

EFFECT OF SOIL PH ON METRIBUZIN  
[4-AMINO-6-TERT-BUTYL-3-  
(METHYLTHIO)-1,2,4-TRIAZIN-5(4H) ONE]  
ACTIVITY AND FATE IN SOIL

Dissertation for the Degree of Ph. D.  
MICHIGAN STATE UNIVERSITY  
JAMES STEPHEN LADLIE  
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5(4H) ONE] ACTIVITY AND FATE IN SOIL

presented by

**James Stephen Ladlie**

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ABSTRACT

EFFECT OF SOIL PH ON METRIBUZIN [4-AMINO-6-TERT-BUTYL-3-(METHYLTHIO)-1,2,4-TRIAZIN-5(4H)ONE] ACTIVITY AND FATE IN SOIL

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Metribuzin [4-amino-6-tert-butyl-3-(methylthio)-1,2,4-triazin-5(4H)one] activity in the field increased with increasing soil pH. Fall panicum (Panicum dichotomiflorum Michx.) control, number of dead corn (Zea mays L.) and soybean (Glycine max (L.) Merr.) plants, and crop injury ratings increased, whereas, plant height and grain yield decreased as soil pH increased. Metribuzin residue analysis of soil samples showed greater amounts of residue extractable at soil pH 6.7 than 4.6. Metribuzin leaching increased with increasing soil pH in the field. Metribuzin disappearance from soil followed pseudo first-order kinetics. Rate constants increased and the half life of metribuzin decreased as soil pH increased. Rate constants decreased and the half life of metribuzin increased at all soil pH levels as depth of sampling decreased.

Metribuzin phytotoxicity to corn and soybeans grown in the greenhouse increased with increasing soil pH. Microbial degradation decreased as the soil became more acid. Metribuzin and atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] mobility increased with increasing concentration and soil pH.  $^{14}\text{C}$ -metribuzin had greater mobility on soil thin-layer plates than  $^{14}\text{C}$ -atrazine because of differences in water solubility and basicity. The pKa of metribuzin was determined to be  $0.99 \pm 0.08$ . Adsorption increased gradually as the soil pH decreased toward the pKa of metribuzin. Protonation of the amine group with subsequent adsorption to soil colloids was postulated to be the reason for the reduction in phytotoxicity, microbial degradation and mobility of metribuzin in acid soils.

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## INTRODUCTION

Metribuzin is a new selective herbicide, which controls weeds by contact and systemic action, and has provided excellent control of a wide range of broadleaved weeds in field, forage, and vegetable crops. It has been less effective on annual grasses. Because of the wide spectrum of broadleaved weeds controlled by this compound, especially hard-to-control weeds such as cocklebur (7,17,37,100) (Xanthium pensylvanicum Wallr.), jimsonwood (17,37,59) (Datura stramonium L.), velvetleaf (17,37,95) (Abutilon theophrasti Medic.), and common ragweed (17,37,42,43) (Ambrosia artemisiifolia L.), metribuzin has the potential of helping producers increase profits by reducing losses due to weed competition. Therefore, the combination of metribuzin and an effective grass herbicide could provide the farmer with broad spectrum weed control, not previously available for weed control in soybeans (16,36,37,40,42,95), in both seeded and transplant tomatoes (12,13,24,57), and potatoes (41,83).

Metribuzin is the first registered herbicide with 1,2,4-triazinone chemistry (96) and there is little

information available on its persistence and behavior in soil. Knowledge of its behavior in the soil environment is essential in evaluating its safety and full potential as an agricultural tool.

The objectives of these studies were to determine the effect of soil pH on (1) metribuzin activity in relation to crop tolerance and weed control, (2) degradation of metribuzin in soil, (3) adsorption to soil, and (4) relative movement in the soil.

## CHAPTER 1

### LITERATURE REVIEW

Metribuzin is the first commercially available asymmetrical triazine (as-triazine) herbicide. This compound, though structurally different from the symmetrical triazines (s-triazines), has a similar mode of action and wide spectrum broadleaf weed control. The mode of metribuzin action is considered to be the inhibition of photosynthesis in light reaction II (12).

Metribuzin has been used primarily for weed control in soybeans (Glycine max (L.) Merr.), seeded and transplanted tomatoes (Lycopersicon esculentum Mill.) and potatoes (Solanum tuberosum L.). Preemergence and early post-emergence applications have given the best results. Pre-plant incorporated applications have also shown promise on tomatoes and soybeans. Effective rates are 0.28 to 1.12 kg/ha for soybeans and tomatoes (preemergence or preplant incorporated), and 0.56 to 1.12 kg/ha for potatoes (pre-emergence or postemergence) (96). Combinations of metribuzin and an effective grass herbicide, either as a tank mix application or overlay treatment, provides the farmer with broad spectrum weed control. Increased grass control was obtained when metribuzin was used with alachlor

(2-chloro-2',6'-diethyl N-(methoxymethyl) acetanilide), or trifluralin ( $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) on soybeans (14,16,36,37,40,42,95).

Weed control obtained with metribuzin has been acceptable, but soybean (7,27,28,71), potato (41), and tomato (72) tolerance has been variable. This variability is due in part to differences in varietal susceptibility.

Hargroder and Rogers (29) reported that  $^{14}\text{C}$ -metribuzin was readily taken up by soybeans and sesbania (Sesbania punicea (Cav. DC.)) grown in nutrient solution. The herbicide was slowly transported from the roots and concentrated in the foliage. Schumacher (64,66,67) showed that  $^{14}\text{C}$ -labeled metribuzin supplied to the roots of soybean seedlings was readily absorbed and transported to the shoots. The major non-polar metabolite detected in the roots and shoots was the deaminated parent 6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5-(4H)-one (DA). Two additional compounds, the diketo parent 4-amino-6-(1,1-demethylethyl)-1,2,4-triazin-3,5-(2H,4H)-dione (DK) and the deaminated diketo parent 6-(1,1-dimethylethyl)-1,2,4-triazine-3,5 (2H,4H)-dione (DADK), were also detected. The primary metabolic pathway of metribuzin detoxication in soybeans appeared to be the conversion of metribuzin to water soluble metabolites. The amount of  $^{14}\text{C}$  in the polar fraction of plant extracts increased with time.

Fate and Behavior of Herbicides in  
the Soil Environment

Many factors influence the behavior of herbicides in agricultural soils. What happens to a soil applied herbicide depends both on the physical and chemical properties of the herbicide involved and on certain properties of the soil and water. Both herbicide degradation processes and herbicide transfer processes play a part in determining the ultimate fate of the chemicals.

Three specific degradation processes serve to break down the herbicides and change their chemical composition (1) biological decomposition - degradation by a living organism, (2) chemical decomposition - breakdown by a chemical process in the absence of a living organism, (3) photodecomposition - degradation by processes involving activation of the molecule by sunlight (87,91).

There are a number of transfer processes that influence the degradation rate of soil applied herbicides: (1) absorption and exudation by plants and animals, (2) retention in vegetation, (3) adsorption by soil particles, a process by which herbicides transfer from solution or vapor to a solid surface, (4) volatilization, a process by which the herbicide is changed from the solid or liquid state into a gas or vapor form and discharged into the atmosphere, (5) surface runoff; the herbicide may be either dissolved or suspended in water or be adsorbed

to eroding soil particles from treated areas, (6) leaching, and (7) capillary action (91).

All processes involved in herbicide degradation are intimately associated. Adsorption, which directly influences all others, is probably the key process. Living organisms, their metabolic products and residues, and humified organic matter, along with inorganic materials such as clays, and the hydrous oxides of iron and aluminum are soil particulate matter responsible for adsorption and inactivation of herbicides.

The adsorption process greatly affects the absorption rate of chemicals by plants and soil organisms. Thus, adsorption helps determine herbicide performance. Adsorption also influences leaching, capillary action and volatility of a herbicide through attachment of the chemical to soil particles.

The discussion in this review will be restricted to soil pH and its effect on herbicide activity, adsorption, leaching, and degradation of certain groups of herbicides.

### Factors Influencing Adsorption of Herbicides

#### A. Physico-Chemical Character of Adsorbate

The following properties determine the role of the adsorbate in adsorption of herbicides by soil colloids (6):  
(1) chemical character, shape, and configuration,

(2) acidity or basicity of the molecule (pKa or pKb), (3) water solubility, (4) charge distribution on the organic cation, (5) polarity, (6) molecular size, and (7) polarizability. There are many ways in which each of these properties of the adsorbate may be manifested in the overall adsorption reaction. It should be realized that more than one of these factors may be, and probably are, operating simultaneously.

Chemical Character, Shape, and Configuration of the Adsorbate.--Four factors determine the role of the chemical character of the adsorbate in the overall adsorption reaction according to Bailey and White (5): (1) nature of the functional group, (2) nature of the substituting groups, (3) position of the substituting group with respect to the functional group, and (4) presence and magnitude of unsaturation in the molecule. Molecular configuration and shape are important in determining if there can be rotation about a double bond which, in turn, may influence the orientation of molecules at the colloidal surface. The type of molecular orientation may, in turn, determine the contribution of each type of bonding mechanism and thus the overall adsorption potential.

Bailey et al. (6) in a study relating the effect of functional group, nature, and position of ring substitution to the magnitude of adsorption by a wide variety of compounds, concluded that the chemical character of the



molecule affects retention by colloidal systems in three different ways as it: (1) determines if the molecule is fundamentally acidic or basic in character and its relative strength, (2) affects the water solubility of the molecule, and (3) determines the relative importance to (1) and (2) of Van der Waals type forces.

Dissociation Constant.--The pKa values represent the pH level at which one-half of the species in solution is present in the cationic form and one-half is in the molecular form. Since ionic species are more water soluble than molecular species, basic herbicides have higher solubilities at low pH levels than they do at neutral pH levels (82).

The pKa of a compound indicates the degree of acidity or basicity that a compound will exhibit and therefore should be very important in determining both the extent of adsorption and the ease of desorption by colloidal systems (5).

The effect of pKa on the adsorption of a basic compound of varying chemical character by montmorillonite has been studied by Bailey et al. (6). Through the use of adsorption isotherms, the adsorption of such basic compounds as s-triazines, substituted ureas, phenylcarbamates, anilides, and anilines on montmorillonite was investigated. They concluded that the major factor governing the magnitude of adsorption by different chemical families basic

in character is the dissociation constant of the adsorbate. The higher the so-called basicity of the pesticide the greater is its adsorption by acid soil particles (94). Talbert and Fletchall (75) studied the adsorption of five s-triazines by 25 different soil types, the extent of adsorption being expressed by means of distribution coefficients,  $K_d$  (amount absorbed at equilibrium concentration remaining in equilibrium solution). The degree of adsorption based on the averaged  $K_d$  values was propazine [2-chloro-4,6-bis(isopropylamino)-s-triazine] (2.0) < atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] (2.7) < simazine [2-chloro-4,6-bis(ethylamino)-s-triazine] (3.7) < prometone [2,4-bis(isopropylamino)-6-methoxy-s-triazine] (7.8) < prometryne [2,4-bis(isopropylamino)-6-(methylthio)-s-triazine] (9.1). The methylmercapto- and methoxy-derivatives are much more basic in chemical character ( $pK_a$  4.2 to 4.8) than are the chloro derivatives ( $pK_a$  1.5 to 2.0) which probably accounts for the observed differences in adsorption. Similar results were reported by Harris (30) for the same series of s-triazines.

From a consideration of the  $pK_a$  of the s-triazines, the basicity of the s-triazines disregarding their groups on the 4 and 6 positions are in the order hydroxy > methoxy > methylmercapto > chloro (4,84). Weber (84) noted for the methoxy-analogues that basicity increased with increasing number of carbons on the amino alkyl



groups. In both cases increasing basicity can be explained in terms of the presence of more nucleophilic groups on the molecule. Carringer and Weber (15) studied the adsorption of five s-triazines and one as-triazine (metribuzin) from aqueous solutions by organic soil colloids and Na<sup>+</sup>-saturated montmorillonite clay at pH levels from 1.0 to 6.5. Maximum adsorption occurred at pH levels in the vicinity of the pKa values of the respective compounds. The amounts adsorbed by montmorillonite clay were dependent upon the molecular structure of the compounds and pH of the suspension. Comparisons of s-triazines substituted in the 4 and 6 positions with monoalkylamino groups indicated decreased adsorption by montmorillonite in the order: 4,6-bis(n-propylamino) > 4-n-propylamino-6-ethylamino > 4,6-bis(isopropylamino). Adsorption of all five s-triazines was much greater than the adsorption of the as-triazine at all pH levels. Differences in adsorption were attributed to differences in basicity, water solubility, and steric effects.

The basicity of the desorbing agent appears to be important in the overall adsorption-desorption reaction, especially if the adsorbed material is basic in nature. Raman and Mortland (56) have studied charge transfer reactions at clay mineral surfaces by infrared spectroscopy. They concluded the proton transfer from the protonated species adsorbed on the clay surface to an

uncharged molecule at the clay surface was dependent upon the relative basicities of the two interacting compounds as well as the relative concentrations or activities of the reactants and the products.

Water Solubility.--Metribuzin has a water solubility of 1220 ppm at 20°C (96). The water solubility of metribuzin is high compared to the s-triazines. Atrazine for example, has a water solubility of only 70 ppm (96).

There appears to be a relationship between water solubility and extent of adsorption, but only within family of compounds. Bailey et al. (6) compared the extent of adsorption of a wide variety of basic herbicides onto sodium and hydrogen montmorillonite. On the basis of these findings, Bailey et al. (6) concluded that within a chemical family or within an analogue series basic in chemical character, the magnitude of adsorption is related to and governed by the degree of water solubility.

Talbert and Fletchall (75) reported that there was greater adsorption of the methoxy- and methylmercapto-derivatives than there was of the chloro-s-triazine derivatives, indicating there was a direct relationship between water solubility and adsorbability. However, it should be recalled that not only does the water solubility increase among the chloro-, the methoxy-, and the methylmercapto-derivatives, but also that the methoxy- and methylmercapto-derivatives are more basic than are the chloro-derivatives.

Hance (26) studied the adsorption by soils of ureas and their derivatives and found no relationship between adsorption and water solubility.

For a particular family of adsorbates, several factors may be interacting to determine whether there is a direct relationship between water solubility and adsorbability. These may include such factors as surface acidity and relative polarity of the adsorbent (5).

#### B. Physico-Chemical Character of Adsorbent

Nature and Properties of Soil Colloids.--The chemical and physical properties of the soil are controlled by constituents with highly reactive surfaces. Since high specific surface is associated with small particle size, the colloidal fraction of the soil will be the dominant factor in influencing interaction between herbicide molecules and the soil.

The colloidal fraction, having the most reactive surface, can be divided into the organic matter (humin, humic acid, and fulvic acids) and clay fraction (5). A major factor that needs to be considered in evaluating the relative importance of organic matter and clay in herbicide adsorption is that, in mineral soils, the two are intimately bound together, probably as a clay-metal-organic complex. Thus, two major types of adsorbing surfaces are normally available to the herbicide, namely, clay-humus and clay alone (73).

Humic substances, which represent the most active fraction of the organic matter in most soils, can best be described as a series of highly acidic, yellow to black colored, high-molecular weight polyelectrolytes whose ability to combine with herbicides is due primarily to their high content of oxygen containing functional groups, including COOH, phenolic-, aliphatic- and enolic-, and heterocyclic-OH, and C=O structures of various types. Amino, heterocyclic amino, imino, and sulfhydryl groups may also be present. The low-molecular-weight fulvic acid have lower carbon contents but higher oxygen contents than the humic acids. Fulvic acid contain substantially more COOH groups than humic acid. The total acidities of fulvic acids (usual range of 890 to 1,400 meq/100g) are considerably higher than humic acid (usual range of 485 to 870 meq/100g). Both COOH and acidic OH groups contribute to the acidic nature of these substances, with COOH being the most important (5,73,99).

The crystalline clays can be divided into two main structural groups on the basis of the ratio of silicate to aluminum layers (5,86). Montmorillonite, a 2:1 type structure, is characterized by having a large surface area and a high exchange capacity. Illite, a non-expanding 2:1 type structure, has a lower cation exchange capacity. Kaolinite, a 1:1 structure, has the lowest surface area and cation exchange capacity. The causes of the cation-exchange capacity of the clay minerals originates from

broken bonds, isomorphous substitution, and dissociation of hydrogen ions of exposed hydroxyls. Broken bonds around the edges of the silica-alumina units would give rise to unsatisfied charges, which would be balanced by adsorbed cations. Substitutions within the lattice structure of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium, for trivalent aluminum in the octahedral sheet result in unbalanced charges in the structural units of some clay minerals. The hydrogen of exposed hydroxyls may be replaced by a cation which might be exchangeable. However, it seems probable that such hydrogen would be relatively tightly held as compared with those associated with broken bonds and hence, in the main, not replaceable (5,76).

The total charge on soil colloidal materials can be separated into two categories, one of which is called the permanent charge, and the other the pH-dependent charge. Permanent charge results from isomorphous substitution and gives to these clay minerals properties of strong acids. About 80% of the CEC at pH 7.0 of montmorillonite and vermiculite is due to isomorphous substitution. The balance derives mainly from broken bonds in the silica layer and is pH-dependent (5,76).

Weak acid groups in soil organic matter include carboxyls and quinone hydroxyls which buffer over a range from pH 3.0 to pH 10.0 and phenolic hydroxyls, dienols and



other groups which buffer only in the alkaline range. In soil mineral fractions, pH-dependent negative change is associated with broken bonds at the edges of the silica layer of crystalline alumino-silicate clays and with silica complexed with hydrated iron and aluminum oxides in amorphous clay colloids. The acid groups associated with silicon buffer over a slightly acid to alkaline pH range (5,73,76,99).

Sites of positive change are also present in soils and are pH-dependent. They appear in the acid range through protonation of broken edge alumina in crystalline layer silicates and protonation of hydrated iron and aluminum oxides in amorphous clay fractions. Protonation of amine groups also gives rise to sites of positive change in the organic fraction of soils. There is a wide range in basicity of amine groups in soil organic matter, and some of the more basic groups may be protonated in the alkaline range (5,73,76,99).

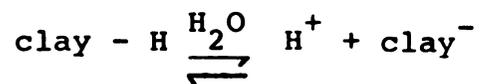
The pH-dependency of weak acid groups and of protonation reactions involving basic groups in mineral and organic colloids contribute importantly to the pH-dependency of binding and activity of both cationic and anionic herbicides in soils (5,99).

Soil pH.--The acidity of a soil is usually measured in an aqueous suspension. The composition of the

soil solution affects the acid-alkaline character of the soil. The water and ions organized by the mineral surface also affect acidity. Because many reactions are pH sensitive, the nature of soil acidity is an important consideration in the soil environment (63,70).

Soil pH is normally measured with a glass electrode in soil:water suspensions of from 1:1 to 1:2.5 for convenience. However, dilution can change the relative ion dissociation from the clay surfaces and a junction potential at the reference electrodes can introduce error; therefore, the environmental pH of the organic molecule lying next to an air dry clay surface may be entirely different than that measured by the glass electrode in a suspension (63,70).

The characteristic of acid solutions is based on the activity of the hydrogen ion ( $H^+$ ). An acid when mixed with water dissociates or ionizes into hydrogen ions and the accompanying anions, as represented by the clay-hydrogen complex:



The  $H^+$  ions to the right indicate "active" acidity, and the more the reaction tends toward that direction, the greater the activity of the  $H^+$  and the stronger the acid is said to be. The clay-hydrogen complex on the left side of the equation is the "potential" acidity (76).

According to generally held views, acidity in soils has several sources: humus or organic matter, aluminosilicate clays, hydrous oxides of iron and aluminum, soluble salts, carbon dioxide, nitrification, and the biological oxidation of reduced sulfure compounds (76).

The pH dependency of acidic functional groups in soil organic matter is an important factor influencing the behavior of cationic and weakly basic herbicides (99).

Surface Acidity.--It has been recognized for some time that the activity of protons in the bulk suspension and the activity of protons at or in close proximity to the colloidal surface may differ drastically. The term "surface acidity" as applied to soil systems is the acidity at or in close proximity to the colloidal surface and reflects the ability of the system to act both as a Bronsted acid and a Lewis acid. This is a composite term which reflects both the total number of acid sites and their relative degree of acidity (5).

Bailey and White (5) state that surface acidity is probably the most important property of the soil or colloidal system in determining the extent and nature of adsorption and desorption of basic organic compounds as well as determining if acid-catalyzed chemical degradation occurs.

The nature and properties of water in the interfacial region differ from those of bulk water (5). Hecht et al (33) have shown that water adsorbed by



montmorillonite has a higher degree of dissociation than that of normal water. The NMR studies of Ducros and DuPont (21) showed that the degree of dissociation of adsorbed water in montmorillonite is at least 1,000 times higher than that in liquid water. The clay surface increases in acidity or proton donating properties as the water content is decreased (98).

There is overwhelming evidence, mainly from infrared studies, that there is protonation of compounds basic in chemical character both by clays where hydrogen and aluminum are the predominant exchangeable cation and also those saturated with transition, alkaline, and alkali metal cations (5). The kind of metal cation occupying exchange sites will largely determine the acidity of the clay surface. Thus, molecules like urea may be protonated on  $H^+$  or  $Al^{+++}$  montmorillonite, but not when the clay is saturated with  $Ca^{++}$  or  $Na^+$ .

Bailey et al. (6) concluded from an adsorption study of adsorbates of widely differing chemical character and basicity that the surface acidity of montmorillonite is three to four pH units lower than the pH of the bulk solution.

A summary of recent investigations clearly indicates that the protonation of organics in the interfacial region of clays is a function of basicity of the molecule, the nature of the exchangeable cation, water content of

the system, and origin of negative charge in the alumina-silicate (5).

### Soil Adsorption of Herbicides

#### Mechanisms of Adsorption

Adsorption of organic pesticides in soils can be defined as the accumulation of the chemical at the colloid surface which is in contact with the solution. Adsorbed molecules are in equilibrium with molecules in solution, and a number of factors affect this equilibrium.

Several mechanisms or combination of mechanisms can be postulated for adsorption of organic compounds by alumino-silicates and soil organic matter. Some of these are as follows: (1) physical adsorption--adsorption due to Van der Waals forces (a summation of dipole-dipole interaction, dipole induced dipole interactions, and induced dipole-induced dipole interactions, ion dipole interactions), (2) hydrogen bonding, (3) coordination complexes, (4) chemical adsorption, and (5) hydrophobic bonding (5,98,99).

It should be realized that not all mechanisms occur simultaneously; however, two or more may occur simultaneously depending on the nature of the functional groups and acidity of the system.

Chemical Adsorption.--Chemical adsorption by soils and soil constituents can occur by at least four different mechanisms (5,98): (1) ion exchange, (2) protonation at

the silicate surface or colloidal surface by reaction of the base with the hydronium ion on the exchange site, (3) protonation in the solution phase with subsequent adsorption of the organic molecule via ion exchange, and (4) in systems having water of hydration, protonation by reaction with dissociated protons from residual water present on the surface or in coordination with the exchangeable cation.

