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FIELD, GREENHOUSE, AND LABORATORY STUDIES ON THE
EFFICACY AND ACTION OF THE HERBICIDES
SC-0051 AND SC-0774

by

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(ABSTRACT)

SC-0051 and SC-0774 are two experimental herbicides of undisclosed chemistry. A three year field study was conducted to evaluate SC-0051 and SC-0774 for weed control in conventional and no-till corn in Virginia. SC-0051, applied preemergence or postemergence, controlled common lambs-quarters (Chenopodium album L.), common ragweed (Ambrosia artemisiifolia L.), horseweed (Conyza canadensis (L.) Cronq.), common chickweed (Stellaria media (L.) Vill.) and was safe to corn. SC-0051 did not control smooth pigweed (Amaranthus hybridus L.) or giant foxtail (Setaria faberii Herrm.). SC-0774 effectively controlled the rye (Secale cereale) cover crop and large crabgrass (Digitaria sanguinalis (L.) Scop.) but did not control broadleaf weeds or giant foxtail. SC-0774 also caused considerable but temporary corn injury when applied at rates above 1.1 kg/ha. Combinations of SC-0051 and atrazine provided broad spectrum weed control and yields comparable to atrazine plus metolachlor. Field and laboratory studies were conducted to evaluate the effect of soil pH on the soil mobility of SC-0051 and SC-0774 in sandy loam soils. SC-0774 was applied to soils amended to high and low pH and samples were collected by depth throughout the growing season. A method was developed for extracting and quantifying SC-0774 from collected soil samples. Large crabgrass was also used as a bioindicator species for qualitative detection of SC-0774 residues. These studies showed that SC-0774 was significantly more mobile in high pH soil than in low pH

soil. Also, the decreased mobility of SC-0774 at low soil pH lead to decreased corn injury but it increased the soil residual activity of this herbicide. Soil column studies with SC-0774 and SC-0051 showed that the soil mobility of both herbicides increased with increasing soil pH. These herbicides cause reductions in chlorophyll and carotenoid levels in susceptible species resulting in a bleached appearance. The mechanism of this bleaching action is not known. Studies were conducted which examined the effect of SC-0051 on the pigment content and quantity in the susceptible species soybean. High performance liquid chromatography was used to separate, quantify, and identify pigments present in extracts of bleached tissues. The bleaching herbicide norflurazon was also examined for comparison purposes. SC-0051 and norflurazon inhibited the biosynthesis of carotenoids while causing an accumulation of the carotene precursor phytoene and an additional, unidentified pigment that appears to be structurally related to phytoene. This indicates that SC-0051, like norflurazon, inhibits carotenoid formation by blocking the desaturation of phytoene to phytofluene. The uptake and translocation of ^{14}C -SC-0051 into tolerant corn and susceptible soybean seedlings was examined under growth chamber conditions to investigate the basis for the selectivity of this herbicide. Herbicide uptake was similar in both species but the susceptible soybean translocated a higher percentage of the ^{14}C -SC-0051 to the growing point of new tissues than did the tolerant corn. It is proposed that differential translocation plays a role in the crop selectivity of the herbicide SC-0051.

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I. LITERATURE REVIEW

CURRENT CORN WEED CONTROL PROGRAMS

In 1985, nearly 80 million acres of corn were planted in the U.S. with 650,000 acres in Virginia (100). Competition from weeds is estimated to reduce corn yields in the U.S. by approximately 10%. This reduction has a value of several billion dollars (6). Yield reductions are even greater in other corn-producing countries (6). Of the herbicides available for use in corn, only nine are commonly used and fall into five classes: triazines, chloroacetamides, thiocarbamates, phenoxyacetic acids, and benzoic acids.

The commonly used s-triazines are 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 cyanazine (2-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl] amino]-2-methyl propanenitrile). Triazines are generally applied as preemergence treatments for the control of broadleaf weeds and some annual grass species. Atrazine has been used in corn for more than two decades. The relatively low cost combined with its broad spectrum weed control has allowed atrazine to capture 40% of the U.S. corn herbicide market (84). However, the continuous use of

atrazine in corn has induced the development of resistance in weed species previously controlled with triazines. As of 1986, 48 different species of triazine-resistant weeds have been reported worldwide, 18 of which being reported in the United States (54, 55). Triazine-resistant smooth pigweed (Amaranthus hybridus L. # AMACH) and common lambsquarters (Chenopodium album L. # CHEAL) were recently reported in western areas of Virginia and in Maryland (71, 81, 91).

The chloroacetamides alachlor [2-chloro-N-(2,6-diethyl phenyl)-N-(methoxymethyl)acetamide] and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl ethyl)acetamide] are the most commonly used herbicides for controlling annual grasses in corn. They are applied primarily preemergence, and provide good initial control, but may lack sufficient residual activity (100). The thiocarbonates butylate [S-ethyl bis(2-methylpropyl) carbamothioate] and EPTC (S-ethyl dipropyl carbamothioate) are also used to control annual grasses in corn. These compounds also have activity on some perennial species, including yellow nut-sedge (Cyperus esculentus L. # CYPES), and johnsongrass [Sorghum halepense (L.) Pers. # SORHA] (95). Thiocarbonates, however, require incorporation to prevent loss from volatilization and need to be safened to increase crop tolerance.

Dicamba (3,6-dichloro-2-methoxybenzoic acid), a benzoic

acid herbicide, and 2,4-D [(2,4-dichlorophenoxy)acetic acid], a phenoxyacetic acid, are used as postemergence treatments for controlling broadleaf weeds. They are inexpensive and effective, but at normal use rates provide little residual activity. Application timing is critical with these herbicides to avoid stalk brittleness and brace root malformation in corn. These herbicides are also prone to off site movement because of high volatility of some formulations which creates the possibility of injury to susceptible plants nearby.

Herbicide options for postemergence control of grasses in corn are limited. Triazines have some postemergence activity on annual grasses. However, control is acceptable only when grasses are treated before they reach 4 cm in height. The chemical tridiphane [2-(3,5-dichlorophenyl)-2-(2,2,2-trichloroethyl)oxirane], combined with atrazine, has shown promise for controlling seedling grasses (98). However, some research suggests this combination may not be more effective than atrazine alone or cyanazine applied postemergence (72).

Other herbicides used less frequently but which play an important role in corn production include pendimethalin [N -(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine], ametryn [N -ethyl- N' -(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine], and linuron [N' -(3,4-dichlorophenyl)- N -methoxy- N -methylurea]. Pendimethalin is used as a preem-

ergence treatment in areas where velvetleaf (Abutilon theophrasti Medik. # ABUTH) and/or triazine resistant common lambsquarters are problems. Ametryn and linuron are used as post-directed treatments for broad-spectrum weed control and are usually salvage treatments (95).

The development of triazine resistance by many weed species and the need for a more effective postemergence grass herbicide in corn are two areas that need to be addressed by herbicide researchers in university and industry. The herbicides SC-0051 and SC-0774 are two experimental herbicides from a new chemical class that have shown some promise in meeting these needs. These compounds were originally introduced by the Stauffer Chemical Company and are now being developed by ICI Americas, Inc. SC-0051 has shown potential as a preemergence or postemergence herbicide for control of broadleaf weeds and some grasses in corn, wheat, sorghum, and turf (20, 49, 51, 59, 60, 64, 73, 80, 86, 92, 94). SC-0774 has shown potential as a preemergence herbicide for control of grasses and some broadleaf weeds in corn (7, 51, 59, 60, 63, 87).

BASES FOR HERBICIDE SELECTIVITY

Introduction

Selective herbicides control unwanted vegetation while not harming desirable plants. Herbicide selectivity is crucial in agriculture since the benefits of weed control must not be lost to crop injury. Herbicide selectivity is the result of either differences in the response of plant species to an applied herbicide (true selectivity) or in the careful application of a herbicide to maximize contact with undesirable vegetation while minimizing contact with desirable species (placement selectivity).

SC-0051 and SC-0774 are used selectively in corn. The basis for their selectivity is currently unknown, although research has shown that the tolerance of corn to SC-0774 can be increased through the use of chemical safeners (21, 59, 60). The action(s) of these safeners are not known with certainty but safener-induced increases in glutathione and/or glutathione-*s*-transferase enzyme levels have been implicated (15, 52, 53).

Placement Selectivity

The herbicides glyphosate [N-(phosphonomethyl)glycine] and paraquat (1,1'-dimethyl-4-4'-bipyridinium ion) kill almost all plants they contact. These "non-selective" herbicides are used extensively in no-till crop production to

kill weeds present at planting. They have almost no soil activity because they are tightly adsorbed to soil particles and therefore are not available for shoot or root uptake. Therefore, these herbicides are selective by differential placement in time.

Some non-selective herbicides are made "selective" by carefully applying the material in such a way as to maximize contact with weed species while minimizing contact with the crop. Examples include the use of ametryn or linuron as postemergence-directed treatments for control of weeds in corn or the use of glyphosate in a ropewick applicator to control johnsongrass in soybeans [Glycine max (L.) Merr.]. Other methods of placement selectivity include seeding a crop below the herbicide zone [cotton with CDAA (2-chloro-N,N-di-2-propenylacetamide) or placing an adsorptive barrier (activated charcoal) between the crop seed and the herbicide (1)].

True Selectivity

Most commercially important herbicides possess some type of selectivity towards a particular crop. There are several mechanisms by which plant species are able to tolerate potentially lethal herbicide doses. The primary strategy is to minimize the amount of herbicide reaching the biochemical site(s) of action.

There are certain limits to which a plant species can

tolerate potentially lethal herbicide doses resulting in herbicide selectivity. These limits are controlled by the complex interaction between the plants age, stage of development, genetics, morphology, the chemistry of the herbicide, and the environment. Plant age is a factor in that young, actively growing plants are generally more susceptible to herbicide injury. Stage of growth can affect susceptibility as is illustrated by the use of growth regulator herbicides in corn. The recommended time for the application of 2,4-D in corn is before corn gets to be 20-25 cm in height (95). After this time, the corn plant is much more susceptible to growth regulator injury and may develop stalk brittleness and/or brace root malformation.

Genetic differences among plants vary substantially and can affect selectivity. Differences in varietal response of many crops and weed species to herbicides have been documented (1, 74, 95). In most cases, differences in response appear to be due to differences in herbicide uptake and/or metabolism. However in the case of species of common lambsquarters and smooth pigweed showing selectivity to triazine herbicides, resistance results from differences in the molecular structure of the triazine binding protein in the chloroplast, which prevents these herbicides from binding to their active site.

The chemistry of the herbicide can profoundly affect herbicide selectivity. The molecular structure, herbicide

formulation and concentration all play a role. For example, the herbicides metsulfuron-methyl [2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) amino] carbonyl] amino] sulfonyl] benzoic acid] and chlorsulfuron [2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino] carbonyl] benznesulfonamide] are both from the family of sulfonylurea herbicides. These compounds differ by only slight changes in the substituent pattern around the sulfonylurea backbone. Despite their similarities, metsulfuron-methyl is non-selective while chlorsulfuron is used selectively in small grains. An example of selectivity due to formulation is the use of cyanazine for postemergence control of annual grasses in corn. The wettable powder formulation of cyanazine can be used postemergence in corn safely, whereas use of the emulsifiable concentrate formulation often results in substantial corn injury (95). Also, the use of adjuvants can affect selectivity. The herbicide chlorimuron-ethyl is used postemergence in soybeans to selectively remove large-seeded broadleaf weeds. Research has shown that the addition of a crop oil concentrate to enhance weed control also greatly reduces soybean tolerance to this herbicide (93).

Herbicides are selective in that the rates necessary to control weed species are significantly lower than the rates which cause crop injury. Quite often, crop injury occurs in areas where the spray pattern overlaps resulting in a double application of the herbicide. Therefore, careful

sprayer calibration and use of application equipment is essential in maximizing herbicide selectivity.

Two of the most important factors in herbicide selectivity are differential uptake and metabolism. Selectivity resulting from differential uptake may be due to a greater retention of a herbicide on the foliage or to increased penetration into the leaf or roots of weeds versus the crop. Variations in plant shape, leaf position, the presence or absence of leaf hairs, and surface characteristics can lead to differences in foliar retention. Plants with broad, horizontally oriented leaves are more likely to intercept and retain a spray than are plants with thin, vertically oriented leaves such as grasses and sedges. Selective control of broadleaf weeds in onions by postemergence applications of sulfuric acid solutions is thought to be due largely to differential wetting (74).

Several factors appear to influence herbicide penetration across leaf surfaces and into roots (1, 2, 26, 27, 50, 74). Penetration into the leaf is affected mainly by the nature and thickness of the cuticle. The cuticle is a lipoidal, non-cellular, non-living membrane covering the leaves and stems of plants which minimizes water loss and acts as a barrier to the penetration of exogenous materials.

The physicochemical properties of the cuticle in relation to herbicide absorption have been reviewed by several

workers (44, 58) and its importance as a barrier to herbicide penetration has been demonstrated (99). Researchers observed increased herbicide uptake into plants pretreated with chemicals that reduce cuticle thickness over that of untreated plants (28, 99).

The cuticle is a complex matrix made up of an outer layer of epicuticular wax followed by a layer of cutin. Under cutin lies a layer made up primarily of pectins which cover the walls of the underlying cells. The chemical nature of these layers results in a gradient of hydrophobicity. The outer layer of epicuticular wax is composed of complex mixtures of long-chained alkanes, primary and secondary alcohols, ketones, aldehydes, fatty and hydroxy fatty acids and esters (27). Layers with a high alkane or ketone content tend to be relatively hydrophobic, while layers rich in alcohols are more easily wetted (43). Cutin is a polyester of long-chain fatty and hydroxy fatty acids. It has hydrophilic characteristics due to the presence of hydroxyl and carboxyl groups and lipophilic properties due to the presence of methyl and methylene groups. Pectins are primarily polysaccharide polymers of polyuronic acids (32). Their highly hydroxylated nature makes them hydrophilic.

The gradient in polarity present in plant cuticles means polar compounds have considerable difficulty entering the epicuticular wax. However, once they pass this barrier

they enter each succeeding layer more easily. In contrast, nonpolar compounds readily enter the epicuticular wax but have increasing difficulty in passing into each succeeding layer. Thus, the polarity of a herbicide can greatly influence its rate of penetration.

The importance of herbicide uptake through stomata remains controversial. It has been shown that absorption of foliar applied herbicides is generally greater through the abaxial leaf surfaces of dicot weeds (17, 44, 79). This has been partly attributed to the greater number of stomata on that surface. Researchers (24, 34) have shown that under certain conditions, spray solution may move in mass through the stomatal pore or through the cuticle over the guard or accessory cells (which may be more permeable than that over the epidermal cells). The mechanism of pore penetration is complex. The surface tension and contact angle of the droplet as well as the morphology and chemistry of the pore wall must be considered. Penetration of the pore can occur only if the surface tension of the spray droplets is equal to or less than the critical surface tension of the plant surface. The critical surface tension of many cuticular surfaces is approximately 30 dyn/cm, but few commonly used surfactants reduce surface tension below this figure (27). Therefore, it is uncertain whether penetration of the stomatal pore occurs or if it is an important means of herbicide uptake. Some researchers believe that preferential

penetration of the guard cells is more probable than entry via the pore (79).

Some plant species are able to tolerate lethal doses of herbicide by chemically metabolizing the molecule rendering it less phytotoxic. There are many documented mechanisms of herbicide metabolism (41). Some include herbicide decarboxylation, hydroxylation, hydrolysis, and dealkylation, and conjugation to natural substances.

