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EFFECTS OF ATRAZINE RESIDUE ON SOYBEAN (*GLYCINE MAX* (L.) MERR.) GROWTH UNDER THREE TILLAGE SYSTEMS AND VARIOUS HERBICIDES

By

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ABSTRACT

EFFECTS OF ATRAZINE RESIDUE ON SOYBEAN (GLYCINE MAX (L.) MERR.) GROWTH UNDER THREE TILLAGE SYSTEMS AND VARIOUS HERBICIDES.

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Field experiments were initiated in the fall of 1982 to examine the effects of tillage on degradation of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine in soil. Interactions of atrazine residue with two soybean varieties and six soil applied preemergence herbicide treatments were also examined. Parameters used in evaluation included visual ratings of soybean injury and soybean yield. Soil samples were analyzed for atrazine using Soxhlet extraction and quantified by gas chromatography.

Injury ratings at growth stage V4 indicated minimum tillage resulted in greater atrazine injury than moldboard plowing. Metribuzin (4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one) reacted synergistically with atrazine under chisel plowing. This may have been due to the disturbed crop residue layer which allowed the metribuzin to reach the rooting zone and the atrazine residue, which remained in the rooting zone under the chisel plowed system. Tillage had no effect on atrazine distribution between the 0 to 5 and the 5 to 15 cm depths. Percent unextractable atrazine was greater with higher application rates.

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INTRODUCTION

Atrazine is commonly used in corn and sorghum for control of grass and broadleaf weeds throughout the midwestern corn belt. However, under conditions of low moisture, low temperature, high pH, a textured soil, and high application rates, atrazine may persist into the next growing season. This poses a problem if atrazine sensitive crops, such as soybeans, are to be planted the year after atrazine application.

Factors such as tillage, soybean herbicides, and soybean planting practices may be manipulated to reduce possible soybean injury. It is the objective of this thesis to examine these factors.

CHAPTER 1

LITERATURE REVIEW

INTRODUCTION

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] has been effectively used for control of several weeds including common lambsquarter (*Chenopodium album* L.), eastern black nightshade (*Solanum ptycanthum* Dun.), common ragweed (*Ambrosia artemisiifolia* L.), and wild mustard (*Brassica kaber* (DC.) Wheeler), since its development by J. R. Geigy in the mid 1950's (42). Atrazine is commonly used throughout the corn belt of the United States, due to its relatively low cost and high effectiveness. However, the use of atrazine does pose some problems. Recommended rates of atrazine may persist in the soil into the next growing season, causing injury to sensitive crops planted that year. Such crops include oats (*Avena sativa* L.), seedling alfalfa (*Medicago sativa* L.), and soybeans (*Glycine max* (L.) Merr.) (12).

Tillage may influence the carryover of atrazine in soil by burying or diluting the residue (6). Along with mixing the soil, tillage or lack of tillage may influence the soil surface in terms of the amount of plant residue remaining (63). This residue layer may interfere with herbicide distribution on the soil (20) and may aid in moisture conservation (10). Tillage systems also influence the pH of the soil surface by determining if pH altering materials, such as lime or nitrogen fertilizers, can be incorporated (11). The amount of atrazine remaining in the soil also influences crop response. Atrazine persistence is influenced by chemical and microbial degradation, both of which are influenced by temperature, moisture, and light. Soil type also influences herbicide breakdown and is one of the factors regulating how much of the herbicide residue is actually available for plant uptake (16).

Metribuzin (4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one) used on atrazine sensitive crops, such as soybeans, the year following atrazine application may interact with the atrazine residue resulting in increased crop injury (44).

Soybean varieties vary in response to metribuzin (54). This may play a part in reducing potential yield reductions due to atrazine residue and metribuzin application with certain varieties. Seed size and seeding rate have also been reported to reduce yield losses due to atrazine residue (1, 2, 30).

EFFECT OF TILLAGE ON ATRAZINE DISPERSION

Burnside et al. (18) found soil persistence from the subsequent year normal use rates of atrazine was only a minor problem under reduced tillage systems. Atrazine carryover was less of a problem under the reduced than conventional tillage systems in experiments conducted in Nebraska (18). Bauman and Ross (6) also found atrazine persisted longer under chisel or conventional plowing systems than under the coulter tillage system. Kells et al. (41) found the percent of extractable atrazine decreased with time under both no-tillage and conventional tillage systems, however, unextractable radioactivity was always higher under no-tillage. This indicates greater breakdown or adsorption to soil or soil constituents under the no-tillage.

Plant Residue

Under the no-tillage system, plant residue remains on the surface. Walker and Crawford (79) found undecayed plant material did not adsorb the triazine herbicides. Bauman and Ross (6) found that although corn residue intercepted some of the atrazine during application, 86 to 90% was removed from the corn residue 30 days after application and only 1% remained after 90 days. Plant residue did not significantly affect weed control when herbicides were applied at recommended rates, but had an increased influence on control as herbicide rates were reduced (20). Control of foxtail millet (Setaria italice (L.) Beauv.) with atrazine decreased with increasing residue levels when simulated rainfall did not occur (20). Lowder and Weber (46) found atrazine retention by crop residue appeared to be primarily a function of the total amount of rainfall, and secondly, a function of residue type and rainfall patterns. They found one 10 cm rainfall immediately after atrazine application or 7 days after application removed approximately 87 and 77% of the atrazine residue from fresh oats and dry corn residue, respectively. Slightly less atrazine was removed from the residue when four 2.5 cm rainfalls were applied in place of the one 10 cm rainfall (46).

Moisture

Wicks and Smika (85) found soil moisture content to be generally greater without tillage. Blevins (10) saw higher corn yields due to more effective use of soil moisture by no-tillage as compared to conventional tillage. No-tillage treatments had a higher volumetric water content to a depth of 60 cm during most of the growing season. The greatest difference occurred in the upper 0 to 8 cm depth. The decrease in evaporation and the greater ability to store moisture under no-tillage produced a greater water reserve (10). Moschler (50) found that the more efficient use of water under the no-tillage system resulted in more efficient use of lime. This resulted in greater increases in corn yield under the no-tillage system due to lime than under conventional tillage. Associated with the larger yield increases from lime in the no-tillage culture were: 1) higher pH in the upper 0 to 10 cm layer (6.4 vs. 6.0); 2) a greater increase in exchangable calcium, and 3) a reduction in exchangable aluminum in the 0 to 10 cm layer (50). Birk and Roadhouse (9) applied atrazine to a loam soil at rates ranging from 2 to 20 lb/A. Some plots were planted to corn, others were left fallow. At the end of the first sampling season there was appreciably greater residue remaining in the corn plots than in the similarly treated fallow plots. An average of 43.8% of applied atrazine remained in the corn planted plots compared to 18.3% remaining in the fallow plots. The greater persistence was probably due to the much drier soil, which was characteristic of the corn plots during the season (9).

Nitrogen

Acidity also influences the persistence of atrazine in the soil. It has been shown by numerous authors that surface soil pH decreases under no-tillage compared to conventional tillage (7, 11, 22, 31, 51). Since atrazine binding and degradation increases as pH decreases, as shown by Hiltbold and Bauchaman (36), there should be reduced atrazine persistence under the no-tillage system in the surface layer of soil. Blevins (10) found that soil pH was lowered by increasing ammonium nitrate application and was lower with no-tillage than with conventional tillage. The use of $NaNO_3$, a basic forming nitrogen fertilizer, resulted in increased atrazine efficiency and longevity as compared to the use of NH_4NO_3, an acid forming nitrogen fertilizer during a dry year in research reported by Lowder (46). No differences were observed during a wet year.

Lime

Liming significantly increased atrazine efficency and longevity in both no-tillage and conventional tillage systems (8, 46). Kells (41) found the addition of lime under no-tillage resulted in a significantly greater amount of applied atrazine remaining at any point in time. The same was also true under conventional tillage. Lowden (46) found that mean surface soil pH levels during the growing season were higher with no-tillage than with conventional tillage. This was due to retention of lime on the surface under no-tillage compared to mixing in the soil under conventional tillage. No increases in atrazine efficiency or longevity were found in one system over the others (46). Kells (41), using ^{14}C labeled atrazine, found the amount of unextractable radioactivity in the soil under no-tillage increased significantly over time at all levels of surface pH tested. The same was true under conventional tillage. Under no-tillage, 72% of the applied radioactivity remained as atrazine 14 days after application in areas receiving lime and 60% remained as atrazine where no lime was applied. Under conventional tillage 75% of the applied atrazine remained 14 days after treatment in areas receiving lime and 64% remained where no lime was applied. The effect of lime on the amount of parent atrazine present in the soil was found to be directly related to its effect on soil pH (41). Best (105) found that by liming an acid Bladen silt loam from pH 5.5 to 7.5, the phytotoxicity of atrazine and prometryn were increased.

Weed Control

Kells (41) found additions of lime as compared to unlimed treatments resulted in significantly increased weed control with simazine (2-chloro-4,6-bis(ethylamino)-s-triazine) (83 vs. 63%), yield (5930 vs. 5290 kg/ha), and soil pH (5.91 vs. 5.22). Poorest weed control was observed with no-tillage on unlimed plots In studies using atrazine, higher levels of extractable triazine in the soil resulted in significantly better weed control under both no-tillage and conventional tillage. However, at any level of extractable triazine, weed control was always greater under conventional tillage. Under no-tillage 19% weed control was observed in areas where 18% of the applied atrazine remained compared with 76% weed control in areas where 52% remained as atrazine. Under conventional tillage 60% weed control was recorded in areas where 6% of the applied atrazine remained compared with 93% weed control in areas where 52% remained as atrazine (41).

Triplet (75) grew continuous corn under no-tillage and conventional tillage for 7 years to evaluate several herbicides for use in both crop culture systems. The only consistently satisfactory herbicide combination for the no-tillage corn were simazine and paraquat (1,1'dimethyl-4,4'bipyridinium ion). Annual weed population shifted rapidly with different herbicide treatments; fall panicum (Panicum dichotomiiflora Michx.) was the major annual weed where triazines were used as the residual herbicide. After several years of corn growth under no-tillage, hemp dogbane (Apocynum cannibinum L.) became a significant problem in some areas. Corn yields were equal under no-tillage and conventional tillage systems provided weed control was satisfactory (75).

Putnam and DeFrank (54) found cover crops such as rye (Secale cereale L.) or wheat (Triticum aestivum L.) provided excellent weed control in spring drilled peas with no need for other herbicides than that needed for burndown. The use of fall planted cover crops with no-tillage also reduced broadleaf weed population 62-85% in carrots (Davlus carrota L.) and onions (Allium sp.) on organic soil. Residue of spring planted oats, rye, wheat, sorghum (S. vulgare), and sorghum + sudangrass hybrids (Sorghum vulgare sudanenis) reduced weed population 55 to 95% in cucumbers (Cucumis sativus) and snap beans (Phoseolus vulgare L.). This would indicate that less herbicide may be needed for equal weed control under no-tillage when compared to conventional tillage. This is contrary to Kells (42) finding that conventional tillage significantly increases yields, weed control, and soil pH over no-tillage. In Putnam's work a thick crop residue level was left by the solid seeded small grains used. This may explain the better weed control from this crop residue when compared to the corn residue used by Kells.

ATRAZINE DEGRADATION

Once a pesticide is released into the environment, degradation may begin. There are two major mechanisms for atrazine degradation in the soil, microbial and chemical.

Microbial Breakdown

Best and Weber (7) determined the pattern of atrazine degradation was characteristic of non-biological processes. Talbert (72), on the other hand, believed that slow microbial decomposition was the principle process involved in the dissipation of simazine and atrazine. Deactivation occurred only under conditions conducive to microbial growth and little or none occurred in frozen or sterile soil. Inactivation of simazine and atrazine applied at 2.24 kg/ha on field plots as determined by soybean and oat bioassay was most rapid when the soil environment was favorable for microbial growth (67). Skipper (68) postulated degradation by soil microorganisms might be a function of qualitative, as well as quantitative differences in the microbial population. In the soils studied by Skipper, organic matter content and microbial population did not directly relate to atrazine degradation.

Microbial population, temperature, aeration, and moisture, normally vary with depth, consequently rate of atrazine breakdown will likely vary with depth. Atrazine was found to degrade two to three times faster in the top soil than in the subsoil in a Sharpsburg silty clay loam and in a Keith silt loam (59). Harris (32) found atrazine residue at a 38 cm depth had 61% greater persistence than atrazine placed in the top 7.5 cm. Conditions at the surface in terms of organic matter content, temperature, and aeration, were more favorable for degradation. Roeth (59) found atrazine adsorption, microbial population, soil organic matter, and atrazine degradation decreased with increasing depth in the soil horizon.

Microbial Pathways

Skipper and Volk (68) found approximately ten times more $^{14}CO_2$ was evolved from ^{14}C-ethyl atrazine than from ^{14}C-isopropyl atrazine. Microbial attack appears to be predominately on the ethyl side chain of atrazine. Possible degradation pathways of the side chain components of atrazine include: 1) dealkylation of the ethyl side chain by hydroxylation of the carbon atom adjacent to the amino group or 2) dealkylation and deamination of aromatic molecules by monooxygenase. Steric hindrance may limit the availability of the isopropyl side chain to microbial attack. Sirens (66) found atrazine is converted into deethylated atrazine as a major and deisopropylated atrazine as a minor phytotoxic metabolite. Isopropyl and the ring constitutent of atrazine were subject to minimal attack. The hydroxyatrazine ring was attacked more readily than the atrazine ring as shown by Skipper and Volk (68). Skipper and Volk (68) also found evolution of $^{14}CO_2$ from the ethyl side chain component of atrazine varied within soil type, herbicide concentration, moisture content, and air flow rate.

As in most chemical and biological processes, water plays an important role; the degradation of atrazine is no exception. A six fold increase in $^{14}CO_2$ evolution from chain ^{14}C-labeled atrazine occurred with an increase in moisture content from 40 to 80% of field capacity (59). A Woodburn soil at 50, 70, and 90% field capacity respired 5.5, 8.5, and 10.1% of the ^{14}C-ethyl component in 4 weeks, respectively. The lower moisture content may reduce microbial activity, limit atrazine availability, or decrease chemical hydrolysis (68).

Chemical Hydrolysis

Skipper et al. (15) reported chemical hydrolysis of the s-triazines to their hydroxy analogs as the major pathway of degradation in the soil, with microbial attack being of minor importance. Le Baron (45) also found chemical hydrolysis of atrazine to non-phytotoxic hydroxyatrazine to be the predominant route of detoxification of atrazine in soil. Research by Harris (31) indicates that the initial hydrolysis at the two positions of the triazine ring occurred more readily than subsequent degradation steps. Since hydroxylation is a prerequsite for enzymatic fission of the benzene ring, hydrolysis of chloro-s-triazines to hydroxy-s-triazines may also be required for cleavage of the s-triazine ring (24).

Factors such as moisture, soil type, leaching, and temperature, also affect the rate of atrazine degradation. Wilson and Cole (87) found watering soil to field capacity every day increased atrazine degradation compared to watering less frequently or not at all. Sheets and Craft (62) found similar results from their work with diuron (3-

[3,4-dichlorophenyl]-1,1-dimethylurea) and atrazine in which both were lost more rapidly from moist rather than dry soil. Many researchers (15, 16, 31, 60, 76, 77, 78) have found herbicide carryover in forms harmful to plants was less serious in the humid regions, compared to the more arid regions of the United States. Atrazine at 2.2 kg/ha significantly reduced subsequent oat yields in central and western, but not in eastern Nebraska. This may be atributed to the higher rainfall in eastern Nebraska (16). In a study comparing atrazine degradation in central and western Nebraska, Burnside (16) found greater carryover in the drier western locations. An Anselmo silty loam was used in both locations, this indicates the greater moisture in the central region enhanced breakdown.

Burnside (16) found carryover to be greater on coarse textured soils, than on fine textured soils. Soils showing the greatest to least residue were sandy loams, silt loams, and silty clay loams. Soil textures had a greater influence on herbicide carryover than climate (8).

Leaching may decrease atrazine persistence in the rooting zone, by moving it out of the plant rhizosphere. Brinkman (12) found yield reductions were less in 1976 due to abundant rainfall during the later half of 1975, which leached much of the atrazine residue from the rooting zone. Conversly, substantial atrazine remained in the top soil when the 1977 crop was planted, due to the dry weather in the later half of 1976. The amount, frequency, and intensity of rainfall have been shown to be important factors in soil longevity of herbicides by both Burnside (15) and Talbert (72) in separate studies. Bauman (6) also found soil factors to affect the movement and persistence of atrazine under field conditions, along with the amount and frequency of rainfall after application. Ritter (58) concluded that atrazine moves more readily in wet soil than in dry soil. Roger (60) has shown organic matter to be more important in terms of s-triazine leaching than solubility. Once a herbicide is leached into the lower soil profile, its dissipation is markedly reduced.

