to describe pendimethalin degradation, applied at

three initial concentrations, in a silt loam at field capacity, under continuous flood, and under alternative flood conditions. The degradation of several dinitroanilines, including pendimethalin, conformed to first-order kinetics in a Sharkey clay at field capacity and under flood (Savage, 1978).

Use of other models

In some situations, the first-order model has failed to adequately describe dinitroaniline degradation (Brewer et al., 1981; Gingerich and Zimdahl, 1976; Zimdahl and Gwynn, 1977). Barrett and Lavy (1983) concluded that the first-order model did not describe pendimethalin degradation in an air-dry silt loam. Zimdahl et al. (1984) determined that pendimethalin degradation under several soil water content and temperature regimes did not conform to first-order kinetics (Zimdahl et al., 1984).

In situations where the first-order model has failed to adequately describe dinitroaniline degradation, other models, such as a quadratic (Zimdahl and Gwynn, 1977; Zimdahl et al., 1984), asymptotic (Jensen and Kimball, 1980), or complex first-order model (Brewer and Lavy, 1983; LaFleur, 1980; LaFleur et al., 1978; Zimdahl and Gwynn, 1977) have been implemented.

A complex first-order model attempts to describe degradation as a biphasic process with an initial, rapid degradation rate followed by a second, slower degradation rate. For each degradation phase, a first-order regression

slope is empirically fit to the data for each phase (Zimdahl and Gwynn, 1977). This model may account for adsorption equilibria, which is not considered by the first-order model (Hamaker, 1972; Hyzak and Zimdahl, 1974; Zimdahl and Gwynn, 1977).

This technique has been questioned because the point of intersection of the two slopes is not determined accurately, the curvilinear transition between the rapid degradation phase (first line) and the slow degradation phase (second line) is not considered or described, and the determination of fit of data to model is difficult and not easily comparable to the first-order model (Reyes and Zimdahl, 1989).

A variation of the complex first-order model, called the biexponential model, approximates this biphasic process by summing the first- and second-order differential rate equations to give the equation

$$\frac{dC}{dt} = -(k_1C + k_2C^2)$$

where dC/dt is the degradation rate, and k_1 and k_2 are the first- and second-order rate constants. Integration of this equation allows the calculation of concentrations by estimating k_1 and k_2 using nonlinear regression.

Like the complex first-order model, the biexponential model can account for the biphasic nature of pesticide degradation. It also does not require subjective separation of the data into the two phases and can account for the curvilinear transition between the rapid, first phase and the

slower, second phase. This model has been shown to provide a better description of trifluralin degradation, as compared to the nonlinear form of first-order model, in four soils (Reyes and Zimdahl, 1989).

B. MATERIALS AND METHODS

Degradation Models

Models used to describe degradation of pendimethalin and flumetralin, applied alone and in combination, under the experimental conditions described in Chapter II, include the zero-order, first-order, second-order, quadratic, and biexponential. Soil concentration data from the chemical assay were used for modeling the degradation of pendimethalin and flumetralin. Data were grouped into each soil by pesticide by pesticide status by soil water content by temperature combination over each time interval.

Estimating Degradation Constants

Linear regression analysis was used to obtain degradation rate estimates and statistical parameters for each model, except the biexponential model. For this model, estimates for the degradation

equations were obtained through nonlinear regression analysis, and statistical parameters were calculated manually.

For the zero-, first-, second-, and quadratic models, degradation constants were obtained by plotting the appropriate dependent variable as a function of independent variables. Dependent variables were C, $\ln(C/C_0)$, 1/C, and C for zero-, first-, second-, and quadratic models, respectively, where C is the pesticide soil concentration. Time was the only independent variable for the zero-,first-, and second-order models (Atkins, 1986). For the quadratic model, time and $(\text{time})^2$ were used as independent variables. This polynomial term resulted in a curvilinear degradation line (Zimdahl et al., 1984).

