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FACTORS AFFECTING IMAZAQUIN AND AC-263,499
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RESPONSE

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Karen Ann Renner

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FACTORS AFFECTING IMAZAQUIN AND AC-263,499
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By

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ABSTRACT

FACTORS AFFECTING IMAZAQUIN AND AC-263,499 PERSISTENCE IN SOIL AND SUBSEQUENT CORN CULTIVAR RESPONSE

By

Karen Ann Renner

Nine corn (Zea mays L.) cultivars differed in their sensitivity to imazaquin (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl)-3-quinolinecarboxylic acid). Cargill 921, Great Lakes 422, and Great Lakes 5922 were among the more tolerant cultivars, while Pioneer 3737 and Stauffer 5650 were among the less tolerant cultivars. Corn injury was 26% greater across all cultivars the first year of study. Preplant incorporated applications were significantly more persistent than preemergence surface applications of imazaquin as determined by soil extraction and analysis and corn bioassays. There was no effect of spring tillage on injury to corn planted into imazaquin residue. Imazaquin dissipated rapidly during the first 30 days after application. A decreased dissipation rate occurred in the next 120 days.

Adsorption of imazaquin and AC-263,499 (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl)-5-ethyl-3-pyridinecarboxylic acid) on five different soils was very low. Kd values ranged from 0.056 to 0.113 for imazaquin, and 0.060 to 0.761 for AC-263,499. The soil that contained the most organic matter, smectite clay, and iron adsorbed the greatest amount of imazaquin. The soil with the highest silt percentage and lowest pH had the greatest AC-263,499 adsorption. Removal of organic matter had no effect on imazaquin adsorption, but increased AC-263,499 adsorption. Ph was lowered by organic matter removal, which could have effected AC-263,499 adsorption. Adsorption of imazaquin and AC-263,499 decreased as the pH of one soil was increased from 3.0 to 8.0.

Imazaquin was 42% more phytotoxic to corn than AC-263,499 at the same application rate. Soil pH appeared to have no effect on AC-263,499 phytotoxicity to corn. As soil pH increased, phytotoxicity to corn from imazaquin decreased in greenhouse and field studies. Imazaquin injury to corn decreased as the time period between application and corn planting increased. Injury to corn planted in June was less at soil pH 5.8 to 6.2, but pH had no effect on imazaquin injury to corn planted in July and August. Injury to corn planted in four soils decreased over time, with corn grown on the soil containing the highest percentage of smectite clay, organic matter, and iron having the least injury, possibly due to greater soil adsorption.

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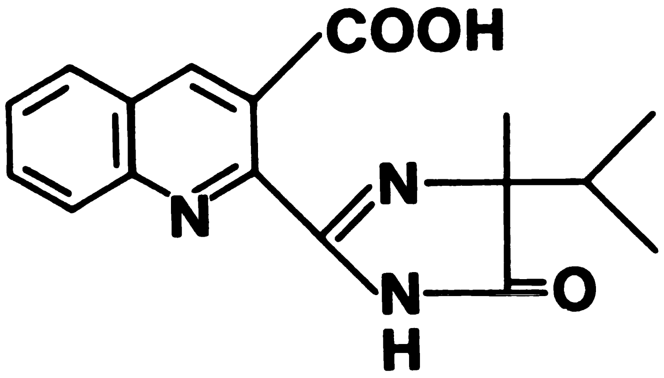
CHAPTER 1

LITERATURE REVIEW

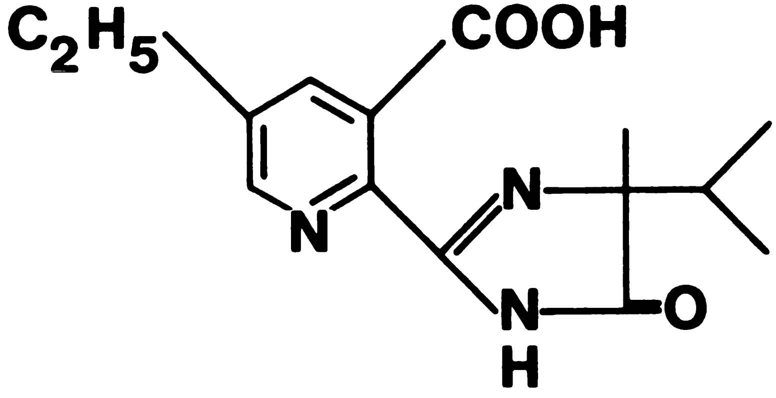
THE IMIDAZOLINONES

Imazaquin (AC-252,214) (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-3-quinolinecarboxylic acid) and AC-263,499 (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-5-ethyl-3-pyridinecarboxylic acid) are two compounds in the imidazolinone class of herbicides (Figure 1). Both compounds can be applied to the soil and incorporated or can remain on the surface. They can also be applied foliarly for postemergence weed control. Soybeans (*Glycine max* (L.) Merr.) are tolerant to imazaquin. Soybeans, field beans (*Phaseolus* sp.), peas (*Pisum* sp.), and seedling and established alfalfa (*Medicago sativa* L.) show tolerance to AC-263,499 (3, 4, 90). These herbicides control both monocots and dicots, with selectivity apparently achieved by differential metabolism of the compounds to non-herbicidal forms (108). Imazaquin controls common cocklebur (*Xanthium strumarium*), common lambsquarter (*Chenopodium album*), smartweed (*Polygonum* sp.), velvetleaf (*Abutilon theophrasti*), redroot pigweed (*Amaranthus retroflexus*), and common ragweed (*Ambrosia artemisiifolia*) when soil-applied (4). Giant foxtail (*Setaria faberi*), velvetleaf, redroot pigweed, and jimsonweed (*Datura stramonium*) are very

Figure 1: The chemical structures of imazaquin and AC-263,499.



Imazaquin



AC - 263,499

susceptible to soil applications of AC-263,499, while yellow nutsedge (Cyperus esculentus), wild proso millet (Panicum miliaceum), crabgrass (Digitaria sp.), and barnyardgrass (Echinochloa crusgalli) are somewhat susceptible (3, 90). Imazaquin and AC-263,499 are translocated in the xylem and phloem to meristematic regions with only a small percentage remaining in the root after root uptake (90, 109). With foliar application, movement occurs both above and below the treated leaf (90, 109). Injury symptoms first appear in meristematic tissue and growth ceases soon after treatment. Chlorosis and tissue necrosis are seen first, followed by dieback of mature plant parts and death of the entire plant within two to three weeks (108, 110). Imazaquin is rapidly metabolized by soybeans, but slowly metabolized by cocklebur (90, 109). Velvetleaf has shown increasing tolerance to imazaquin with age due to greatly reduced absorption by older leaves and more rapid metabolism in older plants. Two-leaf velvetleaf is susceptible while three-leaf velvetleaf appears tolerant to imazaquin (109).

The primary mechanism of action of the imidazolinone herbicides is believed to be inhibition of the biosynthesis of the three branched chain amino acids valine, leucine, and isoleucine, via inhibition of acetohydroxyacid synthase (AHAS) (8, 90, 108). AHAS is one of four enzymes catalyzing the biosynthesis of these amino acids from pyruvate. It is the first enzyme in the biosynthesis of leucine and valine, and the second enzyme in the biosynthesis of isoleucine (8). Protein synthesis is disrupted thus interfering with DNA synthesis and cell growth (90). In maize leaves, DNA synthesis was inhibited in 8 hours with a corresponding decrease in the level of soluble proteins and an increase in the level of free amino acids (110).

Sulfonyl ureas such as chlorsulfuron (2-chloro-N-(((4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino)carbonyl)benzenesulfonamide) are active at different concentrations but produce similar physiological effects and are similar in their mechanism of action (8, 108). Two forms of AHAS may be present in corn (99). Imazaquin activity is on a different form than for chlorsulfuron (99).

Few papers have been published on the persistence and behavior of imazaquin and AC-263,499 in soil. Imazaquin and AC-263,499 are quinoline and pyridine acids, respectively, and are not considered to be volatile (American Cyanamid personal communication). They are both weak acids with pKa values of 3.8 and 3.9, respectively (3, 4). Imazaquin is not chemically hydrolized in the presence of distilled water. In the presence of light under aqueous conditions, rapid photolytic hydrolysis to nonactive metabolites occurs (American Cyanamid, personal communication). It is not known whether this photolytic hydrolysis occurs on the soil surface or how soil moisture levels or soil matrix properties affect this reaction.

Liu found little adsorption of imazaquin on five U. S. surface soils, Ca-montmorillonite, and Ca-organic matter after shaking 20 h at room temperature (72). He found greater adsorption and lesser desorption at low pH levels, with NaCl (0.1 M) more effective than water in displacing the adsorbed herbicide.

AC-263,499 applications of 35 to 140 g ai/ha have no effect on corn (Zea mays L.) or wheat (Triticum aestivum L.) as rotational crops, but could effect cotton (Gossypium hirsutum L.), sorghum (Sorghum bicolor L.), potatoes (Solanum tuberosum L.), rapeseed (Brassica napus L.), sugarbeets (Beta vulgaris L.), and rice (Oryza sativa L.) (90).

Imazaquin rotational restrictions have not been published, but corn injury has been noted the year following imazaquin application (96).

Because of the problem of crop injury from carryover of these herbicides, an approach to the persistence of these compounds can be fourfold: (1) avoid planting a sensitive rotational crop, (2) use a seed or chemical protectant to minimize crop injury to a sensitive crop, (3) plant a resistant variety of a sensitive crop, and (4) alter cultural practices such as tillage, application method, or herbicide rate to reduce the persistence of these compounds in the soil. The following chapters focus on the third and fourth approach in determining the potential use of these compounds in Michigan by altering the persistence so that sugarbeets, potatoes, and corn could be planted as rotational crops after imazaquin or AC-263,499 were used for weed control in soybeans.

CHEMICAL ANTIDOTES

Chemical antidotes (crop safeners) can be used to increase the selectivity of a herbicide so that higher application rates can be used, or the herbicide applied on semi-tolerant crops, or on a crop that has inconsistent tolerance. NA (1H,3H-naptho(1,8cd)-pyran-1,3-dione) is a chemical safener used for many plant species against a wide range of herbicides (58, 99, 111). CDAA (2-chloro-N,N-di-2-propenylacetamide) and R-25788 (N,N-diallyl-2,2-dichloroacetamide) protect corn from EPTC (S-ethyl dipropyl carbamothioate) injury, although their mode of action is not fully understood (111). R-25788 elevates the level of GSH (glutathione), and the activity of several enzymes (99). R-25788 increased the amount of EPTC required to injure corn ten times, and decreased the influence of temperature and moisture on EPTC injury (25, 26). Cyometrinil ((*Z*)-*a*((cyanomethoxy)imino)benzeneacetonitrile) and flurazole (phenylmethyl-2-chloro-4-(trifluoromethyl)-5-thiazole carboxylate) are two protectants that are applied to seed to protect sorghum from metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide), alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide), and acetochlor (2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide) (111). The exact mechanism is not known, although they may compete for sites at which acetanilides act and thus prevent injury (111). Recent work by Rubin and Casida (58) and Hatzios (99) has examined the effect of these protectants on corn to chlorsulfuron. Hatzios found NA the most protective, CGA 43089 (*a*-(cyano-methoxy)-imino-benzeneacetonitrile) and CGA 92194 (*a*-(1,3-doixolan-2-yl-methoxy)-imino-benzeneacetonitrile) partially protective, and R-25788 the least protective when chlorsulfuron was applied preemergence to corn (58). In contrast, Rubin and Casida found chlorsulfuron injury to corn to be alleviated by both NA and R-25788 (99). They found R-25788 effectively protected corn hybrids from chlorsulfuron, and corn inbreds from EPTC. They suggested that R-25788 elevated AHAS activity to compensate for chlorsulfuron-induced inhibition. Two forms of AHAS are present in corn that differ in their sensitivity to chlorsulfuron. R-25788 did not change the proportion of sensitive or insensitive forms, did not function in vitro, and the antidote action therefore appeared to involve enzyme synthesis (99).

Imazaquin is selective for different AHAS forms than chlorsulfuron (99). Barrett found CGA-92194 to protect sorghum from imazaquin injury in field experiments (15, 16). In greenhouse experiments with CGA-92194, flurazole, NA, and R-25788, he found CGA-92184 protected sorghum and corn from imazaquin, whereas R-25788 did not (15). Sorghum was protected more than corn by all four chemical antidotes (15, 16). In further laboratory experiments Barrett found that NA and CGA-92194 reversed imazaquin inhibition of AHAS in vivo in both the dark and the light but did not affect activity in vitro (16). In dark-grown plants, NA and CGA-92194 increased extractable levels of AHAS (16). This did not occur in the light (16). The protectants did not decrease imazaquin uptake or alter distribution, but appeared to increase imazaquin metabolism. Corn varieties varied in their response to imazaquin and degree of imazaquin metabolism (16).

VARIETY TOLERANCE TO HERBICIDES

Differential tolerances of genotypes to the same herbicide have been reported for several crops (7, 16, 25, 34, 45, 82, 96, 98, 101, 138). Tolerant genotypes are useful in physiology studies to determine the basis for herbicide selectivity, the inheritance of resistance to herbicides, the herbicide tolerance in inbred lines in corn breeding, and the development of resistant lines for specific herbicides.

Potato and soybean cultivars were found to vary in tolerance to metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4<u>H</u>)-one) (38, 54, 88). Oplinger found differences of 3-55% leaf kill in soybean injury response to metribuzin (88). Andersen found

80% of the variation in soybean injury response to atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) was attributable to seed size variation (6). Brinkman found tolerance differences among oat (Avena sativa) cultivars to atrazine residues, but concluded that differences did not appear great enough to justify development of tolerant varieties (21). Differential response of corn varieties to herbicides has been extensively reported in the literature (16, 25, 34, 37, 40, 45, 82, 96, 138).

In early studies, resistance of corn plants to simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine) and atrazine was related to stalk rot and corn borer resistance (5). As herbicide resistance increased, the resistance to these insects increased and was correlated to the glucoside level present in the corn plant (5). The MS selection of the maize inbred line GT 112 was very sensitive to atrazine and simazine with plant death occurring before plants reached the height of 15.24 cm. The reaction was controlled by a single recessive gene (34, 45). In contrast, corn tolerance to alachlor has been studied and differential tolerance among inbreds and hybrids occurred (37, 82). However, researchers were unable to use inbred tolerance to predict hybrid tolerance, and no conclusive pattern of alachlor tolerance inheritability was found (37, 82).

Application of diclofop (HOE 23408) ((±)-2-(4-(2,4-dichlorophenoxy)phenoxy) propanoic acid) for volunteer corn (F2 generation) control produced a range of injury responses due to the difference in susceptibility of the inbred lines (7, 40). The gene action was believed to be additive, and controlled by more than one locus (7, 40).

Certain corn lines vary in sensitivity to EPTC and to butylate (S-ethyl bis(2-methylpropyl)carbamothioate) (25, 26, 101, 138, 139). XL 22, XL 43, and XL 80A were found to be the most sensitive to EPTC. Wright found tolerant P3030(N) plants absorbed less and metabolized more butylate than sensitive PAG 644(N) (138). Environmental conditions were found to also be important, with certain hybrids injured more at higher temperatures and others at lower temperatures (139). Burt found EPTC and butylate reduced corn growth more at 30°C than at 20° C (26). An interaction occurred between moisture and temperature with greater injury at 33% moisture than at 15% moisture at 30°C, and the opposite response occurring at 20°C (26). The days prior to corn coleoptile emergence were the most critical time for injury (26), with shallow planted corn exhibiting less injury because the coleoptile emerged quicker (25, 139). Trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine) injured corn with hybrid sensitivity varying with environmental conditions (98). Certain hybrids were more sensitive to trifluralin at 15°C than 25°C, with soil moisture having a lesser but significant effect (98).

An isolation of a maize cell line which is resistant to the imidazolinones has been identified (110). This resistant cell line contains an altered AHAS which is no longer inhibited by the imidazolinones. Resistance is expressed on the whole plant level and appears to be inherited as a single, co-dominant trait (110). American Cyanamid Co. has signed a research agreement with Pioneer Hybrids for further development of the cell line (110).

PESTICIDE PERSISTENCE

The persistence of a herbicide in the soil is a function of the chemical properties of the herbicide, soil properties, and prevailing environmental conditions (2, 23, 29, 60, 61, 64, 80). Ideally a compound should persist long enough to control weeds during the critical weed interference period, but not long enough to lead to herbicide residue problems and injury to rotational crops (11, 61, 74). When herbicide activity is no longer evidenced the herbicide is believed to be non-persistent, when in fact it can still be present in the plant root zone and be unavailable due to immobilization, or be present at a concentration that does not injure the crop or weed species (61). Because of the exceptional bioactivity to corn by the imidazolinones, and the large number of acres rotated to corn from soybeans, an understanding of imazaquin and AC-263,499 persistence in the soil and how it can be altered by environmental and cultural practices is important. Man can alter the persistence of pesticides by changing cultural practices. Changing tillage methods, applying a lower application rate, and using a different application technique are three ways that the persistence of a compound can be altered.

Herbicide persistence can be mechanically altered by tillage that dilutes the herbicide in the plant root zone (111). The extent of detoxification depends on the resulting herbicide concentration and the sensitivity of the rotational crop. Although acute toxicity may be avoided, the prolonged exposure may result in injury as the plants no longer have untreated soil for the roots to grow in (111). Aaberg found no difference in visual injury to alfalfa, soybean, and oats from ethofumesate ((±)-2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methanesulfonate) when the soil was spring plowed or disked prior to planting (1). Trifluralin was found to persist longer where the soil was moldboard plowed instead of disked (36). Triazines remain active longer under conventional plow and chisel plow systems than under no-till situations (17, 113). This was attributed to a lower pH under no-till that causes triazines to bind and become chemically hydrolized, an increase in moisture under no-till that increases hydrolysis, and an increase in organic matter under no-till that increases adsorption (113). However a decrease in soil pH under no-till conditions is not always observed as shown by studies conducted by Lowder and Weber (73). The acidic soil surface in no-till from the application of acidifying nitrogen fertilizer that increases atrazine adsorption and hydrolysis did not occur because the soil surface was limed and the acidic fertilizer effects were negated (73). Kells et. al. found unextractable ^{14}C residues were higher under no-till situations in Kentucky and attributed this to either greater breakdown of atrazine or increased reversible adsorption (66).

Applying minimal rates of a herbicide reduces the concentration of herbicide initially, and increases tolerance to slower degradation rates. Oliver and Frans found the amount of trifluralin remaining in soil was directly correlated to the initial application rate after six months (87). Regardless of environmental conditions, herbicide degradation rates are believed to be independent of initial concentration (142). Buchanan and Hiltbold found no differences in the half life of atrazine at different rates in the south (22). However Hance and McKone found the degradation rate of atrazine and linuron (N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea) decreased as their concentration in the soil increased, possibly due to a limited number of highly active enzyme and chemical reaction sites where degradation of these herbicides in soil could occur (53). The effect of initial concentration on degradation was greater under sterile conditions where microbial degradation was not a factor. They speculated that microbial degradation is not as affected by initial concentration as nonbiological processes (53). Hurle and Walker found a lengthening of the lag phase prior to degradation at higher herbicide concentrations which they attributed to either herbicide toxicity to the degrading organism or inhibition of enzymes necessary for degradation (64). In contrast to this, multiple applications of certain compounds can gradually increase the degradation rate in the soil due to microbial adaptation to the herbicide (111). Low levels of substrate may be insufficient to induce adequate enzyme production or sustain microbe activity, and thus at low concentrations of pesticide, degradation could be very slow (69, 111). Persistence of some herbicides can increase when other pesticides are applied at the same time that are a preferred energy source (111).

Application method can have a significant effect on pesticide persistence. If a compound is volatile or subject to photodecomposition, preemergence surface applications (PES) are less persistent. Walker and Bond found pendimethalin (AC-92,553) (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) more persistent under dry conditions and where incorporated (130). Twenty weeks after application, 80% of the incorporated herbicide could be detected, while only 28% where it was applied PES. They believed this difference would be less in a wetter year. Williams and Eagle found the persistence of dichlobenil (2,6-dichlorobenzonitrile) to be much greater when incorporated due to decreased codistillation and volatility (136). Oliver found 25% of the trifluralin remained four months after application when incorporated to a 10.16 cm depth, but only five percent when incorporated to a five cm depth, and zero when applied on the soil surface (87). In other research where trifluralin was applied at 0.84 and 4.48 kg/ha, 11% remained after forty weeks when incorporated to a five cm depth, and 40% remained where incorporation was to a ten cm depth (103). In contrast, Buchanan found the persistence of atrazine not to differ between PES applications and atrazine applications incorporated to a 10-15 cm depth with two passes of a disk (22). Walker found no difference in herbicide loss between surface and incorporated applications of propyzamide (3,5-dichloro (N-1,1-dimethyl-2-propynyl)benzamide) (127).

Persistence under different application methods can be affected by soil type. Fluridone (1-methyl-3-phenyl-5-(3-(trifluoromethyl) phenyl)-4(1H)-pyridinone) persistence on a Miller clay showed no difference between PPI and PES applications, but was significantly more persistent when incorporated compared to PES applications on a fine sandy loam (14). The authors gave no explanation for this occurrence.

Herbicides are inactivated by biological, chemical, and physical means (9, 11, 23, 31, 60, 61, 80, 111). Inactivation can result from transfer of the pesticide molecule to a location that is unavailable to plants, or transformation of the herbicide to nontoxic forms by degradation. The means and rate of these processes is dependent on the nature of the herbicide and on environmental conditions. Transfer processes that alter the persistence of a herbicide include mechanical dilution or tillage as previously mentioned, leaching, volatilization, plant uptake or release, and soil adsorption (11, 23, 111). Transformation processes include biological transformation by microbes, and nonbiological degradation by chemical and photochemical means. Each of these processes will now be discussed.

TRANSFER PROCESSES

Mechanical Dilution

Tillage was mentioned previously as a cultural method that alters soil persistence of herbicides by removing or diluting the herbicide in the plant root zone.

Leaching and Mobility

Herbicides move in soil by molecular diffusion or by the mass flow of water. Leaching results in herbicide movement out of the plant root zone. Herbicide movement is dependent on water flux, soil-water content, soil texture, and the herbicide concentration in solution. Herbicides may leach under saturated conditions because water is a competitor for soil adsorption sites. Acidic herbicides are more readily leached than neutral or cationic herbicides due to the decreased number of sites in the soil that are positively charged and available for ionic binding of these herbicides (41, 47, 48, 56, 119).

The balance between capillary movement upward and the downward hydraulic gradient create the area in the soil profile where the herbicide will be distributed (41). Herbicide distribution obtained by laboratory leaching experiments is seldom seen under field conditions because frequent changes in water movement direction in the field occur, and/or under laboratory studies adsorption equilibrium is not reached (41, 119). Stoller et. al. found bentazon (3-(1-methylethyl)-(1<u>H</u>)-2,1,3-benzothiadiazin-4(3<u>H</u>)-one 2,2-dioxide) to move with the solvent front in soil thin layer chromotography and soil columns in the laboratory (119). However in the field less than 2% was leached from the top 15 cm of soil. He concluded that less than 1.0 meq/100 kg of soil anion exchange would be required to satisfy the exchange capacity of 3.36 kg/ha of bentazon applied, and therefore the herbicide did not leach in the field (119). In laboratory studies, Grover found picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) to be readily leached in a wave form with the greatest mobility in a fine sandy loam (47, 48). He found picloram to leach farther on sandy soils when the soil column was dry prior to herbicide application because of faster water movement, and on clay soils to leach farther when the column was initially wet because of the increased percolation rate (47). Grover also found picloram to move readily upward when soil columns were subirrigated (47), and Harris had similar results with dicamba (3,6-dichloro-2-methoxybenzoic acid), another acidic herbicide (56). Herr et. al. applied picloram at five rates to three soils and sampled three times (59). Herbicide residues were greatest on heavy textured soils, and little movement below the soil surface occurred. On lighter textured soils movement was detected down to a 61 cm depth, with increasing concentration with increasing depth.

Application rate can alter pesticide movement. Grover found picloram movement in leaching columns did not change when applied at a 1 or 2X rate (47). However Duseja and Holmes found in field studies less trifluralin movement below the application zone at higher application rates (33). They attributed this to the limited solubility of the compound.

Volatilization

Herbicide persistence can decrease immediately if volatility occurs, and therefore herbicides susceptible to volatilization are more effective when incorporated. Soil moisture is important in herbicide volatilization (12, 23, 92, 130). Vapor pressures increase under moist conditions, and herbicide loss from dry soils is less (12, 23, 92, 130). On dry soils volatile herbicides can be adsorbed, but the binding energy is low enough that the herbicide is biologically available. At higher moisture levels, less herbicide is adsorbed resulting in more being susceptible to vapor loss (12,23). Trifluralin was readily volatilized from wet soil, and weed control decreased when incorporation was delayed 96 hours (117). Walker and Bond found trifluralin and pendimethalin to be volatile from a metal surface with a 70% loss in 14 days, and a 95% loss in 28 days (130). On a film of soil particles wetted daily, 95% of the trifluralin and 60% of the pendimethalin were lost in 28 days, but when the soil surface remained dry, only 30% of both compounds were lost in a four week period (139). EPTC volatilization from soil increased as temperature increased when the soil was moist, but temperature had no effect on dry soils (92).

EPTC losses also increased with increased air movement across the soil surface, and was dependent on soil composition (92).

Beestman found 50% of applied alachlor was lost in 12 to 29 days when exposed to 3.2 km/h air movement, with loss dependent on soil type (18). Parochetti found 50% of the alachlor and metolachlor volatilized in 8 days when applied to a glass surface, but only 0.1% volatilized when applied to the soil surface (89).

Plant Uptake and Plant Release

Plant uptake may also remove persistent herbicides from the soil. Once in the plant the herbicide can be metabolized or stored. Plant uptake may cause only temporary removal of a herbicide, as conjugated herbicides can be hydrolytically released during plant decomposition and thus available to the next year's crop (23, 111). Tolerant plant species can be planted to absorb and degrade herbicides when a tolerant crop can be planted into the field containing the persistent herbicide. In contrast, plant roots can release bound herbicide residues, which results in the herbicide appearing to increase in persistence.

In the rhizosphere, plant roots excrete a variety of organic and inorganic compounds that can influence the growth of fungi and bacteria, and change the soil pH (55, 67, 105, 141). Plant roots may thus alter the amount of herbicide available for uptake by controlling the ionic state of the herbicide and penetration into the plant, or by indirectly changing the herbicide's adsorption to the soil colloid, and thus altering herbicide availability (67, 105, 141). All plants can reduce rhizosphere pH when $(NH_4)_2SO_4$ is applied (55). This could increase herbicide adsorption to soil colloids, and/or plant absorption of herbicides that become undissociated at low soil pH (55). Lowering soil pH also disperses humic materials into fibrous networks, which could release herbicides entrapped in internal voids of the organic matter structure (141). Monocots are more effective than dicots at raising the soil pH when $CaNO_3$ is applied (55). This can result in rapid desorption of adsorbed herbicides to the soil. Applications of NH_4^+ can also disrupt ionic bonds and release herbicides. Yee, Weinberger, and Khan studied the release of bound residues of prometryne (N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine) by oats, soybean, and wheat roots (141). Soybeans released 37% of the bound residues and wheat 10% of the bound residues. They attributed this release of bound residues to increased microbial activity in the rhizosphere, because altering soil pH and adding fertilizer did not correlate with the release of bound prometryne (141).

Soil Adsorption

Soil adsorption affects the amount of herbicide available for effective weed control, the amount of herbicide to be leached through the soil profile, and the ability of the herbicide to be microbially degraded (43). As soil adsorption increases the availability and subsequent phytotoxicity to plants decreases (23). Soil adsorption can increase or decrease pesticide persistence (23). Clay has an infinite number of adsorption sites, and the pesticide molecules can be distributed across the clay surface so that interaction with microbes is delayed. Also if pesticides are adsorbed in interlamellar spaces they can be protected from enzymatic attack (43). In contrast, soil adsorption can accelerate degradation by concentrating the enzyme and substrate at one site, and catalyzing nonbiological and biological reactions (43). Therefore soil adsorption can result in less chemical available for plant uptake, but if the herbicide becomes desorbed at a later date, extensive injury to rotational crops may occur (23, 43).

Adsorption of herbicides to soil can be divided into three categories; chemical adsorption, physical adsorption, and hydrogen bonding (2, 12, 27, 43, 80, 91, 118). Types of low energy bonds involved in physical adsorption include van der Waals, charge transfer, and charge dipole bonds. Van der Waals forces are additive and occur by an interaction between polar and polarizable moieties in the pesticide molecule and the ionic charges on soil and the hydration water around the soil micelle (2, 12, 13, 91). Attraction between large herbicide molecules and soil constituents can be great. Charge-transfer bonds between electron deficient aromatic rings and electron rich aromatic rings of organic matter also increase physical adsorption (41). Physical adsorption results in low heats of adsorption and low binding strength (43). Chemical adsorption is due to coulombic forces resulting from charge interactions (shared electrons) and results in higher heats of adsorption and higher binding strength than dipole interactions (2, 43, 91). High energy bonds include ionic bonds and ligand exchange. Ionic chemical bonds occur with cationic herbicides such as paraquat (1,1'-dimethyl-4-4'-bipyridinium ion), weak acids such as benzoic acids, and weak bases such as the triazines (91). Ligand exchange is another type of chemical bonding that can occur between herbicides and transition metals in clays or humics (27). Anions can penetrate the coordination shell of an iron or aluminum atom in the surface of the hydroxide and get incorporated into the surface hydroxyl layer (106). Hydrogen bonding is sometimes considered a third method of adsorption as the forces are intermediate between physical and chemical adsorption (2). Hydrogen bonding involves a bond between two highly electronegative atoms through the medium of a hydrogen atom (2). Hydrogen bonds can occur between adsorbed water and organics or between soil surface groups and organics (41).

Adsorption isotherms are a very useful technique used to characterize properties of herbicide adsorption in the presence of an adsorbing surface such as soil (41, 42, 44, 122). A pesticide solution of known concentration is equilibrated with a given quantity of soil, and the amount of pesticide adsorbed is calculated from the decrease in pesticide concentration in solution. It is usually expressed in umoles adsorbed per gm of soil (x/m). By repeating the measurement at several concentrations, an adsorption isotherm can be obtained by plotting the quantity adsorbed (x/m) versus the herbicide concentration remaining in solution (C) at equilibrium, expressed in umoles/ml of solution. The shape of the isotherm is diagnostic to the mechanism underlying the adsorption process (41, 42). In most instances a straight line can be obtained from the isotherm plot if both x/m and C are plotted as log transformations. The Freundlich adsorption equation is then calculated as $x/m = KC$ to the 1/n power, where K and n are constants. 1/n is the slope of the line and the constant K provides a measure of the extent of adsorption (41, 42, 44, 76). N is usually less than one because the amount of herbicide adsorbed increases less rapidly than the concentration remaining in solution at equilibrium. When n is near unity, the constant K (the distribution coefficient) can be used to describe the partitioning of the herbicide between soil and solution.

The adsorption of a chemical can be described as a partitioning of the chemical between the soil and aqueous medium and is expressed by a partition soil sorption constant Kd (76, 118). The coefficient Kd is = to pesticide adsorbed (umoles/kg of soil) / pesticide in solution (umoles/liter). This constant can be used to provide a measure of the extent of soil adsorption, and determine the importance of various soil parameters on adsorption. Kd is related to the organic content of the soil by the equation Koc = (Kd / % organic carbon) x 100.

Soil adsorption is dependent on experimental conditions, herbicide properties, and soil properties such as the clay content and type of clay, organic matter content, amorphous minerals such as aluminum and iron hydroxides, and soil pH (2, 12, 13, 27, 28, 43, 80, 91, 135, 137). Because the imidazolinones are weak acids, only adsorption of ionic compounds will be discussed.

Herbicide properties such as electronic structure, molecular volume, and water solubility affect herbicide adsorption to the soil matrix (27). Functional and substituting groups are important in soil adsorption, and related positioning can enhance or hinder intramolecular binding (27). Organic compounds are preferentially adsorbed on clays instead of inorganic compounds because of their large size and high molecular weights (27).

Acidic herbicides exhibit specific types of binding to soil. Acidic compounds can physically adsorb to soil. They also can bind with soil through a C=O group, or associate with soil through a water bridge on an exchangeable cation, or through a hydrogen bonding of a carboxyl group to clay via proton association (12, 13). Three mechanisms by which phenoxyalkanoic acids were thought to be bound to soil included van der Waals forces, hydrogen bonds at low soil pH between the carbonyl group of the herbicide and the amino groups of humics or the carboxyl group of the herbicide and the carbonyl or NH groups of organic matter, or via salt linkages with polyvalent cations linking the carboxyl group of humics in the soil with that of the alkanoic acids (83). Frissel found no adsorption of 2,4-D, 2,4,5-T, MCPA (4-chloro-2-methylphenoxy)acetic acid), and DNBP (2-(1-methylpropyl)-4,6-dinitrophenol) to montmorillonite clays, implying none of these types of binding occurred (39). Carringer et. al. summarized the soil adsorption of acidic compounds, and stated that moderate adsorption to organic matter may occur, and very low adsorption to clays and hydrous metal oxides may also occur (28).

Experimental or environmental conditions such as temperature, soil and water ratios, and ionic composition, can alter soil aggregates and change the physical and chemical properties of the soil matrix, thus affecting adsorption (27). Adsorption behavior in the field may differ from herbicide adsorption in the laboratory due to temperature, water, soil pH, or concentration effects (35, 41, 49, 70).

Changing the ratio of soil to solution can change the amount of herbicide adsorbed to soil, and thus change the Kd values. In laboratory studies, increasing the salt concentration and water content of the system increased the adsorption of 2,4,5-T (2,3,5-trichlorophenoxy)acetic acid) on a Palouse silt loam (70). Farmer and Aochi found picloram adsorption to decrease when soil and solution ratios in the laboratory were widened from 1:2 to 1:5 (35). Gerber and Guth increased precision when a soil to water ratio of 1:1 instead of

1:10 was used (41). Grover increased linuron and atrazine adsorption when he changed the soil : water ratio from 1:10 to 4:1 (49).