The classic example of herbicide selectivity due to plant metabolism is that of the triazine herbicides. Triazines control a wide spectrum of broadleaf weeds and some grasses while corn is quite tolerant. Tolerance of corn and several grass species (90) to triazines is the result of rapid metabolism. Corn metabolizes triazines in several ways (41). The most important mechanism appears to be the enzymatic conjugation of triazine herbicides with the tripeptide glutathione (29, 35). The resulting conjugate is not phytotoxic. Corn varieties deficient in the enzyme responsible for catalyzing the conjugation reaction, GSH-s-transferase, are susceptible to atrazine (82) illustrating the importance of this process to corn tolerance. Glutathione conjugation has also been implicated in corn tolerance to the chloroacetamide and the thiocarbamate herbicides (15, 53). Other types of triazine metabolism have also been demonstrated; including N-dealkylation and hydrolysis (39, 83). The role each type of mechanism plays in

the metabolism of triazine herbicides depends upon the particular herbicide and the plant species.

MODES OF ACTION OF BLEACHING HERBICIDES

Introduction

Carotenoids are an important class of pigments found in higher plants, algae, fungi and bacteria. Almost 500 carotenoids have been identified with about 25 % being isolated from higher plants (18). The intense color of carotenoids made them ideally suited to play an important role in the development of such analytical procedures as adsorption chromatography and absorption spectrophotometry. Important carotenoids found in higher plants include α -carotene, β -carotene, lutein, violaxanthin, and neoxanthin. They are found in chloroplasts of photosynthetic tissues as well as in the petals, anthers and pollen of some flowers. Carotenoids found in algal families include fucoxanthin, which is present in Phaeophyceae and gives them a brown color, and carotenoid glucosides which are present in high quantities in blue-green algae.

The presence of carotenoids in higher plants is critical as is illustrated by the inability of mutants lacking carotenoids to survive in the natural environment. Inhibition of carotenoid biosynthesis provides a desirable target for herbicides since this pathway is not present in mammalian systems. Several commercially available herbicides act by inhibiting carotenoid biosynthesis: including the pyridazinones, aminotriazole, some diphenyl ethers and cloma-

zone.

Functions of Carotenoids

Measurements of the action spectrum for photosynthesis indicate that light absorbed by carotenoids (400-500 nm) is photosynthetically active (23). In studies with higher plants and algae, Emerson and Lewis (25) found carotenoids to be roughly half as effective as chlorophyll in photosynthesis, while Tanada (89) found the fucoxanthin in brown algae to be almost as efficient as chlorophyll. Fractions of disrupted chloroplast preparations enriched in PS-I have been shown to contain about 50 carotenoids (mainly carotenes) per molecule of chlorophyll a_{700} . Fractions enriched in PS-II show a similar number (mainly xanthophylls) per molecule of chlorophyll a_{680} . Thus, carotenoids function as accessory pigments in photosynthesis by supplementing the light-harvesting ability of chlorophyll. In order for carotenoids to be effective, absorbed energy must be transferred to chlorophyll. This involves resonance transfer of energy from carotenoids to chlorophyll (32).

The most important function of carotenoids is preventing photodynamic damage in the chloroplasts. Photodynamic damage occurs when oxygen in the first excited singlet state is formed in vivo. Atmospheric oxygen exists in the ground state as a triplet, in which valence electrons have paired spins, while most organic molecules exist as ground

state singlets, in which valence electrons have opposite spins. Reaction between a ground state triplet molecule and a ground state singlet molecule is a spin-forbidden process. For this reason, organic molecules are able to exist in the atmosphere (21% oxygen) without being oxidized. Normally, photosynthesis is carried out by chlorophylls in the first excited singlet state. However, in the presence of excess quanta, some chlorophyll may be converted via intersystem crossing (conversion of an electron from one type of excited state to another type) to the metastable triplet excited state. Chlorophyll in the excited triplet state is capable of reacting with oxygen (spin-allowed process) to form singlet oxygen and ground state chlorophyll. Singlet oxygen is highly reactive and capable of oxidizing chlorophyll and membrane lipids, which can lead to a loss of plant color (bleaching) and eventually plant death.

Carotenoids are known to protect plants from photodynamic damage in three different ways. First, carotenoids are able to quench about 90% of the chlorophyll excited to the first triplet state. Ground state carotenoids are able to react with excited triplet chlorophyll molecules to form ground state singlet chlorophyll and excited triplet carotenoids. Excited triplet carotenoids do not transfer their energy to oxygen, instead, they lose energy through intersystem crossing and the vibrational cascade (electrons falling from high energy vibrational levels to lower energy

levels within the same excited state). Energy is ultimately lost as heat. In this mechanism, carotenoids compete with oxygen for reacting with triplet chlorophyll. Secondly, carotenoids are able to quench excited triplet oxygen directly and efficiently (99.999%). In this reaction, ground state carotenoids quench singlet oxygen to form ground state triplet oxygen and excited triplet carotenoids. Triplet carotenoids are harmlessly converted to ground state carotenoids as described above. A third and less important protective mechanism exhibited by carotenoids in preventing photodynamic damage is acting as a preferred substrate for oxidation by singlet oxygen. The minor importance of this mechanism is illustrated by the fact that only one in every one thousand molecules involved in quenching is oxidized (32).

An additional process involving carotenoids is the xanthophyll cycle which occurs in higher plants, bryophytes, ferns and algae. In higher plants, the carotenoid zeaxanthin is converted to its epoxide derivative violaxanthin. This reversible reaction occurs on the thylakoid membrane and requires light, oxygen, and two equivalents of NADPH. Despite work done in identifying the reactions in the xanthophyll cycle, the function(s) remains obscure. Some researchers (78) speculate that the xanthophyll cycle is involved in oxygen transport, while others postulate that it functions in the destruction of reducing equivalents at

their site of formation within the chloroplasts which may improve the ATP/NADPH ratio (36).

Carotenoid Biosynthesis

Investigations into the biosynthesis of carotenoids began in the 1950's and were spurred on by rapid advances in establishing the pathway of sterol biosynthesis. The first unified hypothesis for carotenoid biosynthesis in higher plants was proposed by Porter and Lincoln in 1950 (68). In the early 1960's, the pathway of the formation of the C-40 skeleton from acetate was generally accepted as being the same as for the sterol precursor squalene with the exception that the final condensation involves two molecules of the C-20 compound geranylgeranyl pyrophosphate. By 1970, the biosynthetic pathway to the C-40 carbon skeleton, the desaturation of phytoene, and the formation of cyclic carotenes could be outlined with reasonable confidence. The biosynthetic pathway is outlined in Figure 1. With the exception of the general isoprenoid pathway, the enzymes for these reactions are compartmentalized in the chloroplasts of higher plants (45).

Mechanisms of Action of Bleaching Herbicides

As mentioned above, several herbicides cause bleaching in susceptible plant species by inhibiting carotenoid bios-

ynthesis. These herbicides exhibit a "direct effect" on carotenoids by preventing their formation, leaving chlorophylls unprotected from photodynamic damage. Some herbicides, however, cause a mild form of bleaching as a result of their action on the photosynthetic apparatus. Herbicides that exhibit this "indirect effect" on plant pigments include the triazines, the substituted ureas, and the diphenylethers. These herbicides produce toxic oxygen species inside the chloroplast which destroy pigments. In the case of the PS inhibitors, the toxic oxygen species is singlet oxygen. Photosynthetic inhibitors act by blocking photosynthetic electron flow which prevents absorbed light energy from being used to do photochemistry. Since excess quanta are available to chlorophyll, singlet oxygen production increases dramatically. This overwhelms the carotenoid-based protective mechanisms and bleaching occurs. In the case of the diphenyethers, the toxic oxygen species are peroxides formed within the chloroplasts. The peroxidative activity of the diphenyether oxyfluorfen has been shown to degrade carotenes, xanthophylls, chlorophylls, the thylakoid membrane, and results in bleaching (75).

Herbicides that affect carotenoid biosynthesis directly, act by interfering with the function of one or more of the enzymes involved in the synthesis of carotenoid precursors. Britton (9) divides the biosynthetic pathway of carotenoids into five stages (the general isoprenoid

pathway, the formation of phytoene, the desaturation reactions, cyclization reactions, and oxygen introduction reactions) and emphasizes the suitability of the enzymes in each of these stages as herbicide targets. He concludes that the enzymes associated with the desaturation reactions are the most susceptible sites for herbicide interference. His conclusions are supported by experimental evidence. In fact, clomazone is the only bleaching herbicide reported that inhibits carotenoid biosynthesis by interfering with enzymes other than the desaturation enzymes.

In 1970, Burns, Buchanan, and Carter (11) found that the bleaching herbicides aminotriazole, dichlormate, and pyrichlor induced the accumulation of compounds other than carotenes in carotene fractions isolated in hexane. These compounds exhibited absorption maxima at shorter wavelengths than did typical carotenes and proved to be the carotenoid precursors phytoene and phytofluene. Levels of these precursors are normally too low for detection. Two years later, Bartels and McCullough found similar results with the bleaching herbicide norflurazon (5). In 1983, Sandmann et al. (77) examined twelve bleaching herbicides with diverse chemical structures and found that every herbicide which reduced carotenoid levels also lead to the accumulation of phytoene and phytofluene. The only exceptions were two diphenylethers which bleached plants through peroxidative activity. The authors concluded that inhibi-

tors of carotenoid biosynthesis affect the same target: the phytoene-desaturation complex. They also suggested that although the structures of the herbicides inhibiting phytoene desaturation vary greatly, they may compete with phytoene for the catalytic site of the phytoene-desaturase complex.

In 1985, Duke and Kenyon (22) reported that the bleaching herbicide clomazone inhibited carotenoid biosynthesis but did not cause an accumulation of phytoene and phytofluene. They also found that this herbicide greatly slowed or prevented the Shibata shift (spectral changes observed on illuminated etiolated seedlings due to the conversion of chlorophyllide to chlorophyll by the addition of phytol during chlorophyll biosynthesis). Along with bleaching, clomazone also inhibits the longitudinal growth between internodes of susceptible species. This symptom was overcome by applications of gibberellic acid (76) implying that gibberellin synthesis may also be affected. Sandmann and Boger (76) concluded that the various effects of clomazone could be explained by a single enzyme target in the terpenoid biosynthetic pathway between acetate and geranylgeranyl pyrophosphate. This conclusion explains the lack of phytoene and phytofluene accumulation.

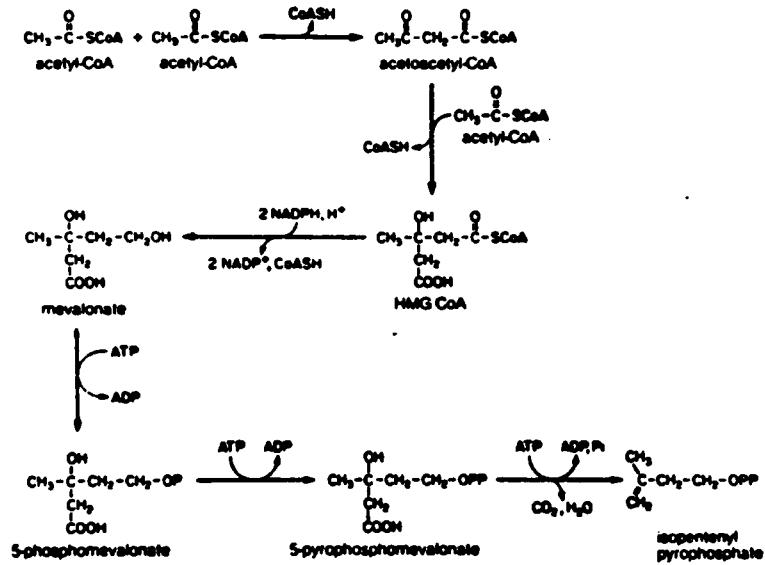
More recently, Soeda and Uchida (85) reported that the compounds 1,3-dimethyl-4-(2,4-dichlorobenzoyl)-5-hydroxypyrazole and some new herbicidal compounds including

2-(2,4-dichlorobenzoyl)-cyclohexane-1,3-dione inhibited carotenoid biosynthesis while causing an accumulation of phytoene. Britton et al (10) showed that the herbicide diflufenican [N-(2,4-difluorophenyl)-2-(3-trifluoromethyl-phenoxy)-3-pyridine carboxamide] inhibited carotenoid biosynthesis and caused the accumulation of phytoene, phytofluene and hydroxy-phytoene.

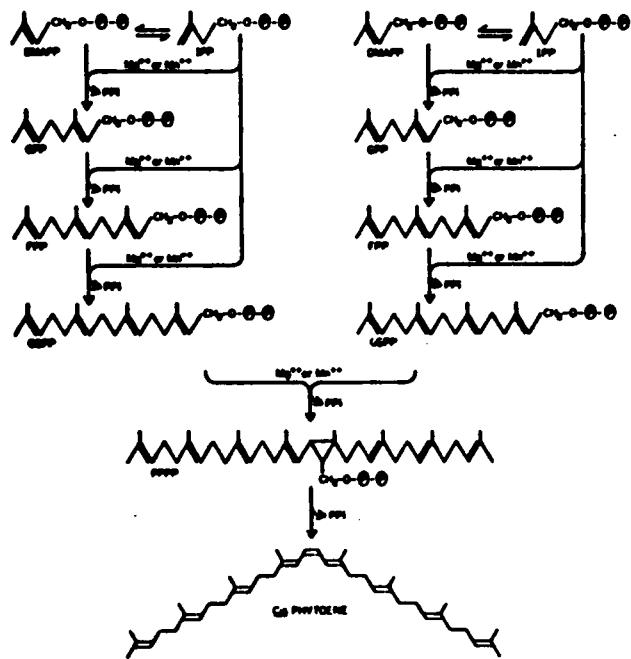
The herbicides SC-0051 and SC-0774 cause strong bleaching symptoms on susceptible species. Researchers (21, 66, 67) studying these compounds have recently shown that these symptoms are accompanied by a decrease in both chlorophyll and carotenoid levels in plant tissues. This indicates that bleaching induced by SC-0051 and SC-0774 may be due to the inhibition of carotenoid biosynthesis. To date, no work has been published which investigates the mechanism by which SC-0051 and/or SC-0774 reduce pigment levels.

In summary, the primary function of carotenoids in higher plants is to protect chlorophyll from photo oxidation. Inhibition of carotenoid biosynthesis is a desirable target for herbicides since this process is not present in mammalian systems. Many chemicals are known to inhibit carotenoid biosynthesis and some have commercial applications. Almost all of the known inhibitors act at the same site: the phytoene-desaturation complex (14). The one known exception is clomazone. Research suggests that this herbicide may act in the terpenoid biosynthetic pathway

between acetate and geranylgeranyl pyrophosphate (76).

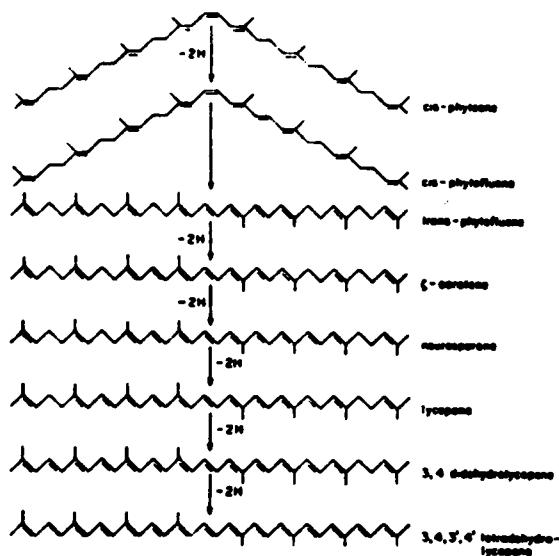


The general isoprenoid pathway

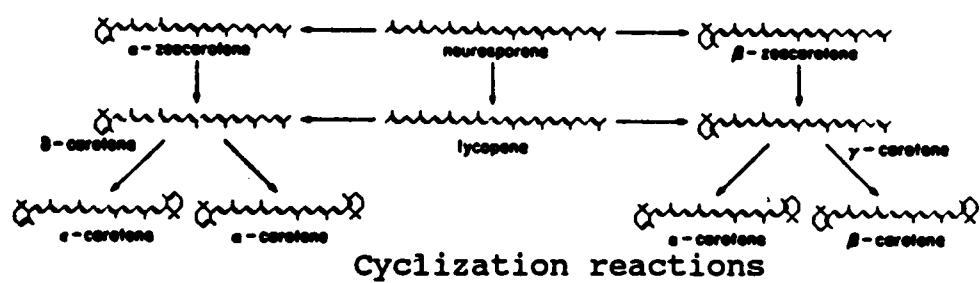


Phytoene formation

Figure 1. The carotenoid biosynthetic pathway (45).