Protonation. As indicated earlier under the topic of surface acidity, adsorption may occur due to protonation at or near the colloidal surface. This process involves the uptake of a proton from the soil-water system by a neutral molecule to become a positively charged ion. This is a very important adsorption mechanism, especially in regard to the adsorption of pesticides basic in chemical character, such as the s-triazines, as-triazines, and triazoles.

Russell et al. (60) found that the amitrole (3-amino-s-triazole) molecule became protonated upon adsorption on the surface of montmorillonite to produce a 3-amino-triazolium cation. The infrared spectrum of a  $Mg^{++}$  saturated montmorillonite exposed to a solution of the neutral 3-aminotriazole was remarkably similar to that of a montmorillonite saturated with the 3-aminotriazolium cation. This indicated that the water associated with the

$Mg^{++}$  ions was more highly dissociated and furnished a proton which was accepted by the amitrole.

The nature of the cation appears to be of great importance in the ability of the interfacial region to protonate organic bases and, also, on the magnitude of protonation and adsorption. Russell et al. (60) found that protonation of amitrole decreased in the order aluminum > magnesium and > calcium. He attributed this to the decreasing polarizing power of the cation.

Another example of protonation of pesticides at colloidal surfaces is the interaction of s-triazines with montmorillonite (60,20). Infrared studies showed that the s-triazines such as propazine and atrazine were protonated when adsorbed on the surface of montmorillonite. This protonation and subsequent hydrolysis was attributed to the surface acidity of the mineral surfaces. Protonation and hydrolysis of several of the s-triazines occur in aqueous systems only at pH values of three or lower. Yet propazine and atrazine, when adsorbed on montmorillonite saturated with basic cations such as  $K^+$ ,  $Mg^{++}$ ,  $NH_4^+$ ,  $Na^+$ ,  $Li^+$ , and  $Ca^{++}$ , were found to be protonated and hydrolyzed as a result of the interaction with the cation-water-clay system.

McGlamery and Slife (48) found that the amount of atrazine adsorbed on humic acid was pH-dependent; large quantities of atrazine were adsorbed at low pH values.

They also reported very little atrazine desorption at acid pH values from the humic complex. Adsorption also increased with increasing temperature. The opposite effect usually is noted in intact soil systems, and it is normally concluded that physical bonding accounts for retention which is reversible to increasing temperature. The data of McGlamery and Slife (48) suggest that a chemical bond was formed (22).

#### Occurrence of Adsorption

The properties of the clay-water system influence the properties of both the adsorbent and adsorbate. The pH of the soil solution will determine the degree of dissociation or association of adsorbate, the exact extent being a function of the actual value of the pKa of the adsorbate (5). Therefore, whether a compound is present in the molecular, the cationic or anionic form can affect the extent and magnitude of adsorption and the strength by which the adsorbed species is held, since the energy of adsorption may be vastly different between the dissociated and the associated form (5). Bailey et al. (6) found that regardless of the chemical character of the adsorbate, adsorption occurred to the greatest extent on the highly acid hydrogen-montmorillonite (pH 3.35) compared to the near neutral sodium-montmorillonite (pH 6.8). The same authors concluded that the magnitude of adsorption of organic compounds with widely different chemical character was governed by three factors: (1) pH of the clay system,

(2) water solubility, and (3) the dissociation constant of the adsorbate. These studies reported that the adsorption of acidic-type compounds was dependent upon the pH of the suspension, while the adsorption of a basic compound was dependent upon the surface acidity.

Bailey et al. (6) studied the effect of pH on the adsorption of a wide variety of chemically basic and acidic compounds by montmorillonite and concluded that: (1) maximum retention of basic compounds would be expected to occur when the surface acidity was at least one to two pH units lower than the lowest dissociation constant of the molecule, (2) adsorption of basic compounds will be principally due to Van der Waals forces where the surface acidity is more than two pH units lower than the dissociation constant, (3) the surface acidity of montmorillonite appears to be three to four pH units lower than the pH of the bulk solution.

Weber (84,86) demonstrated for a series of s-triazine compounds that the maximum adsorption on montmorillonite occurred at a suspension pH in the vicinity of the pKa value of each compound. A further lowering of the pH resulted in some desorption of the s-triazine compounds which was attributed to competition of the protonated species with  $H^+$ . An alternate explanation would be that the low pH released  $Al^{+++}$  from the clay lattice which would be a greater competitor than would  $H^+$  to displace

the protonated organic cation from the exchange complex (51). This result is directly opposite that found by Frissel and Bolt (24) for the adsorption of chloro-s-triazines at three to four pH units above the dissociation constant, adsorption started to increase as pH decreased down to pH 1.0; the amount of adsorption was essentially exponential in nature.

In an adsorption study of simazine with 18 soils from the southeastern United States, Nearpass (52) found that the extent of adsorption was not significantly correlated with soil pH, but was highly significantly correlated with organic matter content and titratable acidity. Nearpass (53), studying the effect of the predominating cation on the adsorption of simazine and atrazine found that adsorption was governed largely by the hydrogen ion activity relationship which occurred between the solution and the solid phase of the soil. At equal concentrations, atrazine was less strongly adsorbed than simazine.

The adsorption of purines, pyrimidines, and their nucleosides by  $\text{Na}^+$ -,  $\text{Li}^+$ -,  $\text{Ca}^{++}$ -, and  $\text{Mn}^{++}$ -montmorillonite over a pH range of 2 to 12 was found to be pH dependent, greater adsorption occurring as the pH decreased (44). Adsorption was postulated to occur primarily as a cation exchange reaction under acid conditions.

## Influence of Soil pH on Herbicides

### Phytotoxicity

The phytotoxicity of various soil-applied herbicides are affected by many factors, some of which are climate, microbial decomposition, plant species in the application area, and adsorption by soil (69).

Hydrogen ions in the soil associate with basic herbicides to form positively charged substances that are readily adsorbed by soil particles. Since it takes free hydrogen ions in the soil to form these cationic compounds, and since free hydrogen ions are present only in acid conditions, it means these compounds are strongly adsorbed in highly acid soils. In neutral or alkaline soils these compounds remain primarily in a non-ionized (molecular) form and are held much more weakly by soil particles. This means more of the chemical is available in non-acidic soil. Hartwig (31), Best et al. (9) reported that liming of acid soils will improve the effectiveness of the triazine herbicides. Liming to near neutral or alkaline pH will also have an effect on the rate of biological or chemical degradation of these chemicals, since the chemicals are more readily available for plants, micro-organisms, and chemical reactions when they are in the soil solution.

The pH dependent adsorption and hydrolysis of basic pesticides in soil systems has been found to affect the biological availability of these compounds. Leefe

(46) measured greater damage to strawberries from simazine on soils which were limed as compared to unlimed soils. He attributed the lower activity on the acid soils to increased hydrolysis of simazine. Weber et al. (92), Weber and Best (88), and Best and Weber (8) showed that soil pH greatly affected the phytotoxicity and persistence of soil-applied prometryne. The much lower activity which occurred in systems at pH 4.5 as compared with systems at pH 6.5 was attributed to increased adsorption by clay and organic soil colloids. Best et al. (9) have recently obtained analogous results in limed versus unlimed soils in field studies. Atrazine and prometryne were much more phytotoxic when applied to limed soils at pH 7.0 than when applied to unlimed soils at pH 5.0. Corbin et al. (19) studied the influence of soil pH (4.3 to 7.5) on the phytotoxicity of herbicides incorporated into high organic soils. Phytotoxicity increased as the soil pH increased and reached a maximum at pH 6.5 for the weak bases, prometone and amitrole.

#### Leaching, Movement and Solubility

The movement of a basic herbicide placed on or within the soil may influence both its effectiveness and its potential as a contaminant in adjacent soil, water or air. Movement may occur while in solution or adsorbed on migrating soil particles, or by transfer vapors and by

diffusion if an activity gradient exists (11,34).

Upchurch and Pierce (77,78) indicated that at least two steps are involved in the movement of a herbicide downward in soil: (1) entrance of the herbicide into solution, and (2) adsorption of the herbicide to soil particles. These two processes, solution and adsorption, may be affected by several variables. A survey of s-triazine mobility literature by Helling (34) suggested that triazines have low to moderate mobility, dependent on the soil adsorptive capacity and the triazine adsorptive strength.

Helling (34) reviewed the parameters influencing movement of s-triazine herbicides in soils: (1) adsorption, (2) solubility, (3) flow rate and amount, (4) formulation, (5) rate of pesticide application, and (6) rate of degradation.

Adsorption is probably the most significant factor affecting the overall behavior of s-triazine herbicides in soils. The rate and extent to which a compound is adsorbed and subsequently desorbed will govern its movement and leaching in soils and its susceptibility to degradation. Scott et al. (68) indicated that the magnitude of the diffusion coefficient of  $^{14}\text{C}$ -metribuzin in Dubbs soil depends primarily upon the amount in the adsorbed phase and on the moisture content. The adsorbed phase diffusion coefficients were less than the apparent self-diffusion

coefficients and decreased with decreasing soil water content. Since negative adsorbed phase diffusion coefficients were observed at the lower soil water contents, the data suggested that the amount of metribuzin in the adsorbed phase increased as soil water content decreased. Savage (62), studying the mobility of metribuzin over a wide range of soil texture, organic matter content, and chemical properties, found a significant negative correlation between  $R_f$  values and clay content, while a significant positive correlation was observed between  $R_f$  value and sand content. The relative movement of metribuzin in soil was not correlated significantly with soil organic matter content. The order of decreasing mobility of seven s-triazines (57) seems to coincide with increasing relative adsorption (6,52,75). Adsorption of simazine by 18 acid soils was highly correlated with organic matter and titratable acidity, and somewhat less correlated to clay content (52). A reduction in pH increases the adsorption of basic herbicides, as documented and discussed previously. The pH effect is predominantly on the herbicide itself. This increased adsorption of various s-triazines by clay or organic matter is generally considered a result of protonation of the somewhat basic molecule (3,5,6,24,30,75). McGlamery and Slife (48) showed atrazine adsorption on Drummer clay loam soil increased markedly as the pH decreased below six; desorption increased as pH and

temperature increased. Adsorption on humic acid (from leonardite) was ten-fold greater at pH 2.5 than at 7.0. Since the process was irreversible, atrazine would thus be rendered immobile to leaching in this model system. Best et al. (10), Best and Weber (8), studying the effect of soil pH on s-triazine dissipation using a balance-sheet approach, reported that plant uptake and leaching occurred to a greater extent in the more alkaline soil. Nearpass (52) found the mobility of simazine was greater in limed than unlimed soil, and suggested that decreased adsorption occurred at increased pH. The nature of the adsorbate and of specific adsorbents in soils also influence adsorption and movement of herbicides (3). Weber (84) compared adsorption of 13 s-triazines on montmorillonite. Maximum adsorption occurred near the pKa of each compound.

The solubilities of herbicides and salts of herbicides that may form in the soil are important properties affecting leaching (50,54). Correlation of solubility and adsorption with movement suggested that solubility may be important in initial movement from the point of application whereas adsorption may be the determining process later. Thus, adsorption in general will be a more accurate indicator of overall potential movement than will be solubility (11). In theory, however, low solubility may limit the ability of a chemical to diffuse into water moving gravitationally or by capillarity (34). It appears that increased solubility may correlate with decreased adsorption

(and therefore, increased mobility) for some individual classes of compounds (34). Bailey et al. (6) concluded that the magnitude of adsorption of s-triazines on H-montmorillonite was directly related to and governed by the degree of water solubility, with the exception of atrazine. The order of adsorbability was simetone [2,4-bis(ethylamino)-6-methoxy-s-triazine] > atratone [2-(ethylamino)-4-(isopropylamino)-6-methoxy-s- triazine] > prometone > trietazine [2-chloro-4-(diethylamino)-6-(ethylamino)-s-triazine] > propazine > atrazine. Adsorption on Na<sup>++</sup>-montmorillonite also decreased in this order. The leaching of seven triazines in sandy loam corresponded rather poorly with solubility; Rogers (57) concluded that measurement of relative adsorption was a better predictor.

Ward and Weber (82) studied the aqueous solubility of alkylamino-s-triazines as a function of pH and molecular structure. In general, solubilities of 2-OH, 2-OCH<sub>3</sub>, and 2S-CH<sub>3</sub> triazines increased significantly only at pH 3.0 or lower; and of 2-Cl triazines, at pH 2.0 or lower. Results indicated that structural changes at either the 2-position or 4,6-position significantly affected solubility. Increased solubility was associated with increased basicity of the 2-substituent and decreased size and steric hindrance of the 4,6-N-alkyl substituents. Correlation of pKa values and solubilities at low pH suggest that protonation occurs at an endocyclic nitrogen atom.

### Degradation and Biodegradation

Biodegradation is a significant factor affecting the residual life and toxicity of many pesticides in soils. There is considerable evidence indicating that soil microorganisms can utilize s-triazine compounds as a source of energy (23,38,55). Numerous s-triazine degrading microorganisms have been isolated and identified (38). Dealkylation appears to be the major mechanism involved in the microbial degradation of chloro-s-triazines (39, 47). Evolution of  $^{14}\text{CO}_2$  from microbial systems treated with  $^{14}\text{C}$ -ring-labeled s-triazines has been reported (39, 47). These observations indicate that ring cleavage may occur, however limited it might be. In nearly all cases only low levels of  $^{14}\text{CO}_2$  (zero to four percent) have been evolved from microbial systems treated with ring-labeled s-triazines. This would indicate that the s-triazine ring structure is somewhat resistant to microbial attack (38).

Hawck and Stephenson (32) suggested that the symmetrical resonating structure of s-triazine molecules contributed to differences in degradation rates. Asymmetrical chlorotriazines were degraded more quickly than the corresponding symmetrically substituted chloro-triazines. They suggested that polymerization resulting in an increased symmetry would lead to stability, whereas labile products of biochemical transformations tend toward asymmetry.

The as-triazines represent a new class of herbicides and there is little information available on their persistence and behavior in soil. Lay and Ilnicki (45) used an oat (Avena sativa L.) and cucumber (Cucumis sativa L.) bioassay and observed a 90% loss of metribuzin phytotoxicity in 42 days from a Sassafras loam soil. Hyzak and Zimdahl (35) reported the half-life of metribuzin in sandy loam soil to be 46 days at 20°C and 16 days at 35°C. The loss of metribuzin was linear at both temperatures. Rates of 1.12 and 2.24 kg/ha, applied in the field, remained in the upper 5 cm of the soil profile, and the pattern of herbicide degradation followed that found in the laboratory study at 20°C. First-order kinetics best described the rate of degradation. Waggoner et al. (79) studied the degradation of metribuzin in mineral and muck soils under laboratory conditions. Deamination and thiodealkylation resulted in three metabolites: DA, DK, DADK. Schumacher (64,65) showed that <sup>14</sup>C-metribuzin was degraded to <sup>14</sup>CO<sub>2</sub> in soil. The metabolism of metribuzin was independent of soil organic matter content and was not increased by amendment with glucose and yeast extract. Metribuzin metabolism was inhibited in autoclaved soils. CO<sub>2</sub> evolution from <sup>14</sup>C-3 and <sup>14</sup>C-5 metribuzin applied to soils indicated that the triazine ring was degraded in a stepwise manner and C-3 was released more readily than was C-5. The primary soil metabolite was DADK.

The influence of metribuzin on soil microbial activity is not known. Lay and Ilnicki (45) reported that metribuzin at 0.29 to 0.56 kg/ha had no effect on the number of soil microorganisms present. Avrik et al. (2) reported a 60% decrease in the number of soil algae in soil treated with 10 ppm of metribuzin. Chlorella sp. and Anabaena sp. appeared to be more resistant to the chemical than other species studied.

Soil pH may directly or indirectly influence the detoxication of herbicides by affecting the ionic or molecular character of the chemical, the ionic character of soil colloids, the cation exchange capacity, and the inherent capacity of microbial populations to respond to a given chemical (18).

Soil pH, moisture content, and aeration affect the activities of soil microorganisms. Soil bacteria and actinomycetes are most active in near neutral or alkaline, moist soils (80), whereas soil fungi are generally more active in soil under low moisture conditions (49) and lower pH levels (81). Since so many soil fungi appear to be involved in biodegradation of s-triazines, one might expect decomposition to occur more rapidly in acid soils of low moisture content. However, this is not the case. Persistence of several s-triazines is less in moist soils than in dry soils (74). Adsorption of atrazine and simazine varies inversely with pH (30,75).

Obien and Green (55), examining soil characteristics such as pH, organic matter content, and atrazine adsorption, revealed that low pH appeared to be more closely related to the rapid degree of atrazine degradation than the other soil properties. Hydroxyatrazine was the main degradation product. It was concluded that chemical degradation (hydrolysis) was the major pathway of atrazine loss in the soils. A similar observation was made by Weber et al. (92) who found that the phytotoxicity of prometryne to wheat (Triticum aestivum L. em Thelli) was inversely related to soil acidity, i.e., lower phytotoxicity was obtained at pH 4.5 than at pH 6.5 in the presence of montmorillonite clay or organic matter. They attributed this result to increased adsorption of the protonated prometryne associated with a decrease in pH of the medium. Chemical hydrolysis of the triazines was catalyzed by adsorption on clay and organic matter (1,61). Corbin and Upchurch (19) found no influence of pH on the detoxication of prometone. Some of the possible factors given for the observed persistence are (1) inhibition of microbial growth at the chemical concentrations used, with subsequent failure of the microorganisms to produce detoxifying enzymes within the allocated time period, (2) low chemical solubility with a resultant low uptake by the primary microflora, (3) strong adsorptive bonds between the chemicals and soil colloids, coupled with a low availability to the microbial population. The pH of the soil environment

has a profound effect upon the inherent capacity of the microbial population to respond to chemical changes in the environment and exerts a vital role in the interactions which eventually result in the partial or total inactivation of the herbicide substrate (19). The dipyridylum herbicide diquat<sup>2+</sup> [6,7-dihydrodipyrido(1,2-a',2',1'-c)-pyrazidinium dibromide] is strongly adsorbed by montmorillonite and not readily extractable (93,90). Weber and Coble (89) showed that the addition of montmorillonite clay in an amount calculated to adsorb one-half of the <sup>14</sup>C-diquat reduced the <sup>14</sup>CO<sub>2</sub> detected.

Best and Weber (8) found the pattern of atrazine degradation was characteristic of nonbiological processes, while prometryne degradation was by microbial action. The higher amounts of extractable prometryne in the acid soils suggested that the adsorption to soil colloids offered some protection from microbial degradation. Unlike atrazine, prometryne was relatively stable in the acidic environment surrounding these colloids (97). In the pH 7.5 soil, more of the prometryne molecules were in the soil solution and consequently available to plants and microbes.

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## CHAPTER 2

### EFFECT OF SOIL PH ON METRIBUZIN ACTIVITY AND DISSIPATION IN FIELD SOILS

#### Abstract

Metribuzin [4-amino-6-tert-butyl-3-(methylthio)-1,2,5-triazin-5(4H)one] activity in the field increased with increasing soil pH. Fall panicum (Panicum dichotomiflorum Michx.) control, number of dead corn (Zea mays L.) and soybeans (Glycine max (L.) Merr.) plants, and crop injury ratings increased, whereas, plant height and grain yield decreased as the soil pH increased. Metribuzin residue analysis of soil samples showed greater amounts of residue extractable at soil pH 6.7 than 4.6. Metribuzin leaching increased with increasing soil pH. Metribuzin disappearance from soil followed pseudo first order-kinetics. Rate constants increased and the half life of metribuzin decreased as soil pH increased. Rate constants decreased and the half life of metribuzin increased at all soil pH levels as depth of sampling decreased. The decreased activity and decreased rate of metribuzin dissipation at lower soil pH is likely due to protonation and increased adsorption.

### Introduction

Adsorption of the s-triazines by soil colloids is dependent on the pH of the system, and many plant studies (6,7,12,16,21) have shown that the s-triazines are generally less phytotoxic under acid conditions than under basic conditions. This increased adsorption of various s-triazines by clay or organic matter is generally considered a result of protonation of the somewhat basic molecule (3,4,5,10,21). It is apparent that the reduction in herbicide concentration resulting from adsorption by soil colloids results in less herbicide available for absorption by plant roots (3,24). Although the adsorption of the compounds by the soil colloids is in most cases reversible, the decrease in the rate of uptake as a result of dilution reduces herbicidal activity of the chemicals (3,24).

The order of decreasing mobility of seven s-triazines (18) seems to coincide with increasing relative adsorption (17,21). Savage (19) studying the mobility of metribuzin over a wide range of soil texture, organic matter content, and chemical properties, found significant negative correlation between Rf values and clay content, while a significant positive correlation was observed between Rf value and sand content. The relative movement of metribuzin in soil was not correlated significantly with soil organic matter content. Scott et al. (20)

indicated that the magnitude of the diffusion coefficient of metribuzin in Dubbs soil depended primarily upon the amount in the adsorbed phase and on the moisture content.

Biodegradation is a significant factor affecting the residual life and toxicity of many pesticides in soils. There is considerable evidence indicating that soil microorganisms can utilize s-triazines compounds as a source of energy (15). Hawck and Stephenson (13) found asymmetrical chloro-s-triazines were degraded more quickly than the corresponding symmetrical substituted chloro-s-triazines. Gysin (11) suggested that methylthio-s-triazines are more readily degraded than chloro-s-triazines. Best and Weber (6), using a balance-sheet approach, found atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] degradation was characteristic of nonbiological process, while prometryne [2,4-bis(isopropylamino)-6-(methylthio-s-triazine)] degradation was probably by microbial action. Extractable atrazine after 5 months amounted to 35% of the initial amount in the pH 7.5 and 11% in the pH 5.5 soil, while prometryne occurred as 10% of the original concentration in the pH 7.5 soil and 42% in the pH 5.5 soil. Waggoner et al. (22) studied the degradation of metribuzin in mineral and muck soils under laboratory and field conditions. Deamination and thio-dealkylation resulted in three metabolites:  
6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5-(4H)-

one (DA); 4-amino-6-(1,1-dimethylethyl)-1,2,4-triazin-3,5-(2H,4H)-dione (DK); 6-(1,1-dimethylethyl)-1,2,4-triazin-3,5-(2H,4H)-dione (DADK). Schumacher<sup>1</sup> showed that <sup>14</sup>C-ring-labeled metribuzin was degraded to <sup>14</sup>CO<sub>2</sub> in soil. The metabolism of metribuzin was independent of soil organic matter and was not increased by amendment with glucose and yeast extract. The primary soil metabolite was DADK. Hyzak and Zimdahl (14) reported the half-life of metribuzin in sandy loam soil to be 46 days at 20°C and 16 days at 35°C. The loss of metribuzin was linear at both temperatures. Rates of 1.12 and 2.24 kg/ha, applied in the field, remained in the upper 5 cm of the soil profile, and the pattern of herbicide degradation followed that found in the laboratory study at 20°C.

Soil pH may directly or indirectly influence activity and detoxication of herbicides by affecting the ionic or molecular character of the chemical, the ionic character of soil colloids, the cation exchange capacity, and the inherent capacity of microbial population to respond to a given chemical (8).

The objectives of this study were to determine the effect of soil pH on metribuzin activity and dissipation in field soil.