Polar organic chemicals and water compete for soil adsorption sites in ion-dipole and coordination reactions, and with water for ligand positions around soil cations (122). Some organic compounds won't be adsorbed by clay from water suspensions because they cannot compete with the large number of water molecules present. In air dry soils they may adsorb and may or may not be displaced from soil when water is added (136). Moisture has a large effect on pesticides if polarizable moieties such as C=O, NH_2, and COOH are present (91). Amitrole (1_H_-1,2,4-triazol-3-amine) can become protonated by highly polarized water molecules that directly coordinate with aluminum, magnesium, and calcium cations, and when protonated are stable to leaching (100). Clay can bind pesticides through bonds that are resistant to leaching, while organic matter may form bonds under dry conditions that are released when moisture is added (81,91). When soil drys it is never completely dehydrated. The increased dissociation of the water remaining at the clay surface is an important aspect of clay-water interactions from the standpoint of pesticide adsorption. Burnside and Fenster found carryover of atrazine, propazine (6-chloro-_N,N'_bis(1-methylethyl)-1,3,5-triazine-2,4-diamine), and linuron to be greatest on coarse textured soils in drier regions of Nebraska (24). Research on fluridone under field and laboratory conditions showed persistence in a Miller clay to be significantly less than on a coarse textured Lufkin sandy loam (14). Although there were little differences in fluridone concentrations remaining after 60 days, thereafter residues decreased much more rapidly on the Miller clay, where 10% remained one year after treatment compared with 20% on the sandy loam (14). Soil properties therefore play an important role in the adsorption and persistence of pesticides to soil. The mechanism of pesticide binding to the clay fraction of the soil has been studied in greater detail than soil organic matter or other portions of the soil matrix.

Silicate clay minerals consist of stacked layers of silica and alumina sheets (122). Clay minerals including montmorillonite and vermiculite are considered expanding and limited-expanding clays, respectively. Their specific surfaces are 500-750 m^2/g and have cation exchange capacities (CEC) of 80-200 meq/100 g. Other clays such as kaolinite and illite are non-expanding clays and have specific surfaces of 25-125 m^2/g and CEC's of 2-40 meq/100 g (135).

Kaolinitic clays consist of one sheet of silica and one sheet of aluminum with the tips of the silica oxygen tetrahedrals projecting into the hydroxyl plane of the aluminum octahedrals and replacing two thirds of the hydroxyl ions (122, 135). Kaolinitic calys thus have crystal edges containing exposed groups of $Al(OH)_2^+$ or $Al(OH)^{+2}$ that are important sites in adsorption. They make up 10-20% of the total crystal area, while in montmorillonitic soils they make up only 5% (122). Thus surface reactions such as anion exchange are more pronounced on kaolinite, and organic compounds having functional groups that can capture an electron via a hydrogen bond such as nitrite or carbonyl would preferentially adsorb on these edges of kaolinite (2, 104). However only 2,4-D and chloramben (3-amino-2,5-dichlorobenzoic acid) have exhibited this behavior and conflicting reports have found 2,4-D phytotoxicity to be similar on kaolinitic clays and montmorillonitic clays, reflecting no increase in adsorption (107).

Montmorillonite is a 2:1 clay containing one layer of alumina between two silica layers. The side by side arrangement of silica - oxygen tetrahedrals results in no hydrogen bonding between layers (122). This weak attraction between oxygens lets this mineral expand as water enters and hydrates the exchangeable interlayer cations (122, 135). Small uncharged polar groups of organic compounds compete for the same ligand sites as water around the cation (122, 136). The extent to which the interlamellar surface can sorb organic molecules depends on the nature of the exchange cation on the clay, the degree of clay hydration, and the properties of the organic molecules (43). The nature of the exchangeable cation is important as it determines the surface acidity. Montmorillonite clays are negatively charged due to isomorphous substitution of magnesium for aluminum, and this resulting negative charge is satisfied by exchangeable cations on the soil surface (122, 127, 136). The greater the affinity of the exchange cations for electrons, the greater the interaction with polar groups of organic molecules capable of donating electrons (135). The most acidic are in order H+ > Fe+3 >Al+3 >Mg+2 > Ca+2 > Na+2 >K+. The compensating cations are also important because they compete with herbicides for binding sites and act as sites in coordination bonds (27). Picloram is believed to form exchange complexes with copper, and to a lesser extent with iron and zinc, and form chelate rings (10). Exchangeable cations also have a predominant influence on the degree of disassociation of water molecules on the soil surface, and cation-water relationships influence the mechanism of adsorption of pesticides such as ion exchange and protonation (136).

Adsorption to Soil Organic Matter

Soil organic matter can be classified into two main groups, nonhumic and humic substances (106, 118, 137). Unaltered plant and animal material, proteins, fats, waxes, and resins are non-humic substances (118). Humic substances are chemically and biologically modified substances consisting of a series of highly acidic, colored, high molecular weight substances, with a high content of oxygen-containing groups such as carboxylic, phenolic, and aliphatic groups (106, 118, 134, 137). These acidic groups have pH dependent ionization and can form ionic bonds with ionized molecules, and participate in cation-dipole bonds (27). The aromatic portion of the soil organic matter can form charge transfer complexes or hydrogen bonds with pesticides (118). Most organic matter is colloidal in nature, and associated with the inorganic fraction to form a clay-humus complex (23, 118). This complex is the site of soil adsorption and biological and nonbiological degradation (23, 118). The large surface area and chemical nature explain the high adsorptive capacity of organic matter (118).

Two major adsorptive surfaces are available to a herbicide; the clay fraction and the clay-humus fraction (118). When soils contain 8% organic matter or less, both the clay and organic fractions contribute to adsorption (118). Soils having greater than 8% organic matter, probably adsorb pesticides exclusively on organic matter surfaces (118). Upchurch found a 5X herbicide rate increase required on a soil containing 20% organic matter compared to a soil with 4% organic matter for twelve cotton herbicides (124). For soils with similar textures and organic matter contents, the organic matter contribution to adsorption would be greater on kaolinitic soils because of the lower CEC of kaolinitic clays (118).

Soils differ in their organic matter quantitatively and qualitatively. The percentage of organic matter as fats, waxes, and resins can range from 2 to 20%, the protein from 15 to 45%, and the carbohydrates from 5 to 25% (118). These fractions have different affinities for herbicides.

Organic matter is often cited as the most important soil parameter in correlating pesticide persistence in the soil (23, 118, 124, 134, 137). Upchurch investigated soil factors affecting diuron (_N_'-(3,4-dichlorophenyl)-_N,N_-dimethylurea) phytotoxicity and concluded that soil organic matter was the most important factor (124). However anionic chlorinated aliphatic acids and benzoic acids including chloramben have shown limited adsorptive response to organic matter (23). Organic anion adsorption by anion exchange on organic matter is not believed to occur because anions are readily released by water. Adsorption to organic matter must therefore be by weak physical forces or hydrogen bonding, and not by anion exchange (134).

Adsorption by Amorphous Fe and Al

Amorphous sesquioxides such as aluminum and iron oxides serve as cementing agents and coat clay and organic matter (2). They have similar surface areas to montmorillonite, are positively charged, and have a high anion exchange capacity (12). These iron and aluminum hydrous oxides exist in crystalline and amorphous forms and are in intimate contact with the surface of soil colloids. Positive adsorption sites exist on aluminum and iron hydroxides below soil pH of

8.0. Organic anions such as acidic pesticides can be associated with these charges by coloumbic attraction. The anions can be displaced by raising the soil pH to 8 or 9 (27, 106, 133). In adsorption isotherm studies using different adsorbents, iron oxides adsorbed 6% of the picloram, and organic matter only 1.9% (19). Chlorsulfuron had very low adsorption on four soils with Kd values less than 0.28, but had greater adsorption on aluminum oxide resins (123).

Soil pH Effect on Adsorption of Ionic Compounds

Soil pH may influence the activity and detoxification of a herbicide by changing the ionic character of the herbicide and the soil colloids, or changing the microbial population (10, 19, 30, 32, 35, 46, 62, 64, 70, 84, 107, 121, 122, 123, 128, 132). Organic colloids, and to a lesser extent clay, have a pH-dependent charge (118, 134, 137). The pKa of the acidic groups in soil humus is approximately 5.2, and at a pH of 7.0, 85% of these are ionized (118). The organic matter contribution to the soil CEC increases as soil pH increases, and at a pH of 7.0, 50% of the CEC is due to these pH dependent charges, while at a soil pH of 5.0, only 25% of CEC is due to these charges (118). At high soil pH values, the H^+ disassociates, and the acidic functional groups can react with divalent cations to form chelate bridges (137). Adsorption of many compounds is dependent on soil pH, and because soil acidity can be altered by common agronomic practices such as liming and fertilizing, the effect of soil pH on herbicide adsorption and degradation is important (78, 84).

Ionizable herbicides are affected by soil pH changes. The pH of the soil surface is one to two units below the measured pH of a soil-water suspension (12). Basic herbicides adsorb at 1-2 pH units above their pKa values, and acidic herbicides become undissociated 1-2 units above their pKa value (12). An assumption is made that the pKa of a molecule does not change when the molecule comes in close proximity to the clay mineral surface. This may not be valid as the magnitude of the force fields on the surface or highly active protons may induce a change in the pKa of the molecule (13). Friessel and Bolt found that the adsorption of ionic herbicides increased as the soil pH decreased, with the soil pH of maximum and minimum adsorption being a function of the specific compound (39). Fluridone is a weak base with a pKa of 1.7, and adsorption increased at lower soil pH values due to protonation (112). S-triazines were shown to be less phytotoxic at low soil pH values due to protonation and resulting adsorption (77). Weber found triazine adsorption to increase as soil pH decreased, with maximum adsorption near the pKa of each specific triazine herbicide (132). Soil adsorption of most weak acid herbicides is relatively low. Dicamba, picloram, and 2,4-D have Kd values of 0.08, 0.04 to 0.49, and 0.14 to 3.38, respectively (48). Harter and Ahlrichs found 2,4-D, aniline, urea, and chloramben to protonate and adsorb 2-3 units higher than what would be predicted by their pKa values (57).

At soil pH values greater than pKa values, acidic herbicides exist in the anionic form, and negative charges on the soil colloids repel anionic herbicides and increase the concentration available for plant root uptake (78, 84). Activity in soils of undissociated anionic pesticides is determined by the interaction with organic materials, and hydrogen bonding to undissociated acid and carbonyl groups of organic matter can occur (137). Increasing the soil pH may make organic matter structure more compact. Herbicides become excluded, and phytotoxicity to plants is increased (112). Hiltbold and Buchanan found the persistence of atrazine to increase with increasing soil pH and heavier texture due to decreased hydrolysis (62). Chlorsulfuron is a weak organic acid with a pKa of 3.8. Phytotoxicity to corn is greater at a pH of 6.9 than at a pH of 5.9 to 4.2 (78, 84). Similar results of increased phytotoxicity at higher soil pH values have been found for 2,4-D and dicamba (30). Corbin et. al. found no change in phytotoxicity from soil pH of 4.3 to 7.5 for chloramben and picloram, and found dalapon phytotoxicity to increase as the soil pH decreased (30). Activity in soils of anionic pesticides at soil pH values where they are associated is determined by the interaction with organic materials (137). Hydrogen bonding to undissociated acid and carbonyl groups of organic matter can occur (137). Decreased activity above the pKa value of an acidic herbicide may reflect adsorption or complexation with hydroxides or oxides of iron and aluminum, or alternatively, an increase in polarity and dissociation making the chemical unfavorable for uptake (137). Picloram had some adsorption at soil pH values of 6.5 to 7.5 due to bridging to divalent metal ions, or because of hydrogen bonding, or because of some other mechanisms (83).

Soil pH can can change herbicide solubility and possibly change soil adsorption. Bailey and White found adsorption of ureas and s-triazines increased as the solubility increased (13). Burns however found the adsorption of ureas to increase as the solubility decreased (23). Harris and Warren found no relationship between solubility and adsorption of diquat (6,7-dihydrodipyrido(1,2-a:2',1'-c)pyrazinediium ion), CIPC (1-methylethyl 3-chlorophenylcarbamate), DNBP, and atrazine

(56). Adams stated that as water solubility decreased, the hydrophobic nature of pesticides should increase (2), and Carringer et. al. stated that nonionic pesticides with low water solubilities should adsorb the most (28).

Soil pH can affect the degradation of herbicides (123). Dalapon degraded most rapidly at a soil pH of 6.5 (30). 2,4-D and dicamba degraded most rapidly at a soil pH of 5.3 (30). Ph had no effect on chloramben and picloram degradation. Increased hydrolysis can occur at low soil pH values, and decreased degradation could occur due to increased soil adsorption, hydrolysis, or because of soil pH influence on the microbial populations (64).

Desorption

When compounds are released from soil the process is called desorption. The extent of desorption can be partial, completely reversible, or completely irreversible (118, 137). Desorption is important in longterm persistence of compounds in soil. Chemicals that are completely desorbed from clays are often incompletely desorbed from organic materials (118).

TRANSFORMATION PROCESSES

Transformation processes occur by biotic and abiotic means, and it is often difficult to distinguish between the two (11). Commonly used methods of sterilization such as autoclaving produce chemical and physical changes in the soil that may alter the degradation of organic molecules by nonbiological means (11).

Biological Transformation

Herbicides can be degraded by algae, actinomycetes, bacteria, fungi, and possibly extracellular enzymes (11, 60, 61, 65, 69). Microbes degrade herbicides by a number of reactions including oxidation, reduction, hydrolysis, decarboxylation, deamination, dealkylation, and conjugation (11, 60, 61, 65, 69). Conditions that promote the growth of microorganisms often accelerate the rate of degradation. These factors include temperature, moisture, soil pH, cation exchange capacity, soil type and structure, organic matter content, oxidation-reduction potential, and dissolved oxygen levels. (11, 61, 65, 69, 111).

Microbial degradation is dependent on the threshold level of pesticide required for optimum utilization by microbes (69, 111). If there is no microbial degradation of an applied pesticide, degradation is either dependent on concentration and not enough herbicide was applied, or the pesticide fails to induce the enzymes required by soil microbes to utilize the pesticide carbon for growth, or the pesticide is unable to penetrate the microbial cells, or the steric configuration prevents or hinders microbial attack (60, 61). Organisms that are naturally present often cannot produce the enzymes required to transform the herbicide to an intermediate that can enter into common metabolic pathways and be completely mineralized (69). Certain chemical groups appear to increase chemical persistence, and include amines, methoxys, sulfonates, nitro groups, m-chlorines, ether linkages, and branched carbons (69). Usually a lag phase is seen prior to microbial degradation. If there is none, it may be that microbial breakdown is not involved, or alterrnatively, there are already organisms present in abundance that posess the constitutive enzymes required for degradation, and no lag phase occurs (60, 65).

Adsorption of herbicides to soil components can reduce biodegradation, since the pesticide would be unavailable to microorganisms (11, 60). Organic matter can enhance microbial degradation by enhancing the growth and population of the microbes. However large amounts of organic matter can retard degradation by increasing pesticide adsorption and reducing the availability to microbes by providing a preferred carbon source that is utilized for energy instead of the herbicide (60, 111).

Nonbiological Degradation

Hydrolysis

Nonabiotic degradation of herbicides can occur in the air, water, and soil by both chemical and physical processes (9, 11, 23, 31). Initial degradative reactions may be nonbiological and further degradative processes biological, or vice versa (11). Herbicides can be oxidized, reduced, hydrolyzed, and epoxidized, and nucleophilic displacement reactions or free radical induced reactions can occur (9, 31). Hydrolysis reactions are more rapid in soil than aqueous systems due to catalysis of reactions by sorption, especially at more acidic soil pH levels (9). High organic matter content can increase hydrolysis due to additional nucleophilic sources, and because more acidic surfaces are available for hydrolytic adsorption (111). Chemical hydrolysis occurred with the chloro-s-triazines and organo-p-insecticides (9), and more recently with the sulfonylureas (115).

Photolysis

Two types of photolysis occur in nature; direct and indirect photolysis (74, 79). Direct photolysis occurs when the herbicide absorbs the radiation from the sun and undergoes a chemical reaction. This type of transformation can occur in aqueous systems (79). In indirect photolysis, another material such as a soil component, absorbs the sunlight and initiates a chemical reaction that transforms the pesticide (74, 79). Many organic chemicals can sensitize, induce, or enhance photochemical reactions, while other organics can slow down or quench reactions (74, 79) Photolysis is influenced by the light intensity and wavelength. UV light of 290-340 nm is important in photolysis reactions, as UV light less than 285 nm is absorbed by ozone and not available to cause photolysis (9). Only pesticides that absorb light above 285 nm are expected to undergo photodecomposition unless a photosensitizer induces photolysis (9).

Photoproducts and photolysis rates of several pesticides are affected by the soil particle size, the organic matter content, the mineral base, the light absorbing character of the soil, and the soil-moisture content (79). Herbicide photolysis is reduced on soils compared to aqueous solutions or on a glass surface (23, 79, 89, 130). The major limiting factors to photolysis in soils is the adsorption of light energy by other soil components that decreases the energy available to the herbicide, and the non-penetration of light below the soil surface (9). In soils and natural waters, light attenuation can significantly reduce photolysis rates as the herbicide is mixed vertically in the soil and water profile, and light is completely adsorbed in the upper soil or water layer (79). Klehr found 80% of thidiazuron (1-phenyl-3-(1,2,3-thiadiazol-5-yl)-urea) applied to soil thin layer plates was photolyzed (68). He attributed the other 20% that did not undergo photolysis to penetration of the applied herbicide solution into deeper soil layers impenetrable to sunlight (68). Nilles and Zabik found the photolysis of fluchloralin (N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)benzenamine) was reduced on soil thin layer plates compared to photolysis in a methanol:water solution (85). They also found that photolysis of bentazon on soil resulted in formation of a dimer that they didn't find as a photoproduct in aqueous solution, and concluded that soils contained transition metals that coordinated two bentazon molecules and held them in direct proximity for coupling (86). Liang and Lichtenstein found the most and least loss of azinphosmethyl (O,O-Dimethyl S-((4-oxo-1,2,3-benzo-triazin-3(4H)-yl)methyl)phosphorodithioate) on glass plates and on soils, respectively. Increased unextractable bound residues were produced by irridating soils having high organic matter and moisture content, showing the role these parameters played in hydrolysis (71). When soil moisture was increased to 12%, the photolysis of profenofos (O-(4-bromo-2-chlorophenyl)-O-ethyl S-propyl phosphorothioate) and diazinon (O-O-Diethyl O-(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothioate) increased, photolysis of carbaryl (1-napthyl N-methylcarbamate) decreased, and there was no change in parathion (O,O-diethyl O-p-nitrophenyl phosphorothioate) photolysis (79). Increased rates of a pesticide for weed control when surface applied may indicate that photolysis is occurring. Wright found that three to five times the rate of trifluralin was needed for chemical weed control when applied PES than when incorporated, and he concluded that photodecomposition or volatility must be occurring (140).

Rate of Herbicide Degradation

By summing all transformation processes for a given pesticide, a degradation rate can be determined and used to predict persistence. Conflicting degradation rates in the literature may be due to environmental conditions. It is difficult in field studies to distinguish the contribution of degradation from other processes in the disappearance of a chemical (29). Surface runoff, leaching, plant uptake, and volatility must be assessed before degradation can be quantified (29). Soil moisture and temperature can alter the rate and the transformation processes and thus change the persistence of a pesticide in the soil. Field measured half-lives are often shorter than in the laboratory due to multiple degradative pathways and the influence of soil moisture content, temperature and substrate concentration (125). Regardless of environmental conditions, herbicide degradation rates are believed to be independent of initial concentration (111, 142). However Hamaker and Goring (51), and Cheung and Lehmann (29) stated that it would be unreasonable to assume a simple rate law, and at very high and very low concentrations the kinetics of herbicide degradation are very different. Hamaker and Goring felt pesticide turnover was a complex process, and when the initial concentration of herbicide is added to soil there is a period of rapid degradation (51). Over time, a greater percentage of herbicide becomes 'less available', and degradation slows until it reaches a steady state and the degradation rate is determined by a labile pool. Hurle and Walker agreed that the rate of pesticide degradation is disproportionately slower at low residual concentrations, and proposed a two compartment soil model with available and nonavailable areas for pesticide location, with only available areas subject to degradation (64). Dissipation of fluridone was found to be very slow following initial rapid disappearance during the first 90 days (14). Zimdahl and Gwynn saw initial rapid loss of trifluralin followed by a much slower reaction rate (142). Duseja and Holmes found that trifluralin persistence in the field dropped rapidly within 9 days after application to one third and one fifth remaining in the 0 to 10 cm depth on a loam and clay soil, respectively (33). Five months after application, only 2.1% and 0.4% of the initial amount applied remained on the loam and clay soils, respectively. In another study trifluralin concentrations decreased rapidly to 10 to 15% of the initial application within one-half year after application, with only 20% remaining after 43 days, followed by a more gradual decrease over time (93). Savage showed similar results on two different soils using trifluralin and nitralin (4-(methylsulfonly)-2,6-dinitro-N,N-dipropylbenzenamine) with 60 ppbw remaining after eight months, and 30 ppbw remaining after 18 months (102). In contrast, Hance and McKone found the degradation rate of atrazine and linuron to increase at low concentrations, suggesting a saturation of active degradation sites at high herbicide concentrations (53).

ENVIRONMENTAL CONDITIONS AFFECTING TRANSFER AND TRANSFORMATION PROCESSES

Soil Moisture

Soil moisture influences transfer and transformation processes, thus altering the persistence of herbicides in soil (2, 20, 23, 24, 75, 126). Excessive soil moisture may leach the compound out of the soil profile and reduce damage to susceptible crops, but this may result in other environmental problems. Soil moisture can alter the vapor pressure of compounds, making them more volatile under moist conditions (23, 130). Adequate soil moisture increases plant uptake during the growing season which may or may not result in decreased persistence, depending on whether the compound is degraded within the plant prior to plant residues being returned to the soil (23). Increased plant phytotoxicity can occur as moisture increases due to an increased amount of herbicide being taken up with water and accumulating in the plant (126). Yearly variations in plant response to herbicides reflect the difference in herbicide availability to the plant. Changing moisture levels in the soil alter the distribution between the sorbed and solution phases, change the rate of herbicide movement by molecular diffusion or mass flow, and change the amount of herbicide translocated in the plant (126).

Adsorption of pesticides to soil colloids may be affected by soil moisture (12, 126). More EPTC is adsorbed in the air dry state than at field capacity (12). For non-volatile herbicides, phytotoxicity increases under moist conditions as less herbicide is adsorbed to the soil making more available for plant uptake (23, 24). Dry soils increase herbicide persistence as there is less competition for adsorption sites by water. Water is very polar and strongly adsorbed to the soil matrix. At low moisture levels the number of water molecules competing for soil adsorption sites decreases, and less polar organic compounds can then adsorb to soil (23). Secondly, higher concentrations of pesticides due to low moisture results in herbicide precipitation out of solution (23,91). At low soil moisture levels the herbicide concentration per unit volume increases, and crystallization can occur that results in decreased herbicide bioactivity (23). Sandy soils have lower water-holding capacities, which may result in herbicide precipitation occurring. Loss of material to the solid phase can be termed sorption to avoid the implication of precipitation or adsorption (106).

The soil moisture content and the method in which water is added to soil is critical in determining herbicide availability (20, 50, 52). When isoproturon (N,N-dimethyl-N'-(4-(1-methylethyl)phenyl)urea) was applied to soil, plants were severely injured after watering from above, but not after sub-irrigation (20). When the soil surface was very moist prior to herbicide application, adsorption was 'normal' and the herbicide leached, especially if watered frequently from above. Hall et al found that metsulfuron (2-(((((4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino)carbonyl)amino)sulfonyl)benzoic acid), chlorsulfuron, picloram, and clopyralid (3,6-dichloro-2-pyridinecarboxylic acid) all showed little activity in sub-irrigated pots when the herbicides were applied to the surface of dry soils (50). When applied to moist soils and sub-irrigated all herbicides showed activity on Canada thistle (Cirsium arvense) except for chlorsulfuron (50). They concluded that either the herbicide was adsorbed on dry soil surfaces and couldn't be displaced by water, or the herbicide precipitated on the dry soil surface and failed to leach. Hance and Embling applied linuron, metribuzin, and simazine to soil that was wetted to 20% field capacity, and to dry soil that was wetted to 20% field capacity 10 minutes or 24 hours after herbicide application (52). When they extracted samples of the soil solution with a pressure membrane cell they found much lower concentrations of herbicide where the soil had remained dry for 24 hours after herbicide application prior to rewetting. They concluded that application to air dry soil makes a herbicide inaccessible to some of the water that is applied later, and the soil moisture content at the time of application is therefore a very important factor in performance variability of soil-applied herbicides (52).

Soil moisture can affect biological and nonbiological transformation (23, 75, 79, 111, 127). Microbial activity is regulated by soil conditions, as 50-75% of field capacity and 25-35°C are optimum for microbial growth (111). Pronamide degradation at 23°C increased as soil moisture increased from 3.5 to 12.0% with the half-life decreasing from 78 to 29 days (127). Pesticide degradation in soils at 15 bars was slower than at one bar, and more bound residues were formed in moist soils than under very dry conditions at 15 bars (94).

Nonbiological transformations are slower under dry conditions (23, 24, 31, 74, 79). Dry soils result in reduced photolysis for some herbicides, and chemical breakdown is decreased because water is needed for hydrolytic transformations and oxidation reactions (23). However in dry soils water is more dissociated, and this may lead to acid-catalyzed hydrolysis (23). Generally pesticides persist longer in dry cool regions than moist warm regions (24). However in a study with ethofumesate, there was a 90% loss in activity over a 12 day period when applied to dry soil, and no loss when applied to a wet soil (75). The authors felt this activity loss could be from volatilization, photodecomposition, increased microbial degradation, adsorption, or chemical decomposition (75). They concluded that volatilization from a dry soil was less likely and microbial degradation on dry soils was also less likely. The ethofumesate loss occurred in the greenhouse where UV light couldn't penetrate, so photodecomposition was not believed to be the cause. Chemical adsorption was ruled out because compounds weren't released when refluxed with methanol. They concluded that ethofumesate chemical decomposition increased on dry soil. Soil adsorption was greater so chemical hydrolysis increased, and this coupled with the pH of the water film being lower under dry conditions caused increased hydrolysis under dry conditions (75).

Soil Temperature

Soil temperature affects transfer processes such as volatilization, and transformation processes such as chemical degradation and microbial decomposition (23, 91). Higher temperatures increase herbicide volatilization as vapor pressure is temperature dependent. Higher temperatures can either increase or decrease plant uptake. Under adequate moisture conditions, increased temperature will increase plant uptake. However under drouth conditions, higher temperatures can cause reduced plant uptake or plant death.

Transformation processes are dependent on soil temperature, and the degradation rates of most soil-applied herbicides increase with temperature (94, 128, 142). Zimdahl and Gwynn found the degradation of three dinitroanilines in the soil to be directly correlated to soil temperature and soil moisture content (142). They found first order degradation at 15°C,but not at 30°C where they had initial rapid loss, and then a slower dissipation rate (142). Rao et al found degradation rates for nine pesticides on seven soils weren't associated with soil, organic carbon, soil pH, cation exchange capacity, percent clay, or total bacteria or fungal propagules, but rather the soil-water content and soil temperature (94). Soil temperatures less than 25°C had a greater influence on degradation, causing a rapid decrease in the degradation rate. When soil temperatures were above 25°C a slight increase in the degradation rate occurred (94). Temperatures may also affect pesticide binding by altering the solubility of the herbicide. As temperature increases the solubility of some pesticides increases, and sorption decreases (91).

STUDYING PERSISTENCE OF HERBICIDES

Residue Sampling

Field residue sampling results show significant variability in the amount of pesticides persisting in the soil which limits precision (63, 95, 97, 120, 129, 131). Variability may be from application method, soil variability, sampling procedure, extraction efficiencies, and other analytical error (63, 95, 97, 114, 116, 120, 129, 131). The herbicide application method can be a major factor in causing increased variability in detectable residue levels (97, 120, 129, 131). Wauchope et. al. found disk harrow incorporation resulted in redistribution of trifluralin, producing areas of poor weed control and other areas of crop damage (131). Robinson found a coefficient of variation (CV) of 42-114% when 0.84 kg/ha of nitralin was applied and incorporated with a disk harrow (97). Concentrations varied widely in soil samples five cm apart, which explained why plant response varied in the treated field. In other research, the wide variability found in simazine recovery persisted throughout the 112 day period that soil cores were taken (129). The CV was reduced to 14% when simazine was applied to smaller plots with a knapsack sprayer. Taylor et. al. found measurements of dieldrin (hexachloro-epoxy-octahydro-endo, exo-dimethanonapthalene) residues to have a 50 -fold variation, and felt it was due to either spray coverage or redistribution of herbicide by disking to a 7.5 cm depth (120). By increasing the number of cores taken per plot from eight to thirty, the CV was lower (120). They attributed this to the irregular herbicide distribution. Hormann et. al. concurred, and felt that analytical error was only a small fraction in overall variability, with sampling error giving the greatest variability (63). Twenty cores per plot taken systematically reduced the CV to 20% (63).

In the soil, physical, biological, and chemical processes which transport and transform the pesticide in the field vary with the differing composition of the soil area (95). These varying soil properties lead to different dissipation rates, resulting in increased sample variation over time (95).

Residue sampling is also complicated by the fact that pesticide extraction efficiency is difficult to determine. When pesticide residues age they become more resistant to solvent extraction due to adsorption to soil colloids and diffusion into the interior of the humic colloids (114, 116). This makes it difficult to determine a true extraction efficiency as fortified soil results could be largely different than the extraction efficiency from field treated soils (114, 116).

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CHAPTER 2

RESPONSE OF CORN CULTIVARS TO IMAZAQUIN

ABSTRACT

Nine corn (Zea mays L.) cultivars differed in their response to imazaquin[1] (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-3-quinolinecarboxylic acid) applied from 35 to 280 g ai/ha, as measured by fresh shoot and adventitious root weight and length. Cargill 921, Great Lakes 422, and Great Lakes 5922 cultivars were among the more tolerant cultivars in both years of study, while Pioneer 3737, Northrup King 9410, DeKalb-Pfizer Trojan 1100, and Stauffer 5650 were among the less tolerant varieties both years. There was no cultivar tolerant to imazaquin across all application rates in both years of the study. There was less corn injury from imazaquin in the second year, and preplant incorporated applications caused significantly more injury than preemergence surface applications. Lack of rainfall the second year limited movement of imazaquin in the soil profile. Increased sorption to soil and decreased availability to plant roots especially from preemergence surface applications, resulted in reduced corn injury.

[1] AC-252,214 Code Number. American Cyanamid Co. Princeton, NJ 08540.

INTRODUCTION

Imazaquin is a selective herbicide for grass and broadleaf weed control in soybeans (Glycine max (L.) Merr.). Plant uptake of imazaquin is by both the root and shoot, with apoplastic and symplastic translocation to meristematic regions (13). Only a small percentage of imazaquin remains in the root after root uptake (13). Plant growth ceases, tissue chlorosis and necrosis develop, and plant dieback and death occur in two to three weeks (14). The primary mechanism of action of imazaquin is believed to be inhibition of the enzyme acetohydroxyacid synthase (AHAS) that catalyzes the biosynthesis of the three branched chain amino acids valine, leucine, and isoleucine (2, 14). Differential metabolism of imazaquin apparently determines crop and weed selectivity (13).

Little information is available regarding the behavior and persistence of imazaquin in soil (8, 9, 10). Rotational crop restrictions for imazaquin have not been published, but injury to corn (Zea mays L.) has occurred when planted the year following imazaquin application in soybeans (9, 10). The persistence of imazaquin in soil has not been related to any specific soil or edaphic factor, and cultivar tolerances have not been correlated to instances of corn injury.

Differential tolerance of crop cultivars, including corn, to several herbicides has been reported. These herbicides include atrazine

(6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine), simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine), alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide), diclofop ((±)-2-(4-(2,4-dichlorophenoxy)phenoxy)propanoic acid), trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine), butylate (S-ethyl bis(2-methylpropyl)carbamothioate), and EPTC (S-ethyl dipropyl carbamothioate) (1, 4, 5, 6, 7, 11, 17, 18). Temperature and moisture conditions alter hybrid sensitivity (5, 11, 18).

Field studies were conducted in 1984 and 1985 to determine if corn cultivars varied in response to imazaquin, and if environmental conditions alter corn varietal response.

MATERIALS AND METHODS

Field plots were prepared on May 16, 1984 and May 8, 1985 on a Capac sandy loam (Aeric Ochraqualfs, fine-loamy, mixed, mesic) with 2.1% organic matter, a pH of 6.4, 57% sand, 26% silt, 17% clay, a cation exchange capacity of 10.1, and <1 and 43 ppm of extractable aluminum and iron, respectively. The experimental design was a three factor factorial arranged in a randomized complete block design with four replications. The factors were imazaquin rate, application method, and corn cultivar. Eight plots (9.14 by 12.2 m) (two per replication) were treated with imazaquin at 35, 53, 70, 140, and 280 g ai/ha with a tractor-mounted boom sprayer at 215 L/ha and 206 kPa. Four plots (one per replication) were incorporated immediately with one pass using a Triple K Danish s-tine field cultivator[2] set at an incorporation depth of 6 cm. One plot in each replication did not receive imazaquin and served as the control. Nine corn varieties per plot were planted at a 4 cm depth. The nine hybrids were Great Lakes 422, Great Lakes 5922, Cargill 921, Pioneer 3901, Pioneer 3737, Northrup King 9410, DeKalb-Pfizer Trojan 1100, Stauffer 5650, and Funks G-4342. Twenty-eight days after planting, four plants per hybrid per plot were dug from the field, and fresh shoot and adventitious root length and weight measured. All measurements were converted to a percentage of the control plants for the respective cultivar to eliminate growth differences among cultivars. Results were not combined over years due to significant interactions of years with herbicide rate, application method, and cultivar. All measured parameters gave similar results. Shoot length measurements had greatest precision, so when data is presented for one parameter it will be for shoot length.

