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Detection and Description of Sulfonylurea Herbicide Breakdown in Soil

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DETECTION AND DESCRIPTION OF SULFONYLUREA HERBICIDE BREAKDOWN IN SOIL

BY

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This dissertation is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy, and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this dissertation does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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MAP

DETECTION AND DESCRIPTION OF SULFONYLUREA HERBICIDE BREAKDOWN IN SOIL

Abstract

MARK A. PETERSON

Corn (Zea mays L. 'Sokota TS60'), grain sorghum [Sorghum bicolor (L.) Merr. 'Sokota 844'], and flax (Linum usitatissimum L. 'Culbert 79') were tested to determine suitability for petri dish bioassays of chlorsulfuron {2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) amino]carbonyl]benzenesulfonamide}, metsulfuron {2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino] carbonyl]amino]sulfonyl]benzoic acid} and chlorimuron {2-[[(4-chloro-6-methoxypyrimidine-2-yl)amino carbonyl] aminosulfonyl]benzoic acid, ethyl ester}. Sorghum was not an acceptable bioassay species. Corn had a significant response to all three herbicides. Flax was the best indicator species in both soil types tested.

The effects of herbicide concentration, temperature, moisture, and pH on decomposition rate of chlorsulfuron and metsulfuron were studied. Both chlorsulfuron and metsulfuron deviated from first-order kinetics. The Arrhenius equation was used to describe temperature influence and gave thermal activation values of 21.1 and 22.8 kcal/mole for chlorsulfuron and metsulfuron,

respectively. Moisture response was curvilinear for both compounds as was pH response. The influence of the factors examined in this work was almost identical for both herbicides.

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LIST OF ABBREVIATIONS

Abbreviation	Definition
ai	active ingredient
C	degrees Celsius
cal	calories
cm	centimeter
d	days
deg	degree
g	grams
g/ha	grams per hectare
K	degrees Kelvin
kcal/mole	kilocalories per mole
kg/ha	kilograms per hectare
M	molar
m	meter
mm	millimeter
ppbw	parts per billion by weight
w	weeks

INTRODUCTION

Persistence of pesticides in the environment is of concern to many people. Growers require pesticides which are effective for a long enough period of time to protect a crop for an entire growing season but which will degrade to non-phytotoxic levels before a susceptible crop is planted. The longer a pesticide persists in the environment the greater the possibility that it will be moved from its intended site of use and affect non-target organisms by such means as leaching or runoff.

The sulfonylurea herbicides are a relatively new group of compounds. As a group, they are known for their ability to control a wide variety of weeds at rates of less than 11 g ai/ha. They are soil active and can persist in soil at phytotoxic levels for a few weeks up to several years depending on the member involved and various edaphic and environmental factors. Chlorsulfuron was the first sulfonylurea to be successfully developed and marketed. It controls a variety of broadleaf weeds and some important grasses in small grains (34). The persistence of chlorsulfuron in soils varies widely depending on location and soil type. In northern states such as Idaho and North Dakota, 35 g ai/ha has caused substantial injury to corn (Zea mays L.) planted 36 months

after application (13, 44). On the other hand, 70 g ai/ha in Virginia caused no injury to corn planted only 10 months after application (14). A study in Kansas indicated no injury to grain sorghum (Sorghum bicolor L.) the year following postemergence application of 0.04 kg ai/ha on winter wheat (33). However, 0.018 kg ai/ha caused significant injury to grain sorghum in Texas, possibly due to the soil type, the dry climate, or a combination of the two (51). In South Dakota, chlorsulfuron can persist for more than one growing season to injure corn, flax, grain sorghum, soybeans, and sunflowers (37).

Metsulfuron is similar to chlorsulfuron in selectivity and spectrum of weeds controlled, but may be less persistent in soil than chlorsulfuron (1). chlorimuron has recently been labeled for use on soybeans in southern portions of the corn belt, but is of limited use in northern areas due to carryover injury to corn (11). Thiameturon [3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid] has been test in cereals and is reported to be safe for use in areas where sensitive broadleaf crops are rotated with cereals (4).

Since the sulfonylureas represent a range of soil half-lives they could become a very useful weed control

tool. By choosing the proper sulfonylurea herbicide or combination of sulfonylureas, a grower could obtain weed control for one to several growing seasons with only one application. However, before this becomes a reality, we must first be able to quantitatively predict levels of sulfonylurea residue at a given time under specified edaphic and environmental conditions.

The objectives of these studies were: 1) Establish a sensitive sulfonylurea bioassay. 2) Determine what kinetics law should be applied to chlorsulfuron and metsulfuron decomposition in soil. 3) Determine the quantitative effects of soil temperature, moisture, and pH on chlorsulfuron and metsulfuron decomposition in soil. 4) Compare the relative decomposition rates of chlorsulfuron and metsulfuron.

REVIEW OF THE LITERATURE

Herbicide Bioassay

Before a researcher can model the decomposition of a herbicide in the soil there must be a reliable method for the quantitative detection of the compound of interest. Sulfonylurea herbicides are usually applied at rates below 11 g ai/ha, resulting in soil residues which must be measured in parts per billion. Chromatographic analysis at this level can be difficult (52). Certain plant species can respond to these low soil residue levels (8). Bioassays may be the only practical detection method for these herbicides until new chromatographic procedures are discovered.

Plants exhibit a variety of responses to herbicides depending on the species and mode of action of the particular herbicide involved. A bioassay must use a plant species which gives a gradual reaction in response to increasing herbicide rate. Common field and garden crops such as oats, corn, sorghum, soybeans, cucumbers, and sunflowers have been used for bioassays(7,10, 21, 31, 41). Weed species are seldom used, probably due to their lesser genetic uniformity.

A major disadvantage of many bioassays is that they require long periods of time in order for the plants

to show a significant response to the herbicide. Small pot bioassays utilizing higher plants can require 3 to 4 weeks before plant heights or weights are sufficiently different to give an indication of herbicide concentration. Similarly, visual symptoms may not be fully expressed for several weeks. A time saving approach which often works well for herbicides which inhibit meristematic activity is the petri dish bioassay. In most petri dish bioassays, seeds of the test species are placed in small petri dishes containing anywhere between 20 and 150 g of soil or some other medium containing the herbicide. The petri dishes are then moistened and incubated for several days in a constant temperature chamber. At the end of the incubation period, seedling root or shoot growth is measured. This type of bioassay has been used successfully for a number of herbicides (7,10, 24, 26, 35). In many instances, seeds are pregerminated and sorted for uniformity before being planted. Petri dish bioassays do not appear to work well for photosynthetic inhibitors. Brattain, et al, found the petri dish method to be relatively insensitive for measurement of atrazine [6-chloro-N-ethyl-N'-(1-methyl-ethyl)-1,3,5-triazine-2,4-diamine] soil residues (7).

Most published chlorsulfuron bioassays have utilized corn as an indicator crop (3, 4, 21, 32).

However, some of the results have been extremely variable. Other plant sensitive plant species should be tested to determine if a better sulfonylurea bioassay can be developed.

Chlorsulfuron and Metsulfuron Degradation in Soil

A number of scientists have been interested in modeling pesticide fate in the environment. Modeling the fate of pesticides in the soil usually considers the basic routes a pesticide takes once it is in the soil. These main routes are sorption, leaching, volatilization, photodecomposition and degradation (45). Sorption, leaching, volatilization, and photodecomposition can sometimes be estimated from the chemical properties of a pesticide. Degradation, however, can not be so easily estimated due to the complexity of the systems involved. This pathway collectively considers both biological and chemical means of breakdown with the relative importance of each depending on the pesticide involved and on the soil environment. For example, herbicides such as picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) and the dinitroanilines degrade mainly by microbial action (17, 20, 29). In other pesticide families non-biological decomposition may play an important role.

The triazine herbicides can be degraded by soil microorganisms, but much of the initial loss of the molecule's phytotoxicity is due to an adsorption catalyzed hydrolysis to hydroxy analogs (5, 6, 28).

The most basic property of pesticide decomposition is the pattern of disappearance with time. Hamaker examined decomposition kinetics in detail and felt that the determination of a rate law was an important prerequisite to quantitative modeling of a pesticide's persistence (16). First-order kinetics are often encountered or assumed to hold for most herbicides (45). The equation for a first-order reaction is:

$$dc/dt = \text{Rate} = kc$$

where c = concentration,t = time, and k is the rate constant. In this case a plot of the logarithm of concentration against time gives a straight line with slope proportional to the rate constant. If $t_{1/2}$ is considered to be the half-life (time required for 50% degradation), it may be related to the rate constant by the following equation:

$$t_{1/2} = 0.6932/k$$

In such a situation herbicide half-life is independent of initial concentration. It has been proposed that since the concentration of a pesticide is small relative to other soil constituents, the concentration of the pesticide is the limiting factor in the decomposition reaction and that first-order kinetics should apply (53). Hamaker disagreed with this position and indicated that such a generalization was not supported by experimental data (16). Hurle and Walker cited numerous examples of studies which indicated kinetic orders either greater or less than one (22). Rate laws other than first-order have been proposed (16, 22). One type is referred to as the power rate model and is described by the generalized equation:

$$\text{Rate} = dc/dt = kc^n$$

where c is concentration, k is a rate constant, and n is the order of the reaction. Another type is known as the hyperbolic rate model and is described by the generalized equation:

$$\text{Rate} = dc/dt = (k_1 c) \; / \; (k_2 + c)$$

where k_1 is a maximum rate which is approached with

increasing concentration and k_2 is a pseudoequilibrium constant (16). Michaelis-Menton kinetics are a form of the hyperbolic rate concept which are usually applied to enzyme systems in living organisms. Since many pesticide decomposition reactions are thought to occur through microbial enzyme systems, several researchers have applied this approach to pesticide modeling (17, 18, 29, 36).

While most pesticides are subject to action of microbial enzymes, some compounds may become an energy source for some portion of the soil microflora. Often a portion of the microbial population becomes adapted to using a particular pesticide as an energy source. In such cases, decomposition may proceed slowly for a period of time until the adapted microbes multiply to significant levels. This lag phase is then followed by a more rapid rate of decomposition. The presence of a lag phase in the decomposition pattern of a pesticide may make the kinetics of the breakdown more complex. In one instance a combination of two first-order rate equations was used to describe the decomposition of 2,4-D [(2,4-dichlorophenoxy) acetic acid] in soil (36).