Desaturation reactions



Cyclization reactions

Figure 1. (continued)

**FACTORS AFFECTING THE MOBILITY OF HERBICIDES
IN THE SOIL**

Introduction

Soil applied herbicides are subjected to many physical, chemical, and biological phenomena which affect their availability to target plants. These phenomena include degradative activities such as chemical, microbial and photochemical degradation, and mass transfer phenomena such as leaching, movement in surface runoff and erosion, and volatility. All of these processes affect the concentration of herbicide available for weed control and therefore the efficacy of the product. An understanding of the degree to which these processes affect new herbicides is important to maximize their performance. To date, no work has been published which examines factors affecting the mobility or persistance of SC-0051 or SC-0774 in the soil. However, scientists at the Stauffer Chemical Company have determined that the water solubility of SC-0774 increases with increasing pH. Therefore, soil pH may influence the mobility of this herbicide. Much has been written on the degradative activities that occur in soil (33, 37, 46, 62, 69, 70) and will not be covered in this chapter. Rather, a review of the physical and chemical factors that affect the soil mobility of herbicides is presented.

The ability of a herbicide to move in the soil is

influenced by a number of factors; including soil adsorption, herbicide water solubility, and herbicide volatility. The four principal means for pesticide transport within soils are 1) diffusion in the airspace of the soil, 2) diffusion in soil water, 3) downward flowing water, and 4) upward moving water (3). Movement by diffusion would be important for only those pesticides of high volatility. Since most soil applied herbicides have a relatively low vapor pressure, movement by this type of diffusion is minimal. There are, however, some instances (thiocarbamate herbicides, clomazone) where diffusion through soil air spaces may be significant. Diffusion through water is not considered an important transport mechanism for herbicides in soil. Calculations (3) have indicated that it would take several years for a surface applied herbicide to migrate by diffusion to a depth of two feet in a moist soil. Downward movement of herbicides by percolation or upward movement by evapo-transpiration appears to be the most important means of pesticide transport through the soil profile (3).

To understand or predict the mobility of a herbicide in soil, one must understand the physical and chemical properties of both the herbicide and the soil to which it is to be applied. The factors to be discussed in this review include the chemical structure of the herbicide and the soil properties that influence adsorption: soil texture, organic matter content and soil pH.

Chemical Structure

The chemical and physical properties of a molecule are determined by its molecular structure. Therefore, the structure of a molecule will greatly affect its interaction with a solvent or an adsorbent. A chemical's character, size and configuration, acidity or basicity, water solubility, charge distribution and polarizability all affect the adsorption-desorption by soil colloids (3, 46). The charge distribution in a molecule is one of the most important factors influencing the physical properties of both water solubility and adsorptivity. The charge may be weak, arising from unequal distribution of electrons producing polarity in the molecule, or it may be strong resulting from ionic dissociation.

Charge distribution can be affected by the presence and position of functional groups on the molecule. Functional groups that appear to be very important in herbicide adsorptivity are carboxyl, carbonyl, hydroxyl and amino groups. Other less important groups include trifluoromethyl groups and halogens. Carbonyl groups, trifluoromethyl groups, and halogens are electronegative and attract electron density within a molecule. This results in uneven distribution of electron density and increases the overall polarity of a molecule. Hydroxyl, carbonyl and amino groups are able to form hydrogen bonds with polar molecules

which increase water solubility and binding to some soil components. Amino groups can become protonated, depending on their pK_b and the pH of their environment. The resulting cation may adsorb tightly to anionic soil particles.

Adsorption is the physical and/or chemical attachment of a compound to a surface resulting in the formation of some type of bond. Bonds may be of high or low energy. High energy bonds include ionic and ligand exchange bonds. Ionic bonds can occur between organic ions and positive or negative electrical charges located at the adsorbent surface (examples include the bipyridyliums and the phenoxyacetic acids). Ligand exchange bonds form when one or more ligands on a pesticide molecule are replaced by the adsorbent molecule. The necessary condition for this phenomenon is that the adsorbent molecule be a stronger chelating agent than the replaced ligands. An example is the binding of s-triazines on the residual transition metals of humic acid (38, 46).

Low energy bonds include charge-dipole bonds, hydrogen bonds, charge transfer bonds, and Van der Waals bonds. Charge-dipole bonds result when electrical charges on adsorbents attract polar molecules. Hydrogen bonds result from the attraction of partially positive protons to some partially negative group and have been suggested as a mechanism of adsorption of carbamates (65, 4) and atrazine (14) to montmorillonite. Charge transfer bonds form when elec-

trons are transferred between the surface of the adsorbent and the organic molecule. Compounds containing either bonds or lone pairs of electrons can give rise to such interactions. Some evidence implicates this mechanism in the adsorption of bipyridylium cations on clays (40, 47). Finally, Van der Waals bonds are simply due to dispersion forces and are thought to exist with all herbicides (13).

Soil Texture

Soil texture is determined by the relative proportions of particles of various size in a given soil. Particles are classified by size into three groups: sand, silt and clay. Sand is defined as particles ranging in size from 0.05 to 2 mm and are primarily made up of quartz (SiO_2). Silt is defined as particles ranging from 0.002 to 0.05 mm and are also primarily made up of quartz. Clays are particles smaller than 0.002 mm and are primarily made up of silicon and/or aluminum and magnesium. The small size and fine subdivisions of silt and in particular clay dramatically increases their surface area. This is illustrated by the fact that a fine colloidal clay has about 10,000 times as much surface area as the same weight of medium-sized sand. The specific surface area of colloidal clay ranges from about 10 to 10,000 m^2/g while that of the smallest silt particles and fine sand are 1 and 0.1 m^2/g respectively (8). Since the adsorptive properties of particles

are surface phenomena, it is clear that clay content plays a most important role in determining a soils adsorptive capacity.

Organic Matter

Organic matter content is another important factor in determining the adsorptive capacity of soils, particularly for those compounds that do not ionize. The organic matter in a soil consists of a complex mixture of compounds which are generally grouped into what are called non-humic and humic substances. Non-humic substances include those organic compounds with definite chemical characteristics such as carbohydrates, proteins, amino acids, fats, waxes, and low molecular weight organic acids. These compounds are subject to microbial and chemical degradation and are generally short lived in the soil.

Humic substances, on the other hand, are quite stable being resistant to microbial and chemical degradation and make up the bulk of the organic matter in a soil. Humic substances are acidic, dark colored, predominantly aromatic, hydrophilic and range in molecular weight from a few hundred to several thousand. The large surface area and complex chemical nature of humic substances impart their high adsorptive properties. They have been shown to form ionic bonds with ionized molecules (57), participate in cation-dipole bonds (12,) and charge transfer complexes

(42). Hydrogen bonding is also thought to play an important role in the adsorption of pesticides to organic matter (13). Weber et al. recently found a high correlation between humic acid content in soils and herbicide bioactivity (97).

Soil pH

Much work has been done investigating the influence of soil pH on the adsorption of herbicides (4, 30, 61, 88) with varying results. The nature and magnitude of the effect depends upon the chemistry of the pesticide and the composition of the soil. Bailey et al. (4) concluded that the magnitude of adsorption of organic compounds with widely different chemical character is governed by three factors: 1) the pH of the clay system, 2) the water solubility of the compound, and 3) the dissociation constant of the compound. These researchers also found that the adsorption of acidic-type compounds was dependent upon the pH of the suspension, while the adsorption of basic compounds was dependent upon the surface acidity. Surface acidity is the acidity at or in close proximity to the colloid surface. It is differentiated from the acidity in the bulk solution (measured by pH) because the activity of protons in the bulk suspension and the activity of protons at or near the colloid surface can differ drastically (3).

Most of the research done on the effect of pH on herbi-

cide adsorption was conducted on *s*-triazines and phenoxyacetic acids. Talbert and Fletchall (88) and McGlamery and Slife (61) found that atrazine adsorption onto soil and humic acid increased with decreasing soil pH. The protonation of amino groups on triazine molecules increases with decreasing pH, with the resulting cation being readily adsorbed to anionic soil particles. Weber (96) studied the adsorption of 13 related *s*-triazines and found that adsorption was influenced by the dissociation constant (pK_a) of the amino group on the herbicides. Frissel and Bolt (30) and Bailey et al. (4) found that the pH of montmorillonite determined the type of adsorption of 2,4-D. At a pH below 4, 2,4-D was positively adsorbed (adsorbed to negatively charged particles), when the pH was above 4, the adsorption was negative (adsorbed to positively charged particles). Some work (31, 56) indicates the effect of pH on adsorption depends upon the nature of both the adsorbents and adsorbates.

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II. FIELD EFFICACY STUDIES WITH THE HERBICIDES SC-0051 AND SC-0774 IN CORN (ZEA MAYS)

INTRODUCTION

Corn and soybeans are two major agronomic crops that provide an economic incentive to the agrochemical industry for the development of herbicides. Throughout the late 1970's and early 1980's, many new products from several new chemical classes (i.e. diphenylethers, imidazolinones, sulphonylureas) were introduced which revolutionized weed control in soybeans. In contrast, few new products and no new chemical classes have been introduced for corn.

The herbicide market for corn has been dominated by a small number of products from five chemical classes: triazines, chloroacetanilides, thiocarbamates, phenoxyacetic acids, and benzoic acids. Though products from these families have provided adequate, economical weed control for many years, there remains a need for new products in corn. The lack of postemergence grass herbicides for corn and the development of triazine resistant weed species, that increases the need for new broadleaf herbicides with soil residual activity (4, 5), are two areas that need to be addressed.

SC-0051 and SC-0774 are two experimental herbicides

from a new chemical class. SC-0051 has provided preemergence and postemergence control of broadleaf weeds in corn and small grains (2, 3, 6, 7, 8, 9, 10, 13) while SC-0774 has shown potential as a preemergence herbicide for control of annual grasses in corn (1, 3, 6, 7, 11). This research was conducted to evaluate SC-0051 and SC-0774 for weed control in conventional and no-till corn in Virginia.

MATERIALS AND METHODS

Ten studies investigating SC-0051 and SC-0774 were conducted during the 1985 through 1987 growing seasons in conventional and no-till corn. Research was conducted on a State sandy loam soil (Typic Hapludults) near Painter, VA. Herbicides were applied in 235 L/ha water at 275 kPa pressure using flat fan tips¹. Each plot consisted of 4-row plots with the center two rows treated. The treated area was 2.5 m wide by 6 m long in no-till studies and 2 m wide by 6 m long in conventional corn studies. Information concerning the planting date, tillage, variety planted, application time, weed species and weed density in these studies is presented in Tables 1 and 2.

Environmental conditions varied with years. Rainfall received at the location of these studies is presented in

¹TeeJet 8003 tips. Spraying Systems Co., Wheaton IL 60287.

Table 3. Growing conditions were good in 1985 with adequate moisture being received throughout the growing season. The spring of 1986 was dry with only 9 cm of rain received from April through June. Corn establishment in 1986 was assisted with irrigation which also influenced preemergence herbicide activity. In 1986, weeds were under drought stress at the time of postemergence applications. In 1987, spring moisture was adequate but the summer was dry with only 10 cm of rain being received from July through September.

Corn injury was rated 2 to 3 weeks after herbicide applications. Weed control was rated at the beginning, middle, and end of the growing season with data from the following ratings being presented. Control of the rye cover crop and winter annual weed species was rated 2 to 8 weeks after herbicide application. Horseweed and large crabgrass ratings taken 15 to 17 weeks after application are presented. Ratings for preemergence control of smooth pigweed, common lambsquarters, common ragweed, and giant foxtail taken 12 to 16 weeks after application are presented, while postemergence control of these same weeds rated 6 to 13 weeks after application are presented. Plots were harvested and shelled grain yields, adjusted for moisture, were determined.

The experimental design used in these studies was a randomized complete block with 3 replications in 1985 and 4

replications in 1986 and 1987 except where noted otherwise. Data were analyzed statistically by analysis of variance and means were compared using Fisher's LSD procedure. Orthogonal contrasts were also made where appropriate. Although much of the research was repeated over years, treatments were modified over time to make practical comparisons based on previous years' results and to maximize experimental efficiency. Since all treatments and rates were not identical from year to year, studies are presented individually by year.

RESULTS AND DISCUSSION

No-till corn. Both SC-0051 and SC-0774 were active on vegetation present at planting and on later germinating weeds. However, the spectrum of weeds controlled by SC-0051 and SC-0774 differed considerably. SC-0051 was active primarily on broadleaf weeds, while SC-0774 was active primarily on grass species. SC-0051 provided greater than 90% control of the winter annual broadleaf species wild lettuce, common chickweed, and horseweed but failed to control the rye cover crop (Tables 4 and 5). This herbicide also provided excellent residual control (99%) of common lambsquarters but did not control (<50%) smooth pigweed or large crabgrass. SC-0051 did not injure corn in these studies.

In contrast, SC-0774 controlled the rye cover crop (90 % at 1.1 kg/ha) and provided residual control of large crabgrass (Tables 4 and 5). SC-0774 also controlled common lambsquarters but was weak on other broadleaf weeds in these studies. Treatments containing SC-0774 at 0.8 to 1.3 kg/ha were superior to treatments containing metolachlor for residual control of large crabgrass (Table 6). SC-0774 caused temporary corn injury in some studies (Table 6). Injury symptoms included bleaching of the new growth of seedling corn. Corn recovered, however, within 1-2 weeks with no loss of plant vigor being observed by mid-season and yields were not affected.

While neither SC-0051 nor SC-0774 alone provided adequate broad-spectrum weed control, combinations of SC-0051 plus SC-0774 provided weed control and yields comparable to atrazine plus metolachlor (Tables 5 and 6). Combinations of SC-0774 plus atrazine controlled common chickweed, horseweed, and large crabgrass, but failed to control smooth pigweed (Table 6). A combination of SC-0051 and atrazine provided broad-spectrum weed control that was superior to control achieved with atrazine plus metolachlor.

Although these herbicides were active on existing weed species, their action was slow, requiring as much as 2 weeks for complete control. This slow action allowed winter annual weed species to compete with seedling corn for moisture and nutrients. For this reason, combinations of

SC-0051 plus SC-0774 applied early preplant, at planting, and at planting plus paraquat were compared to measure the effect of application timing and paraquat on weed control and corn yields. Reduced control of the rye cover crop and reduced residual control of large crabgrass occurred when these herbicides were applied early preplant compared to applications made at planting (Table 7). The addition of paraquat to SC-0051 plus SC-0774 significantly improved overall weed control which resulted in increased corn yields. The lack of residual large crabgrass control in treatments which failed to control the rye cover crop suggests that much of the applied herbicide was intercepted by the cover crop and did not enter the soil. The addition of the non-selective herbicide apparently increased the amount of SC-0051 and SC-0774 reaching the soil surface, thus improving residual control. The rapid death and decay of the rye cover crop provided by paraquat may allow for the release of intercepted herbicide residues which may then enter the soil.