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<sup>1</sup>Schumacher, R. W. 1974. Metabolism of metribuzin in soybeans and soil. Ph.D. Thesis. University of Kentucky, Lexington, Kentucky. 176 pp.

## Materials and Methods

### Field Experiments

Field experiments were conducted in 1972, 1973, and 1974 at East Lansing, Michigan to study the effect of soil pH on metribuzin phytotoxicity to soybeans and corn. The experiments were conducted on Hillsdale sandy clay loam, East Lansing, Michigan, containing 1.5% organic matter with a pH adjusted over a 15-year period with ammonium sulfate, calcium nitrate or dolomitic limestone (26). The soil mechanical analyses were similar at all five pH levels; OM (1.5%), sand (53%), silt (22%), and clay (25%). Treatments were replicated four times in a completely randomized block design. There were variations within the pH ranges given, over the four replications. Metribuzin was applied preemergence at 0.00, 0.56, 0.84 and 1.12 kg/ha with a tractor-mounted sprayer that delivered 215 L/ha. Two rows of corn 'Michigan 400' and two rows of soybeans, 'Wirth' (1972), 'Hark' (1973), and 'Swift' (1974) were planted in each plot. Plot size was 3.0 m x 7.6 m with four rows in 0.76 m row widths. Planting dates were June 3, 1972, May 17, 1973, and May 22, 1974. Rainfall (Table 1) occurred within 7 days after application in all three years. All untreated and treated plots were hand weeded as needed early in the growing season. Population counts and injury ratings (0 = no injury; 10 = complete kill) were measured one month after planting. Plant height was measured six

Table 1.--Rainfall data for 1972, 1973, and 1974 Soils Farm, East Lansing, Michigan.

Year	April	May	June	July	Aug.	Sept.	Oct.	Total
	(cm)							
1972	8.54	7.46	6.04	6.29	8.89	10.67	7.87	55.75
1973	10.00	12.64	9.30	2.21	5.69	8.33	5.59	53.77
1974	5.18	11.78	4.42	3.89	9.86	7.01	2.82	44.96

weeks after planting. At maturity grain yields were recorded. Due to the effect of pH on plant growth at the different pH levels, population counts and injury ratings were expressed after subtracting the control at the given pH range. Plant height and grain yield were reported as percent of the control at the given pH range. Weed control ratings were recorded on a 0 to 10 scale (0 = no control and 10 = complete control) for fall panicum late in the growing season.

#### Field Residue Study

Field residue analyses were conducted at the previously described plots. Soil samples were taken from the 1.12 kg/ha metribuzin treated plots in 1973 and 1974. A split-plot design was used with soil pH as main plots and dates of sampling as subplots. Metribuzin had been used on the plots in 1972, therefore, samples were collected before application in 1973, and 1974 to establish residue

levels from application the previous year. Samples were collected in 1973 at 15, 36, 77, and 150 days and in 1974 at 3, 21, 84, and 142 days after herbicide application. Depths of sampling were 0.0-5.0, 5.0-10.0, and 10.0-20.0-cm. At each sampling date, subsamples were taken from each main plot, extracted and analyzed separately. Rainfall for 1973 and 1974 is given in Table 1. After each sampling date, the soil was air-dried, screened, thoroughly mixed, and frozen prior to analysis.

The amount of herbicide present was determined by Soxhlet extraction and gas chromatograph analysis (14). Herbicide standards were prepared to check extraction efficiency by dissolving the analytical grade compound (99 to 100% purity) in distilled acetone. Fifty grams of soil, pH levels 4.6, 5.6, and 6.7, were placed in beakers and 5 ml of acetone solution were uniformly pipetted over the soil surface. The herbicide was thoroughly mixed with the soil to yield a uniform concentration of 1.0 and 0.1 ppm, w/w basis. The soil and herbicide were allowed to equilibrate for 48 hours. The 50 grams of soil were extracted in a Soxhlet apparatus with 250 ml of 80% methanol for five hours with a recycling time of approximately five minutes. After extraction, 25 ml of distilled water was added to the extractant and the solvent was evaporated to 20 to 30 ml. The aqueous phase was extracted with one 50 ml and two 25 ml aliquots of glass distilled

benzene to bring the final volume to 100 ml. The aqueous-benzene mixture was vigorously shaken for 10 to 15 seconds and allowed to separate into its respective phases. Thirty grams of anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was added to each bottle. The aqueous phase was drained into a beaker and discarded. The samples were then placed in a refrigerator until analysis. Samples from the field plots were handled as previously described.

Herbicide concentrations in the benzene extracts were determined with a gas chromatograph equipped with a Beckman helium arc discharge electron-capture detector. A 183 cm by 2 mm (I.D.) glass column was packed with 80/100 mesh Chromosorb Gas-Chrom Q coated with 3% SE-30. Injector, column, and detector temperatures were 250, 190, and 310°C, respectively. Helium at a flow rate of 40 ml/min was used for the carrier gas. Under these conditions, a retention time of 1.85 min was obtained. The range of linearity was from 0.05 ng to 5 ng, and the detection limit of the method was 0.01 ppm in soil. Herbicide content was determined by comparing peak heights from sample to peak heights of known standards. A series of standards of different concentrations of herbicide was injected to determine the range of linearity and sensitivity before, during, and after each day's run of samples. Known soil pH standards were extracted and analyzed to determine extraction efficiency at the different soil pH levels.

## Results and Discussion

### Effect of Soil pH on Metribuzin Activity in the Field

Metribuzin activity in the field increased with increasing soil pH (Tables 2 to 6). Fall panicum control increased with increasing soil pH (Figure 1). Metribuzin applied at 0.84 and 1.12 kg/ha gave similar results, however, there were greater differences between pH ranges at the 0.56 kg/ha rate than at the higher application rates (Table 2). It can be postulated that the reduction in herbicide concentration by soil colloids resulted in less absorption by the fall panicum roots at the lower application rate.

Phytotoxicity to corn and soybean also increased as the soil pH increased (Figures 2 and 3). Corn was a more sensitive indicator of the metribuzin pH response than soybean. Because of the variation of soil pH within the four replications in a given pH range, pH levels were not always significantly different. This held true for all parameters measured, especially at the 0.56 kg/ha metribuzin rate. However, correlations, with soil pH obtained from field data were 0.971 and 0.977 for corn injury ratings and grain yield at 1.12 kg/ha metribuzin in 1972 (Figures 4 and 5). Injury ratings as an indication of vigor and stand reduction were taken one month after planting. Corn injury showed a positive correlation with increasing soil pH (Figure 4). Corn injury (Table 3)

Table 2.--The effect of soil pH on metribuzin toxicity to fall panicum.<sup>a</sup>

pH Range	Metribuzin (kg/ha)								
	0.56		0.84		1.12				
	1972	1973	1974	1972	1973	1974			
4.5-4.9	4.4 a	7.5 a	5.4 a	6.6 b	8.3 abc	7.0 b	6.9 bc	7.5 ab	7.3 bc
5.0-5.4	8.5 bcd	8.4 bc	6.9 b	7.6 bcd	8.3 abc	7.8 bcd	9.8 d	9.4 d	9.0 de
5.5-5.9	9.0 cd	8.8 cd	7.8 bcd	9.7 d	9.5 d	8.4 bcde	9.8 d	9.0 cd	10.0 e
6.0-6.4	9.5 d	9.1 cd	9.7 e	9.6 d	9.4 d	8.8 cde	9.7 d	9.1 cd	9.8 e
6.5-6.9	9.9 d	9.0 cd	9.5 e	9.8 d	9.1 d	9.7 e	9.9 d	9.4 cd	9.9 e

(% of control) bc

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>0 = no control; 10 = complete control.

<sup>c</sup>Weed control ratings for fall panicum control were recorded late in the growing season.

Table 3. The effect of soil pH on metribuzin phytotoxicity to corn in the field, measured by visual injury ratings.<sup>a</sup>

pH Range	Metribuzin (kg/ha)								
	0.56		0.84		1.12				
	1972	1973	1974	1972	1973	1974			
4.5-4.9	1.4 ab	2.2 ab	1.3 ab	2.4 abc	3.7 abcd	2.3 abc	0.5 a	2.5 abc	0.0 a
5.0-5.4	1.5 ab	2.0 a	1.3 ab	2.5 abc	4.0 abcde	1.8 ab	1.7 ab	5.0 cde	2.3 abc
5.5-5.9	1.7 ab	2.0 a	2.5 bc	2.2 abc	4.0 abcde	3.0 bcd	2.3 abc	6.5 ef	4.8 cde
6.0-6.4	2.5 abc	3.0 abc	3.0 bcd	3.4 bc	4.5 abcde	3.0 bcd	3.7 bc	5.7 def	5.0 de
6.5-6.9	2.2 abc	3.4 abcd	3.7 bcde	4.3 c	4.8 bcde	4.7 cde	4.5 c	7.5 f	5.7 e

(Injury rating minus control at given pH level)<sup>bc</sup>

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>0 = no injury; 10 = complete kill.

<sup>c</sup>Injury rating made on vigor and stand one month after planting.

Table 4.--The effect of soil pH on metribuzin phytotoxicity to corn in the field, measured in grain yield (kg/ha).<sup>a</sup>

pH Range	Metribuzin (kg/ha)					
	0.56		0.84		1.12	
	1972	1974	1972	1974	1972	1974
	(% of control)					
4.5-4.9	92 bc	93 d	88 bc	88 cd	104 c	84 bcd
5.0-5.4	86 bc	88 cd	80 b	90 cd	86 bc	81 bcd
5.5-5.9	90 bc	86 cd	85 bc	79 bcd	57 a	77 bcd
6.0-6.4	87 bc	74 bc	80 b	77 bcd	57 a	69 b
6.5-6.9	81 b	81 bcd	57 a	69 b	46 a	54 a

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

Table 5.--The effect of soil pH on metribuzin phytotoxicity to soybean in the field, measured by visual injury ratings.<sup>a</sup>

pH Range	Metribuzin (kg/ha)								
	0.56		0.84		1.12				
	1972	1973	1972	1973	1972	1973			
4.5-4.9	1.5 abc	0.5 a	0.8 abcd	1.8 abc	2.5 bcdef	0.4 ab	0.3 a	2.0 abcd	0.0 a
5.0-5.4	1.3 abc	1.1 ab	0.6 abc	1.5 abc	3.8 efgh	0.6 abc	1.0 ab	3.3 cdefgh	1.4 bcde
5.5-5.9	1.4 abc	1.7 abc	1.3 bcde	2.6 bc	3.5 defgh	1.5 bcde	2.6 bc	4.2 gh	1.8 cdef
6.0-6.4	1.6 abc	2.5 bcdefg	1.5 bcde	1.9 abc	4.0 fgh	2.0 def	2.1 bc	3.8 efgh	2.7 fg
6.5-6.9	1.8 abc	2.2 bcde	2.0 ef	2.8 c	4.0 fgh	2.8 fg	2.8 c	5.0 h	3.8 g

(Injury rating minus control at given pH range)<sup>bc</sup>

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>0 = no injury; 10 = complete kill.

<sup>c</sup>Injury rating made on vigor and stand one month after planting.

Table 6.--The effect of soil pH on metribuzin phytotoxicity to soybean in the field, measured in grain yield (kg/ha).<sup>a</sup>

pH Range	Metribuzin (kg/ha)								
	0.56		0.84		1.12				
	1972	1973	1974	1972	1973	1974			
4.5-4.9	98.6 ab	93.6 a	96.3 bc	91.9 ab	97.7 a	97.9 bc	101.9 b	98.5 a	109.4 c
5.0-5.4	97.2 ab	86.5 a	94.7 abc	92.6 ab	83.5 a	96.7 bc	88.4 ab	85.1 a	92.0 ab
5.5-5.9	82.3 ab	85.6 a	92.8 abc	76.4 ab	81.9 a	90.8 ab	70.5 ab	80.1 a	84.6 ab
6.0-6.4	85.9 ab	81.0 a	90.8 ab	79.3 ab	81.0 a	88.9 ab	72.7 ab	71.2 a	83.7 ab
6.5-6.9	82.1 ab	78.3 a	88.8 ab	70.0 ab	70.5 a	87.1 ab	62.2 a	64.2 a	77.9 a

(% of control)

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

Fig. 1.--Weed control with metribuzin at two soil pH levels. Treatment (A) check (B) metribuzin 1.12 kg/ha at pH range of 6.5 to 6.9 and (c) metribuzin 1.12 kg/ha at pH range of 4.5 to 4.9.



**C**  
Fig. 1

Fig. 2.--Metribuzin phytotoxicity to corn and soybean over several soil pH levels.  
Treatment (A) metribuzin 1.12 kg/ha at pH range of 6.5 to 6.9 (B) check  
pH range 6.5 to 6.9 (C) metribuzin 1.12 kg/ha at pH range of 4.5 to 4.9  
and (D) check at pH range 4.5 to 4.9.

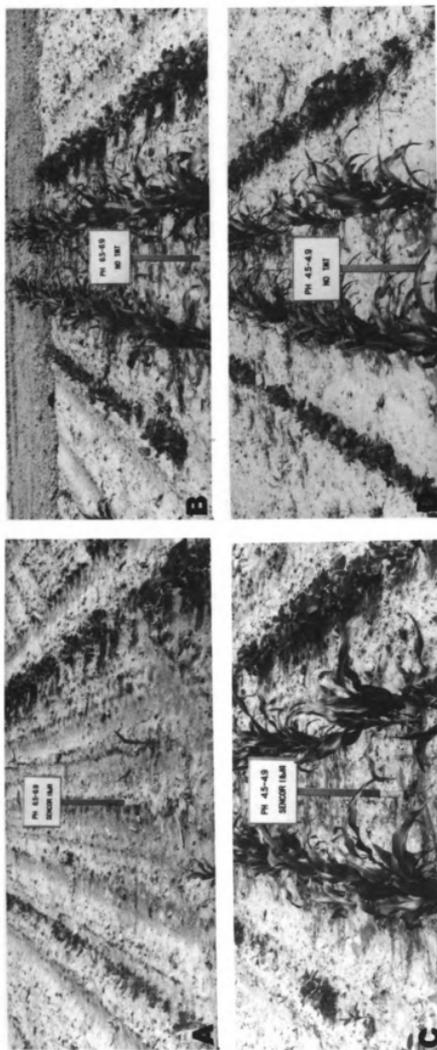


Fig. 2

Fig. 3.--Metribuzin phytotoxicity to corn and soybean at several soil pH levels. Treatment (A) check at pH range 6.5 to 6.9 (B), (C), (D), (E), and (F) metribuzin 1.12 kg/ha with pH ranges of 6.5 to 6.9, 6.0 to 6.5, 5.5 to 5.9, 5.0 to 5.4, and 4.5 to 4.9, respectively.

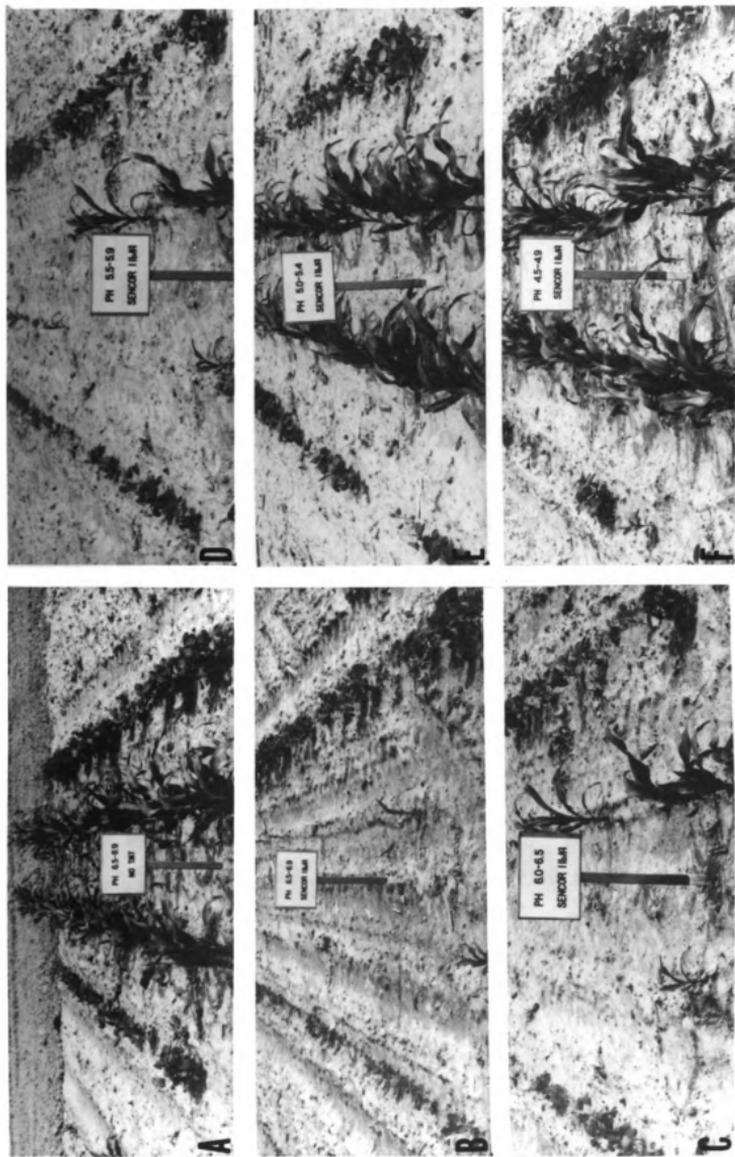


FIG. 3

Fig. 4.--Corn injury (rating 0 = no injury; 10 = complete kill) minus control at given pH range. Metribuzin applied at 1.12 kg/ha in 1972.

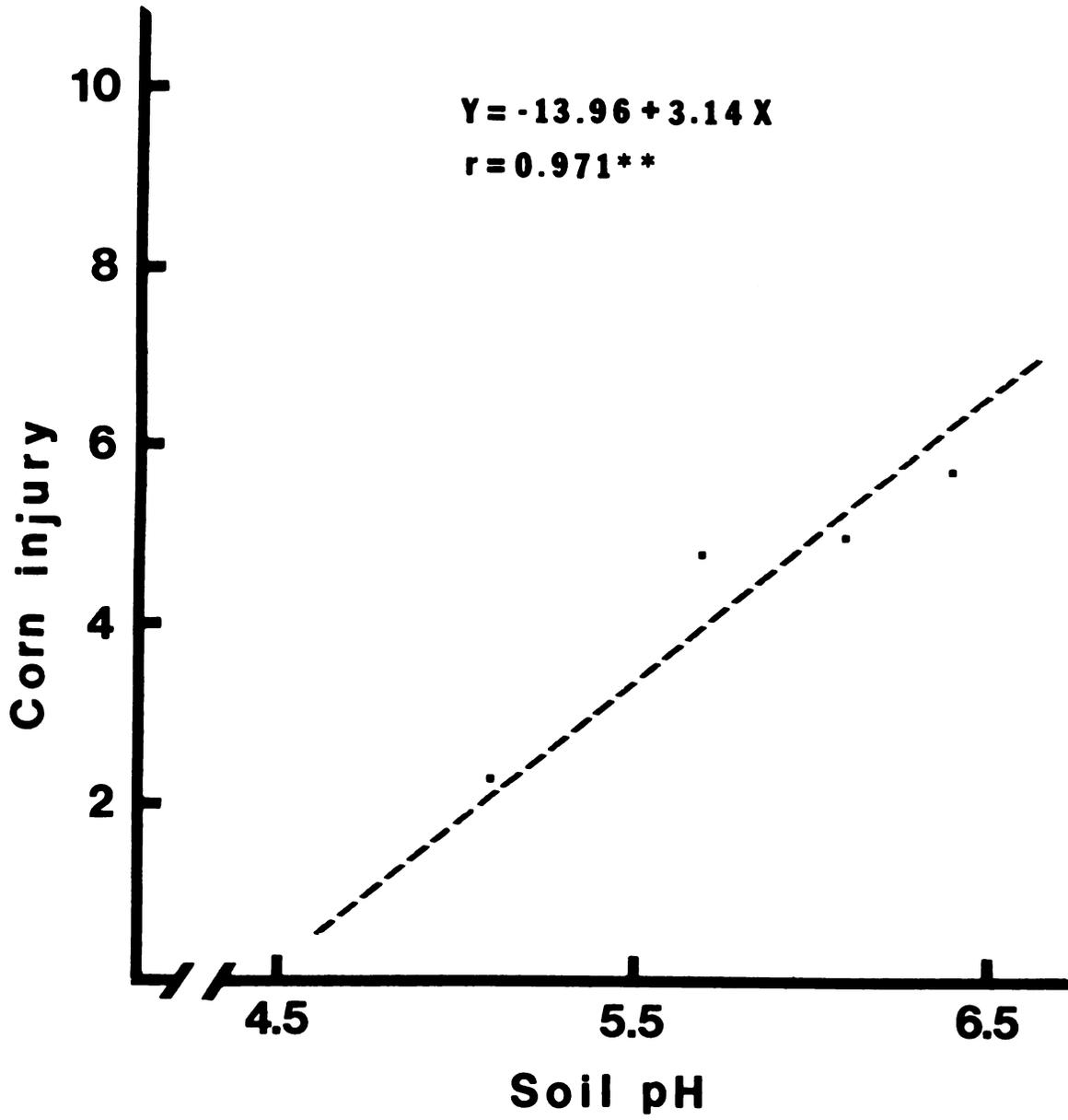


Fig. 4

Fig. 5.--Corn yield as percent of control. Metribuzin applied at 1.12 kg/ha in 1972.