For the biexponential model, degradation estimates were obtained by nonlinear regression of the equation

$$C = \frac{k_1 C_0}{(k_1 + k_2 C_0)e^{k_1 t} - k_2 C_0}$$

where C is concentration at time t, k_1 and k_2 are the degradation constants, t is time, and C_0 is the initial concentration.

Evaluating Model Performance

Performance of each model for each treatment combination was evaluated by comparison of coefficients of determination (r^2). For the

biexponential model, coefficients of determination were calculated using the equation

$$r^2 = \frac{\textit{corrected regression SS}}{\textit{corrected total SS}}$$

where the corrected regression SS (sums of squares) is the corrected total SS - error SS.

The mean r^2 for each model within soils, pesticide by pesticide status, soil water contents, and temperatures were calculated and used to evaluate and compare model performance under experimental conditions.

C. RESULTS AND DISCUSSION

Coefficients of determination (r^2) for these data represent the portion of the total variation in the dependent variable accounted for by the relationship to the independent variable(s). Values for r^2 can range from 0 to 1, with 0 indicating that none of the variation was accounted for by the model, and 1 indicating that all of the variation was accounted for by the model. The closer r^2 is to 1, the better the fit of the model to the data. Values for r^2 were determined for each soil, pesticide, soil water content, and temperature by model combination. The pesticide by model combination was further subdivided to include the pesticide status effect to determine if any difference in r^2 values occurred between each pesticide, applied alone

and in combination.

Influence of Soil on Model Performance

Values for r^2 for soils within models indicated that the highest mean values were obtained with Norfolk soil for each model, followed by the Dickson, Decatur, and Sequatchie soils (Table 16). Mean r^2 values for each model within soils indicated that the biexponential model gave the best fit of data for each soil, followed by the quadratic, first-, second-, and zero-order models. There was very little difference in r^2 between the first- and second-order models in each soil. Values for r^2 varied widely within each soil by model combination, as indicated by the high standard deviations. In the Decatur soil, r^2 values ranged from 0.24 to 0.92 for the first-order model, and from 0.53 to 0.99 for the biexponential model.

Influence of Pesticides on Model Performance

Values of r^2 for pendimethalin and flumetralin, applied alone and in combination, within each model indicated higher r^2 for pendimethalin than with flumetralin (Table 17). Also, very little difference existed between pendimethalin alone and pendimethalin applied in combination with flumetralin or between flumetralin alone and flumetralin applied in

Table 16. Coefficients of determination for degradation models within the Decatur clay loam, Dickson silt loam, Norfolk loamy sand, and Sequatchie loam soils[a].

Soil	Degradation models				
	Zero	First	Second	Quadratic	Biexp.[b]
	(r^2)				
Decatur	0.64 (0.18)	0.70 (0.23)	0.65 (0.23)	0.76 (0.17)	0.82 (0.16)
Dickson	0.65 (0.10)	0.67 (0.11)	0.67 (0.12)	0.78 (0.11)	0.83 (0.10)
Norfolk	0.71 (0.17)	0.74 (0.19)	0.74 (0.19)	0.80 (0.14)	0.85 (0.11)
Sequatchie	0.55 (0.15)	0.57 (0.18)	0.56 (0.19)	0.67 (0.16)	0.76 (0.14)

[a]Mean values for coefficients of determination (r^2) are for each model within a soil, averaged over pesticide, pesticides status, soil water content, and temperature. Values are followed by their respective standard deviations in parenthesis.

[b]Abbreviation for the biexponential model.

Table 17. Coefficients of determination for degradation models for pendimethalin and flumetralin, applied alone and in combination[a].

Pesticide[b]	Degradation models				
	Zero	First	Second	Quadratic	Biexp.[c]
	(r^2)				
Pend (alone)	0.69 (0.13)	0.75 (0.16)	0.73 (0.15)	0.82 (0.11)	0.89 (0.09)
Flum (alone)	0.58 (0.18)	0.58 (0.20)	0.58 (0.21)	0.66 (0.16)	0.73 (0.13)
Pend (comb)	0.71 (0.09)	0.75 (0.12)	0.73 (0.14)	0.82 (0.07)	0.88 (0.07)
Flum (comb)	0.58 (0.18)	0.59 (0.21)	0.58 (0.22)	0.69 (0.17)	0.76 (0.14)

[a]Mean values for coefficients of determination (r^2) for each model within a pesticide are averaged over soil, soil water content, and temperature. Means are followed by their respective standard deviations in parenthesis.