SC-0051 controlled wild lettuce, and horseweed, two important broadleaf weeds in no-till corn that are not adequately controlled by paraquat. The addition of SC-0051 to paraquat could increase control of these two species and also provide residual control of common lambsquarters and other broadleaf weeds. SC-0774 possessed burndown activity on the rye cover crop and provided better residual control

of large crabgrass than did metolachlor. Combinations of SC-0774 with a broadleaf herbicide could be effective in situations where large crabgrass is a problem.

Conventional Corn. As in no-till corn, SC-0051 primarily controlled annual broadleaf weeds with SC-0774 being most active on grasses; neither herbicide was adequate when applied alone. Postemergence applications of SC-0051, at rates of 0.6 kg/ha and above, provided complete control of common lambsquarters and common ragweed, but provided erratic control (70 % in 1986 and 10 % in 1987) of giant foxtail (Tables 8 and 9). The addition of 1.1 kg/ha of atrazine significantly improved residual giant foxtail control which resulted in high corn yields (Tables 8 and 9). Combinations of SC-0051 plus atrazine provided weed control and corn yields comparable to those obtained with postemergence combinations of tridiphane plus atrazine. However, despite the high degree of activity on several broadleaf weeds, SC-0051 failed to adequately control smooth pigweed (Table 11).

Preemergence treatments of SC-0774 failed to provide adequate control (<80%) of common lambsquarters, common ragweed, or giant foxtail (Tables 8, 9 and 10). Also, combinations of SC-0774 and SC-0051 were not as effective as SC-0051 plus metolachlor for control of giant foxtail (Table 11). As in no-till corn, sporadic but temporary

corn injury occurred in treatments containing SC-0774 at rates above 1.1 kg/ha.

In both conventional and no-till corn, SC-0051 applied preemergence or postemergence controlled many broadleaf weeds, suppressed some grasses, and was safe to corn. This herbicide was very active on common lambsquarters and common ragweed but did not adequately control smooth pigweed. The combination of SC-0051 plus atrazine, applied preemergence or postemergence, provided consistant, broad-spectrum weed control and corn yields that were comparable to those obtained with atrazine plus metolachlor or atrazine plus tridiphane. Because of the high level of common lambsquarters control, this combination might also be an effective postemergence alternative for the control of triazine resistant common lambsquarters.

SC-0774 controlled large crabgrass more effectively than did metolachlor in no-till corn and possessed considerable foliar activity on the rye cover crop. However, SC-0774 did not adequately control giant foxtail in conventional corn and induced occasional corn injury in conventional and no-till corn. Considering the weaknesses of this herbicide, and the effectiveness of other preemergence grass herbicides currently available for corn, the potential use of SC-0774 may be limited.

Table 1. Treatment information for preemergence applicacations of SC-0051 and SC-0774 in no-till and conventional corn.

Planting date	Tillage	Variety	Application time	Species	Density (No/m ²)
April/18/85	no-till	Pioneer 3378	1		
April/26/85	conv.	Pioneer 3378	0		
April/07/86	no-till	Gutwein 698	3	rye STEME ERICA	190 5% ^b 32
April/10/87	no-till	Gutwein 698	1	DIGSA	120
April/10/87	no-till	Gutwein 698	5	ERICA AMACH DIGSA	1 4 100
April/10/87	no-till	Gutwein 698	5	ERICA	0.1
April/09/87	conv.	Gutwein 698	1		

^aDAP - days after planting.

^bpercent ground cover.

Table 2. Treatment information for postemergence applications of SC-0051 in no-till and conventional corn.

Planting date	Tillage	Variety	Application time	Species	Growth stage		
			(DAP ^a)				
April/18/85	no-till	Pioneer 3378	20	corn ERICA	4 leaf 0-25		
April/26/85	conv.	Pioneer 3378	12	corn CHEAL PANDI	3-4 leaf 0-2 1-2 leaf		
April/08/86	conv.	Gutwein 698	31	corn CHEAL AMBEL SETFA	4 leaf 0-8 2-6 leaf 2-6 leaf		
April/09/87	conv.	Gutwein 698	22	corn CHEAL AMBEL SETFA	2-3 leaf 0-3 0-3 0-3		

^aDAP - days after application.

Table 3. Rainfall by month at
Painter, VA.

<u>YEAR</u>	<u>APR</u>	<u>MAY</u>	<u>JUN</u>	<u>JUL</u>	<u>AUG</u>	<u>SEP</u>
	(cm)					
1985	1.1	8.2	10.0	7.9	4.9	15.3
1986	3.3	0.7	4.8	12.6	21.5	1.8
1987	7.4	3.7	10.7	3.0	2.4	5.0

Table 4. Preemergence and postemergence weed control with SC-0051 and SC-0774 in no-till corn in 1985.

Herbicide	Rate	Application ^a	Control						
			timing	Rye	DIGSA	LACSE	CHEAL	STEME	Yield
	(kg ai/ha)			(%)					(kg/ha)
SC-0051	1.1	PRE	12	50	87	94	99	4500	
SC-0051	1.6	PRE	25	63	91	99	99	4210	
SC-0051	2.2	PRE	33	85	99	99	99	3940	
SC-0774	0.6	PRE	73	65	40	94	88	2450	
SC-0051	0.6	POST	--	58	94	99	--	4420	
SC-0051	1.1	POST	--	79	91	99	--	5280	
SC-0051	1.6	POST	--	83	99	99	--	4680	
LSD (0.05)			7	10	19	5	9	970	

^aPRE = applied preemergence

POST = applied postemergence

Table 5. Preemergence weed control with SC-0051 and SC-0774 in no-till corn in 1986.

Herbicide	Rate (kg ai/ha)	Control					Yield (kg/ha)
		Rye	DIGSA (%)	ERICA	AMACH		
SC-0051	0.3	5	0	18	3	----	
SC-0051	0.6	8	0	87	39	----	
SC-0051	1.1	0	0	96	48	1330	
SC-0774	0.6	55	40	8	0	----	
SC-0774	1.1	90	33	30	0	----	
SC-0774	1.6	92	79	74	8	1300	
SC-0051 + SC-0774	1.1 1.1	89	76	91	60	4580	
Paraquat + Atrazine + Metolachlor	0.6 1.3 1.6	98	43	92	65	4000	
LSD (0.05)		12	18	22	22	670	

Table 6. Preemergence weed control with combinations of SC-0051 and SC-0774 in no-till corn in 1987^a.

Herbicide	Rate (kg ai/ha)	Control						Yield (kg/ha)
		Corn bleach	STEME	ERICA	AMACH	DIGSA		
		(%)						
Control	---	0	0	0	0	0	0	120
SC-0774 + Atrazine	0.8 1.3	25	99	99	26	83	3740	
SC-0774 + Atrazine	1.1 1.1	35	99	99	23	88	3810	
SC-0774 + Atrazine	1.3 1.1	35	99	99	58	92	4410	
SC-0774 + SC-0051	0.8 1.1	23	87	99	57	88	3860	
SC-0774 + SC-0051	1.1 1.1	33	93	99	47	87	3700	
SC-0774 + SC-0051	1.3 1.1	42	95	99	30	90	3600	
SC-0051 + Metolachlor	1.1 1.6	12	85	99	17	67	3680	
SC-0051 + Atrazine	1.1 1.3	12	99	99	80	82	4240	
Atrazine + Metolachlor	1.3 1.6	0	99	96	42	48	3310	
LSD (0.05)		20	6	3	24	7	1070	
Significance ^b :								
SC-0774	SC-0774							
+	+							
Atrazine vs. SC-0051	NS	**	NS	NS	NS	NS	NS	

^aMeans are averages of three replications.

^bIndicated orthogonal contrasts were significant at the 1% (**) level or were nonsignificant (NS).

Table 7. Effect of timing of application and paraquat on the efficacy of combinations of SC-0051 and SC-0774 for weed control in no-till corn in 1987^a.

Herbicide	Rate (kg ai/ha)	Growth stage	<u>Control</u>			
			Corn bleach (%)	Rye (%)	DIGSA	Yield (kg/ha)
CONTROL	---		0	0	0	100
SC-0774 +	0.8	EPRÉ	0	31	5	890
SC-0051	1.1					
SC-0774 +	1.1	EPRÉ	3	34	8	1780
SC-0051	1.1					
SC-0774 +	1.3	EPRÉ	4	65	15	1800
SC-0051	1.1					
SC-0774 +	0.8	PRE	1	55	56	2320
SC-0051	1.1					
SC-0774 +	1.1	PRE	5	64	69	2140
SC-0051	1.1					
SC-0774 +	1.3	PRE	6	75	85	2670
SC-0051	1.1					
SC-0774 +	0.8	PRE	2	99	75	4220
SC-0051 +	1.1					
Paraquat	0.6					
SC-0774 +	1.1	PRE	4	99	84	3750
SC-0051 +	1.1					
Paraquat	0.6					
SC-0774 +	1.3	PRE	9	99	94	4350
SC-0051 +	1.1					
Paraquat	0.6					
Atrazine +	1.3	PRE	0	99	85	3760
Metolachlor +	1.6					
Paraquat	0.6					

LSD (0.05)	5	16	12	1230
Significance^b:				
EPR vs. PRE	NS	**	**	*
EPR vs. PRE + Paraquat	*	**	**	**
PRE vs. PRE + Paraquat	NS	**	**	**

aAll paraquat treatments contained 0.25% surfactant. All other treatments contained 1% crop oil concentrate.

bIndicated orthogonal contrasts were significant at the 5% (*) or 1% (**) level or were nonsignificant (NS).

Table 8. Preemergence and postemergence applications of SC-0774 and SC-0051 for weed control in conventional corn in 1986.

Herbicide	Rate (kg ai/ha)	Growth Stage	Control			Yield (kg/ha)
			CHEAL	AMBEL	SETFA	
SC-0774	0.6	PRE	75	33	56	3060
SC-0774	0.8	PRE	81	40	70	4130
SC-0774	1.6	PRE	84	44	70	3840
Aalachlor	2.2	PRE	81	15	99	4200
SC-0051	0.6	POST	99	99	34	4390
SC-0051	1.1	POST	99	99	45	4800
SC-0051	1.6	POST	99	99	68	4440
SC-0051 + Atrazine	1.1	POST	99	99	84	5700
Tridiphane + Atrazine	0.8 1.6	POST	99	97	85	4940
LSD (0.05) Significance ^a :			10	18	18	1130
SC-0051 vs. SC-0051 + Atrazine			NS	NS	**	NS

^aIndicated orthogonal contrasts were significant at the 1% (**) level or were not significant (NS).

Table 9. Preemergence applications of SC-0774 and postemergence applications of SC-0051, alone plus atrazine in conventional corn in 1987^a.

Herbicide	Rate	Growth Stage	Control			Yield (kg/ha)
			CHEAL	AMBEL	SETFA	
			(kg ai/ha)	(%)		
SC-0774	1.3	PRE	--	53	57	2080
SC-0774	1.6	PRE	--	73	73	3500
SC-0051	0.6	POST	99	99	0	1970
SC-0051	1.1	POST	99	99	7	2190
SC-0051	1.6	POST	99	99	7	2680
SC-0051 + Atrazine	0.6 1.1	POST	99	99	68	4070
SC-0051 + Atrazine	1.1 1.1	POST	99	99	73	4290
SC-0051 + Atrazine	1.6 1.1	POST	99	99	64	3820
Tridiphane + Atrazine	0.6 1.6	POST	99	97	97	4190
LSD (0.05)			0	25	25	930
Significance ^b :						
SC-0051 vs.			NS	NS	**	**
SC-0051 + Atrazine						

^aMeans are averages of three replications.

^bIndicated orthogonal contrasts were significant at the 1% (**) level or were not significant (NS).

Table 10. Weed control and corn bleached with preemergence applications of SC-0774 plus atrazine or plus SC-0051 in conventional corn in 1987.

Herbicide	Rate (kg ai/ha)	Corn bleach	<u>Control</u>			Yield (kg/ha)
			AMBEL (%)	SETFA		
SC-0774 + Atrazine	0.6 1.1	3	99	76		3400
SC-0774 + Atrazine	0.8 1.1	3	99	86		3030
SC-0774 + Atrazine	1.1 1.1	19	99	79		3190
SC-0774 + Atrazine	1.3 1.1	21	99	82		3400
SC-0774 + SC-0051	0.6 1.1	8	99	51		2500
SC-0774 + SC-0051	0.8 1.1	8	99	38		2980
SC-0774 + SC-0051	1.1 1.1	15	99	66		3060
SC-0774 + SC-0051	1.3 1.1	30	99	58		3050
Metolachlor + 1.6 Atrazine 1.3		0	99	83		3330
LSD (0.05) Significance ^a :		8	0	23		820
SC-0774 + SC-0774 + Atrazine vs. SC-0051	NS	NS	**	NS		

^aIndicated orthogonal contrasts were significant at the 1% (***) level or were not significant (NS).

Table 11. Postemergence weed control with low rates of SC-0051 in conventional corn in 1987.

Herbicide	Rate	Control					Yield (kg/ha)	
		CHEAL	AMBEL	AMACH	SETFA			
		(%)						
		(kg ai/ha)						
SC-0051 +	0.2	99	99	5	79	3170		
SC-0774	0.8							
SC-0051 +	0.3	99	99	25	69	2970		
SC-0774	0.8							
SC-0051 +	0.6	99	99	60	83	3000		
SC-0774	0.8							
SC-0051 +	0.2	95	93	18	89	3550		
Metolachlor	1.6							
SC-0051 +	0.3	99	97	23	88	3160		
Metolachlor	1.6							
SC-0051 +	0.6	99	99	65	85	3630		
Atrazine	1.1							
LSD (0.05)		4	2	26	13	550		
Significance ^a :								
SC-0774 vs. Metolachlor		NS	**	NS	**	*		

^aIndicated orthogonal contrasts were significant at the 5% (*) or 1% (**) level or were not significant (NS).

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III. THE INFLUENCE OF SOIL pH ON THE MOBILITY OF SC-0774 AND SC-0051 IN SOIL

INTRODUCTION

Soil-applied herbicides must enter the soil, either by leaching or by mechanical incorporation, to be effective. The mobility of herbicides in soil is influenced by a number of factors, including the soil texture, organic matter, pH, the chemistry of the herbicide, and rainfall amounts (1, 3, 4, 10). Recent concerns on the impact of agrichemicals on ground water contamination has sparked new interest in the movement of pesticides in the soil. SC-0774 and SC-0051 are experimental herbicides, from a new chemical class, that selectively control grasses and broadleaf weeds when applied preemergence in corn (2, 6, 7, 8, 9). Little is known about the mobility of these herbicides in soil, but technical data indicate that both are subject to leaching on light, sandy soils and that their water solubilities are pH dependent¹.

During the 1986 growing season, at the Eastern Shore Agricultural Experiment Station in Painter, VA, SC-0774-

¹Stauffer Chemical Co. 1987. Technical information report on SC-0051 and SC-0774. Mountain View Research Center, Mountain View, CA 94042.

and SC-0051-induced bleaching symptoms were observed in the new growth of weeds after rainfall events that occurred 12 weeks after application. These injury symptoms suggested that SC-0051 and SC-0774 residues remained in the soil in significant quantities late in the growing season. This research was conducted to investigate the mobility and residual characteristics of SC-0051 and SC-0774 in sandy loam soils.

MATERIALS AND METHODS

Soil Type. The soil type at the experiment station is a State Sandy Loam (Typic Hapludults), consisting of 67% sand, 28% silt, 5% clay, and 1% organic matter. The soil pH ranged from 5.2 to 5.6.

pH Amendments. Field soil pH was amended by applications of hydrated lime or elemental sulfur. Lime was applied in the fall of 1986 at a rate of 4170 kg/ha. Sulfur was applied in the winter of 1986 at a rate of 1020 kg/ha. These applications resulted in a pH near 4 at the soil surface in sulfur treated soils and a pH near 6 at the surface in lime treated soils. The differences in soil pH were less at lower depths (Table 3) but became greater as the growing season progressed. The field was to be planted no-till, so the lime and the sulfur were incorporated by rainfall only. A second site was chosen to further inves-

tigate the mobility of these herbicides. The soil at this location was not ammended and the pH and was found to be near 5 (Table 3).