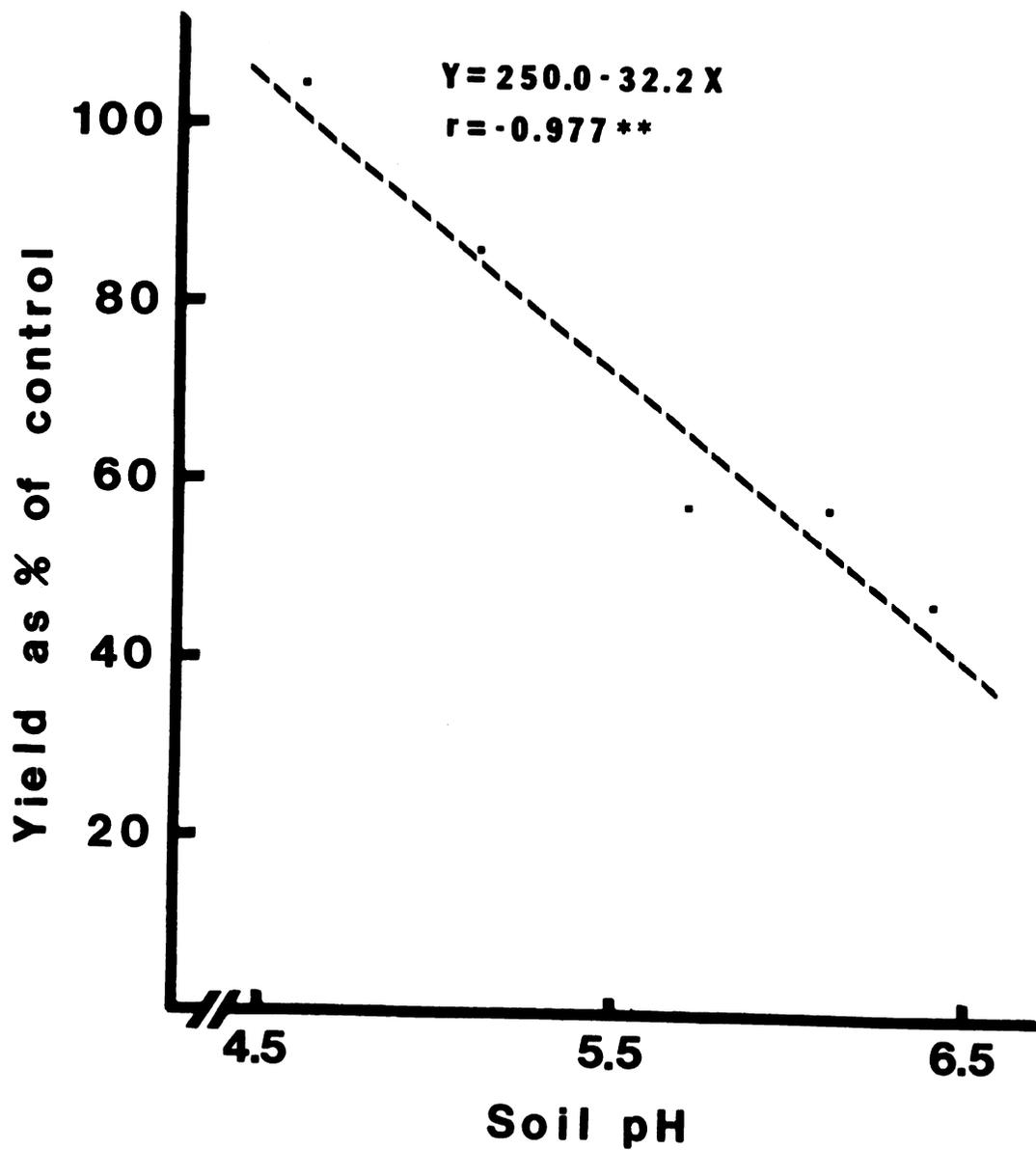


Fig. 5

showed significant differences between pH ranges at 1.12 kg/ha. Corn yields were not taken in 1973 because of dry conditions during silking and pollination, which resulted in the lack of ear development. Corn yield for 1972 as percent of control gave a negative correlation with increasing soil pH (Figure 5). Significant differences occurred between the high and low pH ranges at 0.84 and 1.12 kg/ha (Table 4). Soybean injury (Table 5) was significantly different at 0.56 kg/ha in 1973 and 1974. Soybean yield showed significant differences from the high and low pH ranges in 1972 and 1974 at 1.12 kg/ha (Table 6). Number of dead corn and soybean plants increased and plant height as percent of control decreased with increasing soil pH (see Appendix A to F). Soybeans more readily overcame injury seen earlier in the growing season than corn as indicated by final grain yield.

There appeared to be a dividing line at pH range 5.0 to 5.4, between slight injury and severe injury at the 1.12 kg/ha rate (Figure 3). This was apparently the effect of soil pH on the adsorption of metribuzin on soil colloids. It can be postulated that a reduction in herbicide concentration resulting from adsorption by soil colloids resulted in less absorption by plant roots below this pH range. Metribuzin activity continued to increase with increasing soil pH. Surface acidity is probably the most important property of the soil or colloidal system in determining the extent and nature of adsorption and

desorption of basic organic compounds (4). Bailey et al. (5) found the surface acidity of montmorillonite appears to be three to four pH units lower than the pH of the bulk solution. As the pH decreases, the adsorption of the protonated s-triazine molecule was attributed to cation exchange and to complexing of the s-triazine molecules with hydrogen ions on the clay surface (24). Weber (23) found that maximum adsorption of 13 s-triazines occurred in the vicinity of the dissociation constant of each compound. Frissel and Bolt (10) found for the adsorption of chloro-s-triazines, however, that about 3 to 4 pH units above the dissociation constant adsorption started to increase as pH decreased down to pH one. The pKa of metribuzin was found to be  $0.99 \pm 0.08$  (see Chapter 3). The same mechanism of protonation and adsorption by the soil colloids appears to be taking place with metribuzin as seen with the s-triazines. Greenhouse data on phytotoxicity to corn and soybean grown in a nutrient-sand culture versus soil at comparable pH levels supported the field data. Corn and soybeans grown in soil and treated with metribuzin showed a pH-sensitive response with a reduction in dry weight per plant as pH increased. Whereas, in sand culture there was no difference in the reduction in dry weight as pH increased (see Chapter 3).

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Effect of Soil pH on Metribuzin  
Dissipation in the Field

Metribuzin residue analysis of soil samples from the field showed greater amounts of residue extractable at soil pH 6.7 than 4.6 (Tables 7 and 8). The increase in residue may be due to less adsorption by the soil. The data in Table 7 also shows that as the pH increased leaching also increased, most likely due to the higher concentration of unbound metribuzin at the highest soil pH value. Most of the metribuzin was found in the upper 5 cm of the soil profile. Extraction efficiency of metribuzin from soil standards at 0.1 ppmw were 95% at pH 6.7, 87% at pH 5.6, and 63% at pH 4.6. In 1973 and 1974 extraction efficiency was found to also increase as soil pH increased in the field plots. Leaching of metribuzin after 7.1 cm of rainfall in 1973, increased with increasing soil pH. This is an indication of increased adsorption as pH decreased.

Metribuzin dissipation followed pseudo first-order kinetics (Tables 7 and 8) which is an approximation of first-order kinetics (9). These results were similar to Hyzak and Zimdahl (14). Data was plotted as first-order plots relating the log of soil concentration (ppbw) of metribuzin at soil pH levels 4.6, 5.6, and 6.7 at 0.0 to 5.0, 5.0 to 10.0, and 10.0 to 20.0-cm depths versus time (Figures 6, 7, and 8). Linear regression analysis indicated that the mean data points fit two lines, high

Table 7.--Effect of soil pH on metribuzin residue in soil, following application of metribuzin (1.12 kg/ha) in the field.<sup>a</sup>

pH	Depth (cm)	Soil concentration of metribuzin					
		Days after application					
		1973			1974		
		15 <sup>b</sup>	36 <sup>c</sup>	150 <sup>d</sup>	3 <sup>e</sup>	21 <sup>f</sup>	142 <sup>g</sup>
		(ppbw)					
4.6	0.0-5.0	191 e	48 bc	17 a	671 b	44 a	21 a
	5.0-10.0	67 c	23 ab	15 a	31 a	18 a	19 a
5.6	0.0-5.0	236 f	49 bc	16 a	986 c	37 a	23 a
	5.0-10.0	116 d	33 ab	16 a	42 a	16 a	21 a
6.7	0.0-5.0	298 g	73 c	17 a	1143 d	66 a	21 a
	5.0-10.0	192 e	30 ab	16 a	23 a	16 a	21 a

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

Rainfall since application: <sup>b</sup>7.1-cm, <sup>c</sup>11.9-cm, <sup>d</sup>34.0-cm, <sup>e</sup>0.3-cm, <sup>f</sup>4.4-cm, <sup>g</sup>29.0-cm.

Table 8.--Correlation values (r) of the log of concentration remaining in the soil with pH, first-order rate constant (k), half lives (t 1/2) of metribuzin in soil at three pH levels and at three depths, following application of 1.12 kg/ha in the field, 1973.

pH	Depth (cm)	Days after application					
		15 to 77			36 to 150		
		Correlation values (r)	k (day <sup>-1</sup> )	t 1/2 (days)	Correlation values (r)	k (day <sup>-1</sup> )	t 1/2 (days)
4.6	0.0-5.0	-.932	3.38 x 10 <sup>-2</sup>	21	-.940	9.29 x 10 <sup>-3</sup>	74
	5.0-10.0	-.839	2.01 x 10 <sup>-2</sup>	34	-.998	3.84 x 10 <sup>-3</sup>	180
	10.0-20.0	-.914	1.11 x 10 <sup>-2</sup>	62	-.996	4.04 x 10 <sup>-3</sup>	171
5.6	0.0-5.0	-.887	3.38 x 10 <sup>-2</sup>	20	-.996	9.90 x 10 <sup>-3</sup>	70
	5.0-10.0	-.896	2.71 x 10 <sup>-2</sup>	26	-.998	9.09 x 10 <sup>-3</sup>	76
	10.0-20.0	-.798	1.49 x 10 <sup>-2</sup>	46	-.962	5.66 x 10 <sup>-3</sup>	122
6.7	0.0-5.0	-.955	3.79 x 10 <sup>-2</sup>	18	-.944	1.25 x 10 <sup>-2</sup>	55
	5.0-10.0	-.858	3.64 x 10 <sup>-2</sup>	19	-.951	5.66 x 10 <sup>-3</sup>	122
	10.0-20.0	-.812	1.86 x 10 <sup>-2</sup>	37	-.983	5.05 x 10 <sup>-3</sup>	136

Fig. 6.--Metribuzin degradation rate as the log of concentration in soil at pH 4.6 at three soil depths following application of 1.12kg/ha in the field in 1973.

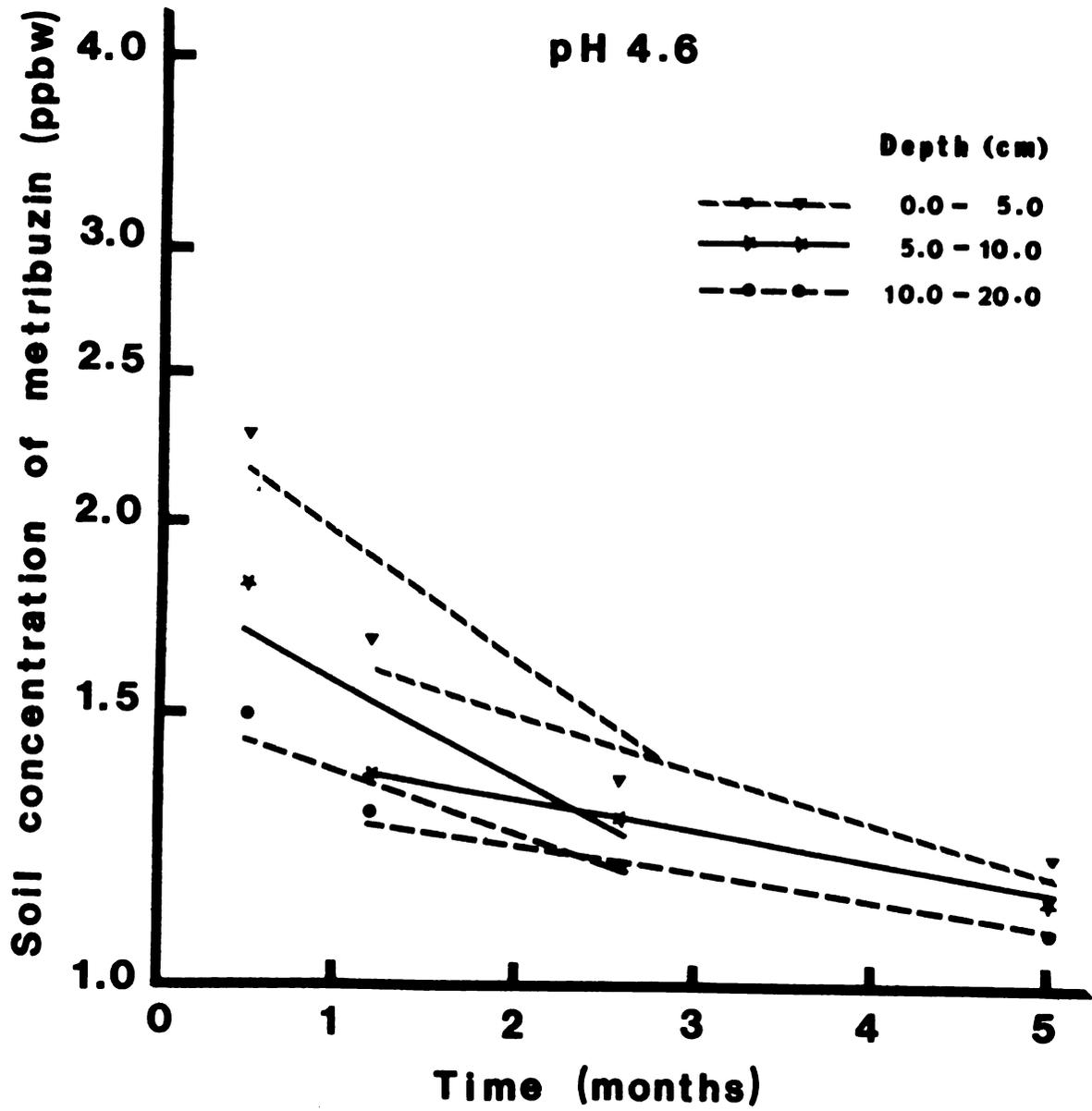


Fig. 6

Fig. 7.--Metribuzin degradation rate as the log of concentration in soil at pH 5.6 at three soil depths following application of 1.12 kg/ha in the field in 1973.

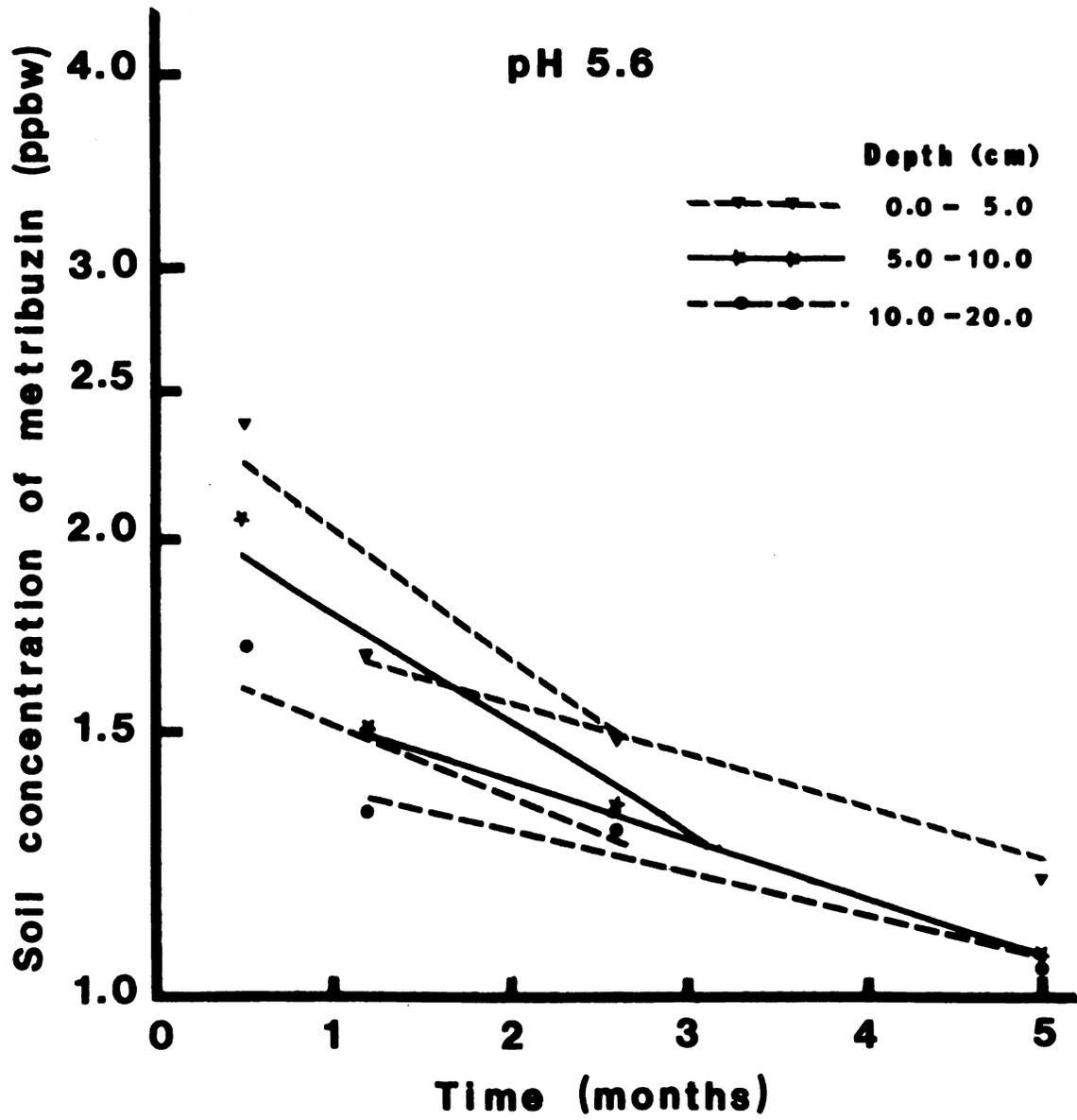


Fig. 7

Fig. 8.--Metribuzin degradation rate as the log of concentration in soil at pH 6.7 at three soil depths following application of 1.12 kg/ha in the field in 1973.

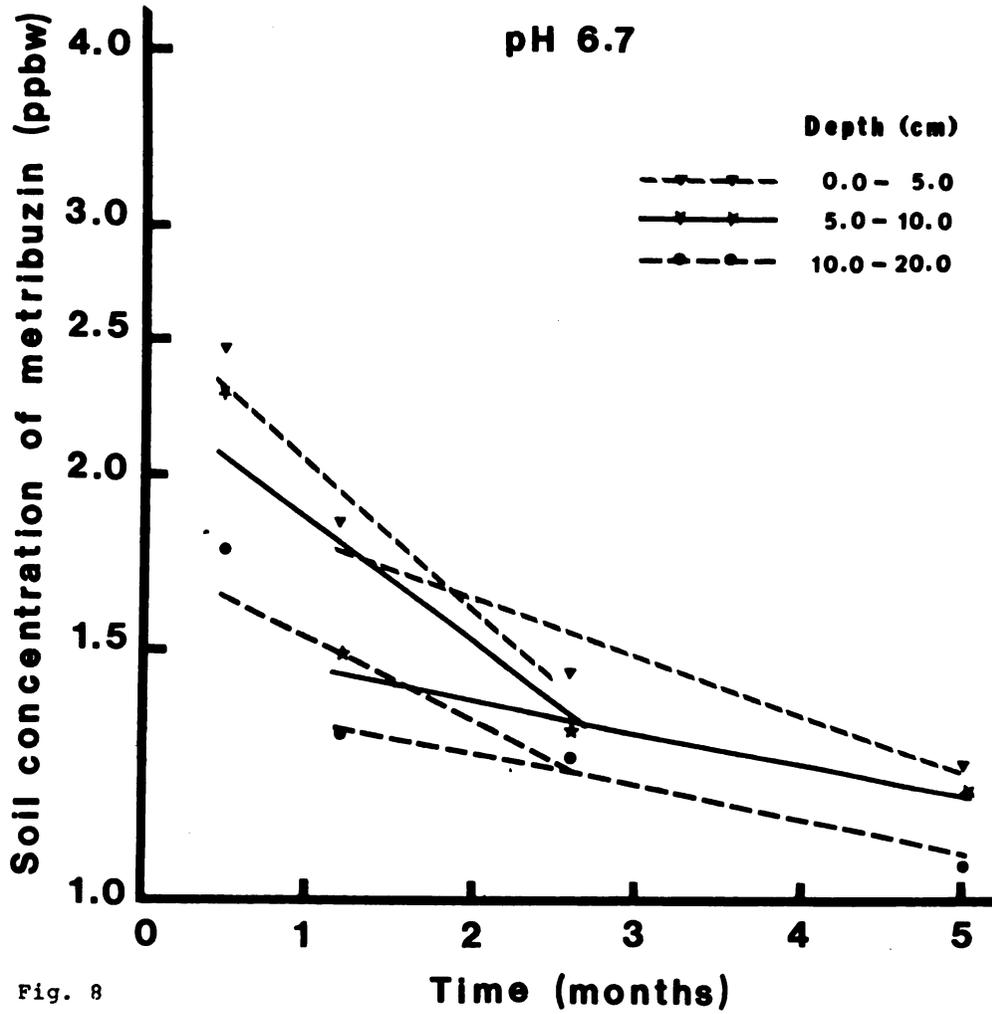


Fig. 8

correlation was obtained when two lines were drawn to represent the rate of degradation (Table 7). Rate constants increased and the half life of metribuzin decreased as soil pH increased. Rate constants decreased and the half life of metribuzin increased at all soil pH levels as depth of sampling decreased (Table 8). There was no indication of a lag period for metribuzin at any of the pH levels or depths of sampling.

Hyzak and Zimdahl (14) found that the pattern of degradation of metribuzin and two analogs in the field fit one straight line. However, Figures 6 to 8 indicate that metribuzin dissipation may best be represented by three or more straight line correlations. Rate constants and half lives observed are dependent on several factors. The values obtained are dependent on rainfall, depth of sampling, time and soil pH (Table 8). Caution should be used in extrapolating degradation patterns and predicting half lives and the kinetic rate law. This value may not be constant, and will change over time, as indicated above.

The decreased rate of metribuzin degradation as soil pH decreased is very likely due to increased adsorption. Hyzak and Zimdahl (14) reported that decreased rate of degradation of metribuzin and two analogs below 0.1 ppm at 35°C may have been due to adsorption. Several investigators have shown that the decomposition of organic

compounds is greatly altered when adsorbed on soil colloids (1,2,24,25). A slow release of metribuzin into the soil solution may have resulted in a reduced rate of degradation by soil microorganisms. Schumacher<sup>1</sup> reported the as-triazine ring appeared to be broken down in a stepwise fashion and C-3 was released as  $^{14}\text{CO}_2$  at a faster rate than C-5 of the as-triazine ring. This would suggest that ring cleavage and subsequent metabolism occurred secondarily to ring substituent metabolism. If substituent metabolism process was significant in soil and necessary for ring cleavage and subsequent metabolism, then it is likely that the rate of substituent metabolism and thus degradation may be reduced if metribuzin was protonated and adsorbed to soil colloids in acid soils.

#### Acknowledgment

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<sup>1</sup>Ibid.

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### CHAPTER 3

#### EFFECT OF SOIL PH ON METRIBUZIN PHYTO- TOXICITY, MICROBIAL DEGRADATION, ADSORPTION, AND MOBILITY

##### Abstract

Metribuzin [4-amino-6-tert-butyl-3-(methylthio)-1,2,5-triazin-5(4H)one] phytotoxicity to corn (Zea mays L.) and soybeans (Glycine max (L.) Merr.) increased with increasing soil pH. Microbial degradation decreased as the soil became more acid. Metribuzin and atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] mobility increased with increasing concentration and soil pH. <sup>14</sup>C-metribuzin had greater mobility on soil thin-layer plates than <sup>14</sup>C-atrazine because of differences in water solubility and basicity. Adsorption increased with decreasing soil pH. The pKa was determined to be 0.99 ± 0.08. Adsorption increased gradually as the soil pH decreased toward the pKa of metribuzin. Protonation of the amine group with subsequent adsorption to soil colloids was postulated to be the reason for the reduction in phytotoxicity, microbial degradation, and mobility of metribuzin at low pH levels.