[b]Pesticide treatments are pendimethalin (pend), alone and in combination with flumetralin (comb), and flumetralin (flum), alone and in combination with pendimethalin (comb).

[c]Abbreviation for the biexponential model.

combination with pendimethalin. Thus, presence of both pesticides in soil did not appear to influence fit of data to any model for either pesticide. For models within pesticide treatments, r^2 values were again highest for the biexponential model, followed by the quadratic model. The order of the remaining models was generally first-, second-, and zero-order, with little difference between any of these models for pendimethalin, and essentially no difference for flumetralin. Variation in r^2 was high for most pesticide treatment by model combinations, with flumetralin exhibiting more variation than pendimethalin treatments, as indicated by their respective standard deviations.

Influence of Soil Water Content on Model Performance

Values for r^2 for soil water content treatments within each model indicated only small differences between treatments, with slightly higher values at the high water content, (-33 kPa) compared to the low water content (-100 kPa) (Table 18). For models within soil water contents, ranking of the models was similar to that found for models within soils and within pesticide treatments, where the highest r^2 values were found for the biexponential model, followed by the quadratic, first-, second-, and zero-order models. Wide variation in r^2 values occurred for most model by soil water content combinations, with greater variation at -100 than at -33 kPa.

Table 18. Coefficients of determination for degradation models at soil water contents of -33 and -100 kPa.[a].

Soil Water Content	Degradation models				
	Zero	First	Second	Quadratic	Biexp.[b]
(kPa)	(r^2)				
-33	0.65 (0.14)	0.68 (0.17)	0.66 (0.18)	0.77 (0.13)	0.82 (0.11)
-100	0.63 (0.18)	0.66 (0.21)	0.65 (0.21)	0.74 (0.17)	0.81 (0.15)

[a]Mean values for coefficients of determination (r^2) for each model within soil water content are averaged over soil, pesticide, pesticide status, and temperature. Means are followed by their respective standard deviations in parenthesis.

[b]Abbreviation for the biexponential model.

Influence of Temperature on Model Performance

Higher r^2 values were obtained at 30 C within each model than at 15 C (Table 19). This difference in r^2 values between temperatures was much more than observed between soil water contents. Ranking of models within each temperature again followed the same general pattern as with soils, pesticide treatments, and soil water contents. Variation in means was greater at 15 C than at 30 C.

Generally, all models provided a better fit of data for treatments where half-lives were shorter, or degradation rates were faster. Values for r^2 were higher for pendimethalin treatments, which had shorter half-lives than flumetralin treatments. This was also true for soil water content and temperature treatments, where higher r^2 values were obtained at -33 kPa compared to -100 kPa, and at 30 C compared to 15 C. This was not the case for soils, where no general pattern was observed between r^2 values and mean half-life values for soils (as determined in Chap II).

Results reported here agree with those reported by Barrett and Lavy (1983), who used the first-order model to describe pendimethalin degradation under various soil water regimes. At a soil water content of -30 kPa, pendimethalin degradation was adequately described by the first-order model, where half-life was calculated to be 59 d. However for air-dried soil, there was only negligible dissipation of pendimethalin, and

Table 19. Coefficients of determination for degradation models at temperatures of 15 and 30 C[a].

	Degradation models				
Temp	Zero	First	Second	Quadratic	Biexp.[b]
(C)	(r^2)				
15	0.58 (0.19)	0.58 (0.21)	0.56 (0.22)	0.68 (0.18)	0.75 (0.15)
30	0.70 (0.09)	0.76 (0.11)	0.74 (0.11)	0.81 (0.08)	0.88 (0.07)

[a]Mean values for coefficients of determination (r^2) for each model within temperature are averaged over soil, pesticide, pesticide status, and soil water content. Means are followed by their respective standard deviations in parenthesis.