Herbicide breakdown, by both biological and nonbiological means, decrease with the reduced soil temperature or increasing depth in the soil horizon (59). Atrazine was found to degrade two to three times faster in the top soil than in the subsoil of a Sharpsburg silty clay loam and a Keith silt loam by Skipper (68). Each 10^{o} temperature increase from 10 to 30^{o}C caused the degradation rate to increase two to three times in these soils. Similar results were found by McCormick and Hiltbold (48). Talbert (72) found atrazine, as well as diuron, to be lost more rapidly during high temperatures, rather than low temperatures. Atrazine was found to be increasingly volitile from soil with increasing temperatures by Kearney et al. (39). They also showed that volitility from soil ceased with leaching. Jordan (38) showed photodecomposition to stop with leaching.

Wolfe (88) found direct photolysis of the s-triazines exposed to visible light was so low that it is not likely to have environmental importance. Gast (23) was able to show losses of simazine and atrazine activity when dry surface treated soil was irradiated with ultraviolet and infrared light, losses were reduced in wet soil. The direct photolysis of s-triazine herbicides in water and alcoholic solutions at 253.7 nm resulted in the nucleophilic displacement of the R_1 substitute and formation of hydroxyl and alkoxy derivatives, respectively (52). Rijte (57) found the rate of photodegradation was affected by the pH of the reaction mixture. The rate of reaction increased as the pH decreased, indicating that photodegradation will increase at a lower pH. One of the primary photodegradation products was the deethylated s-triazine.

Soil Clay

Armstrong et al. (1) and Harris (31) showed atrazine in contact with soil was degraded more rapidly than atrazine in aqueous solution. This would suggest that soil, or some soil constituent, catalyzed degradation. Both attributed the increased degradation to a non-biological constituent, which catalyzed atrazine to 2-hydroxyatrazine.

Crystalline clays bind herbicides via their exchange sites. These sites originate from broken bonds, isomorphic substitution, and dissociation of hydrogen ions of exposed hydroxyls (22). Broken bonds result in unsatisfied charges around the edges of silica-aluminum units. Unsatisfied charges also result from isomorphic substitutions of an ion, usually Al^{3+} for a lower valance ion usually Mg^{2+} in the octahedral sheets of clay particles. The exposed oxygen of hydroxyl groups may result in unsatisfied charges if the hydrogen is removed. This, however, is unlikely due to the light association of the hydrogen to the hydro group. These unsatisfied charges may be satisfied hydroxyls with cationic herbicides, such as atrazine (5, 22, 74).

Soil texture differences had a greater influence than did climatic differences across Nebraska (16). This may be due to different types and amounts of clays and/or organic matter. Weber and Coble (32) reported a reduction in microbial attack on diquat (6,7-dehydrodipyrid (1,2-:2',1'-c) pyrazinediium ion) when the herbicide was adsorbed by montmorillonite. The adsorbtion of atrazine by montmorillonite in the neutral Coker clay soil may protect the atrazine molecule from microbial attack (31). Baily (4) found the surface acidity of montmorillonite to be 3 to 4 pH units lower than the suspension pH, which would result in greater adsorption of atrazine. No adsorption of atrazine was reported with kaolinite by Talbert (73).

Soil Organic Matter

Although certain clays may adsorb triazines, organic matter is most highly related to adsorption and/or phytotoxicity of the chloro-s-triazines (31, 49, 53, 56, 63, 69, 72). Grover (25) found by adding organic matter to a Regina heavy clay soil, that the phytotoxicity from simazine to oats was reduced. Walker and Crawford (79) extensively studied the role of organic matter in the adsorption of triazine herbicides by soils and found that undecayed plant material was not very adsorptive.

Studies with mixtures of clay and organic matter by Hance (27) showed they associate in a manner which reduced the total surface availability for herbicide adsorption. He suggests that in the soil, little of the clay mineral surface will be accessible to the herbicide molecule. Talbert (73) found that increasing amounts of organic matter and/or clay in a soil, generally were associated with increased adsorption of the triazine herbicides. The availability of soil applied s-triazine herbicides generally decreases as clay and/or organic matter increases (64, 84).

Soil pH

The adsorption of simazine by 18 soils was not correlated significantly with soil pH, but was correlated significantly with percent clay and highly significantly with organic matter and titratable acidity (19). Kells et al. found the amount of unextractable atrazine was greatest in areas where surface pH was less than 5.0 compared with areas where the surface pH was greater than 6.5. Best and Weber (7) found more rapid hydrolysis of atrazine to hydroxyatrazine in soil of pH 5.5 than 7.4. Hiltbold and Buchanan (13) found persistence of atrazine was positively related to soil pH. They also found that the extent of the pH effect varied with soil type. The effect of pH in McLaurin sandy loam amounted to 8 to 9 days longer persistence per unit increase in pH. In a Hartsells fine sandy loam 9 to 13 day increase in persistence was found per unit increase in pH. A 29 day increase in persistence was found in a Decator clay loam (36). The pka value represents the pH level at which one-half of the species in solution is present in the ionic form. Since ionic species are more water soluble than molecular species, basic herbicides, such as atrazine, have higher solubilities at low pH levels than at neutral pH levels (80). Weber also found that the higher the basicity of a pesticide the greater it will be adsorbed by acid soil particles. Maximum adsorption was found to occur at pH levels in the vicinity of the pka value for the triazine herbicides (83). Atrazine has a pKa of 1.68, which indicates maximum adsorption will occur at a pH of around 1.68. Under more acid conditions than the pKa of the adsorbent, hydrogen cations compete with the triazine molecule for the binding site (5). Because weakly basic herbicides are protenated in acid soil systems and are ionicly adsorbed by negatively charged colloids, pH exerts a strong influence over both adsorption and hydrolysis of atrazine (11, 65).

Colloidal surface pH may be 3 to 4 orders of magnitude lower than the pH of the soil solution (84). The Stern theory states that as distance from the soil colloid decreases, the percent H^+ ions increase. Therefore, in the soil solution near the soil colloid the concentration of H^+ is much greater than in the overall solution. This results in a lower pH near the colloidal surface. pH is normally measured and reported from the soil solution. Atrazine adsorption and degradation occur at the colloidal surface, thus, the colloidal surface pH governs the reactions (84).

Buckhanam and Hiltbolt (13) reported atrazine half-lives of 10, 20, and 30 days for various soils in Alabama. They believed the difference in half-life between soils was associated with greater influence of pH on atrazine persistence between these soils. Soil colloidal properties determine the distribution of atrazine between the adsorbed and solution phases. Degradation, in the form of chemical hydrolysis, takes place on the colloidal surface. Since lowering the pH of the soil solution lowers the acidity of the soil colloid and protonates the atrazine molecule, lowering the pH of the soil solution creates an environment conducive for the adsorption of atrazine and thus the hydrolysis to the inactive hydroxy form (13).

Hance (27) found adsorption of two substituted ureas, monuron and diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), were independent of pH or exchange capacity. The adsorption of the triazines were influenced by both factors. Hance postulated that the ureas were adsorbed by coordination complexes with exchange cations, while the triazines are adsorbed by a combination of these two plus protenation and consequently ion exchange reactions. The importance of each process being determined by pH, exchangable cations, and the characteristic of the adsorbate molecule (27). In separate studies Harris (29), McGlamery (49), and Talbert (73) found atrazine adsorption to increase with decreasing pH. Colbert (19) found adsorption of atrazine, along with other triazines, to decrease on natural and limed soils as soil pH increased.

Of the colloidal fraction, organic matter has the most reactive surface. This includes humin, humic and fulvic acids. The clay fraction makes up the rest of the reactive surface (5). Stevenson (70) found that organic matter and clays are bound intimately together, probably via metal ions. Thus, there are two major adsorbing surfaces available to herbicides, the clay-metal-organic matter complex and clay alone. Nearpass found adsorption of simazine by 18 soils was not correlated significantly with pH, but was correlated significantly with percent clay and highly significantly with organic matter and titratable acidity (51). Swain (71) found dissipation rate and atrazine adsorption were both correlated with organic carbon content of the soil, which ranged from 1.43 to 0.73%. No correlation between either dissipation rate or adsorption and clay content were found even though clay content ranged from 37 to 78%. A possible explanation for this may be the type of clay present. A clay such as kaolinite would have very little adsorption capacity. The organic matter may have also masked any effect of the clay. Weber (83) found the adsorption of the _s_-triazines were due to the complexing of the triazine molecules with functional groups on the organic colloids and/or adsorption of _s_-

triazine cations by ion exchange forces. The ratio of the amount of herbicide adsorbed to the amount in equilibrium solution (Kd) for a given s-triazine and exchange remained relatively constant over a range of concentrations (73). Four factors determined the role of the chemical character of the adsorbate in the overall adsorption reaction according to Baily and White (5): 1) nature of the functional groups; 2) nature of the substituting groups; 3) position of the substituting group with respect to the functional groups, and 4) magnitude of unsaturation in the molecule.

Baily et al. (5) believes there are several factors, such as surface acidity and relative polarity of the adsorbent that determines whether there is a direct relationship between water solubility and adsorbability. There appears to be a relationship between water solubility and the extent of adsorption, but only within certain families of compounds (4). An inverse relationship occurs for the chloro series of s-triazines. The solubility of the series of compounds increases as the side chain length increases, with the exception of atrazine.

Temperature also affects adsorption of the triazines. Talbert (73) found that increasing temperature and pH resulted in decreased adsorption of simazine and atrazine. Harris (29) and McGlamery (49) also found increasing temperatures caused adsorption of atrazine to decrease.

ATRAZINE - METRIBUZIN INTERACTIONS

Although atrazine residue alone may result in soybean injury, the addition of metribuzin in combination with atrazine residue may result in increased injury.

Soil pH has an effect on the activity of both metribuzin and atrazine. The phytotoxicity of both components increase with increasing soil pH (34). Best (8) found that liming increased the ^{14}C-concentration present in the shoots of corn (Zea mays L.), cotton (Gossypium hitsutum L.) and soybeans from soil treated with ^{14}C ring-labeled atrazine. Increasing pH resulted in increased activity of metribuzin expressed as weed control and crop injury (43). Atrazine at 10^{-5} and 10^{-6} M concentrations in a sand culture nutrient solution during early growth of "Swift" soybean seedlings decreased ^{14}C-metribuzin uptake and movement into 12 day-old soybean shoots (44). However, 10^{-7} M atrazine increased C^{-14} metribuzin in the shoots by increasing stomatal aperture and subsequent transpiration. Conditions favoring the synergistic interactions were low atrazine levels, which increased soybean transpiration, high metribuzin rates, and high soil pH levels (44). Atrazine applied in nutrient solution to corn, cotton, and soybeans reduced transpiration both in intact plants and excised shoots. This effect occurs only in the light. Microscopic examination revealed that atrazine caused closure of the stomates (86). Smith and Buchholtz (69) also found atrazine to reduce transpiration and stomatal aperature at concentrations of 10^{-6} molar and above. Sheet (64) showed a close correlation between herbicide uptake and the amount of water transpired (64). Transpiration rates in darkness were positively correlated with stomatal aperture. Stomatal closure after treatment with atrazine at high concentrations or opening under sub-lethal levels of atrazine appeared to result from fluctuating CO_2 levels in the guard cells and substomatal cavities. This resulted from atrazine inhibiting CO_2 fixation in the chloroplasts (62, 86). Ladlie et al. (44) found that atrazine at 10^{-6} M reduced transpiration and stomatal aperture. However, atrazine concentration of 10^{-7} and 10^{-8} M increased stomatal aperture over the control and uptake and translocation of 10^{-5} M ^{14}C-metribuzin was dependent on the atrazine concentration. Stomatal opening or closing would appear to be a result of atrazine concentration and environmental conditions in a field situation. Stomatal closure due to atrazine was confirmed by Wills (26), who found that atrazine caused transpiration reduction, stomatal closure, and an initial increase in the water content of cotton. Imbamba (37) found that atrazine did not cause stomatal closure in CO_2-free air. Because atrazine blocks the Hill reaction from occurring ($2\ H_2O\ \ 4H + O_2 + 4e^-$). No reducing power is available to convert CO_2 into glucose. Therefore, CO_2 levels build up from respiration, which in turn causes the CO_2 sensitive guard cells to close. This then results in reduced transpiration (37).

A synergistic interaction occurred with 0.07 and 0.28 kg/ha atrazine and 0.56 kg/ha metribuzin (44). Soybean growth was stimulated with 0.07 kg/ha of atrazine. Atrazine rates of above 0.28 kg/ha appeared to overload the system, and the interaction was more additive than synergistic. Higher rates of metribuzin of 0.56 and 0.84 kg/ha were needed to show synergistic effects with atrazine at 0.28 kg/ha

(44). Atrazine at 0.14 kg/ha and metribuzin at 0.56 kg/ha applied under field conditions intersected synergisticly to reduce soybean growth. In the greenhouse a number of combinations with atrazine at 0.07 kg/ha or greater and metribuzin and 0.56 kg/ha and greater interacted synergisticly to reduce soybean fresh and dry weight 30 days after planting (44).

Over a soil pH range of 4.6, 5.6, and 6.7 atrazine-metribuzin interactions were more apparent as the soil pH increased (44). Soybean plants grown in culture solutions containing various atrazine concentrations showed increased or decreased ^{14}C-metribuzin uptake and plant transpiration, depending on the concentration of atrazine used in the preconditioning solution. Greater ^{14}C-metribuzin moved into the shoot and transpiration increased over the control at 10^{-7} M concentration of atrazine. Atrazine concentrations of 10^{-5} and 10^{-6} M inhibited transpiration and net uptake. Ladlie et al. (44) concluded the basis for the interaction was the effect of atrazine on the transpiration of the soybean plant and the associated increase or decrease in uptake of metribuzin. Synergistic interactions occurred when atrazine at subtoxic levels increased stomatal opening and increased transpiration, resulting in increased metribuzin uptake. The interaction was most apparent at high soil pH levels. An additive interaction appeared to result from higher concentrations of atrazine, which caused a reduction in transpiration (44).

Uptake and translocation of root fed atrazine increased as temperature increased. Greater uptake and translocation of atrazine occurred under low rather than high relative humidity (81).

VARIETAL RESPONSES

Researchers have found ways to reduce triazine injury to sensitive crops grown in atrazine treated soils. Hardcastle (28) found metribuzin by variety interactions existed as indicated by soybean stand height and yield reduction. Oplinger (55) showed tolerant varieties such as A78-123018, had minimal leaf kill of 3% when 3/4 lb/A of metribuzin was applied. Sensitive varieties, such as NK-1884, resulted in 55% leaf kill at the same rate. Average leaf kill for all varieties tested equalled 17%. Brinkman and Harvey (12) found differences in oat cultivars in tolerance to atrazine residue, but differences were not great enough to justify development of tolerant varieties.

Anderson (1) measured soybean varietal tolerance to atrazine by recording the percent reduction in dry weight compared to each varieties untreated check. Tolerance thus measured generally increased as seed size increased. Regression analysis indicated that 80% of the variation in response was attributed to variation in seed size. One possible explanation of these results may be that as atrazine was gradually dissipated during the test, the large seeded strains survived on food reserved in the cotyledons until concentrations reached a non-lethal level. The small-seeded strains may not have had enough reserves to survive until a non-lethal level was reached. Another explanation may be the larger seedling produced by larger seeds may have had a smaller absorbing surface related to the total seedling volume than did seedlings produced by small seeds.

Anderson also found that increasing soybean seeding rates 1.5 to 2.0 times can compensate for losses of yield that would be caused from atrazine carryover or excess metribuzin application (2).

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CHAPTER 2

FACTORS EFFECTING SOYBEAN RESPONSE TO ATRAZINE RESIDUE

ABSTRACT

Field experiments were initiated in the fall of 1982 to examine the effects of tillage on degradation of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) in soil. Interactions of atrazine residue with two soybean varieties and six soil applied preemergence herbicide treatments were also examined. Parameters used in evaluation included visual ratings of soybean injury and soybean yield.

Injury ratings at growth stage V4 indicated that minimum tillage, such as no-tillage and chisel plowing, resulted in greater atrazine injury than moldboard plowing. Metribuzin (4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one) at 0.42 kg/ha resulted in the greatest injury of the soybean herbicides tested, regardless of atrazine residue levels.

Metribuzin reacted synergistically with atrazine under chisel plowing. This may have been due to the disturbed trash layer, which allowed the metribuzin to reach the rooting zone and the atrazine residue, which remained in the rooting zone under the chisel plowed system.

Chloramben (3-amino-2,5-dichlorobenzoic acid) at 3.36 kg/ha resulted in decreased yields under no-tillage. combination of chloramben, lack of rainfall for incorporation, and a light textured soil, may have led to inhibition of root development, which in turn may have resulted in moisture stress and reduced yields. Due to a disturbed trash layer under the chisel and moldboard tillage, moisture stress masked the effect of chloramben.