### Introduction

Relatively little information is available on the behavior of the as-triazines in soil as compared to the s-triazines.

The rate and extent to which a compound is adsorbed and subsequently desorbed may govern its biological toxicity. Adsorption of the s-triazines by soil colloids is dependent on the pH of the system, and many studies with plants have shown that the s-triazines are less phytotoxic under acid soil conditions than under basic conditions (22). Talbert and Fletchall (19) found that an increase in pH resulted in the decreased adsorption of simazine [2-chloro-4,6-bis(ethylamino)-s-triazine] and atrazine by soils. McGlamery and Slife (16) found that atrazine adsorption onto soil humic acid isolated from leonardite increased as pH decreased.

Surface acidity is probably the most important property of the soil or colloidal system in determining the extent and nature of adsorption and desorption of basic organic compounds (6). Bailey et al. (5) found the surface acidity of montmorillonite appears to be three to four pH units lower than the pH of the bulk solution. As the pH decreases, the s-triazine molecule becomes protonated. Adsorption at pH levels in which the compounds were in the cationic form was attributed to cation exchange and to complexing of the s-triazines

molecules with hydrogen ions on the clay surface (22). Weber (23) also showed that the pH of the system and the molecular structure of the s-triazines influenced their adsorption on organic soil colloids in a matter analogous to their adsorption on clay minerals. Adsorption of the compounds was attributed to the complexing of the s-triazines molecules by ionizable  $H^+$  ions on functional groups of the organic colloids and adsorption of the protonated species by cation exchange.

Soil microorganisms are involved in the degradation of s-triazine herbicides. Chemical hydrolysis is probably the major detoxification method of chloro-s-triazines in soil systems, whereas methylthio-s-triazine detoxication is believed to be dependent upon microbial action (13). In nearly all cases only low levels of  $^{14}CO_2$  (0 to 4%) have been evolved from microbial systems treated with  $^{14}C$ -ring-labeled s-triazines. This would indicate that the s-triazine ring structure is fairly resistant to microbial attack (13). Hawck and Stephenson (10) suggested that the symmetrical resonating structure of the s-triazine molecule contributed to differences in degradation rates. Asymmetrical chloro-triazines were degraded more quickly than the corresponding symmetrically-substituted chloro-triazines. They suggested that polymerization resulting in an increased symmetry would lead to stability, whereas labile products of biochemical

transformation tend toward asymmetry. Schumacher<sup>1</sup> reported <sup>14</sup>C-ring-labeled metribuzin was degraded to <sup>14</sup>CO<sub>2</sub> in soil. CO<sub>2</sub> evolution from <sup>14</sup>C-3 and <sup>14</sup>C-5 metribuzin applied soils indicated that the as-triazine ring was degraded in a stepwise manner and C-3 was released more rapidly than was C-5. This would suggest that ring cleavage and subsequent metabolism occurred secondarily to ring substituent metabolism. Lay and Ilnicki (15) used an oat (Avena sativa L.) and cucumber (Cucumis sativus L.) bioassay and observed a 90% loss of metribuzin phytotoxicity in 42 days from a Sassafras loam soil. Hyzak and Zimdahl (12) reported the half-life of metribuzin in sandy loam soil to be 46 days at 20 C and 16 days at 35 C. The loss of metribuzin was linear at both temperatures.

Soil pH may directly or indirectly influence the detoxication of herbicides by affecting the ionic or molecular character of the chemical, the ionic character of soil colloids, the cation exchange capacity, and the inherent capacity of the microbial population to respond to a given chemical (7).

The order of decreasing mobility of seven s-triazines seems to coincide with increasing adsorption

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<sup>1</sup>Schumacher, R. W. 1974. Metabolism of metribuzin in soybeans and soil. Ph.D. Thesis. University of Kentucky, Lexington, Kentucky. 76 pp.

(5,18,19). Nearpass (17) found the mobility of simazine was greater in limed than unlimed soil and it was suggested that decreased adsorption occurred at increased pH.

The objectives of this study were to determine the effect of soil pH on metribuzin (1) activity, (2) microbial degradation, (3) adsorption to soil, and (4) mobility in soil, and to determine the dissociation constant of metribuzin and show a relationship to adsorption.

### Materials and Methods

#### Phytotoxicity

Greenhouse studies were conducted to compare the activity of metribuzin on 'Wirth' soybean and 'Michigan 400' corn grown in soil and nutrient-sand culture at five pH levels. Soil was collected from a field site of Hillsdale sandy loam (Table 1), East Lansing, Michigan, containing 1.5% organic matter and with a pH which had been adjusted over a 15-year period with ammonium sulfate, calcium nitrate or calcium carbonate to 4.6, 5.1, 5.6, 6.1, and 6.7 (24). The pH levels in nutrient-sand culture were adjusted to those of the field. The soil mechanical analysis were similar at all five pH levels. This soil was also used for the study of the pH effect on microbial degradation, adsorption, and mobility of metribuzin.

Seven soybean and corn seeds were planted in washed No. 7 graded quartz sand and soil in 295-ml paper

Table 1.--Physical and chemical properties of Hillsdale soil, East Lansing, Michigan.<sup>a</sup>

Soil type	Texture	Percent <sup>b</sup>			pH	ppm							
		Sand	Silt	Clay		OM	P	K	Ca	Mg	Na	Fe	SO <sub>4</sub>
Hillsdale	Sandy clay loam	53	22	25	1.5	4.6	148	85	80	20	53	80	10
					1.7	5.1	148	97	97	160	53	64	9
					1.4	5.6	66	85	400	40	34	32	15
					1.0	6.1	118	92	240	75	54	44	20
					1.5	6.7	127	103	640	95	49	44	16

<sup>a</sup>Soil analysis performed by the Michigan State University Soil Testing Laboratory, East Lansing, Michigan.

<sup>b</sup>The soil mechanical analysis was similar at all five pH levels.

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cups These paper cups with drainage holes in the bottom were placed in plastic 295-ml cups to allow for subirrigation by daily additions of nutrient solution or distilled water to promote optimum growth. The nutrient solution was Hoagland's No. 1 solution, with pH levels adjusted to that of the soil. A preemergence application of metribuzin at 0.28, 0.56, 0.84, and 1.12 kg/hg at 935 L/ha and 2.11 kg/cm<sup>2</sup> pressure was applied to the soil and nutrient-sand culture. Containers were then placed in the greenhouse at 20 to 30 C with natural illumination supplemented with fluorescent lighting. Plants were thinned to five in number after emergence. After 30 days, height, fresh and dry weight of the soybean and corn plants were measured. All treatments were arranged in a completely randomized design with four replications. The data presented are the means of two experiments, expressed as percent of control.

#### Microbial Degradation and <sup>14</sup>CO<sub>2</sub> Release

Metribuzin degradation in the variable pH soils was investigated in the following way. Soils from the field test plots were collected in August and a 25 g portion of soil was placed in a 300-ml flask. The soils received 5 ml of  $6.3 \times 10^{-4}$  M NH<sub>4</sub>NO<sub>3</sub> while the sodium azide (NaN<sub>3</sub>) treated soils received 5 ml of  $6.3 \times 10^{-4}$  M NH<sub>4</sub>NO<sub>3</sub> plus  $3.9 \times 10^{-2}$  M NaN<sub>3</sub> per flask. The sodium

azide treatment approximates sterilization without altering the soil physical or chemical properties. A 1-ml portion of radioactive  $^{14}\text{C}$ -metribuzin (.0256  $\mu\text{Ci}$ ; Sp. act. = 1.5 mCi/mM) was added to each flask. A 2-ml plastic beaker containing 1-ml of 1 M KOH was suspended in the flask to collect the  $^{14}\text{CO}_2$ . The flask was sealed with a rubber stopper and placed in a room at  $25 \pm 2$  C under low light intensity. The flasks were sampled at one week intervals for 12 weeks after treatments. At sampling time, the content of the 2-ml beaker were placed in a vial containing 15 ml of 1:1 (v/v) CAB-O-SIL<sup>R</sup> solution: 60 g naphthalene, 4 g PPO, 0.2 g POPOP, 100 ml methanol, 20 ml ethylene glycol filled to a liter with p-1,4-dioxane. The contents of the vials were shaken to assure even distribution and radio-assayed by scintillation spectrometry. The treatments were replicated two times in a completely randomized design. The data presented are the means of two experiments.

#### Determination of the Dissociation Constant (pKa)

The dissociation constant of metribuzin was determined spectrophotometrically (1,21). The pH meter was standardized with buffers at pH 4, 7 and 10 at room temperature. A 125-ml portion of  $10^{-4}$  M solution of (99-100% purity) technical grade metribuzin was titrated from pH 5.5 to pH 0.0 with 6.0 N HCl and from pH 5.5 to

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pH 12.0 with 1 N NaOH. The analytical wavelength used for determination of the isoelectric point was 264 nm. The isoelectric point was determined by finding the point of most rapid change in optical density and through the use of the equation for determining pKa (3). The titration was repeated several times with similar results.

### Adsorption Study

Adsorption of  $^{14}\text{C}$ -metribuzin (sp. act. = 1.5 mCi/mM) was determined using slight modifications of the adsorption procedure developed by Talbert and Fletchall (19). With the soil previously air-dried and later screened through a 1 mm sieve, one gram was weighed into a 15-ml centrifuge tube and 5 ml of 0.0112  $\mu\text{Ci}/5\text{ ml}$  solution of  $^{14}\text{C}$ -metribuzin was added. The solution added to the test tube had been adjusted to the pH of the soil. The tube was stoppered with a polyethylene-covered rubber stopper. Each sample was equilibrated for 24, 72, 144, and 288 hr at 25 C in a horizontal shaker reciprocating at 120 strokes per minute. The sample was centrifuged at 12,000 x g for 20 minutes. A 0.5 ml sample of the supernatant was removed and placed in 15 ml of a scintillation solution consisting of 0.1 g of 1,4-bis [2-(4-methyl-5-phenyloxazolyl)]-benzene (dimethyl-POPOP), 5.0 g of 2,5-diphenyloxazole (PPO), 50 g of naphthalene, 380 ml of toluene, 380 ml of 1,4-dioxane, and 240 ml of absolute ethanol. The samples

were counted for 10 minutes and metribuzin adsorption was determined by comparing the radioactivity in a sample with soil to a sample of solution without soil (79.4 nM  $^{14}\text{C}$ -metribuzin/test tube). The difference was considered to be the quantity of herbicide bound and was expressed as a percent of  $^{14}\text{C}$ -metribuzin adsorbed.

The effect of soil pH on adsorption of metribuzin was also studied by Soxhlet extraction and gas chromatograph analysis (12). The same soil used in the previous adsorption studies was used. Herbicide standards were prepared by dissolving the analytical grade metribuzin (99 to 100% purity) in distilled acetone. Fifty grams of soil, pH levels 4.6, 5.6, and 6.7, were placed in beakers and 5 ml of acetone solution were uniformly pipetted over the soil surface. The herbicide was thoroughly mixed with the soil to obtain a uniform concentration of 1.0 and 0.1 ppm, w/w basis. The soil and herbicide were allowed to equilibrate for 48 hours. The 50 grams of soil were extracted in a Soxhlet apparatus with 200 ml of 80% methanol for five hours with a recycling time of approximately five minutes. After extraction, 25 ml of distilled water was added to the extractant and the solvent was evaporated to 20 to 30 ml. The aqueous phase was extracted with one 50 ml and two 25 ml aliquots of glass distilled benzene to bring the final volume to 100 ml. The aqueous-benzene mixture

was vigorously shaken for 10 to 15 seconds and allowed to separate into its respective phases. Thirty grams of anhydrous sodium sulfate was added to each bottle. The aqueous phase was drained into a beaker and discarded. The samples were then placed in the refrigerator until analysis.

Herbicide concentration in the benzene extracts was determined with a gas chromatograph equipped with a Beckman helium arc discharge electron-capture detector. A 183 cm by 2 mm (I.D.) glass column was packed with 80/100 mesh Chromosorb Gas-Chrom Q coated with 3% SE-30. Injector, column, and detector temperatures were 250, 190 and 310 C, respectively. Helium at a flow rate of 40 ml/min was used for the carrier gas. Retention time of 1.85 min was obtained. The range of linearity was from 0.05 ng to 5 ng, and the detection limit of the method was 0.01 ppm in soil. Herbicide content was determined by comparing heights of sample to peak heights of known standards. A series of standards of different concentrations of herbicide was injected to determine the range of linearity and sensitivity before, during, and after each day's run of samples.

#### Mobility on Soil Thin-Layer Plates

The procedure of Helling (11) was used for making soil thin-layer plates using a standard thin-layer

chromatographic spreader. Soil collected from the field at variable pH levels was air dried and screened through a 500  $\mu\text{m}$  screen. Duplicate 20 by 20 cm plates were coated with a 500  $\mu\text{m}$  thick layer of soil at pH levels 4.6, 5.1, 5.6, 6.1, and 6.7. The plates were allowed to dry and then spotted 2 cm from the bottom with 0.005 and 0.10  $\mu\text{Ci}$  of  $^{14}\text{C}$ -metribuzin and  $^{14}\text{C}$ -atrazine in 10  $\mu\text{l}$  of solution. The plates were allowed to equilibrate for 30 minutes. The lower 5 mm of each plate was then submerged in water and allowed to chromatograph ascendingly to a distance of 15 cm above the origin. The plates were air-dried for 24 hr and exposed to Kodak no-screen medical x-ray film for 14 days. The frontal movement, or Rf values were calculated from the radioautographs. After radioautography, consecutive 0.5-cm zones were removed. Direct liquid scintillation radioassay of  $^{14}\text{C}$ -labeled herbicide in soil was used (14). The data presented are the means of two experiments replicated twice.

## Results and Discussion

### Effect of Soil pH on Metribuzin Phytotoxicity

Metribuzin phytotoxicity on corn and soybeans increased with increasing soil pH (Tables 2 and 4). Whereas, in a nutrient-sand culture adjusted to comparable soil pH levels, there was no reduction in plant dry weight as pH increased. The nutrient-sand culture

showed only a herbicide rate response (Tables 3 and 5). However, in soil with the same rate of metribuzin at soil pH levels 4.6, 5.1, 5.6, 6.1, and 6.7 phytotoxicity increased as soil pH increased (Tables 3 and 5). There was significant difference between the high and low pH levels. Figure 1 shows the effect of soil pH on metribuzin phytotoxicity to soybeans. The parameters of plant height and fresh weight also showed the soil pH response. Similar results were observed in field studies (see Chapter 2). The lack of plant uptake of metribuzin at low soil pH levels could be due to rapid microbial degradation, adsorption to the soil, lack of plant absorption, or several of these factors.

#### Effect of Soil pH on Microbial Degradation and $^{14}\text{C}$ Release

$^{14}\text{C}$ -5-ring-labeled metribuzin was readily degraded in the soil over a 12-week period (Table 6). Treatment of the soil with sodium azide drastically reduced the evolution of  $^{14}\text{C}$  release from the soil (Figure 2). Degradation of metribuzin increased with the increasing soil pH (Figure 3). All soil pH levels were significantly different from each other. Figure 4 shows a highly significant positive correlation of percent  $^{14}\text{C}$  evolved as  $^{14}\text{C}$  on soil pH. The percent of  $^{14}\text{C}$  evolved as  $^{14}\text{C}$  at pH 4.6 and 6.7,  $\pm$  sodium azide, was 4.6 versus 0.4 and 17.9 versus 1.1 respectively. The reduction in evolution

Table 2.--Effect of soil pH on metribuzin phytotoxicity to corn as measured by reduction in dry weight of 1-month-old corn plants.

pH	Metribuzin (kg/ha)			
	0.28	0.56	0.84	1.12
	(% of control) <sup>a</sup>			
4.6	93.0 j	78.9 ghi	82.0 ghij	61.3 cde
5.1	91.1 ij	76.3 fgh	66.0 def	56.9 bcd
5.6	86.1 hij	70.9 efg	59.3 bcde	53.1 bcd
6.1	81.5 ghij	64.4 def	54.9 bcd	47.0 ab
6.7	71.9 efg	60.4 cde	49.5 abc	39.9 a

<sup>a</sup>Means with common letters are not significantly different at the 5% level by Duncan's multiple range test.

Table 3.--Effect of pH on metribuzin phytotoxicity to corn grown in a nutrient-sand culture, measured as reduction in dry weight of 1-month-old corn plants.

pH	Metribuzin (kg/ha)			
	0.28	0.56	0.84	1.12
	(% of control) <sup>a</sup>			
4.6	43.9 fg	34.5 cde	26.5 abc	23.9 ab
5.1	42.4 efg	30.0 bcd	21.8 ab	22.1 ab
5.6	46.1 g	24.5 ab	21.3 ab	20.8 a
6.1	34.5 cde	26.3 abc	24.0 ab	23.3 ab
6.7	36.1 def	28.5 abcd	22.4 ab	19.9 a

<sup>a</sup>Means with common letters are not significantly different at the 5% level by Duncan's multiple range test.

Table 4.--Effect of soil pH on metribuzin phytotoxicity to soybeans as measured by reduction in dry weight of 1-month-old soybean.

pH	Metribuzin (kg/ha)			
	0.28	0.56	0.84	1.12
	(% of control) <sup>a</sup>			
4.6	101.81 i	96.6 hi	87.4 gh	73.0 ef
5.1	95.5 hi	96.8 hi	86.8 fgh	64.3 cd
5.6	85.4 efgh	80.4 efg	71.3 de	48.0 b
6.1	95.5 hi	78.3 defg	57.0 bc	46.3 b
6.7	75.0 defg	71.6 de	53.5 bc	24.3 a

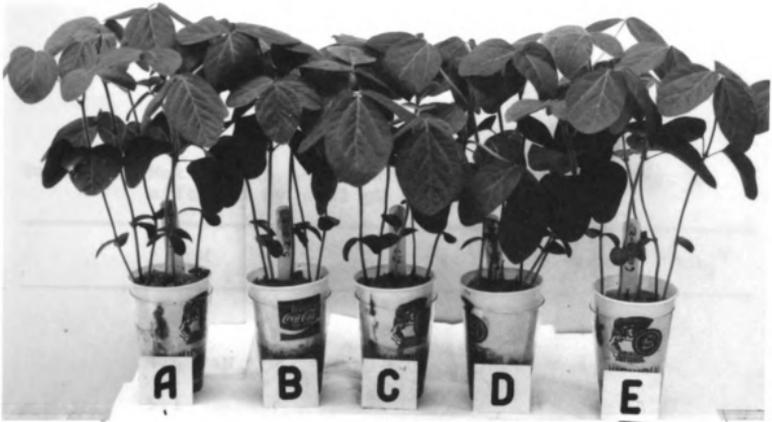
<sup>a</sup>Means with common letters are not significantly different at the 5% level by Duncan's multiple range test.

Table 5.--Effect of pH on metribuzin phytotoxicity to soybeans grown in a nutrient-sand culture, measured as reduction in dry weight of 1-month-old soybean.

pH	Metribuzin (kg/ha)			
	0.28	0.56	0.84	1.12
	(% of control) <sup>a</sup>			
4.6	54.5 c	20.4 b	19.9 b	14.6 ab
5.1	56.9 c	17.8 ab	17.6 ab	11.9 ab
5.6	48.8 c	16.8 ab	11.1 ab	8.8 a
6.1	55.3 c	18.8 ab	13.4 ab	12.5 ab
6.7	54.4 c	17.4 ab	11.9 ab	11.3 ab

<sup>a</sup>Means with common letters are not significantly different at the 5% level by Duncan's multiple range test.

Fig. 1.--Soil pH effect on tolerance of soybeans to metribuzin (0.00 and 0.56 kg/ha). Soil pH from left to right (A) 4.6 (B) 5.1 (C) 5.6 (D) 6.1 and (E) 6.7.



SENCOR  
**0.0** KG/HA



SENCOR  
**0.56** KG/HA

Fig. 1

Table 6.--Metribuzin degradation to CO<sub>2</sub> in 12 weeks, as affected by soil pH and sodium azide.

pH	% <sup>14</sup> C evolved as <sup>14</sup> CO <sub>2</sub> <sup>b</sup>
4.6	4.6 c
4.6 NaN <sub>3</sub>	0.4 a
5.1	8.6 d
5.6	10.2 e
6.1	13.5 f
6.7	17.9 g
6.7 NaN <sub>3</sub>	1.1 b

<sup>a</sup>Means within columns followed by similar letters are not significantly different at the 5% level by Duncan's multiple range test. The sodium azide treatment approximates sterilization.

<sup>b</sup>0.0256 μCi/flask.

Fig. 2.--Effect of soil pH and sodium azide on the degradation of  $^{14}\text{C}$ -5-labeled metribuzin to  $^{14}\text{CO}_2$  at pH 4.6 and 6.7 + sodium azide.

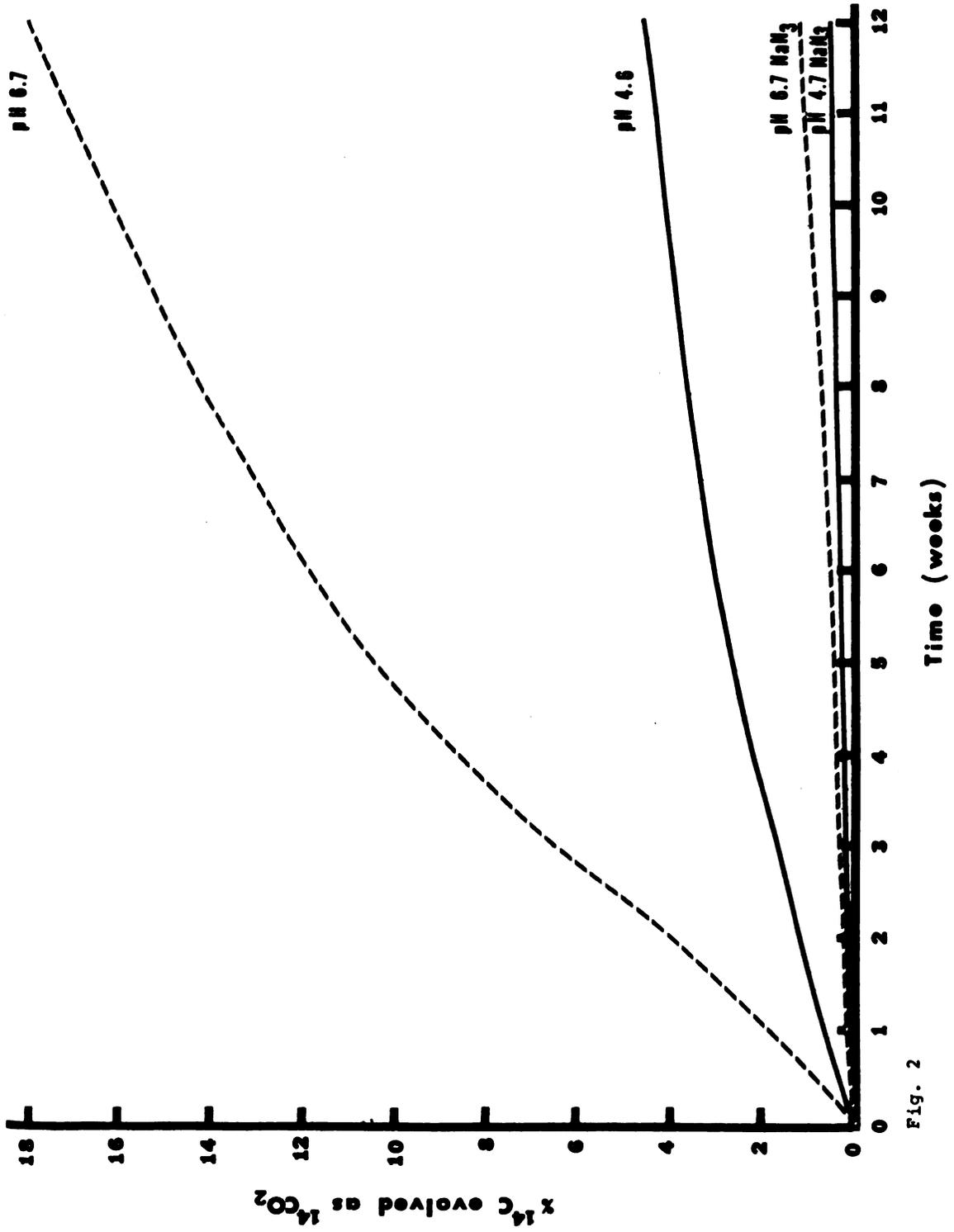


Fig. 2

Fig. 3.---Effect of soil pH on the degradation of  $^{14}\text{C}$ -5-labeled metribuzin to  $^{14}\text{CO}_2$  at pH 4.6, 5.6, and 6.7.