[b]Abbreviation for the biexponential model.

degradation did not follow the first-order degradation model. Brewer et al. (1981) found that fit of first-order model decreased as persistence increased. For a half-life of 15.1 wk, the correlation coefficient was -0.81, while for a half-life of 7.4 wk, the correlation coefficient was -0.95. Conflicting results were obtained by Zimdahl and Gwynn (1977) for three dinitroanilines. They found that degradation of trifluralin, benefin, and an unnamed compound was adequately described by the first-order model at 15 C, but not at 30 C. At the higher temperature, a complex first-order model was used, giving a better description of the data than the first-order model. The complex first-order model is similar to the biexponential model used in this study, in that both attempt to describe pesticide degradation as a biphasic process.

The biexponential model was superior for describing degradation of both pesticides under all conditions compared to other models, including the first-order model. Reyes and Zimdahl (1989) reported similar results with trifluralin, where biexponential model was superior to first-order model in 15 out of 25 data sets. This would indicate that pendimethalin and flumetralin degradation does follow a two phase degradation process. The superiority of quadratic model to the first-order model in this experiment was similar to results reported by Zimdahl et al. (1984), where pendimethalin degradation in three soils, under different soil water content and temperature conditions, was not adequately described by the first-order model, but was by the

quadratic model. The zero- and second-order models also failed to adequately describe pendimethalin in their study.

The use of the quadratic model does not allow for prediction of future concentrations of pesticides. It can only predict pesticide concentrations within the time frame of the experiment. For this study, that time period would be 180 d. With the addition of the polynomial term, $(time)^2$, to the quadratic model, the characteristic U-shaped curve of the quadratic model is formed, thus making prediction of future pesticide concentrations impossible.

Wide variation in r^2 values for each model by treatment combination would indicate that none of these models is ideal for describing either pendimethalin or flumetralin degradation under all possible conditions. Since persistence and r^2 values were influenced by soil and environmental factors, it would be necessary to incorporate these parameters into each model. This would allow more adequate description of pesticide degradation under the wide range of conditions that were imposed here, and would also occur in the field.

CHAPTER IV

SUMMARY

Several conclusions can be formulated from these results on the influence of soil and environmental factors on pendimethalin and flumetralin persistence. The soils used in this study had a significant influence on the soil persistence of these pesticides. Wide variation in the measured values of soil properties obviously influenced the half-lives observed in each soil, as indicated by the significant soil effect in the data analyses. However, the failure of any one soil factor to be highly correlated with pesticide half-life, even though some properties were significantly correlated, would indicate that the effect of soil on pesticide persistence is a result of the interaction of several soil properties, rather than a single property.

The pesticide differences detected indicate that flumetralin is generally much more persistent than pendimethalin. This statement must be qualified due to the significant decrease in flumetralin half-life observed in the Dickson silt loam soil. Higher microbial activity in the Dickson soil could have been the cause for the increased degradation rate of flumetralin, although this would require verification.

Although the differences between each pesticide's half-life when

applied in combination compared to its half-life when applied alone were large in some cases, they were generally not significant. Half-lives of the pesticides were as long as 300 to 400 d in some treatments. Application rates for both pesticides were three to four times the maximum rates specified on their respective labels. This could have resulted in the half-lives to be longer than under normal conditions. Half-life data in this study were determined under non-field conditions and were used as a means for comparison between treatments. These half-life values cannot be applied to field situations, although the effect of the treatments on pesticide persistence can be applied with caution.

The soil water contents used in this study did not produce a significant difference between the half-lives of pendimethalin or flumetralin. This does not indicate a lack of influence of soil water content on pendimethalin or flumetralin persistence. Obviously a wider difference in soil water content treatments was needed.

The influence of temperature on pendimethalin and flumetralin persistence was quite high as one would expect. Variation in response of pesticides to temperature resulted in differences in activation energies, indicating possible differences between degradation pathways between pesticides and between soils.