RESULTS AND DISCUSSION

In 1984, the main effects of application method, imazaquin rate, and corn cultivar were highly significant. A highly significant interaction occurred for application method by imazaquin application rate (Table 1). The interaction can be explained by the preplant incorporated (PPI) applications causing less injury than preemergence

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[2] Manufacturer. Kongskilde, Box 88, Exeter, Ontario.

Table 1: Application method and imazaquin rate interaction in 1984.

Imazaquin Rate g ai/ha	Application Method	
	Preplant incorporated shoot length[a]	Preemergence surface shoot length
	--------------------(% of control)----------------	
35	67 a	73 a
53	59 b	69 a
70	56 bc	51 c
140	36 de	41 d
280	27 f	31 ef

[a] Values followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test. Statistical comparisons are valid across rows and between columns.

surface (PES) applications at 70 g ai/ha, while at all other rates PPI applications caused 4 to 10% more injury. The magnitude of the significance of the interaction was considerably less than the significance of the main effects.

The main effect of application method was highly significant in 1984. PPI applications of imazaquin reduced corn height 4% more compared to PES applications. Corn injury increased significantly as imazaquin application rate increased (Figure 2). Corn cultivars in 1984 showed great differences in tolerance to imazaquin across all application rates and methods (Table 2). Cargill 921, Pioneer 3901, and Great Lakes 422 were among the more tolerant cultivars for all measured parameters.

In 1985, all main effects were highly significant, and a highly significant interaction occurred between application method and corn cultivar (Table 3). This interaction was significant because of the 33 to 39% increase in injury to Stauffer 5650 and Northrup King 9410 when imazaquin was incorporated compared to surface applications, and a lesser difference in injury due to application method found for the cultivars Pioneer 3737 and Dekalb-Pfizer Trojan 1100. There was no significant difference in the effect of application method on cultivar injury to the other five hybrids, and this difference in response among cultivars in 1985 caused the corn cultivar by application method interaction. When analysis of variance was evaluated including the control plants, no significant difference in injury to the nine cultivars at any imazaquin application rate compared to the controls for PES applications occurred. All nine varieties at all application rates for PPI applications, exhibited injury as measured by all four

Figure 2: The effect of imazaquin application rate on fresh shoot and root weight and length in 1984.

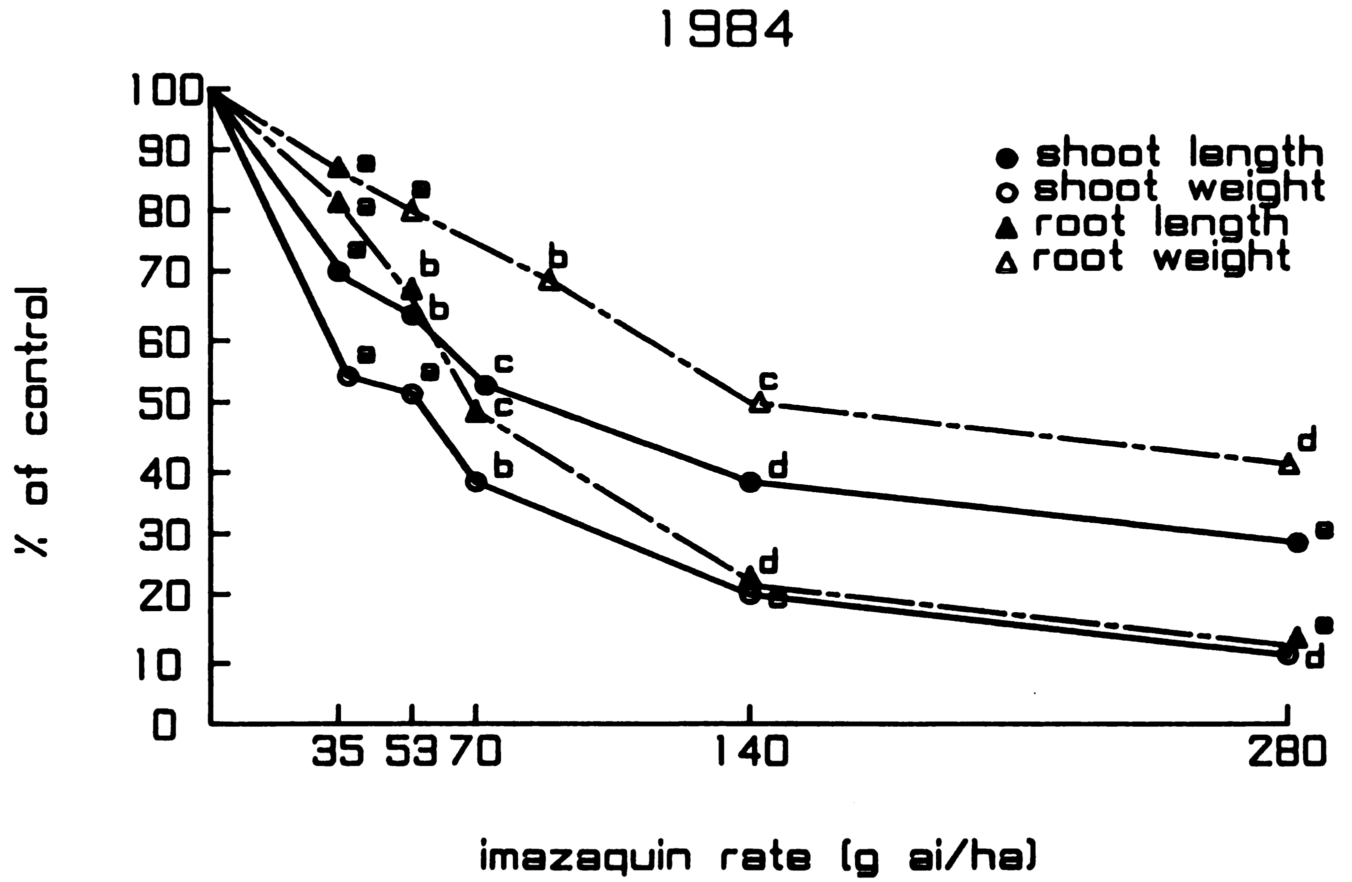
1984
% of control
100
90
80
70
60
50
40
30
20
10
0
35
53
70
140
280
imazaquin rate (g ai/ha)
● shoot length
○ shoot weight
▲ root length
△ root weight
a
b
c
d

Table 2: Corn cultivar response to imazaquin in 1984 across all herbicide rates and application methods.

Cultivar	Shoot length[a]
	---(% of control)---
Cargill 921	61 a
Great Lakes 422	55 bc
Pioneer 3901	59 ab
Great Lakes 5922	52 cd
Northrup King 9410	49 de
DeKalb-Pfizer Trojan 1100	41 f
Stauffer 5650	46 ef
Funks G 4342	51 c-e
Pioneer 3737	45 ef

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

Table 3: The influence of corn cultivar and imazaquin application method on corn shoot length in 1985.

	Application Method	
	Preplant incorporated	Preemergence surface
Cultivar	Shoot length[a]	Shoot length
	----------------(% of control)-------------------	
Cargill 921	84 a-d	93 ab
Great Lakes 422	75 c-f	88 a-d
Pioneer 3901	71 d-f	82 a-d
Great Lakes 5922	89 a-c	93 ab
Northrup King 9410	66 ef	100 a
DeKalb-Pfizer Trojan 1100	71 d-f	92 a-c
Stauffer 5650	50 g	90 a-c
Funks G 4342	75 c-f	81 b-e
Pioneer 3737	63 f-g	85 a-d

[a] Values followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test. Statistical comparisons are valid across rows and between columns.

parameters. Therefore evaluation of cultivar response to imazaquin in 1985 can be made only with PPI applications.

PES applications caused 18% less injury than PPI applications, which resulted in a highly significant main effect. As the imazaquin application rate increased, injury to corn decreased (Figure 3), but there was less corn injury across all imazaquin application rates in 1985 than 1984.

Less corn injury occurred in 1985 compared to 1984 across all imazaquin application rates, and PPI applications gave significantly more corn injury than PES applications. In 1984, 9.14 cm of rain fell in the 28 days after imazaquin application and corn planting, with 7 cm of this rain falling during the first 10 days after planting (Table 4). In 1985, a total of 3.96 cm of rain fell in the 28 days after application and corn planting, with only 0.91 cm of this rain falling during the first 10 days. The increased moisture level in 1984 appeared to increase the availability of imazaquin to corn by decreasing soil sorption. Imazaquin did not leach out of the corn root zone and was available for uptake. In 1985 rainfall was very limited, PES applications failed to move into the corn root zone to be available for root uptake, resulting in decreased corn injury in 1985, especially for PES applications.

Changing moisture levels in the soil alter the herbicide distribution between the sorbed and solution phases, and change the rate of herbicide movement by diffusion and mass flow (3). At low moisture levels the number of water molecules competing for soil adsorption sites decreases so herbicides can adsorb, and a higher concentration of herbicide per water volume at low soil moisture levels

Figure 3: The effect of imazaquin application rate on fresh shoot and root weight and length in 1985.

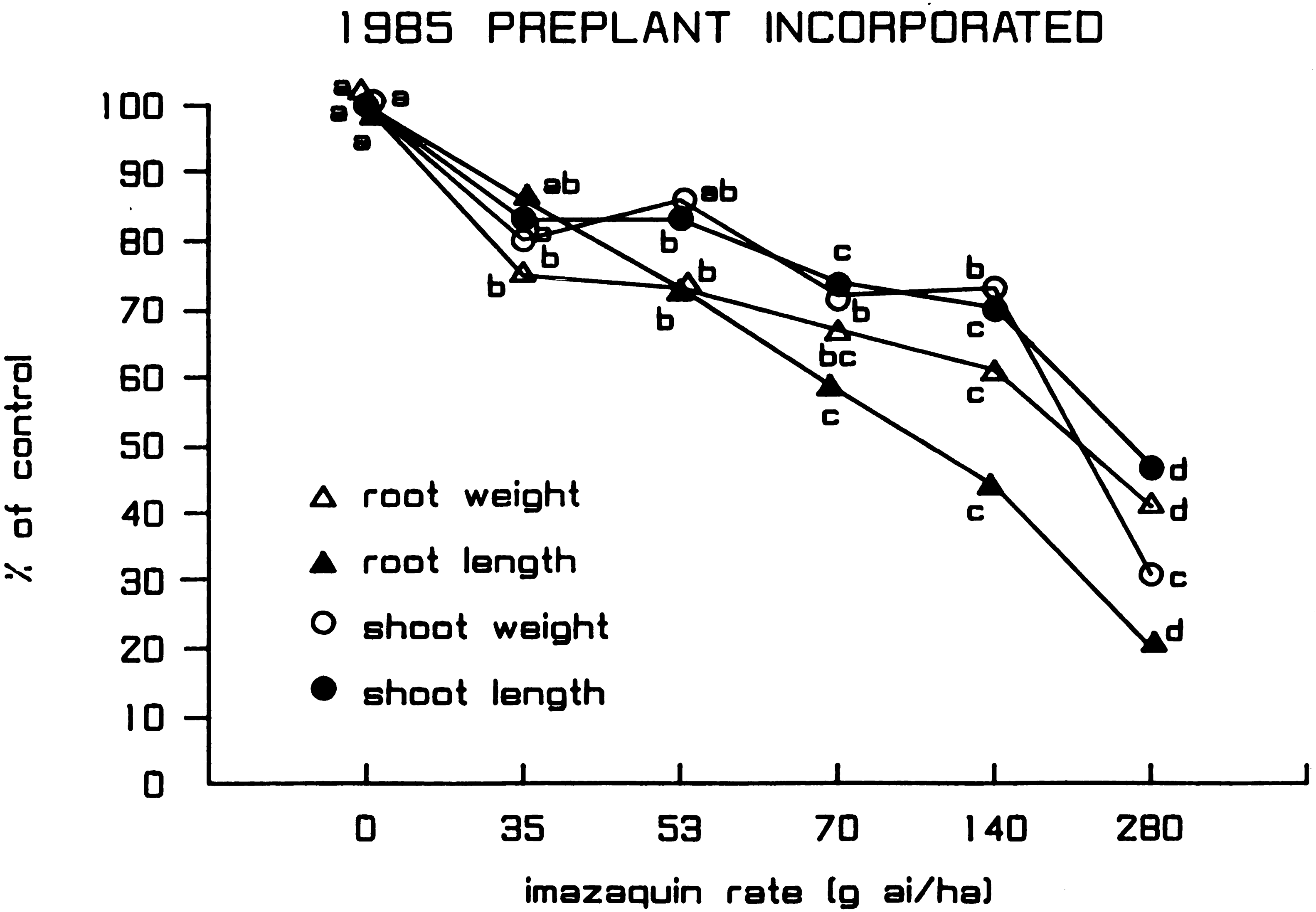
1985 PREPLANT INCORPORATED
% of control
100
90
80
70
60
50
40
30
20
10
0
imazaquin rate (g ai/ha)
0
35
53
70
140
280
△ root weight
▲ root length
○ shoot weight
● shoot length
a
a
a
a
ab
b
b
b
ab
b
b
b
c
b
bc
c
b
c
c
c
d
d
c
d

Table 2: Rainfall summary for 1984 and 1985. Corn was planted and imazaquin applied on May 16, 1984 and May 8, 1985.

Days after application and planting	1984	1985
	-------------cm	-------------
1	--	--
2	.08	--
3	.23	--
4	.13	--
5	.03	--
6	.76	--
7	2.87	.10
8	--	.08
9	.28	.18
10	2.62	--
11	.08	--
12	--	--
13	1.83	1.14
14	.10	--
15	--	--
16	--	--
17	--	--
18	--	--
19	--	1.40
20	--	.53
21	--	--
22	--	--
23	--	.53
24	.18	--
25	--	--
26	--	--
27	--	--
28	--	--
Total	9.14	3.96

can result in the herbicide precipitating out of solution and becoming unavailable for plant uptake (3). Both of these processes may be reasons for the lack of corn injury seen in 1985, especially for PES applications where it appeared that no imazaquin reached the corn root zone to be available for plant uptake.

Soil moisture also influences plant transpiration, which can change the amount of herbicide taken up and translocated by plants. Corn cultivar uptake in 1984 may have exceeded the ability of corn to metabolize imazaquin. This may be cultivar dependent. Sander and Barrett found differences in hybrid tolerance to imazaquin, and differential metabolism was given as the explanation (12).

Corn cultivars varied in their response to imazaquin. Cargill 921, Great Lakes 422, and Great Lakes 5922 were among the more tolerant hybrids both years. Stauffer 5650, Dekalb-Pfizer Trojan 1100, Northrup King 9410, and Pioneer 3737 were among the more susceptible cultivars both years. In greenhouse studies, researchers found Cargill 921, Pioneer 3901, and Great Lakes 422 to be more tolerant to imazaquin, with a GR_{50}= 46 g ai/ha (12). Northrup King 9410, Stauffer 5650, and Pioneer 3737 were in a more sensitive group, with a GR_{50}= 23 g ai/ha (12). The response of Great Lakes 5922 was intermediate between the less and more tolerant groups. Uptake, translocation, and metabolism studies with Pioneer 3737 and Cargill 921 found no differences in enzyme activity or selectivity between cultivars, and no differences in uptake and translocation (12). However on a percentage basis, significantly less radioactive imazaquin and more unextractable and radioactive metabolites were extracted from the root of the tolerant cultivar Cargill 921, and differential metabolism was given as the explanation for varietal tolerance (12).

It appeared that cultivar response may be involved in incidences where imazaquin injured corn planted as the rotational crop after soybeans. It is not known if genetic variation in the parent lines contributed to the observed varietal differences, as the parent lines of these nine hybrids are not known. Researchers have identified a maize cell line containing an altered AHAS enzyme that is no longer inhibited by the imidazolinones (14). The resistance is inherited as a single, co-dominant trait and is expressed on the whole plant level (14). By developing a cultivar tolerant to imazaquin, injury to corn from imazaquin persisting in the soil may be avoided.

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CHAPTER 3

INFLUENCE OF HERBICIDE APPLICATION METHOD, RATE, AND TILLAGE ON IMAZAQUIN PERSISTENCE IN SOIL

ABSTRACT

Preplant incorporated (PPI) applications of 280 and 70 g ai/ha of imazaquin[1] (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-quinolinecarboxylic acid) had significantly greater persistence than preemergence surface (PES) applications across all soil depth increments from 0 to 23 cm throughout the growing season in 1985. In 1984 there was no statistical difference between PPI and PES applications, but a similar trend was evident. Imazaquin disappeared rapidly both years during the first 30 days after PPI and PES applications. A subsequent decrease in the dissipation rate occurred in the next 120 days of the growing season. There was no significant difference in residue remaining from 60 to 150 days after application where 280 and 70 g ai/ha of imazaquin were incorporated or surface-applied in 1984, or where 280 g ai/ha was incorporated in 1985. There was no significant difference in imazaquin remaining from 30 to 150 days after application for PES applications of 280 g ai/ha in 1985, and

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[1] Code Number AC-252,214. American Cyanamid Co. Princeton, NJ 08540.

for PPI and PES applications of 70 g ai/ha in 1985. Injury to corn (Zea mays L.) planted in 1985 was greatest where imazaquin had been incorporated at 140 and 280 g ai/ha in 1984. PES applications of 140 g ai/ha in 1984 did not reduce corn height significantly when compared to the control plants grown where no imazaquin had been applied in 1984. Reduction in corn height occurred from PPI imazaquin applications in 1984 at 53, 70, 140 and 280 g ai/ha, and PES applications of 70 and 280 g ai/ha. Spring tillage had no significant effect on corn injury, as there was no difference between corn grown in spring moldboard plowed versus disked ground, across both corn hybrids, application methods, and herbicide rates.

INTRODUCTION

Imazaquin is registered for use in soybeans (Glycine max (L.) Merr.) as a preplant incorporated (PPI), preemergence (PES), and postemergence (POE) herbicide. Imazaquin controls both monocots and dicots at soil application rates of 70 to 280 g ai/ha by inhibiting the enzyme acetohydroxyacid synthase that is involved in the biosynthesis of leucine, valine, and isoleucine (26). Little information is available regarding the fate of imazaquin in soil. Reports have indicated persistence problems can occur in the northern United States when corn is planted as the rotation crop [2].

[2] Personal Communication. American Cyanamid Co. Princeton, NJ 08540.

Herbicide persistence in soil is a function of the chemical properties of the herbicide, soil properties, environmental conditions, and cultural practices (1, 3, 6, 7, 15, 20, 27). Changing tillage methods, applying a lower herbicide rate, and using a different application technique are three methods, that when implemented, alter the persistence and/or distribution of a herbicide in soil and may reduce rotational crop injury.

Herbicide persistence may be mechanically altered by tillage that moves or dilutes the herbicide in the plant root zone. The success of this method on reducing phytotoxicity to crops is dependent on the resulting herbicide concentration and crop plant sensitivity (27).

Lower application rates can reduce the amount of herbicide remaining in the soil if degradation rate is independent of initial concentration (7, 12, 14, 15, 32). However, researchers found the degradation rates of fluridone (1-methyl-3-phenyl-5-(3-(trifluoromethyl)phenyl)-4(1H)-pyridinone), trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine), nitralin (4-(methylsulfonyl)-2,6-dinitro-N,N-dipropylbenzenamine), and other pesticides were biphasic (4, 7, 8, 12, 15, 23, 24, 32). Rapid degradation occurred initially, followed by a slower degradation rate at lower residual concentrations. In contrast to these results, researchers have found the degradation rates of atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and linuron (N'-3,4-dichlorophenyl)-N-methoxy-N-methylurea) to increase at lower concentrations (13).

Application method has a significant effect on herbicide persistence, especially if a compound is volatile or subject to photodecomposition (2, 6, 8, 18, 19, 22). PES applications of pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine), trifluralin, and dichlobenil (2,6-dichlorobenzonitrile) were more persistent when incorporated than when applied to the soil surface (21, 25, 30, 31). Herbicides that are not volatile or subject to photodegradation such as atrazine and pronamide (3,5-dichloro (N-1,1-dimethyl-2-propynyl)benzamide) have shown application technique to have no effect on pesticide persistence (5, 29). Fluridone persistence on a Miller clay was the same whether incorporated or surface-applied, but on a fine sandy loam persistence was significantly greater for PPI applications (4).

Because of the sensitivity of corn to imazaquin, and the common rotation of soybeans to corn, knowledge of how imazaquin persistence in soil can be altered by cultural practices is needed. The experiment objectives were to determine a) if application method influences imazaquin distribution in the soil b) if application techniques alter persistence, c) if application rate influences persistence, and d) the effect of spring tillage on altering imazaquin phytotoxicity to corn.

MATERIALS AND METHODS

Persistence and distribution of imazaquin. Field plots were prepared on May 16, 1984 and May 8, 1985 on a Capac sandy loam (Aeric Ochraqualfs, fine-loamy, mixed, mesic) having 2.1% organic matter, a soil pH of 6.4, 57% s, 26% si, 17% cl, cation exchange capacity (cec) of 10.1, and <1 ppm of aluminum and 43 ppm of iron. Eight plots (3.05 m by 9.14 m) received imazaquin at 0, 35, 53, 70, 140, and 280 g ai/

ha. Four plots of each application rate were incorporated immediately with one pass using a Triple K danish tine field cultivator[3] set at a 5 cm depth. The design was a randomized complete block with four replications. Immediately after application 20 soil cores per plot from the 280 and 70 g ai/ ha plots were taken to a 10 cm depth in 1985. The cores were grouped together from each plot and fractionated into increments of 0 to 2.5 cm, 2.5 to 5.0 cm, 5.0 to 10.0 cm. 10.0 to 15.0 cm, and 15.0 to 23.0 cm depths, placed in plastic bags and frozen within 2 h of collection until analysis. Corn was planted in 1984 and 1985 and grew throughout the season. Soil cores were removed 30, 60, 90, and 150 days after imazaquin application in 1984, and 0, 15, 30, 60, 90, and 150 days after application in 1985. The imazaquin concentration present in the soil samples was determined by gas liquid chromatography.

Soil extraction and analysis. The following soil extraction and analysis procedure was made available by American Cyanamid Company. Soil samples of 100 g from each soil depth, application rate, time interval, and replication were weighed into 250 -ml Erlenmeyer flasks. Separate 50 g soil samples were dried in an oven overnight to determine the moisture percentage for each sample. Two hundred ml of 0.5N sodium hydroxide in water was added to each flask, the flasks sealed with parafilm-covered rubber stoppers, and shaken for 1 h on a wrist action shaker at 200 strokes/min. After shaking, the extracts were

[3] Kongskilde, Thames Road East, Box 880, Exeter, Ontario.

transferred into polypropylene centrifuge bottles using 100 ml of additional extracting solvent to wash the contents from the flasks, and centrifuged at 1050 x g for 20 min. The solution was transferred to a new centrifuge bottle, with the remaining soil centrifuged at 1050 x g for 5 min with 100 ml of methanol. This was combined with the first extract, the pH lowered to 2.0 with 6<u>N</u> hydrochloric acid in water to precipitate out the humics, and centrifuged at 1050 x g for 5 min. The supernatent was decanted, filtered through glass wool, and transferred to a 1 -L separatory funnel. The remaining humic acid precipitate was centrifuged at 1050 x g for 5 min with 100 ml of 0.1<u>N</u> hydrochloric acid in 75% methanol : 25% water and then filtered through glass wool into the same separatory funnel. The aqueous solution was partitioned once with 200 ml and once with 100 ml of methylene chloride. Any emulsions that formed were broken by drawing off the lower phase of methylene chloride plus the emulsion into a 250 -ml separatory funnel. The emulsions would break during transfer. The pKa of imazaquin is 3.8 [2], so the imazaquin was in the nonionic form and partitioned into the methylene chloride. The lower methylene chloride phases were drained each time into a 500 -ml round bottom flask and the combined extracts evaporated to less than 0.5 ml. Ion exchange chromatography was used for further cleanup using a 500 mg quarternary amine column[4] that was prepared by forcing in succession 3 ml of hexane, 3 ml of methanol, 3 ml of distilled water, and 3 ml of pH 7.0 phosphate buffer through the column. The imazaquin residue remaining in the round bottom flasks was

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[4] Baker - 10SPE, No. 7091-3. J. T. Baker Chemical Co., Phillipsburg, NJ.

dissolved in 5 ml of pH 7.0 phosphate buffer which changed the imazaquin to the anionic form, forced through the ion exchange column, and the eluate collected in a beaker. This step was repeated with an additional 5 ml of buffer. The combined eluates received an additional 40 ml of buffer, the pH was adjusted to 2.0 with 1N hydrochloric acid, and then transferred to a 500 -ml separatory funnel. Imazaquin now in the nonionic form was then partitioned once with 50 ml and once with 25 ml of methylene chloride, and the combined methylene chloride phases were evaporated to less than 0.5 ml in a 250 -ml round bottom flask. Fifty ml of methanol was added to each sample and vacuum evaporated twice to ensure methylene chloride removal and the final imazaquin residue dissolved in 1 ml of methanol. In addition to the field samples, untreated soil was fortified with imazaquin and extracted to determine an extraction efficiency which was ± 20%. All residue levels reported (in ppb) have not been adjusted for extraction efficiency.

The 1 ml imazaquin samples were derivatized with TMAH (trimethylanilinium hydroxide)[5] prior to injection on a Tracor Model 560 gas liquid chromatograph equipped with a Model 702 nitrogen-phosphorus detector. The column was 92 cm by 2 mm I. D. glass packed with 10% OV-101 on 80/100 mesh Supelcoport. The operating temperatures for the injection port, column, and detector were 255, 255, and 265°C, respectively. Helium carrier gas flow was 25 ml/min, and hydrogen and air flow rates were 2.0 ml/min and 120 ml/min, respectively. Five μl

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[5] Cat. No. 303097. TMAH 0.2M in Methanol. Supelco, Incorporated.

injections of all samples were made and peak heights and retention time compared to injections each day and every 2 h of the standard curve of analytical grade imazaquin. The sensitivity of the method was 5 ppb, and retention time approximately four minutes. Peak heights were converted to ng by extrapolation from the standard curves each day and a mathematical equation (ppb = ng/5 x 1000 / sample weight in g corrected for moisture) used to convert ng to ppb in each soil sample.

Spring tillage. The 1984 imazaquin plots were split by tillage on April 24, 1985, with half of each plot moldboard plowed and the other half tilled by two passes with a disk set at 15 cm. All plots were field cultivated and planted to corn (Pioneer 3901 and 3744) on May 7, 1985. Alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide) plus atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-amine) both at 3.36 kg/ha were applied for grass and broadleaf control. The heights of four plants per hybrid per plot were measured on June 28, 1985 and height measurements converted to a percent of the control plant heights in each replication that were growing on soil where no imazaquin was applied in 1984. In this way the tillage effect on corn growth would not be a factor affecting imazaquin injury evaluations.

RESULTS AND DISCUSSION

Persistence and distribution of imazaquin. Imazaquin distribution and persistence in 1984 in the top 23 cm of the soil profile during the growing season is shown for PPI and PES applications of 280 g ai/ha in

Figures 4 and 5, respectively. Thirty days after application (d.a.a.) 34, 14, 8, 10, and 9 ppb remained at descending depth increments where surface-applied, and 60, 24, 11, 5, and 5 ppb where incorporated. There was 43% less imazaquin remaining in the 0 to 2.5 cm increment, and 27% less in the 5.0 to 10.0 cm depth increment for PES imazaquin applications, compared to PPI applications. Sixty d.a.a., there was 31 and 53% less imazaquin remaining in PES applications in the 0 to 2.5, and the 2.5 to 5.0 cm increments, respectively. One hundred and fifty d.a.a. there was less residue remaining in the 2.5 to 5.0 cm depth for PES applications.

In 1985 samples were taken immediately and 15 days after application to measure application accuracy and determine imazaquin persistence levels during the first month after application. Accurate application and a rapid decrease in persistence over time occurred for PPI (Figure 6) and PES (Figure 7) applications of 280 g ai/ha of imazaquin. Incorporation distributed imazaquin in the top 10 cm of the soil profile. Residues in the top 2.5 cm decreased during the first 60 d.a.a., increased the next 30 days, and then decreased during the next 60 days. Residues in the 2.5 to 5.0 cm increment and the 5.0 to 10.0 cm increment decreased during the first 60 days, and then increased in the next ninety days. Surface applications of 280 g ai/ha showed no detectable imazaquin below 5 cm depth, and residues in both the 0 to 2.5 and 2.5 to 5.0 increments decreased over time. More imazaquin remained at all depth increments at all sampling times when incorporated. There was a greater magnitude of difference in imazaquin remaining between the two application techniques in 1985 compared to 1984 (Figures 4 and 5).

Figure 4: Imazaquin distribution and persistence in the soil profile in 1984 where 280 g ai/ha was applied and incorporated.

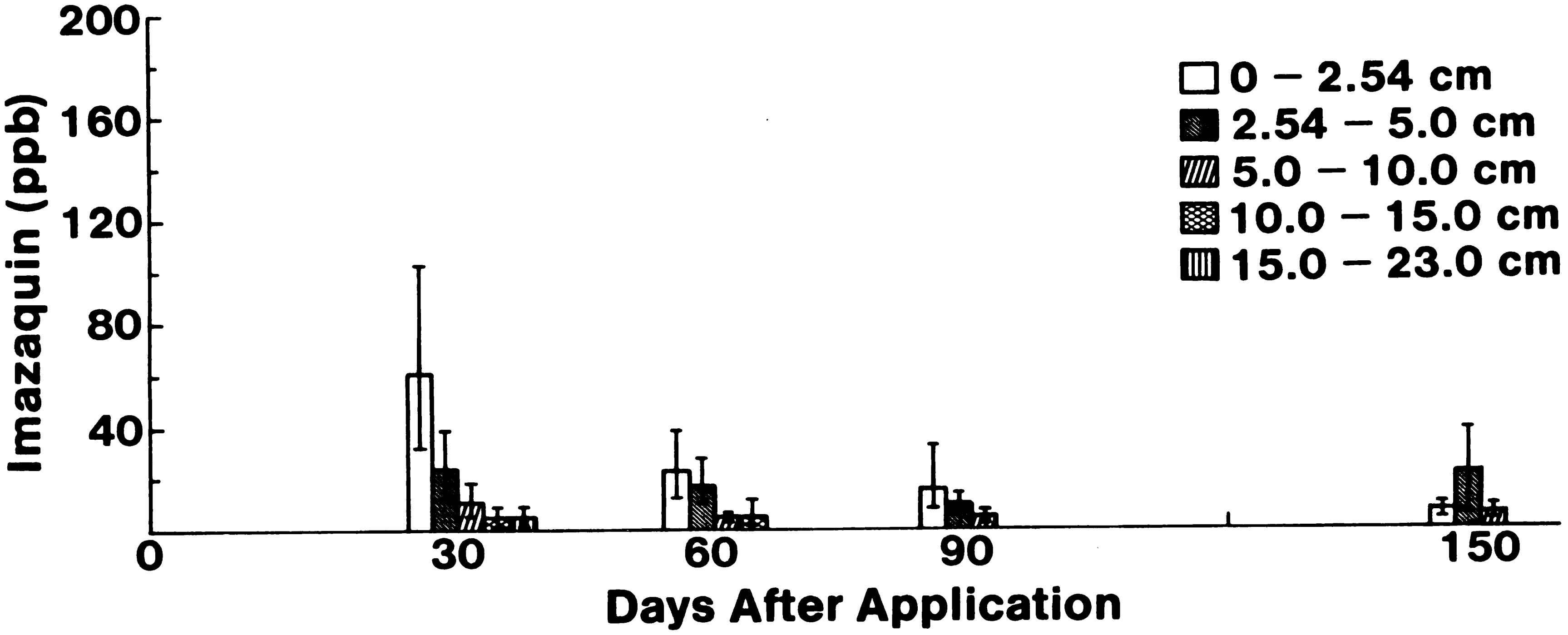
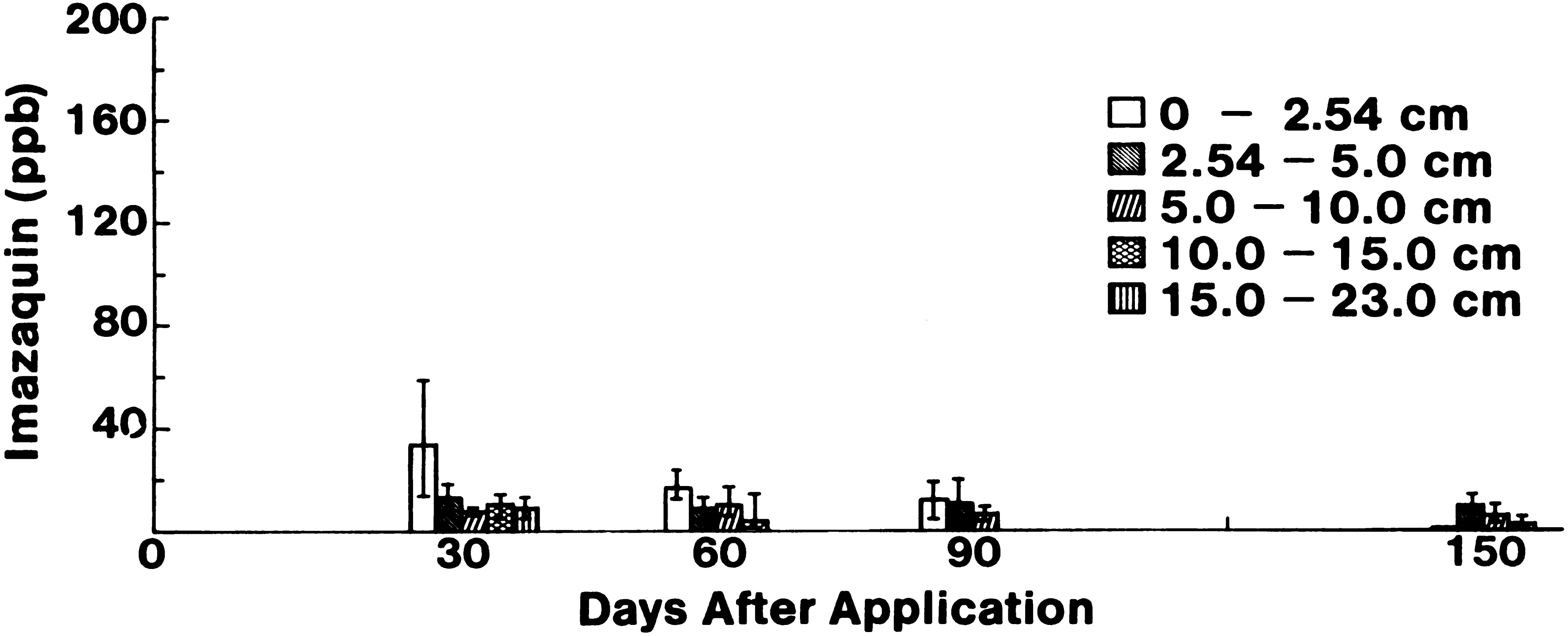

Imazaquin (ppb)
200
160
120
80
40
0
30
60
90
150
Days After Application
☐ 0 – 2.54 cm
■ 2.54 – 5.0 cm
▨ 5.0 – 10.0 cm
▩ 10.0 – 15.0 cm
▥ 15.0 – 23.0 cm

Figure 5: Imazaquin distribution and persistence in the soil profile in 1984 where 280 g ai/ha was preemergence surface-applied.