Soil temperature can influence both chemical and biological degradation reactions. An often used relationship in the description of temperature effects is

the Arrhenius equation:

$$k = Ae^{-E/RT}$$

where k is the rate constant at temperature T (degrees Kelvin), R is the gas constant (1.986 cal deg^{-1} $mole^{1}$), and E is the activation energy of the reaction. In general, most pesticides degrade at a very low rate when temperatures are near 0 C (16, 22). At this temperature, biological activity is low and free water for chemical hydrolysis reactions is limited. As temperature increases degradation rates tend to increase. Breakdown mechanisms involving microorganisms often exhibit an optimum temperature value which corresponds to the maximum growth rate of the population involved. Since the Arrenhius equation does not provide for a temperature maximum, it may be inappropriate for describing temperature effects on decomposition when microbial breakdown is dominant.

Soil moisture is another factor which affects breakdown. Usually the relationship between soil moisture and degradation rate is described empirically due to a lack of a theoretical basis which is widely applicable. In general, pesticide decomposition rates are slow in air dry soil and steadily increase as soil moisture levels

increase to field capacity. The effect of anaerobic conditions which occur at saturation varies with the pesticide involved (16, 22).

Alan Walker has constructed several persistence models which combine temperature and moisture effects on herbicide degradation (46, 47, 49). One of his first published models described the persistence of napropamide [N,N-diethyl-2-(1-naphthalenyloxy)propanamide] (46). First-order kinetics were used as a basis for his model. From laboratory moisture and temperature experiments he described the effects of moisture and temperature on napropamide half-life. He then used a computer program to simulate soil moisture and temperature in a field situation and subsequently used these values to model the breakdown of napropamide. This model has also been applied to simazine (6-chloro-N,N'-diethyl-1,3,5 -triazine-2,4-diamine), atrazine, propyzamide [N-(1,1-dimethyl-propynyl)-3,5-dichlorobenzamide], linuron [N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea], trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl) benzenamine], metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one],and chlorsulfuron (47, 49). In spite of their simplicity and the fact that they do not account for dissipation pathways such as adsorption, volatilization, and leaching, Walker has found

his models to be reasonably accurate for determining herbicide persistence in the field, depending on the soil type and herbicide involved. But since his models do not include the effects of factors such as texture, organic matter, and pH, they may not be widely applicable to other soil types.

The effects of soil factors such as pH, organic matter, and texture vary widely depending on the pesticide involved. They are the most difficult factors to study due to the numerous interactions possible. It is also hard to obtain a range of values for a given soil factor while keeping other soil properties constant. Walker and Thompson studied the decomposition of simazine, linuron, and propyzamide in 18 soils with a range of soil properties (48). Using regression analysis, the authors attempted to determine the correlation between degradation rate and soil parameters such as organic matter content, clay content, pH, available P and K, and soil respiration. A significant correlation between linuron degradation and respiration, organic matter, and clay content was discovered. Simazine decomposition was related to pH, but the correlation was low ($r = 0.57$). With propyzamide there was no significant relationship between degradation and any of the soil properties studied. In a similar study, Meikle et al. could only

account for 27% of the variation in picloram decomposition using a multiple regression equation which included soil temperature, moisture, organic matter, and pH (29). On the other hand, a study of PCP (pentachlorophenol) degradation in ten different soils was able to produce an equation which accounted for 68% of the variation in breakdown rates (27). One of the most extensively studied soil factors is pH. The pH of a soil can affect the pesticide molecule and influence reactions involved in its breakdown. Adsorption catalyzed decomposition of the triazine herbicides is an example of a breakdown reaction which is influenced by pH (5, 6, 12, 28). Corbin and Upchurch found significant pH effects on the decomposition of dicamba (3,6-dichloro-2-methoxybenzoic acid), 2,4-D, dalapon (2,2-dichloropropanoic acid), amitrole (1H-1,2,4-triazol- 3-amine), vernolate (S-propyl dipropylcarbamothioate), diuron [N'-(3,4-dichlorophenyl)-N,N-dimethylurea], chloramben (3-amino-2,5-dichlorobenzoic acid), picloram, trifluralin, isocil, and prometon [6-methoxy-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine] (12).

Preliminary research indicates that a major mechanism of decomposition for the sulfonylurea herbicides is hydrolysis of the parent molecule into non-phytotoxic products with further breakdown by microorganisms (50).

Hydrolysis of sulfonylurea herbicides is thought to be enhanced by high temperature, the presence of free moisture and low pH (34, 49). Soil pH has been demonstrated to have a very significant affect on residual chlorsulfuron activity with a rapid increase in carryover potential as pH increases from 5.0 to 7.0 (15, 37).

Although hydrolysis appears to be a key step in the breakdown of sulfonylurea herbicides, a recent paper indicated that microbial action makes a significant contribution to chlorsulfuron decomposition in soil (25). Under alkaline soil conditions, chlorsulfuron degrades 10-12X faster in non-sterile soil than in sterile soil. However, in soils with relatively lower pH values chemical hydrolysis becomes dominant and the difference between sterile and non-sterile soil is less. Chlorsulfuron is a weak organic acid with a pka of 3.8 and exists in an anionic form at most soil pH values (42). Therefore chlorsulfuron does not adsorb well to clay minerals which have a net negative charge but does adsorb to organic matter (30, 42). Adsorption to organic matter is pH dependent with increased adsorption at lower soil pH values (42). The half-life of chlorsulfuron decreases as soil temperature and moisture increase. In one instance, chlorsulfuron half-life in a silty clay loam soil with a pH of 7.7 decreased from 231.7 days at 10 C to 63 days at

40 C (43). The same study showed increasing moisture content from 25 to 50% of field capacity caused the degradation rate to increase by 46%. Estimates of chlorsulfuron half-life in soil have ranged from 9 to 232 days depending on soil type, temperature, and moisture (43, 49).

While a significant amount of work concerning chlorsulfuron fate in soil has been published, only a small amount has been published with regard to metsulfuron. Metsulfuron is reported to be less persistent than chlorsulfuron (1). However, a recropping study in North Dakota compared metsulfuron and chlorsulfuron and concluded that carryover injury to eight different crops was significantly higher with metsulfuron when both compounds were applied at the same rates (44).

MATERIALS AND METHODS

Sulfonylurea Bioassay

Chlorsulfuron Bioassay. Corn, grain sorghum, and flax were tested for suitability as chlorsulfuron bioassay indicators. Samples of surface horizons from two different soil types were used. Chlorsulfuron is highly active in the Great Bend soil (Udic Haploborolls; fine-silty, mixed) and relatively less active in the Brookings soil (Pachic Udic Haploborolls; fine-silty, mixed) (37). The characteristics of these soils are presented in Table 1. The third soil listed in Table 1 was used in other experiments to be described later. Sand, silt, and clay contents were determined using the pipet method (3). Soil pH was measured in a 1:1 soil:water suspension with a glass electrode. Soil organic matter was determined by a modified Walkley-Black procedure (23). Moisture content at 1/3 bar was determined using a pressure plate (3). A 4.47×10^{-3} M solution (ai basis) of chlorsulfuron was prepared using the 75% dry flowable formulation of the compound. This solution was then applied to each of the three soils at a rate of 1 ml of solution/1000 g of soil to reach a soil concentration of 16 ppbw. The treated soil was mixed in a twin shell blender for 90 minutes. Lower concentrations

Table 1. Characteristics of surface (Ap) horizons used in bioassay and degradation studies.

Soil	Sand	Silt	Clay	Organic Matter	1/3 bar Moisture	pH
	---------- (%) ----------					
Brookings	19	51	30	3.5	28	5.3
Great Bend	5	61	34	2.5	35	6.5
Vienna	42	37	21	3.5	22	5.3

of herbicide were made by diluting treated soil with untreated soil and mixing for 90 minutes. Concentrations used for these studies were 4, 2, 1, 0.5, 0.25 and 0.125 ppbw. Seeds of the test crops were placed in 55 mm plastic petri dishes and covered with 20 g of soil. Corn was pregerminated for 36 h at 30 C. One pregerminated corn seedling per dish was used. Six ungerminated grain sorghum seeds were used in the sorghum test and 12 ungerminated flax seeds were used in the flax test. The planted dishes were then watered with a hand held squeeze bottle, placed in aluminum pans lined with moist paper towels, covered with aluminum foil, and incubated for 5 days at 30 C. For corn the length of the radicle was measured. For sorghum the length of the longest root for each of three representative seedlings was measured. For flax the length of the entire seedling for each of four representative seedlings was measured. Representative seedlings for sorghum and flax were chosen by discarding the longest and shortest seedlings in each dish and selecting seedlings of medium length. Eight replications of each concentration were used and the experiment was repeated twice. The data were examined by use of the analysis of variance and regression analysis (38,40).

Chlorimuron and Metsulfuron Bioassay. In order to test suitability of corn, flax, and grain sorghum as

bioassay indicators for chlorimuron and metsulfuron, three concentrations (0, 0.25, and 2.0 ppbw) of each of the two herbicides were prepared in a manner similar to that used for chlorsulfuron. Bioassays were carried out using the same procedure as for chlorsulfuron. The Great Bend soil was used in these experiments. Mean root lengths for corn and sorghum, and mean seedling lengths for flax were compared using the analysis of variance and the Waller-Duncan K-ratio t-test with a K-ratio of 100 (P=0.05) (38).