The biological assay detected similar differences between the treatments as observed in the chemical assay data. However the failure of

the assay to estimate soil concentrations of the pesticides indicated that this assay technique was not as sensitive to changes in pesticide concentrations between samples as the chemical assay. The observed response for the combination of pendimethalin and flumetralin was greater than the expected response, using percent of untreated control as the method of corn shoot height data transformation, indicating that the interaction effect was antagonistic. Differences in these results from previous research on the interaction of pendimethalin and flumetralin is likely due to the plant species used to indicate the biological response. Phytotoxicity of a pesticide on a plant species within a plant family is variable as is the phytotoxicity of several pesticides within a chemical family on a single plant species.

The accurate estimation of pendimethalin and flumetralin soil concentrations by the models used in this study is possible in some situations, but not advisable in all situations. Future work involving modeling of pendimethalin, flumetralin, or any dinitroaniline should incorporate specific environmental and soil variables into the model to account for the variation in degradation that does occur with these factors.

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APPENDIX

Table A1. Soil concentrations of pendimethalin and flumetralin, applied alone and in combination, each at a rate of 4 $\mu g\ g^{-1}$ of soil, in a Decatur clay loam adjusted to two soil water contents and incubated at two temperatures for five time intervals[a].

Pesticide	Soil Water Content	Temperature	Time				
			0	30	60	120	180
	(kPa)	(C)	($\mu g\ g^{-1}$ of soil)				
Pendimethalin (alone)	-33	15	4.00	3.12	2.30	1.91	1.17
		30	4.00	1.43	0.58	0.37	0.14
	-100	15	4.00	3.10	2.46	2.14	1.36
		30	4.00	1.37	0.73	0.42	0.18
Flumetralin (alone)	-33	15	4.00	3.43	3.11	3.14	2.67
		30	4.00	2.64	2.41	2.25	1.71
	-100	15	4.00	3.28	3.06	3.38	2.74
		30	4.00	2.98	2.90	2.38	1.83
Pendimethalin (combination)	-33	15	4.00	3.38	1.89	2.40	1.22
		30	4.00	1.72	0.69	0.49	0.21
	-100	15	4.00	3.38	2.43	2.49	1.71
		30	4.00	1.72	1.36	0.55	0.34
Flumetralin (combination)	-33	15	4.00	3.63	2.73	3.37	2.99
		30	4.00	2.90	2.43	2.21	1.91
	-100	15	4.00	3.51	2.77	3.39	2.88
		30	4.00	3.26	2.91	2.33	2.05

[a]Soil concentration means are averaged over four replications.

Table A2. Soil concentrations of pendimethalin and flumetralin, applied alone and in combination, each at a rate of 4 $\mu g\ g^{-1}$ of soil, in a Dickson silt loam adjusted to two soil water contents and incubated at two temperatures for five time intervals*.

Pesticide	Soil Water Content	Temperature	Time 0	30	60	120	180
	(kPa)	(C)	($\mu g\ g^{-1}$ of soil)				
Pendimethalin (alone)	-33	15	4.00	3.21	3.19	3.39	2.84
		30	4.00	2.52	2.27	2.08	1.95
	-100	15	4.00	3.14	3.17	2.80	2.79
		30	4.00	2.82	2.56	2.59	2.26
Flumetralin (alone)	-33	15	4.00	3.22	3.21	2.87	2.69
		30	4.00	3.21	3.34	2.29	2.36
	-100	15	4.00	3.41	3.20	3.07	2.58
		30	4.00	3.54	3.16	2.87	2.66
Pendimethalin (combination)	-33	15	4.00	3.17	3.23	2.76	2.96
		30	4.00	2.33	2.66	2.12	1.58
	-100	15	4.00	3.35	3.32	3.17	2.95
		30	4.00	2.58	2.70	2.63	2.12
Flumetralin (combination)	-33	15	4.00	3.32	2.66	1.89	2.67
		30	4.00	2.67	2.62	2.77	1.55
	-100	15	4.00	3.45	3.02	2.84	1.95
		30	4.00	2.66	2.94	2.39	1.62

*Soil concentration means are averaged over four replications.