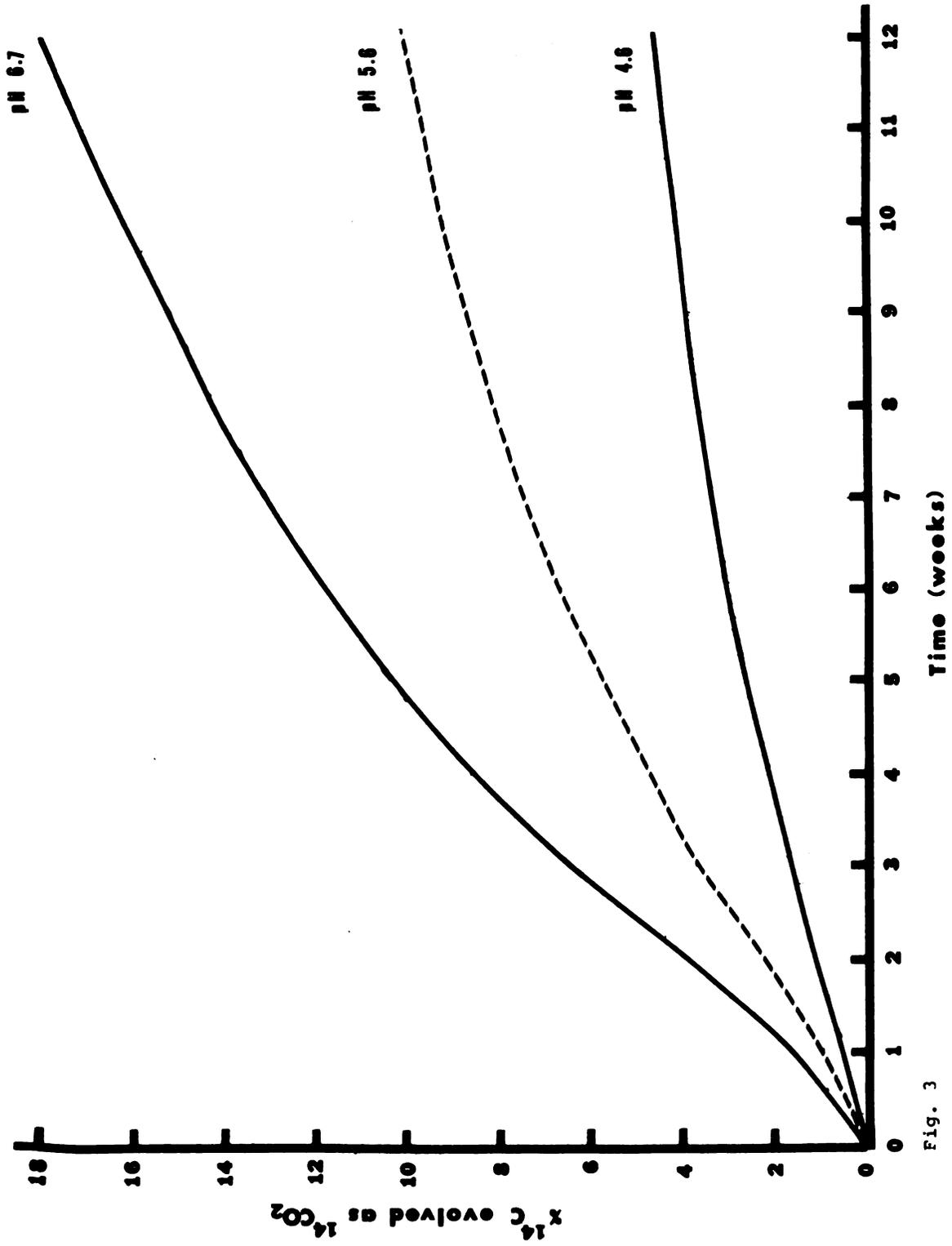


Fig. 3

Fig. 4.--Positive correlation with soil of percent  $^{14}\text{C}$   
evolved as  $^{14}\text{CO}_2$  in 12 weeks.

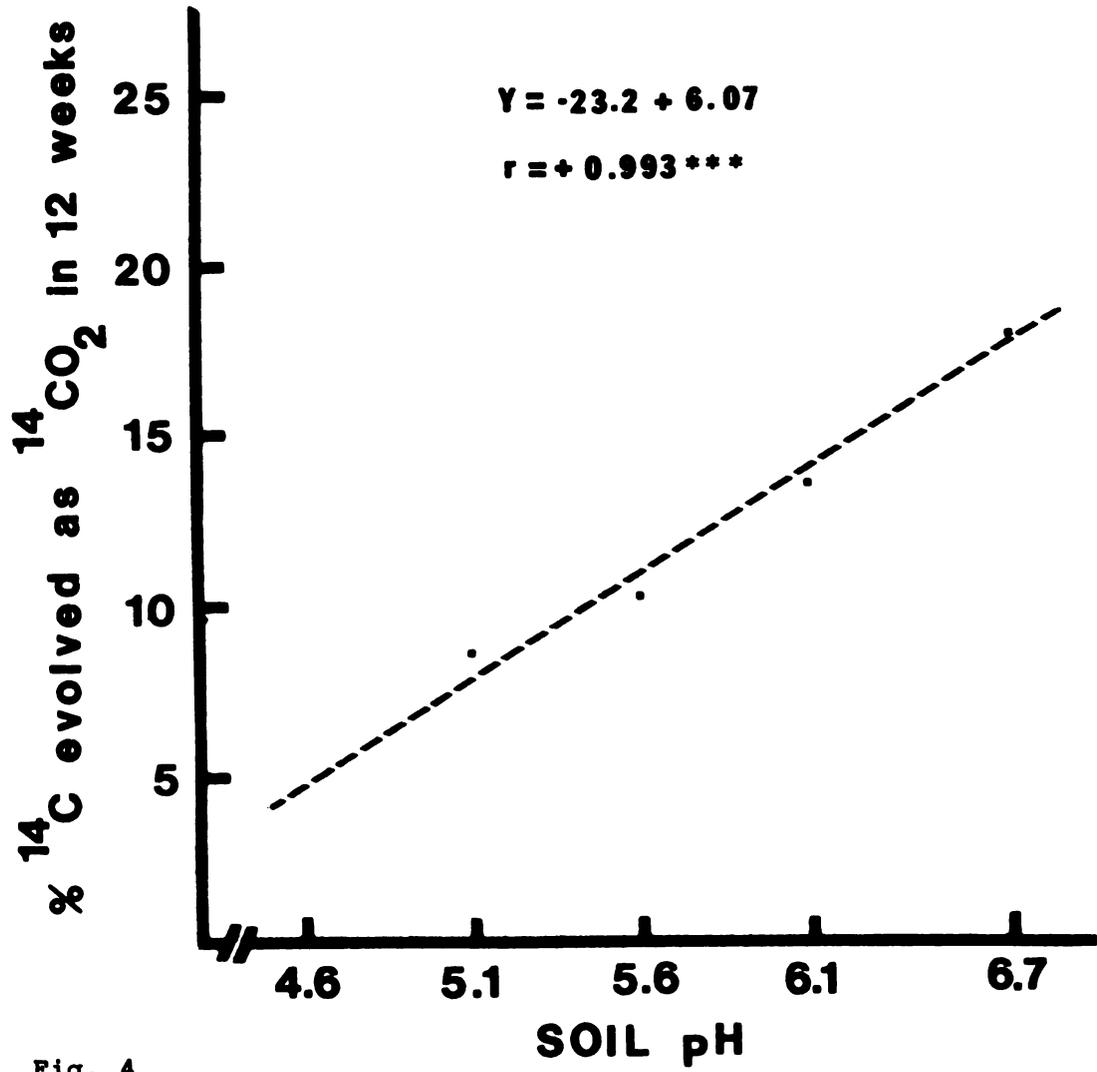


Fig. 4

of  $^{14}\text{CO}_2$  due to the addition of sodium azide, was significant at both pH levels.

There are a number of reasons why metribuzin degradation may be reduced as the pH of the soil decreased: (1) metribuzin may have been bound more tightly to the soil and thus was less available to the organisms in acid soils, (2) variation in the microorganism population over the pH range studied, and (3) a pH effect on microbial metabolism over the pH range studied. The most plausible explanation for the decreased rate of metribuzin degradation in acid soil, appears to be adsorption. Several investigators (2,3,12,22) have suggested that a substrate readily consumed by the soil microflora can be protected if it becomes adsorbed or deposited at microsites inaccessible to soil microorganisms. If the chemical hydrolysis process was significant in soil, then it is likely that the rate of hydrolysis and thus degradation may be reduced if Metribuzin is adsorbed to soil colloids (12).

#### Determination of the Dissociation Constant (pKa)

Figure 5 shows the spectrophotometric determination of the pKa of metribuzin at 264 nm and the resulting plot of absorbance versus pH. The pKa of metribuzin is  $0.99 \pm 0.08$  compared to atrazine with a pKa of 1.68 (22) and propazine with a pKa of 1.85 (22). Figure 6 shows the chemical structure of propazine and the proposed

Fig. 5.--The spectrophotometric determination of the pKa of metribuzin at 264 nm.

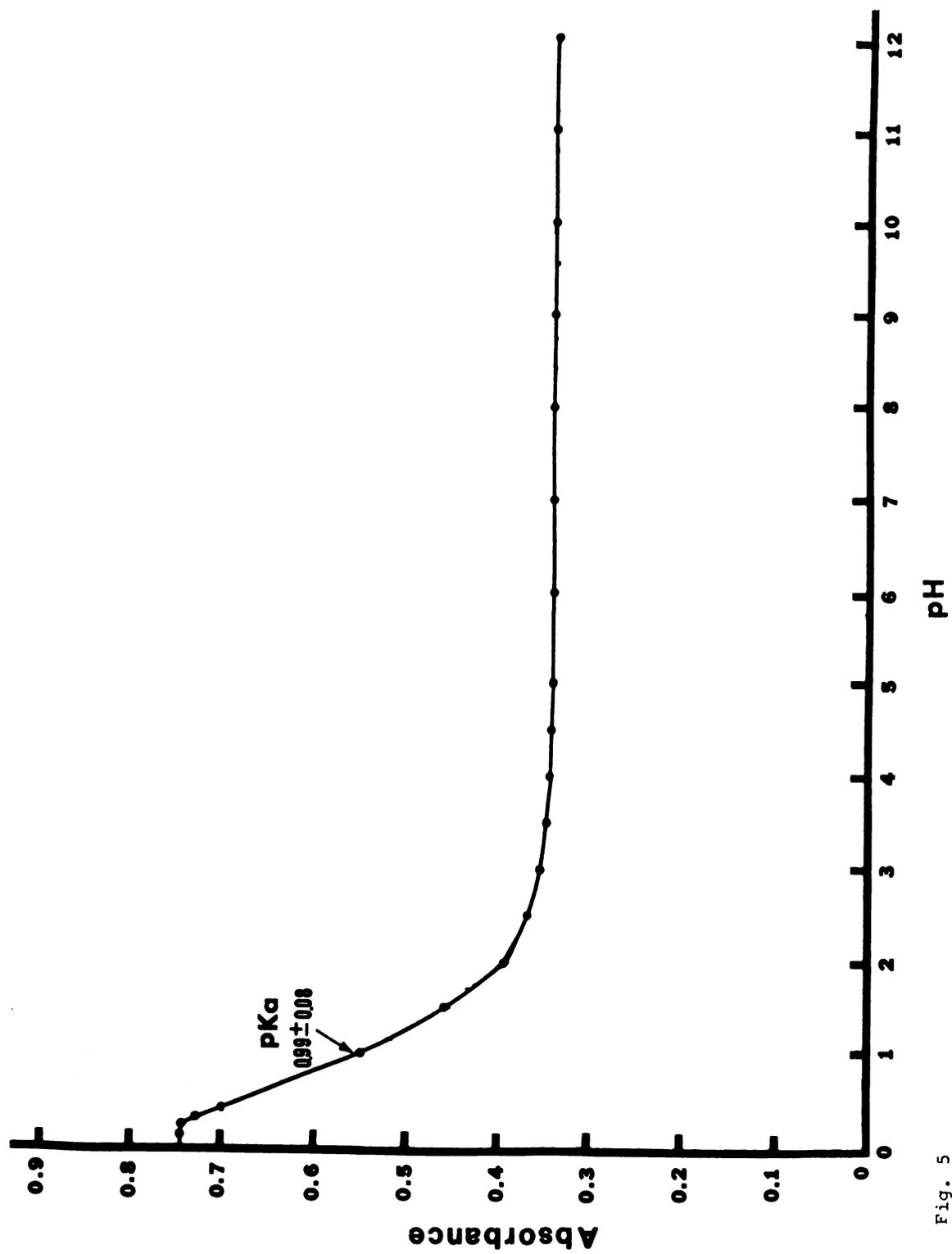
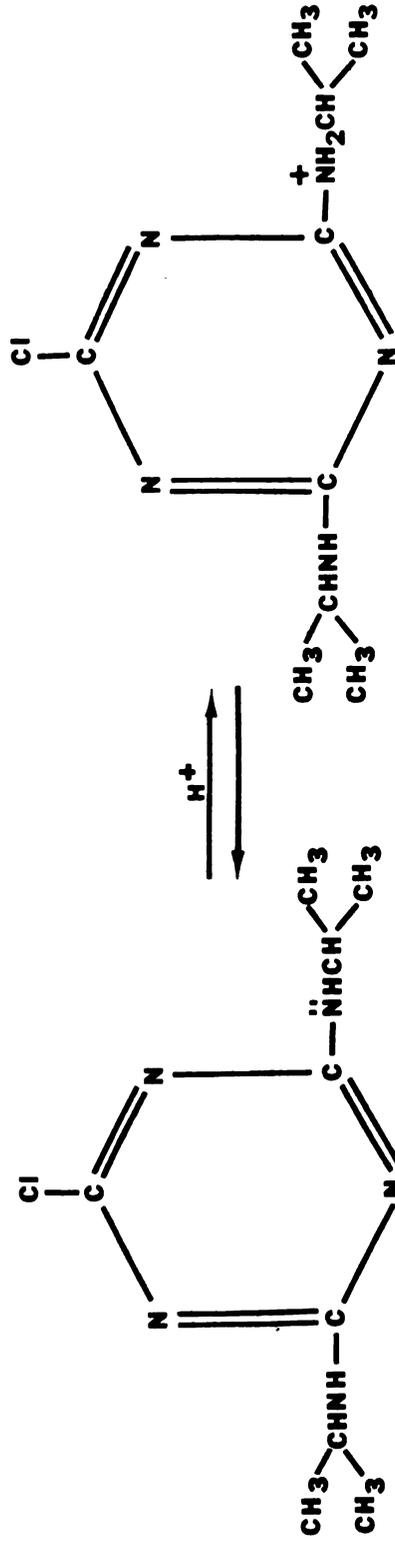


Fig. 5

Fig. 6.--Chemical structure of propazine and the proposed ionization equation (22).



$pK_a = 1.85$

**Propazine**

Fig. 6

ionization equation (22). Figure 7 shows the chemical structure of metribuzin and proposed ionization equation.

The pKa of a compound indicates the degree of acidity or basicity that a compound will exhibit and therefore is important in determining both the extent of adsorption by and the ease of desorption from colloidal systems. There may be other possible ionization equations for metribuzin.

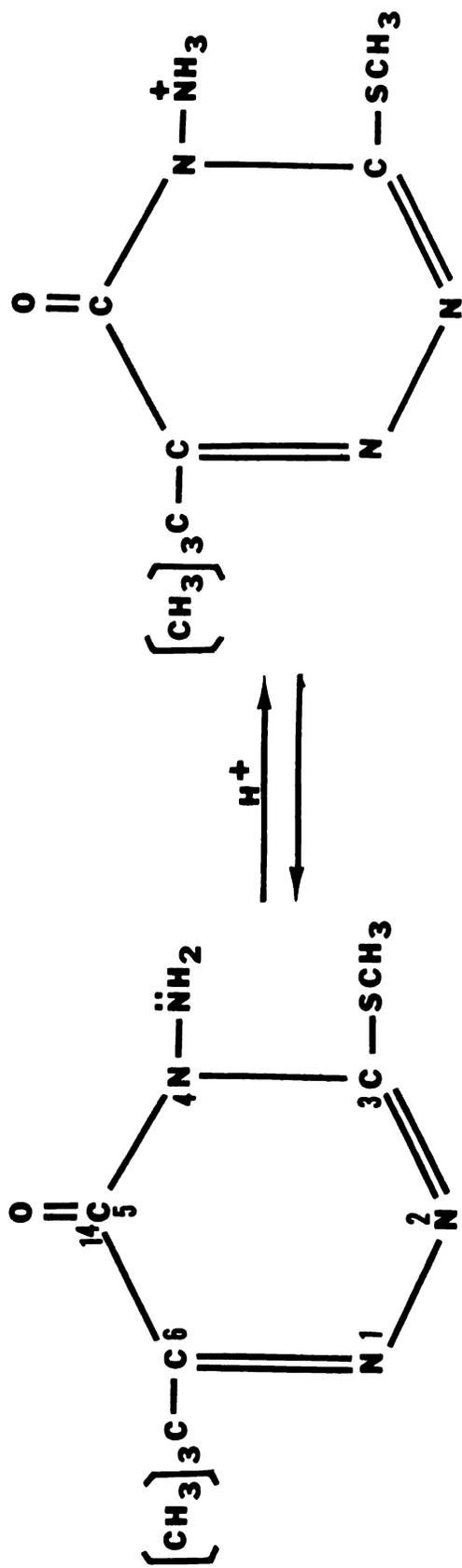
#### Effect of Soil pH on Metribuzin Adsorption

The adsorption of  $^{14}\text{C}$ -metribuzin increased with time and with a decrease in soil pH (Table 7). The differences between the five soil pH levels were significant.

The pH of the soil had an influence on the extraction efficiency of metribuzin from the soil (Table 8). There were significant differences between the three soil pH levels at both the 1.0 and 0.1 ppmw. A greater percentage of metribuzin was extracted at the higher concentration (1.0 ppmw). As soil pH decreased, the percentage of metribuzin extracted at both 1.0 and 0.1 ppmw decreased, indicating that more metribuzin was bound to the soil at the lower pH levels.

The above findings of metribuzin activity in relation to soil pH are similar to those found with s-triazines. In an adsorption study of 13 related s-triazines on montmorillonite, Weber (20) found that the

Fig. 7.--Chemical structure of metribuzin and the proposed ionization equation.



$pK_a = 0.99 \pm 0.08$

## Chemical structure of metribuzin and proposed ionization equation

Fig. 7

Table 7.--<sup>14</sup>C-metribuzin adsorption by Hillsdale sandy clay loam at various pH levels.

pH	Time after treatment (hr)				Average
	24	72	144	288	
	<sup>14</sup> C-metribuzin adsorption <sup>a</sup> (% adsorption) <sup>b</sup>				
4.6	15.6 f	17.8 h	21.1 i	27.1 k	20.4 e
5.1	12.4 cd	13.0 d	18.5 h	21.9 j	16.4 d
5.6	10.4 b	11.8 c	16.8 g	20.8 i	14.9 c
6.1	9.9 ab	10.6 b	13.8 e	17.9 h	13.0 b
6.7	9.2 a	10.2 b	11.7 c	15.5 f	11.6 a

<sup>a</sup>Means followed by similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>79.4 nM/test tube.

Table 8.--Extraction efficiency of metribuzin from Hillsdale sandy clay loam at several pH levels.<sup>a</sup>

Soil pH <sup>b</sup>	% extraction efficiency	
	1.0 ppm	0.1 ppm
6.7	99.1 c	95.3 c
5.6	90.6 b	87.2 b
4.6	71.1 a	63.2 a

<sup>a</sup>Means within columns followed by similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>Hillsdale sandy clay loam (Table 1).

maximum adsorption of all the compounds occurred at a pH in the vicinity of the dissociation constant of each compound. It has also been reported by Bailey (5) that the surface acidity of montmorillonite clay appears to be three to four pH units lower than the pH of the bulk solution. The pKa of metribuzin has been reported here to be  $0.99 \pm 0.08$ . Considering the surface acidity of clays and the pKa of metribuzin, one can postulate that similar mechanisms of adsorption are involved with metribuzin at low pH values as with the s-triazines. Frissel and Bolt (8) reported also, with the chloro-s-triazines, that at about three to four pH units above the dissociation constant adsorption started to increase as pH decreased.

#### Effect of Soil pH on Mobility of Metribuzin and Atrazine

Greater movement of metribuzin and atrazine, with the water front, was observed as pH and herbicide concentration increased on soil TLC plates. Table 9 shows the effect of concentration and pH on atrazine movement. There was a noticeable increase in movement of metribuzin (Table 10) compared to atrazine (Table 9). Figures 8 and 9 show the quantitative movement of <sup>14</sup>C-labeled herbicide with distance. Atrazine moved less and more remained at the origin compared to metribuzin. More atrazine was adsorbed at the origin at pH level 4.6 than at the higher pH levels (Figure 10) compared to

Table 9.--Effect of soil pH on the mobility of  $^{14}\text{C}$  atrazine on soil TLC plates.

pH	$^{14}\text{C}$ Rf <sup>a</sup> atrazine	
	<u>0.05 <math>\mu\text{Ci}</math></u>	<u>0.10 <math>\mu\text{Ci}</math></u>
4.6	.25 a	.26 ab
5.1	.27 b	.27 b
5.6	.29 c	.31 d
6.1	.31 d	.32 d
6.7	.32 d	.34 e

<sup>a</sup>Means followed by similar letters are not significantly different at the 5% level by Duncan's multiple range test.