Chlorsulfuron and metsulfuron degradation

Surface soil from a Vienna loam series (Udic Haploborolls; Fine loamy, mixed) was used in all degradation experiments (Table 1). For the pH study the pH was adjusted to values of 6.2, 7.3, and 7.8 by adding 1, 4, or 16 g of hydrated lime per 1000 g of soil. The amended soil was wetted to 66% of field capacity and maintained at 30 C for 1 week before use to allow the samples to reach pH equilibrium. Fifteen hundred g of treated soil placed in polyethylene bags. Herbicide concentration was 16 ppbw for the moisture, temperature, and pH studies. Concentrations of 16, 8, and 4 ppbw were used in the kinetics study. Distilled water was added to

bring the samples to a soil moisture content of approximately 90% of field capacity for the kinetics study, 66% for the temperature and pH studies, or 90, 66, 38, or 11% for each treatment in the moisture study. The bags were kept at 5 C for 24 h to allow for adsorption equilibrium after which time a baseline sample (time = 0) of 250 g was removed from each bag. These samples were allowed to air dry and the concentration of each herbicide was determined using the flax bioassay described previously. After sampling the bags were then weighed and placed in a constant temperature chamber at 30 C except in the temperature study in which case the bags were placed in separate temperature chambers at 5, 20, 30, or 40 C. Further samples were removed for bioassay 5, 15, 35, and 75 days after the 0 day sample. Soil moisture content was periodically checked by reweighing and adding sufficient deionized water to the bags to bring them back to the recorded weight. All degradation experiments were conducted in a randomized complete block design with treatments blocked by time and 5 replications.

Analysis. Three different rate laws were applied to the data for each herbicide: a hyperbolic rate law, a power rate law, and a first order rate law. The equations for each rate law along with the corresponding integrated forms are shown in Table 2. The

method of Hamaker was used to test for fit to hyperbolic kinetics (16). Over relatively short time spans first order kinetics can be applied to decomposition. The rate constant for a first order reaction can derived from a linear regression of the logarithm of the concentration and time, with time as the independent variable. The product of this first order rate constant and the initial concentration of herbicide will equal the calculated rate of decomposition at time zero. Hyperbolic kinetics can be inverted to give the following linear form:

$$1/\text{rate} = (k_2/k_1)(1/c) + 1/k_1$$

Linear regression of the calculated initial rates for several initial concentrations will give estimates for the values of k_2/k_1 and $1/k_1$ which can then be solved for the values of k_1 and k_2. The coefficient of determination for the linear regression (r^2) can be used to indicate how well the data fit hyperbolic kinetics. The power rate model was tested by using a non-linear regression technique (39) in conjunction with the integrated form of the power rate equation. Values of the order of the reaction were determined for chlorsulfuron and metsulfuron. First order kinetics were tested by using regression analysis in conjunction with the

integrated form of the first order rate equation.

The influence of temperature, moisture, and pH on chlorsulfuron and metsulfuron degradation were determined by calculating the rate constant (k) value at each level. Equations describing the effect of each variable on the rate constant were determined using non-linear regression. The Arrhenius equation was used to express the relationship between degradation rate and soil temperature. Relationships between chlorsulfuron and metsulfuron degradation and moisture and pH were fitted empirically using regression analysis.

Table 2. Rate law equations[1].

Rate Law	Integrated Form
Hyperbolic:	
$dC/dt=(k_1)(C)/k_2 + C$	$C + k_2\log(C)=Co + k_2\log(Co) + k_1t$
Power:	
$dC/dt=kC^n$	$C=[(n-1)kt + Co^{1-n}]^{1/1-n}$
First-Order:	
$dC/dt=kC$	$\log(Co/C) = kt$

[1]C = Concentration at time t; Co = initial concentration; k_1, k_2, and k are rate constants.

RESULTS AND DISCUSSION

Sulfonylurea bioassay

Figure 1 illustrates the response of grain sorghum to increasing rates of chlorsulfuron. For both soil types there was no significant decrease in the length of sorghum roots from additions of chlorsulfuron. This is surprising in light of the fact that grain sorghum is sensitive to chlorsulfuron in the field (13,37). Considerable injury was noticed when grain sorghum was planted where chlorsulfuron had been previously applied at the same site where the Great Bend soil was collected (37). Grain sorghum has also been successfully used as a bioassay crop for chlorsulfuron in small pot bioassays (15). It may be that chlorsulfuron does not act on primary root growth in grain sorghum but works mainly on shoot meristem tissue. The petri dish bioassay tested here was conducted in the dark and did not allow shoots to develop normally.

Corn radicle length did decrease significantly with increasing chlorsulfuron rate (Figure 2). This effect was observed in both soil types, however the nature of the response differed between the two soil types. Chlorsulfuron was much less active in the Brookings soil

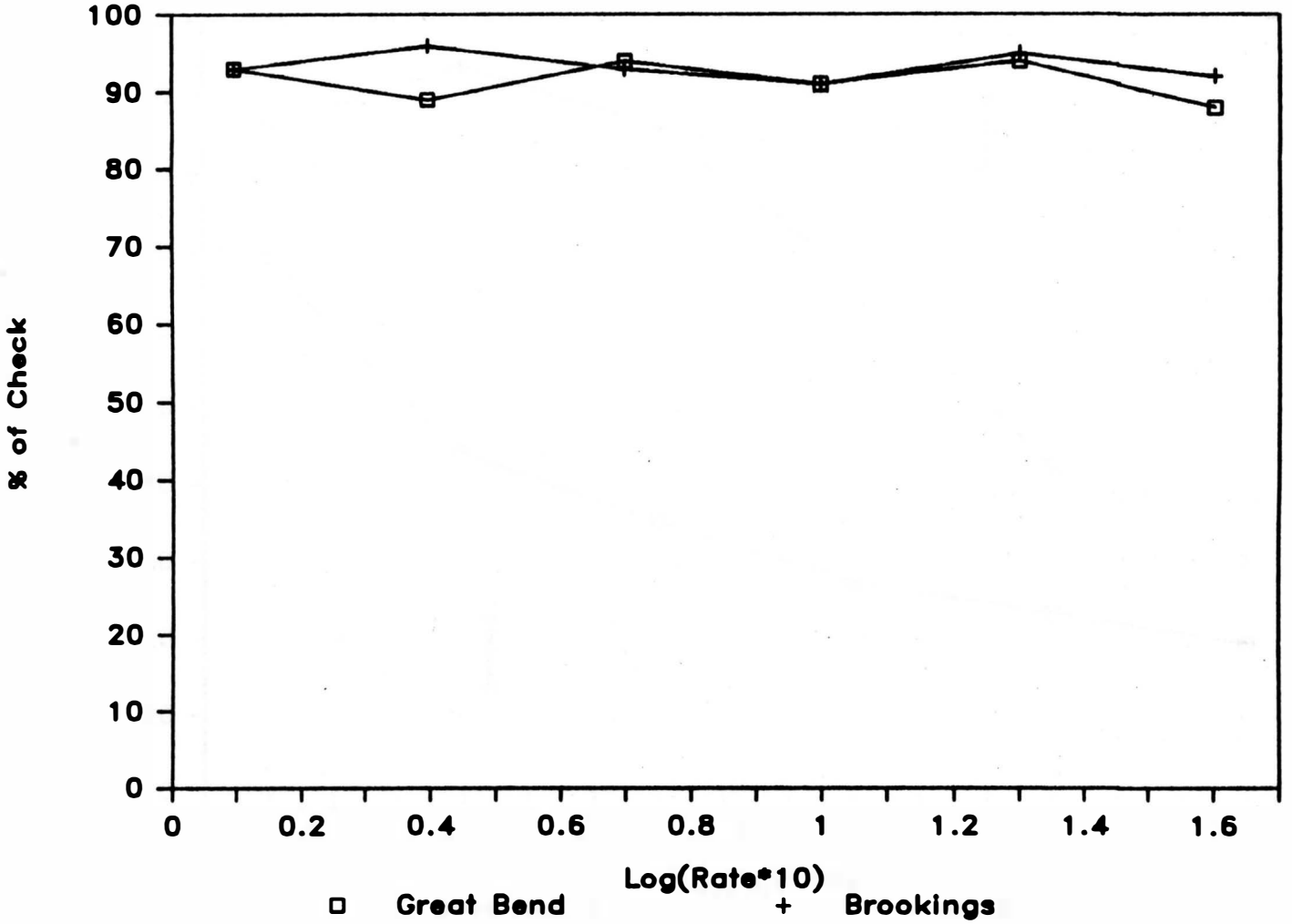

Figure 1. Effect of chlorsulfuron on grain sorghum root length. Data points correspond to 0.125, 0.25, 0.50, 1.0, 2.0, and 4.0 ppbw of chlorsulfuron. No significant differences were determined at the 0.05 significance level for either soil type.