Imazaquin (ppb)
200
160
120
80
40
0
30
60
90
150
Days After Application
□ 0 – 2.54 cm
▨ 2.54 – 5.0 cm
▨ 5.0 – 10.0 cm
▩ 10.0 – 15.0 cm
▥ 15.0 – 23.0 cm

Figure 6: Imazaquin distribution and persistence in the soil profile in 1985 where 280 g ai/ha was applied and incorporated.

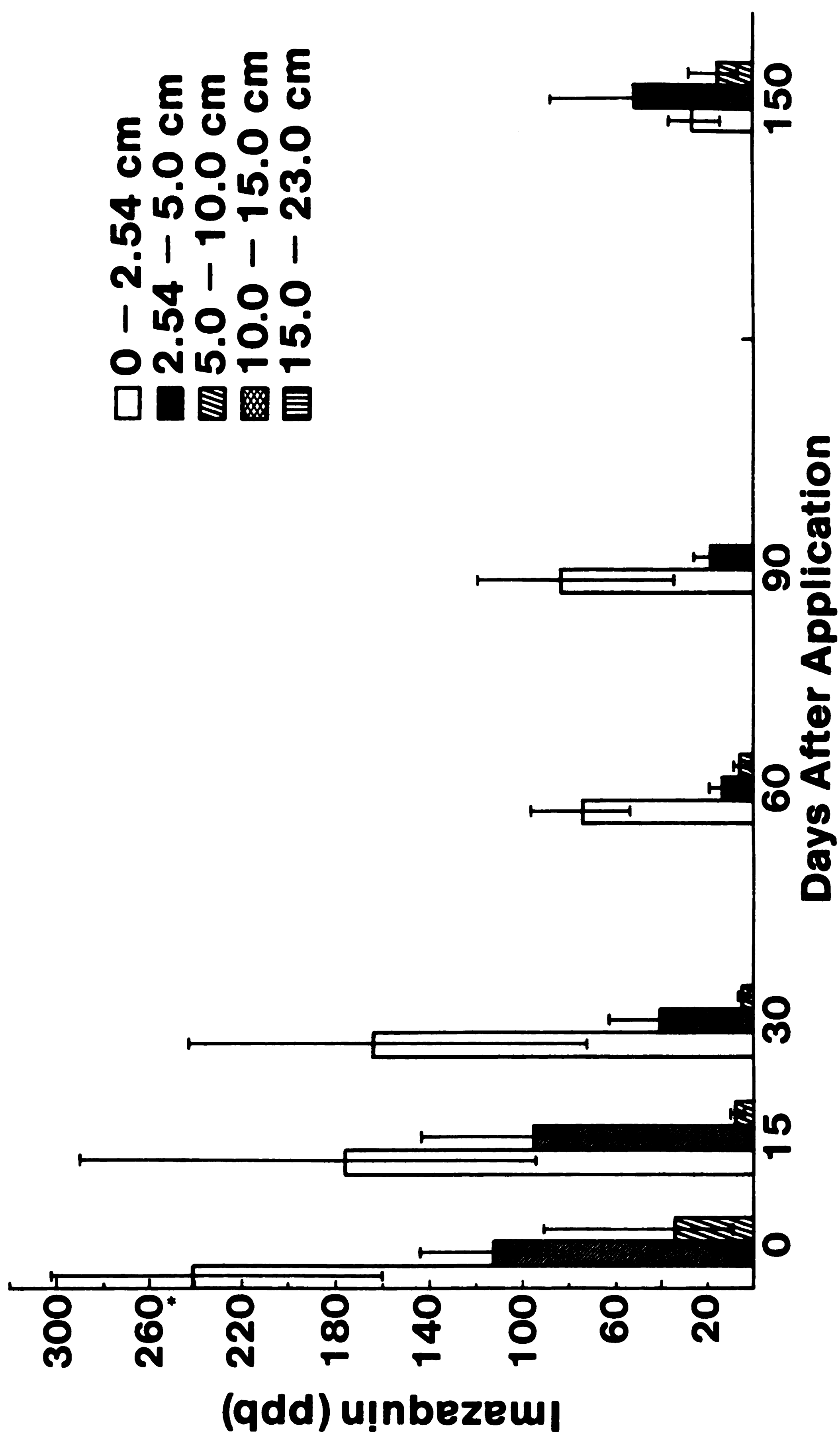
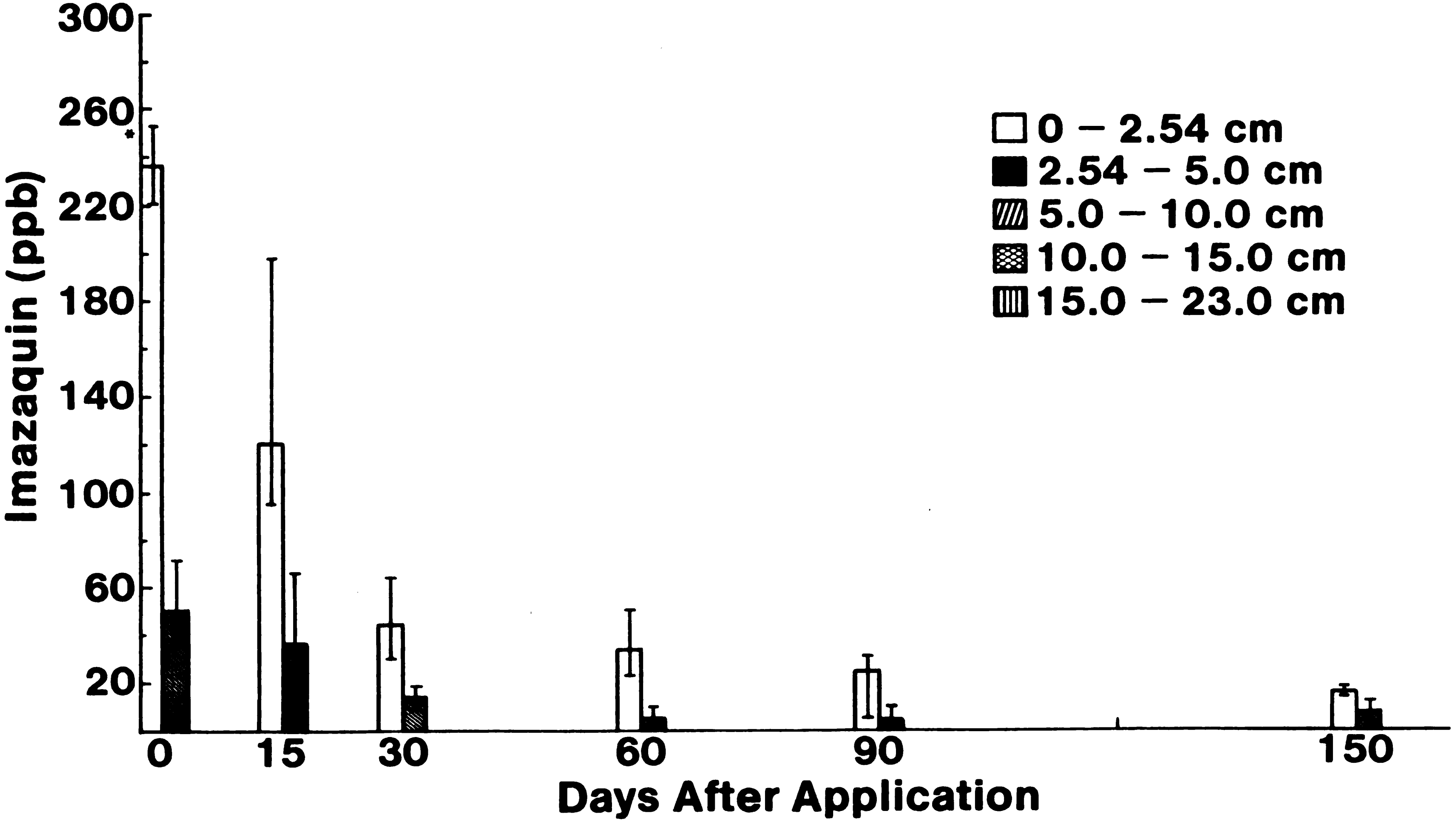

Imazaquin (ppb)
300
260*
220
180
140
100
60
20
0
15
30
60
90
150
Days After Application
□ 0 — 2.54 cm
■ 2.54 — 5.0 cm
▨ 5.0 — 10.0 cm
▩ 10.0 — 15.0 cm
▥ 15.0 — 23.0 cm

Figure 7: Imazaquin distribution and persistence in the soil profile in 1985 where 280 g ai/ha was preemergence surface-applied.


Imazaquin (ppb)
300
260*
220
180
140
100
60
20
0
15
30
60
90
150
Days After Application
□ 0 – 2.54 cm
■ 2.54 – 5.0 cm
▨ 5.0 – 10.0 cm
▩ 10.0 – 15.0 cm
▥ 15.0 – 23.0 cm

Soil cores were also extracted and analyzed from 1984 and 1985 for PES (Figures 9 and 11) and PPI (Figures 8 and 10) imazaquin applications of 70 g ai/ha. In 1984 imazaquin was not detected below 5 cm in the soil profile for either application technique. The most imazaquin was detected in the top 2.5 cm when surface-applied, and it was more evenly distributed across the top 5.0 cm when imazaquin was incorporated. Soil samples from 1985 depict some movement of imazaquin to the 5.0 to 10.0 cm depth under both application methods. More imazaquin was detected in 1985 (Figures 10 and 11) than in 1984 (Figures 8 and 9), regardless of application method. In 1985, PPI applications of imazaquin has greater persistence than PES applications during the first 30 d.a.a.. This trend was reversed at the 60 d.a.a. sampling date. However at 150 d.a.a., PES application residues were lower in the top 2.5 cm compared to PPI applications.

A summary of imazaquin persistence in the soil profile was made by adding the ppb remaining in each depth increment. The differences in soil volume of the depth increments were accounted for. Results of the 280 g ai/ha applications are given in Figure 12. In 1984 there was no significant difference between PPI and PES applications, and no statistical difference in residues remaining from 60 to 150 days after application. In 1985, the application method and sampling date were highly significant. PPI applications persisted significantly more than PES applications at each sampling date. There was no statistical decrease in imazaquin remaining for both applications methods from 60 to 150 days after application. When imazaquin was applied at 70 g ai/ha (Figure 13) the main effects of application method and sampling date were signficant in both 1984 and 1985. In 1984 there was a

Figure 8: Imazaquin distribution and persistence in the soil profile in 1984 where 70 g ai/ha was applied and incorporated.

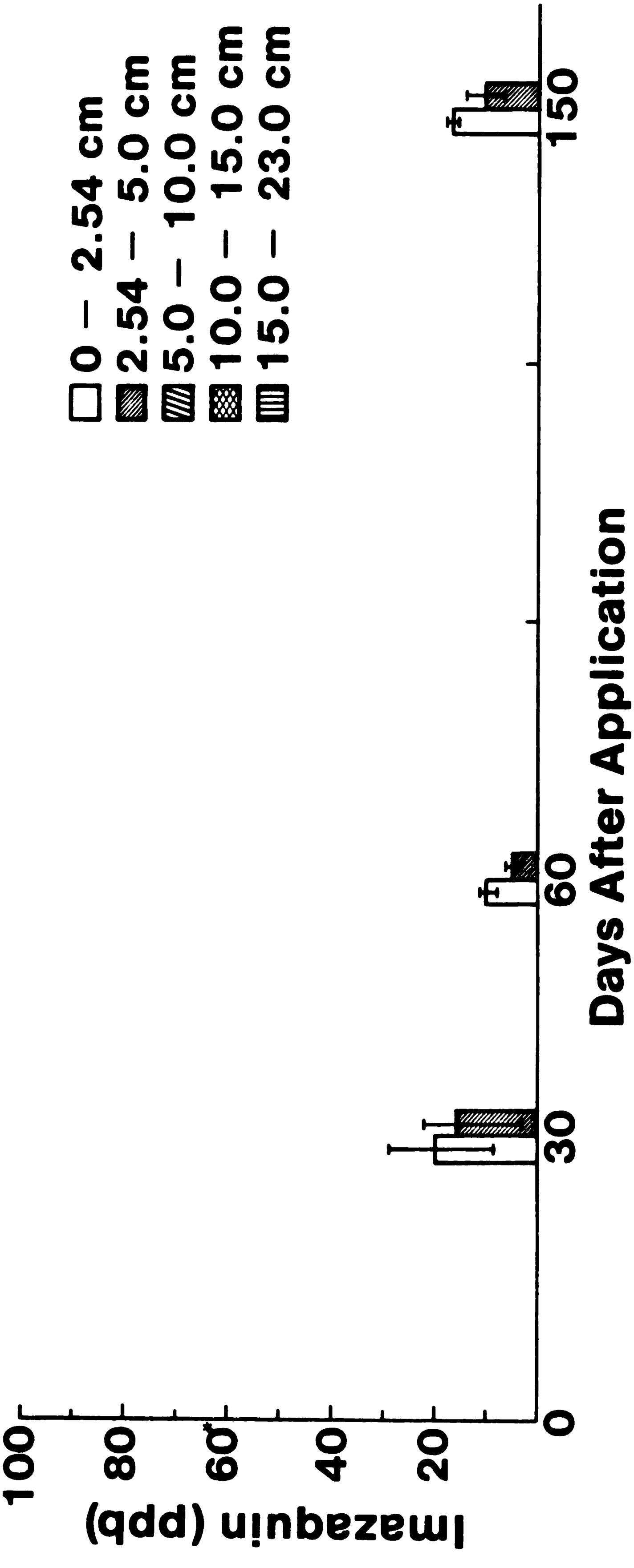

Imazaquin (ppb)
100
80
60
40
20
0
30
60
150
Days After Application
☐ 0 — 2.54 cm
▨ 2.54 — 5.0 cm
▨ 5.0 — 10.0 cm
▩ 10.0 — 15.0 cm
▥ 15.0 — 23.0 cm

Figure 9: Imazaquin distribution and persistence in the soil profile in 1984 where 70 g ai/ha was preemergence surface-applied.

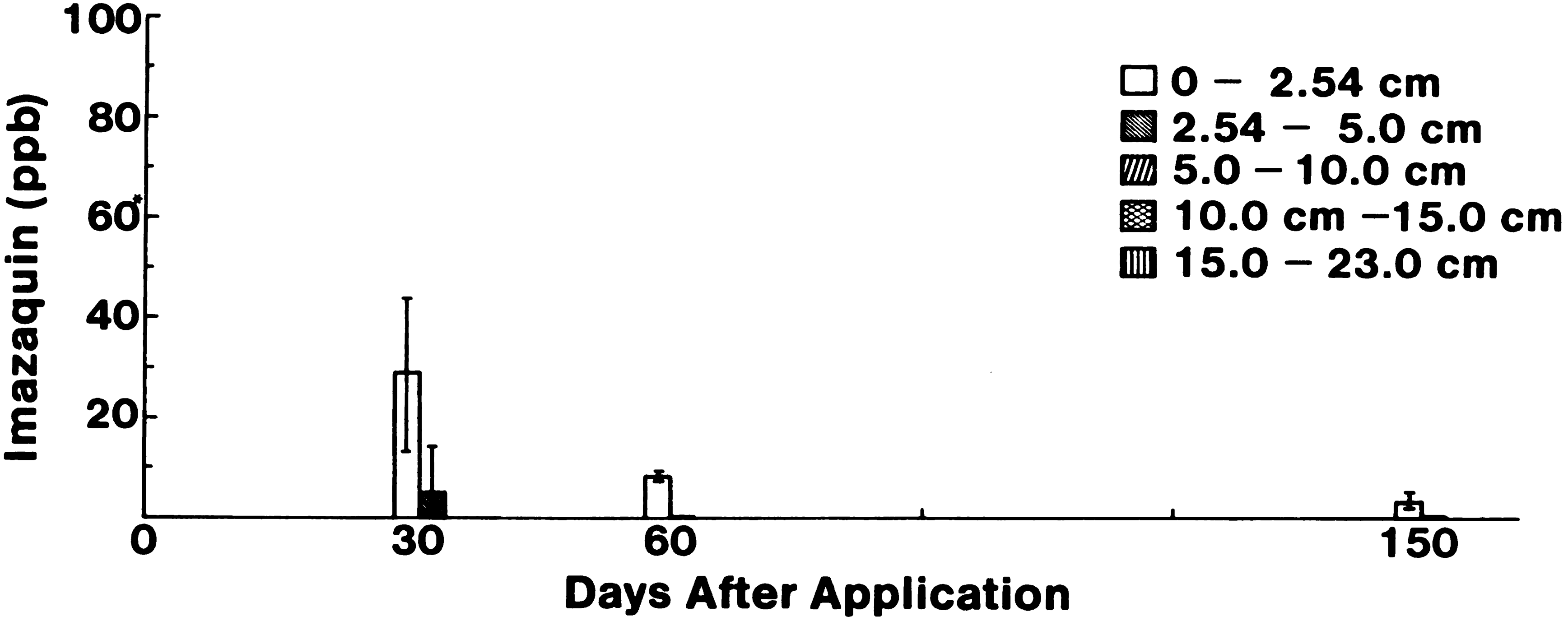

Imazaquin (ppb)
100
80
60
40
20
0
30
60
150
Days After Application
□ 0 – 2.54 cm
▨ 2.54 – 5.0 cm
▨ 5.0 – 10.0 cm
▨ 10.0 cm –15.0 cm
▥ 15.0 – 23.0 cm

Figure 10: Imazaquin distribution and persistence in the soil profile in 1985 where 70 g ai/ha was applied and incorporated.

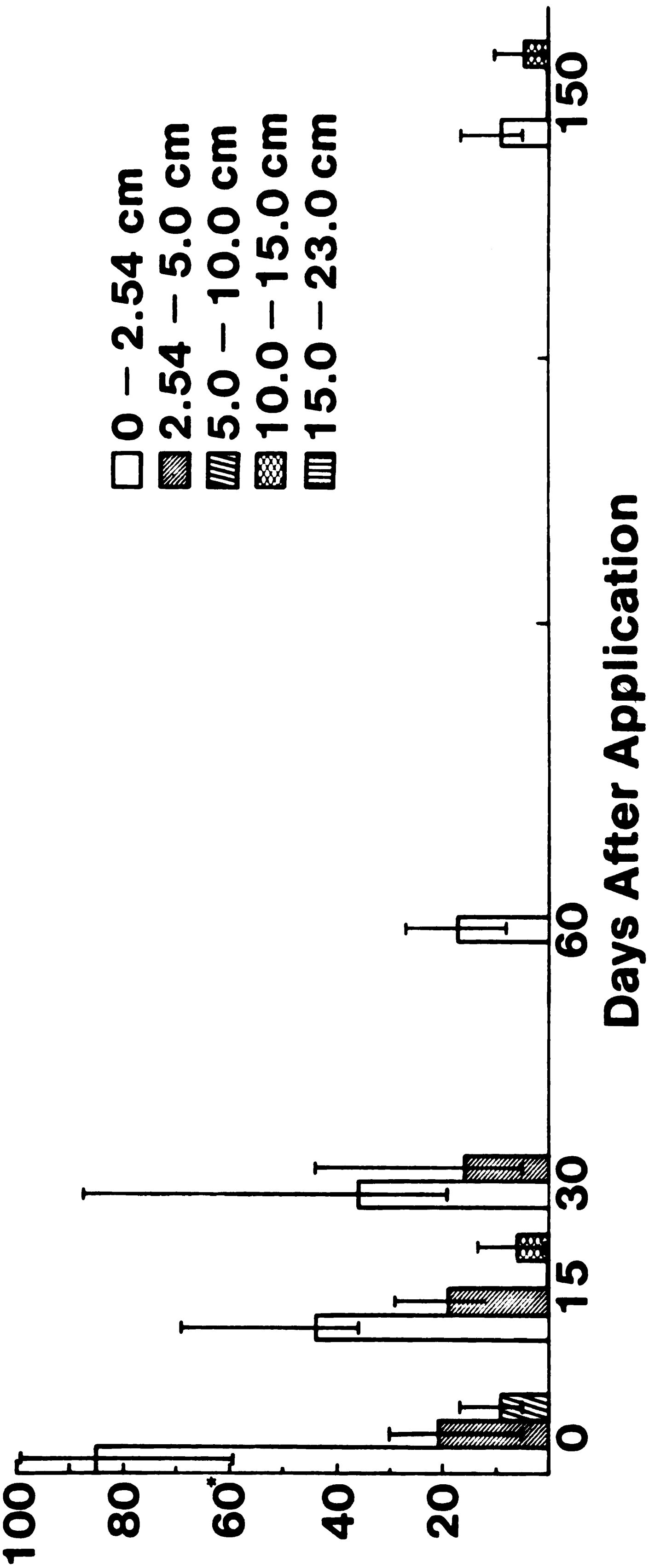

Imazaquin (ppb)
100
80
60*
40
20
0
15
30
60
150
Days After Application
0 — 2.54 cm
2.54 — 5.0 cm
5.0 — 10.0 cm
10.0 — 15.0 cm
15.0 — 23.0 cm

Figure 11: Imazaquin distribution and persistence in the soil profile in 1985 where 70 g ai/ha was preemergence surface-applied.

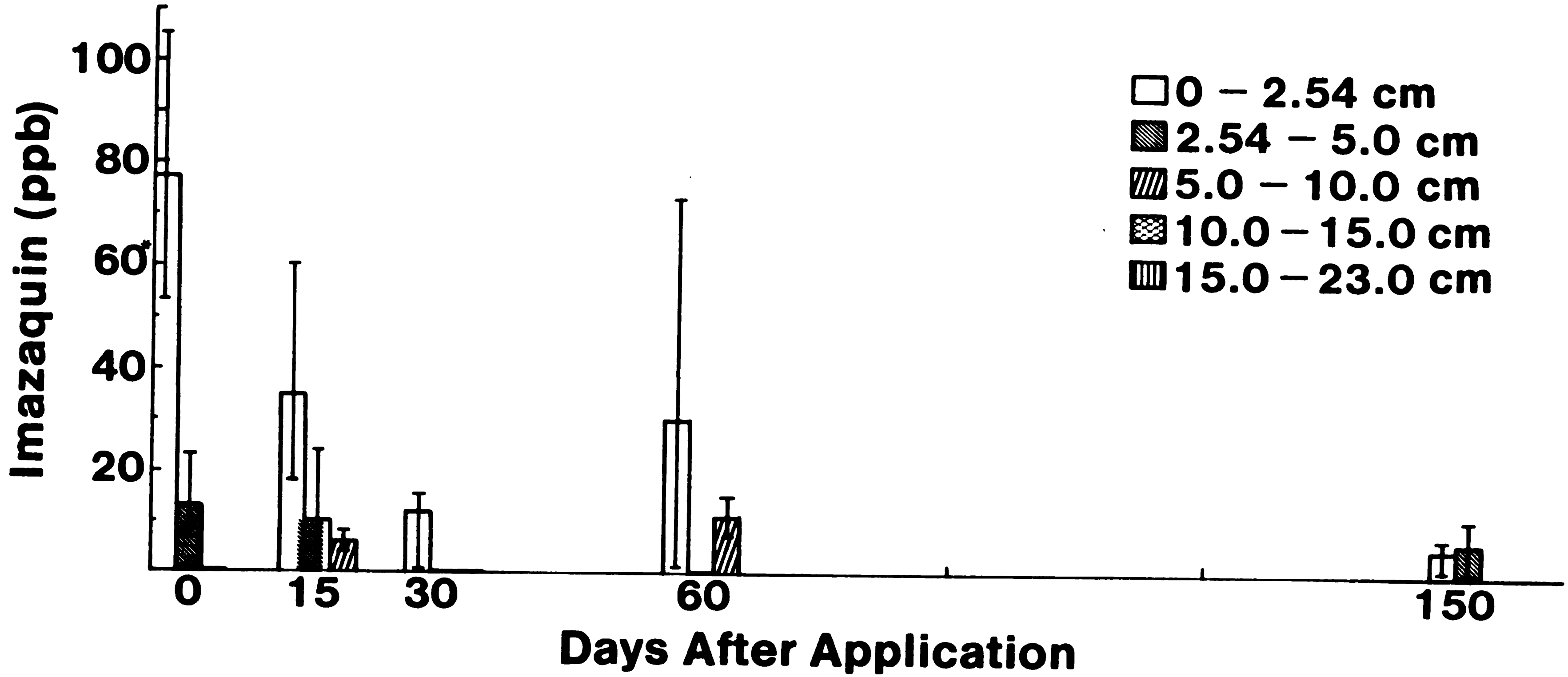

Imazaquin (ppb)
100
80
60
40
20
0
15
30
60
150
Days After Application
□ 0 – 2.54 cm
▨ 2.54 – 5.0 cm
▨ 5.0 – 10.0 cm
▨ 10.0 – 15.0 cm
▥ 15.0 – 23.0 cm

Figure 12: Imazaquin dissipation in 1984 and 1985 for preplant incorporated and preemergence surface applications of 280 g ai/ha.

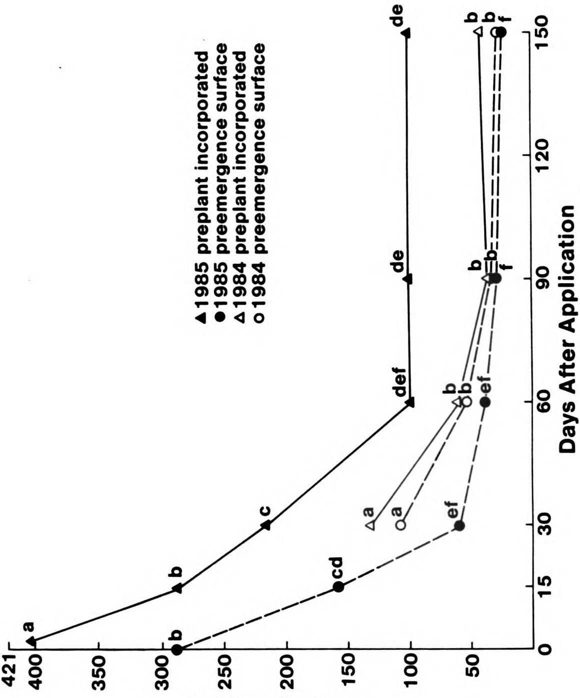
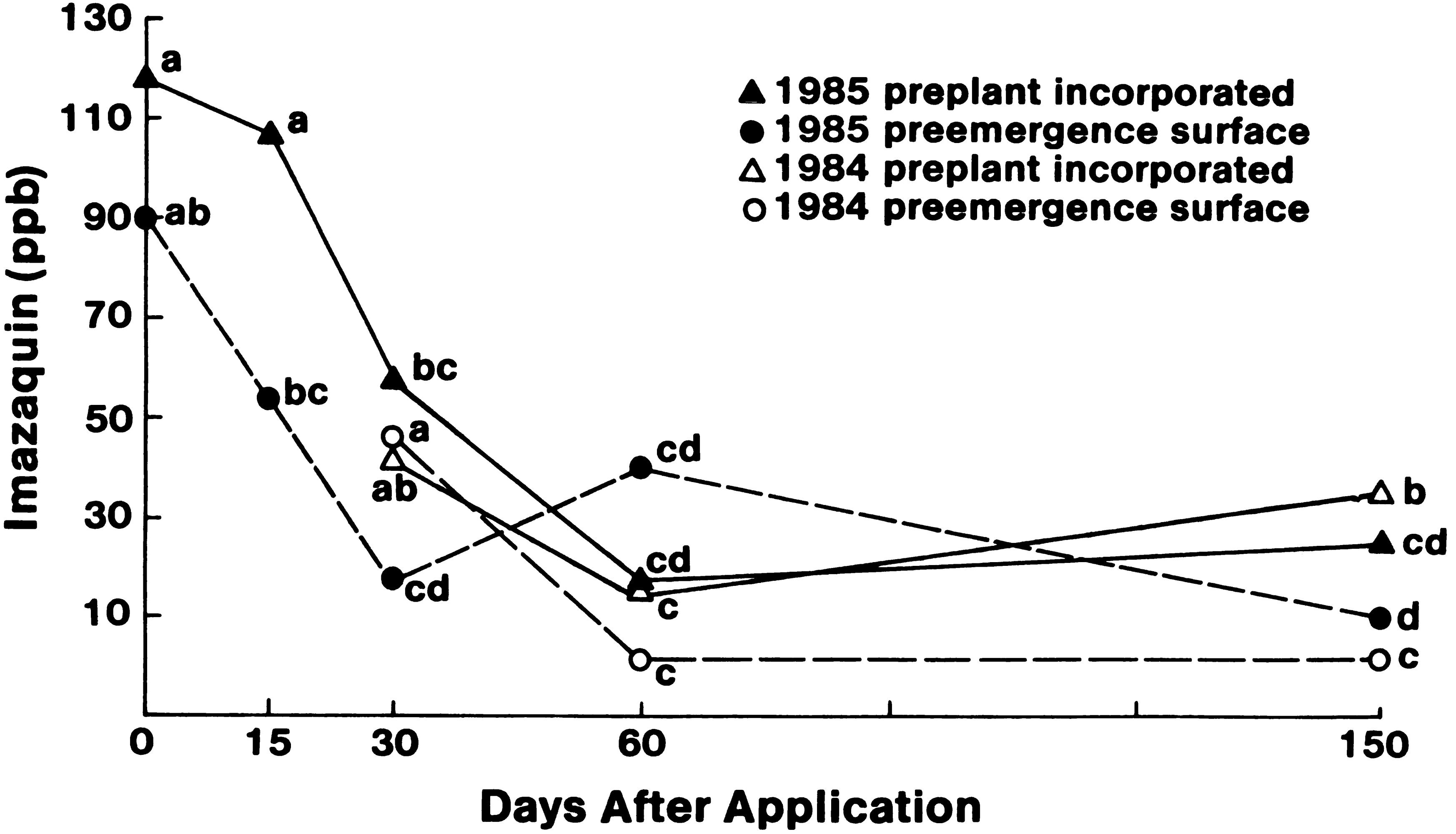

▲1985 preplant incorporated
●1985 preemergence surface
△1984 preplant incorporated
○1984 preemergence surface
Imazaquin (ppb)
421
400
350
300
250
200
150
100
50
Days After Application
0
15
30
60
90
120
150
a
b
c
def
de
de
b
cd
ef
ef
f
f
a
a
b
b
b
b
b
b

Figure 13: Imazaquin dissipation in 1984 and 1985 for preplant incorporated and preemergence surface applications of 70 g ai/ha.


▲ 1985 preplant incorporated
● 1985 preemergence surface
△ 1984 preplant incorporated
○ 1984 preemergence surface
Imazaquin (ppb)
130
110
90
70
50
30
10
0
15
30
60
150
Days After Application
a
a
bc
cd
cd
ab
bc
cd
cd
d
a
c
c
ab
c
b

significant interaction between application method and sampling date because of the significant increase in imazaquin remaining at 150 days after the PPI application, and no corresponding increase in the PES application. In 1985, PPI applications persisted significantly more than PES applications at all sampling dates except at 60 d.a.a..

There was an initial rapid decrease in persistence, followed by a slower dissipation rate for all application rates and techniques. The estimated half-lives in 1984 of PPI applications were 30 days for 280 g ai/ha and 36 days for 70 g ai/ha. PES applications estimated half-lives were < 30 days for 280 g ai/ha and 32 days for 70 g ai/ha. In 1985, the estimated PPI half-lives were 52 and 48 days for 280 and 70 g ai/ha, respectively, and 20 and 23 days for PES applications of 280 and 70 g ai/ha, respectively. Half-life estimations differed more with the year and application technique, than the initial herbicide rate applied.

The pesticide residues remaining in the field reflect the combined influence of transfer processes such as leaching, plant uptake, volatility, and soil adsorption, and transformation processes including microbial and photolytic degradation (3, 6, 7, 12, 14, 20, 27). These processes can be affected by environmental conditions such as soil moisture and temperature, and cropping systems and soil management (7). Imazaquin dissipation in the field is the result of a combination of the above mentioned processes.