Table A3. Soil concentrations of pendimethalin and flumetralin, applied alone and in combination, each at a rate of 4 $\mu g\ g^{-1}$ of soil, in a Norfolk loamy sand adjusted to two soil water contents and incubated at two temperatures for five time intervals[a].

Pesticide	Soil Water Content	Temperature	Time 0	30	60	120	180
	(kPa)	(C)	----------($\mu g\ g^{-1}$ of soil)----------				
Pendimethalin (alone)	-33	15	4.01	3.36	3.44	3.24	2.87
		30	4.01	2.95	2.61	2.38	1.46
	-100	15	4.01	3.68	3.19	3.08	2.68
		30	4.01	2.99	2.61	2.22	1.72
Flumetralin (alone)	-33	15	4.01	3.72	3.39	3.38	3.37
		30	4.01	3.44	3.05	3.21	2.67
	-100	15	4.01	3.51	3.31	3.88	3.24
		30	4.01	3.51	3.26	2.93	2.64
Pendimethalin (combination)	-33	15	4.01	3.35	3.15	3.04	2.55
		30	4.01	2.78	2.52	2.17	1.37
	-100	15	4.01	3.22	3.17	3.07	2.82
		30	4.01	3.05	2.59	2.18	1.79
Flumetralin (combination)	-33	15	4.01	3.38	3.28	3.27	2.90
		30	4.01	3.09	3.01	2.75	2.57
	-100	15	4.01	3.25	3.42	3.28	3.24
		30	4.01	3.36	2.93	2.83	2.71

[a]Soil concentration means are averaged over four replications.

Table A4. Soil concentrations of pendimethalin and flumetralin, applied alone and in combination, each at a rate of 4 $\mu g\ g^{-1}$ of soil, in a Sequatchie loam adjusted to two soil water contents and incubated at two temperatures for five time intervals[a].

Pesticide	Soil Water Content	Temperature	Time 0	30	60	120	180
	(kPa)	(C)	($\mu g\ g^{-1}$ of soil)				
Pendimethalin (alone)	-33	15	3.96	3.18	2.85	2.91	2.60
		30	3.96	2.27	1.60	1.65	1.30
	-100	15	3.96	3.19	2.74	2.94	2.50
		30	3.96	2.45	1.85	1.90	1.31
Flumetralin (alone)	-33	15	3.96	3.35	3.39	3.31	3.14
		30	3.96	2.92	2.88	2.69	2.24
	-100	15	3.96	3.41	3.22	3.27	3.25
		30	3.96	2.94	2.84	2.94	2.53
Pendimethalin (combination)	-33	15	3.96	3.37	2.95	2.92	2.73
		30	3.96	2.45	1.93	1.67	1.25
	-100	15	3.96	3.46	3.36	3.27	2.97
		30	3.96	2.52	2.48	2.02	1.58
Flumetralin (combination)	-33	15	3.96	3.35	3.40	3.27	3.20
		30	3.96	3.00	2.88	2.89	2.34
	-100	15	3.96	3.38	3.20	3.28	2.95
		30	3.96	3.11	3.30	3.11	2.46

[a]Soil concentration means are averaged over four replications.

VITA

Jeffrey Eric Herrmann was born in Fort Lee, Virginia, on February 15, 1963. He attended grade schools in Illinois and Missouri before relocating with his parents and three brothers to Madisonville, Kentucky, in 1976. He attended Madisonville-North Hopkins High School, from which he graduated with honors in 1981. In August 1981, he enrolled at the University of Kentucky in Lexington and was awarded a Bachelor of Science degree in Agronomy in May, 1985. He continued his education at the University of Kentucky in the Department of Agronomy, under the direction of Dr. Jones H. Palmer and Dr. Gary K. Palmer. He received a Master of Science degree in Crop Science in December, 1987.

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