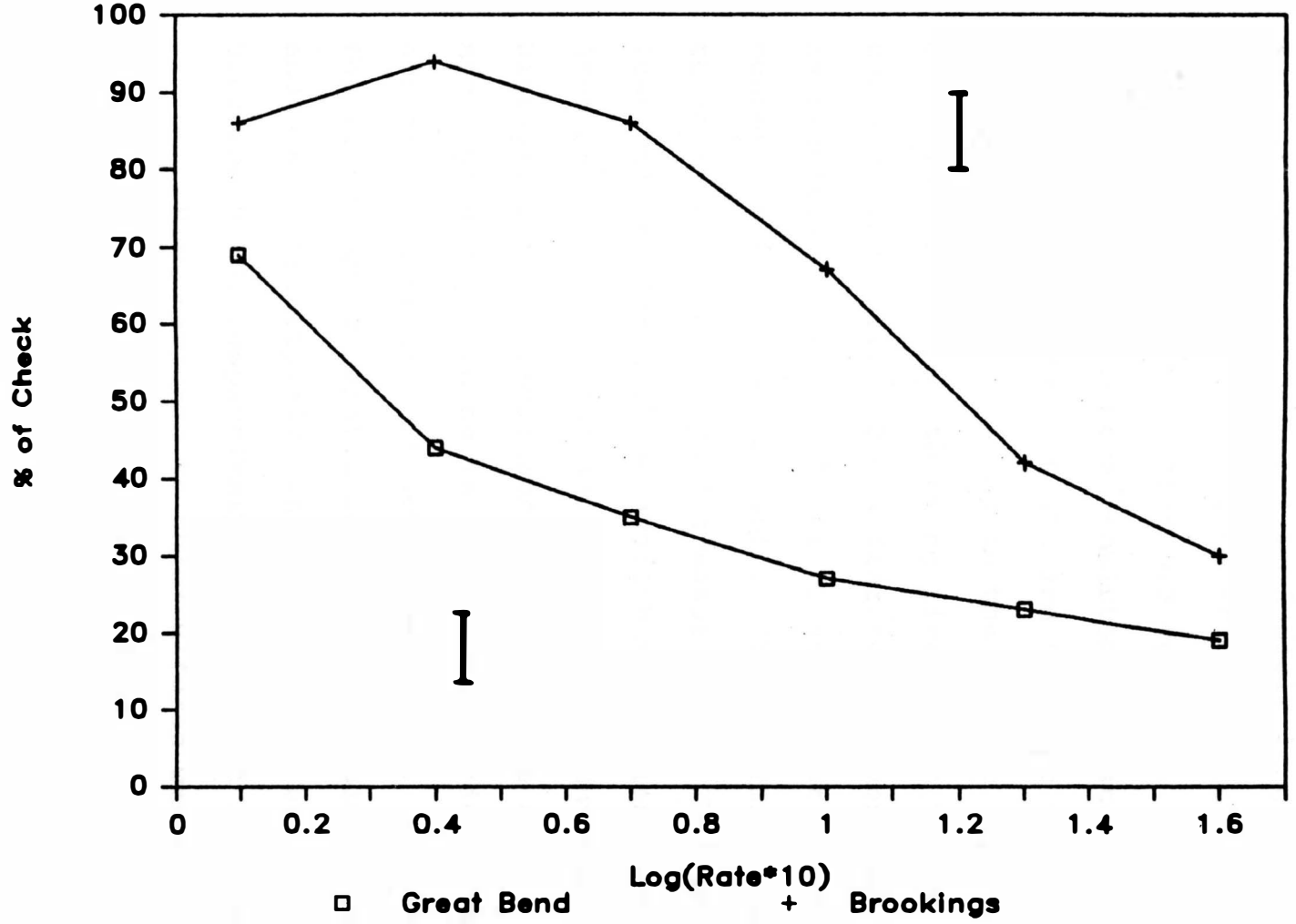

Figure 2. Effect of chlorsulfuron on corn radicle length. Data points correspond to 0.125, 0.25, 0.50, 1.0, 2.0, and 4.0 ppbw of chlorsulfuron. Vertical bars represent LSD values at the 0.05 significance level for each soil type.

than in the Great Bend soil. Radicle length reduction was inconsistent in the Brookings soil when chlorsulfuron concentration was less than 0.5 ppb. The response in the Great Bend soil was more consistent. A steep drop in corn radicle length between 0.125 and 0.25 ppb was followed by a more gradual decrease up to the 4.0 ppb level. This curve is also closer to being linear than the curve for the Brookings soil. The difference between the two soils is probably due to the lower pH and higher organic matter content of the Brookings soil. Chlorsulfuron adsorption to soil increases as pH decreases (42). This would cause less chlorsulfuron to be available for plant uptake in the Brookings soil. Hsiao and Smith also found the corn root bioassay for chlorsulfuron to be variable and non-reproducible in soils with high organic matter contents and relatively low soil pH (21). Values of r^2 for linear and quadratic regressions (Table 3) were 0.60 and 0.67, respectively, in the Brookings soil and were 0.62 and 0.69, respectively, in the Great Bend soil.

Flax response to chlorsulfuron was similar in both soils (figure 3). However, seedling lengths were greater in the Brookings soil. The effect of increasing chlorsulfuron rate on flax seedling length was more linear than with corn. Values of r^2 (Table 3) were the same for linear and quadratic regressions in the Brookings soil

Table 3. Linear and quadratic regression coefficients for chlorsulfuron effects on corn and flax growth.

Crop	Soil	Regression[1]	A	B1	B2	r^2
Corn	Brookings	Linear	104	-18.7	----	0.60
		Quadratic	89	6.2	-6.4	0.67
	Great Bend	Linear	62	-13.4	----	0.62
		Quadratic	73	-31.1	4.5	0.69
Flax	Brookings	Linear	97	-11.0	----	0.63
		Quadratic	94	-6.7	-1.1	0.63
	Great Bend	Linear	88	-16.4	----	0.72
		Quadratic	81	-4.2	-3.1	0.75

[1]General equation forms are:

$$Y = A + B1*X \quad \text{(Linear)}$$

$$Y = A + B1*X + B2*X^2 \quad \text{(Quadratic)}$$

where Y = radicle length of corn or seedling length of flax, and X = the natural log of the chlorsulfuron concentration in ppb.

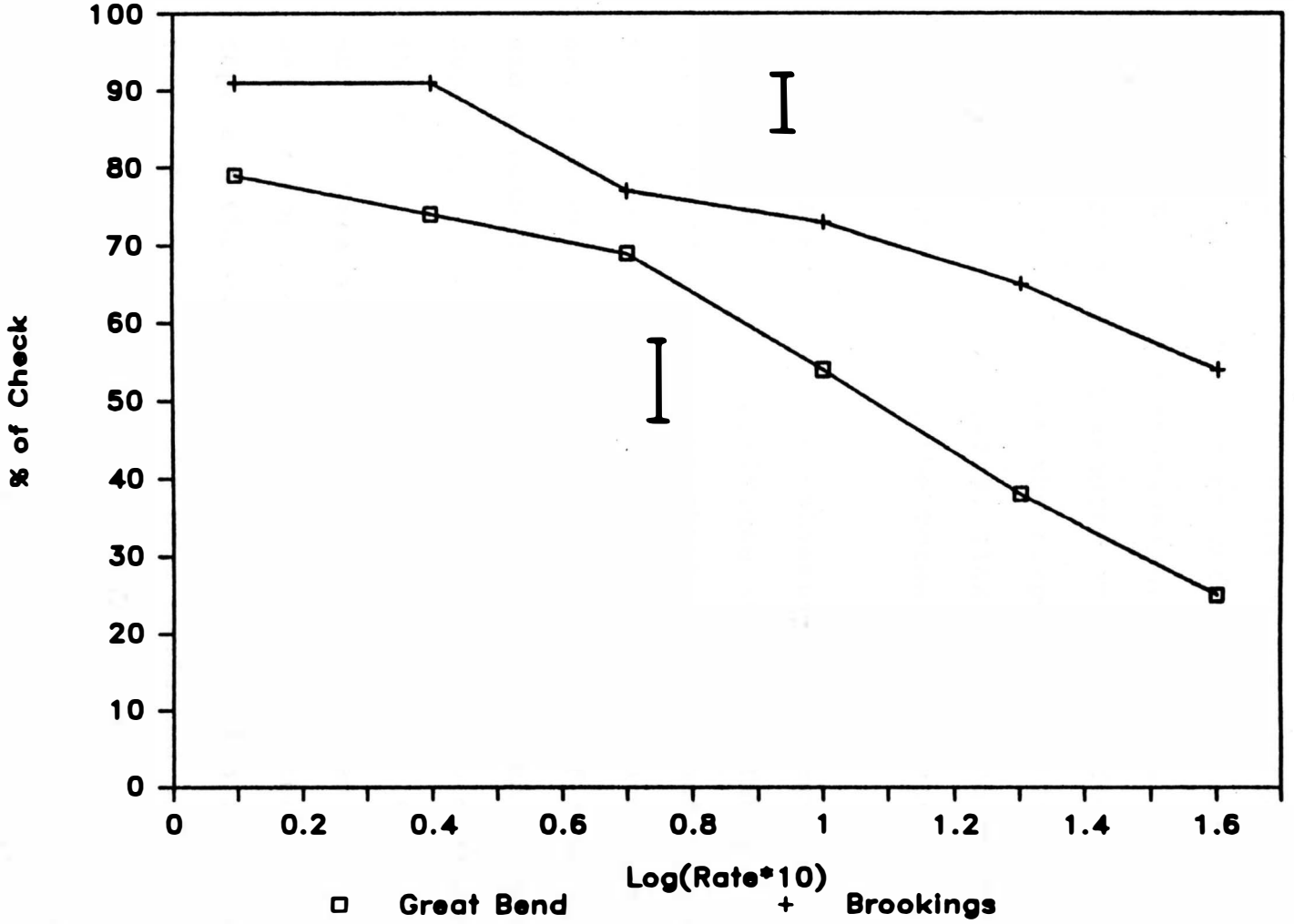

Figure 3. Effect of chlorsulfuron on flax seedling length. Data points correspond to 0.125, 0.25, 0.50, 1.0, 2.0, and 4.0 ppbw of chlorsulfuron. Vertical bars represent LSD values at the 0.05 significance level for each soil type.

(0.63). Quadratic regression of the response in the Great Bend soil resulted in a r^2 value of 0.75 as opposed to 0.72 for the linear regression. There was no difference between the seedling lengths at 0.125 and 0.25 ppb in the Brookings soil. Since the response to chlorsulfuron was linear in both soil types, flax appears to be the best bioassay indicator of the three crops tested in these studies.

Flax is also a satisfactory bioassay crop for other sulfonylurea herbicides as well. Table 4 contains the means of the root or shoot lengths that correspond to rates of 0, 0.25, and 2.0 ppb of chlorimuron and metsulfuron. Means of seedling length of flax were significantly different at all three rates of each compound. Corn radicle lengths were also different at all three rates of each compound. Mean root lengths of sorghum were different for all three rates of metsulfuron. However, sorghum root lengths could not separate the 0.25 ppb rate of chlorimuron from the 0.0 rate. All of these tests were conducted using the Great Bend soil and the results probably represent a better response than would have been seen in the Brookings soil.

The results of these experiments indicate that a petri dish bioassay can be a rapid, reliable means of detecting sulfonylurea herbicides in soil. Either corn or

Table 4. Effect of metsulfuron and chlorimuron on corn flax, and grain sorghum.

Crop[1]	Rate	Metsulfuron	Chlorimuron
	(ppb)	(mm)	
Corn	0.0	160 a	160 a
	0.25	132 b	120 b
	2.0	71 c	68 c
Flax	0.0	123 a	128 a
	0.25	95 b	100 b
	2.0	57 c	67 c
Sorghum	0.0	295 a	290 a
	0.25	273 b	273 a
	2.0	251 c	248 b

[1]Radicle lengths for corn and sorghum. Total seedling length for flax.

flax can be used while grain sorghum does not provide satisfactory results with this type of bioassay. Flax appears to be a better bioassay crop than corn due to its more linear response.