INTRODUCTION

It is not uncommon for atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) applied one year to persist into the next growing season in sufficient concentration to cause injury to sensitive crops planted the following year (1, 3). Tillage influences the degradation and distribution of herbicide residues within the soil profile, which may alter the degree of crop injury the following year (3). Kells (13) found the rate of unextractable ^{14}C-atrazine from soil to be greater under no-tillage compared to conventional tillage. Burnside (7) also found atrazine carryover to be less of a problem under reduced tillage systems compared to conventional tillage. Similar results were found by Bauman and Ross (3).

Numerous authors have found pH to be directly linked to the rate of atrazine degradation (4, 5, 12, 13, 15). In an experiment by Best and Weber (4) 35% of the applied atrazine was recovered 5 months after application in a soil of pH 7.5, while only 11% was recovered in 5 months at pH 5.5. Hiltbold and Buchanan (12) found atrazine persistence to be linked to soil texture as well as to pH. An 8 to 9 day increase in persistence occurred in a McLaurin sandy loam per unit pH increase, while a 29 day increase occurred in a Decatur silt loam.

Most forms of ammonium nitrogen fertilizers are acid forming and their continued use lowers the soil pH (24). Lower and Weber (15) found by using $NaNO_3$, a basic nitrogen fertilizer, as the nitrogen source atrazine efficacy and longevity were increased compared to the use of NH_4NO_3, an acid nitrogen fertilizer. The use of acidifing nitrogen fertilizer in a no-tillage system results in an acid soil surface (13, 16, 22). This results in greater adsorption of atrazine to the soil (10, 16, 18, 20, 25), which in turn leads to more rapid degradation by means of chemical hydrolysis (2, 4, 11, 13, 15).

Similarly, if lime were added to the soil surface in a no-tillage situation, an alkaline surface layer would develop, resulting in decreased atrazine degradation (15, 17). Ladlie (16) reported atrazine residue in the soil may interact with metribuzin, resulting in increased injury to soybeans (Glycine max (L.) Merr.).

Reduced tillage systems also affect the soil surface in terms of the plant residue remaining. It was once thought that the plant residue would strongly adsorb preemergence herbicides (8). Groover (9), however, showed that picloram (4-amino-3,5,6-trichloropicolinic acid) was not adsorbed on either wheat (Triticum aestivum L.) straw or cellulose. Walker and Crawford (62) also showed that undecayed plant material left on the soil surface did not readily adsorb herbicides. Data from Bauman (3) showed 96 to 90% of the atrazine intercepted by corn (Zea mays L.) residue was lost 30 days after application and only 1% remained 90 days after application.

Elbach (8) found plant residue did not significantly affect weed control when herbicides were applied at the recommended rates, but had an increased influence as rates were reduced. Atrazine retention by crop residue appears to be primarily a function of the total amount of rainfall received and secondly dependent upon residue type and rainfall pattern (15). One 10 cm rain applied immediately or 7 days after atrazine application, removed approximately 87 and 77% of the residue from fresh oat (Avena sativa L.) plants and dry corn trash, respectively. Slightly less was removed when rainfall was applied as four 2.5 cm rains (15).

Blevins (6) found no-tillage treatments had higher volumetric moisture contents to a depth of 60 cm during most of the growing season. The greatest difference occurred in the 0 to 6 cm depth. Soil moisture curves showed different water withdrawal patterns between no-tillage and conventional tillage. The decrease in evaporation and the greater ability to store moisture under no tillage produced a greater water reserve.

Residue cover after tillage is dependent on both the crop being tilled under and the type of tillage method employed. The amount of residue left on the soil surface with a chisel plow varies from 10 to 20% with 4 10.2 cm twisted shanks to 50% or greater with narrow points. The percent residue left on the surface is also dependent on the number and type of secondary tillage operations employed in seedbed preperation (8).

MATERIALS AND METHODS

A field study examining the effects of tillage systems and atrazine residue levels on soybean growth was initiated in the fall of 1982. The site selected was a Kalamazoo loam (Typic Hapludalf, fine-loamy, mixed mesic, 0 to 2% slope, pH 6.8) at the Kellogg Biological

Research Station in southwestern Michigan. This site had no recent history of triazine use.

In the fall of 1982 three tillage systems were initiated into soybean stubble, these systems being no-tillage, chisel plowing, and moldboard plowing.

Four strips of each tillage system were arranged into four blocks in a split plot design. A split plot design was needed due to the impracticality of tilling individual plots. A soil finisher was used to prepare a seedbed on the chisel and moldboard plowed areas in the spring of 1983, prior to planting. Corn ('Pioneer 3747') was planted the second week of May in the same direction tillage was conducted.

Atrazine was then applied perpendicularly to the tillage systems at rates of 0, 1.12, or 2.24 kg/ha. Application of all rates were made across all tillage systems in strips within each replication. This was done to reduce complexity in application of the atrazine as well as later herbicide applications. Alachlor at 2.24 kg/ha along with 0.56 kg/ha paraquat plus X-77[1] was also applied to all plots for grass control and for burndown on the (1/4% v/v) no-tillage plots, respectively. Corn was harvested in the fall and the stalks chopped. Fall tillage was then implemented with each tillage area receiving the same tillage as in 1982.

In the spring of 1984, seedbeds on the moldboard and chisel plowed strips were prepared using a soil finisher. Each sub sub-plot (tillage system x atrazine rate) was subdivided into six sub-plots with each

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[1]X-77 is a nonionic surfactant composed of a mixture of alkylarylpolyoxyethyene glycols, free fatty acids, and isopropenol.

receiving a different soybean herbicide treatment. The treatments included were: a) an untreated check, b) chloramben at 3.36 kg/ha, c) metribuzin at 0.42 kg/ha, d) metribuzin at 0.56 kg/ha, e) linuron at 0.84 kg/ha, and f) linuron at 1.12 kg/ha. Treatments were applied May 21st, 3 days after planting. The entire location was treated with 2.8 kg/ha of alachlor, the no-tillage plots also received 0.56 kg/ha paraquat + X-77 (1/4% v/v). All treatments were applied 207 kilopascals in 215 L/ha of water with a compressed air mounted sprayer on a cub tractor.

Two group II soybean varieties were planted in each plot, Northrup King 1492 and Corsoy 79. Corsoy 79 was chosen because of its popularity and its moderate tolerance to metribuzin. NK 1492 was chosen due to its high tolerance to metribuzin. The rational for using two varieties was to check for varietal responces due to tillage, atrazine residue, and soybean herbicides.

Visual injury evaluations were taken at the V2, V4, and V7 growth stages. Ratings were made on a 0 to 10 scale, based on reduction in plant vigor and visible signs of herbicide injury, such as leaf chlorosis and necrosis. Yields were determined by harvesting 11.1 meters of the one row plots. Yields were calculated based on 13.0% moisture.

RESULTS AND DISCUSSION

No differences in yield occurred between Corsoy 79 and Northrup King 1492, due to tillage systems (Table 1). Varietal responses due to atrazine treatment, when averaged over soybean herbicide treatments, existed at soybean growth stages V4 and V7 (Table 2). This occurred

Table 1. The effect of tillage on varietal differences in soybean yield averaged over atrazine treatments.[a]

Tillage System	Soybean Yield	
	Corsoy 79	Northrup King 1492
	(kg/ha)	
No-tillage	1134 A	1176 A
Chisel plowed	648 B	546 B
Moldboard plowed	786 B	486 B

[a]Means within columns or rows followed by the same letter are not significantly different at the 10% level according to Duncan's multiple range test.

Table 2. Varietal responses, in terms of injury, to atrazine residue under chisel plowing.[a]

Atrazine Rate	Growth Stage	Variety: Corsoy 79	Variety: Northrup King 1492
(kg/ha)		(% Injury)	
	V2		
0		5 C	3 C
1.12		16 B	14 B
2.24		28 A	24 A
	V4		
0		5 D	1 D
1.12		14 C	16 C
2.24		31 B	37 A
	V7		
0		4 C	1 D
1.12		7 C	5 CD
2.24		15 B	20 A

[a]Means within growth stages followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

only at the high atrazine levels (2.24 kg/ha) under the chisel plowed system. Corsoy 79 appeared more tolerant to atrazine than Northrup King 1492, but differences were relatively small (Table 2).

Soybean herbicide treatments resulted in varietal responses only under moldboard tillage at growth stage at V2 (Table 3). Metribuzin resulted in greater injury to Corsoy 79 than to Northrup King 1492. It has previously been shown that Northrup King 1492 is relatively tolerant to metribuzin when compared to other commonly grown U.S. varieties, including Corsoy 79 (19).

It is believed this interaction occurred only under moldboard plowing, due to the zero crop residue cover under this tillage system (Appendix A) and to the dry spring in 1984 (Appendix B). Under the moldboard system, no crop residue remained on the soil surface to intercept the metribuzin application. No-tillage and chisel plowed plots retained a 45 and 75% residue cover, respectively. Under normal rainfall conditions, crop residue may not have been important, however, without sufficient rainfall the metribuzin may have remained on the crop residue off the soil surface longer on the chisel and no-tillage plots. With chisel plowing, metribuzin application resulted in greater injury to Corsoy 79, however, this was only significant at the 10% level. Chisel plowing left a 45% crop residue cover, which may have allowed more of the metribuzin to reach the soil. No difference in injury occurred under no-tillage, where a 75% residue cover remained (Table 3).

Due to the limited varietal interactions and the small differences, which occurred in the existing interactions, only the widely-used Corsoy 79 variety was used in the remainder of the analysis.

Table 3. Varietal response to soybean herbicides under three tillage systems averaged over atrazine rates at growth stage V2.[a]

Tillage	Soybean Herbicide	Rate	Variety: Corsoy 79	Variety: Northrup King 1492
		(kg/ha)	(% Injury)	(% Injury)
No-tillage				
	Chloramben	3.36	4 C	6 C
	Metribuzin	0.42	13 AB	13 A
	Linuron	0.84	4 C	4 C
	Untreated	-	4 C	8 BC
Chisel plowed				
	Chloramben	3.36	9 C	7 C
	Metribuzin	0.42	24 A	17 AB
	Linuron	0.84	12 BC	11 BC
	Untreated	-	12 BC	12 BC
Moldboard plowed				
	Chloramben	3.36	4 BCD	8 BC
	Metribuzin	0.42	13 A	6 BCD
	Linuron	0.84	4 BCD	6 BCD
	Untreated	-	2 D	1 D

[a]Means within tillage system followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

The greatest series of interactions occurred at growth stage V4. Metribuzin interacted with both rates of atrazine, which resulted in increased injury (Table 4).

Ladlie et al. (14) also found metribuzin to interact with atrazine residue, resulting in increased soybean injury. Synergistic interaction occurred when sublethal atrazine rates increase soybean transpiration and subsequently, increase metribuzin uptake.

Tillage accomplished two functions, first, atrazine was buried and/or diluted under the moldboard system and was left in place under both no-tillage and chisel plowing. This resulted in equal injury under no-tillage and chisel plowing, both of which were greater than under moldboard plowing (Figure 1). Secondly, the crop residue levels under each tillage system were altered.

Under the moldboard system, metribuzin reached the soil surface unimpeded, but the atrazine had been diluted, thus there was no interaction between tillage, atrazine and metribusin (Figure 2). However, metribuzin did result in increased injury under moldboard plowing at both atrazine rates, compared to the other soybean herbicide treatments at growth stage V2 (Figure 3). This did not occur under the chisel or no-tillage systems (Figure 4, 5). Metribuzin did not cause increased soybean injury at growth stage V4, probably due to either increased degradation by the time the plants grew to this growth stage or by the soybean root system growing out of the herbicide containing soil zone (Table 4).

No-tillage left the atrazine residue intact, but the high crop residue level appears to have inhibited from metribuzin reach the root zone (Figure 2). Sufficient rainfall to incorporate the metribuzin into the root zone did not occur.

Table 4. The effect of soybean herbicides on injury with increasing atrazine rates at growth stage V4 under three tillage systems.[a]

			Atrazine (kg/ha)		
Tillage	Soybean Herbicide	Rate	0	1.12	2.24
		(kg/ha)	(% Injury)		
No-tillage					
	Chloramben	3.36	0 J	0 J	18 C-H
	Metribuzin	0.42	3 IJ	5 HIJ	18 C-H
	Linuron	0.84	0 J	5 HIJ	18 C-H
	Untreated	-	0 J	10 F-J	28 BCD
Chisel plowed					
	Chloramben	3.36	3 IJ	13 E-J	25 B-E
	Metribuzin	0.42	0 J	23 C-F	38 A
	Linuron	0.84	0 J	10 F-J	30 ABC
	Untreated	-	0 J	13 E-J	25 B-E
Moldboard plowed					
	Chloramben	3.36	0 J	3 IJ	5 HIJ
	Metribuzin	0.42	3 IJ	3 IJ	18 C-H
	Linuron	0.84	0 J	0 J	20 C-G
	Untreated	-	0 J	3 IJ	8 G-J

[a]Means within columns or rows followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

Figure 1. Soybean injury in 1984 under no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB), following atrazine application in 1983. No herbicide was applied in 1984.

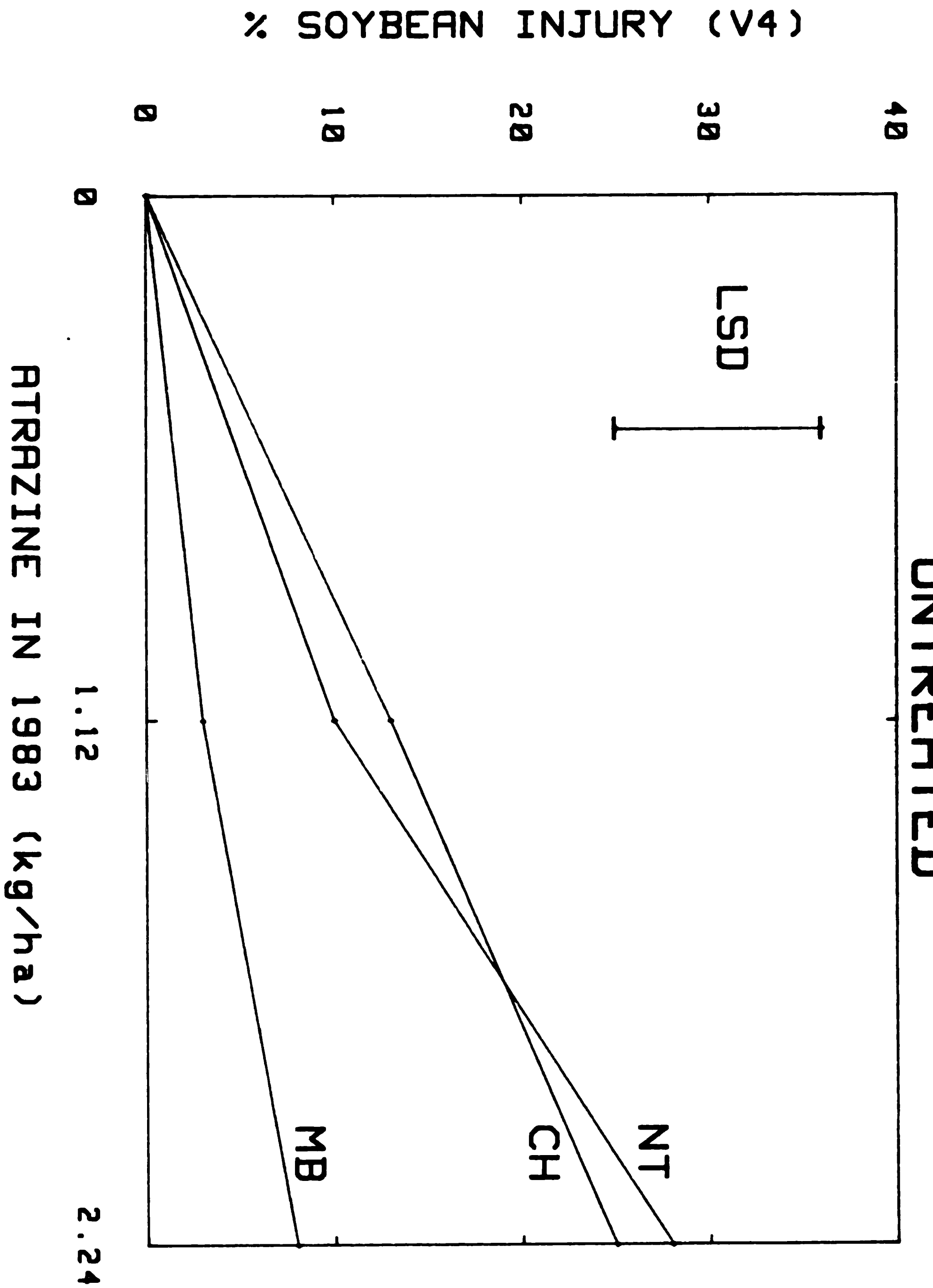

UNTREATED
% SOYBEAN INJURY (V4)
0
10
20
30
40
LSD
NT
CH
MB
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

Figure 2. Soybean injury in 1984 under no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB), following atrazine application in 1983. Metribuzin was applied preemergence in 1984.