Table 10.--Effect of soil pH on the mobility of  $^{14}\text{C}$  metribuzin on soil TLC plates.

pH	$^{14}\text{C}$ Rf <sup>a</sup> metribuzin	
	<u>0.05 <math>\mu\text{Ci}</math></u>	<u>0.10 <math>\mu\text{Ci}</math></u>
4.6	.50 a	.51 ab
5.1	.51 ab	.52 bc
5.6	.52 bc	.53 cd
6.1	.54 de	.56 f
6.7	.58 g	.60 h

<sup>a</sup>Means followed by similar letters are not significantly different at the 5% level by Duncan's multiple range test.

Fig. 8.--Effect of concentration on movement of atrazine at pH 6.7, using soil thin-layer chromatography. Radioactivity per (0.5-cm) segment (% total recovery) versus cm.

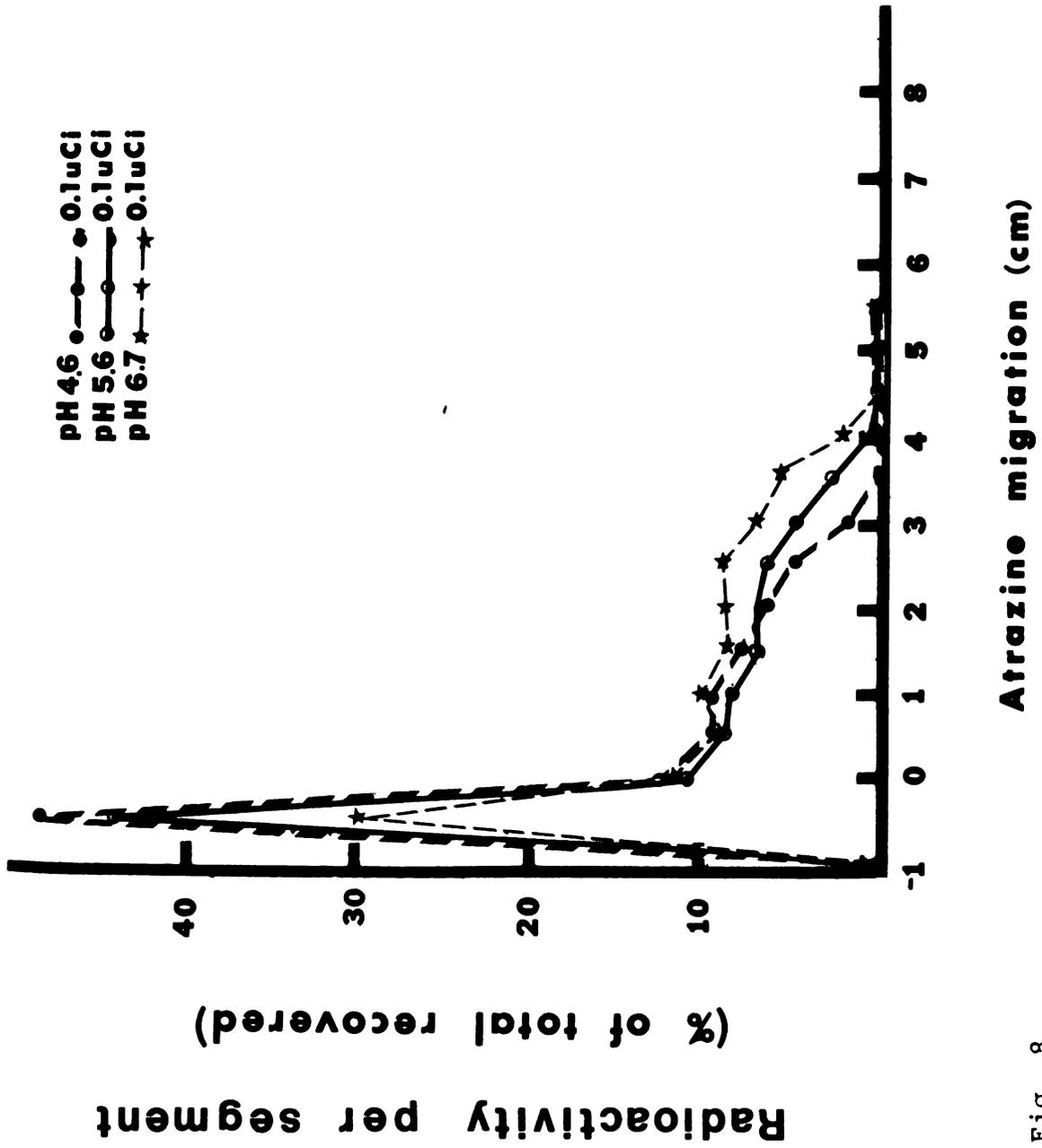


Fig. 8

Fig. 9.--Effect of concentration on movement of metribuzin at pH 6.7, using soil thin-layer chromatography. Radioactivity per (0.5-cm) segment (% total recovery) versus cm.

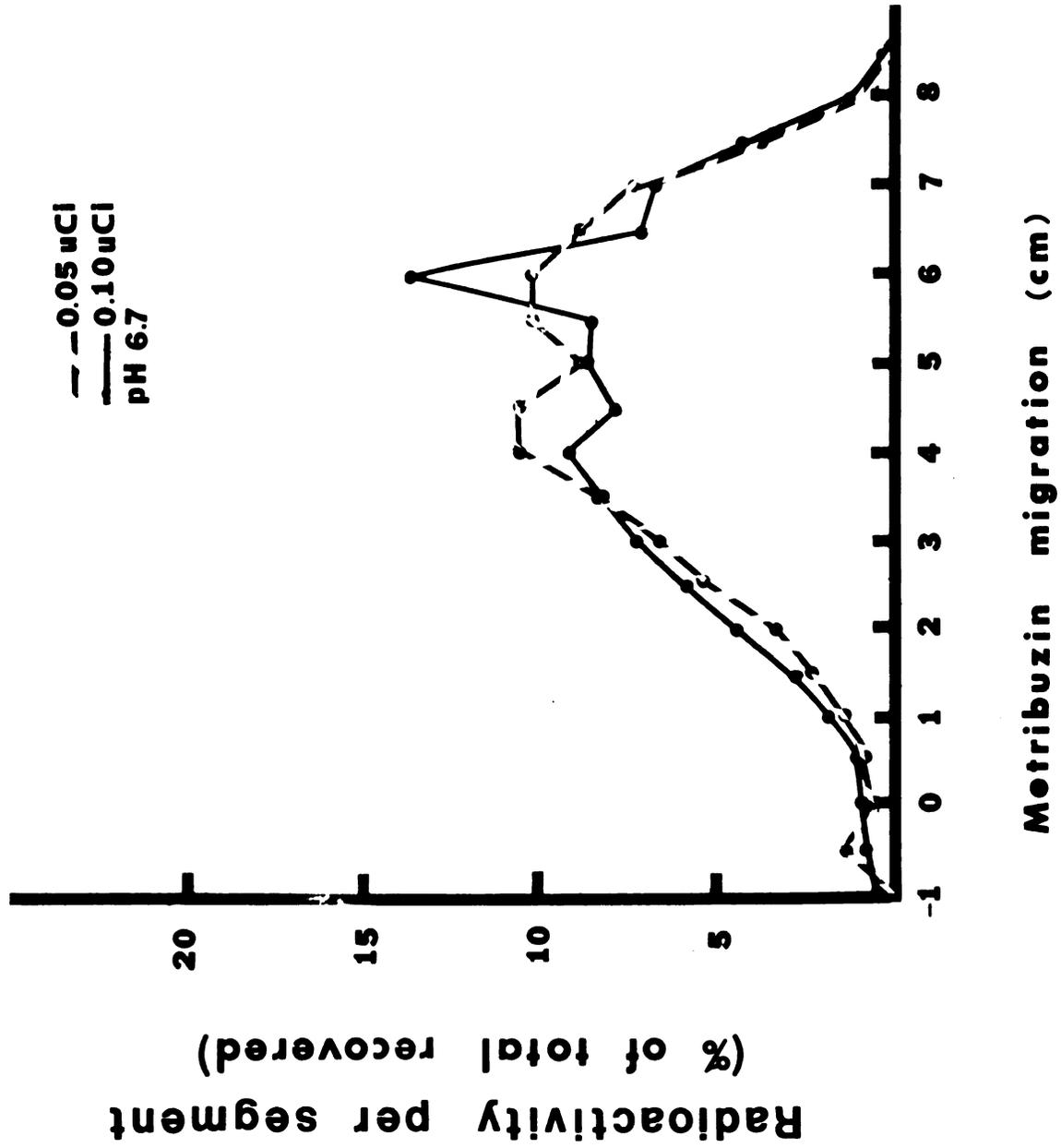


Fig. 9

Fig. 10.--Effect of soil pH on movement of  $^{14}\text{C}$ -atrazine, using soil thin-layer chromatography. Radioactivity per (0.5 cm) segment (% of total recovery) versus cm.

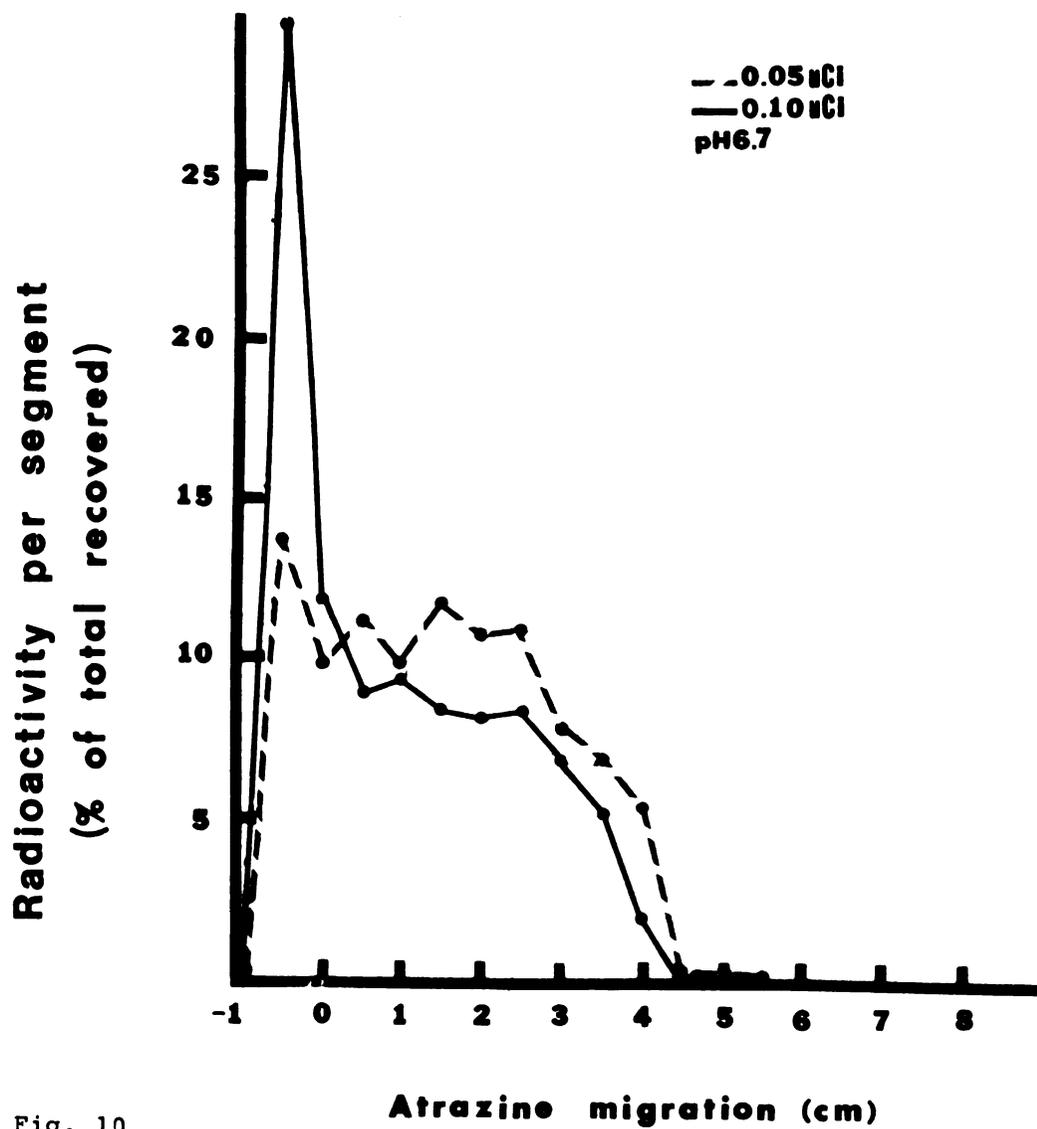


Fig. 10

metribuzin (Figure 11). The degree of adsorption at the origin at all three pH levels was less with metribuzin than with atrazine, whereas, mobility was greater. Differences in adsorption and movement may be attributed to differences in water solubility, basicity, and steric effects. All three herbicide properties would affect the entrance of the compound into solution and adsorption to soil particles. Metribuzin with a water solubility of 1200 ppm would enter into solution more quickly than atrazine. Atrazine is more basic in chemical character than is metribuzin which probably accounts for the observed differences in adsorption.

#### Summary

Studies with soils of varying pH indicate that metribuzin phytotoxicity increased with increasing soil pH. Whereas, in the nutrient-sand culture, there was no reduction in dry weight as pH increased. Microbial degradation increased as the soil pH increased. With 4.6% and 17.9 %  $^{14}\text{CO}_2$  being released at soil pH 4.6 and 6.7 respectively. Adsorption increased with decreasing soil pH. The dissociation constant was determined to be  $0.99 \pm 0.08$ . The dissociation constant was shown to be important in determining the adsorption by colloidal systems. Positive adsorption increased gradually as the soil pH decreased toward the pKa of metribuzin. Thus, adsorption and not microbial degradation, is the reason

Fig. 11.--Effect of soil pH on movement of  $^{14}\text{C}$ -metribuzin, using soil thin-layer chromatography. Radioactivity per (0.5 cm) segment (% of total recovery) versus cm.

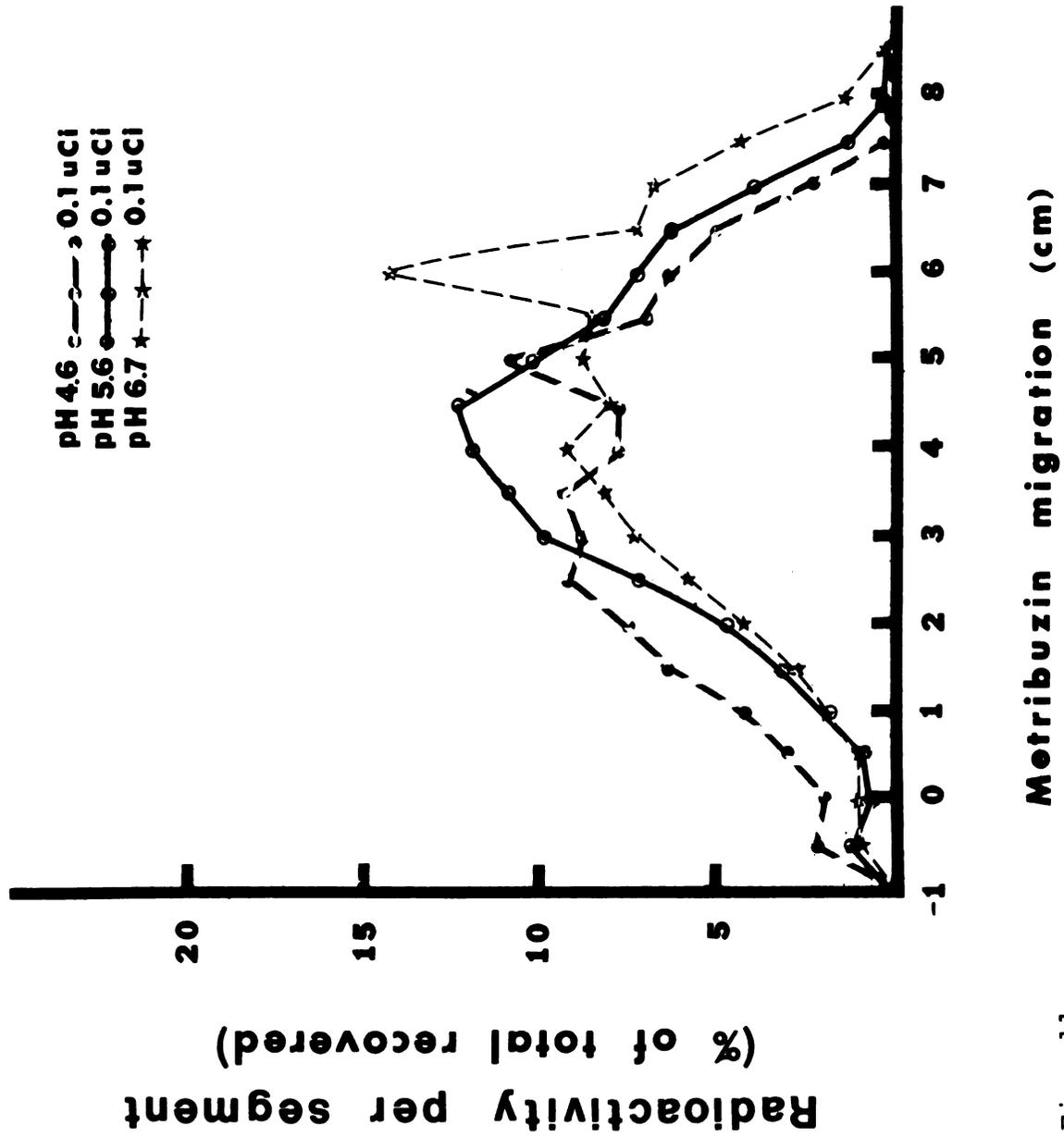


Fig. 11

for the decreased phytotoxicity observed at low pH levels on corn and soybeans. This is postulated to occur through protonation of the amine group on metribuzin; which increases with a decrease in soil pH.  $^{14}\text{C}$ -metribuzin and  $^{14}\text{C}$ -atrazine mobility increased with increasing concentration and soil pH. Metribuzin was shown to be more mobile on soil thin-layer plates than atrazine. A greater percentage of atrazine was adsorbed at the origin of application and not allowed to migrate with the water front.

#### Acknowledgment

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## CHAPTER 4

### SUMMARY AND CONCLUSIONS

Field, greenhouse and laboratory studies were initiated to determine the effect of soil pH on metribuzin activity, dissipation, microbial degradation, adsorption, mobility in soil, and to determine the dissociation constant and show how it relates to adsorption.

Metribuzin activity in the field increased with increasing soil pH at 0.56, 0.84 and 1.12 kg/ha. Fall panicum control, number of dead corn and soybean plants, and crop injury ratings increased, whereas plant height and grain yield decreased as the soil pH increased. The lack of plant uptake of metribuzin at low soil pH levels could be due to rapid microbial degradation, adsorption to the soil colloids, lack of plant adsorption, or several of these factors.

Greenhouse data on phytotoxicity to corn and soybeans grown in a nutrient-sand culture versus soil at comparable pH levels supported the field data. Corn and soybeans grown in soil and treated with metribuzin showed a pH-sensitive response with a reduction in dry weight per plant as pH increased. Whereas, in nutrient-sand culture there was no difference in the reduction in dry weight as

pH increased. Reduction in herbicide concentration resulting from adsorption by soil colloids results in less absorption by plant roots at lower pH levels as observed in the field and greenhouse. Adsorption studies support these observations, with increased adsorption as soil pH decreases.

Metribuzin residue analysis of soil samples from the field showed greater amounts of residue extractable at soil pH 6.7 than 4.6. Most of the metribuzin was found in the upper 5 cm of the soil profile. Metribuzin leaching increased with increasing soil pH. This is an indication of increased adsorption as pH decreased. Metribuzin disappearance from field soil followed pseudo first-order kinetics. Rate constants increased and the half life of metribuzin decreased as soil pH increased. Rate constants decreased and the half life of metribuzin increased at all soil pH levels as depth of sampling decreased. Laboratory studies on microbial degradation of  $^{14}\text{C}$ -5-labeled metribuzin showed decreased  $^{14}\text{CO}_2$  release as the soil became more acid. These results and those from the field indicate that metribuzin is being bound more tightly to the soil colloids and thus unavailable to the microorganisms in acid soils. If the substituent metabolism process is significant in soil and necessary for ring cleavage and subsequent metabolism, then it is likely that the rate of substituent metabolism and thus

degradation may be reduced if metribuzin was protonated and adsorbed to soil colloids in acid soils.

Metribuzin and atrazine mobility increased with increasing concentration and soil pH.  $^{14}\text{C}$ -metribuzin had greater mobility on soil thin-layer plates than  $^{14}\text{C}$ -atrazine. A greater percentage of atrazine was adsorbed at the origin of application and did not migrate with the water front. Differences in adsorption and movement were attributed to differences in water solubility, basicity, and steric effects. All three herbicide properties would effect the entrance of the compounds into solution and adsorption to soil colloids.

Adsorption increased with decreasing soil pH. The dissociation constant was determined to be  $0.99 \pm 0.08$ . The dissociation constant was shown to be important in determining the adsorption by colloidal systems. Positive adsorption increased gradually as the soil pH decreased toward the pKa of metribuzin. This is postulated to occur through protonation of the amine group on metribuzin, which increases with a decrease in soil pH. Adsorption at pH levels in which metribuzin is in the cationic form was attributed to cation exchange and to complexing with hydrogen ions on the soil colloids. Similar results are known to occur with the s-triazines.

Thus, protonation with subsequent adsorption to soil colloids was shown to be the reason for the reduction in activity, microbial degradation and mobility of metribuzin as soil pH decreases.

## APPENDICES

## APPENDIX A

Fig. A-1.--Number of dead corn plants per plot minus the control value at each given pH range. Metribuzin applied at 1.12 kg/ha in 1972.