Chlorsulfuron and metsulfuron degradation

Logarithmic plots of the decomposition of three initial starting concentrations of chlorsulfuron and metsulfuron are shown in Figures 4 and 5. Measured starting concentrations averaged over the 5 replications were 3.06, 6.85, and 11.95 ppb for chlorsulfuron, and 4.09, 7.47, and 12.78 ppb for metsulfuron. The difference between these and the application concentrations of 4, 8, and 16 ppb is probably due to adsoption during the 24 h equilibrium period. If first-order kinetics are assumed, the half-life ($t_{1/2}$) of the two compounds can be calculated by the following formula:

$$t_{1/2} = 0.6932/k$$

in which k is the first order rate constant. The first-order half-life for chlorsulfuron in this work is 15.4 days in a loam soil with a pH of 5.3 maintained at 90% of field capacity and 30 C. The first-order half-life

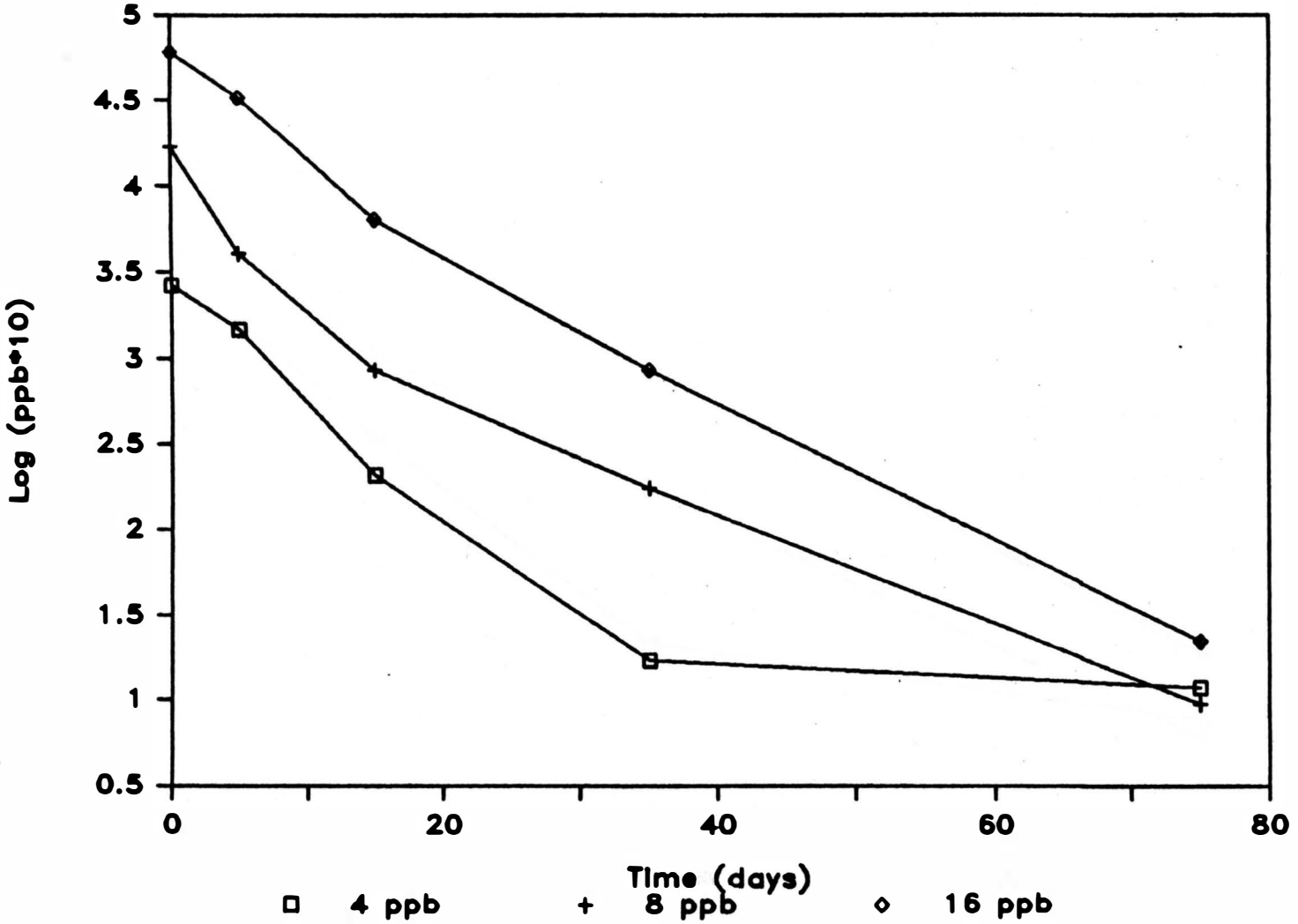

Figure 4. Decomposition of chlorsulfuron in a Vienna loam soil under 3 different starting concentrations.

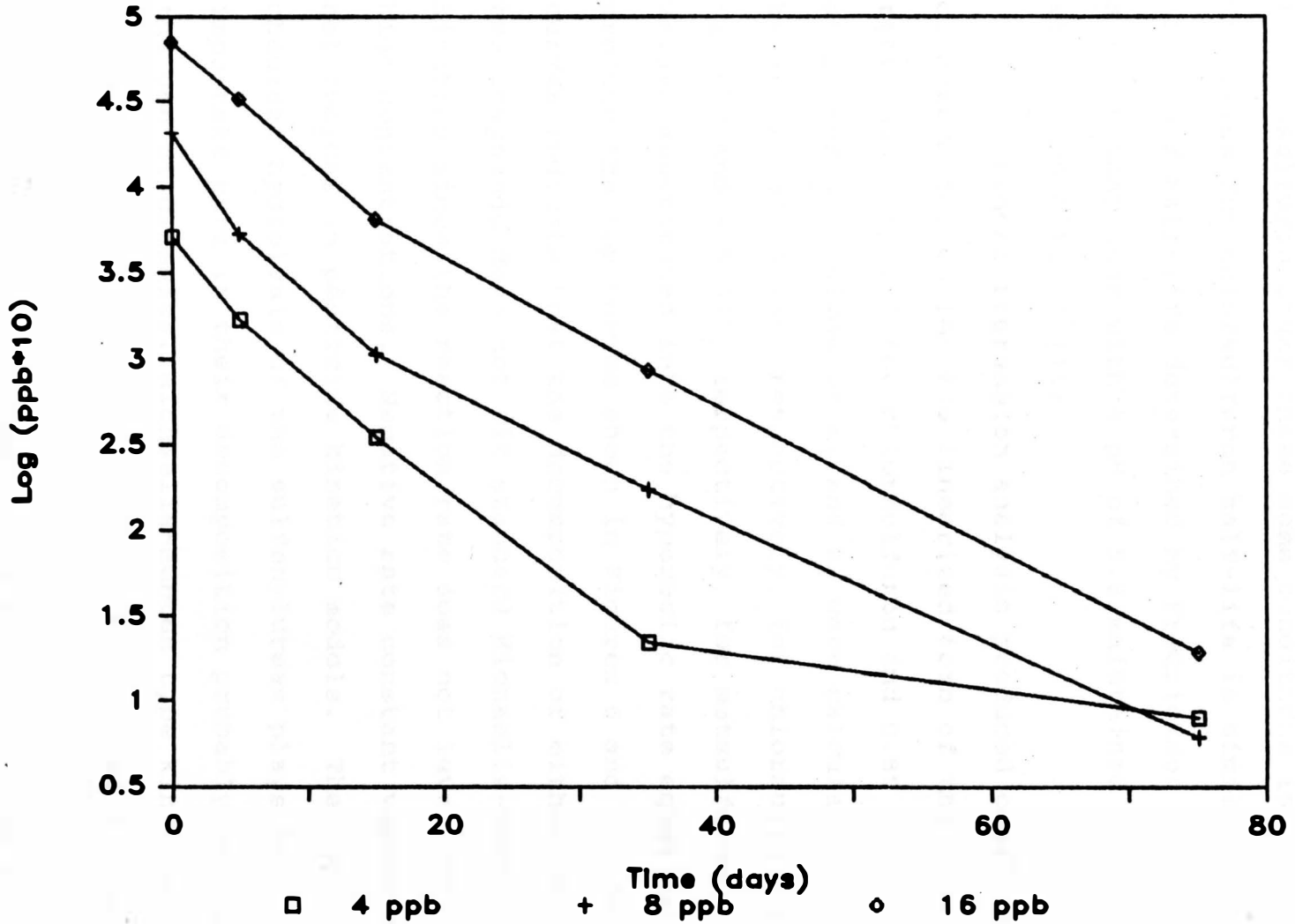

Figure 5. Decomposition of metsulfuron in a Vienna loam soil under 3 different starting concentrations.

for metsulfuron under these same conditions is 14.2 d. The value for chlorsulfuron half-life is similar to the 13.3 days half-life determined by Fredrickson and Shea for a silty clay loam with a pH of 5.6 maintained under similar conditions (15).

Linear regression analysis produced coefficients of determination for the linearized form of the hyperbolic rate model of 0.94 for chlorsulfuron and 0.88 for metsulfuron. Values of k_1 and k_2 were calculated to be -4.12 and -63.66, respectively, for chlorsulfuron and -5.7723 and -85.387, respectively, for metsulfuron. These values substituted into the hyperbolic rate equation produce the top curves shown in Figures 6 and 7. Both curves indicate that the decomposition of either of these two compounds does not fit standard Michaelis-Menten kinetics since the reaction rate does not level off at high concentrations. Negative rate constant values are not logical in pesticide kinetics models. The fact that chemical hydrolysis of the sulfonylureas plays an important part in their decomposition probably precludes the use of classical Michaelis-Menten type kinetics. Neither hyperbolic curve is characteristic of a purely biological reaction.