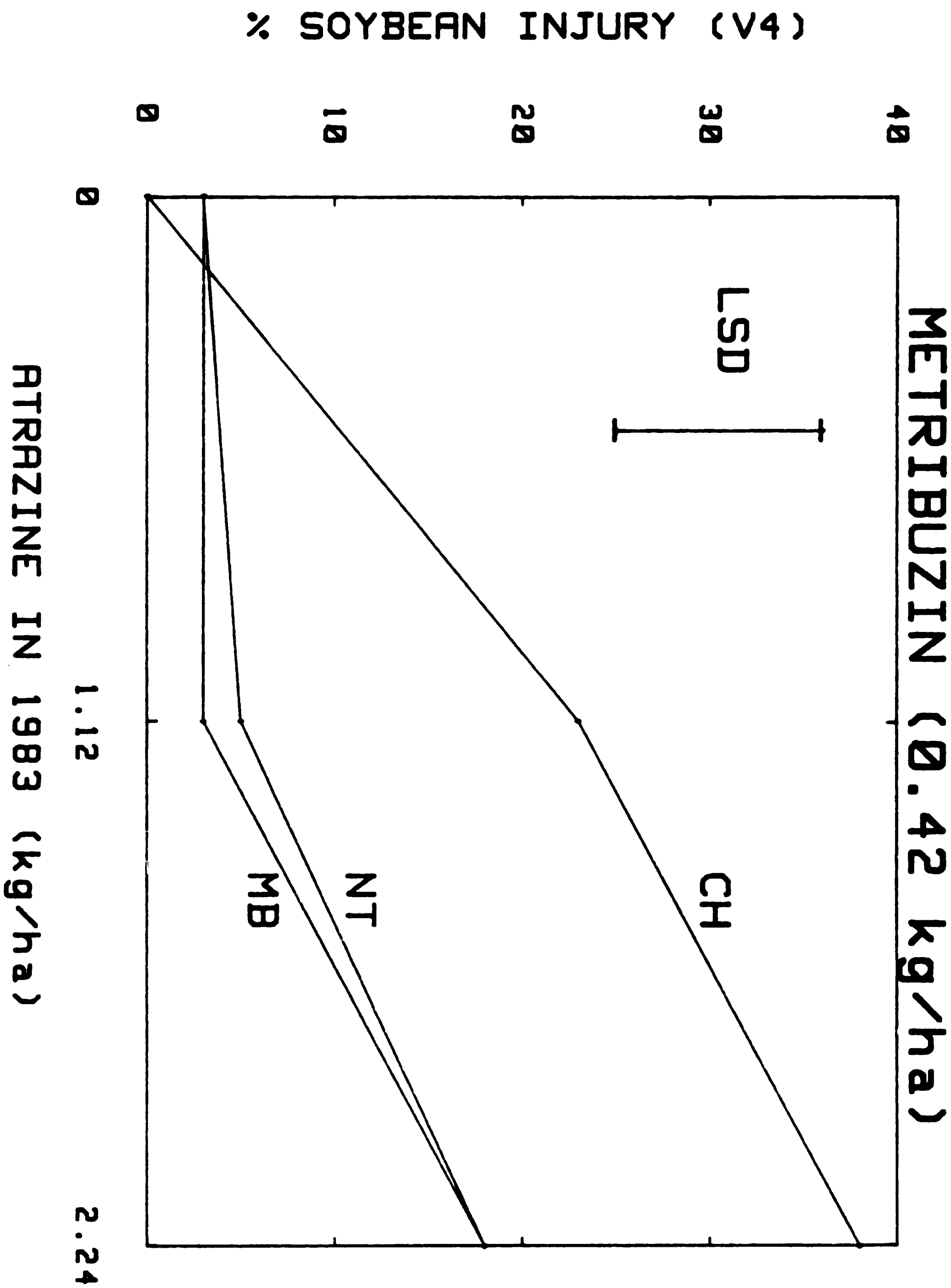

METRIBUZIN (0.42 kg/ha)
% SOYBEAN INJURY (V4)
0
10
20
30
40
0
1.12
2.24
LSD
CH
NT
MB
ATRAZINE IN 1983 (kg/ha)

Figure 3. Soybean injury in 1984, under moldboard plowing, following atrazine application in 1983. Metribuzin (MET), chloramben (CHL), or linuron (LIN) were applied in 1984, or no application was made (UNT).

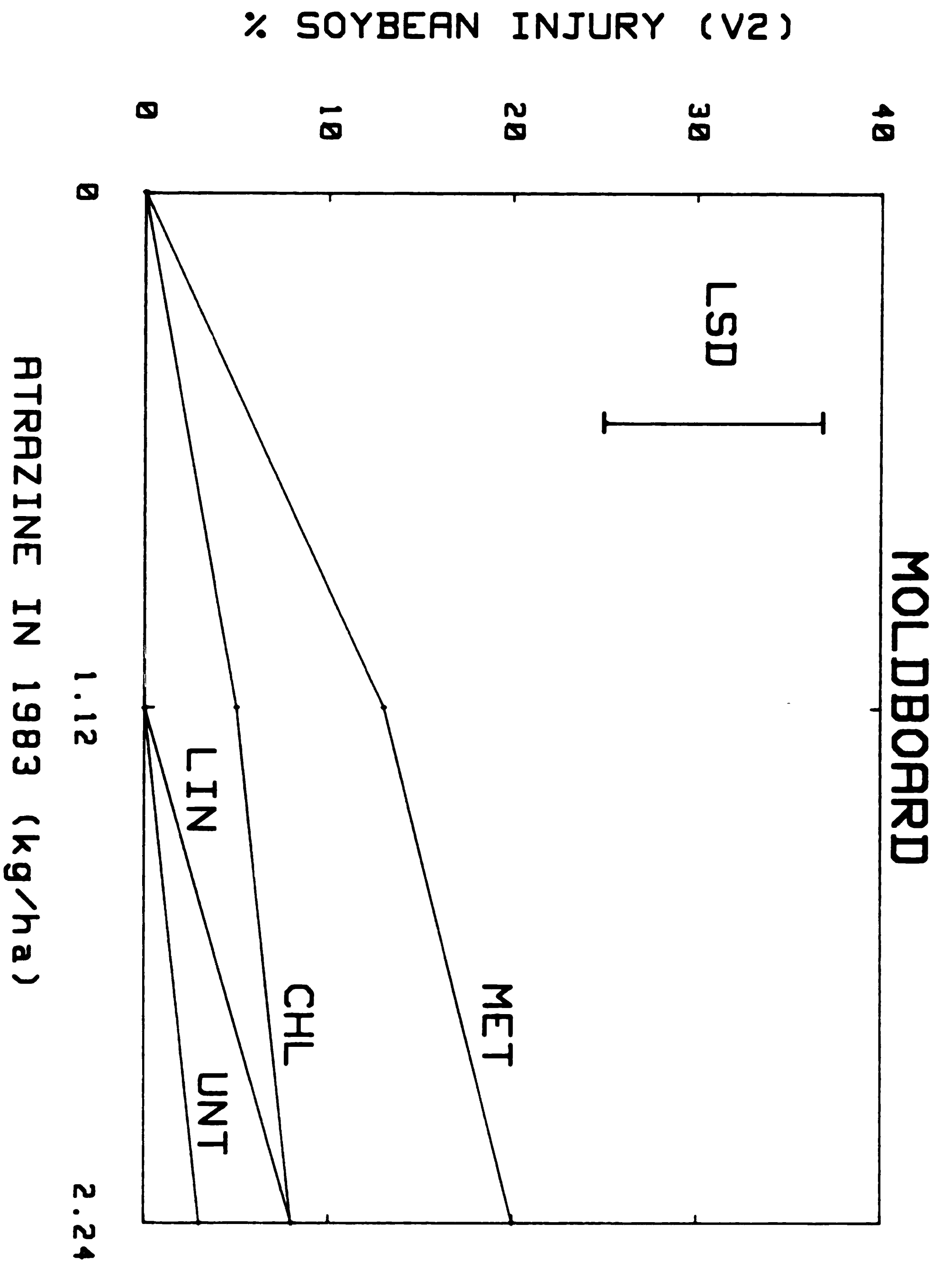

MOLDBOARD
% SOYBEAN INJURY (V2)
0
10
20
30
40
LSD
MET
CHL
LIN
UNT
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

Figure 4. Soybean injury in 1984, under chisel plowing, following atrazine application in 1983. Metribuzin (MET), chloramben (CHL), or linuron (LIN) were made in 1984, or no application was made (UNT).

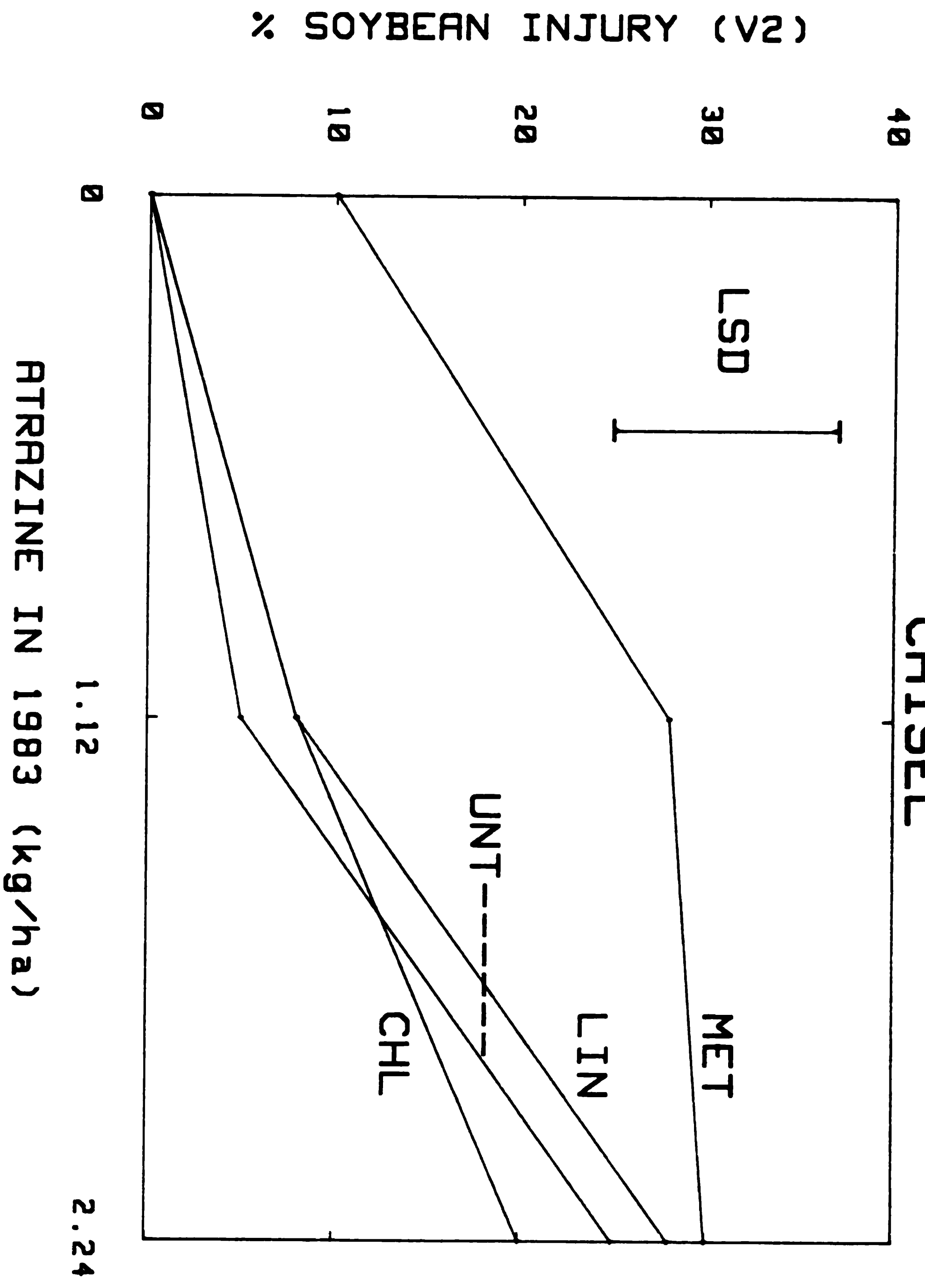
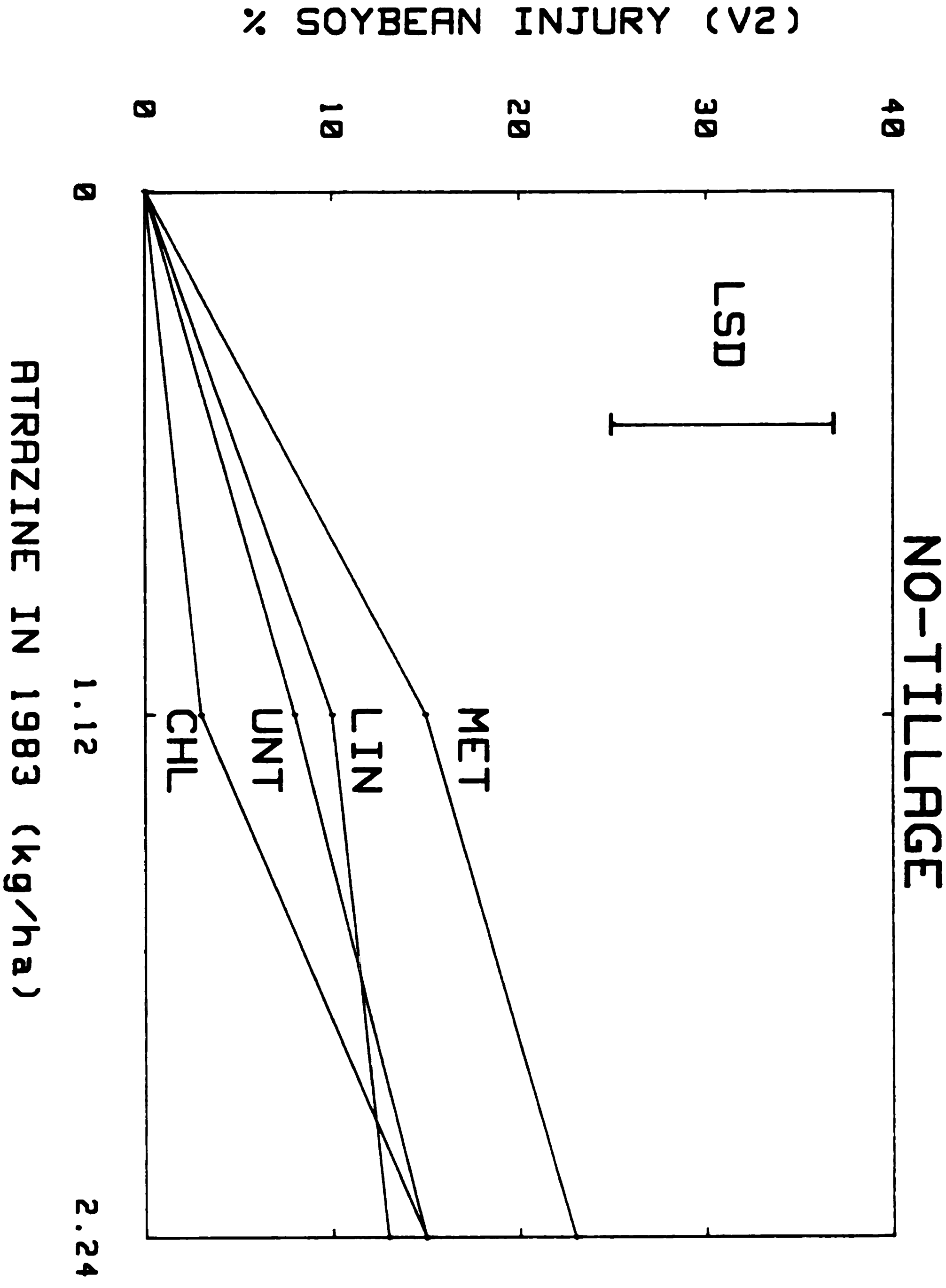

CHISEL
% SOYBEAN INJURY (V2)
0
10
20
30
40
LSD
MET
LIN
UNT
CHL
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

Figure 5. Soybean injury in 1984, under no-tillage, following atrazine application in 1983. Metribuzin (MET), chloramben (CHL), or linuron (LIN), were applied in 1984, or no application was made (UNT).