For soil column studies, soil from an adjacent site was used to maintain consistency in soil type. Soil pH was amended to pH 3, 4, 5, and 6, by the dropwise addition of either 35% H₂SO₄ or 35% NaOH to a soil, water slurry (2:1 w/w). These solutions were added over a period of 24 to 36 hours, until the pH of the slurry stabilized at the desired pH. The soil solutions were then dried at room temperature and mixed thoroughly before use.

Herbicide applications. Herbicides were applied for field studies in 235 L/ha water at 275 kPa pressure using flat fan tips². Plots were 2.5 m wide by 6 m long with 4 rows per plot. The 2 center rows were treated leaving untreated guard rows as controls.

Soil Sampling. Soil samples from field studies in 1986 and 1987 were collected using stainless steel soil probes with internal diameters of 2.5 cm. Samples were separated by depth into 2.5 cm sections. Herbicide treatments were replicated 4 times in the field with 5 to 10 samples collected from each replicate. The samples were composited by treatment and depth, mixed thoroughly, and frozen until analyzed. In 1986, soil samples were collected 16 weeks

²TeeJet 8003 tips. Spraying Systems Co., Wheaton IL 60287.

after herbicide application from soils treated with 1.1 kg/ha SC-0051, 1.7 kg/ha SC-0774, and 1.1 kg/ha SC-0051 plus 1.7 kg/ha SC-0774 in no-till corn. In 1987, samples were collected 2, 5, 10, 18 and 24 weeks after application from soils treated with 1.1 kg/ha SC-0774 in no-till corn.

Soil Column Preparation. Soil columns consisted of ten 2.5 cm sections of PVC pipe with an internal diameter of 2.5 cm stacked and taped together. The bottoms were sealed with glass wool. Soil added to each column was compacted to a density of approximately 1.3 g/cm³, then saturated with tap water (pH near 6.5). One hundred ug of either SC-0774 or SC-0051 was applied by pipette (in 1 ml of water) to the soil surface then dried overnight. Fifty ml of tap water was leached through the columns over a period of 24 to 48 h. The column components were separated and seeded with large crabgrass. Large crabgrass was used as a bio-indicator species because it is highly susceptible to these herbicides (Table 1).

Bioassay Technique. Twenty to 30 g of the soil samples collected from the field were placed in plastic medicine cups. Large crabgrass seed was mixed into the top 2 mm of the sample. Herbicide residues were detected by visual estimates of percent bleaching.

Herbicide Extraction. No extraction information was available for SC-0774 at the time that these experiments were conducted so the following method was developed. Soil

samples (100 g) were placed in 250 ml centrifuge bottles with 50 ml of tap water. Three ml of 35% NaOH was added followed by 50 ml of nanograde hexanes. The solutions were shaken vigorously and allowed to stand for several minutes. Five ml of 35% H₂SO₄ was added and the solutions were shaken again for several minutes followed by centrifugation for 4 minutes at 5,000 rpm. The hexanes layer was removed and collected. An additional 50 ml of hexanes were added followed by vigorous shaking and centrifugation. The hexanes were collected and the procedure was repeated a third time. The extracts were combined and concentrated under a stream of air. The residues were washed into a 25 ml bottles with reagent grade acetone and concentrated to approximately 0.5 ml under a stream of air. The residues were washed into 1.5 ml micro-centrifuge tubes with acetone and evaporated to dryness. A final volume of 200 ul of acetone was added. The samples were frozen until analyzed.

Quantification of SC-0774 by Scanning Densitometry. Two ul aliquots of each sample were placed on 10 by 10 cm Whatman silica gel high performance thin layer chromatography plates with fluorescent indicator. The SC-0774 in the samples was separated from impurities by chromatography using a solvent system consisting of ethyl acetate, acetone, ammonium hydroxide (66:30:4 v/v/v). The quantity of SC-0774 in the samples was determined by scanning densitometry at a scanning rate of 1 cm/sec with a wavelength of

285 nm. Calibration curves were created for each plate from absorbance values obtained from SC-0774 standards ranging in concentration from 20 to 1000 ng. The detection limit for this procedure was 20 ppb SC-0774 soil concentration.

Statistical Analysis. Data were analyzed statistically using analysis of variance with means being compared by Fisher's Protected LSD at the 5% level. Orthogonal contrasts were made where appropriate. Factorial analysis of variance indicated a significant interaction between soil depth and soil pH factors for both field and soil column studies. For this reason, mean separation values are presented which compare the effect of soil pH on the mobility of SC-0774 within individual depth levels.

RESULTS AND DISCUSSION

Extraction Method. A rapid, inexpensive method was developed for extracting SC-0774 from a sandy loam soil. The extraction efficiency for this method was approximately 85% at soil concentration of 1 ppm SC-0774 and was unchanged over a 10 week period (Table 4). Extraction efficiency improved slightly as the SC-0774 concentration was lowered (Figure 1). Presoaking the soil samples in a basic solution substantially improved recovery (data not presented). Apparently at high pH, SC-0774 is ionized and readily desorbs from soil surfaces. Then, after subsequent

acidification, the herbicide enters the organic phase more readily than it readsorbs to soil particles.

Soil Mobility Studies. Studies in 1986 indicated that residues remained in this sandy loam soil 4 months after application at levels high enough to bleach large crabgrass (Table 2). Also, the residues were concentrated near the soil surface in contradiction to the technical information. The soil pH at the site of these experiments was found to be 5.2.

Since the water solubilities of these herbicides are pH dependent, the effect of soil pH on the mobility of SC-0774 was examined. Soil ammended with lime and sulfur resulted in adjustments to pH near 4 and 6. At the site with no adjustment, the soil pH was near 5 (Table 3). The distribution of SC-0774 in the soil was significantly affected by soil pH. In soil of pH 4, SC-0774 remained concentrated near the soil surface, while in pH 6 soil, it moved into lower depths (Figure 2). SC-0774 residue levels were very low in soils collected from our second site (pH near 5). This site had a rye cover crop and apparently most of the SC-0774 applied was absorbed in the rye so little entered the soil. Residues detected from this location were, however, concentrated at the soil surface (Figure 6). These findings were supported by soil column studies (Figures 3 and 4) which showed that the soil mobility of SC-0774 and SC-0051 increased with increasing soil pH. Despite the

increased mobility at high pH, no residues were detected from field samples collected below 10 cm (data not presented).

Soil pH also affected the efficacy and persistence of SC-0774. Early season corn injury was significantly higher in SC-0774 treatments applied to pH 6 soils as compared to the same treatments applied to pH 4 soils (Figure 5). Control of yellow nutsedge by SC-0774 and SC-0051 was not affected by pH in 1987. However, residues persisted in low pH soils 13 months after application at levels high enough to bleach yellow nutsedge and significantly reduce the numbers of nutsedge plants present in 1988 (Table 6). Bleaching of yellow nutsedge was not observed in high pH soils in 1988. Using large crabgrass as a bio-indicator, herbicide residues fell below detection limits 10 weeks after application to high pH soils (Figure 6). Residues, however, remained high enough in the top 2.5 cm to bleach large crabgrass 24 weeks after application to low pH soils.

These results indicate that soil pH must be considered when using herbicides from this family. At high pH (>6), the potential for herbicide leaching increases dramatically. This could affect weed control and increase the potential for ground water contamination. At low pH (<5), the potential for carryover of herbicide residues increases which could restrict crop rotation.

Table 1. The susceptibility of large crabgrass to SC-0051 and SC-0774^a.

	<u>Concentration (ppm)</u>				
	0.1	0.5	1	2.5	5
	<u>Bleached</u>				
(%)					
SC-0051	15	82	97	99	99
SC-0774	0	79	90	97	99

^aMeans are averages of 2 replications repeated in time.

Table 2. SC-0774 residues present by depth as detected by large crabgrass 16 weeks after application in 1986^a.

Depth (cm)	SC-0051 1.1 kg/ha		
	+		
	SC-0051 1.1 kg/ha	SC-0774 1.7 kg/ha	SC-0774 1.1 kg/ha
	<u>Bleached</u>		
(%)			
0-2.5	0	25	93
2.5-5.1	0	0	3
5.1-7.6	0	0	0
7.6-10.1	0	0	0

^aMeans are averages of 3 replications repeated in time.

Table 3. The soil pH measured at the beginning and end of the 1987 growing season and one year later.

Depth (cm)	Low pH			High pH			Site 2	
	5/87	11/87	4/88	5/87	11/87	4/88	5/87	11/87
0-2.5	3.9	3.2	4.0	5.8	6.3	7.0	4.8	4.8
2.5-5.1	4.7	3.4	4.0	5.8	5.9	6.7	4.8	4.7
5.1-7.6	5.1	3.7	4.3	5.8	5.7	6.2	5.1	4.6
7.6-10.1	5.3	3.9	4.5	5.5	5.5	6.1	4.8	4.7

Table 4. The effect of time on the extraction efficiency of 1 ppm SC-0774 from sandy loam soils.

Weeks After Treatment	Extraction Efficiency (%)
1 week	88
4 weeks	85
6 weeks	82
10 weeks	86

*means are averages of 2 replications.

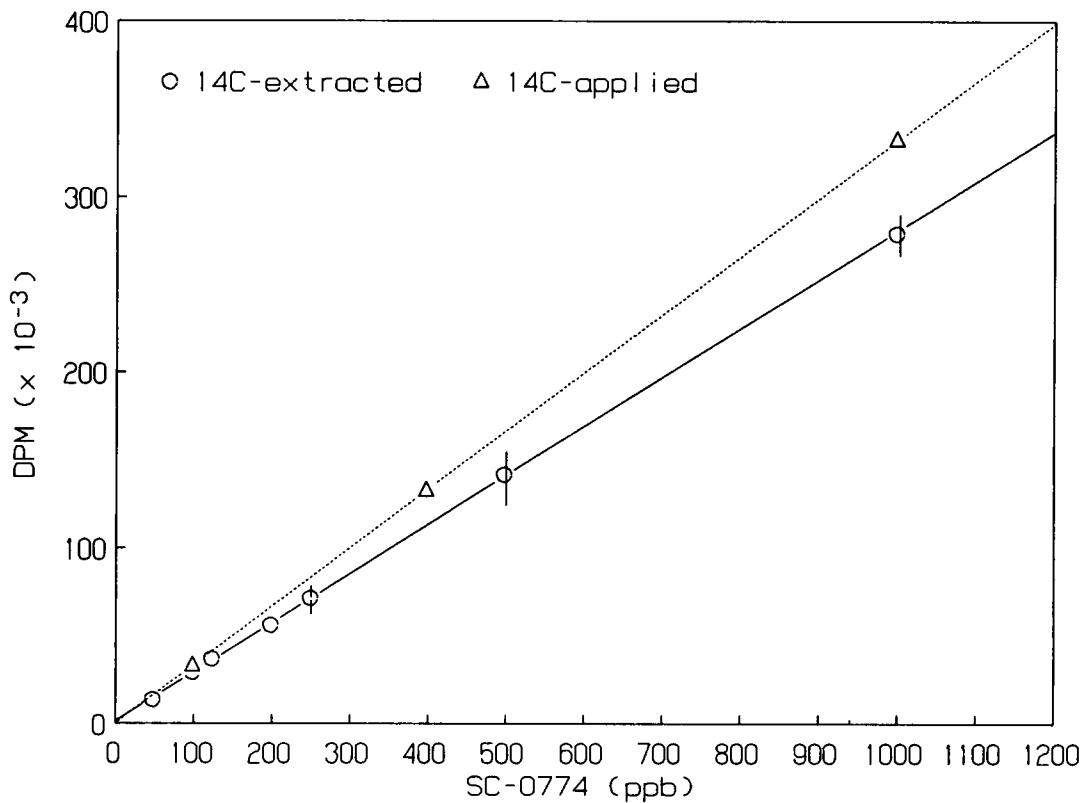
Table 5. The effect of soil pH on yellow nutsedge control by SC-0774 and SC-0051 from April 1987 herbicide applications^a.

Herbicide	Rate (kg/ha)	Growth stage	b pH	Yellow nutsedge		
				Control (%)	Plants (No/plot)	Bleached (%)
Control	--	--	high	0	4290	0
SC-0774	1.1	PRE	high	5	3170	0
SC-0774 + SC-0051	1.1	PRE				
SC-0774 + SC-0051	1.1	PRE	high	25	2320	0
Atrazine	0.6	POST				
SC-0774 + Atrazine	1.1	PRE	high	10	3490	0
Control	--	--	low	0	2800	0
SC-0774	1.1	PRE	low	10	2130	18
SC-0774 SC-0051	1.1	PRE				
SC-0774 SC-0051	1.1	PRE	low	50	600	50
SC-0774 SC-0051	0.6	POST				
SC-0774 Atrazine	1.1	PRE	low	20	640	29
Atrazine	1.3	PRE				
LSD (0.05) Significance: ^c				20	1220	11
high vs low pH				NS	*	*

^aMeans are averages of 4 replications.

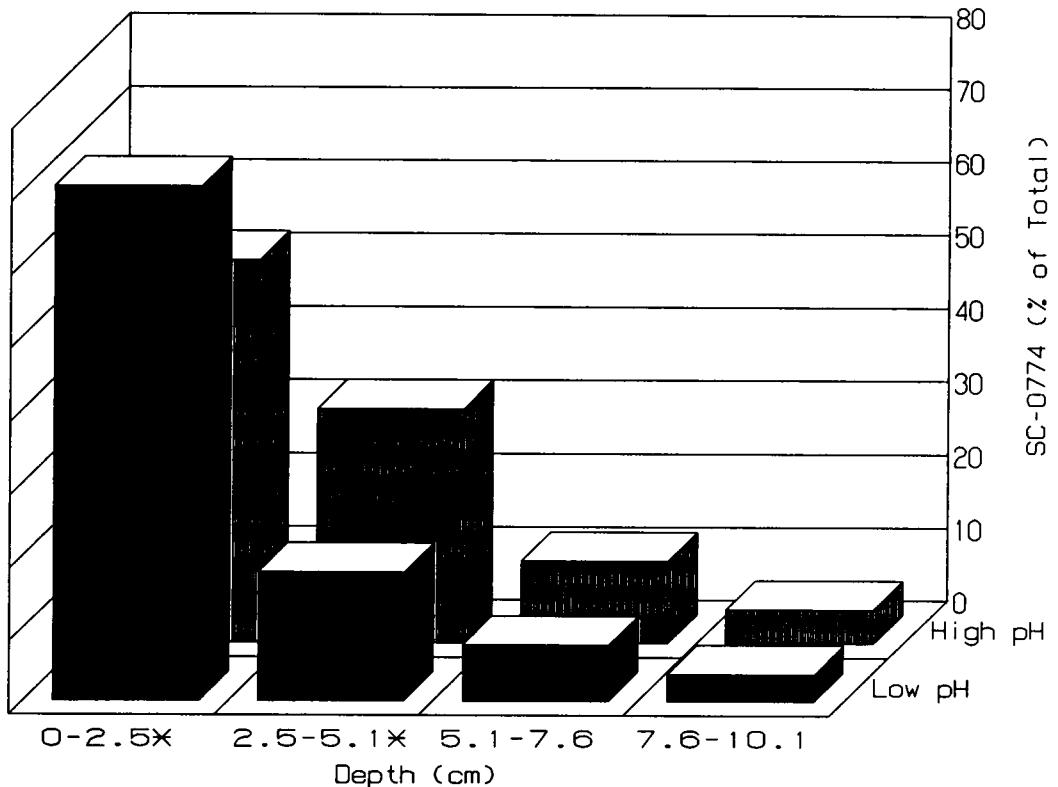
^bHigh pH = pH near 6, low pH = pH near 4

^cSignificant at the 0.01 level (*) or was not significant (NS).