Very little imazaquin was detected below the top 10 cm of the soil in either year for both application techniques and rates. Imazaquin could have leached below the 23 cm sampling depth and not been present for detection. Imazaquin is an acidic herbicide, and acidic herbicides are more readily leached than cationic or nonionic pesticides due to a small number of sites in soil that are positively charged and available for anionic binding (1, 9, 10, 11). However only yearly rainfall totals within the first month after application correlate with decreased persistence due to leaching (Table 5). Less imazaquin remained in 1984 where 11.33 cm of rain fell in the first 30 d.a.a., compared to 1985 rainfall of 4.27 cm in the first 30 d.a.a.. Yet, over 15.8 cm of rainfall occurred both years between 90 and 150 d.a.a., and imazaquin residues did not decrease substantially either year during this time period.

Table 5. Summary of rainfall in 1984 and 1985 occurring between each of the imazaquin soil sampling periods.

Rainfall Summary

Time increment (d.a.a.)	1984	1985
	------------- cm	----------------
0 to 15	11.20	1.47
15 to 30	0.13	2.79
30 to 60	1.35	5.82
60 to 90	6.25	5.56
90 to 150	15.77	19.28

Plant uptake may have been an important factor in decreasing imazaquin persistence over time (7). In 1984, the 11.33 cm of rainfall received in the 30 days following imazaquin application and corn planting would have resulted in increased movement of the herbicide to the plant root and increased plant uptake. This may have resulted in the lower herbicide residues remaining in the soil cores in 1984. In 1985, only 4.34 cm of rain fell in the 30 days after application and planting, and greater imazaquin residues remained in the soil cores. The removal of the herbicide by corn would be permanent if metabolized within the plant, or temporary if it was only conjugated and then hydrolytically released later during plant decomposition (6, 27).

Application method may have a significant effect on pesticide persistence, as persistence decreases immediately if the herbicide is volatile or subject to photodecomposition (2, 6, 8, 18, 19, 22, 23, 30). Imazaquin is not believed to be volatile, but is subject to photolytic hydrolysis [2]. The two major limiting factors to photolysis in soils is adsorption of light by other soil components that decreases available energy, and the non-penetration of light below the soil surface (2, 3, 6, 18, 19). Herbicides such as pendimethalin and trifluralin that are subject to volatility and photodecomposition have shown increased persistence when incorporated and when incorporated to deeper depths (21, 25, 30). Photolytic hydrolysis may be a factor causing the decreased persistence of PES imazaquin applications. Rainfalls within 30 d.a.a. could cause photolytic hydrolysis of imazaquin to occur on the soil surface, and to a lesser extent in the top 2.5 cm soil depth. Capillary water movement during the growing season could move imazaquin applied by either application method to the soil surface and subject it to continued photolytic hydrolysis. The extent of capillary water and imazaquin movement is not known.

Imazaquin rapidly dissipated during the first 60 d.a.a. under both application rates and techniques in 1984 and 1985. A slower rate of loss occurred during the remainder of the growing season. The level of imazaquin at which dissipation slowed varied with the year and application method. The dissipation rate slowed at 100 ppb and 50 ppb for PPI and PES applications, respectively, at 280 g ai/ha in 1985, and approximately 55 ppb for 1984 PPI and PES applications, respectively, of 280 g ai/ha. The slower degradation rate occurred at lower concentrations for the 70 g ai/ha applications. These results agree with Hamaker and Goring (12) and other researchers who found biphasic degradation rates occurred with numerous pesticides (4, 8, 15, 23, 24, 32). A greater percentage of the herbicide remaining is believed to become less available over time. Degradation slows until a steady state is reached, and the degradation rate determined by a labile pool (12). Pesticide degradation was disproportionately slower at low residual concentrations, and Hurle and Walker proposed a two compartment model containing available and non-available compartments, with only herbicides in available areas subject to degradation (15). The non-available areas appear to be dynamic and change with environmental conditions, as evidenced by the differences in the imazaquin level at which degradation appeared to slow. The validity of the hypothesis of too low a concentration of imazaquin to support microbial populations is questionable. The hypothesis that imazaquin became increasingly less available over time due to increased adsorption may be a better explanation for the experimental results.

Decreased persistence of imazaquin during the growing season may result from decreasing extraction efficiency of imazaquin over time on field treated soils. When pesticide residues age they become more resistant to solvent extraction because of adsorption to soil colloids and diffusion into the interior of humic colloids (28). It is difficult to determine true extraction efficiency as fortified soils in the laboratory can have extraction efficiencies different than field treated soils, and the difference is difficult to quantify.

Spring tillage. There was no significant difference in corn cultivar response to imazaquin, so results were pooled over cultivars and the main effects of tillage and herbicide treatment, and their interaction evaluated. There was no interaction between tillage and treatments (Figure 14). There was no signifiant effect of spring tillage on corn injury, as neither moldboard plowing or disking altered the amount of injury to corn planted in 1985. Corn roots growing for 60 days after planting had proliferated throughout the 23 cm soil profile and could not grow in untreated soil (27).

The effect of herbicide treatment was highly significant (Figure 15). Imazaquin residues of 42 and 25 ppb remained in October 1984 from PPI and PES applications of 280 g ai/ha, respectively. Twenty-seven and 4 ppb remained from PPI and PES applications, respectively, of 70 g ai/ha. A reduction in corn height occurred from both PPI and PES applications of 280 g ai/ha, and injury was significantly greater from PPI applications of 140 g ai/ha compared to surface application. Where 70 g ai/ha was applied, there was no difference in plant height between PPI and PES applications, but corn height was reduced

Figure 14: Effect of spring tillage on imazaquin injury to corn across all imazaquin treatments.

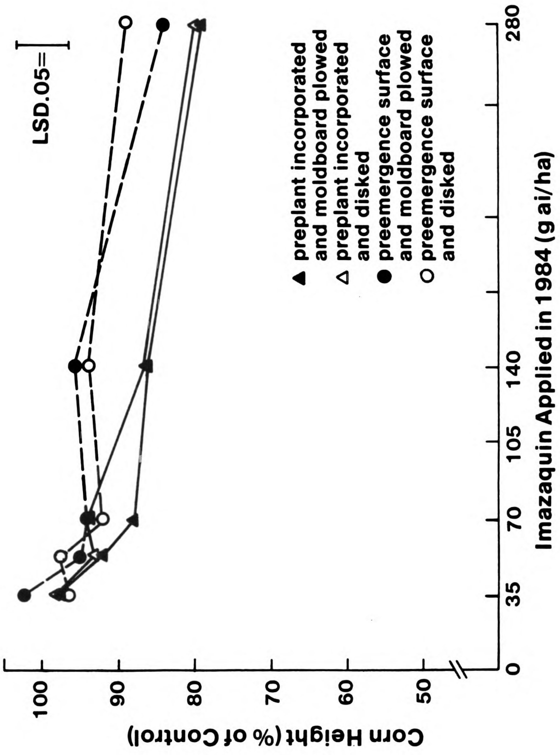
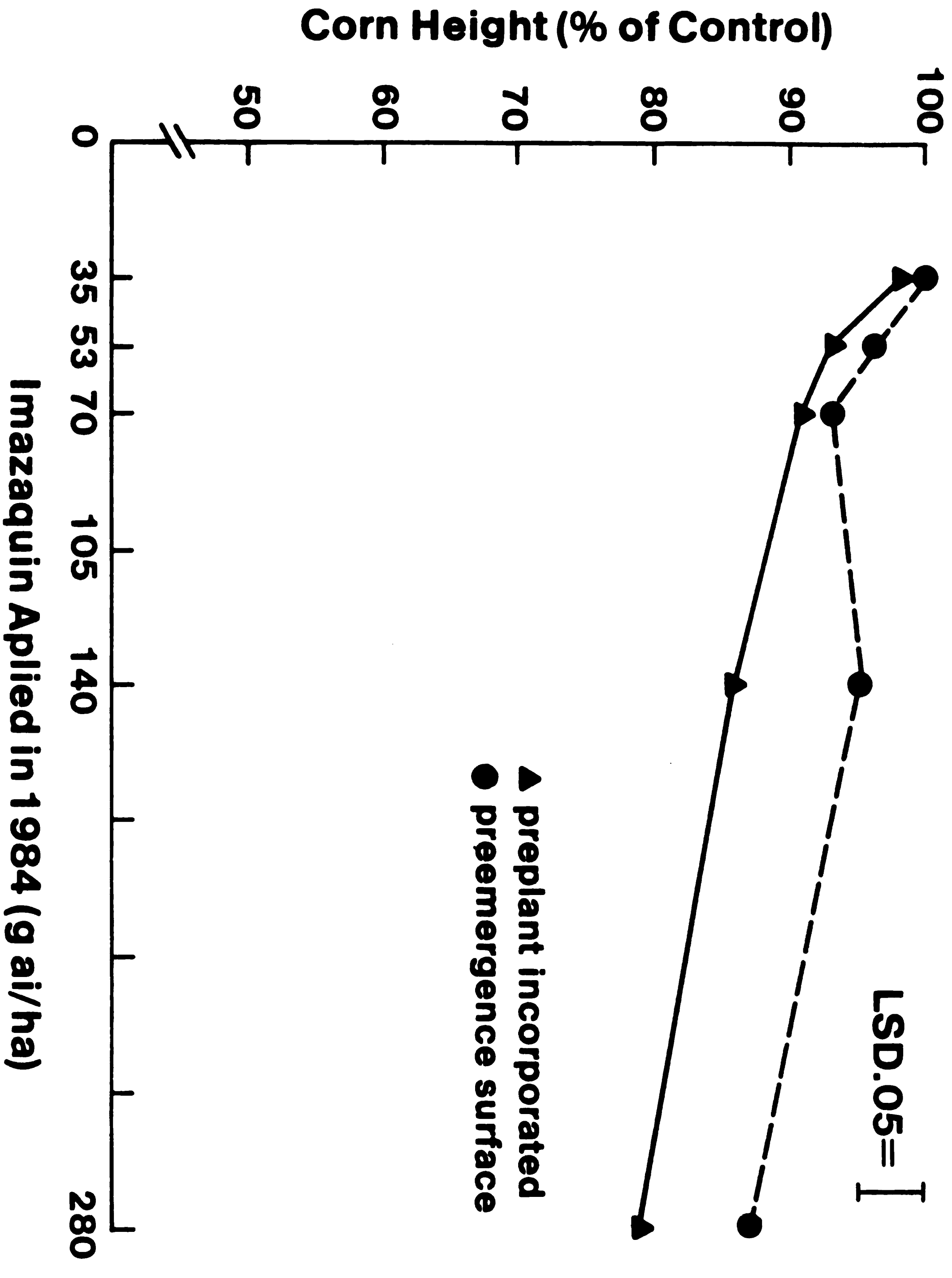

LSD.05=
▲ preplant incorporated and moldboard plowed
△ preplant incorporated and disked
● preemergence surface and moldboard plowed
○ preemergence surface and disked
Corn Height (% of Control)
100
90
80
70
60
50
0
35
70
105
140
280
Imazaquin Applied in 1984 (g ai/ha)

Figure 15: Effect of imazaquin applications from 1984 on corn height in 1985.


Corn Height (% of Control)
100
90
80
70
60
50
0
35
53
70
105
140
280
Imazaquin Aplied in 1984 (g ai/ha)
LSD.05=
▲ preplant incorporated
● preemergence surface

significantly from the control. Possibly more imazaquin remained than the 6 ppb detected by gas chromatography. Therefore, 42 and 25 ppb remaining in the soil in early October 1984 significantly injured corn planted on May 8, 1985 regardless of tillage. Increased corn injury occurred where imazaquin was incorporated at 140 and 280 g ai/ha, reflecting increased persistence of incorporated imazaquin treatments.

ACKNOWLEDGEMENTS

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CHAPTER 4

INFLUENCE OF SOIL PROPERTIES ON ADSORPTION, PERSISTENCE AND AVAILABILITY OF IMAZAQUIN AND AC-263,499

ABSTRACT

Studies were conducted to evaluate the effect of soil type on adsorption, persistence, and availability of imazaquin[1] (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1_H_-imidazol-2-yl)-3-quinolinecarboxylic acid) and AC-263,499 (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1_H_-imidazol-2-yl)-5-ethyl-3-pyridinecarboxylic acid) to corn (_Zea mays_ L.). Adsorption of imazaquin and AC-263,499 were low for all five soils tested. Kd values ranged from 0.056 to 0.113 for imazaquin, and 0.060 to 0.761 for AC-263,499. The Kilmanagh soil that contained the most organic matter, smectite clay, iron, and had the highest soil pH adsorbed the most imazaquin. The Decatur soil adsorbed the most AC-263,499, with the Kilmanagh soil having the second greatest adsorption. When organic matter was removed from a Capac sandy loam, there was little change in imazaquin adsorption but a large increase in adsorption of AC-263,499. The soil pH decreased from 6.4 to 4.63 when

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[1] AC-252,214 code number. American Cyanamid Company. Princeton, NJ 08540.

the organic matter was removed with hydrogen peroxide, which appeared to affect adsorption of AC-263,499 more than imazaquin. AC-263,499 adsorption on the Decatur silty clay loam was much greater than imazaquin adsorption, due to either the lower soil pH or the high silt percentage increasing adsorption of AC-263,499. Corn injury from imazaquin at 105 g ai/ha was 42.5% greater than from AC-263,499 across all soil types. This occurred because of increased availability of imazaquin or increased corn sensitivity to imazaquin. Injury to corn by imazaquin and AC-263,499 decreased over time, with the exception of AC-263,499 in experiment 1. The Kilmanagh sandy clay loam had the least corn injury for both herbicides over time, but corn responded differently on the Greenville sandy clay loam in the two experiments.

INTRODUCTION

Imazaquin and AC-263,499 are selective herbicides for grass and broadleaf control in soybeans (Glycine max (L.) Merr.). Little information is available regarding the behavior of these herbicides in soil. Soil properties alter the adsorption of herbicides to soil, and their subsequent soil persistence and availability to plants.

The persistence of a herbicide in soil is a function of the chemical properties of the herbicide, soil properties, and environmental conditions (1, 3, 5, 7, 14, 23). When herbicide activity is no longer observed the herbicide is believed to be dissipated, when in fact it could be adsorbed to soil material or diluted below the threshold level of the bioassay species (13). Herbicides are inactivated by transfer mechanisms that result in the herbicide being unavailable to plants, and by transformation mechanisms that change the herbicide to nontoxic forms (2, 3, 5, 8, 13, 23). Transfer processes that alter soil persistence include soil adsorption, mechanical dilution, leaching, volatilization, and plant uptake (3, 5, 8, 10, 11, 12, 23). Transformation processes include microbial degradation and nonbiological degradation by chemical and photochemical means (2, 3, 5, 13, 15, 18). The means and rates of these processes are dependent on the herbicide, soil, and environmental conditions.

Soil adsorption affects the amount of herbicide available for effective weed control, the amount that will leach through the soil profile, and the ability of the herbicide to be microbially or nonbiologically degraded (10). As adsorption increases, the availability and subsequent phytotoxicity to plants decreases. Adsorption can accelerate or slow degradation dependent on whether the pesticide is adsorbed into interlamellar spaces where it may be protected from microbial attack, or adsorption may increase degradation because the enzyme and substrate are concentrated at one site and biological and nonbiological reactions are catalyzed (10).

Soil adsorption in the field may differ from adsorption measured in the laboratory due to temperature, water content, soil pH, or concentration effects (8, 12, 16). Herbicides and water compete for adsorption sites. Water can occupy positions around soil cations, reducing available binding sites for herbicide molecules (6). Soil moisture has a large effect on polar pesticide groups, such as carbonyls, amines, and carboxylic acids (21). Some organic herbicides are not adsorbed when water is present, but in air dry soils they are adsorbed, and may or may not be displaced by the addition of water (19, 21, 22, 26). At low soil moisture levels precipitation of herbicides can occur, resulting in less herbicide available for plant uptake (5).

Adsorption of acidic compounds can occur on clay, metal oxides, and organic matter, and can be dependent on soil pH (1, 4, 6, 25, 28). Smectite clays have greater surface area than kaolinitic clays and can expand when hydrated due to the weak attraction between oxygen layers (26). Herbicides can adsorb into the expanded inner layers and bind to the substituted interlayer cations (26). The greater the affinity of these exchangeable cations for electrons the greater the interaction with polar groups on the herbicides capable of donating electrons. Hydrogen, iron, and aluminum cations are the most acidic, and have the greatest affinity for these electrons (28). Kaolinitic soils have exposed aluminum hydroxides on the clay crystal edges that make up a large portion of the cation exchange capacity (cec) and are important sites for anionic adsorption (26, 28). Aluminum and iron hydroxides exist in crystalline and amorphous forms, have similar surface areas as smectite, and have high anionic exchange capacities (1, 4, 6, 27). Organic matter contains carboxylic and phenolic groups that have pH dependent ionization with pKa values of approximately 5.2 (25). At high soil pH levels, ionized acidic functional groups can react with polyvalent cations to form chelate bridges with acidic herbicides (29). Ph also affects ionic herbicides as they become undissociated when the suspension pH is 1 to 2 units above their pKa or lower (4). At pH values greater than their pKa values, acidic herbicides exist largely in the anionic form and are repelled by negatively charged soil colloids. Increasing concentrations are then available for root uptake. This has been shown recently with the acidic herbicide chlorsulfuron

(2-chloro-N-(((4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino)carbonyl) benzenesulfonamide) (17, 20).

Acidic herbicides exhibit different types of binding to the soil matrix (4, 25, 28). Physical adsorbtion can occur at low soil pH levels when herbicides are in the molecular form, or hydrogen bonding at low pH levels with the carbonyl, amino, and carboxyl groups of soil humus can occur (4, 25). Herbicides also bind with polyvalent cations which can bind both the carboxyl group of the herbicide and the carboxyl group of humics. Binding of the herbicide to polyvalent cations on clay may also occur (4, 25). Anionic herbicides can bind via water bridges or by anion exchange on the positive sites of aluminum and iron polyhydroxy complexes, or by penetrating the shell of iron and aluminum in the surface of hydroxides and becoming incorporated into the interlayer of the clay (1, 6, 27). The type of binding that occurs is dependent on the percentage and type of clay, the aluminum and iron content, the percentage of organic matter, and the soil pH of the soil system. The relationship of these variables in different soils is important in determining how each of these factors affect herbicide adsorption, and resulting persistence and availability. Therefore experiments where conducted to determine a) the adsorption of imazaquin and AC-263-499 on five different soils and one soil with organic matter removed, and b) the availability and persistence of imazaquin and AC-263,499 on four of the soils.

MATERIALS AND METHODS

Characteristics of the five soils used in the following experiments are given in Table 6.

Adsorption study. Soils were air dryed and sieved through a 2 -mm sieve. Organic matter was removed from the Capac sandy loam by a hydrogen peroxide treatment. Hydrogen peroxide was added in 50 ml increments to soil contained in a beaker until all organic matter was oxidized. The soil was then leached with distilled water to remove hydrogen ions. To determine equilibration time, 5 g of soil and 5 ml of a 0.5 ppm ^{14}C-imazaquin (specific activity of 4.61 µCi/µM) and ^{14}C-AC-263,499 (7.23 µCi/µM) were weighed into 30 -ml glass centrifuge tubes. sealed with parafilm-covered rubber stoppers, and gently shaken on a reciprocal shaker at 23°C at 70 strokes/min. Tubes were removed at 0, 4, 8, 12, 24, and 36 h, and centrifuged for 15 min at 12,350 x g. Two 1 ml samples were removed from each tube and added to glass scintillation vials containing 15 ml of a water-accepting scintillation solution.[2] The samples were radioassayed on a liquid scintillation spectrometer.

To determine adsorption, 5 g of soil were placed in 30 -ml glass centrifuge tubes and 5 ml of the appropriate concentration of ^{14}C-imazaquin or ^{14}C-AC-263,499 at 2.0, 0.5, 0.25, and 0.02 ppm in

Table 6: Characteristics of soils utilized in soil adsorption and availability studies.

Soil	Classification	pH	Sand	Silt	Clay	Organic Matter	Cation exchange capicity	ppm	
		%					(meq/100 g)	Al	Fe
Capac sandy loam	Aeric Ochraqualfs, fine-loamy, mixed, mesic	6.4	57	26	17	2.1	10.1	< 1	43
Kilmanagh sandy clay loam	Aeric Haplaquepts, fine-loamy, mixed, honacid, mesic	7.3	51	24	25	3.1	12.3	1	68
Kalamazoo sandy loam	Typic Hapludalfs, fine-loamy, mixed, mesic	6.5	58	31	11	1.8	7.3	< 1	26
Greenville sandy clay loam	Rhodic Paleudults, clayey, kaolinitic, thermic	6.6	59	11	29	1.2	5.0	4	25
Decatur silty clay loam	Rhodic Paleudults, clayey, kaolinitic	5.9	18	53	29	2.0	7.1	1	25

distilled water added. Maximum concentrations of both herbicides equilibrated with soil were 30 times below the solubility of the acid form of the compounds to prevent precipitation. Tubes were sealed with parafilm-covered rubber stoppers, taped securely, and gently shaken at 23°C on a reciprocal shaker at 70 strokes/min for 10 h. Samples were then centrifuged at 12,350 x g for 15 min, and two 1 ml aliquots of the supernatent were pipetted into separate glass scintillation vials containing 15 ml of water-accepting scintillation solution.[2] These were radioassayed on a liquid scintillation spectrometer. Differences in radioactivity between known standard concentrations and the supernatents of the samples were assumed to be due to soil adsorption. The experiments were repeated twice with each treatment replicated 3 times. The herbicide adsorbed (ng per g of soil) was plotted on the *y* axis, and the equilibrium concentration of herbicide remaining (ng per ml of solution) plotted on the x axis. Plots of each herbicide and soil were linear without log transformation. Regression equations were then calculated for each soil and herbicide treatment without log transformations, and single t-tests were used to compare the slopes of the lines, and determine if they were different from zero and from each other (24). Distribution coefficients (Kd) were calculated to express the ratio of the amount of ^{14}C-herbicide adsorbed to the amount remaining in solution at equilibrium (8, 9).

[2] Safety-solve, high-flash point cocktail. Research Products. International Corp. Mount Prospect, IL 60056.

Persistence and Availability study. Imazaquin and AC-263,499 were applied at 105 g ai/ha to 1100 -ml pots containing 500 cc of each of the first four soils listed in Table 1. The herbicides were thoroughly mixed throughout the 7.6 cm soil depth. Sixty ml of water was added to each pot to bring the soils to approximately 25% of their field capacity, and the pots covered with polyethylene wrap[3] that is oxygen but not water permeable. Each herbicide was applied to 12 pots of each soil, and 12 pots of each soil did not receive herbicide and were used as controls. Three pots of each herbicide applied to 4 soils plus 3 control pots of each soil were immediately placed in the freezer. The remaining pots were divided into 3 groups that were considered the replications and placed in 3 growth chambers. All chambers were set at 26°C and 16°C for day and night temperatures, respectively. Sixteen h of light was supplied by inflorescent tubes and incandescent bulbs supplying from 120 to 190 $\mu E \cdot m^{-2} \cdot s^{-1}$ of photosynthetically active radiation. Pots were maintained in the growth chambers until removal of 12 pots of each herbicide treatment plus the controls at 30, 60, and 120 days after initial application. Removed pots were immediately placed in the freezer. Sixty ml of water was added to each pot in the growth chambers every 30 days to maintain moisture levels. After 120 days all pots were removed from the freezer, equilibrated to 23°C for 2 days, and then the soil was transferred to 600 -ml pots. Three corn 'Stauffer 5650' seeds per pot were planted to a 3.5 cm depth. Corn was grown for 21 days in the greenhouse and thinned to two plants/pot after

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[3] Sysco Plastic Wrap. Sysco Corporation. Houston, Texas 77002.

7 days. Temperature was maintained at a maximum of 27°C during the day and a minimum of 16°C at night. Supplemental lighting was supplied by high pressure metal halide lamps to provide a 16 h photoperiod and 360 $\mu E \cdot m^{-2} \cdot s^{-1}$ of photosynthetically active radiation. Plants were watered each day with approximately 120 ml of water, and alternated surface and sub-irrigated. After 21 days, shoot fresh weight and height were measured, averaged for each pot, and then converted to a percentage of the weight or height of the control plants grown on that soil and in that replication that received zero herbicide so that any effect of soil type on plant growth would be eliminated. The experiment was repeated twice, and results were not combined because there was an interaction between experiments and soil type. Injury to corn grown on the Greenville soil was significantly different in each experiment. In both experiments, shoot height and weight gave similar results, and only fresh shoot height data will be presented.

RESULTS AND DISCUSSION

Adsorption study. The equilibrium time for soil adsorption of ^{14}C-imazaquin and ^{14}C-AC-263,499 was 4 h, with no additional adsorption in the next 32 h (data not shown). Soil adsorption was low on all five soils for both herbicides (Figures 16 and 17). Increasing the volume of solution to 10 ml did not increase adsorption (data not shown). Very low adsorption is typical of acidic herbicides such as chlorsulfuron, picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid), and 2,4-D ((2,4-dichlorophenoxy)acetic acid) (11, 12, 27). Low Kd values of 0.03 to 0.49, 0.03 to 0.3, 0.14 to 3.38, and 0.54 to 0.123

Figure 16: The adsorption of imazaquin on five soils.

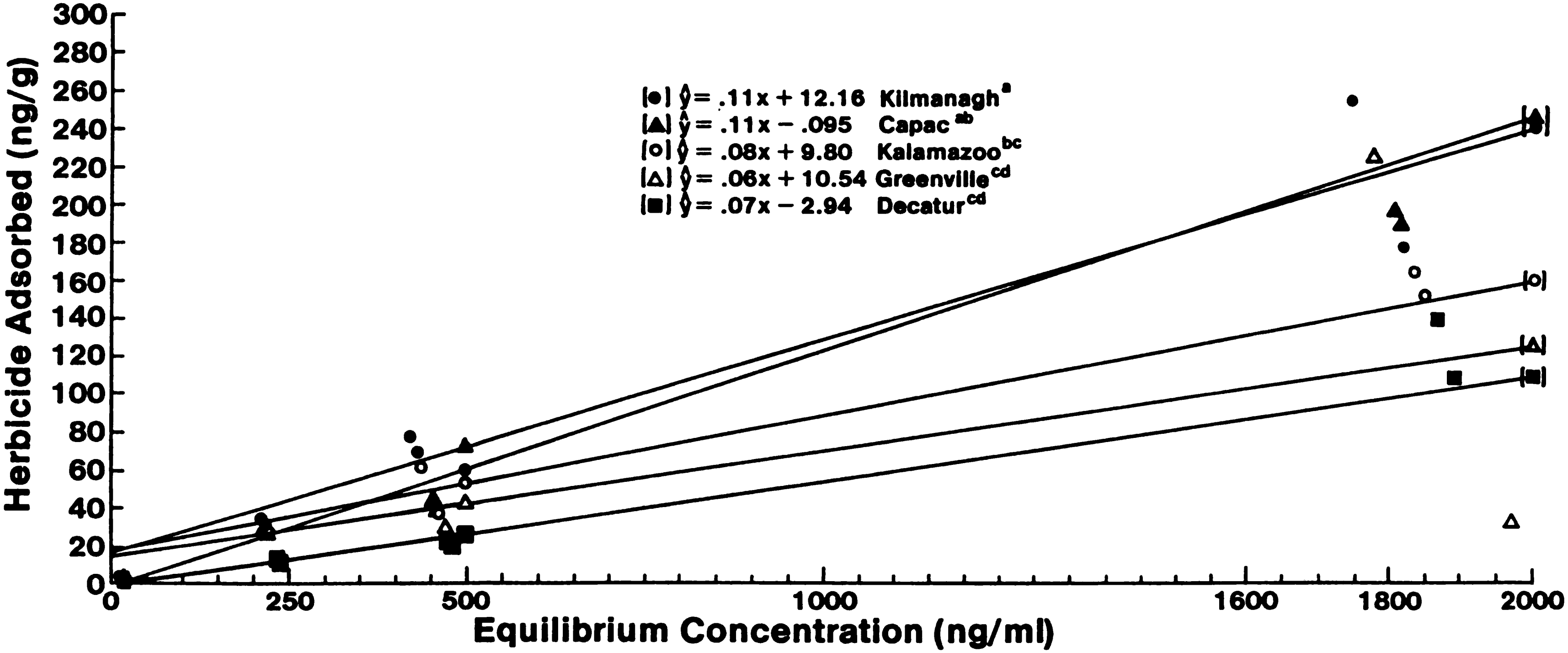
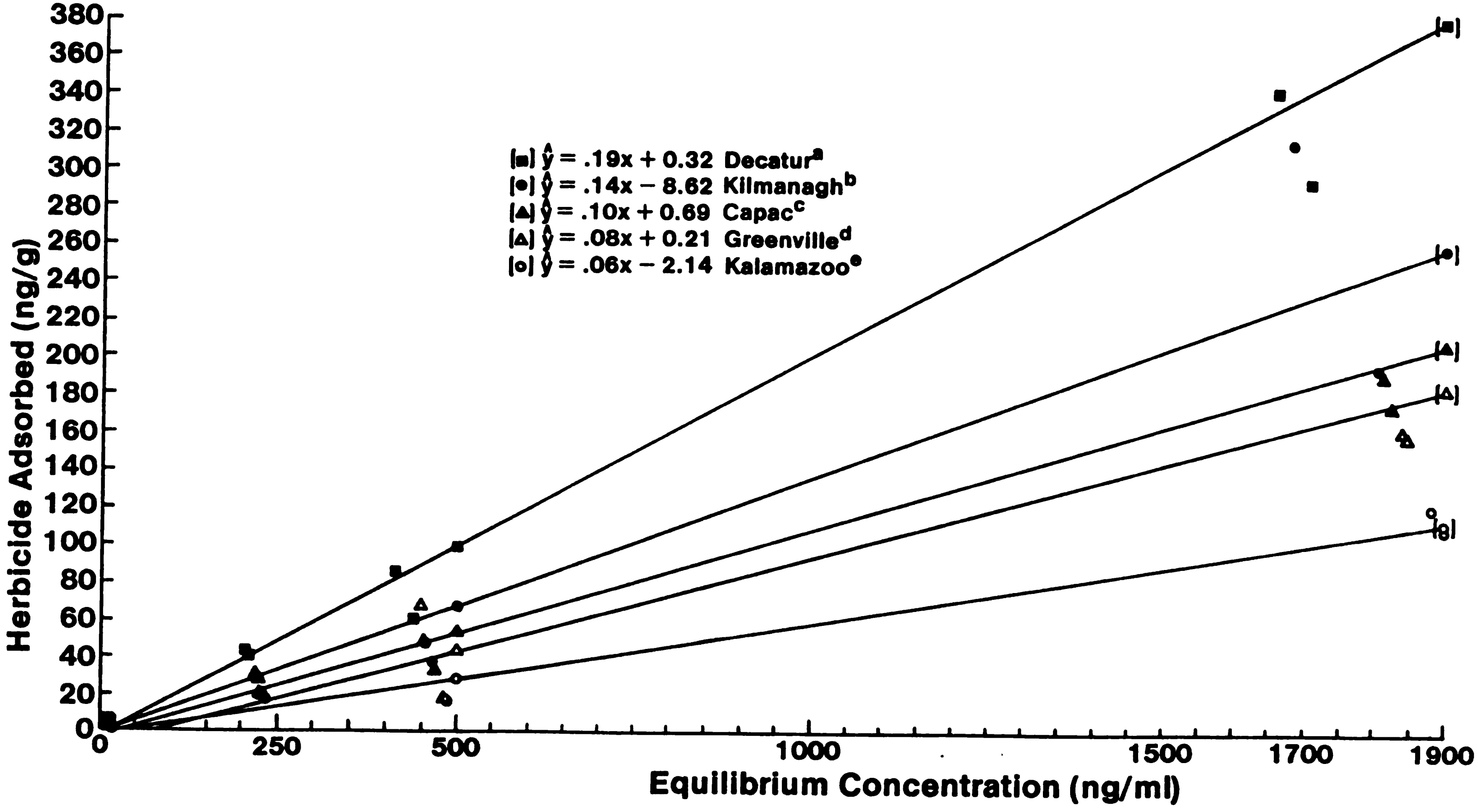

[●] $\hat{y}$ = .11x + 12.16 Kilmanagh^{a}
[▲] $\hat{y}$ = .11x − .095 Capac^{ab}
[○] $\hat{y}$ = .08x + 9.80 Kalamazoo^{bc}
[△] $\hat{y}$ = .06x + 10.54 Greenville^{cd}
[■] $\hat{y}$ = .07x − 2.94 Decatur^{cd}
Herbicide Adsorbed (ng/g)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0
250
500
1000
1600
1800
2000
Equilibrium Concentration (ng/ml)

Figure 17: The adsorption of AC-263,499 on five soils.


Herbicide Adsorbed (ng/g)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
Equilibrium Concentration (ng/ml)
0
250
500
1000
1500
1700
1900
[■] $\hat{y}$ = .19x + 0.32 Decatur[a]
[●] $\hat{y}$ = .14x − 8.62 Kilmanagh[b]
[▲] $\hat{y}$ = .10x + 0.69 Capac[c]
[△] $\hat{y}$ = .08x + 0.21 Greenville[d]
[○] $\hat{y}$ = .06x − 2.14 Kalamazoo[e]
[■]
[●]
[▲]
[△]
[○]

were found for picloram, dicamba (3,6-dichloro-2-methoxybenzoic acid), 2,4-D, and chlorsulfuron, respectively (11, 12, 27). Calculated Kd values for imazaquin and AC-263,499 are given in Table 7. The first four soils listed adsorbed significantly more imazaquin than the Greenville and Decatur soils. These four soils are smectite based and have increasingly higher Kd values as the percentage of smectite clay is increased. All Kd values for AC-263,499 were significantly different from each other as determined by single t-tests (24). There was no significant difference at the 10% level between imazaquin and AC-263,499 adsorption on the Capac sandy loam and also on the Greenville sandy clay loam soils. The greatest difference in soil adsorption between imazaquin and AC-263,499 occurred on the Decatur silty clay loam, and on the Capac sandy loam with organic matter removed (Figures 18 and 19).