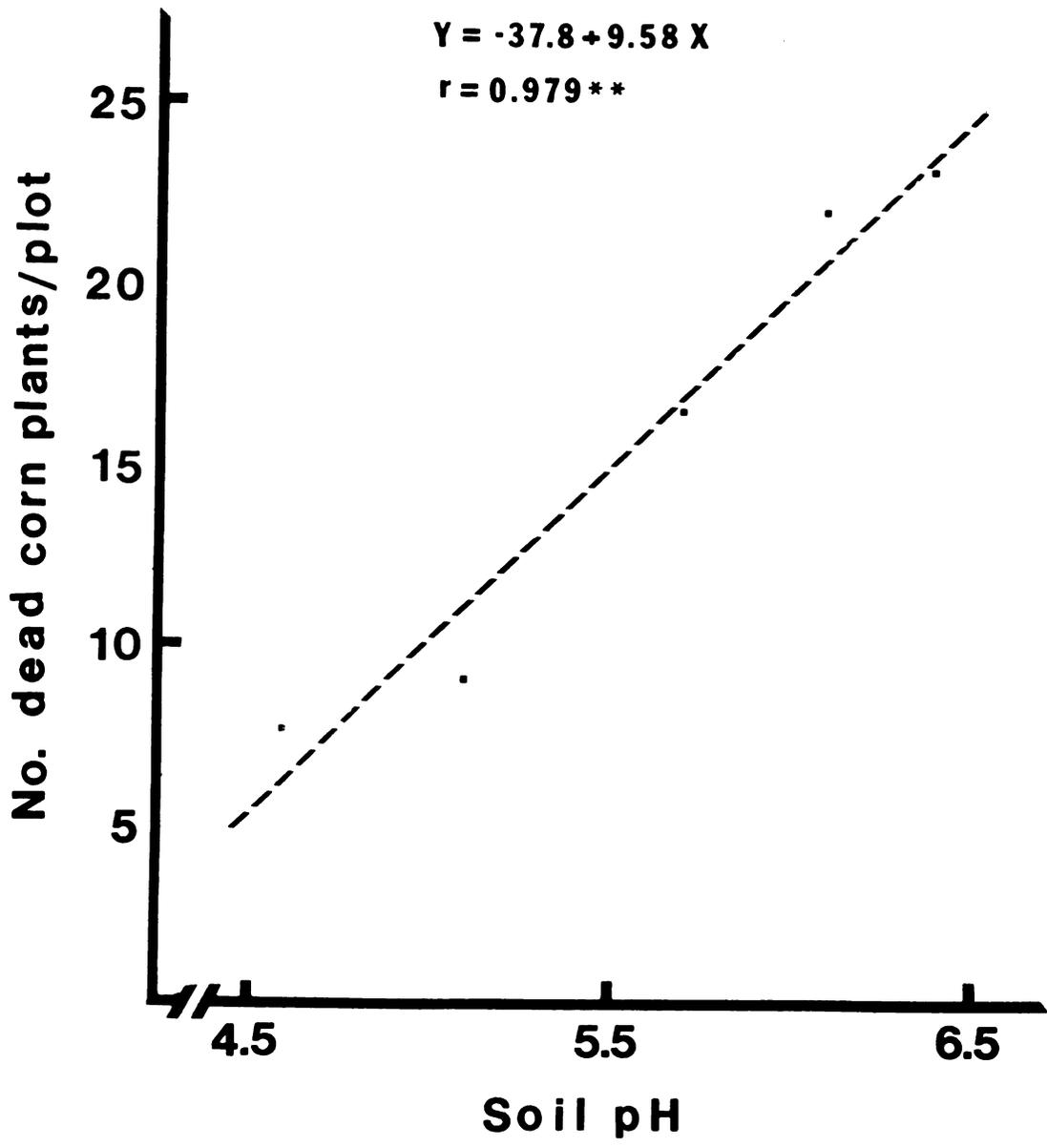


Fig. A-1

APPENDIX B

Table B-1.--The effect of soil pH on metribuzin phytotoxicity to corn in the field, measured as number dead plants per plot.<sup>a,c</sup>

pH Range	Metribuzin (kg/ha)								
	0.56		0.84		1.12				
	1972	1973	1974	1972	1973	1974			
4.5-4.9	2.5 ab	0.5 a	0.5 a	7.5 ab	3.3 a	0.8 a	7.7 ab	5.8 ab	2.0 ab
5.0-5.4	5.3 ab	1.3 a	0.8 a	8.0 ab	4.2 ab	1.5 ab	9.0 b	8.7 bc	3.5 b
5.5-5.9	1.3 a	2.0 a	2.0 ab	7.8 ab	4.5 ab	4.0 b	16.5 cd	12.5 c	9.0 cd
6.0-6.4	7.5 ab	3.0 a	2.0 ab	15.0 c	8.5 bc	7.0 c	22.0 de	13.5 c	10.0 de
6.5-6.9	7.5 ab	3.0 a	3.2 ab	18.2 cde	20.0 d	10.7 de	23.2 e	21.0 d	12.0 e

(No. dead corn plants--minus control at given pH range)<sup>b</sup>

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>Measurements were taken one month after planting.

<sup>c</sup>Rainfall of 1.3 cm one day after application may have accounted for the increased number of dead plants per plot area in 1972.

APPENDIX D

Fig. D-1.--Corn height as percent of control. Metribuzin applied at 1.12 kg/ha in 1972.

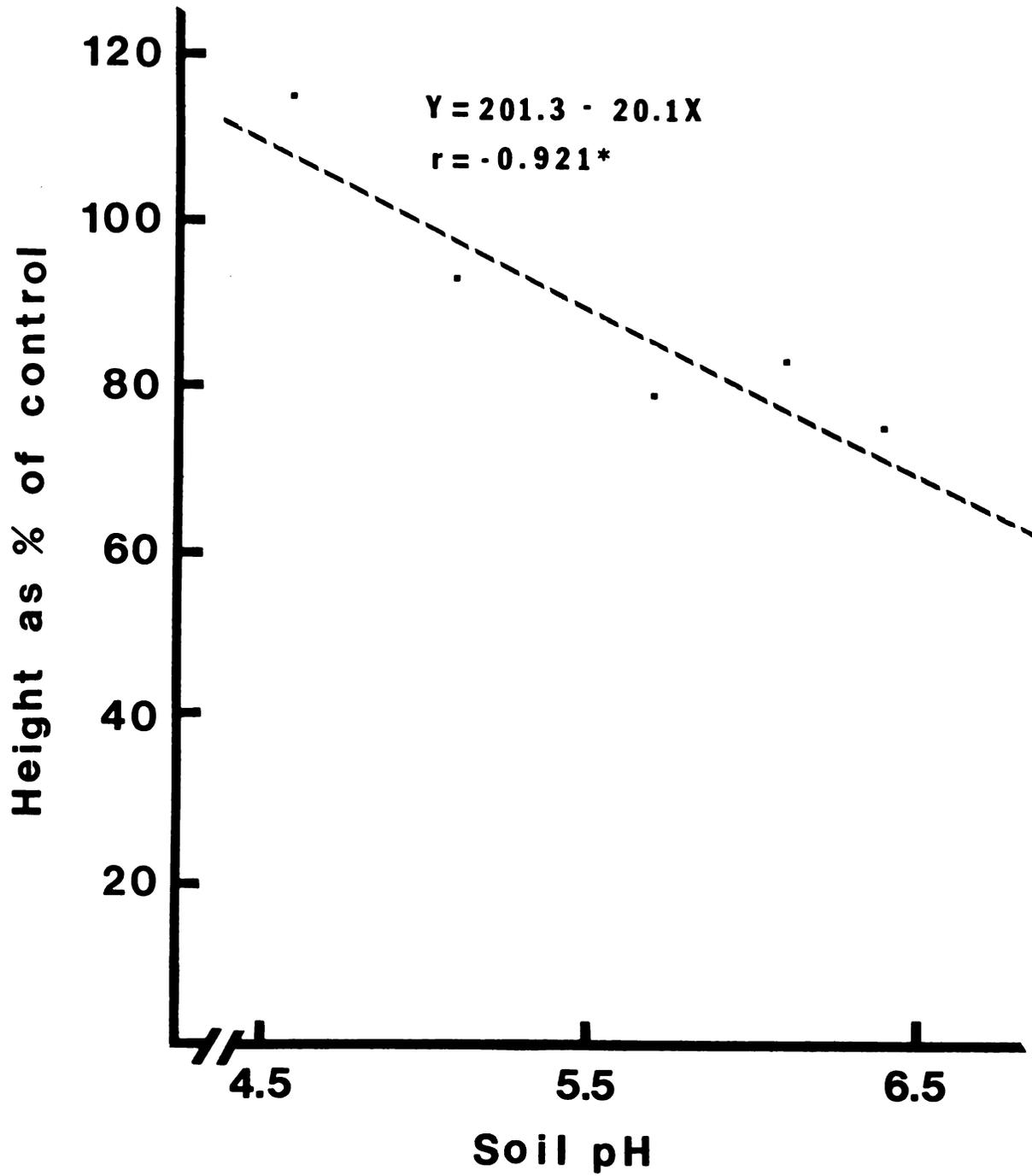


Fig. D-1

APPENDIX E

Table E-1.--The effect of soil pH on metribuzin phytotoxicity to corn in the field, measured as reduction in plant height.

pH Range	Metribuzin (kg/ha)																	
	0.56		1973		1974		0.84		1.12									
	1972	1973	1972	1973	1974	1974	1972	1973	1972	1973	1974							
4.5-4.9	89	a	81	fg	94	de	85	a	65	cde	88	bcd	115	b	63	cde	103	e
5.0-5.4	87	a	82	fg	91	cd	86	a	61	cd	87	bcd	93	ab	54	bc	87	bcd
5.5-5.9	92.2	ab	84	g	91	cd	87	a	67	cdef	85	bcd	79	a	40	a	78	ab
6.0-6.4	89	a	78	efg	86	bcd	85	a	68	cdef	83	bc	83	a	44	ab	81	abc
6.5-6.9	82	a	72	defg	82	abc	74	a	55	bc	78	ab	75	a	33	a	72	a

(% of control) bc

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>Measurements were taken to the highest point of top hanging leaf on the plant.

<sup>c</sup>Height measurements taken six weeks after planting.

APPENDIX F

Table F-1.--The effect of soil pH on metribuzin phytotoxicity to soybean in the field, measured as reduction in plant height.<sup>a</sup>

pH Range	Metribuzin (kg/ha)								
	0.56		0.84		1.12				
	1972	1973	1974	1972	1973	1974			
4.5-4.9	87 ab	97 f	101 bc	91 bc	79 abcd	91 ab	105 c	83 cde	113 c
5.0-5.4	91 bc	99 f	90 ab	92 bc	82 bcde	88 ab	98 bc	78 abcd	93 ab
5.5-5.9	93 bc	94 ef	88 ab	84 ab	80 bcd	88 ab	86 ab	70 ab	84 ab
6.0-6.4	89 abc	87 def	88 ab	87 ab	79 abcd	81 a	90 abc	70 abc	81 a
6.5-6.9	87 ab	78 abcd	86 ab	72 a	67 a	81 a	81 ab	67 a	76 a

(% of control)<sup>bc</sup>

<sup>a</sup>Means of each year's data with similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>Measurements were taken to the tip of the growing point.

<sup>c</sup>Height measurements taken six weeks after planting.

APPENDIX G

Fig. G-1.--Soil pH effect on metribuzin (1.12 kg/ha) phytotoxicity to corn  
and soybeans.

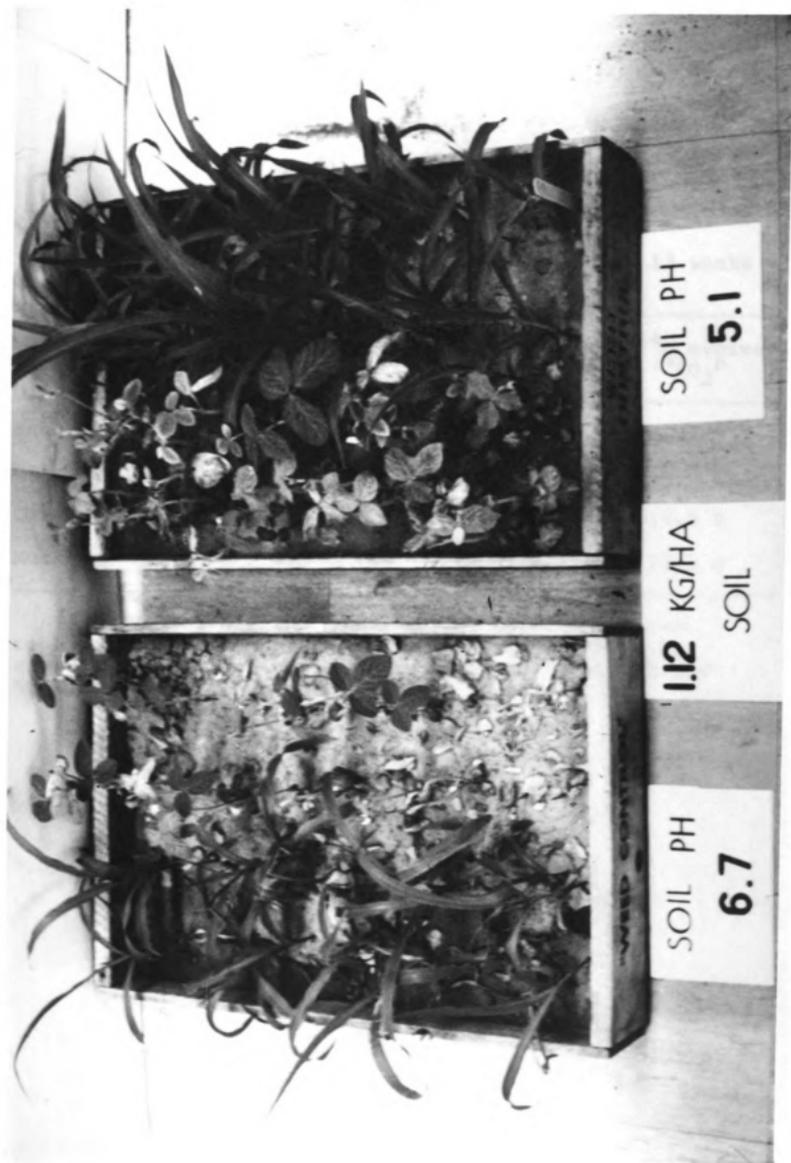


Fig. G-1

APPENDIX H

Table H-1.--<sup>14</sup>C-metribuzin degradation to CO<sub>2</sub> in 12 weeks as affected by soil type.<sup>a</sup>

Soil Texture	Sand %	Silt %	Clay %	OM %	pH	% <sup>14</sup> C evolved as <sup>14</sup> CO <sub>2</sub> <sup>b</sup>
Sandy loam	65	18	17	2.5	6.2	16.6 a
Clay loam	44	25	31	2.5	7.5	30.3 d
Clay loam	39	24	37	3.2	8.0	18.6 b
Muck					7.6	23.1 c

<sup>a</sup>Values are the means of two experiments two replications per experiment. Means in a followed by similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>0.0256 μCi/flask

APPENDIX I

Tabl3 I-1.--The effect of soil type on adsorption of <sup>14</sup>C-metribuzin.<sup>a</sup>

Soil Type	Clay %	Organic matter %	pH	Time after treatment (hr)		
				6	12	24
Conover sandy clay loam	29.7	2.7	5.7	5.1 a	7.7 b	9.2 c
Toledo clay loam	71.7	3.8	7.4	12.2 d	14.4 e	15.5 ef
						16.6 f

<sup>a</sup>Values are the means of two experiments with two replications each. Means followed by similar letters are not significantly different at the 5% level by Duncan's multiple range test.

<sup>b</sup>79.4 nM added/test tube

APPENDIX J

Fig. J-1.--Metribuzin degradation rate as the log of concentration in soil at three pH levels at a depth of 0.0-5.0-cm, following application of 1.12 kg/ha in the field in 1973.

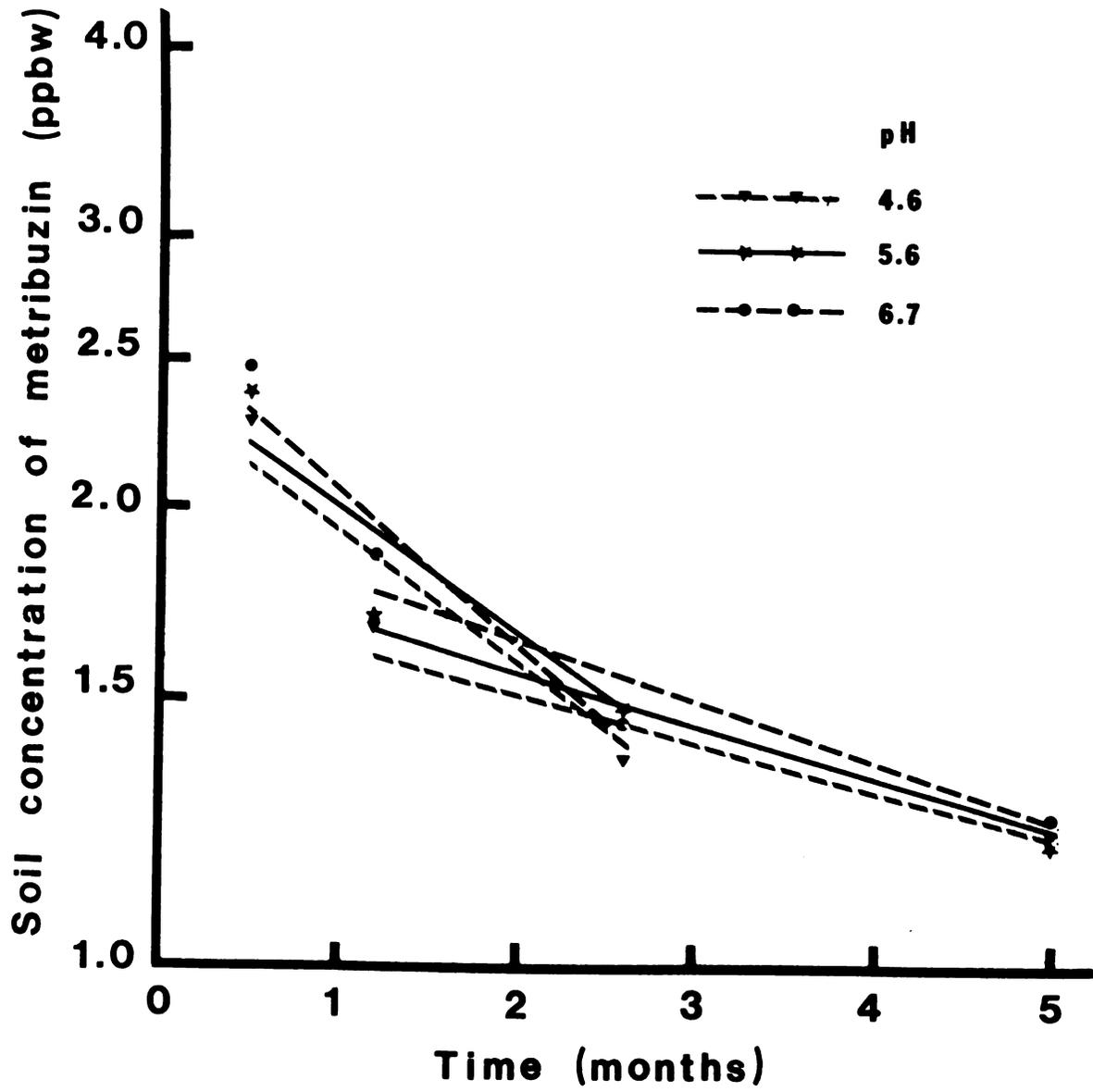


Fig. J-1

## APPENDIX K

Fig. K-1.--Metribuzin degradation rate as the log of concentration in soil at three pH levels at a depth of 0.0-5.0-cm, following application of 1.12 kg/ha in the field in 1974.

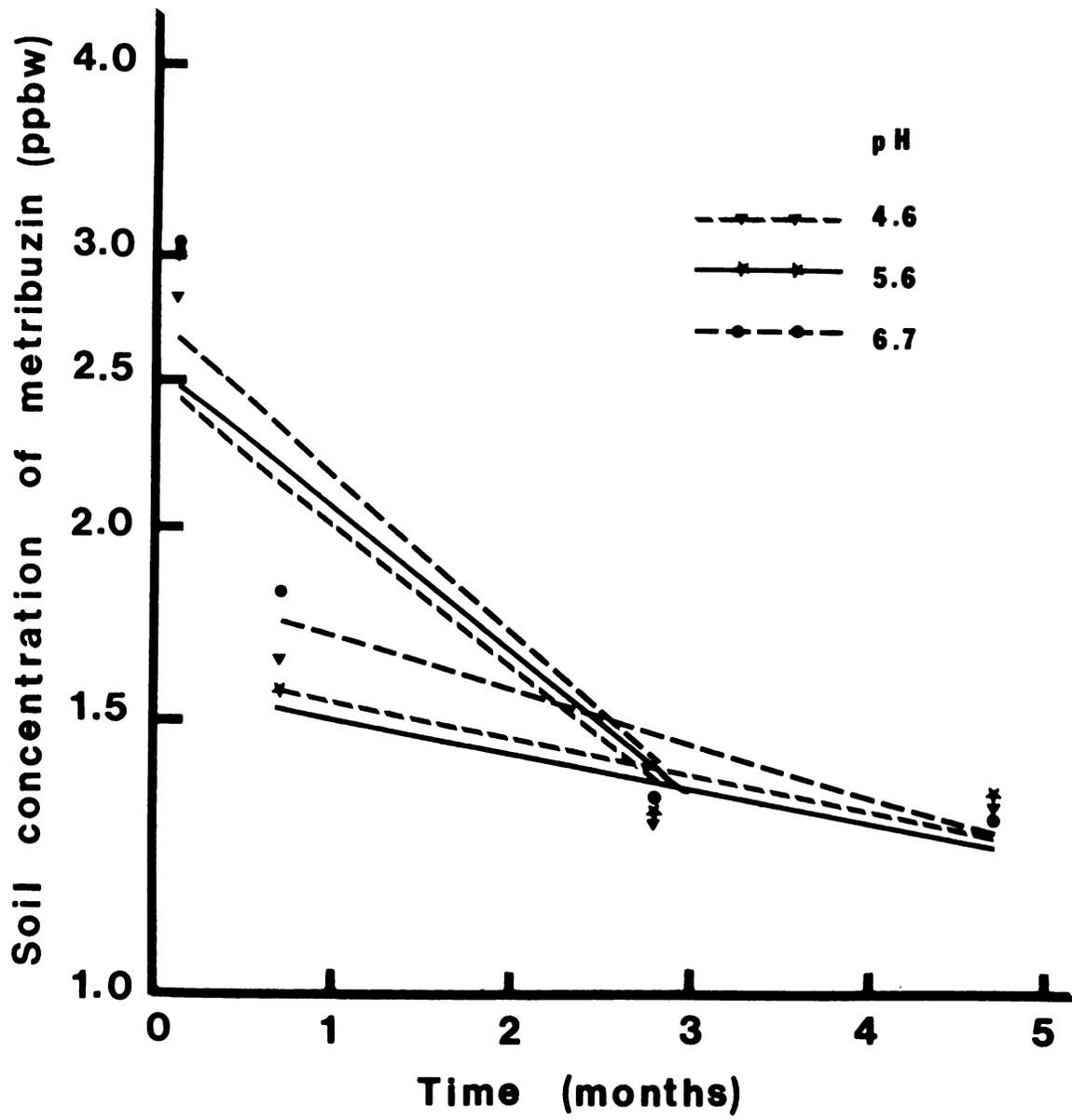


Fig. K-1

## APPENDIX L

### Modified No. 1 Hoagland's Solution

1.	1 M $\text{KH}_2\text{PO}_4$	2 ml/L
2.	1 M $\text{KNO}_3$	2 ml/L
3.	1 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	3 ml/L
4.	1 M $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2 ml/L
5.	1.5 g/L $\text{MnCl}_3 \cdot 4\text{H}_2\text{O}$	
	2.5 g/L $\text{H}_3\text{BO}_4$	
	0.1 g/L $\text{ZnCl}_2$	1 ml/L
	0.05 g/L $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	
	0.05 g/L $\text{MoO}_3$	
6.	26.3 g/L Sequestrene <sup>R</sup>	1 ml/L
	pH 6.5 to 6.8 with 1 M NaOH	