^aMeans are averages of 2 replications, with confidence limits at the 0.1 level.

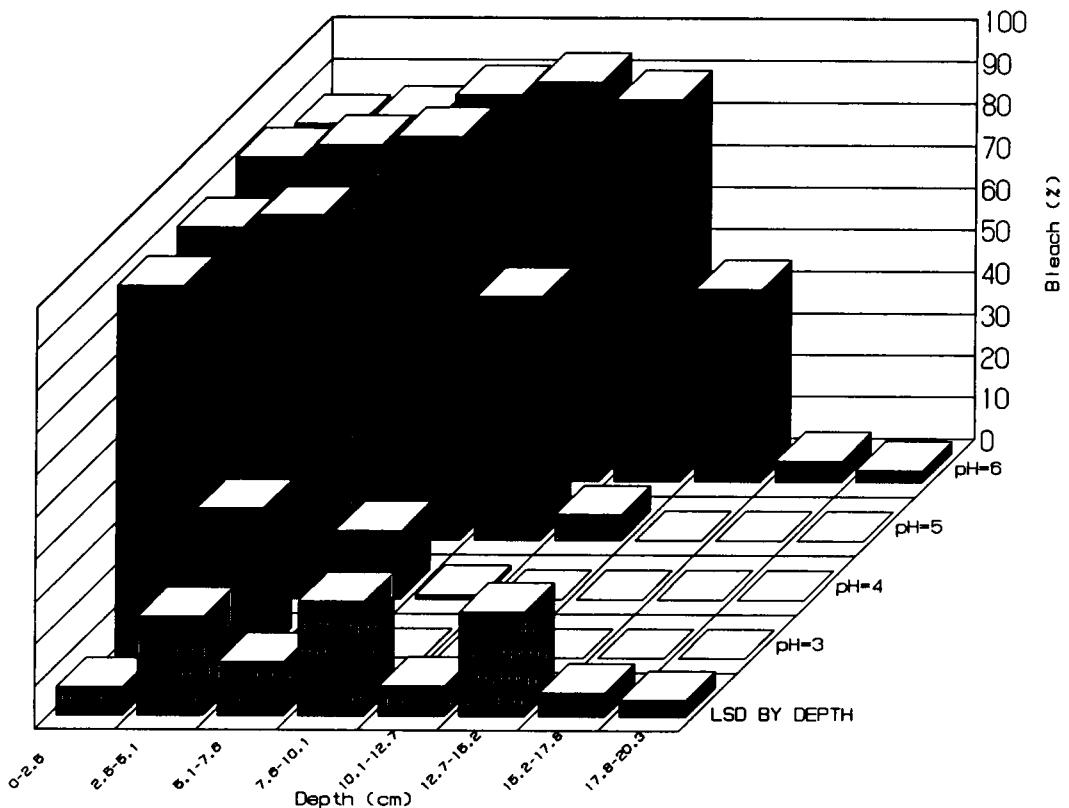
Figure 1. The recovery of ¹⁴C-SC-0774 from sandy loam soils^a at soil concentrations ranging from 50 to 1000 ppb.



^aMeans are averages of 3 sampling times.

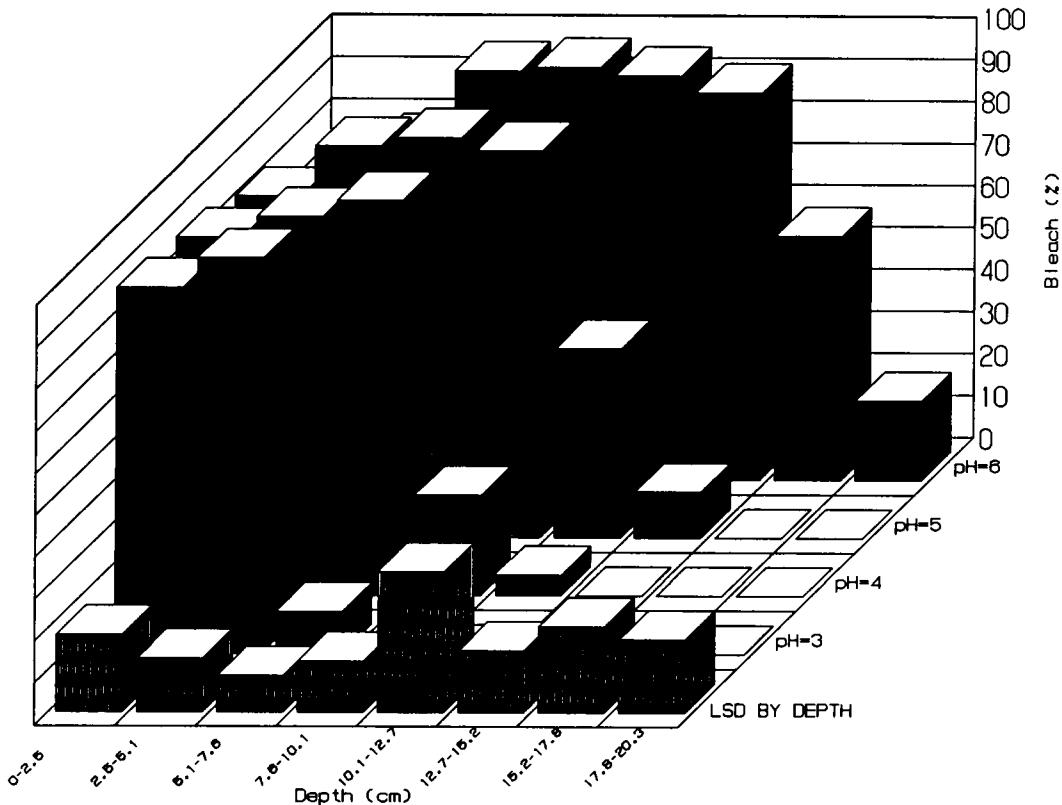
*Significant at the 0.01 level.

Figure 2. The effect of soil pH on the distribution of recovered SC-0774 from field soil samples^a.



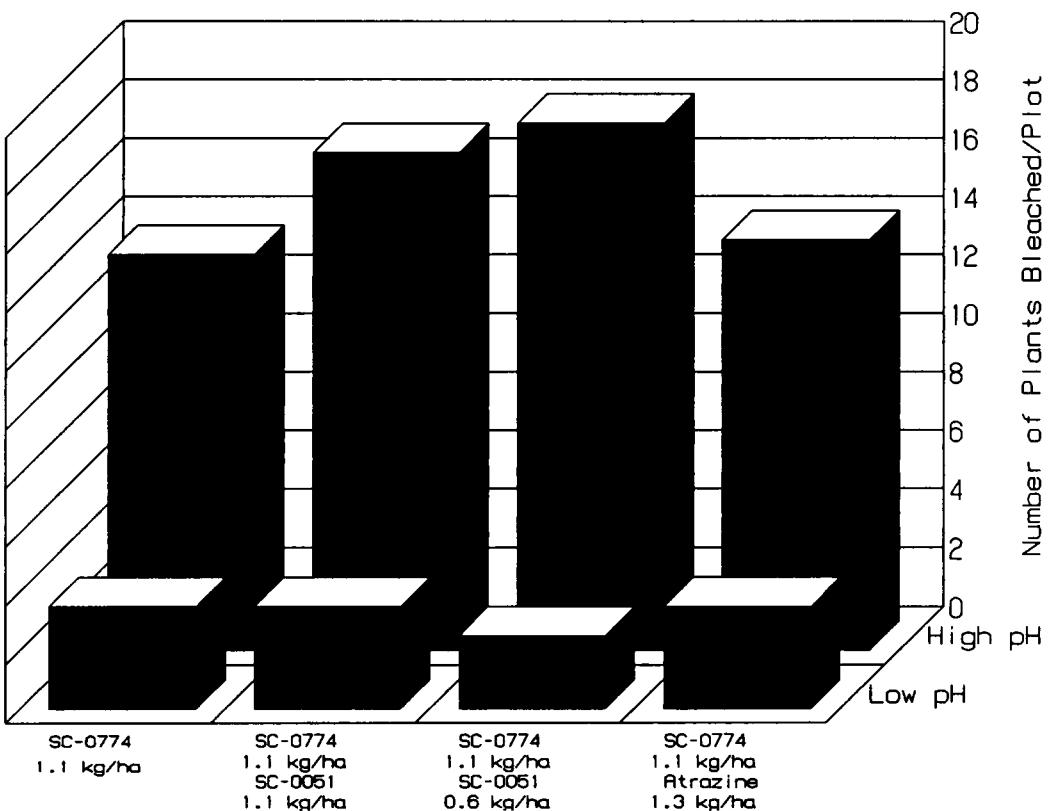
^aMeans are averages of 2 replications repeated once.

Figure 3. The effect of soil pH on the mobility of SC-0774 in sandy loam soils^a as detected by large crabgrass.



^aMeans are averages of 2 replications repeated once.

Figure 4. The effect of soil pH on the mobility of SC-0051 in sandy loam soils^a as detected by large crabgrass.



^aMeans are averages of 4 replications.

Figure 5. The effect of soil pH on SC-0774 induced corn bleaching.

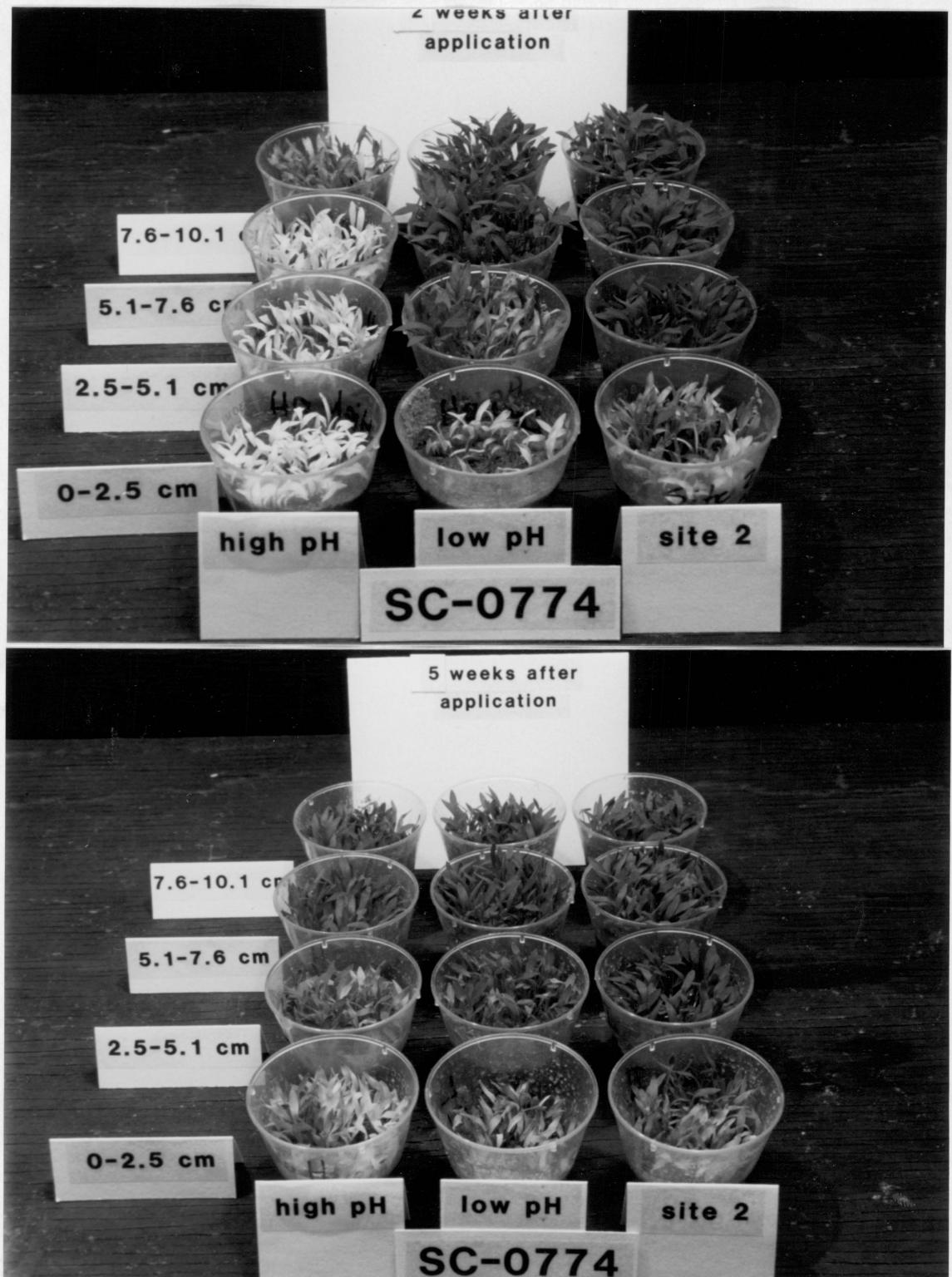


Figure 6. The effect of soil pH on the dissipation of SC-0774 residues over time detected by large crabgrass.

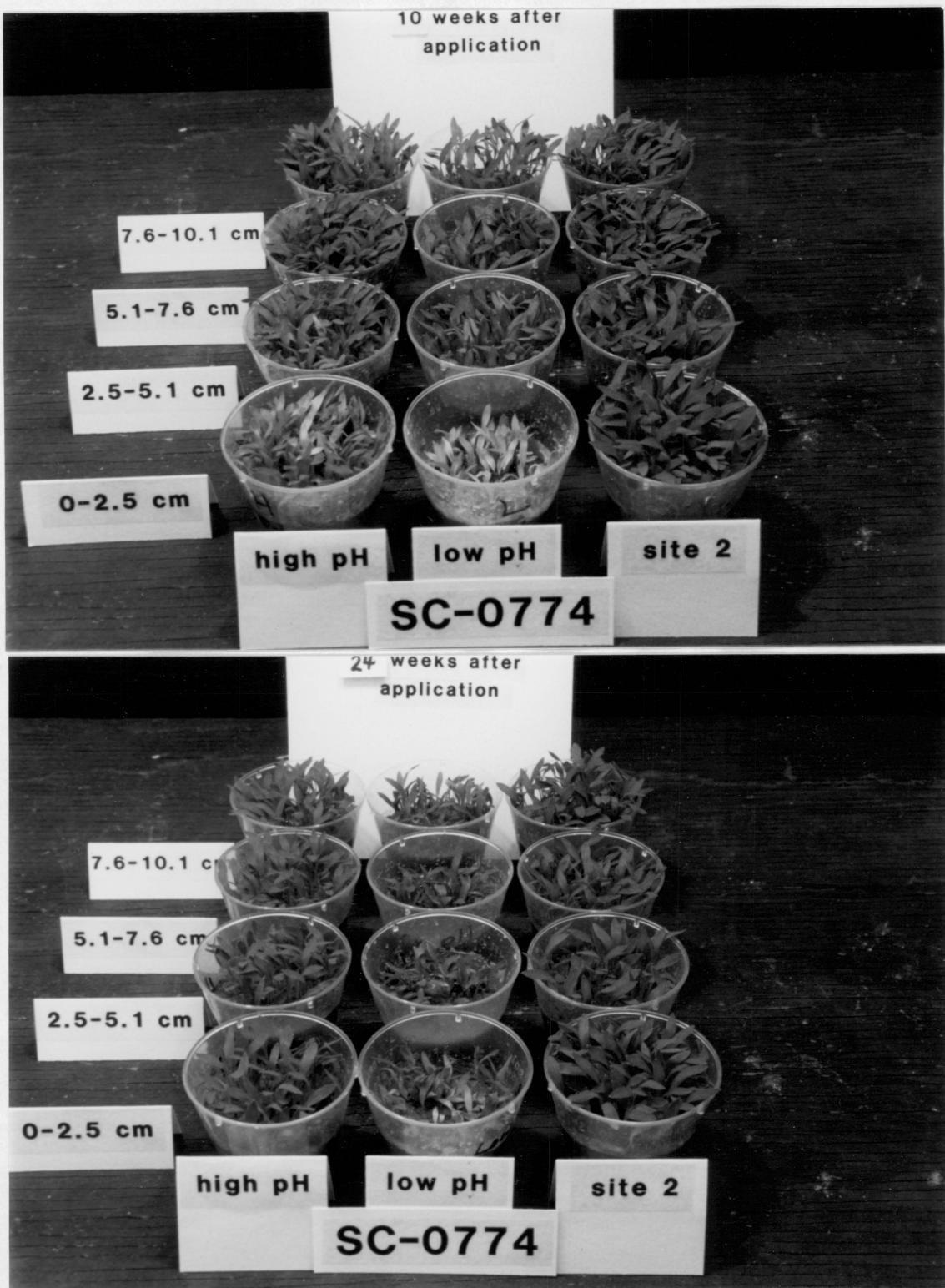


Figure 6. (Continued)

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IV. MECHANISM OF ACTION STUDIES WITH THE HERBICIDE SC-0051

INTRODUCTION

SC-0051 is an experimental herbicide that has shown promise for the selective control of many broadleaf weeds and some grasses in corn, sorghum, and wheat (5,7,8,9,12, 15,16). This herbicide causes reductions in chlorophyll and carotenoid levels in plant tissues (10) resulting in a bleached appearance in susceptible plant species. The exact mechanism of the bleaching effects of this herbicide is unknown.