NO-TILLAGE
% SOYBEAN INJURY (V2)
0
10
20
30
40
LSD
MET
LIN
UNT
CHL
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

Chisel plowing loosened the soil as opposed to turning it over as in moldboard plowing, therefore, the atrazine residue remained relatively undisturbed. Chisel plowing does, however, incorporate some of the surface plant residue into the soil. When metribuzin was applied under this tillage system, more of it may have reached the soil due to the reduction in plant residue cover. This resulted in a three-way interaction between atrazine, metribuzin and the chisel plowing system at growth stage V4 (Figure 2). Under chisel plowing sublethal levels of atrazine may have increased transpiration which in turn may have increased metribuzin uptake and therefore resulted in increased injury. Chloramben and linuron were not involved in three-way interactions with tillage, varieties or atrazine residue levels (Figures 6 and 7).

No interactions between tillage, soybean herbicides and atrazine residue levels occurred at growth stage V7 (Figures 8, 9 and 10). Atriazine and/or metribuzin may have degraded to levels low enough not to show interactions with tillage or each other. Another explanation may be that at this stage the root system may have grown past the herbicide containing soil zone. During a dry year, such as 1984, the root system may have grown deeper in seach for water. A combination of these explanations is probably the case.

Atrazine application independently influenced injury at all growing stages, (Table 2), along with interacting with both soybean herbicides and tillage at V4 (Table 4). As expected, soybean injury increased as atrazine rate increased.

Although tillage did not significantly influence yield at the 5% level according to Duncan's Multiple Range Test, it did at the 10%

Figure 6. Soybean injury in 1984, under no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB), following atrazine application in 1983. Chloramben was applied preemergence in 1984.

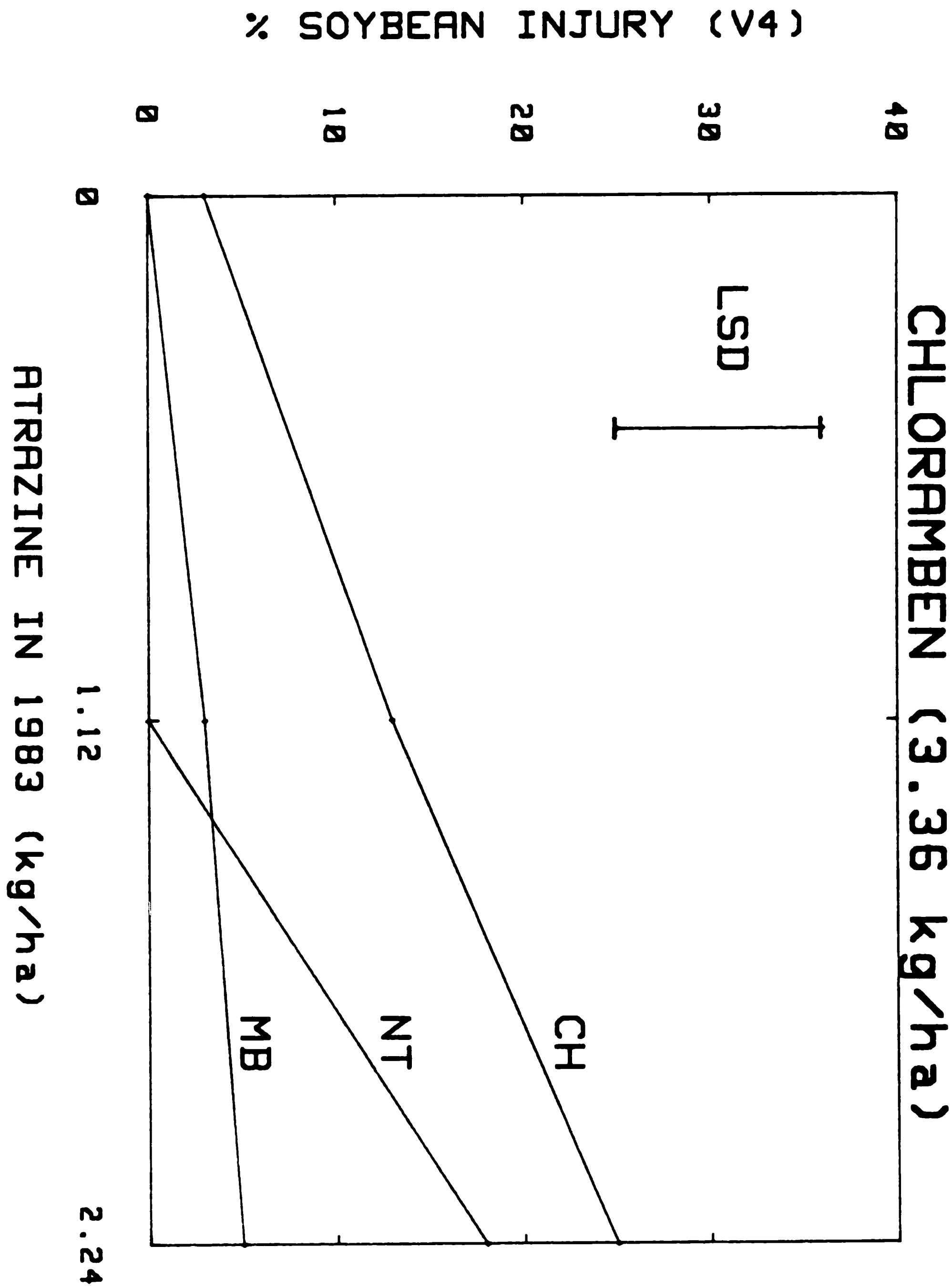

CHLORAMBEN (3.36 kg/ha)
% SOYBEAN INJURY (V4)
ATRAZINE IN 1983 (kg/ha)
LSD
CH
NT
MB
0
10
20
30
40
0
1.12
2.24

Figure 7. Soybean injury in 1984, under no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB), following atrazine application in 1983. Linuron was applied preemergence in 1984.

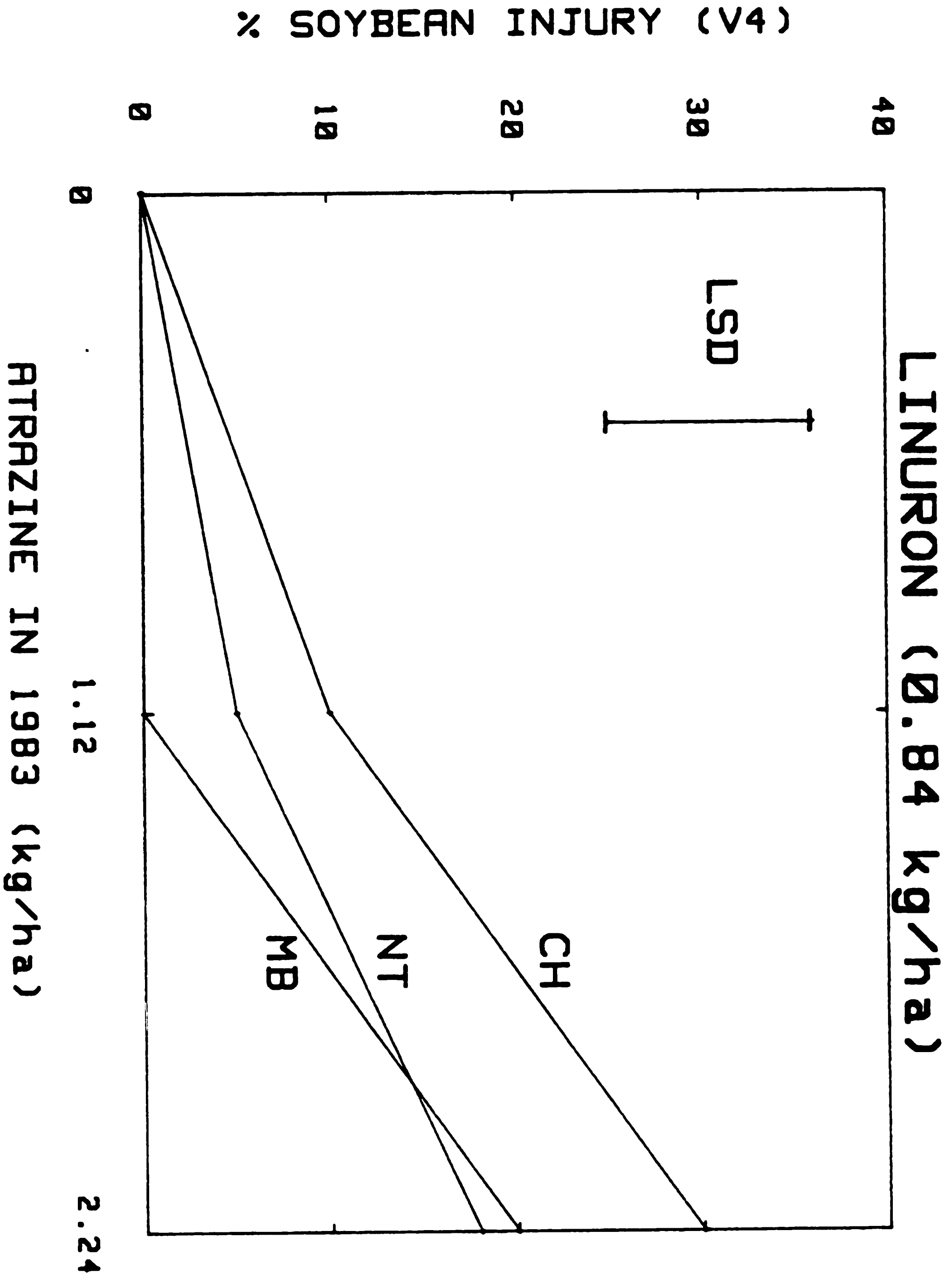

LINURON (0.84 kg/ha)
% SOYBEAN INJURY (V4)
0
10
20
30
40
LSD
CH
NT
MB
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

Figure 8. Soybean injury in 1984, under moldboard plowing, following atrazine application in 1983. Metribuzin (MET), chloramben (CHL), or linuron (LIN), were applied in 1984, or no application was made (UNT).

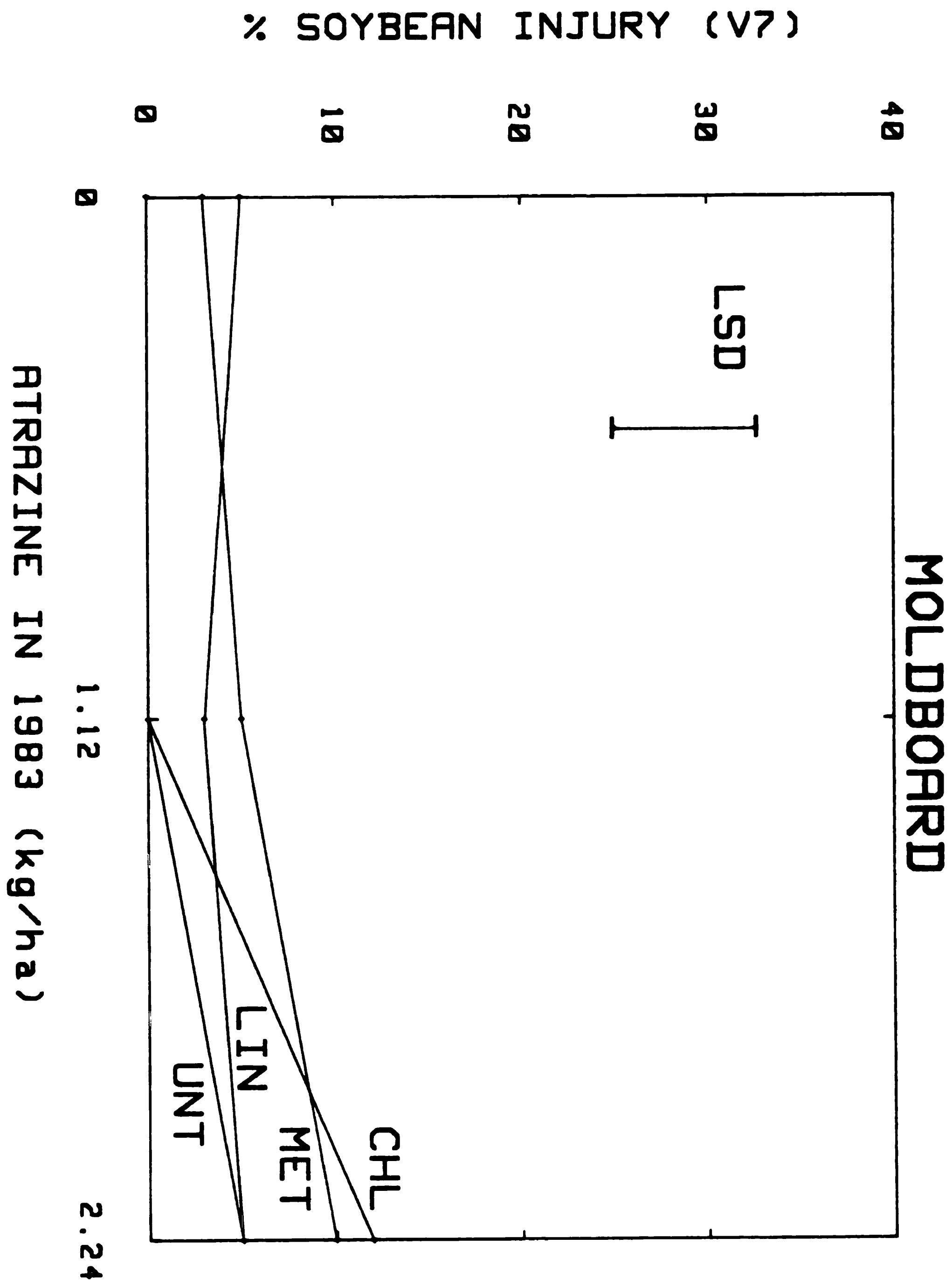

% SOYBEAN INJURY (V7)
0
10
20
30
40
MOLDBOARD
LSD
CHL
MET
LIN
UNT
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

Figure 9. Soybean injury in 1984, under no-tillage, following atrazine application in 1983. Metribuzin (MET), chloramben (CHL), or linuron (LIN), were applied in 1984, or no application was made (UNT).