Examining the soil characteristics, we found the pH of the Decatur soil was significantly lower and the percentage of silt significantly higher than all other soils. Low soil pH or high silt content may be important in AC-263,499 adsorption to kaolinitic soils. When the organic matter was removed from the Capac sandy loam there was no significant difference in imazaquin adsorption, but a significantly greater increase in AC-263,499 adsorption (Figure 19). When organic matter was removed, the soil pH dropped from 6.4 to 4.63. Adsorption of acidic herbicides has been shown to increase when in the molecular form (4, 17, 20). Increased adsorption of AC-263,499 may have occurred because at the lower pH an increased amount of both herbicides existed in the nonionic form. AC-263,499 in the molecular form may have higher affinity to clays than the molecular form of imazaquin, and result in

Table 7. Calculated distribution coefficents (Kd) for imazaquin and AC-263,499 on five soils.

Soil	Imazaquin	AC-263,499
	----------- Kd[a]	---------
Capac sandy loam	.105^{ab}	.098^{d}
Capac sandy loam w/out organic matter	.094^{ab}	.761^{a}
Kilmanagh sandy clay loam	.113^{a}	.145^{c}
Kalamazoo sandy loam	.081^{bc}	.060^{f}
Greenville sandy clay loam	.056^{cd}	.085^{e}
Decatur silty clay loam	.066^{cd}	.192^{b}

[a] Kd values followed by the same letter are not significantly different from each other at the 5% level using single t-test comparisons. Comparisons of letters between herbicide columns are not valid.

Figure 18: The adsorption of imazaquin and AC-263,499 on a Decatur silty clay loam soil.

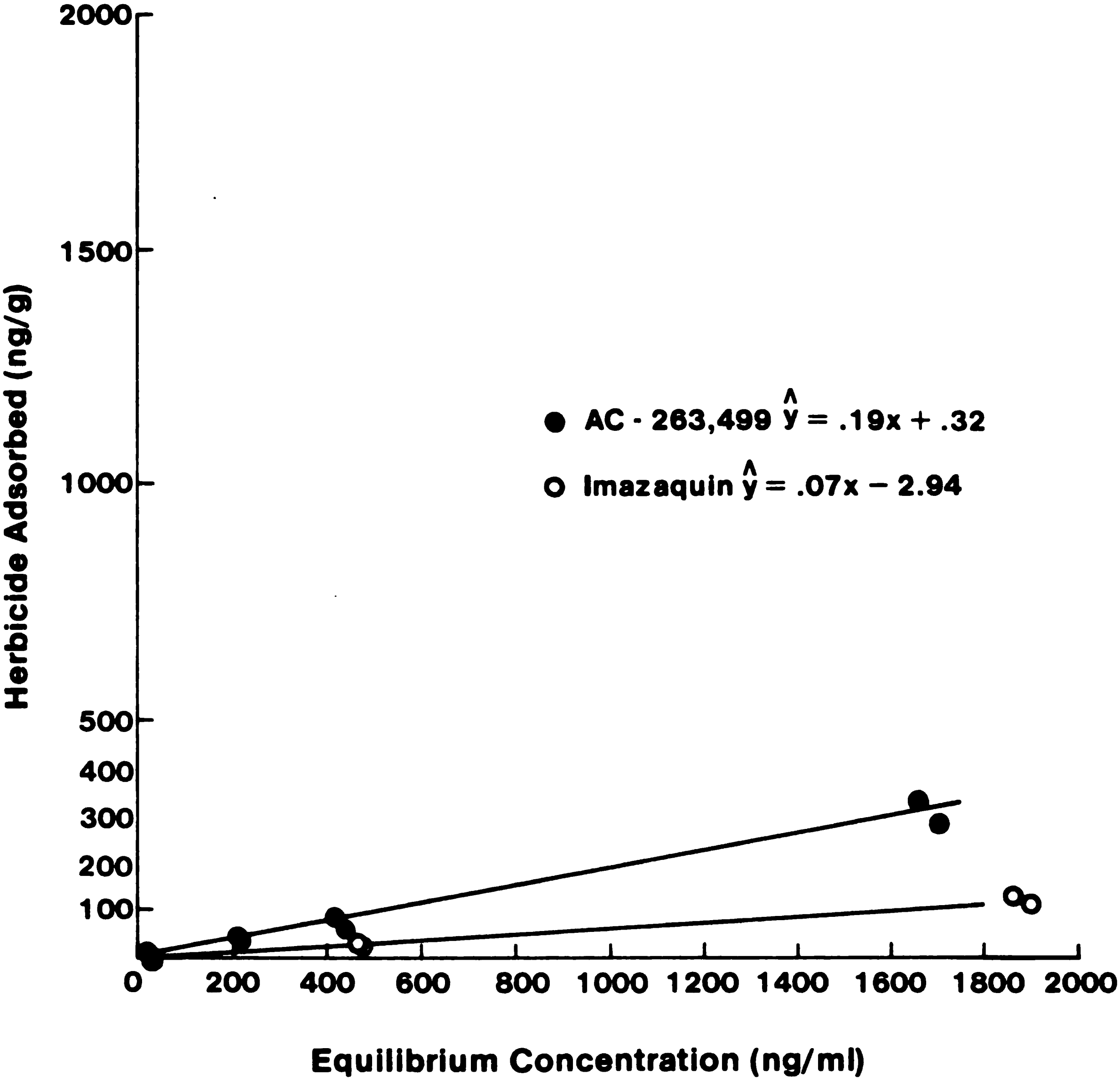
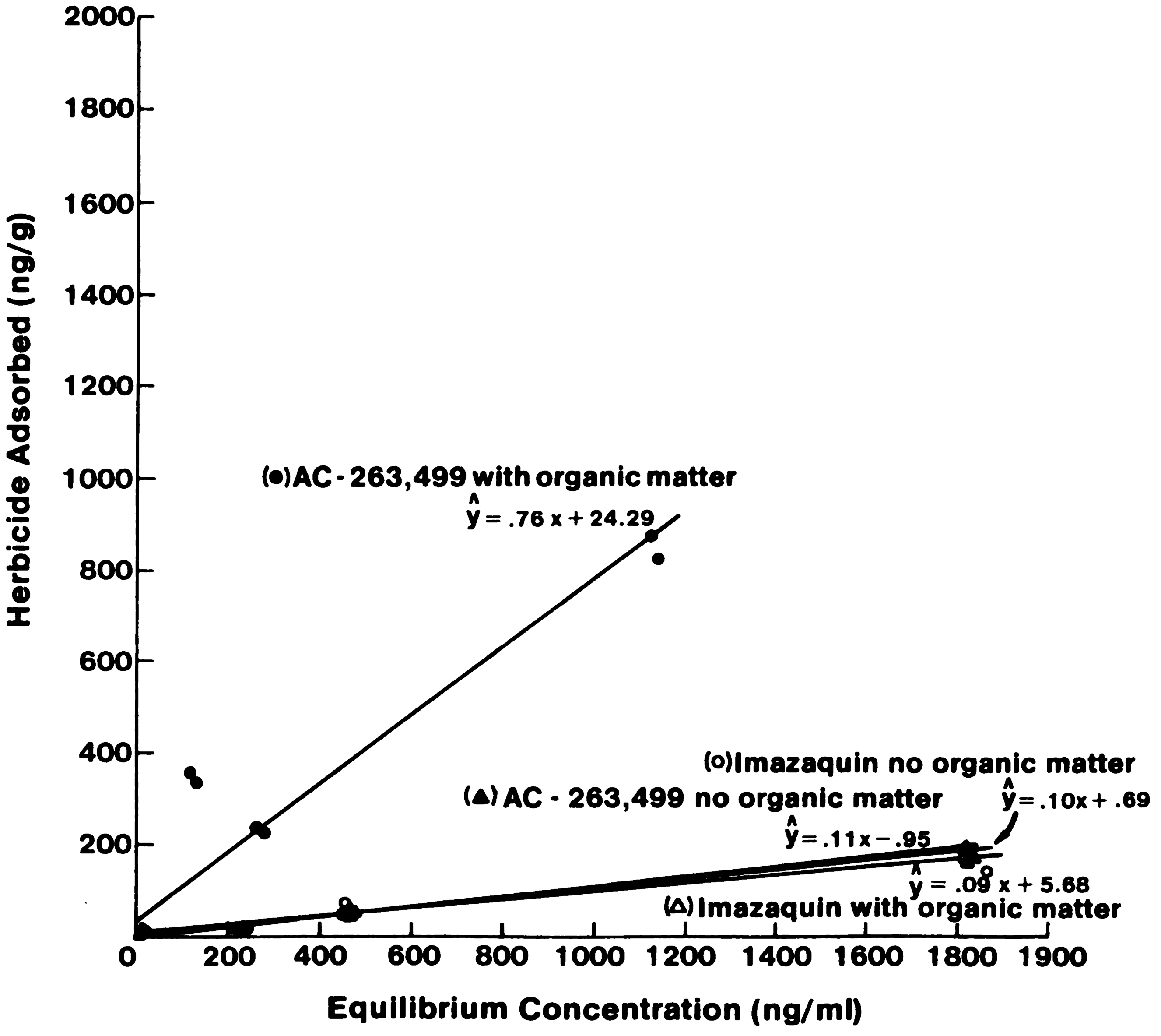

Herbicide Adsorbed (ng/g)
2000
1500
1000
500
400
300
200
100
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Equilibrium Concentration (ng/ml)
● AC - 263,499 $\hat{y} = .19x + .32$
○ Imazaquin $\hat{y} = .07x - 2.94$

Figure 19: The adsorption of imazaquin and AC-263,499 on a Capac sandy loam soil without and with 2.1% organic matter.


Herbicide Adsorbed (ng/g)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
200
400
600
800
1000
1200
1400
1600
1800
1900
Equilibrium Concentration (ng/ml)
(●)AC - 263,499 with organic matter
ŷ = .76 x + 24.29
(○)Imazaquin no organic matter
ŷ = .10x + .69
(▲) AC - 263,499 no organic matter
ŷ = .11x − .95
ŷ = .09 x + 5.68
(△) Imazaquin with organic matter

increased adsorption.

Low adsorption of imazaquin and AC-263,499 occurred because the herbicides were in the anionic form and repelled from the predominantly negatively charged soil surfaces. The ionic form of both herbicides are highly water soluble, and may have greater affinity for the aqueous medium. Low adsorption is consistent with results reported for other acidic compounds (4, 23, 27, 20). Positive charges in soil from aluminum and iron hydroxides or other sites could account for limited adsorption of the ionic forms of imazaquin and AC-263,499, as could weak physical adsorption of the molecular form of these compounds existing in solution (25). In the presence of excessive water, neither imazaquin or AC-263,499 were competitive with water for soil sorption sites. Under varying moisture conditions in field and greenhouse studies, differences in soil adsorption could occur and alter herbicide availability to plants.

Persistence and Availability studies. The main effects of herbicide, soil, and removal date, and the herbicide by removal date interaction were highly significant in both experiments. Corn injury from imazaquin and AC-263,499 applied at 105 g ai/ha was 42.5% greater from imazaquin across all soil types and removal dates (Figure 20). Imazaquin was more available to corn due to more favorable uptake or decreased soil binding, or corn may be more susceptibile to imazaquin. Structurally the two herbicides are similar (Figure 21), and increased susceptibility of corn to imazaquin may be a better explanation.

The effect of soil type on imazaquin availability to corn across both herbicides and removal dates is shown in Figure 22, and for each

Figure 20: Corn response to imazaquin and AC-263,499 across all four soils and removal dates.

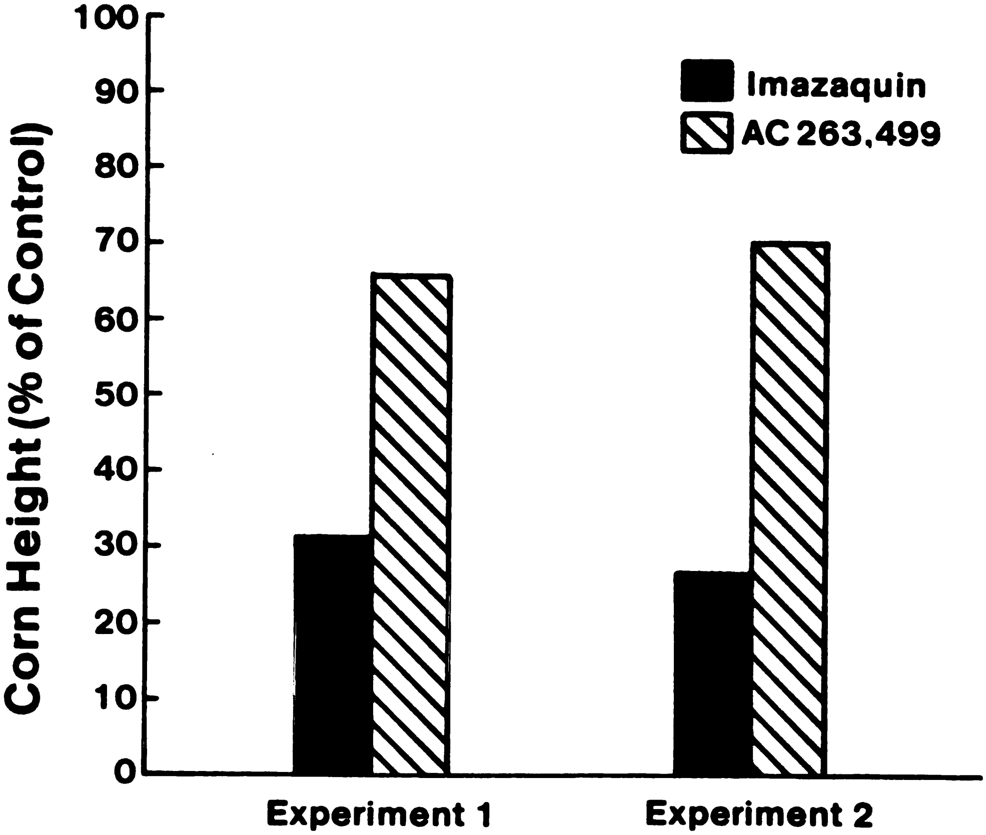
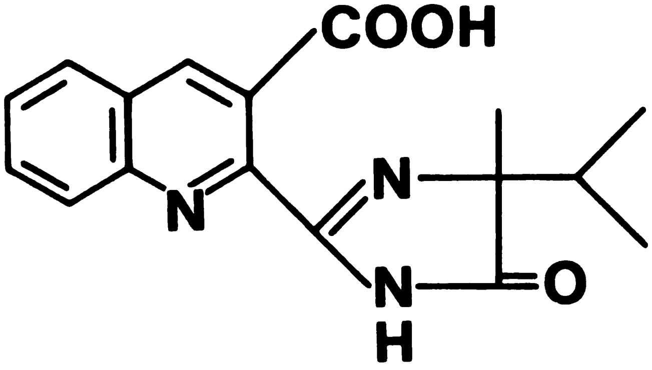
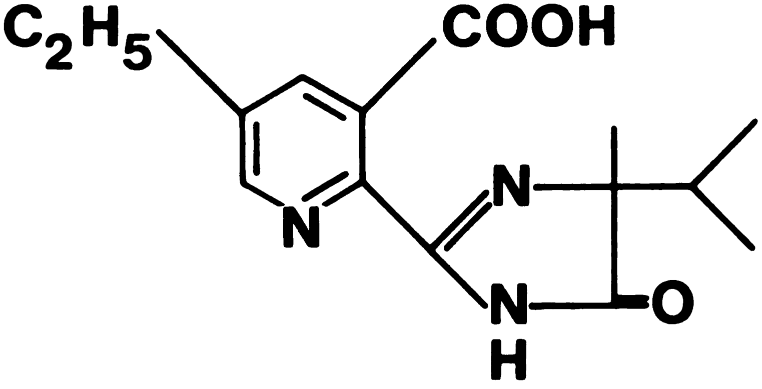

Corn Height (% of Control)
100
90
80
70
60
50
40
30
20
10
0
Imazaquin
AC 263,499
Experiment 1
Experiment 2

Figure 21: The chemical structures of imazaquin and AC-263,499.

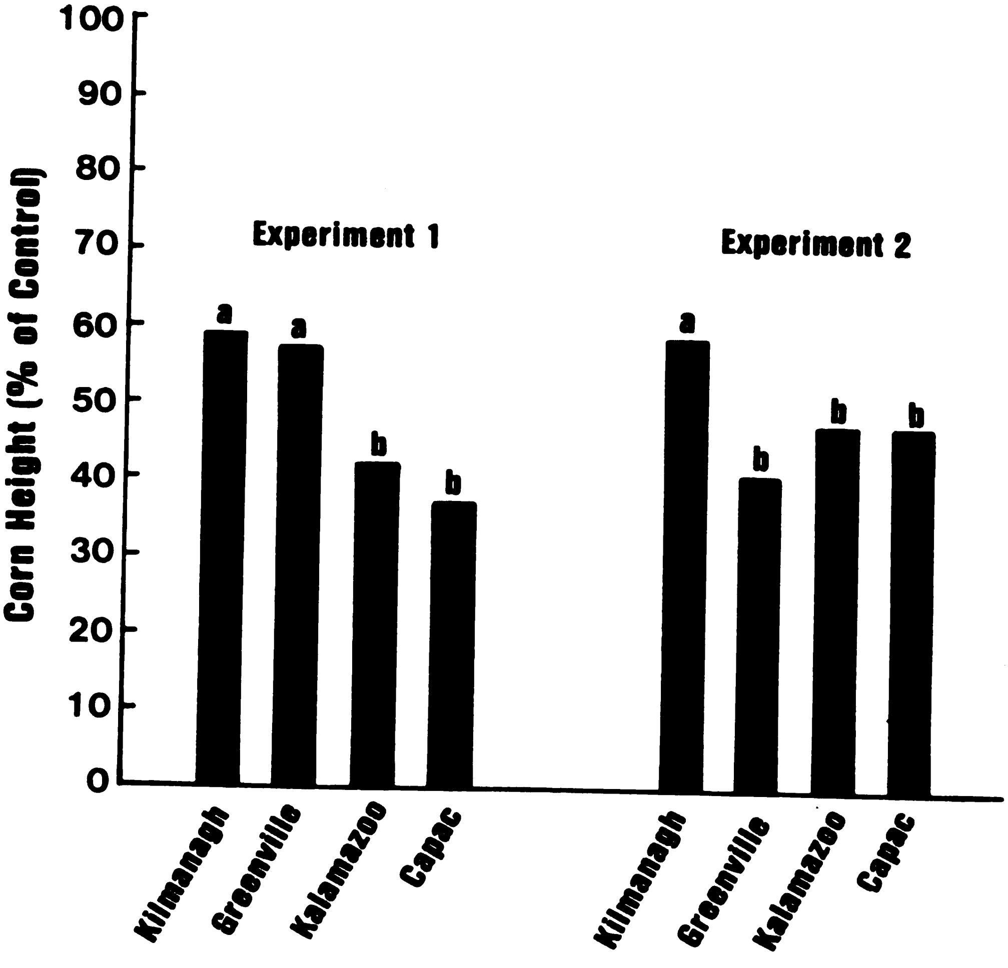


Imazaquin



AC - 263,499

Figure 22: Corn height reduction from imazaquin and AC-263,499 across all herbicides and removal dates.

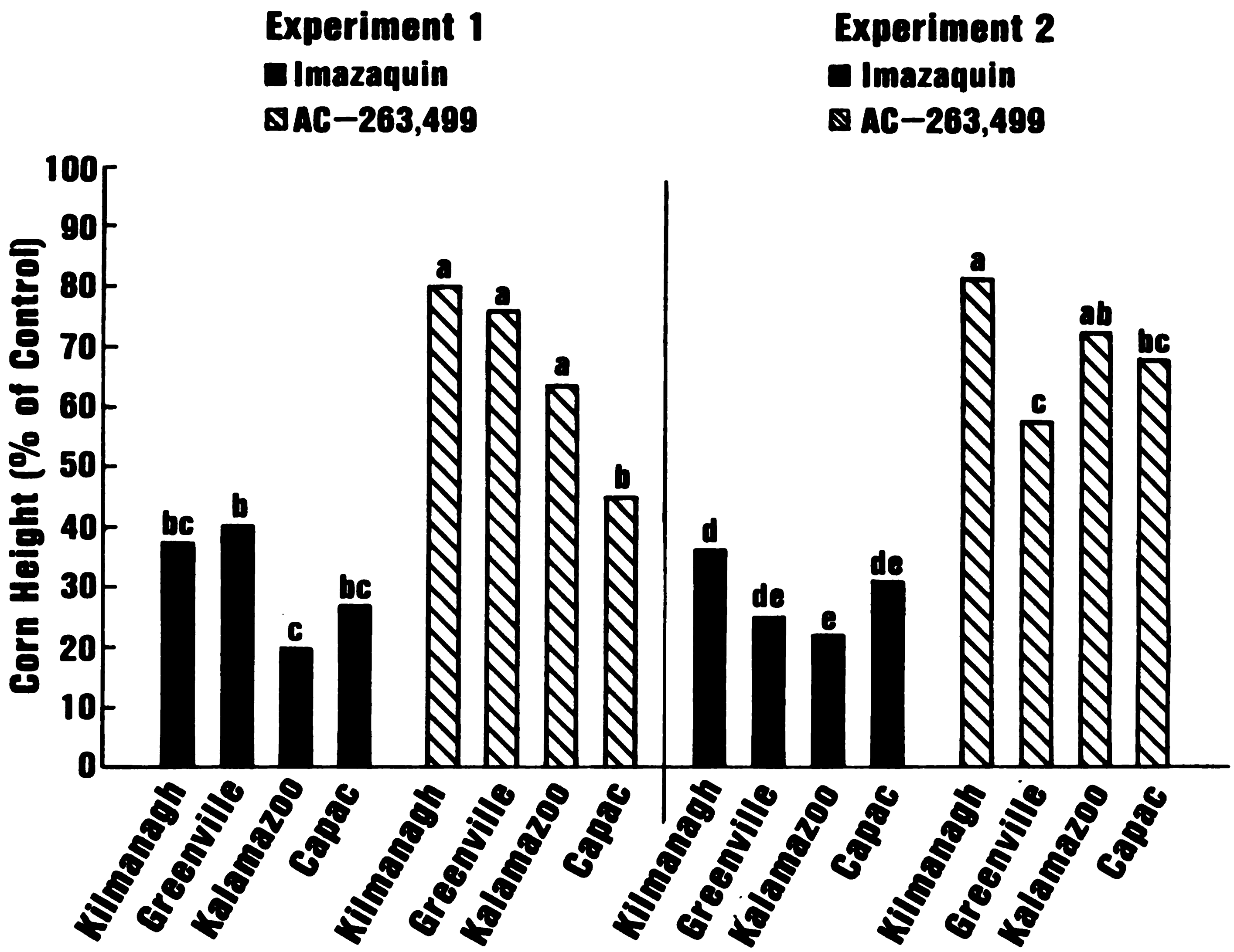

Corn Height (% of Control)
100
90
80
70
60
50
40
30
20
10
0
Experiment 1
Experiment 2
a
a
b
b
a
b
b
b
Kilmanagh
Greenville
Kalamazoo
Capac
Kilmanagh
Greenville
Kalamazoo
Capac

herbicide alone in Figure 23. In both experiments, corn grown on the Kilmanagh sandy clay loam had the least injury. This may be because of increased adsorption to this soil. In the adsorption experiments, both herbicides had greatest adsorption on this soil of the four soils used in this study. In experiment 1, corn grown on the Greenville sandy clay loam was not injured more than corn grown on the Kilmanagh soil. However in experiment 2, corn grown on the Greenville soil had the greatest injury. Therefore it is not clear which response is to be expected.

The Greenville soil was kaolinitic, and had a high sand content of 59%, and a low organic matter content of 1.2%. If these herbicides adsorb to organic matter, lower adsorption on the Greenville soil would occur and increased availability and corn injury result. However if the herbicides adsorb to clay, kaolinitic soils are believed to have greater adsorption capacity for anionic herbicides than smectites because a larger portion of their surface area is composed of aluminum hydroxides that can be positively charged (26, 28). However in the laboratory adsorption studies this was not shown, because this soil had a lower Kd value compared to the Kilmanagh soil for both herbicides. Therefore adsorption under saturated conditions would be less and corn injury would increase, confirming the findings of experiment 2.

The Greenville soil would have a very low water holding capacity because of the kaolinitic nature, and high sand and low organic matter content. Bioavailability of a herbicide is a function of the water content of soil, and at low soil moisture levels the concentration of herbicide per unit volume increases and precipitation may occur, resulting in decreased bioactivity (5). Sandy soils such as the

Figure 23: Corn height reduction from imazaquin and AC-263,499 for each soil across all removal dates.


Experiment 1
■ Imazaquin
▨ AC–263,499
Experiment 2
■ Imazaquin
▨ AC–263,499
Corn Height (% of Control)
100
90
80
70
60
50
40
30
20
10
0
bc
b
c
bc
a
a
a
b
d
de
e
de
a
c
ab
bc
Kilmanagh
Greenville
Kalamazoo
Capac
Kilmanagh
Greenville
Kalamazoo
Capac
Kilmanagh
Greenville
Kalamazoo
Capac
Kilmanagh
Greenville
Kalamazoo
Capac

Greenville hold less water and thus a lower amount of herbicide may remain in solution. Once crystallized the soil may not be able to retain enough water for the herbicide to dissolve into solution and be available again for plant uptake (5). This would not have occurred in laboratory adsorption studies because concentrations were well below solubility limits, and the moisture amount was constant. However, the Kilmanagh soil had the least corn injury in both experiments. The water holding capacity of the Kilmanagh soil would be greater than the Greenville soil because of the smectite nature and high organic matter content, and precipitation would be less likely to occur. Herbicides would be more available for plant uptake. Since this did not occur, it appeared that soil adsorption would be a better explanation for the herbicide availability behavior in the Greenville soil, and experiment 2 results of greater corn injury on the Greenville soil would be consistent with soil adsorption behavior.

Correlation coefficients of soil properties for the availability and persistence of imazaquin and AC-263,499 at 0 day and 120 day removal dates showed very low correlations of any soil parameter to corn injury from imazaquin at 0 days (Table 8) (24). AC-263,499 exhibited a negative correlation to the percentage of clay in experiment 2, however both kaolinite and smectite clays were present in this analysis, and the percentage of sand or the cec were better correlation parameters. At the 120 day removal date, both soil persistence and availability were involved in decreasing corn injury. There were no significant correlation coefficients in experiment 1 for either herbicide, or in experiment 2 for AC-263,499. In experiment 2 imazaquin had a strong negative correlation with the percentage of sand

Table 8: Correlation coefficients* (r) of soil properties to the availability and persistence of imazaquin and AC-263,499.

	r Values							
	0 Days				120 Days			
	Imazaquin		AC-263,499		Imazaquin		AC-263,499	
	Ex. 1	Ex. 2	Ex. 1	Ex. 2	Ex. 1	Ex. 2	Ex. 1	Ex. 2
% O.M.	-.056	.278	-.028	.208	-.189	.798	-.013	.298
% clay	.468	.083	-.368	-.702	.326	.097	.187	.311
% sand	-.105	-.317	.045	-.045	.11	-.774	-.084	-.364
pH	.201	.334	-.092	-.264	.052	.624	.232	.433
CEC	.067	.214	-.071	.300	-.229	.792	-.120	.236

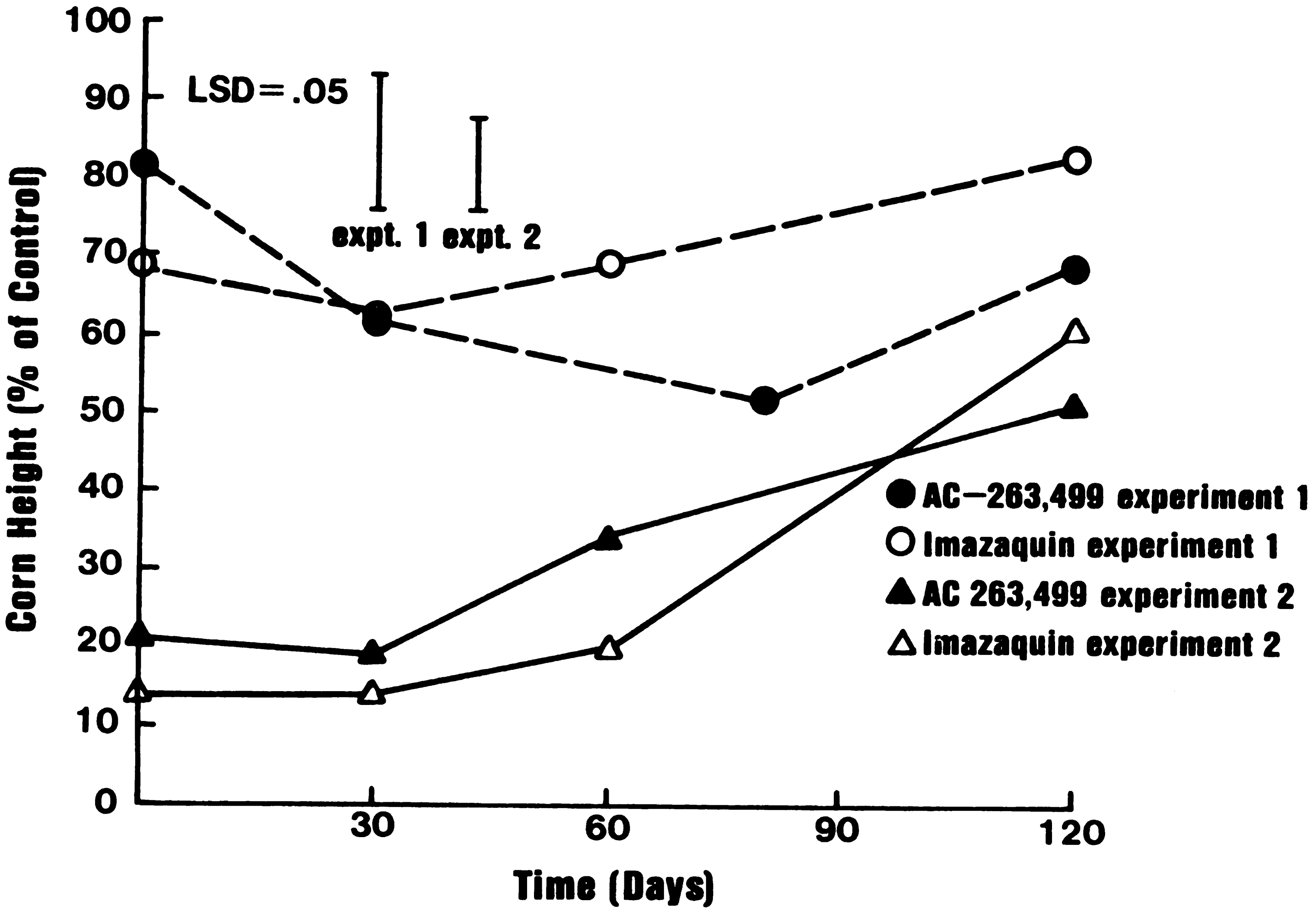
*If r = .5, then 25% of variation in Y is explained by variable X.

and a positive correlation with the percentage of organic matter and the cec. These parameters may be important to the availability and/or persistence of imazaquin. Chlorsulfuron phytotoxicity had a significant positively correlation with organic matter, exchangeable aluminum, and the cation exchange capacity (cec), and had no significant correlation to the percentage of clay (18). Because of the high correlation between each of these soil parameters themselves, it was not possible to isolate which of these parameters was most important to the availability and soil persistence of imazaquin and AC-263,499.

The interaction of the herbicides with removal dates across all soils was highly significant in both experiments (Figure 24). Imazaquin injury to corn decreased over time in both experiments, but the effect of AC-263,499 on corn decreased significantly between the 0 and 4 month removal dates only in experiment 2. Corn height reduction from AC-263,499 at 105 g ai/ha was less than 20% initially in experiment 1, and injury reduction over time was more difficult to quantify because of variability in corn growth. Imazaquin persistence decreased over time because of transformation processes such as microbial and nonbiological degradation, or because of transfer processes such as soil adsorption that resulted in less herbicide available for plant uptake.

Herbicide persistence is a function of the herbicide properties, soil properties, and environmental conditions. It can be altered by transfer processes such as volatilization, leaching, plant uptake, and soil adsorption, and/or by transformation processes such as photodecomposition, microbial degradation, and nonbiological

Figure 24: The removal date by herbicide interaction across all four soils for experiments 1 and 2.


100
90
80
70
60
50
40
30
20
10
0
Corn Height (% of Control)
LSD=.05
expt. 1
expt. 2
30
60
90
120
Time (Days)
● AC—263,499 experiment 1
○ Imazaquin experiment 1
▲ AC 263,499 experiment 2
△ Imazaquin experiment 2

degradation such as hydrolysis (1, 3, 5, 7, 14, 23). Volatility did not occur because of the ionic nature of these herbicides, and because these herbicides were incorporated. Plant uptake was not a factor during the removal time periods prior to corn planting, and leaching could not occur in these pots. Treated soil was not exposed to ultraviolet light either in the greenhouse or growth chambers, so photodecomposition would be unlikely (18). Therefore microbial or nonbiological degradation may have decreased the imazaquin and AC-263,499 remaining over time which resulted in reduced corn injury. Alternatively or concurrently, soil adsorption may have increased over time, and the herbicides became increasingly less available for plant uptake. In adsorption studies, both herbicides had very low adsorption under excessive moisture conditions. It is not known whether changing moisture conditions alter imazaquin and AC-263,499 adsorption to soil. Significant differences in the availability of imazaquin and AC-263,499 on these soils may be due to differences in soil adsorption.

ACKNOWLEDGEMENTS

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CHAPTER 5

EFFECT OF SOIL PH ON IMAZAQUIN AND AC-263,499 ADSORPTION TO SOIL AND PHYTOTOXICITY TO CORN (*Zea mays* L.)