A number of herbicides kill plants by reducing levels of plant pigments. Examples include the pyridazinone herbicides, amitrole, and clomazone. These herbicides inhibit the biosynthesis of carotenoids, leaving chlorophylls unprotected from photodestruction by sunlight (13). Most bleaching herbicides inhibit carotenoid biosynthesis by interfering with the desaturation of phytoene, leading to an accumulation of phytoene, phytofluene and other colorless pigments (1,2,3,4,14). Recently however, the bleaching herbicide clomazone was shown to inhibit carotenoid biosynthesis by inhibiting the formation of terpenoids needed for carotenoid biosynthesis (11). The intent of this research was to examine the effect of SC-0051 on the

distribution and quantity of pigments in the susceptible species soybean.

MATERIALS AND METHODS

Chemicals. Technical grade SC-0051 and norflurazon were used in these experiments. High performance liquid chromatography (HPLC) grade solvents were used for all extractions and chromatographic separations.

Plant Material. Soybean [Glycine max (L.) Merr. 'Essex'] seeds were sown in a potting mixture of sand/peat/weblite (1:1:1, v/v/v) and grown in a growth chamber at 25 C with a 14 hr light ($400 \text{ uE} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), 10 h dark cycle. Treatments were made by pipetting 150 ml of the herbicide solutions [24 mg norflurazon, 3 mg SC-0051 in water, methanol (95:5, v/v)] to the potting mixture when the soybeans had fully expanded unifoliate leaves. These treatments resulted in soil solution concentrations of approximately 20 ppm (w/w) norflurazon and 2.5 ppm (w/w) SC-0051 which provided similar degrees of bleaching symptoms. The bleaching response expressed in soybeans was herbicide dependent. Norflurazon caused bleaching symptoms primarily in the unifoliate leaves (old growth) while SC-0051 caused bleaching symptoms primarily in the first trifoliate (new growth). For these experiments, leaf tissues on each plant showing the greatest amount of bleaching

symptom were selected for pigment analysis.

Pigment Extraction. Leaf tissues (ca. 170 mg fresh wt) were homogenized in a solution of acetonitrile, methanol, methylene chloride, hexanes (40:15:22.5:22.5) for 4 minutes. Extracts were purified by preparative chromatography with C-18 Sep-pak columns using the extraction solvent. Solvents were removed under a stream of nitrogen with mild heat (40 C). Remaining residues were dissolved in 1.0 ml of a solution of acetonitrile, methanol, methylene chloride, hexanes (75:15:5:5) and filtered through a 0.45 um Gelman Acrodisc CR filter before analysis.

HPLC analysis. Fifteen ul portions of the plant extracts were injected into a Hewlet Packard Model 1090 liquid chromatograph with a Hewlet Packard 200 mm by 46 mm Hypersil ODS 5 um C-18 column with a Hewlet Packard 100 mm by 46 mm C-18 pre column. The pigments were separated by gradient elution chromatography. The program consisted of a 2 minute elution with a solution of acetonitrile, methanol, methylene chloride, hexane (75:15:5:5) followed by a gradient change to solution of acetonitrile, methanol, methylene chloride, hexane (40:15:22.5:22.5) over an 18 minute period. The flow rate was 0.50 ml/min and the column temperature was 40 C.

The pigments were detected by a diode array detector monitoring simultaneously at 285, 350 and 430 nm. Pigments were identified by their absorption spectra and retention

times. Quantitative comparisons of pigment levels were made using areas under selected peaks determined by integration.

RESULTS AND DISCUSSION

The effects of SC-0051 and norflurazon on soybean pigment composition are presented in Figures 1, 2, and 3, and in Table 1. Figure 1 shows a typical HPLC chromatogram of a pigment extract obtained from untreated soybeans. Good separation of xanthophylls, chlorophylls a and b, and carotenes was obtained. Figure 2 shows a typical chromatogram of a pigment extract from norflurazon treated soybeans. As reported previously (1), this herbicide caused reductions in the levels of xanthophylls, chlorophylls, and carotenes and induced an accumulation of the carotenoid precursor phytoene. A purified sample of phytoene had absorption maxima at 275, 285, and 297 when measured in petroleum ether. Phytoene was separated into its cis and trans isomers under these chromatographic conditions. Norflurazon also caused the accumulation of an additional, unidentified pigment not previously reported.

An HPLC chromatogram of a typical pigment extract from SC-0051 treated soybeans is shown in Figure 3. Like norflurazon, SC-0051 reduced the level of xanthophylls, chlorophylls, and carotenes while causing an accumulation of the carotene precursor phytoene. SC-0051 also caused the

accumulation of an unidentified pigment. The carotenoid precursor phytofluene, detected by other researchers, was not detected in any of these experiments. Table 1 shows that both norflurazon and SC-0051 reduced the levels of xanthophylls, chlorophylls, and carotenes by more than 90 % while causing more than a 5-fold increase in the levels of phytoene as compared to untreated controls.

Both SC-0051 and norflurazon induced the formation of a pigment not detected in controls. The identity of this compound is unknown but it appears to be a derivative of phytoene. The absorption spectrum of this unknown pigment is similar to that of phytoene (Figures 4 and 5), but its location in the chromatogram indicates that it is more polar. A compound, similar in chromatographic location, induced by the bleaching herbicide diflufenican [N-(2,4-difluorophenyl)-2-(3-trifluoromethylphenoxy)-3-pyridine carboxamide], was detected by Britton et al. (3) and determined to be monohydroxyphytoene. It is therefore possible that this compound is also monohydroxyphytoene.

The results obtained in these studies indicate that SC-0051 behaves similarly to norflurazon; inducing bleaching symptoms by inhibiting the desaturation of phytoene and ultimately the formation of carotenes. These findings, however, do not preclude the possibility of other SC-0051 induced herbicidal effects. Nandihalli and Bhowmik (10) recently reported that SC-0051 reduced chlorophyll **b** levels

to a greater extent than chlorophyll α levels and they suggested that SC-0051 may interfere directly with chlorophyll synthesis. However, preferential reductions in chlorophyll levels by SC-0051 were not observed in these studies and Devlin (6) reported that SC-0774, a structural analogue of SC-0051, preferentially affected chlorophyll α formation. Therefore, the effects of this family of herbicides on chlorophyll biosynthesis, if any, remain unclear.

Table 1. The effect of norflurazon and SC-0051 on pigment composition in soybean^a.

Treatment	Pigment Content				
	Xanthophylls	Chl a	Chl b	Carotenes	Phytoene
	(% of Control)				
Norflurazon	6.5	7.2	7.5	3.4	770
SC-0051	2.8	1.5	2.0	2.1	560

^aData is based on three replications repeated once.

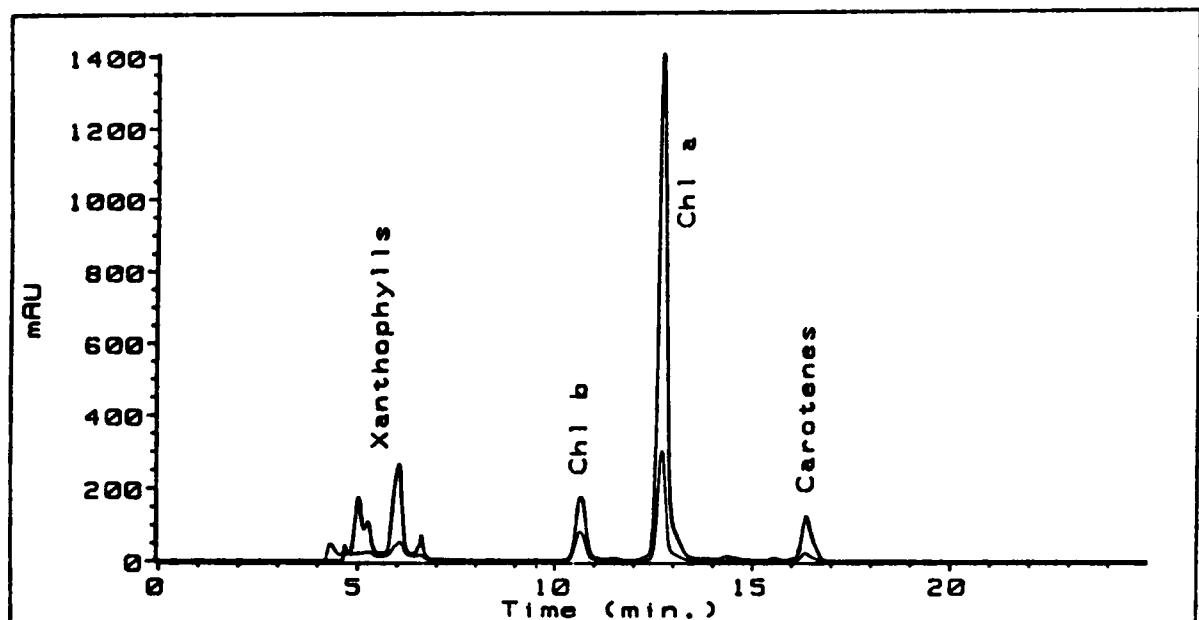


Figure 1. HPLC chromatogram of pigment distribution in untreated soybeans monitored at 430 and 285 nm.

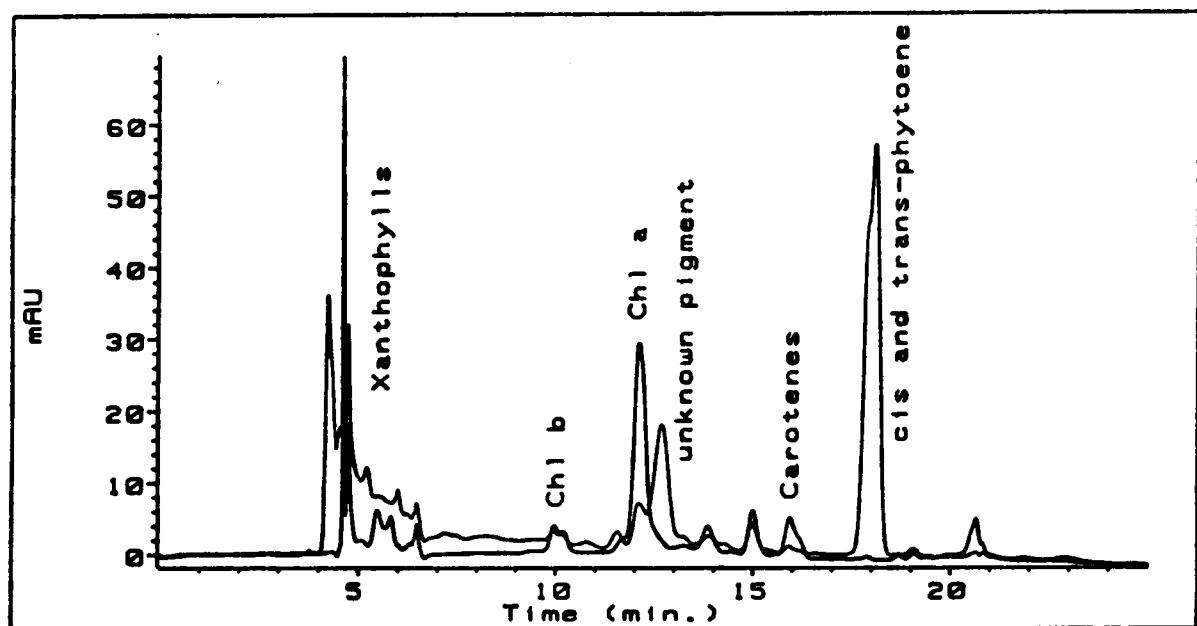


Figure 2. HPLC chromatogram of pigment distribution in norflurazon-treated soybean monitored at 430 and 285 nm.