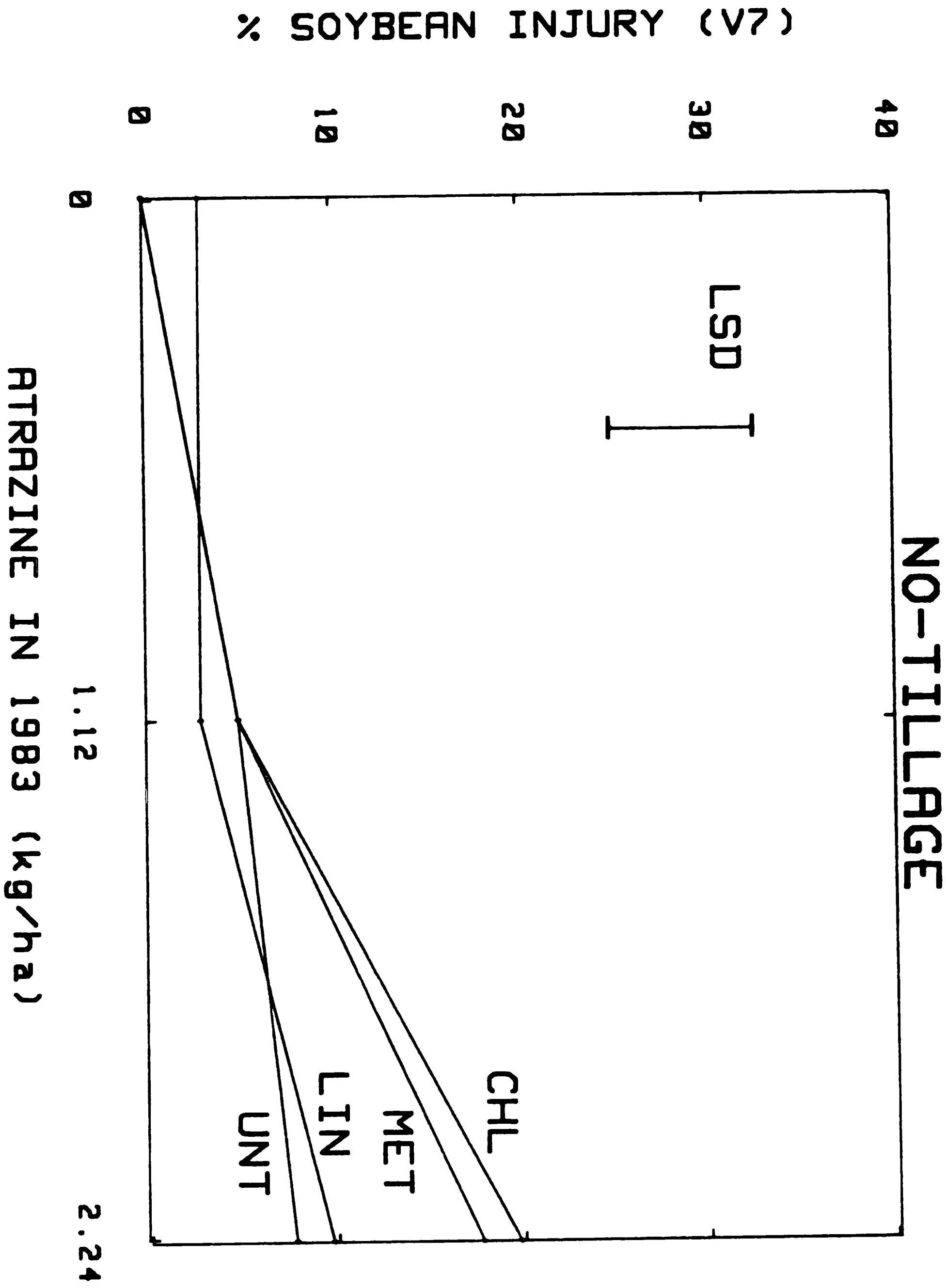
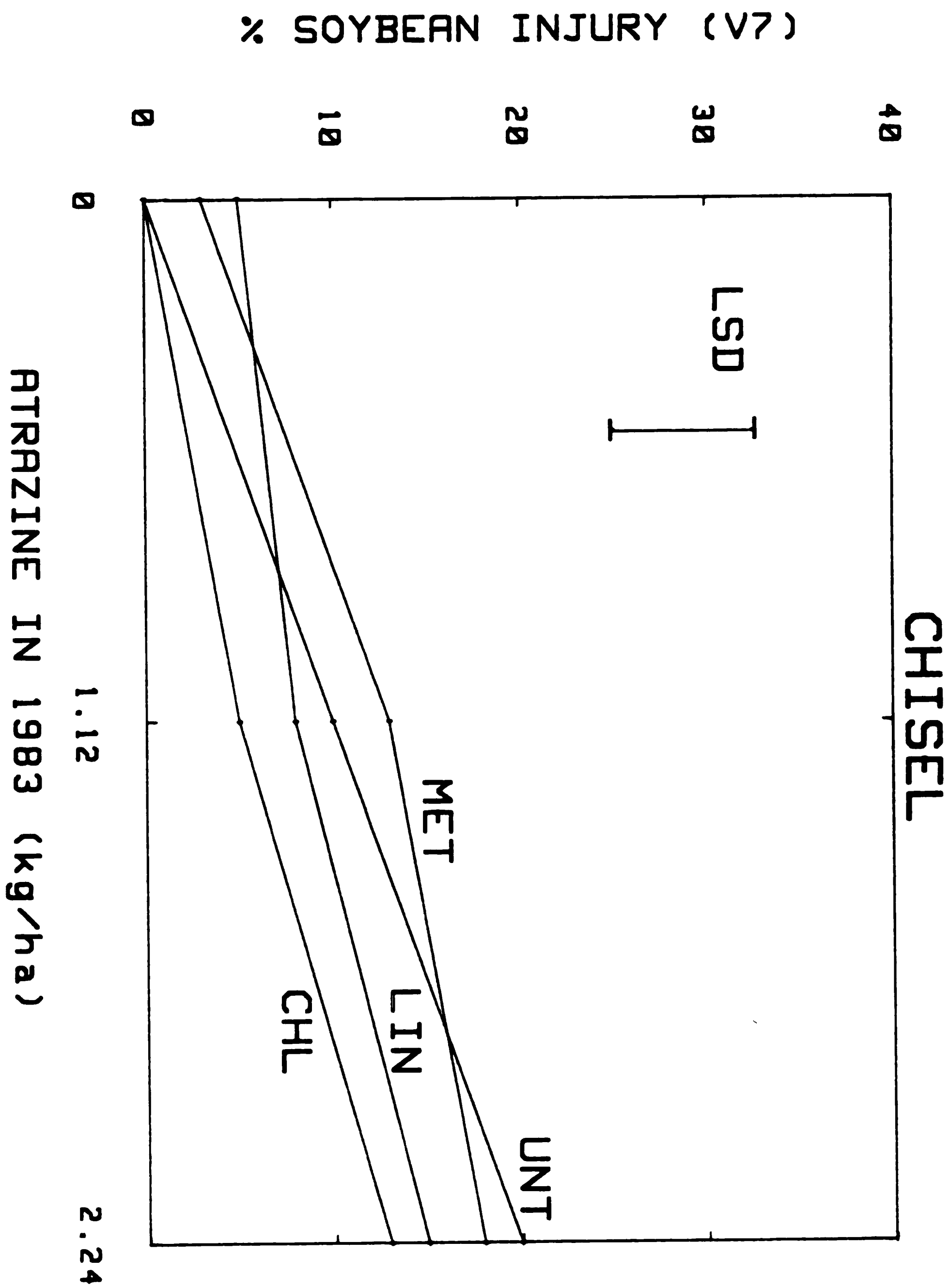

NO-TILLAGE
% SOYBEAN INJURY (V7)
0
10
20
30
40
LSD
CHL
MET
LIN
UNT
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

Figure 10. Soybean injury in 1984, under chisel plowing, following atrazine application in 1983. Metribuzin (MET), chloramben (CHL), or linuron (LIN), were applied in 1984, or no application was made (UNT).


CHISEL
% SOYBEAN INJURY (V7)
0
10
20
30
40
LSD
MET
LIN
CHL
UNT
0
1.12
2.24
ATRAZINE IN 1983 (kg/ha)

level. No-tillage resulted in the greatest soybean seed yields (Table 5). This was probably due to increased moisture conservation under the no-tillage system in response to the high crop residue level.

Tillage interacted with chloramben, resulting in a decrease in yield under the no-tillage system (Figure 11). Chloramben was applied at 3.36 kg/ha on a Kalamazoo loam soil, characterized by mid-summer droughtiness. The effect of this somewhat high rate was compounded by the lack of rainfall, which resulted in the chloramben remaining near the root zone for an extended period of time. This may have inhibited seedling root development, as stated by Ross (20), which would have resulted in increased moisture stress compared to the other soybean herbicide treatments under the no-tillage system.

In the chisel and moldboard tillage systems, the crop residue layer was reduced or non-existent. Therefore, moisture conservation was poor and moisture stress had already occurred in all of the soybean herbicide treatments, which masked any affect of chloramben.

In conclusion, atrazine-metribuzin interactions occurred when both were available for plant uptake. Chisel plowing resulted in the greatest combination of atrazine and metribuzin uptake as shown in terms of injury, at growth stage V4. This interaction was masked in terms of soybean yield due to moisture stress.

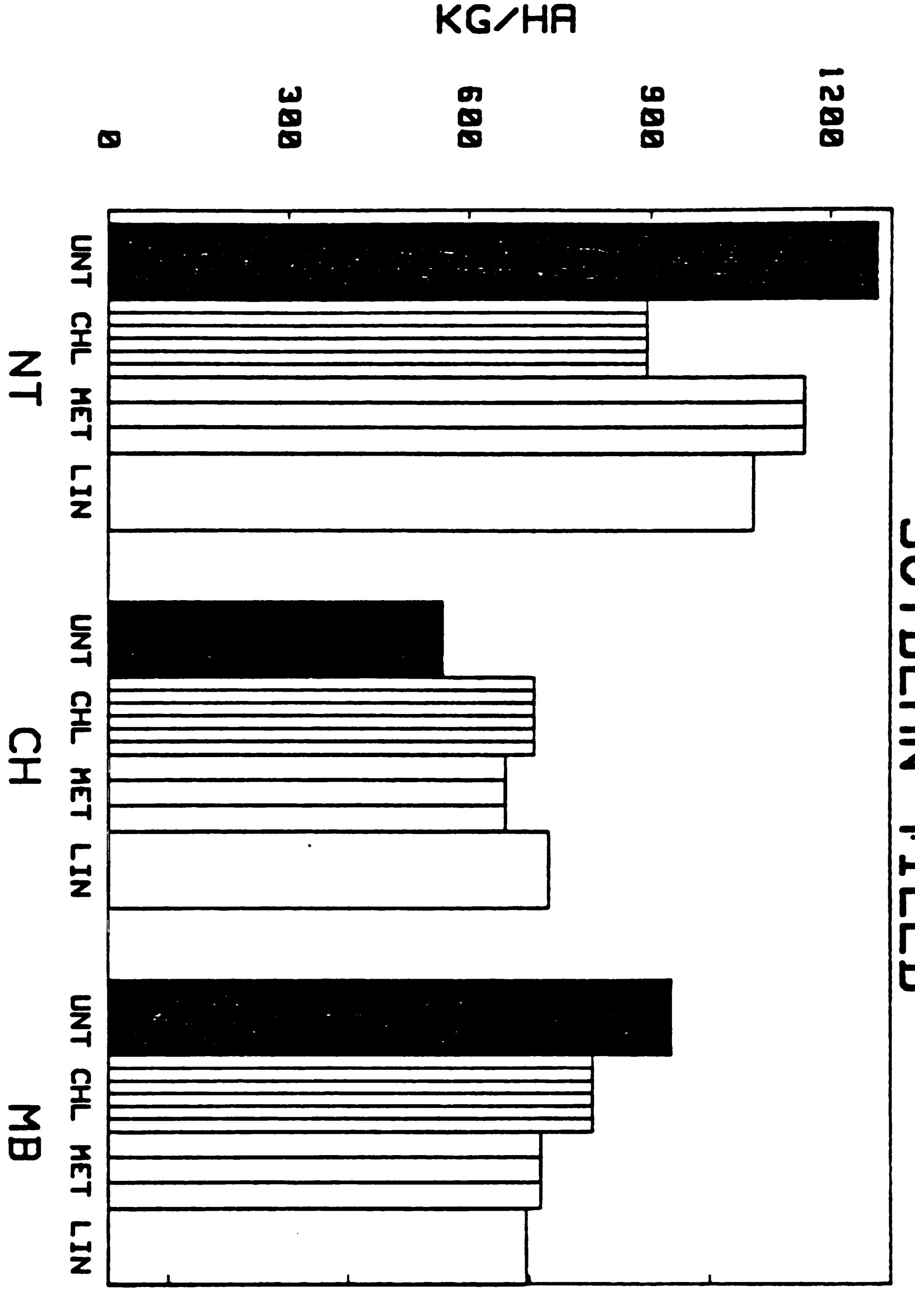
Chloramben inhibited root development, which led to decreased yields due to moisture stress under no-tillage. Drought stress masked this under chisel and moldboard-tillage systems.

Table 5. The effect of tillage system on soybean yield.[a]

Tillage System	Yield
	(kg/ha)
No-tillage	1134 A
Chisel plowed	648 B
Moldboard plowed	786 B

[a]Means followed by the same letter are not significantly different at the 10% level according to Duncan's multiple range test.

Figure 11. The effect of soybean herbicides on yield within three tillage systems, no tillage *NT), chisel plowing (CH), and moldboard plowing (MB). All treatments were maintained in a weed free environment.


SOYBEAN YIELD
KG/HA
0
300
600
900
1200
UNT CHL MET LIN
NT
UNT CHL MET LIN
CH
UNT CHL MET LIN
MB

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CHAPTER 3

ATRAZINE DEGRADATION AND DISTRIBUTION AS EFFECTED BY TILLAGE

ABSTRACT

The effect of tillage systems on atrazine (2-chloro-4-(ethylamino)-6-(isoproplamino)-s-triazine) disappearance and distribution in soil was examined on a Kalamazoo loam (Typic hapludalp, fine-loamy, mixed misc.). Tillage, prior to atrazine application, had no effect on atrazine persistence as measured by extractable atrazine remaining in the soil. No differences were recorded in soil surface pH between tillage systems. Percent extractable atrazine in the soil was greater from the high application rate (2.24 kg/ha) of atrazine compared to the low rate (1.12 kg/ha) at both 133 and 350 days after application, regardless of tillage system.

The majority of extractable atrazine was located in the 5 to 15 cm profile under all tillage systems for both application rates. No differences in atrazine distribution between tillage systems were found within the 0 to 5 and the 5 to 15 cm sampling depth. Tillage systems did not influence atrazine persistence.

INTRODUCTION

Atrazine applied 1 year has the potential to carryover into the next growing season, thereby resulting in injury to subsequently grown crops. Factors which affect the amount of residual left in the rooting zone include degradation and distribution, both of which are influenced by many other factors.

Best and Weber (5) determined the pattern of atrazine degradation was characterized by non-biological processes. Skipper et al. (15) reported chemical hydrolysis of the s-triazines to their hydroxy analogs to be the major pathway of degradation, with microbial degradation being of minor importance.

Chemical hydrolysis of atrazine to non-phytotoxic hydroxy atrazine is considered the predominate route of atrazine detoxication in soil (2). Harris (9) believed that hydrolysis occurred at the 2 position more rapidly than subsequent degradation steps. Armstrong (2) and Harris (9) have both shown atrazine in contact with soil was degraded faster than atrazine in aqueous solution. This suggests soil or some soil constitute catalyzed degradation. Both attributed the increased degradation to a non-biological constitute, which catalyzed atrazine to 2-hydroxyatrazine. The $^{14}CO_2$ evolved from the s-triazine ring ranged from 25 to 40 times greater from hydroxyatrazine than from atrazine (20).

Possible degradation pathways of the side chain components of atrazine include dealkylation of the ethyl side chain along with dealkylation of the isopropyl side chain. Microbial attack appears to be predominately on the ethyl side chain (21). Diethylated atrazine has herbicidal properties which may explain phytotoxity where analytical data indicates low levels of atrazine in soil (18).

Hiltbold and Buchaman (11) found atrazine persistence to increase with increasing pH. Extractable atrazine was greatest where surface pH was greater than 6.5 compared to areas with surface pH's lower than 5.0 (12). This is explained by Best and Weber (5) who found more rapid hydrolysis of atrazine to hydroxyatrazine in soil of pH 5.5, than 7.5. Acidity is probably the most important factor of the soil colloidal system that influences adsorption and desorption as well as acid catalyzed soil degradation (3).

Of the soil constitutes, organic matter is most highly related to atrazine adsorption and phytotoxicity (1, 8, 10, 15, 22, 23). Availability of soil applied s-triazines to plants generally decreases as clay and/or organic matter content increases (24). Texture also influences adsorption and therefore, degradation. McCormick (14) found evolution of CO_2 from a Decatur clay loam was twice that of a Norfolk loamy sand. Hiltbold and Buchaman (11) found persistence of atrazine was positively related to soil pH in three soil types. The pH effect on a McLaurin sandy loam amounted to a 8 to 9 days increase in persistence per unit increase in pH. In a Hartsell's fine sandy loam, a 9 to 13 day increase in persistence was found per unit increase in pH and a 29 day increase was found in a Decatur clay loam (11). Burnside (6) found soil carryover of herbicide residue was greater in coarse as opposed to fine texture soils and in drier regions of Nebraska opposed to more humid regions.

Herbicide carryover in soil in levels toxic to plants is less serious in the humid regions than in the more arid regions of the United States (16, 17). Roeth (16) found that increasing soil moisture from 40 to 80% resulted in 0 to 6-fold increases in $^{14}CO_2$ evolution from chain labeled ^{14}C-atrazine.

Temperature also influences atrazine degradation. McCormick and Hiltbold found atrazine degradation doubled for each 10°C increase in temperature from 10 to 30°. Roeth (16) also found atrazine to be degraded two to three times faster in top soil than in sub-soil of a Sharpeburgh silty clay loam and a Keith silt loam soil. Each 10°C temperature increase from 15 to 35°C resulted in the rate of degradation to double or triple. Once a herbicide is leached into the lower soil profile its dissipation is markedly reduced. One reason for this is herbicide degradation by both biological and non-biological means decrease with reduced soil temperature (15). Microbial activity is also reduced with increasing depth due to decreased oxygen levels (7).

Field studies by Bauman (4) on the persistence of atrazine showed less carryover under coulter than chisel or conventional tillage in the year of application. Burnside (6) found soil persistence of normal use rates of atrazine into the subsequent growing season as a minor problem under reduced tillage systems. Atrazine carryover in soil was less of a problem under reduced tillage systems as compared with prior experiments with conventional tillage systems across Nebraska.

Lowder (13) found surface soil pH levels during the growing season were higher with no-tillage than with conventional tillage, due to the retention of lime on the surface in no-tillage vs mixing with the soil in conventional tillage. Atrazine carryover in soil was less of a problem under reduced tillage systems compared with prior experiments with conventional tillage systems across Nebraska (13).

It is the objective of this study to examine the effects of tillage on the disappearance and distribution of atrazine within the soil profile.