ABSTRACT

Adsorption of ^{14}C-imazaquin[1] (2-((4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-3-quinolinecarboxylic acid) and ^{14}C-AC-263,499 (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-5-ethyl-3-pyridinecarboxylic acid) to soil increased as soil pH decreased from 8.0 to 3.0 in laboratory studies. Significantly more AC-263,499 than imazaquin was adsorbed at all pH levels, with the greatest difference observed at pH 5.5. In greenhouse studies, phytotoxicity to corn (*Zea mays* L.) from imazaquin applied at 26 and 53 g ai/ha decreased as the soil pH increased from 4.7 to 8.5. Soil pH had no effect on AC-263,499 phytotoxicity. Sub-irrigation decreased the degree of corn injury from both herbicides. In field studies with imazaquin at soil pH ranges of 4.0 to 4.8, 5.4 to 5.5, and 5.8 to 6.2, imazaquin injury to corn across all pH levels decreased as the time lapse between herbicide application and corn planting increased. There

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[1] AC-252,214 Code Name. American Cyanamid Company. Princeton, NJ 08540.

was a significant interaction between soil pH and the time of planting. Imazaquin injury to corn decreased at pH 5.8 to 6.2 when corn was planted in June, but there was no significant effect of soil pH when corn was planted in July or August. The soil pH interaction with herbicide rate was significant because there was no response of corn to imazaquin rate at the higher pH level.

INTRODUCTION

Imazaquin and AC-263,499 are selective herbicides for grass and broadleaf control in soybeans (Glycine max (L). Merr.). They are both weak acids with pKa values of 3.8 and 3.9 for imazaquin and AC-263,499, respectively[2]. Little information is available regarding the behavior of these herbicides in soil. Liu (21) found little adsorption of imazaquin on five U. S. soils, Ca-montmorillonite, and Ca-organic matter in laboratory studies. Greater adsorption and lesser desorption was observed at low pH levels. Researchers have studied the effects of different soil properties including soil pH on herbicide adsorption and performance. This has been reviewed by Bailey and White (1). Soil pH can alter the adsorption of ionic herbicides to the soil, and change their availability to weed and crop species (5, 17, 18, 19, 22, 24, 26, 33).

Soil pH may directly or indirectly influence adsorption and activity of ionic pesticides by affecting the ionic character of the

[2] Personal Communication. Gary Mangas. American Cyanamid Company. Princeton, NJ 08540.

organic matter and clay colloids, or the ionization of the herbicide. Organic matter, and to a lesser extent clay, have pH-dependent charges (29, 35). Organic matter contains carboxylic acid and phenolic groups that have pH dependent ionization with pKa values of approximately 5.2 (29, 35). At high pH values, the ionized acidic functional groups can react with polyvalent cations to form chelate bridges with acidic herbicides (30, 35). PH affects herbicide ionization, as herbicides become undissociated when the suspension pH is 1 to 2 units above their pKa or lower (1). At pH values greater than their pKa values, acidic herbicides exist in the anionic form and are repelled by negatively charged soil colloids (8, 14, 22, 24). Friessel and Bolt found that soil adsorption of anionic herbicides such as 2,4-D ((2,4-dichlorophenoxy)acetic acid), 2,4,5-T ((2,4,5-trichlorophenoxy)acetic acid), and MCPA ((4-chloro-2-methylphenoxy)acetic acid) increased as the pH decreased (8). Picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) is an anionic herbicide, and adsorption on clay increased from 0 to 39% as pH decreased from 8.0 to 2.0 (13). Chlorsulfuron (2-chloro-N-(((4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino)carbonyl)benzenesulfonamide) showed little adsorption to soil at pH 7.5, but considerable adsorption on both silty clay loam and sandy loam soils at pH of 4.3 (24). The greatest differences in the pH effect on adsorption occurred with the sandy loam soil. Weak bases such as the triazines have been extensively studied and found to be adsorbed to soil to a greater extent as the pH decreases. This is a result of protonation of the ring nitrogen, with maximum adsorption near their pKa values (17, 33). At higher pH values, increasing concentrations of weak basic and acidic herbicides would be available for root uptake and could cause increased phytotoxicity to sensitive plants. 2,4-D, dicamba (3,6-dichloro-2-methoxybenzoic acid), and chlorsulfuron have exhibited this behavior (5, 22). However Farmer and Aochi (7) found no correlation between picloram injury and soil pH in soils with pH values of 5.6 to 7.4. They did find increased adsorption of picloram to soil in laboratory studies when the pH of the solution was lowered. Corbin (5) found no change in phytotoxicity of picloram or chloramben (3-amino-2,5-dichlorobenzoic acid) as soil pH increased from 4.3 to 7.5. Decreased herbicidal activity above the pKa value of an acidic compound may reflect adsorption or complex formation with hydroxides or oxides of iron and aluminum, or alternatively, an increase in polarity and dissociation of the herbicide molecule resulting in decreased uptake by plants (31, 35).

The amount of herbicide available for effective weed control is determined by adsorption to the soil, the mobility of the herbicide in the soil profile, and whether the herbicide can be degraded (12). Both microbial and nonbiological degradation may be affected by soil pH (18, 27, 31). Dalapon (2,2-dichloropropanoic acid) is degraded most rapidly at pH 6.5, and 2,4-D and dicamba at pH 5.3; whereas, chloramben and picloram degradation were not affected by soil pH. Ph played a significant role in s-triazine and sulfonylurea degradation and persistence due to increased hydrolysis at low pH values and increased adsorption to soil (18, 19, 27).

As soil adsorption increases the availability and subsequent phytotoxicity to plants decreases. Soil adsorption in the field may differ from adsorption measured in the laboratory due to temperature, soil water content, pH, or concentration effects (7, 10, 14, 20, 23).

Herbicides and water compete for adsorption sites in ion-dipole and coordination reactions, and with water for ligand positions around soil cations (4, 30). Soil moisture has a large effect on polar pesticide groups such as carbonyls, amines, and carboxylic acids (25). Some organic chemicals are not adsorbed when water is present, but in air dry soils they are adsorbed, and then are not displaced by the addition of water (25, 30). At very low soil water contents, increased dissociation of water on the soil surfaces coupled with the decreased competition by water for binding sites, can affect pesticide adsorption. Physically adsorbed, but not ionically bound pesticides, may be displaced by water (23, 29, 30).

The soil moisture content and method of water addition to soil has a critical effect on herbicide availability (2, 15, 16, 32). Herbicides applied to dry soil cause less plant injury, as does subirrigation (2, 15, 16). Phytotoxicity of atrazine (6-chloro-*N*-ethyl-*N*'-(1-methylethyl)-1,3,5-triazine-2,4-diamine), simazine (6-chloro-*N*,*N*'-diethyl-1,3,5-triazine-2,4-diamine), and linuron (*N*'-(3,4-dichlorophenyl)-*N*-methoxy-*N*-methylurea) increased as the soil moisture content increased due to differences in herbicide concentration accumulated in the plant (32). In the greenhouse, phytotoxicity increased due to the increased number of roots per soil volume. Daily watering regularly initiated changes in herbicide equilibrium, leading to higher bioavailability of herbicides and increased plant uptake (9, 32).

The total amount of herbicide in solution is a function of the water content of the soil and soil solution pH. Precipitation of herbicides at low moisture levels results in less herbicide available for plant uptake (3). Water solubility of the herbicide is important. The higher the water solubility the less moisture needed for the herbicide to dissolve into solution and be available for plant uptake. Water solubility of acidic herbicides increases as the pH increases. Thus at low soil pH values, sorption of acidic herbicides to soil can increase due to either protonation or neutralization of the acid group or decreased solubility (1, 13, 22).

The purpose of these studies was to a) determine the effect of pH on adsorption of imazaquin and AC-263,499 to soil under laboratory conditions, b) determine if soil pH and watering method altered the availability of imazaquin and AC-263,499 as expressed by corn phytotoxicity in the greenhouse, and c) determine if soil pH altered the persistence and availability of imazaquin in field studies.

MATERIALS AND METHODS

Soils. The soil used in all experiments was a Hillsdale sandy loam (Typic Hapludalfs, coarse sandy, mixed, mesic) with 65% sand, 24% silt, 11% clay, 1.9% organic matter, a pH of 5.5, cation exchange capacity of 5.2 meq/100 g, 6 ppm of extractable aluminum, and 74 ppm of iron. The soil pH was increased with calcium hydroxide and decreased with hydrochloric acid to the levels shown in the studies. The soil was watered to field capacity and incubated for 2 months to allow for equilibration of the base with soil functional groups. The soil was not leached prior to herbicide treatments. In the field study the soil had not been limed for 8 years. Previous plot pH adjustments were achieved with dolomitic lime, calcium nitrate, and ammonium sulfate.

Effect of soil pH on herbicide adsorption to soil. Soils were air dryed and sieved through a 2 -mm sieve after pH adjustment and equilibration to pH levels of 3.0, 5.5, and 8.0. Five g of soil were weighed into 30 -ml glass centrifuge tubes and 5 ml of the appropriate concentration of ^{14}C-imazaquin (specific activity of 4.61 µCi/µM) or ^{14}C-AC-263,499 (specific activity of 7.23 µCi/µM) were added in distilled water at concentrations of 2.0, 0.5, 0.25, and 0.02 ppm. Maximum concentrations equilibrated with the soil were 30 times below the solubility of the acid herbicide form to prevent precipitation of these compounds (3). The glass tubes were sealed with parafilm-covered rubber stoppers, taped securely, and gently shaken at 23°C on a reciprocal shaker for 10 h at 70 strokes/min. Equilibrium was reached in 4 h, with no additional adsorption after 32 h (data not published). Samples were then centrifuged at 12,350 x g for 15 min, and two 1 -ml aliquots of the supernatent were pipetted into separate glass scintillation vials containing 15 ml of water-accepting scintillation solution[3]. These were radioassayed on a liquid scintillation spectrometer, and differences in radioactivity between known standard concentrations and supernatents of the samples were assumed to be due to soil adsorption. The experiments were repeated twice with each treatment replicated three times. Adsorption was then plotted with the herbicide adsorbed (ng per g of soil) on the y axis, and equilibrium concentration of herbicide in solution (ng per ml) on the x axis. Plots of each herbicide at each soil pH were linear. Regression

[3] Safety-Solve, high flash point scintillation solution. Research Products. International Corp. Mount Prospect, IL 60057.

equations were calculated for each soil and herbicide treatment without log transformation, and analyzed to determine if the slopes of the lines were different from 0 and from each other by t-tests (28). Distribution coefficients (Kd) were calculated to express the ratio of the amount of ^{14}C-herbicide adsorbed to the amount remaining in solution at equilibrium (11).

Influence of soil pH on herbicide phytotoxicity to corn in greenhouse studies. Greenhouse experiments were conducted on the Hillsdale sandy loam soil adjusted to pH values of 4.7, 5.7, 6.5, 7.5, and 8.5. Imazaquin and AC-263,499 were applied at 26 and 53 g ai/ha to 500 cc of soil in 600 ml pots and incorporated to a 7.6 cm depth. Four replications at each pH level were left as untreated controls to measure corn growth across all five pH levels. Three corn 'Stauffer 5650' seeds per pot were planted to a 3.5 cm depth. Corn was grown for 21 days in the greenhouse and thinned to two plants/pot after 7 days. Temperature was maintained at a maximum of 27°C during the day and a minimum of 16°C at night. Supplemental lighting was supplied by high pressure metal halide lamps to provide a 16 h photoperiod and 360 $\mu E \cdot m^{-2} \cdot s^{-1}$ of photosynthetically active radiation. After 21 days shoot fresh weight and height were measured, averaged for each pot, and then converted to a percentage of the weight or height of the control plants from that soil pH and replication that received zero herbicide so that any effect of soil pH on plant growth would be eliminated. The treatments were replicated four times and the experiment repeated three times, twice with sub-irrigation of 120 ml/day, and once with surface irrigation of 120 ml/day. Sub-irrigation experiments were combined and averaged, and surface irrigation experiments analyzed separately due to the difference in magnitude of injury resulting from watering method.

Herbicide availability and persistence in the field. Field studies were conducted in 1984 and 1985 on Hillsdale sandy loam soil in a completely randomized design with four replications. Plot pH values were a range in three levels of 4.2 to 4.8, 5.4 to 5.5, and 5.8 to 6.2. Imazaquin was applied at 420, 280, and 140 g ai/ha and incorporated to a depth of 7.6 cm with one incorporation pass using a Triple K Danish s-tine field cultivator [4]. Four plots at each pH level did not receive imazaquin and served as controls. Alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) at 3.36 kg ai/ha and chloramben at 2.0 kg ai/ha were applied for weed control. Corn was planted 30, 60, and 90 days after initial imazaquin application, which corresponded to June, July, and August planting dates. Corn was grown for 21 days, and the fresh shoot and root weight and height of four plants/plot measured. All parameters gave similar results so only shoot height will be presented. In 1984 inadequate weed control due to dry weather resulted in failure of adequate growth for corn planted 60 and 90 days after imazaquin application. All measurements in both years were changed to a percentage of the control plants grown where no imazaquin was applied across the pH levels. In this way the pH effect on corn growth would not be a factor in evaluating imazaquin injury to corn at the various pH levels. Results were not combined over years.

[4] Manufacturer Kongskilde, Eceter, Ontario.

Only a comparison of the corn planted 30 days after imazaquin application in 1984 and 1985 could be made.

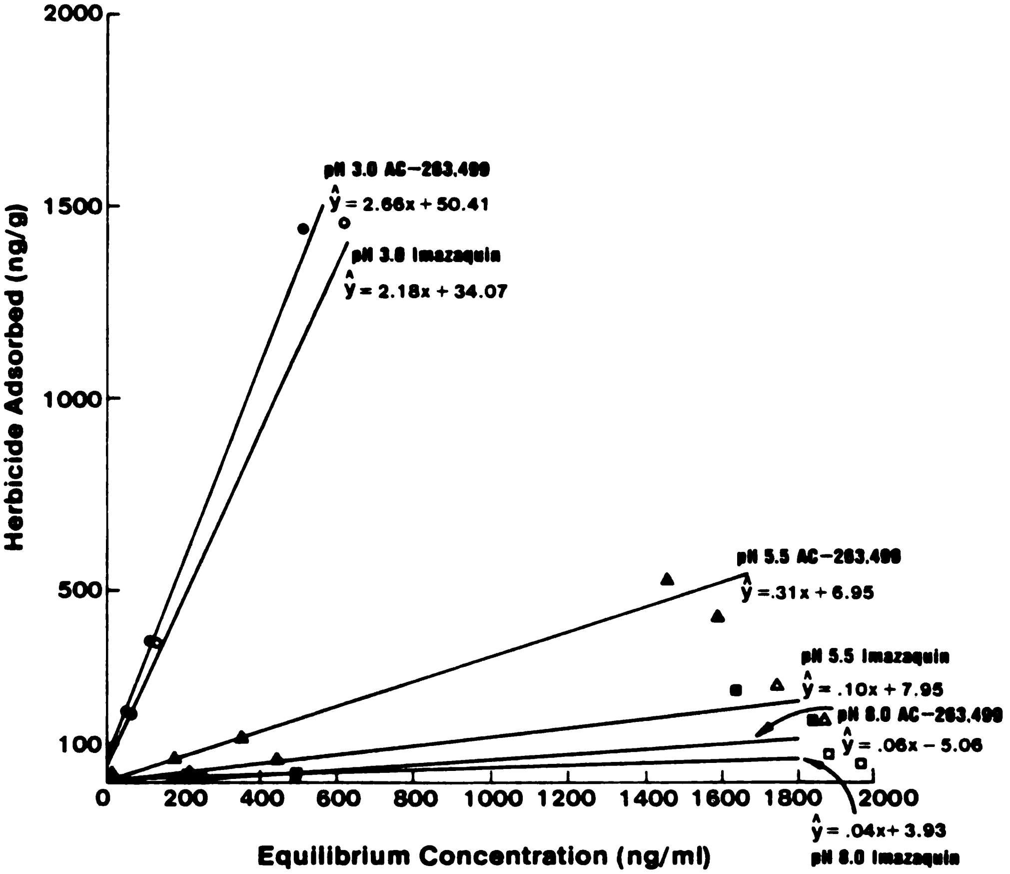
RESULTS AND DISCUSSION

Effect of soil pH on herbicide adsorption to soil. Adsorption of both herbicides to soil increased as soil pH decreased from 8.0 to 3.0 (Figure 25). The amount of herbicide adsorbed increased as herbicide concentration increased. The slopes of the lines plotted for adsorption of imazaquin and AC-263,499 against equilibrium concentration at pH values of 5.5 and 8.0 were less than one, which is a sign of low adsorption typical of acidic herbicides such as chlorsulfuron, picloram, and 2,4-D (13, 14, 31). Calculated Kd values for imazaquin and AC-263,499 are given in Table 9. All Kd values were significantly different from each other at the 5% significance level, using single t-test comparisons (28).

Table 9. Calculated distribution coefficients (Kd) for imazaquin and AC-263,499 on a Hillsdale sandy loam adjusted to three pH levels.

Soil pH	Imazaquin	AC-263,499
	Kd	
3.0	2.184	2.669
5.5	0.103	0.312
8.0	0.036	0.062

Figure 25: The adsorption of imazaquin and AC-263,499 on a Hillsdale sandy loam soil adjusted to three pH levels.


2000
1500
1000
500
100
Herbicide Adsorbed (ng/g)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Equilibrium Concentration (ng/ml)
pH 3.0 AC-263.499
$\hat{y} = 2.66x + 50.41$
pH 3.0 Imazaquin
$\hat{y} = 2.18x + 34.07$
pH 5.5 AC-263.499
$\hat{y} = .31x + 6.95$
pH 5.5 Imazaquin
$\hat{y} = .10x + 7.95$
pH 8.0 AC-263.499
$\hat{y} = .06x - 5.06$
$\hat{y} = .04x + 3.93$
pH 8.0 Imazaquin

The pKa values of imazaquin and AC-263,499 are 3.8 and 3.9, respectively, and the reported water solubilities of the acid forms of imazaquin and AC-263,499 are 60 and 1400 ppm at 25°C, respectively[5]. The ionic forms would be considerably more water soluble. The maximum concentration equilibrated with the soil was 2.0 ppm to prevent precipitation of the acid forms of these compounds under the adsorption isotherm conditions. Solubility effects on adsorption at this concentration should be minute.

Low adsorption of imazaquin and AC-263,499 to soil occurred at soil pH 8.0. At this pH, the herbicides were presumably in the anionic form and were repelled from the predominantly negatively charged soil surface. This is consistent with previous reports for imazaquin and other acidic compounds studied under similar laboratory conditions (7, 13, 20, 21, 22, 23, 31). Positive charges in this soil from aluminum and iron hydroxides or other sites could account for limited adsorption, as could weak physical adsorption of the 0.01% of the herbicide existing in the molecular form at pH 8.0 (29). In the presence of excessive water, neither imazaquin or AC-263,499 were competitive with water for soil sorption sites at pH 8.0, and thus were in solution and available for plant uptake (3).

At soil solution pH 3.0, the herbicides were predominantly in the molecular form and adsorption to soil increased. Protonation of the imidazolinone nitrogens, or the nitrogen on the quinoline or pyridine ring of imazaquin and AC-263,499, respectively, could result in

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[5] Personal Communication. American Cyanamid Company. Princeton, NJ 08540.

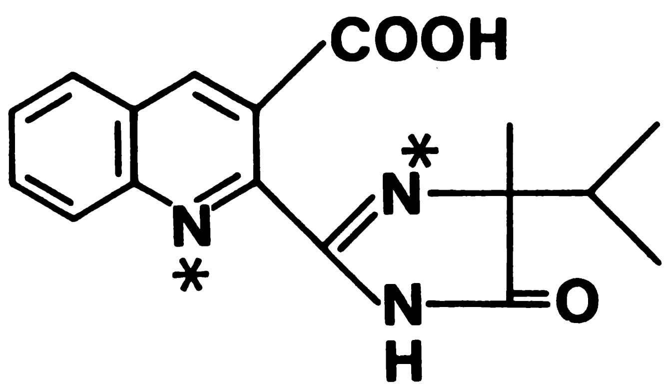
cationic binding of the herbicide to the soil at the low pH (Figure 26). The adsorption capacity of the soil at pH 3.0 was not reached, suggesting binding of the herbicides to the large number of negatively charged sites present on the soil surface. If the herbicides were in the cationic form due to protonation of a nitrogen, their affinity for these negatively charged sites would be dramatically increased. Quinoline molecules in aqueous solutions have a pKa of 5.0, and show increased adsorption to clay surfaces as pH decreased from 8.5 to 6.0 (6).

Adsorption of AC-263,499 was greater than imazaquin across all pH levels, especially at pH 5.5. The pKa values of the carboxylic and phenolic functional groups of organic matter are reported to be 5.0 (29). At pH 5.5 the organic matter present in the molecular form may have a greater affinity for AC-263,499 than imazaquin, causing increased binding to occur. Alternatively, the pKa of AC-263,499 may be higher than 3.9. A higher concentration of the molecular herbicide form would exist at pH 5.5, and be attracted to the soil surface.

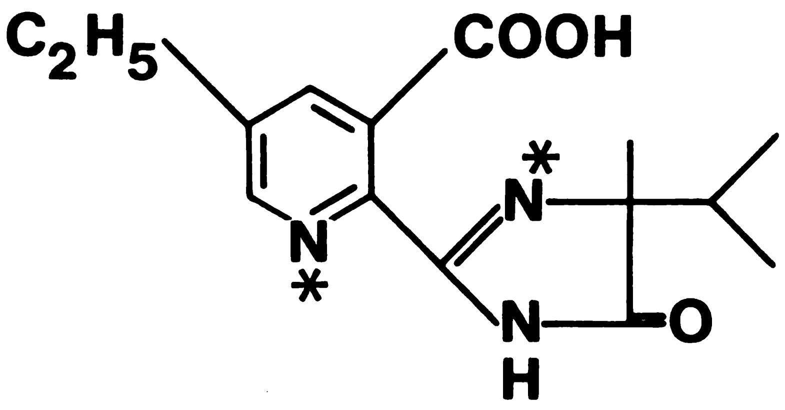
Adsorption to soil of both compounds decreased as pH increased, and AC-263,499 had greater adsorption than imazaquin across all pH levels. Increased availability of imazaquin and AC-263,499 may thus occur as soil pH is increased, and phytotoxicity to sensitive plants increased. Adsorption studies indicated imazaquin may be more available for plant uptake than AC-263,499.

Influence of soil pH on herbicide phytotoxicity to corn in greenhouse studies. Regression analysis of data from surface and sub-irrigated experiments in the greenhouse, showed that corn injury from imazaquin

Figure 26: Chemical structures of imazaquin and AC-263,499, with possible protonation sites denoted with an *.



Imazaquin



AC - 263,499

decreased as the soil pH increased (Figure 27 and 28). Soil pH had no significant effect on AC-263,499 phytotoxicity to corn. This is in disagreement with the adsorption studies conducted under excess water conditions which showed increased adsorption of imazaquin and AC-263,499 as pH decreased.

The decreased imazaquin activity at higher soil pH values indicated that the herbicide was adsorbed or complexed with iron or aluminum hydroxides or other forms of anionic exchange on the soil matrix that were not available in the presence of excessive water. Secondly, increased adsorption at high pH values may result from an increase in polymorphous hydroxides of aluminum and iron. Calcium hydroxide previously added to the soil system to increase the soil pH, released increasing amounts of these polymorphous hydroxides into the soil system. Because the soil was not leached prior to herbicide application, the herbicides may have bound to these polymorphous hydroxides, precipitated out of solution, and been unavailable for plant uptake. Thirdly, the increased polarity and dissociation of these herbicides at higher pH levels may cause them to be unfavorable for plant uptake (35). In studies with excised corn roots[6], the molecular forms of imazaquin and AC-263,499 were more easily adsorbed by plant roots than the ionic forms. This was especially true for AC-263,499. This occurred because the nonionized compounds penetrated the Casparian strip more easily. Therefore as soil pH increased, imazaquin phytotoxicity to corn decreased because of increased soil adsorption or increased polarity that reduced plant uptake.

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[6] Personal Communication. Dale Shaner. American Cyanamid Company. Princeton, NJ 08540.

Figure 27: The effect of soil pH on injury to corn from 26 and 53 g ai/ha of imazaquin and AC-263,499 when surface-irrigated.

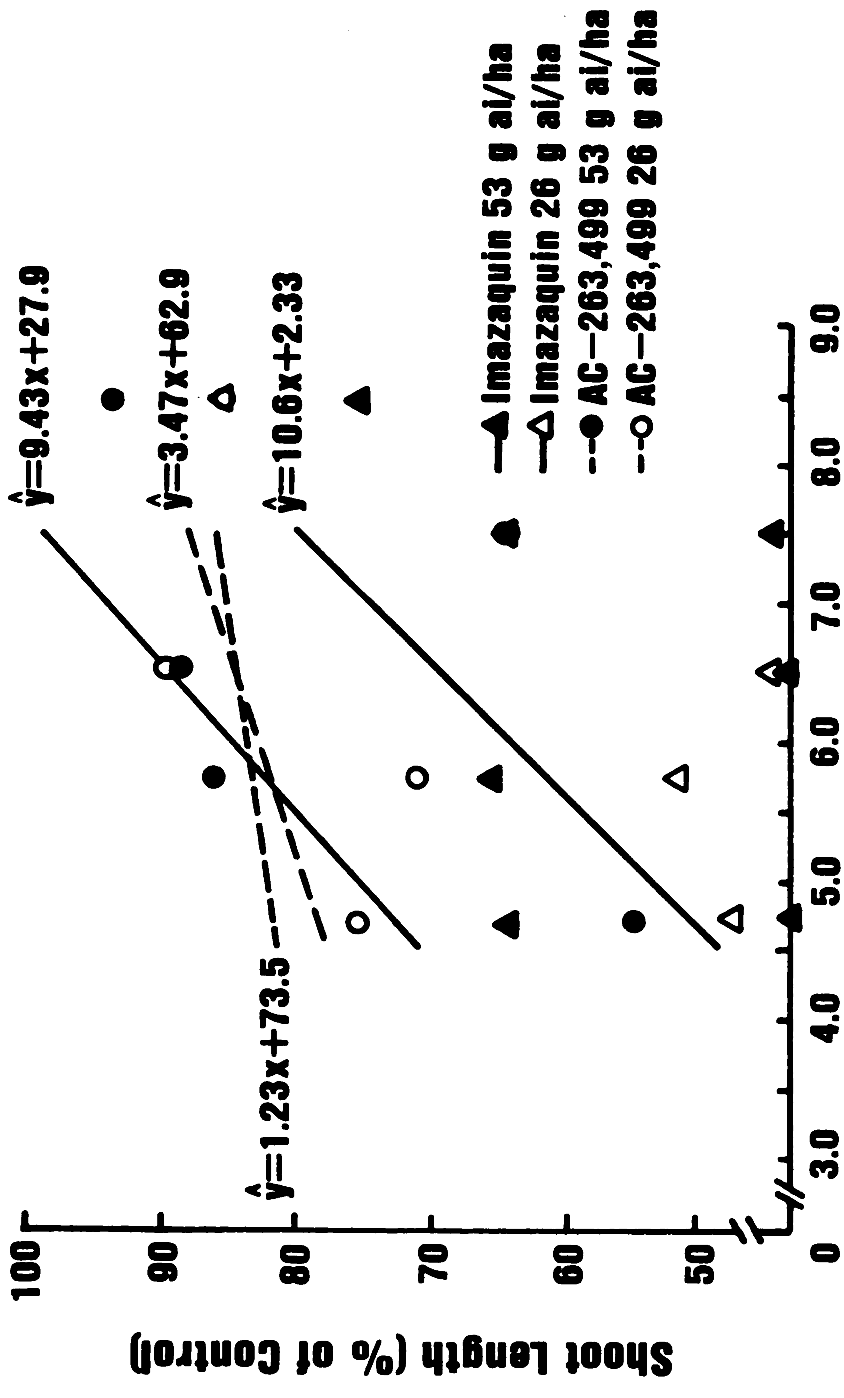
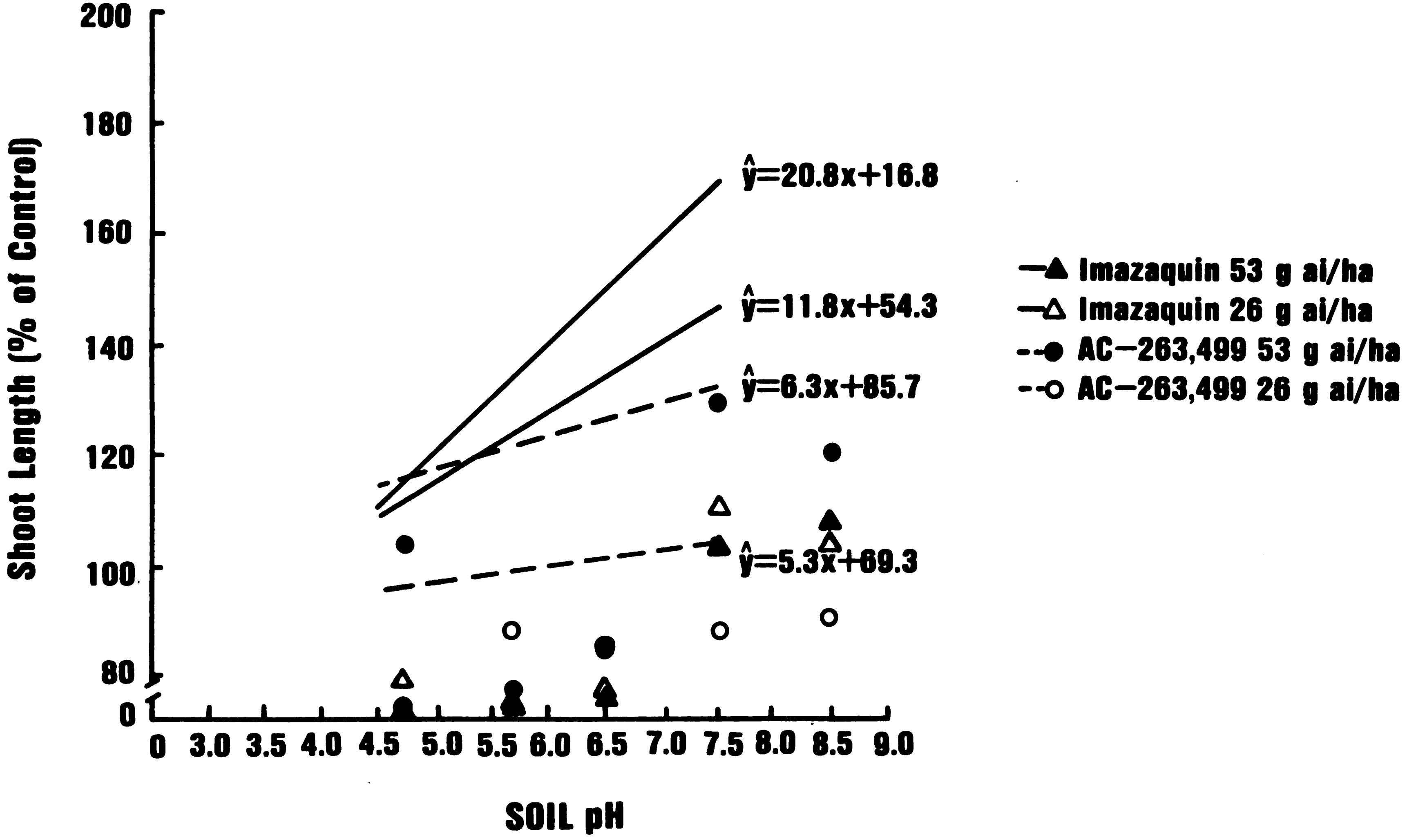

Shoot Length (% of Control)
100
90
80
70
60
50
0
Soil pH
3.0
4.0
5.0
6.0
7.0
8.0
9.0
$\hat{y}$=9.43x+27.9
$\hat{y}$=3.47x+62.9
$\hat{y}$=10.6x+2.33
$\hat{y}$=1.23x+73.5
▲ Imazaquin 53 g ai/ha
△ Imazaquin 26 g ai/ha
● AC—263,499 53 g ai/ha
○ AC—263,499 26 g ai/ha

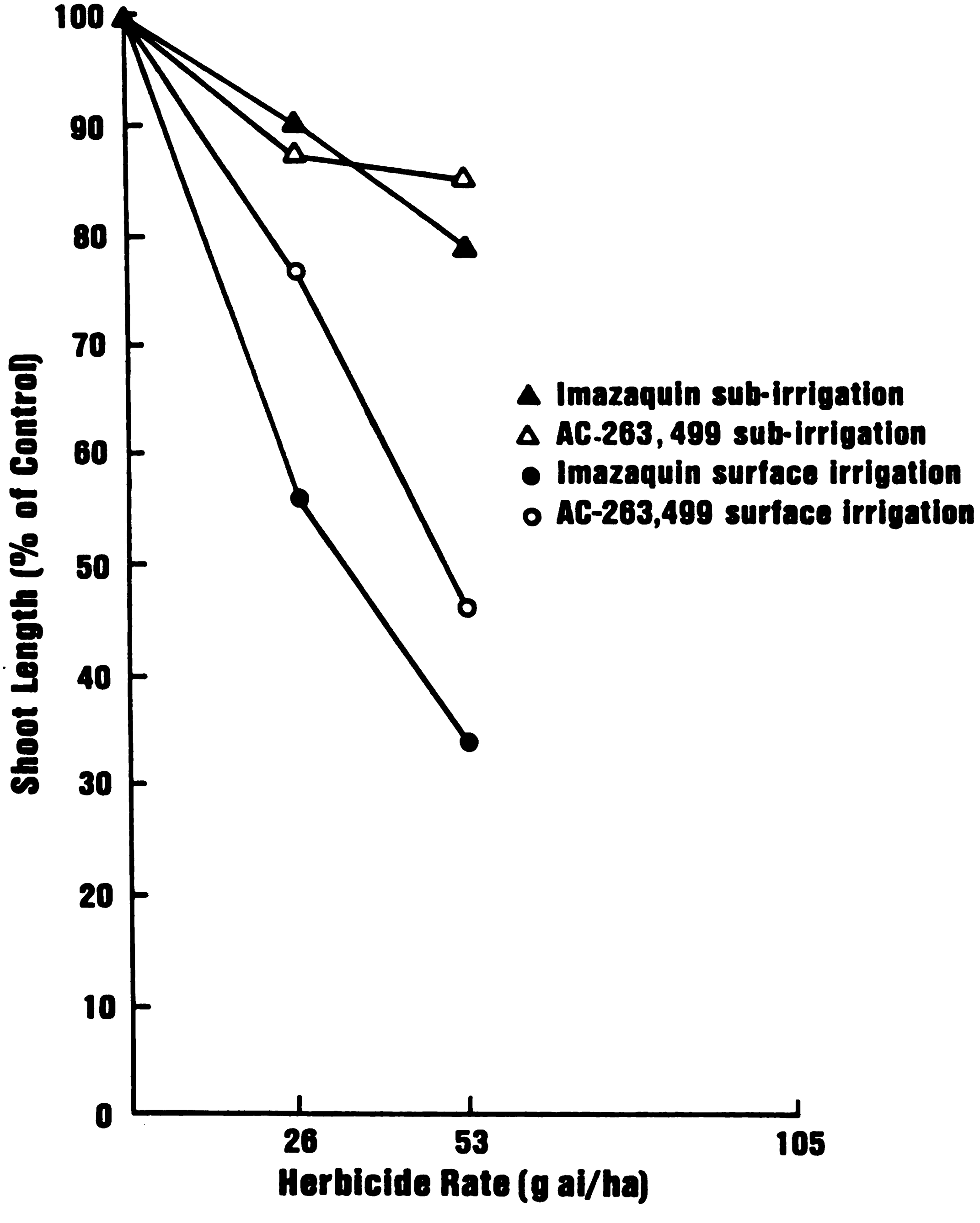
Figure 28: The effect of soil pH on injury to corn from 26 and 53 g ai/ha of imazaquin and AC-263,499 when sub-irrigated.