Non-linear regression of the data using the integrated form of the power rate model produced reaction

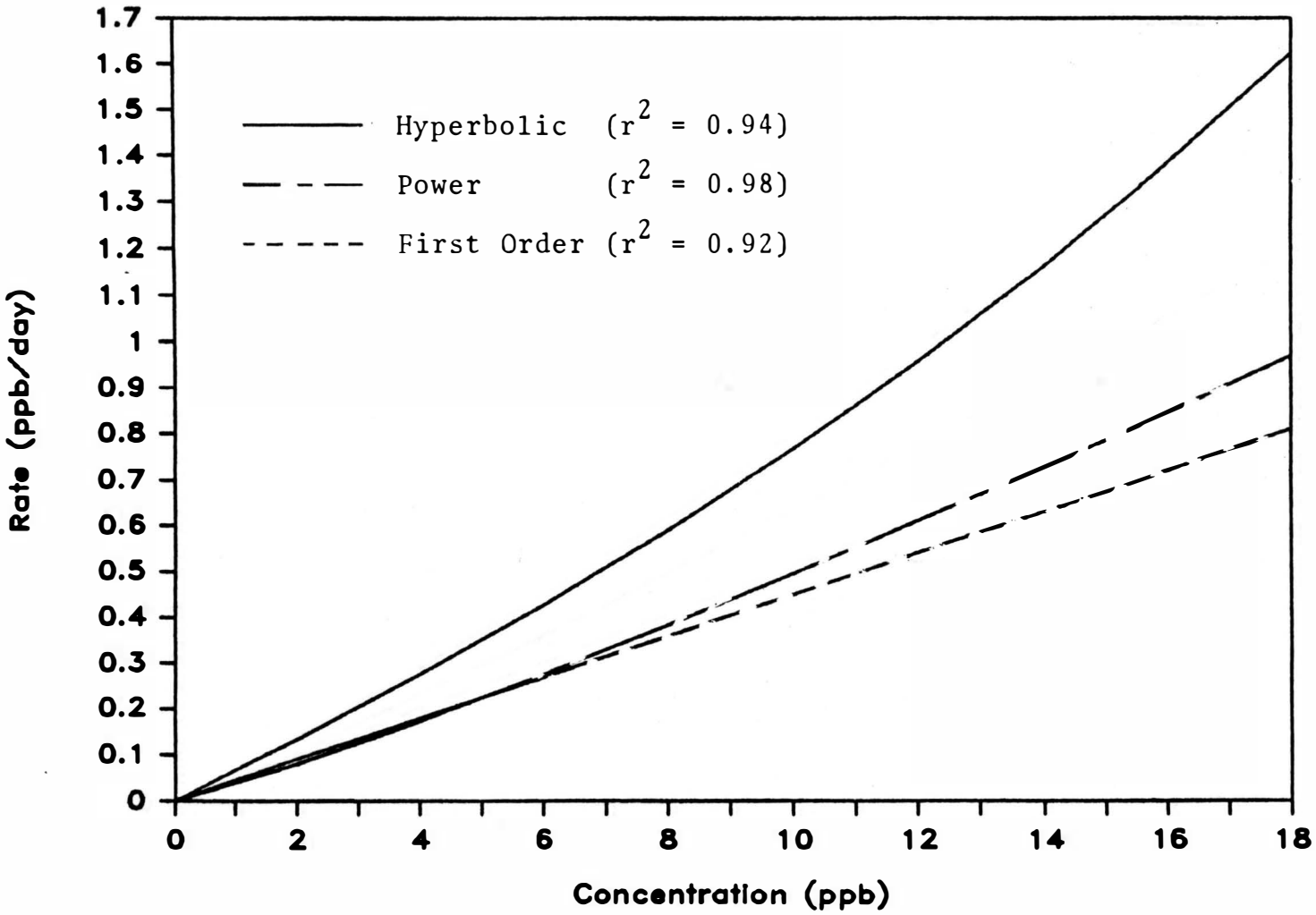

Figure 6. Influence of herbicide concentration on the rate of chlorsulfuron breakdown as determined by hyperbolic, power, and first order rate laws.

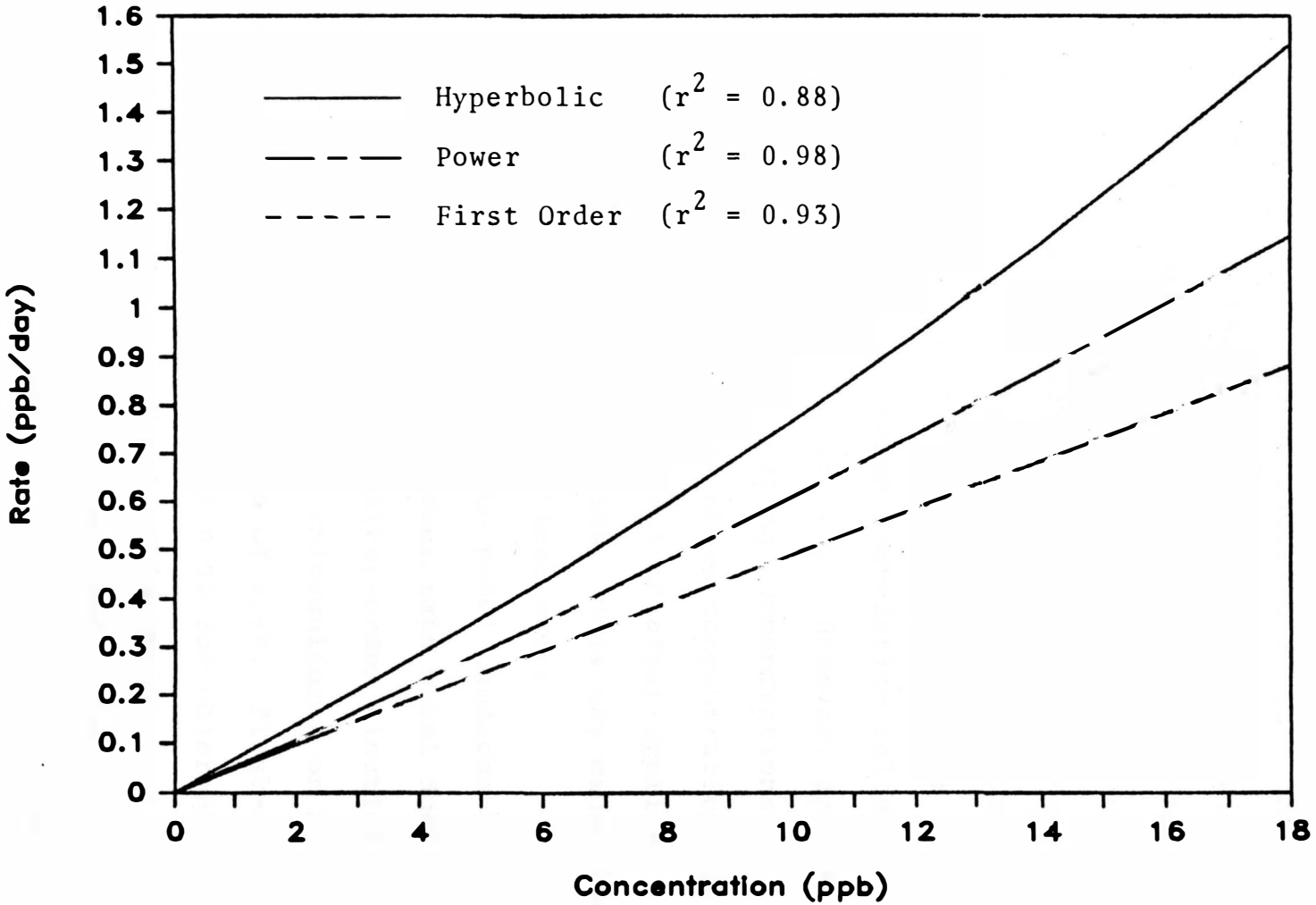

Figure 7. Influence of herbicide concentration on the rate of metsulfuron breakdown as determined by hyperbolic, power, and first order rate laws.

orders of 1.14 ±0.2 for chlorsulfuron and 1.08 ±0.18 for metsulfuron. These values substituted into the power rate equation produce the center curves shown in Figures 6 and 7. In both cases the 95% confidence limits include the value 1.0. This indicates that the kinetics of chlorsulfuron and metsulfuron degradation in soil may not differ significantly from first-order which is represented by the lower lines in Figures 6 and 7. Other research has concluded that chlorsulfuron degradation follows first-order kinetics (1, 15, 43). However, in these cases the authors were using starting concentrations which were several orders of magnitude above concentrations which would be found in field situations after application of standard rates of the herbicide. This may cause the degradation to appear to be first-order.

Though the power rate model produces a value close to 1, the use of the power rate model does provide a better fit to the data than first-order kinetics. A power rate model applied to either chlorsulfuron or metsulfuron degradation gives an r^2 value of 0.98. First-order kinetics produce r^2 values of 0.92 for chlorsulfuron and 0.93 for metsulfuron. Due to this improvement in fit with the power rate model it will be used as basis for further description of chlorsulfuron and metsulfuron degradation. The kinetics studies were conducted at a soil pH of 5.3 in

order to achieve a large amount of decomposition over the 75 days period of the experiment. This aided in the mathematical description of the decomposition process. It has been determined that chlorsulfuron degradation occurs by chemical hydrolysis and metabolism by soil microorganisms and that the balance between these two pathways is determined in large part by the soil pH (25). Due to this two-part degradation scheme it is possible that the rate law may change as pH changes. Further kinetics experiments should be conducted at higher pH levels in order to get analysis of rate laws over a wider range of conditions. However, results from this work indicate that first order kinetics may be an over simplification of sulfonylurea decomposition. The calculation of a rate law from one soil type and application of that rate law to other soil types is a better approach than to simply assume that first order kinetics applies to all situations.