MATERIALS AND METHODS

A laboratory study examining the effects of tillage systems on atrazine distribution and degradation was conducted at the Kellogg Biological Research Station, Hickory Corners, Michigan . In the fall of 1982, three tillage systems were initiated into soybean stubble. These systems being no-tillage, chisel plowing, and moldboard plowing. Atrazine was applied at 0, 1.12, and 2.24 kg/ha across all tillage systems in the spring of 1983, following corn planting.

Soil samples were taken immediately after atrazine application to a depth of 5 cm. After corn harvest, 133 days after atrazine application, soil cores were taken at 0 to 5 and 5 to 15 cm depth.

Tillage was repeated in the fall of 1983. A soil finisher was used to prepare a seedbed on the moldboard and chisel plowed plots in the spring of 1984. Soybeans were then planted. Soil samples were taken at 0 to 5 and 5 to 15 cm depths following planting. All soil cores were stored in cardboard sample boxes and frozen until analysis.

A Soxhlet extraction apparatus was used to extract six soil samples simultaneously. Samples were thawed 48 hours before extraction, allowed to air-dry, and were ground with a porcelain morter and pestle. Ten grams samples were measured using an analytical balance, all stones and large pieces of plant material were removed. The sample was then placed into a single thickness cellulose extraction thimble and 1 to 2 ml distilled water was added. Glass wool was used to cover the soil to avoid soil splashing during reflushing. One-hundred ml of pesticide grade acetone along with 50 ml analytical grade methylene chloride was added to a 250-ml flat bottom boiling flask as the solvent.

The cellulose thimble containing the soil sample was then inserted into the Soxhlet extraction tube. The boiling flask was attached to the bottom on the extraction tube and placed onto a heating pad. Allihn condensers were placed above the extraction tube with cold water running through. The solvents were allowed to reflux 8 hrs ($\pm$ 15 min).

After the heating pad cooled, the flask containing the extracted atrazine was evaporated to near dryness, approximately 2 to 3 ml. This was done to remove the methylene chloride. Methylene chloride has a higher vapor pressure and therefore, volatilized more readily than acetone. The flask was then rinsed with acetone to dilute any remaining methylene chloride and was then evaporated to 2 to 3 ml. Only reagent grade acetone was used throughout the extraction procedure.

The sample was filtered through anhydrovs sodium sulfate into a 10 ml volumetric flask to remove any water. Approximately 5 ml of acetone was sprayed into the flask and swirled around to remove any remaining atrazine, it was then filtered into the volumetric flask. The sample was then brought close to volume by applying acetone through the funnel. This was done to rinse any remaining atrazine from the sodium sulfate into the flask. Final volume was obtained using a buret. The sample was then transfered to a 25 ml glass vial.

Analysis was conducted using a Tractor 560 gas liquid chromatograph with a nitrogen-phosphorus detector. A SE-30 packed column was used with helium at 40 cc/m as the carrier. Temperature was set at 200 C, which along with a .92 m column, resulted in a retention time of approximately 2 min. Hehum was used as the carrier gas.

A standard curve was established each run by injecting 2 ul atrazine standards ranging in concentration from 0.01 to 1.0 ppm. A linear relationship occurred between peak height and atrazine concentration.

When maximum detection occurred, 1 ul of sample was injected and peak height was doubled. Volumes of 2 ul were normally injected per sample. The injection syringe was rinsed in acetone before each injection.

RESULTS AND DISCUSSION

Fall tillage treatments in 1982 had no effect on atrazine dissipation from soil at either high (2.24 kg/ha) or low (1.12 kg/ha) atrazine concentrations 133 days after application in the spring of

1983 (Table 1). This was expected since no acid or alkaline soil surface had developed to influence atrazine degradation (Appendix C). Therefore, disturbing the soil surface through tillage would have no influence on degradation.

The rate of atrazine dissipation was greatest at the 2.24 kg/ha rate, both at 133 and 350 days after application, when compared to the 1.12 kg/ha rate (Tables 1 and 2). This supports Armstrong's (2) conclusion that the dissipation of atrazine conforms to first order reactions in which the rate of degradation is proportional to concentration. The greatest difference between rates of atrazine dissipation occurred 133 days after application. With increasing time the difference in percent degradation decreased. This agrees with the findings of Burschel (7).

By the fall of 1983, the majority of the atrazine remaining in the soil had moved into the 5 to 15 cm depth (Figures 1 to 6). Tillage had no apparent effect on the distribution of atrazine within the two depths, however, with only two sampling depths, the effect of tillage on atrazine distribution cannot be stated conclusively.

Different rates of degradation may have occurred within the two soil depths between the time fall tillage was implemented and spring sampling. Therefore, any differences in atrazine levels cannot be attributed solely to tillage or differential degradation.

Leaching of atrazine has been reported by Rogers (17) to occur in sandy soils and may have been important in this study. Soil was not tested below a 15 cm depth, therefore, no conclusions can be drawn about atrazine leaching.

Table 1. Effect of tillage on atrazine dissipation 133 days after application based on percent extracted following application.

	Unextractable Atrazine (kg/ha)	
Tillage	1.12	2.24
	(%)	
No-tillage	35	73
Chisel-plowed	25	60
Moldboard-plowed	40	66

Table 2. The effect of tillage on atrazine dissipation 350 days after application based on percent extracted following application.

	Unextractable Atrazine (kg/ha)	
Tillage	1.12	2.24
	(%)	
No-tillage	51	77
Chisel-plowed	48	78
Moldboard-plowed	33	67

Figure 1. Atrazine extracted, from a 1.12 kg/ha application rate, in the spring of 1983 (S-83) immediately after application, in the fall of 1983 (F-83) 133 days after application, and in the spring of 1984 (S-84) 350 days after application and after fall-tillage, from the 0 to 15 cm soil profile, under three tillage systems, no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB).

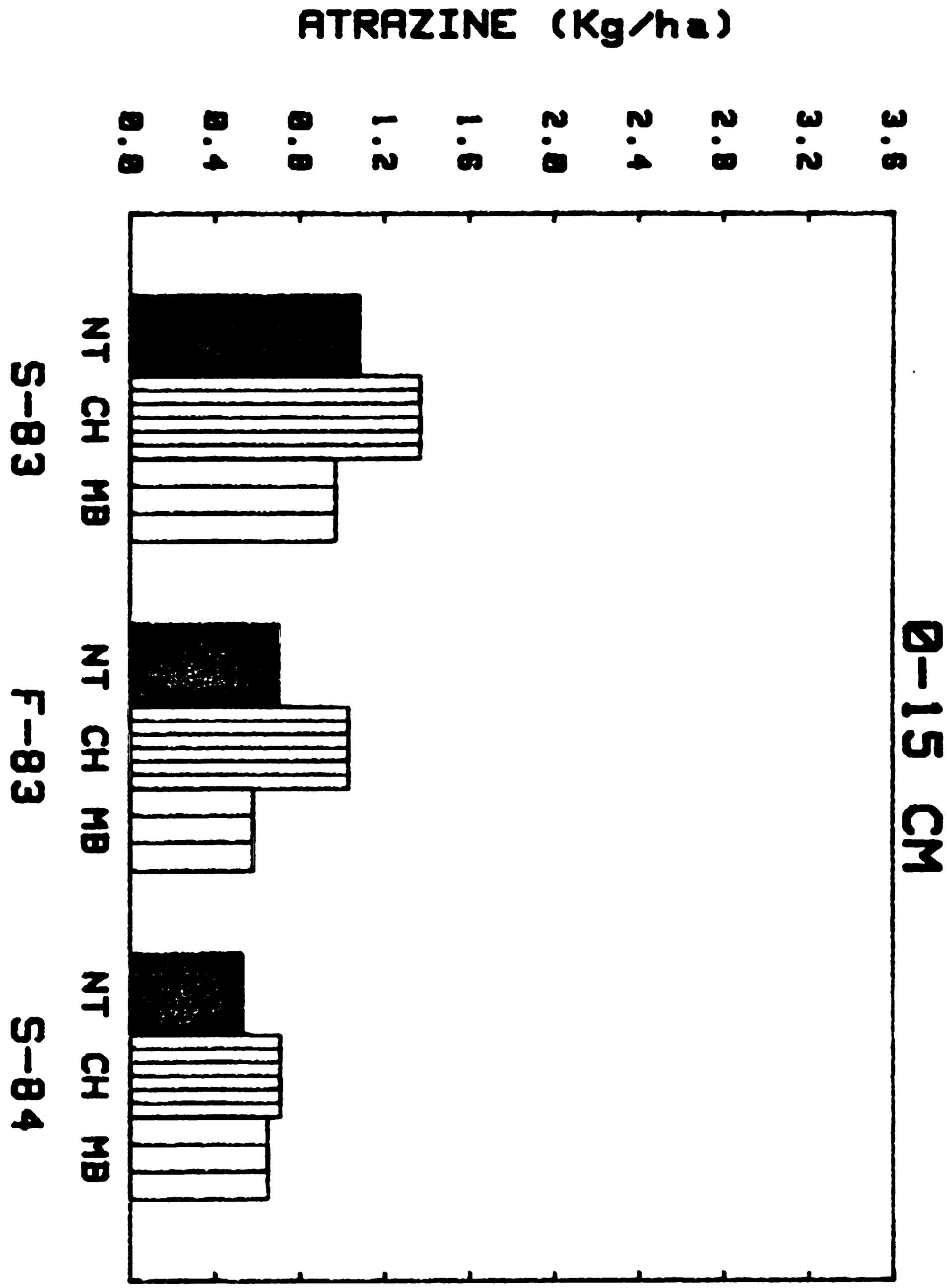
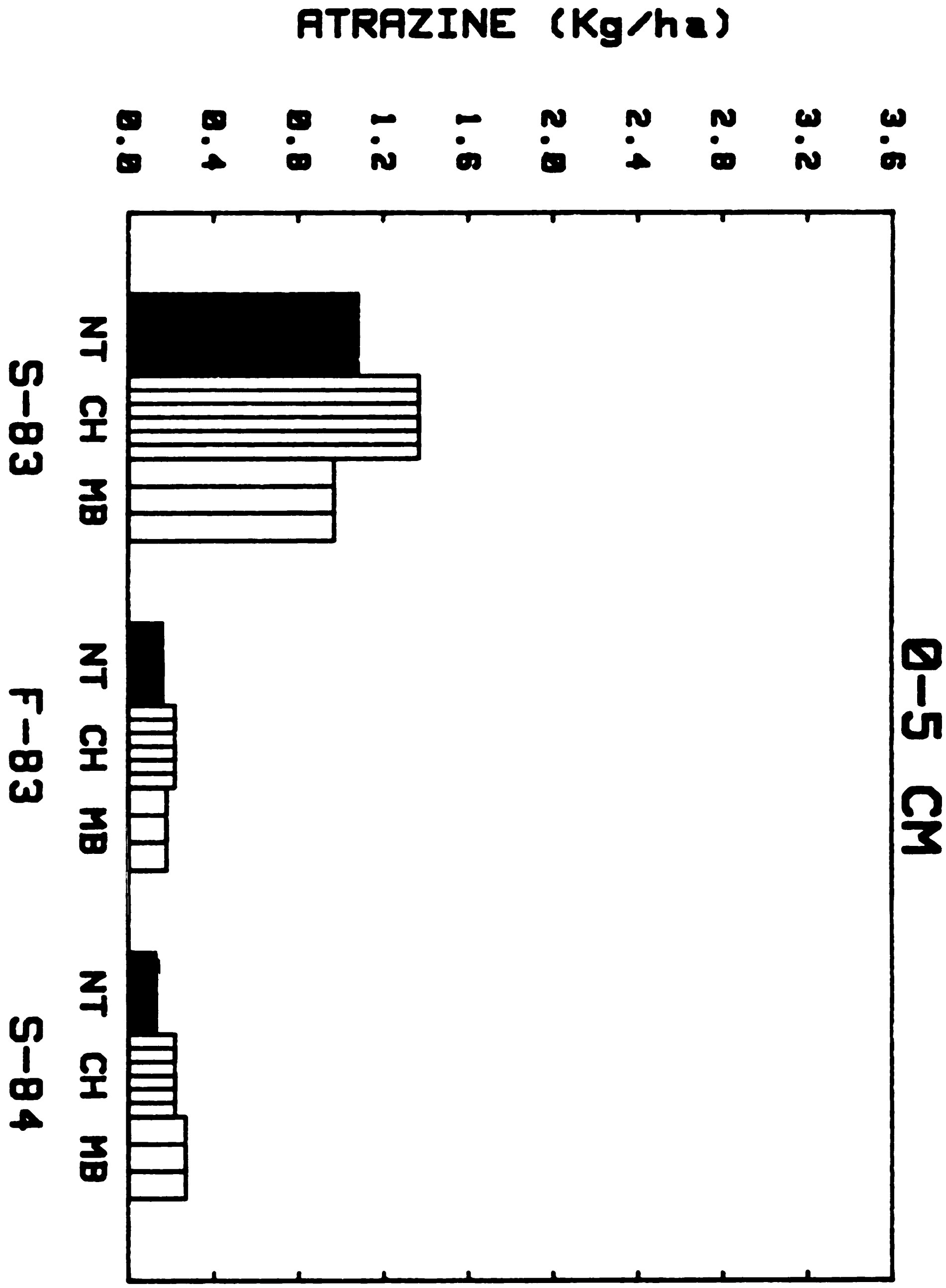

ATRAZINE (Kg/ha)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
0-15 CM
NT CH MB
S-83
NT CH MB
F-83
NT CH MB
S-84

Figure 2. Atrazine extracted from a 1.12 kg/ha application rate, in the spring of 1983 (S-83) immediately after application, in the fall of 1983 (F-83) 133 days after application, and in the spring of 1984 (S-84) 350 days after application and after fall-tillage from the 0 to 5 cm soil profile, under three tillage systems, no-tillage (NT, chisel plowed (CH), and moldboard plowed (MB).



ATRAZINE (Kg/ha)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
0-5 CM
NT CH MB
S-83
NT CH MB
F-83
NT CH MB
S-84

Figure 3. Atrazine extracted, from a 1.12 kg/ha application rate, in the spring of 1983 (S-83) immediately after application in the fall of 1983 (F-83) 133 days after application, and in the spring of 1984 (S-84) 350 days after application and after fall-tillage, from the 5 to 15 cm soil profile, under three tillage systems, no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB).

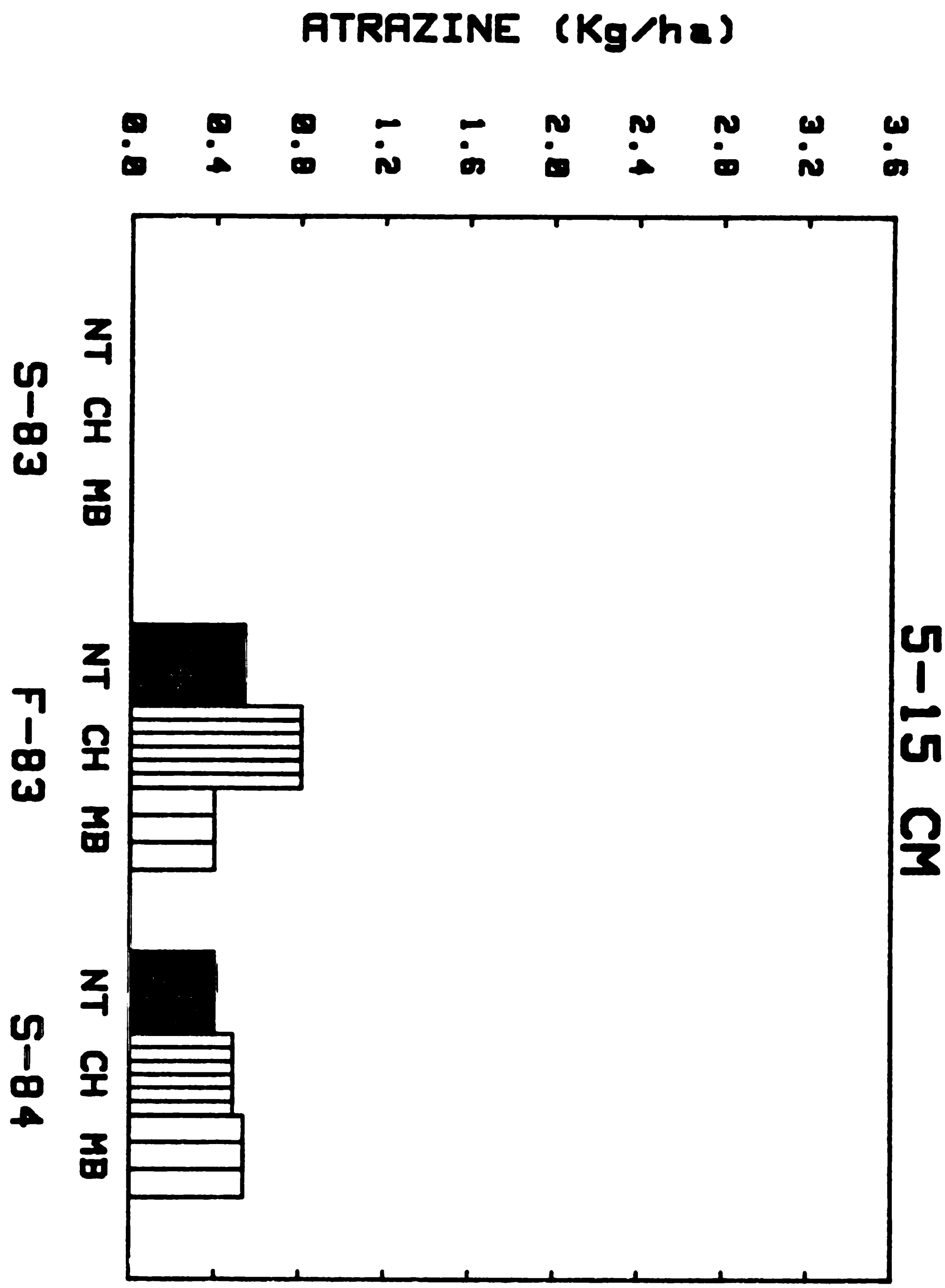

ATRAZINE (Kg/ha)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
5-15 CM
NT CH MB
S-83
NT CH MB
F-83
NT CH MB
S-84

Figure 4. Atrazine extracted, from a 2.24 kg/ha application rate, in the spring of 1983 (S-83) immediately after application, in the fall of 1983 (F-83) 133 days after application, and in the spring of 1984 (S-84) 350 days after application and after fall-tillage, from the 0 to 15 cm soil profile, under three tillage systems, no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB).