Shoot Length (% of Control)
200
180
160
140
120
100
80
0
0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
SOIL pH
ŷ=20.8x+16.8
ŷ=11.8x+54.3
ŷ=6.3x+85.7
ŷ=5.3x+69.3
▲ Imazaquin 53 g ai/ha
△ Imazaquin 26 g ai/ha
● AC—263,499 53 g ai/ha
○ AC—263,499 26 g ai/ha

The method of water addition to the pots altered the degree of corn injury. Imazaquin was 20% more phytotoxic to corn than AC-263,499 on a g/g basis when surface irrigated (Figure 29). Increased soil adsorption of AC-263,499, which was apparent in the adsorption studies, and/or the increased susceptibility of corn to imazaquin on a g/g basis, may account for the difference between imazaquin and AC-263,499 phytotoxicity to corn. There was no significant difference between imazaquin and AC-263,499 injury to corn under sub-irrigation. Injury was 40 to 50% less across all soil pH values and herbicide rates evaluated (Figure 29).

Researchers have shown that the method of water addition to the soil and the soil moisture content at the time of herbicide application are critical in determining herbicide availability (2, 15, 16). Isoproturon (N,N-dimethyl-N'-(4-(1-methylethyl)phenyl)urea) severely injured plants when watered from above but not when sub-irrigated (2). Hall et al. (15) found metsulfuron (2-(((((4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino)carboxyl)amino)sulfonyl)benzoic acid), chlorsulfuron, picloram, and clopyralid (3,6-dichloro-2-pyridine carboxylic acid) showed little herbicide activity on Canada thistle (Cirsium arvense (L.) Scop. CIRAR) when surface-applied to dry soils and sub-irrigated. When the soil surface was moist prior to herbicide application, all herbicides showed activity when surface irrigated and all herbicides but chlorsulfuron when sub-irrigated (15). Hance and Embling (16) applied linuron, metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one), and simazine to moist soil and to dry soil that was wetted to 20% field capacity 10 min and 24 h after herbicide application. Much lower herbicide

Figure 29: Corn height reduction from imazaquin and AC-263,499 across all soil pH levels under surface and sub-irrigation.

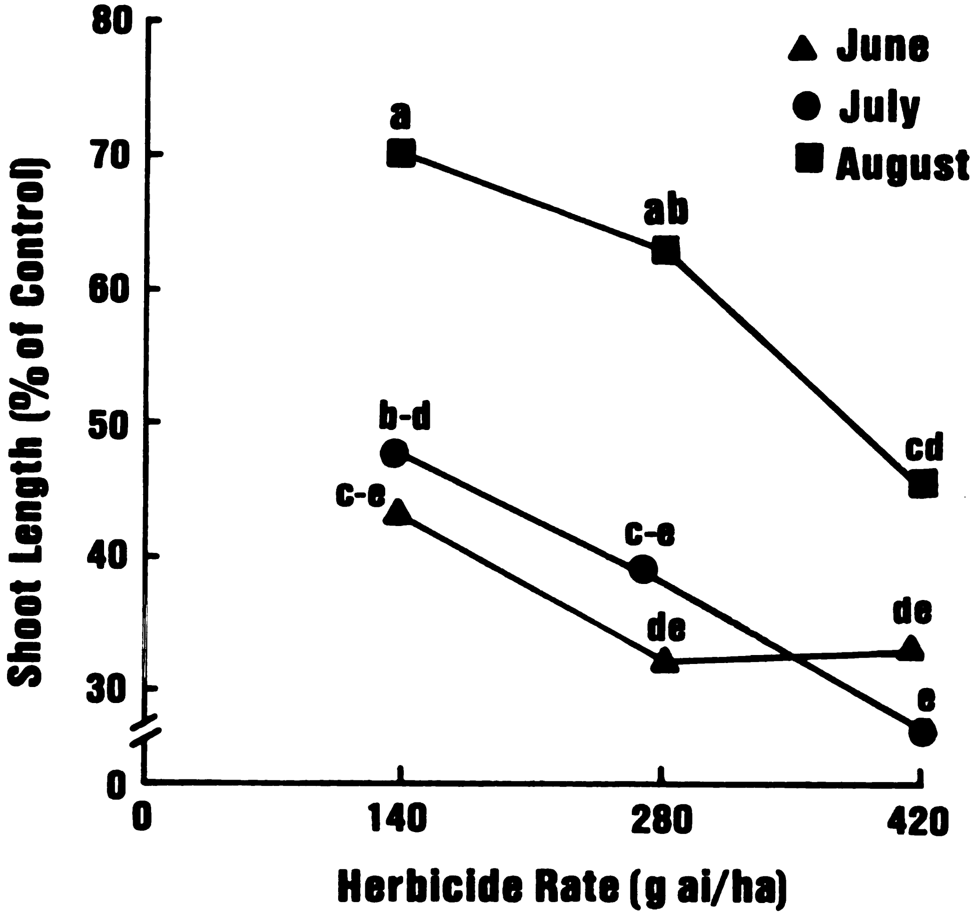

100
90
80
70
60
50
40
30
20
10
0
Shoot Length (% of Control)
26
53
105
Herbicide Rate (g ai/ha)
▲ Imazaquin sub-irrigation
△ AC-263, 499 sub-irrigation
● Imazaquin surface irrigation
○ AC-263,499 surface irrigation

concentrations were extracted with a pressure membrane cell when the soil had remained dry for 24 h after herbicide application prior to rewetting.

In this study, the herbicides were applied to dry soil and incorporated prior to adding water by either method. All water was retained in a second pot, so movement of water between pots or loss of herbicide by leaching could not occur. Root growth appeared similar under both watering systems. Greater injury occurred with surface watering. The herbicide may have moved into the lower soil profile and remained available for uptake under these conditions. With sub-irrigation the herbicides may have moved with capillary water up to the soil surface and were less available for root uptake resulting in decreased corn injury. The herbicides may have adsorbed to the dry soil particles and become inaccessible or unable to be displaced by capillary water movement with sub-irrigation, or precipitated out of solution and become unavailable for plant uptake (2, 15, 16).

Herbicide availability and persistence in the field. The main effect of planting date, and the interactions of soil pH by planting date and soil pH by herbicide rate were significant. In 1985, corn planted in August showed significantly less injury from imazaquin than corn planted in June and July. Soil pH had no significant effect on imazaquin injury to corn planted in June and July (Figure 30). There was more injury to corn planted in June of 1985 than June of 1984 across all pH levels and herbicide rates (Figure 31). Corn growth was reduced 30% when 140 g ai/ha of imazaquin was applied 90 days prior to corn planting in August of 1985.

Figure 30: The effect of planting date on imazaquin injury to corn in 1985 across all pH levels.



Shoot Length (% of Control)
80
70
60
50
40
30
0
0
140
280
420
Herbicide Rate (g ai/ha)
▲ June
● July
■ August
a
ab
cd
b-d
c-e
c-e
de
de
e

Figure 31: The comparison of imazaquin injury to corn planted in June 1984 and June 1985 across all pH levels.

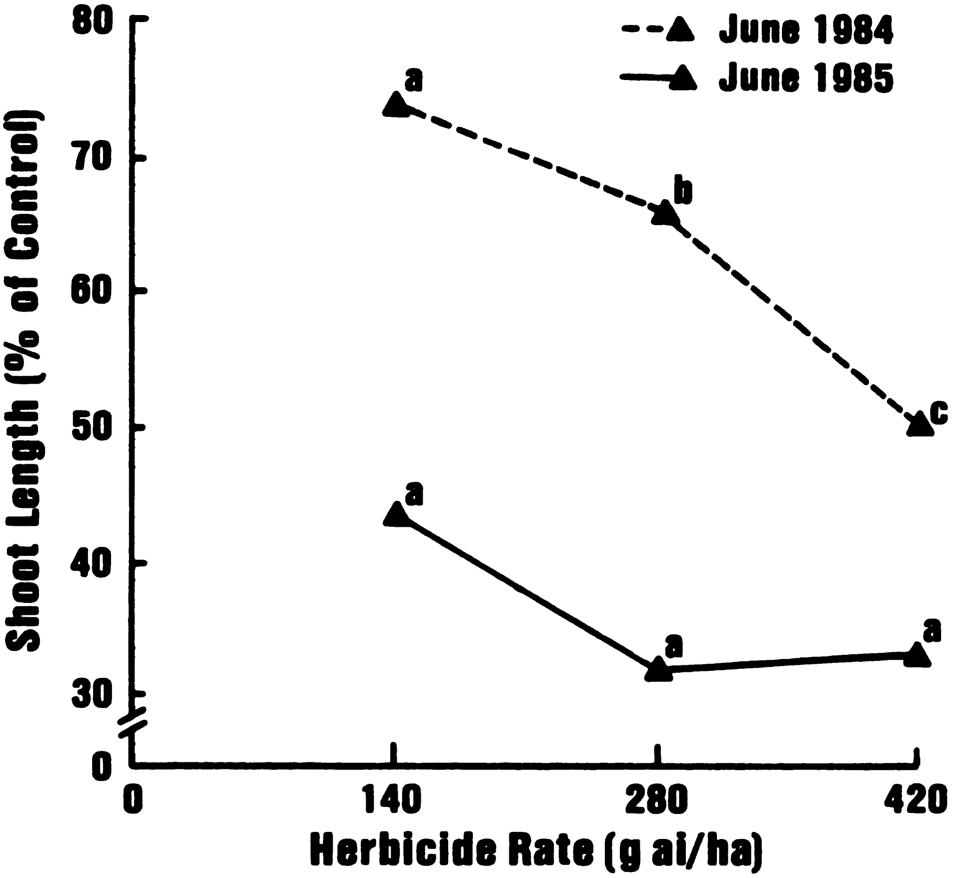
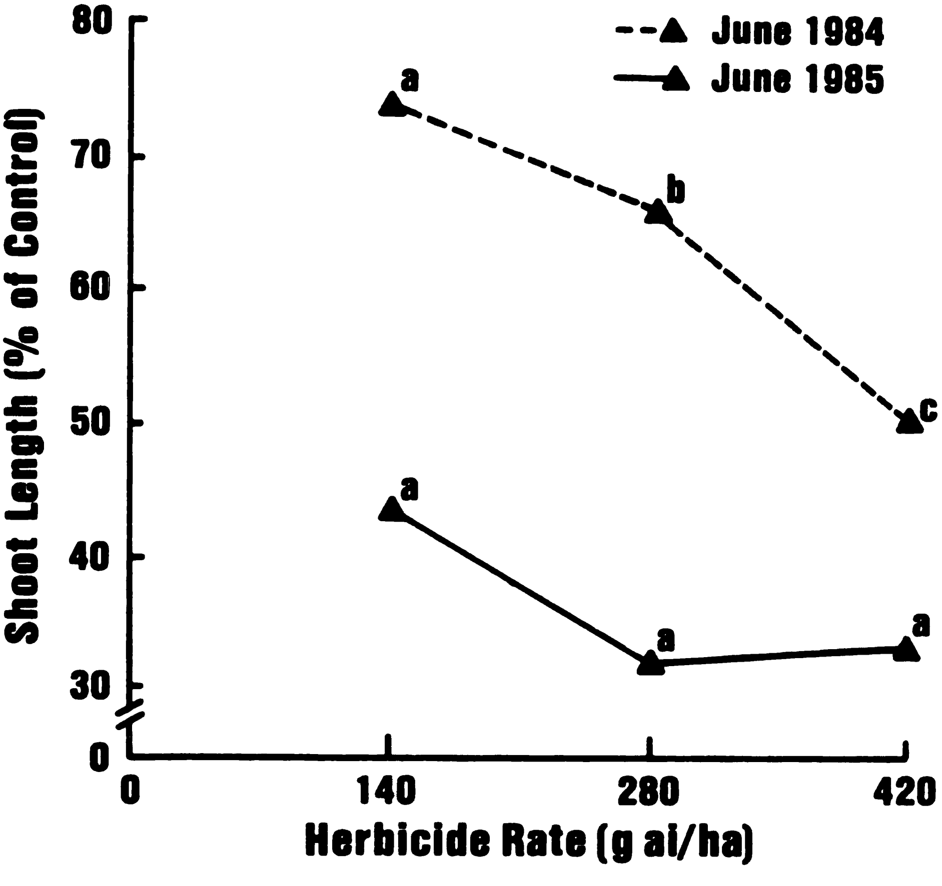

June 1984
June 1985
Shoot Length (% of Control)
80
70
60
50
40
30
0
a
b
c
a
a
a
0
140
280
420
Herbicide Rate (g ai/ha)

Figure 31: The comparison of imazaquin injury to corn planted in June 1984 and June 1985 across all pH levels.


June 1984
June 1985
Shoot Length (% of Control)
80
70
60
50
40
30
0
0
140
280
420
Herbicide Rate (g ai/ha)
a
b
c
a
a
a

Corn planted in July and August of 1985 showed no significant diference in corn injury from imazaquin across all pH levels (Figure 32). A significant decrease in injury to corn planted in June occurred at the higher soil pH level. This increased herbicide phytotoxicity to corn at the higher soil pH level did not occur for corn planted in July and August, possibly because of accelerated degradation at the lower soil pH values that resulted in equal concentrations of imazaquin available in July and August at all soil pH levels. If adsorption increased at lower soil pH values, corn injury would decrease at the lower soil pH, but this did not occur. Hiltbold and Buchanan (18) found atrazine persistence increased as soil pH increased due to decreased adsorption and hydrolysis. It appeared that adsorption of imazaquin increased at higher soil pH in June which caused a decrease in herbicide availability and corn injury. In July, imazaquin was desorbed, and injury was not reduced at the higher soil pH level. This is contrary to results obtained with certain acidic herbicides (18, 22, 24), but similar to picloram and chloramben behavior in the field (5).

The soil pH by herbicide rate interaction across all planting dates occurred because there was not a rate response at the higher pH level (Figure 33). There was no significant difference in corn injury in 1985 at the three pH levels at 140 g ai/ha. At the application rate of 280 g ai/ha, injury to corn was greater at pH values of 4.2 to 4.8 and 5.4 to 5.5.

When the results of the corn planted in June 1984 and June 1985 were compared, there was no difference in corn response to imazaquin application rates at the high pH level in 1985. In 1984, there was not a significant pH by herbicide rate interaction, although more injury at

Figure 32: The effect of soil pH on imazaquin persistence across all imazaquin application rates in 1985.

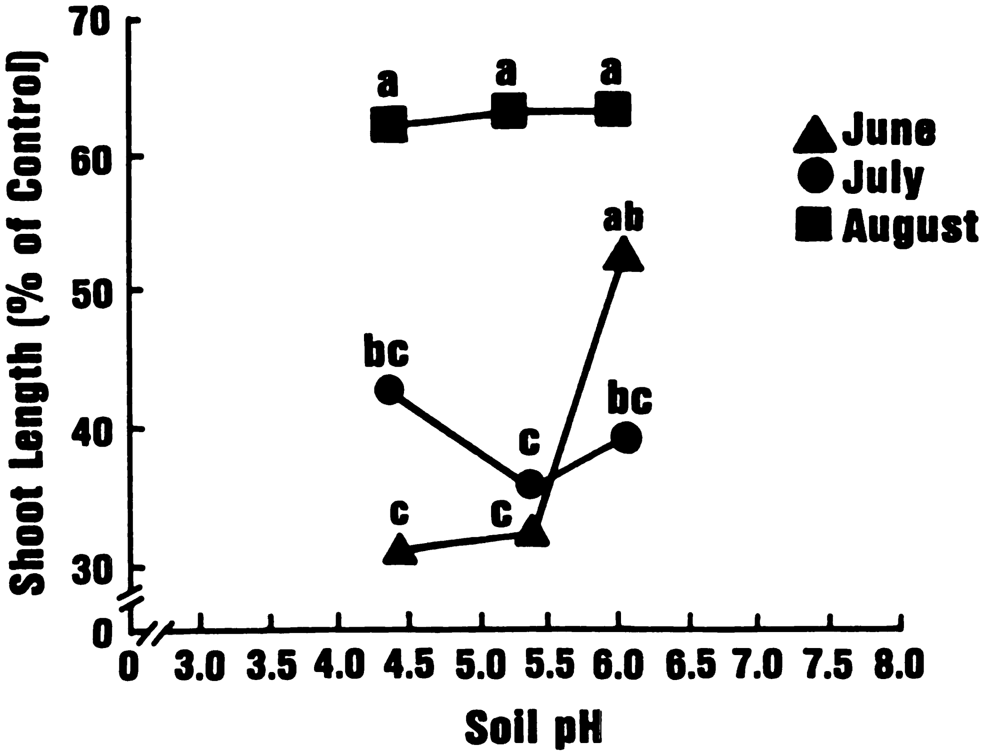
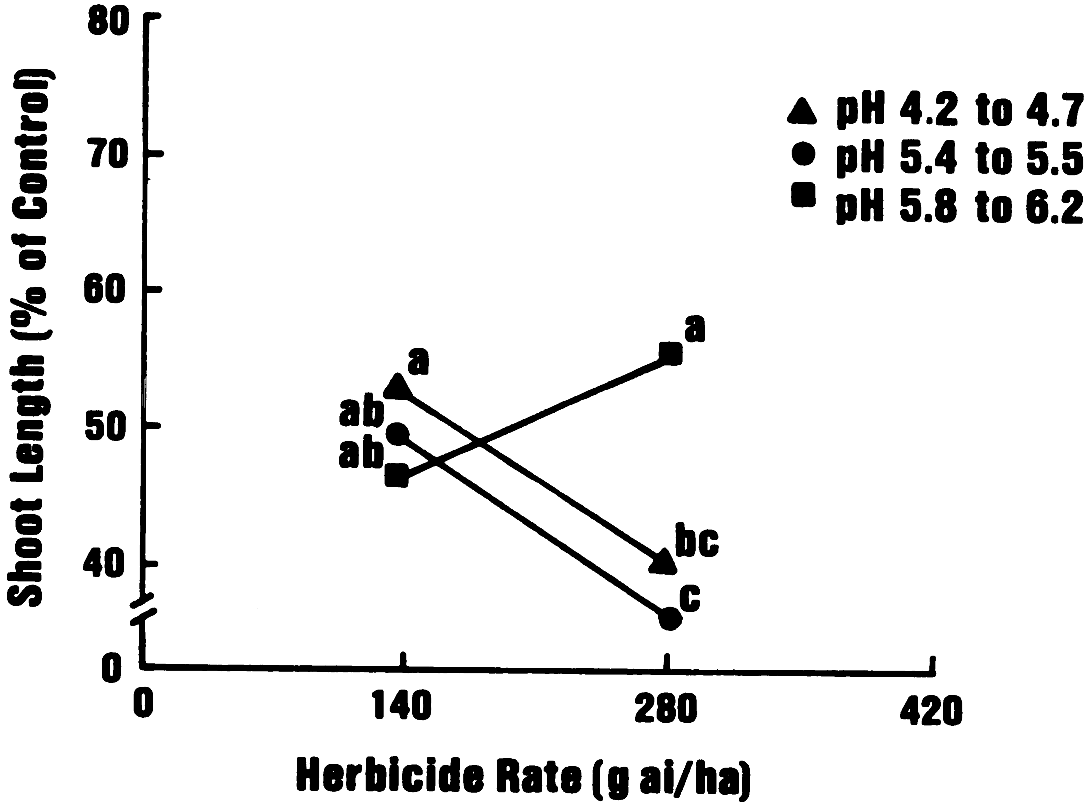

Shoot Length (% of Control)
70
60
50
40
30
0
0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
Soil pH
a
a
a
ab
bc
c
bc
c
c
▲ June
● July
■ August

Figure 33: The effect of soil pH on imazaquin application rate across all planting dates in 1985.


▲ pH 4.2 to 4.7
● pH 5.4 to 5.5
■ pH 5.8 to 6.2
Shoot Length (% of Control)
80
70
60
50
40
0
a
ab
ab
a
bc
c
0
140
280
420
Herbicide Rate (g ai/ha)

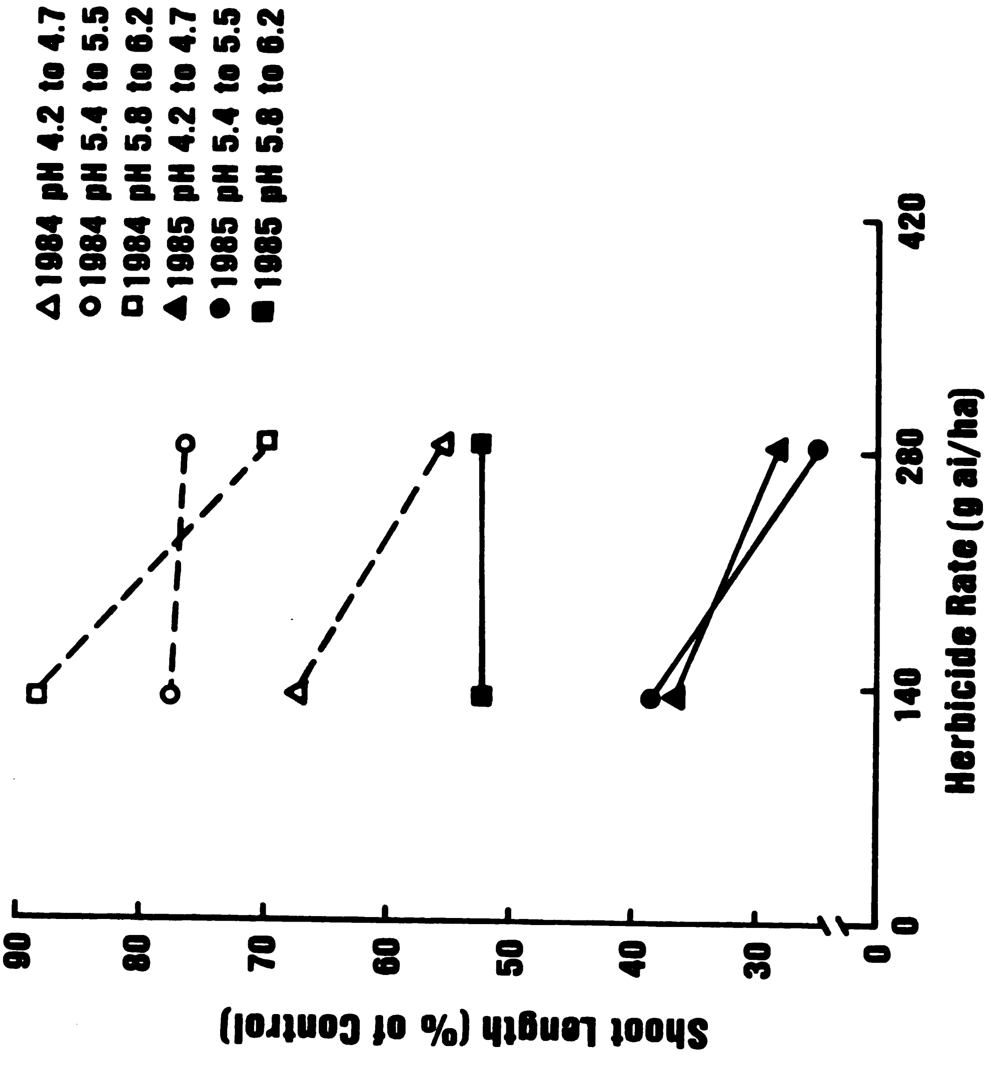
both application rates occurred at the low pH level (Figure 34).

Imazaquin persistence decreased during the growing season across all pH levels. In 1984, 11.25 cm of rain fell in the 30 days prior to planting of corn in June, and only 0.36 cm of rain fell during the 21 day period of corn growth. In 1985, 7.82 cm of rain fell in the 30 days prior to planting of corn in June, and 2.16 cm of rain fell during the corn growth period. In 1985, less imazaquin was taken up by corn due to decreased transpiration because of moisture stress, or because less imazaquin remained in the soil profile.

The corn planted in July 1985 received 11.91 cm of rain prior to planting, and 3.94 cm of rain during the 21 days of corn growth. Corn planted in August received 15.85 cm of rain prior to planting, and 8.61 cm during the 21 days of corn growth. An additional 4 cm of rainfall occurred prior to each planting date, yet there was no difference in injury to corn planted in June and July. Leaching of imazaquin or dilution in the soil profile may not be a factor. The corn planted in August received the most rain during the period of corn growth, yet had the least injury. This is in direct contrast to the increased injury to corn planted in June 1985, compared to the corn planted in June 1984 where very little rainfall occurred during the corn growth period. It is unclear whether moisture prior to or during corn growth is the more important factor in affecting corn injury from imazaquin.

At high soil pH levels, neither imazaquin nor AC-263,499 were adsorbed to soil, and thus increased availability and resulting corn injury should have occurred. However in greenhouse and field studies, a slight increase in corn injury occurred at lower pH values. The increased polarity and dissociation of imazaquin and AC-263,499 at

Figure 34: The effect of soil pH on corn injury from imazaquin at both application rates in June 1984 and June 1985.



△ 1984 pH 4.2 to 4.7
○ 1984 pH 5.4 to 5.5
□ 1984 pH 5.8 to 6.2
▲ 1985 pH 4.2 to 4.7
● 1985 pH 5.4 to 5.5
■ 1985 pH 5.8 to 6.2
Shoot Length (% of Control)
90
80
70
60
50
40
30
0
Herbicide Rate (g ai/ha)
0
140
280
420

higher pH levels may result in unfavorable plant uptake of the anionic herbicide forms. Alternatively, some form of adsorption such as anion exchange may have occurred in greenhouse and field studies under alternating moisture conditions. Imazaquin and AC-263,499 may bind to aluminum or iron hydroxides or other forms of iron present in the soil matrix, as high concentrations of iron were present in this soil.

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CHAPTER 6

SUMMARY AND CONCLUSIONS

Imazaquin and AC-263,499 are selective herbicides for grass and broadleaf weed control in soybeans. They are both weak acids with pKa values of 3.8 and 3.9 for imazaquin and AC-263,499, respectively. Little information is available regarding the behavior of these herbicides in soil. Soil properties can alter the adsorption of herbicides to soil, and their subsequent availability to plants and soil persistence. Because these are acidic herbicides, soil pH may be an important factor influencing their persistence.

Injury to corn has occurred when corn was planted the year following imazaquin application to soybeans. The persistence of imazaquin in soil has not been linked to any specific soil or edaphic factor, or correlated to differences in corn cultivar susceptibility to these herbicides. Experiments were designed to determine corn cultivar response to imazaquin and to determine if herbicide application method and rate, spring tillage, and/or soil pH altered imazaquin persistence in the soil and availability to corn. Soil adsorption studies were designed to determine if any soil property significantly affected adsorption of imazaquin and AC-263,499 and if soil adsorption results reflected availability and subsequent injury to corn grown in various soils.

The nine cultivars differed in their response to imazaquin. Cargill 921, Great Lakes 422, and Great Lakes 5922 were among the more tolerant cultivars, while Pioneer 3737 and Stauffer 5650 were among the less tolerant cultivars. However no cultivar showed tolerance to imazaquin at 70 g ai/ha, which is 50% of the labeled use rate in soybeans. Corn injury was significantly greater across all cultivars in the first year of study. The increased moisture level in the soil that year may have increased the availability of imazaquin to corn by decreasing soil sorption, or possibly root uptake exceeded the ability of corn to metabolize imazaquin.

Imazaquin persistence in the soil was significantly greater when the herbicide was preplant incorporated instead of applied as a preemergence surface application in 1985. Imazaquin dissipated rapidly during the first 30 days after application, and a decreased dissipation rate occurred in the next 120 days. Injury to corn planted in 1985 was greatest where imazaquin had been incorporated at 140 and 280 g ai/ha in 1984. However, injury to corn was evident where PES applications of 70 to 280 g ai/ha were made. There was no significant difference in corn injury from imazaquin between spring moldboard plowed and disked plots across both application methods and herbicide rates.

Soil adsorption of imazaquin and AC-263,499 increased as soil pH decreased from 8.0 to 3.0. However, adsorption was very low for all soils having inherent soil pH values from 5.9 to 7.3. Kd values ranged from 0.056 to 0.113 for imazaquin, and 0.60 to 0.761 for AC-263,499. Soil containing the most organic matter, smectite clay, iron, and the highest inherent pH adsorbed the greatest amount of imazaquin. Soil with the highest silt percentage and lowest pH had the greatest AC-

263,499 adsorption. Removal of organic matter had no effect on imazaquin adsorption, but increased AC-263,499 adsorption.

Imazaquin was 42% more phytotoxic to corn than AC-263,499. Injury to corn on four soils decreased over time, with corn grown on the soil containing the highest percentage of smectite clay, organic matter, iron, and the highest soil pH having the least corn injury. Soil pH had no effect on AC-263,499 phytotoxicity to corn, but as soil pH increased, phytotoxicity to corn from imazaquin decreased. Imazaquin injury to corn decreased as the time period between application and corn planting increased. Injury to corn planted in June was less at soil pH 5.8 to 6.2, but soil pH had no effect on imazaquin injury to corn planted in July and August.

An approach to avoid crop injury due to the persistence of these compounds in soil is suggested by these research results. Development of a corn cultivar tolerant to imazaquin would reduce the risk of injury to corn planted as the rotational crop into a field where imazaquin was applied in soybeans. Lower application rates may result in less imazaquin persisting in the soil. However, the herbicide level at which the dissipation rate slowed varied with the year and method of application more than the herbicide rate applied. Therefore, that may not be the most effective method of avoiding imazaquin persistence. Preemergence surface applications would reduce the degree of imazaquin persistence in the soil. Photolytic hydrolysis or some other transfer or transformation process appeared to decrease the persistence of preemergence surface applications. Different spring tillage methods did not appear to reduce crop injury. Possibly fall tillage may be an effective method in reducing or diluting the herbicide persisting in the soil. AC-263,499 was less injurious to corn, and would be a better choice than imazaquin as a soybean herbicide if corn is planted as the rotational crop.

Adsorption to soil decreased as pH increased from 3.0 to 8.0, and AC-263,499 had greater adsorption than imazaquin across all pH levels. Increased availability of imazaquin and AC-263,499 may occur as soil pH is increased and phytotoxicity to sensitive plants increased. However in greenhouse studies, soil pH had no significant effect on AC-263,499 phytotoxicity to corn, and corn injury from imazaquin decreased slightly as soil pH increased. Herbicide precipitation, changing moisture levels, a difference in soil adsorption under dry conditions, or reduced plant uptake due to increased polarity of the herbicides, could all be factors affecting imazaquin and AC-263,499 availability to plants.

Soil adsorption was very low under excessive moisture conditions in laboratory studies. Alternating moisture conditions may be important in imazaquin and AC-263,499 binding to soil. Further adsorption research with fluctuating moisture levels would be necessary to determine if imazaquin and AC-263,499 adsorption is increased under changing moisture conditions.

It is not clear which soil property, if any, influences the persistence of these herbicides in the soil. Because of the correlation between soil properties such as the cation exchange capacity, the percent of organic matter, and the percent of clay, it cannot be determined which of these would be most important in soil adsorption of herbicides. Soil pH appeared to be important in adsorption under excessive moisture conditions in laboratory studies, but under field conditions pH had a smaller and reversed effect from what occurred in the laboratory. The soil that appeared to adsorb the greatest amount of AC-263,499 had the lowest pH and the highest percentage of silt. The soil that adsorbed the most imazaquin, and had the least corn injury for both herbicides, was the soil that contained the highest percentage of smectite clay, organic matter, iron, and had the highest soil pH. When the organic matter was removed from a soil, imazaquin adsorption was not affected. Further research would need to be conducted to determine the importance of iron in imazaquin and AC-263,499 adsorption, and the importance of kaolinite and smectite clays on herbicide binding. By designing a dynamic system where the affects of wetting and drying cycles on imazaquin and AC-263,499 binding to soil could be studied, the implications of changing moisture levels present in the field environment could be determined. The soil persistence of imazaquin and AC-263,499 may be dealt with on a cultural basis by making only PES applications at low application rates and planting a more tolerant corn cultivar. These herbicides could be used in crop production, but the factors involved in the binding or nontransformation or transfer of these acidic herbicides that results in their lengthy soil persistence need to be determined.