Using the power rate model, the degradation of chlorsulfuron or metsulfuron can be described by the general equation:

$$\text{rate} = kC^n$$

where n = 1.14 for chlorsulfuron and n = 1.08 for

metsulfuron. The rate constant, k, is a function of various environmental and soil factors. Temperature and moisture affect all chemical and biological reactions, and therefore have a strong influence on the decomposition of herbicides. The Arrhenius curves and equations for the two herbicides are shown in Figure 8. This type of equation fits the data well with r^2 values of 0.98 for chlorsulfuron and 0.96 for metsulfuron. The curves are almost identical indicating that the temperature effect is the same for both herbicides. Activation energy (E) values are 21.1 kcal/mole for chlorsulfuron and 22.8 kcal/mole for metsulfuron. The value calculated for chlorsulfuron is larger than the 15.9 kcal determined by Walker and Brown (49). This may be due to the fact that first-order kinetics were assumed in that work. Thirunarayanan et al. determined E values for chlorsulfuron of 8.1 at 10 C, 9.4 at 20 C and 4.9 at 30 C (43). In their analysis they did not include the early portions of the decomposition data which lowered the apparent values of E. The E values determined in this work are similar to the E values determined for the atrazine (9, 19). Activation energy values in this range are considered to be indicative of degradation which is governed more by chemical reactions rather than microbiological processes.

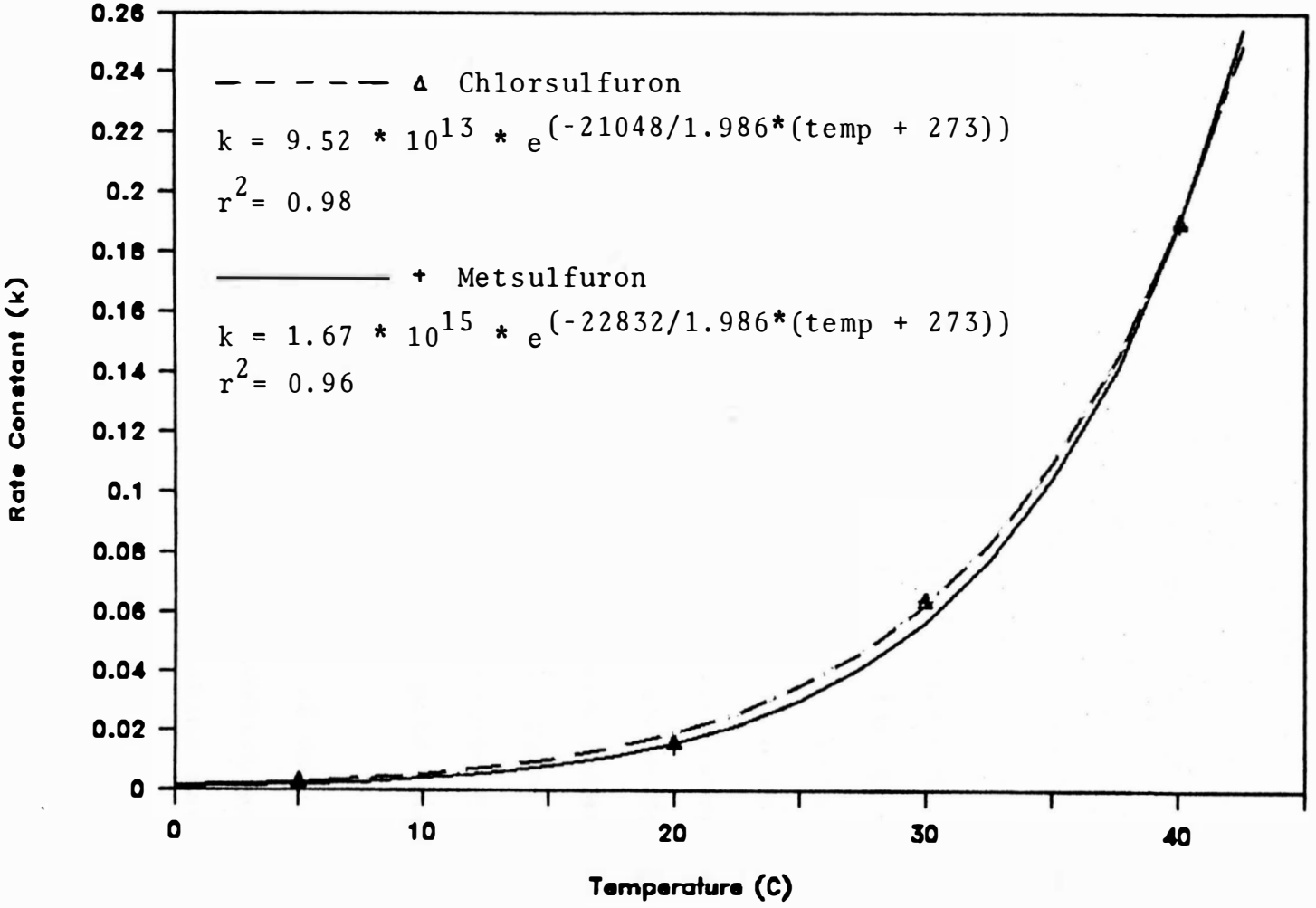

Figure 8. Soil temperature effect on chlorsulfuron and metsulfuron degradation rate constants.

The effect of soil moisture content on chlorsulfuron and metsulfuron degradation is shown in Figure 9. Values for r^2 were 0.96 for chlorsulfuron and 0.90 for metsulfuron. This type of equation has been used previously to describe moisture effects on herbicide breakdown (46, 49). For both herbicides the value of k increases with increasing moisture content from 11% of field capacity up to 90% of field capacity. The response is almost identical for both herbicides up to approximately 50% of field capacity. Above that point the chlorsulfuron rate constant begins to level off while the metsulfuron rate constant continues to increase at the same rate. Since moisture contents above field capacity were not used in this study one cannot determine the effect of saturation on decomposition rate. The change from an aerobic to an anaerobic environment significantly alters the nature of soil reactions both chemical and biological.

Figure 10 shows the effect of soil pH on chlorsulfuron and metsulfuron degradation as determined by these experiments. A quadratic equation satisfactorily describes the relationship between pH and the rate constant for both herbicides. Values of r^2 are 0.91 for chlorsulfuron and 0.96 for metsulfuron. The change in the rate constant between a pH of 5.3 and 7.3 is rapid. Above

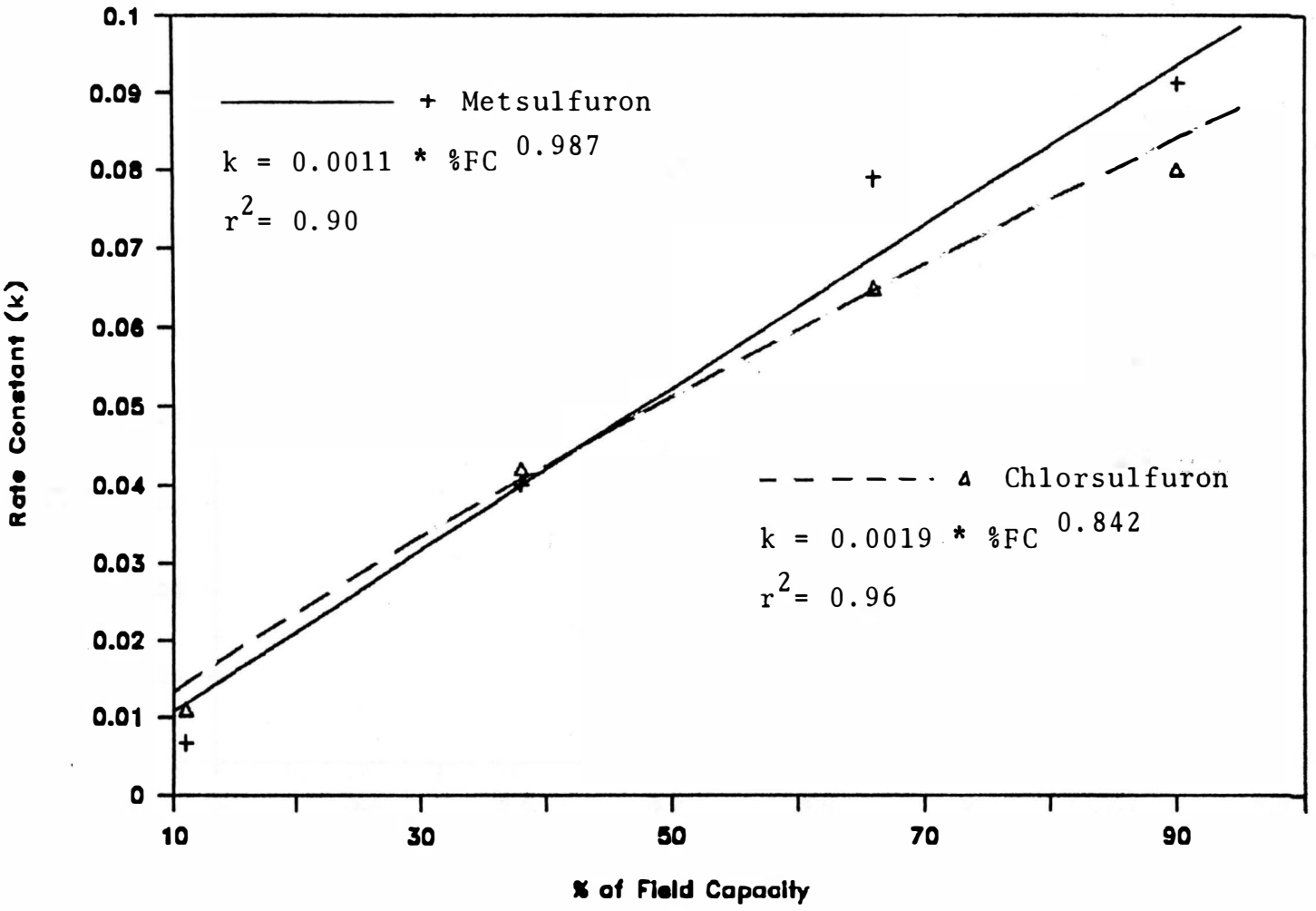

Figure 9. Soil moisture effect on chlorsulfuron and metsulfuron degradation rate constants.