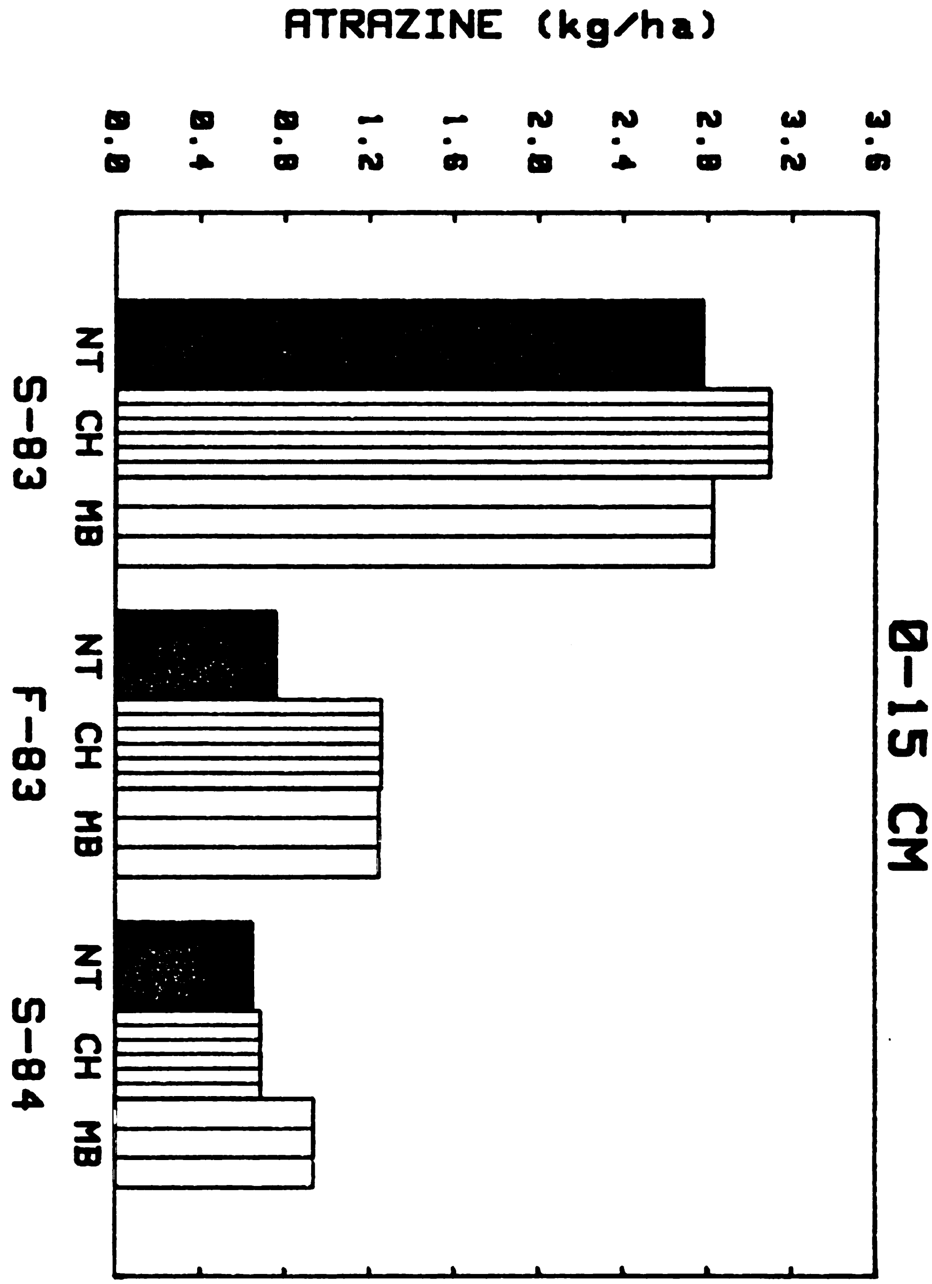

ATRAZINE (kg/ha)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
0-15 CM
NT
CH
MB
S-83
F-83
S-84

Figure 5. Atrazine extracted, from a 2.24 kg/ha application rate, in the spring of 1983 (S-83) immediately after application, in the fall of 1983 (F-83) 133 days after application, and in the spring of 1984 (S-84) 350 days after application and after fall-tillage, from the 0 to 5 cm soil profile, under three tillage systems, no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB).

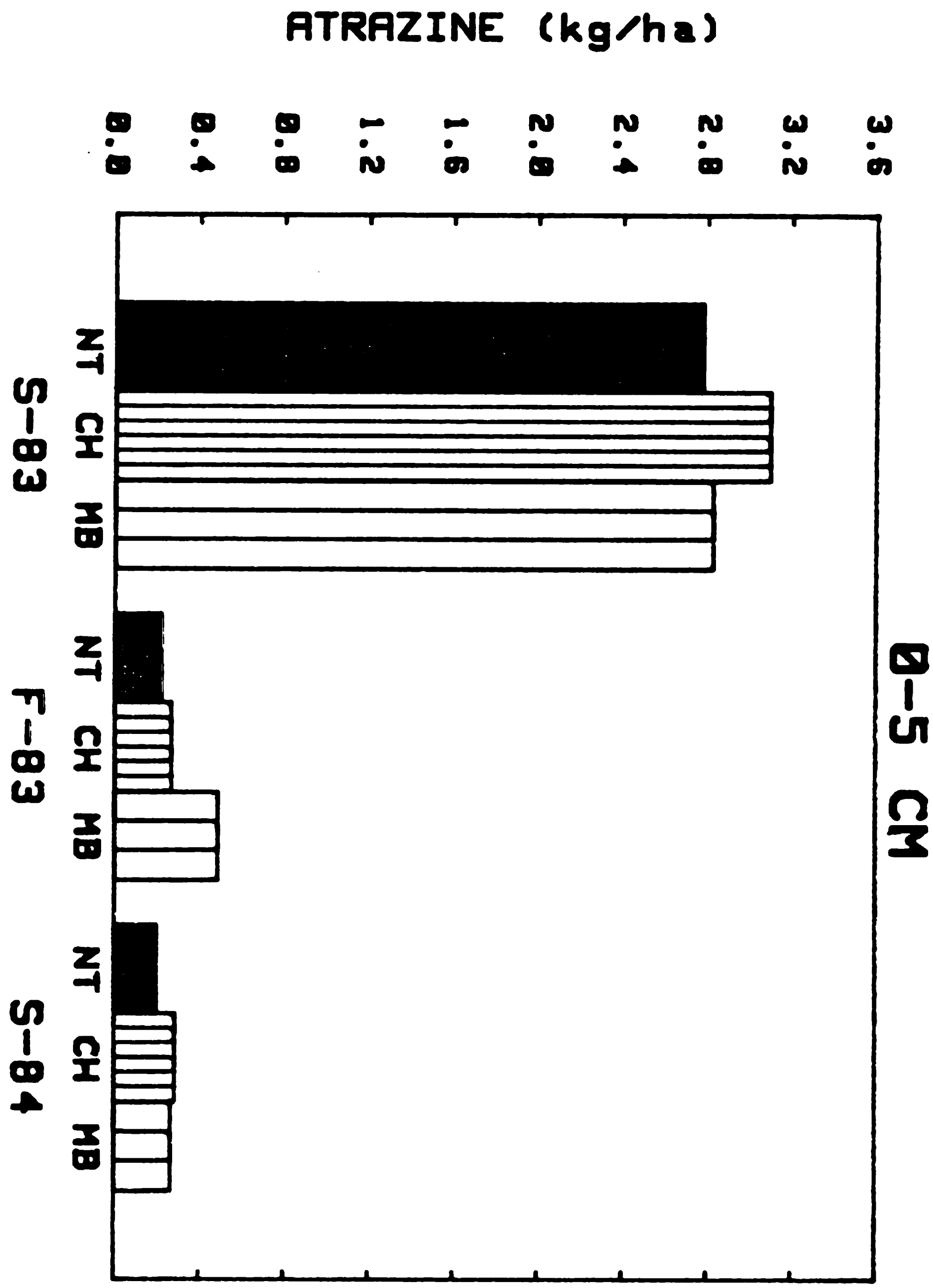
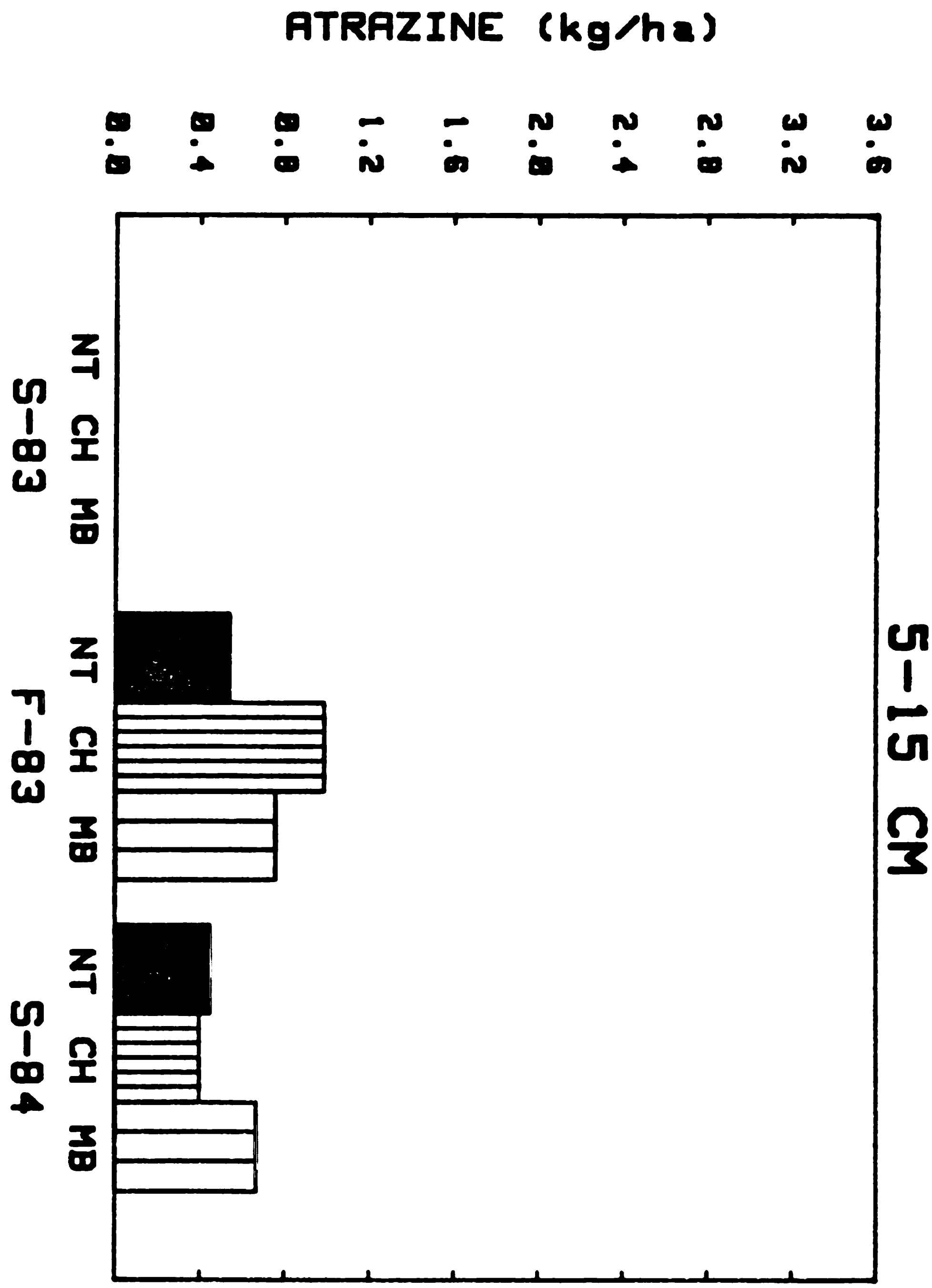

ATRAZINE (kg/ha)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
0-5 CM
NT
CH
MB
S-83
NT
CH
MB
F-83
NT
CH
MB
S-84

Figure 6. Atrazine extracted, from a 2.24 kg/ha application rate, in the spring of 1983 (S-83) immediately after application, in the fall of 1983 (F-83) 133 days after application, and in the spring of 1984 (S-84) 350 days after application and after fall-tillage, from the 5 to 15 cm soil profile, under three tillage systems, no-tillage (NT), chisel plowed (CH), and moldboard plowed (MB).



ATRAZINE (kg/ha)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
5-15 CM
NT CH MB
S-83
NT CH MB
F-83
NT CH MB
S-84

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CHAPTER 4

SUMMARY AND CONCLUSIONS

Soybean (Glycine max (L.) Merr.) injury resulting from atrazine carryover was greatest under minimum tillage compared to moldboard plowing. When sub-lethal rates of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) were available for soybean uptake, transpiration was believed to have increased. This may have led to an increased uptake of metribuzin (4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one), provided it to was available for plant uptake. Both atrazine and metribuzin were available under the chisel plowed system. Moldboard plowing is believed to dilute the atrazine to concentrations too low for increased transpiration. The high crop residue layer on the surface with no-tillage is believed to intercept the metribuzin, making it unavailable for plant uptake.

Chloramben (3-amino-2,5-dichlorobenzoic acid) at high rates on a coarse textured soil, resulted in poor root development due to the lack of sufficient rainfall in which to dilute the chloramben. The reduced yields under the chloramben application resulted in response to greater moisture stress under no-tillage. Moisture stress occurred under all soybean herbicide treatments under chisel and moldboard plowing due to lack of a sufficient plant residue cover for moisture conservation.

Tillage had no measurable effect on the disappearance or distribution of atrazine within the soil profile at depths of 0 to 5 and 5 to 15 cm.

Extractable as a percent of applied, atrazine was greater for the 1.12 kg/ha compared to the 2.24 kg/ha application rate.

In conclusion, the results of this research indicates that tillage does not influence atrazine degradation when no differences in surface soil pH exists between tillage systems. However, tillage does effect the soil surface in terms of the plant residue layer remaining. This residue layer may pose a barrier to herbicide penetration to the soil, this is especially important when adequate rainfall does not occur to incorporate the herbicide. This plant residue layer may also aid in moisture conservation in drouthy years, resulting in increased yields.

APPENDIXS

A. Percent residue cover on the soil surface after tillage prior to herbicide application.

TILLAGE SYSTEM	% RESIDUE COVER
NO-TILLAGE	75
CHISEL	45
MOLDBOARD	0

B. Rainfall at the Kellog Biological Research Station in 1983 and 1984.

MONTH	1983	1984	30 YEAR AVERAGE
	(cm)		
MAY	9.8	11.5	9.1
JUNE	6.7	.7	10.5
JULY	6.7	8.5	8.5
AUGUST	9.1	5.7	8.5
TOTAL	32.3	26.4	36.6

C. Soil pH 0 to 5 cm and 5 to 15 cm for three tillage system.

	DEPTH	
TILLAGE SYSTEM	0 to 5 cm	5 to 15 cm
NO-TILLAGE	6.7	6.9
CHISEL	6.7	7.2
MOLDBOARD	6.9	7.2

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