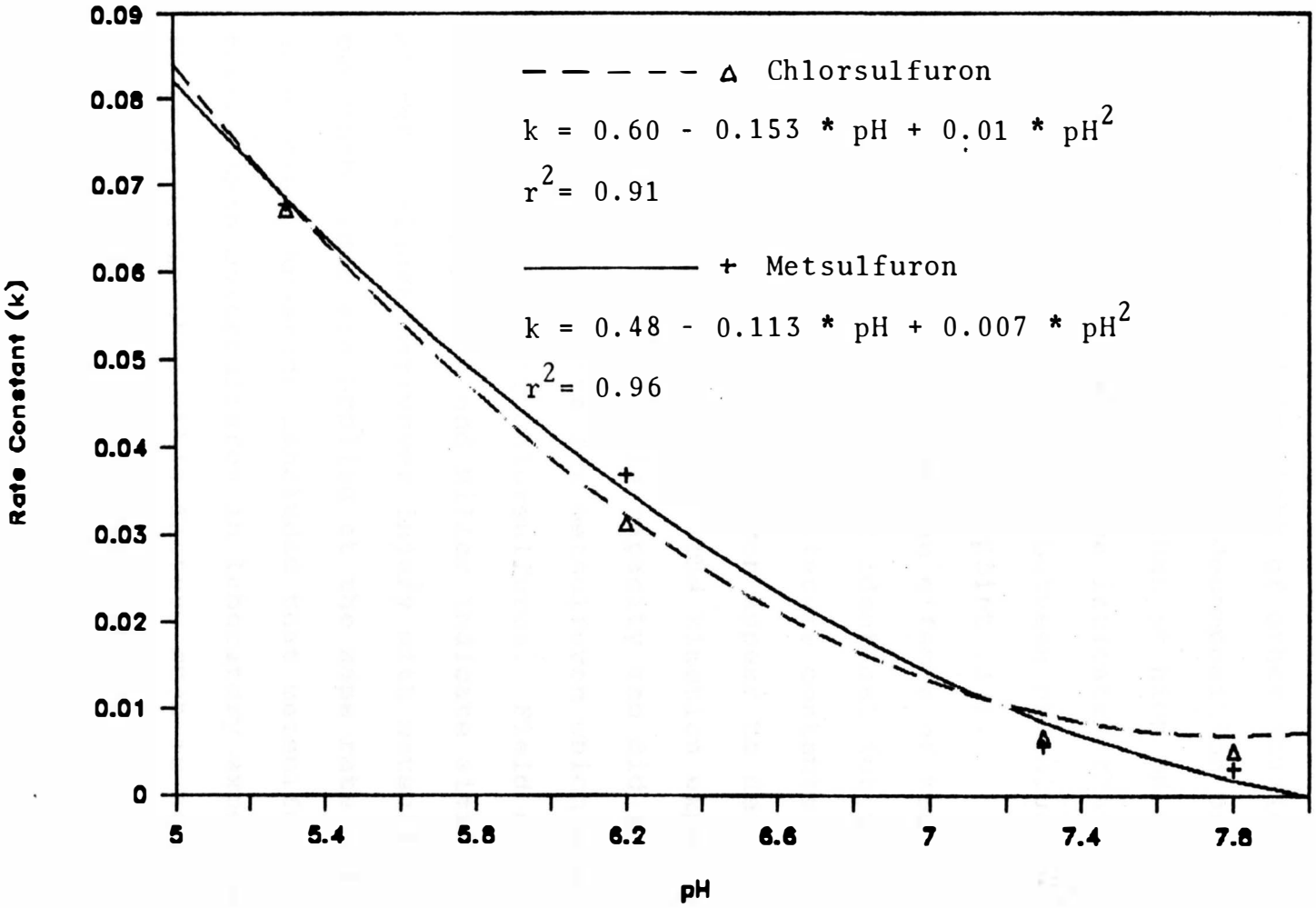

Figure 10. Soil pH effect on chlorsulfuron and metsulfuron degradation rate constants.

this pH the rate constant levels off. This type of response is logical in light of other studies which indicate that chlorsulfuron decomposition proceeds more rapidly at lower pH values than at high pH values (1, 15, 25). Previous field research indicates that chlorsulfuron carryover increases rapidly between pH values of 5.0 and 6.5 leveling off after that point (37).

In these studies the effects of temperature, moisture, and pH were almost identical for chlorsulfuron and metsulfuron. Only at moisture contents above 50% of field capacity did metsulfuron appear to degrade slightly faster than chlorsulfuron. The kinetics experiment was conducted at 90% of field capacity and did indicate a first-order half-life for metsulfuron which was slightly shorter than that of chlorsulfuron. Field studies conducted by Ulrich and Miller indicate similar to slightly higher carryover injury with metsulfuron when the two herbicides are applied at the same rate (44). On the other hand, Anderson concluded that metsulfuron degrades faster than chlorsulfuron in laboratory experiments (1). It is possible that other factors such as soil organic matter may influence chlorsulfuron and metsulfuron differently and possibly cause metsulfuron to degrade more rapidly than chlorsulfuron in some situations.

Simple multiple regression equations were

constructed from these data in a manner similar to that done previously for picloram (29). The basic equation was of the form:

$$k = A + B1(X1) + B2(X2) + B3(X3)$$

where k is the rate constant; X1, X2, and X3 represent the functions determined for temperature, moisture, and pH for each herbicide; B1, B2, and B3 are regression coefficients; and A is the intercept. This procedure produced equations with R^2 values of 0.96 for chlorsulfuron and 0.88 for metsulfuron. Rate constants determined from these equations can then be entered into the integrated form of the power rate law and herbicide concentration can be determined for a given initial concentration and time period. Table 4 shows concentrations calculated to occur after 75 days of decomposition under the various temperature, moisture, and pH levels used in these experiments. The values determined by the bioassay are also presented for comparison. In all cases, the multiple regression equations tend to underestimate the actual concentration. The difference is particularly large for metsulfuron at low temperatures and high pH levels. This demonstrates that such equations are probably unsatisfactory for

Table 5. Comparison of actual and predicted concentrations of chlorsulfuron and metsulfuron after 75 days of decomposition.

Temp	Moist	pH	Chlorsulfuron Actual	Chlorsulfuron Pred.[a]	Metsulfuron Actual	Metsulfuron Pred.[b]
(°C)	(%)		---------- (ppb) ----------			
5	66	5.3	11.71	8.83	12.49	3.44
20	66	5.3	3.81	2.00	3.54	1.19
30	66	5.3	0.56	0.11	0.78	0.08
40	66	5.3	0.49	.00	0.34	.00
30	11	5.3	4.96	3.61	7.37	4.53
30	38	5.3	1.12	0.47	1.55	0.51
30	66	5.3	0.49	0.11	0.54	0.08
30	90	5.3	0.35	0.04	0.52	0.02
30	66	5.3	0.51	0.11	0.50	0.08
30	66	6.2	0.99	0.94	0.51	0.57
30	66	7.3	7.58	5.48	7.86	3.45
30	66	7.8	10.11	6.76	10.84	5.58

[a] $\text{Concentration} = [15^{-0.14} + 0.14 * k * 75]^{-7.14}$

$k = 0.44 + (9.52*10^{13} * 2.72^{-10598 / (\text{Temp} + 273)}) + 0.002 * \text{Moist}^{0.84} - 0.14 * \text{pH} + 0.009 * \text{pH}^2$

$R^2 = 0.96$

[b] $\text{Concentration} = [13^{-0.08} + 0.08 * k * 75]^{-12.5}$

$k = 0.33 + (1.64*10^{15} * 2.72^{-11497 / (\text{Temp} + 273)}) + 0.001 * \text{Moist}^{0.99} - 0.11 * \text{pH} + 0.006 * \text{pH}^2$

$R^2 = 0.88$

predicting herbicide persistence in soil. Equations of this type assume simple additivity between factors and do not take interactions between factors into account. The mathematical relationships determined in this paper provide the basis for comprehensive models of chlorsulfuron and metsulfuron decomposition in field situations. In order to construct useful models of chlorsulfuron or metsulfuron decomposition further work needs to be done to define interactions between factors such as temperature, moisture, and pH. The influence of soil organic matter and its interaction with other soil factors should also be examined.

SUMMARY

Corn and flax were both satisfactory bioassay indicator species for chlorsulfuron, chlorimuron and metsulfuron. Flax response to chlorsulfuron was more linear and consistent between soil types than was the corn response. Therefore, flax is the best suited bioassay indicator of the three species tested.

The effect of herbicide concentration on chlorsulfuron and metsulfuron degradation in soil deviated from first-order. Hyperbolic kinetics did not provide a logical fit to the decomposition data. Fitting the power rate kinetics law to the data determined that the order of the degradation reaction was 1.14 for chlorsulfuron and 1.08 for metsulfuron. Of the three rate laws tested, the power rate model produced the best fit (r^2 = .98) to the decomposition data for chlorsulfuron and metsulfuron.

Soil temperature, moisture, and pH all had a significant influence on the decomposition rate of chlorsulfuron and metsulfuron. As temperature increased, the rate constant for either herbicide increased rapidly. The Arrhenius equation fit the temperature data well (r^2 = 0.98 and 0.96 for chlorsulfuron and metsulfuron, respectively). Thermal activation energies for the two herbicides were 21.1 kcal/mole for chlorsulfuron and 22.8

kcal/mole for metsulfuron. Increasing soil moisture content from 11% to 90% of field capacity increased the rate constant for both herbicides although the effect was not as pronounced as the temperature effect. A simple power function adequately described the moisture effect on the rate constant for chlorsulfuron and metsulfuron (r^2 = 0.96 and 0.90 respectively). Rate constants for metsulfuron were slightly higher than chlorsulfuron rate constants when soil moisture content was above 50% of field capacity. Soil pH effect on decomposition was pronounced for both herbicides. A quadratic equation satisfactorily describe the effect in both cases (r^2 = 0.91 for chlorsulfuron and 0.96 for metsulfuron). Rate constants for both herbicides dropped off rapidly as pH increased from 5.3 to 7.3 at which point they leveled off.

Multiple regression analysis relating chlorsulfuron and metsulfuron rate constants to soil temperature, moisture, and pH simultaneously produced equations that gave satisfactory r^2 values (0.96 for chlorsulfuron and 0.88 for metsulfuron) but consistently underestimated the decomposition rates for both compounds. This points out the deficiencies in using a simple linear additive model in the description of herbicide breakdown in soil. Further research will be

required in order to define interactions between factors such as temperature, moisture and pH. However, the quantitative relationships described in this work will provide a basis for further research which may lead to predictive models of chlorsulfuron and metsulfuron fate in the environment.

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