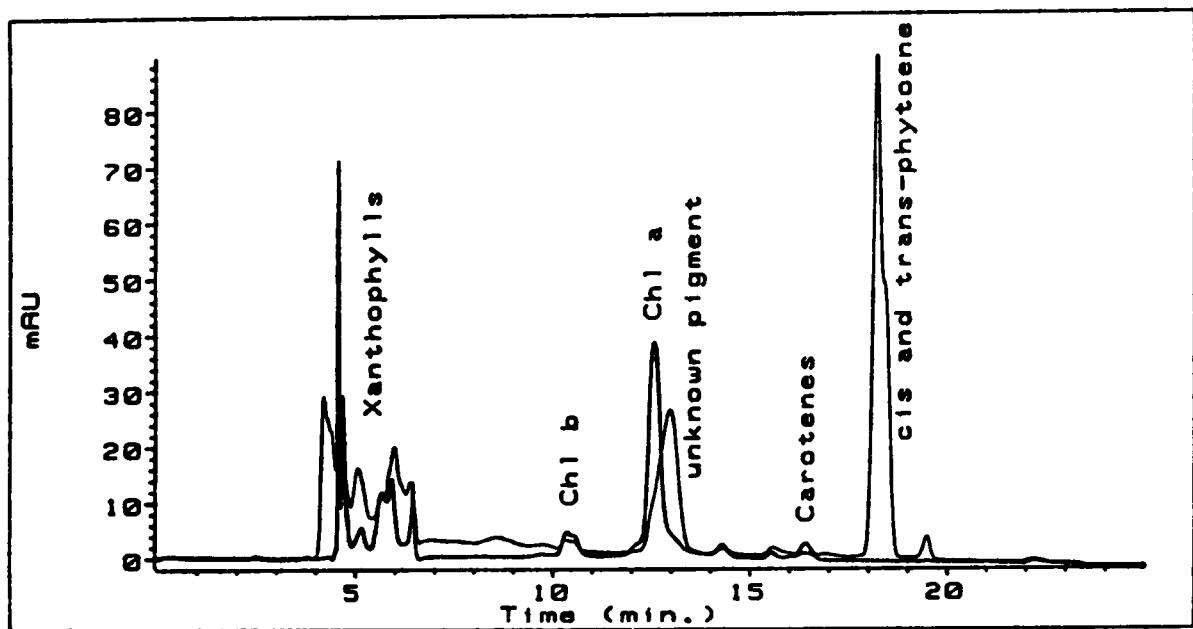
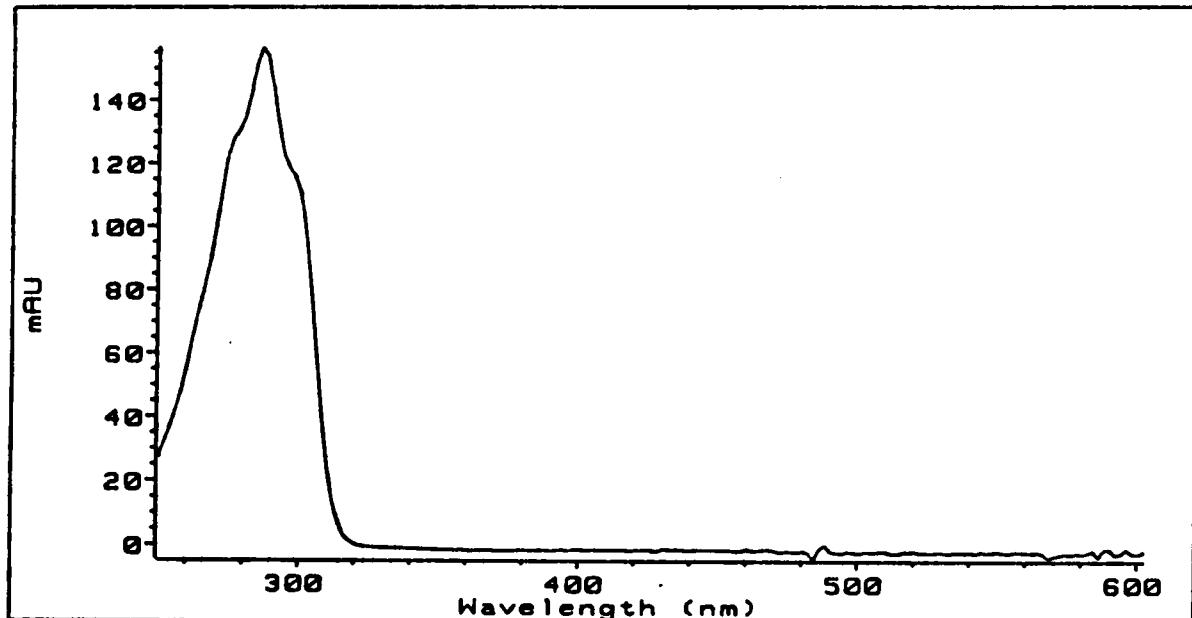
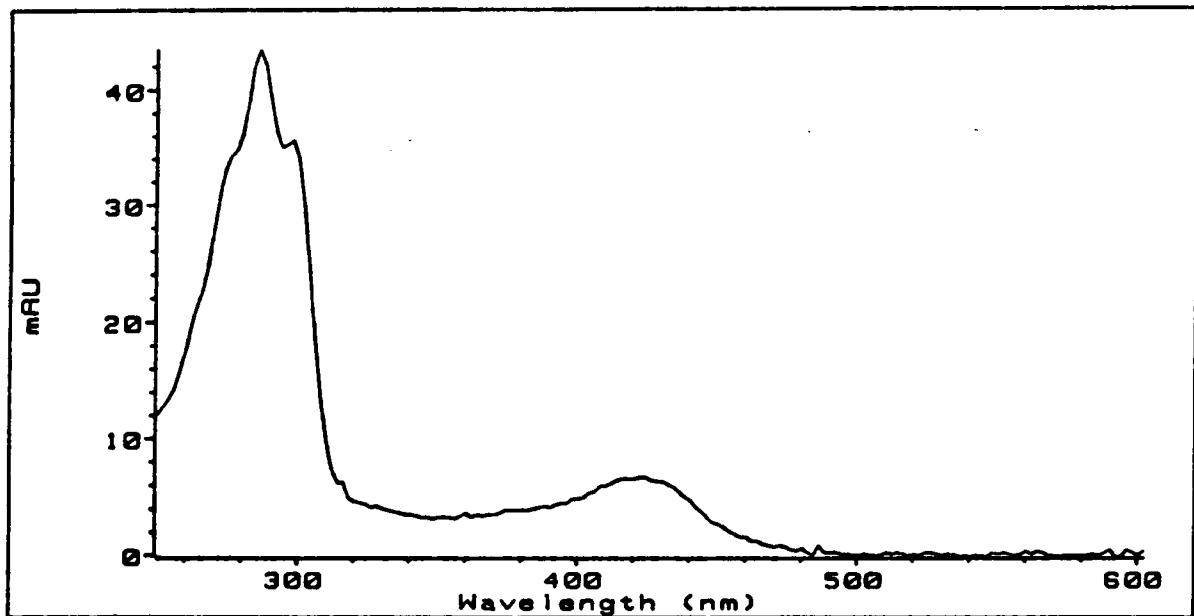


Figure 3. HPLC chromatogram of pigment distribution in SC-0051-treated soybeans monitored at 430 and 285 nm.



^aMeasured in acetonitrile, methanol, dichloromethane, hexane (ca. 45:15:20:20).

Figure 4. Absorption spectrum of phytoene^a extracted from SC-0051-treated soybeans.



^aMeasured in acetonitrile, methanol, dichloromethane, hexane (ca. 55:15:15:15).

Figure 5. Absorption spectrum of an unidentified pigment^a extracted from norflurazon-treated soybeans.

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V. UPTAKE AND TRANSLOCATION OF SC-0051 IN CORN
(*Zea mays*) AND SOYBEANS (*Glycine max*)

INTRODUCTION

SC-0051 is an experimental herbicide that has shown potential for selectively controlling broadleaf weeds and some grasses selectively in corn, sorghum, and wheat (2, 5, 6, 7, 8, 9, 10, 11, 12, 13). Under field conditions, corn tolerates preemergence or postemergence applications of SC-0051 at use rates as high as 2.2 kg/ha, while soybeans are susceptible to use rates as low as 0.3 kg/ha. The basis for this selectivity is not known.

Differential absorption, translocation, and metabolism are recognized as important factors involved in herbicide selectivity (1, 3, 4). The purpose of this study was to determine the role of absorption, translocation, and metabolism in the differential susceptibility of corn and soybeans to SC-0051.

MATERIALS AND METHODS

Plant material. For root uptake studies, corn and soybean seeds were sown in a potting mixture of sand/peat/weblite (1:1:1, v/v/v) until harvested for treat-

ment. For foliar uptake studies, corn and soybean seeds were sown in vermiculite watered with half strength Hoagland's solution. Plants were grown in a growth chamber at 25 °C with a 14 hr light ($400 \text{ uE} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), 10 hr dark cycle throughout the course of these experiments.

Root uptake studies. When corn plants reached 10 cm in height, and when soybean plants had expanding unifoliate leaves, they were transferred to half strength Hoagland's solution for 48 hrs, followed by an additional 48 hrs in full strength Hoagland's solution. Plants were then transferred to 100 ml of full strength Hoagland's solution containing 0.2 uCi of ^{14}C -SC-0051, with an overall SC-0051 concentration of 100 uM. Plants were harvested 12, 48, and 96 hrs after treatment. After washing the roots with running water for 30 seconds, the plants were placed in a drying oven for 48 hrs at 40 °C. Corn plants were divided into roots, and shoots. Soybeans were divided into old leaves (cotyledons and unifoliate leaves), new leaves (trifoliates), and roots and stems.

Foliar uptake studies. When corn plants reached the 3 leaf stage and when soybean plants had one expanding trifoliate, a 20 ul drop [acetone/water (1:1 v/v)] containing 0.1 uCi ^{14}C -SC-0051 (Sp act 10.2 mCi/mmol) was placed on the bottom leaf on corn plants and on one of the unifoliate leaves on soybean plants. Plants were harvested at 12, 48, and 96 hrs. Non-absorbed ^{14}C -SC-0051 was washed from the

treated leaves with a 20 ml stream of acetone. The plants were then oven dried as described above. Corn plants were separated into treated leaf roots, and remaining shoot. Soybeans were separated into the treated leaf, old leaves, new leaves, and roots and stems.

Radioactivity was determined by combustion, and is expressed as disintegrations per minute (dpm) per milligram dry weight of root or leaf tissue. Translocation was determined both qualitatively by autoradiography and quantitatively by radioassay of the various portions of the treated plants.

RESULTS AND DISCUSSION

Uptake studies. There was a significant increase in ^{14}C -SC-0051 uptake over time in both corn and soybeans (Table 1). Considerably more radiolabelled herbicide was absorbed by the foliage of both corn and soybeans than was absorbed by the roots. In both cases, soybeans exhibited herbicide injury symptoms (bleaching) while corn remained uninjured.

There was no significant difference in foliar uptake of ^{14}C -SC-0051 between species. However, soybeans absorbed more herbicide through the roots than did corn. This may be due in part to a more vigorous growth in Hoagland's solution exhibited by soybeans. The transpiration rate for

soybeans in Hoagland's solution was approximately twice that of corn (data not presented).

Translocation of ^{14}C -SC-0051. Radiolabelled SC-0051 rapidly translocated throughout corn plants when applied to the roots or to the foliage (Table 2). The distribution pattern of ^{14}C -SC-0051 in corn seedlings can be seen in the autoradiographs presented in Figures 1 and 2. There was little change in the distribution pattern over time. Herbicide applied to the foliage did not remain in high concentrations in the treated leaf, nor was there an accumulation of ^{14}C -SC-0051 in any portion of the plant.

Radiolabelled SC-0051 rapidly translocated throughout soybean plants when applied to the roots but not when applied to the foliage (Table 3). The distribution pattern of ^{14}C -SC-0051 in soybean seedlings can be seen in the autoradiographs presented in Figures 3 and 4. Foliar applied herbicide remained concentrated in the treated leaf with little movement into the old leaves (unifoliate leaves and cotyledons) or in the roots and stem. Over time there was a significant accumulation of herbicide in the new leaves (trifoliates) of soybeans from both root and foliar applications.

In summary, ^{14}C -SC-0051 was absorbed by the foliage of corn and soybeans more rapidly than by the roots. Soybeans absorbed more herbicide through the roots than did corn, but there was no difference in foliar uptake between

species. SC-0051 rapidly translocated throughout corn plants but was concentrated in the new growth in soybeans.

The visual injury symptoms expressed in soybeans by SC-0051 are bleaching in the newly formed tissues followed by necrosis and plant death. The data in these studies support the visual observations that SC-0051 is translocated preferentially to the most actively growing portions of soybeans. No local accumulation of SC-0051 was observed in corn. Corn tolerates SC-0051 applied to the foliage or to the soil, while soybeans are susceptible to this herbicide applied either way. Since there was difference in foliar herbicide uptake between species and questionable differences in root uptake, selectivity between corn and soybeans is probably not due to differential uptake. Selectivity is more likely due to differential translocation of SC-0051 between these species.

Table 1. ^{14}C -SC-0774 absorption by corn and soybean plants harvested 12, 48, and 96 h after root or leaf treatment^a.

Species	Harvesting time (hrs)	^{14}C -Content	
		Root applied	Foliar applied
Corn	12	65	785
	48	115	880
	96	150	1165
LSD(0.05) ^b		40	405
Soybean	12	90	825
	48	135	1140
	96	275	1420
LSD(0.05) ^b		60	380
Significance: ^c			
Corn vs Soybean		*	NS

^aMeans are averages of 3 replicates repeated.

^bBetween harvesting time, within species and organs.

^cSignificant at the 0.01 level (*) or was not significant (NS).

Table 2. Distribution of absorbed ^{14}C -SC-0051 in corn plants harvested 12, 48, and 96 h after root or leaf treatment^a.

14C-distribution					
Organ treated	Harvesting time	Treated leaf	Roots	Leaves	LSD
	(hrs)	(% of total recovered)			(0.05)
Root	12	--	53	47	13
	48	--	52	48	11
	96	--	50	50	13
LSD(0.05) ^b			12	12	
Leaf	12	41	23	36	39
	48	23	28	49	35
	96	37	15	48	20
LSD(0.05) ^b		35	15	29	

^aMeans are averages of 3 replications repeated in time.

^bBetween harvesting time, within organs.

Table 3. Distribution of absorbed ^{14}C -SC-0051 in soybean plants harvested 12, 48, and 96 h after root or leaf treatment^a.

Organ treated	Harvesting time	Treated	^{14}C -distribution			
			Old ^b leaf	New ^c leaves	Root + stems	LSD
(hrs)		— (% of total recovered) — (0.05)				
Root	12	--	35	25	40	9
	48	--	19	46	35	17
	96	--	26	39	35	16
$\text{LSD}(0.05)^d$			7	16	15	
Leaf	12	83	2	7	8	5
	48	70	2	22	6	7
	96	74	1	14	11	7
$\text{LSD}(0.05)^d$		10	1	4	8	

^aMeans are averages of 3 replications repeated in time.

^bOld leaves includes the cotyledons and unifoliates.

^cNew leaves include all trifoliates.

^dbetween harvesting time, within organs.

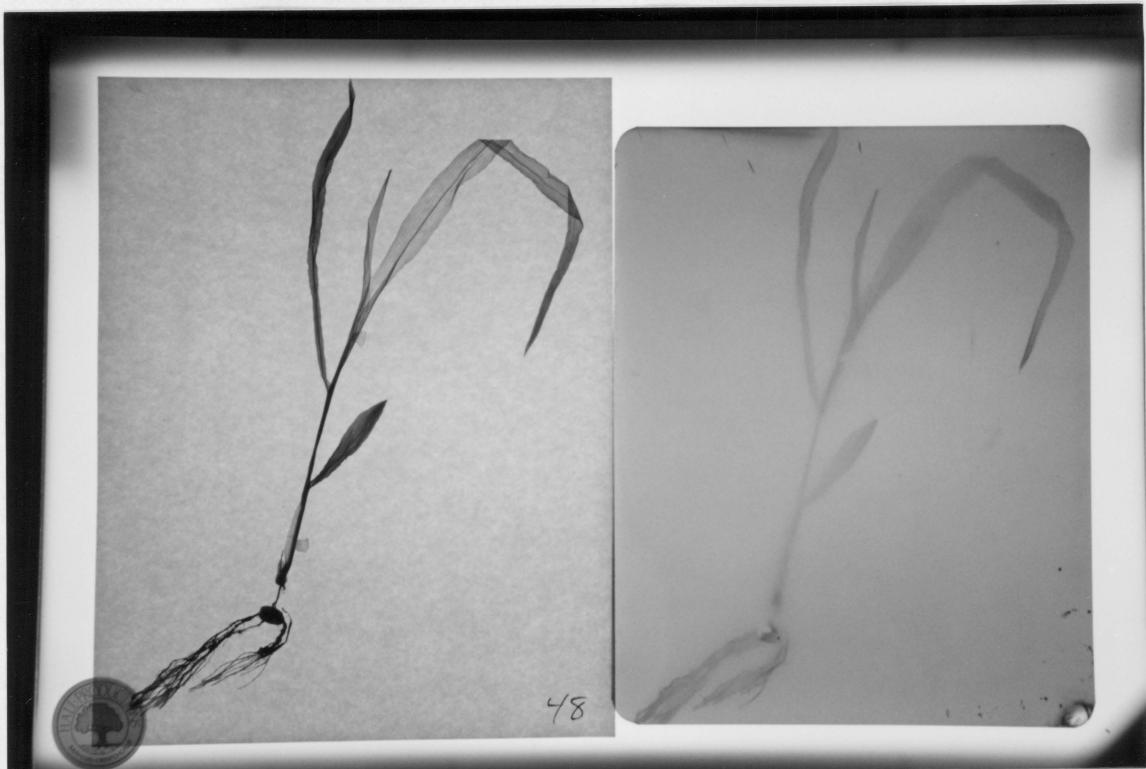


Figure 1. Distribution of root absorbed ^{14}C -SC-0051 in corn seedlings 48 h after application.

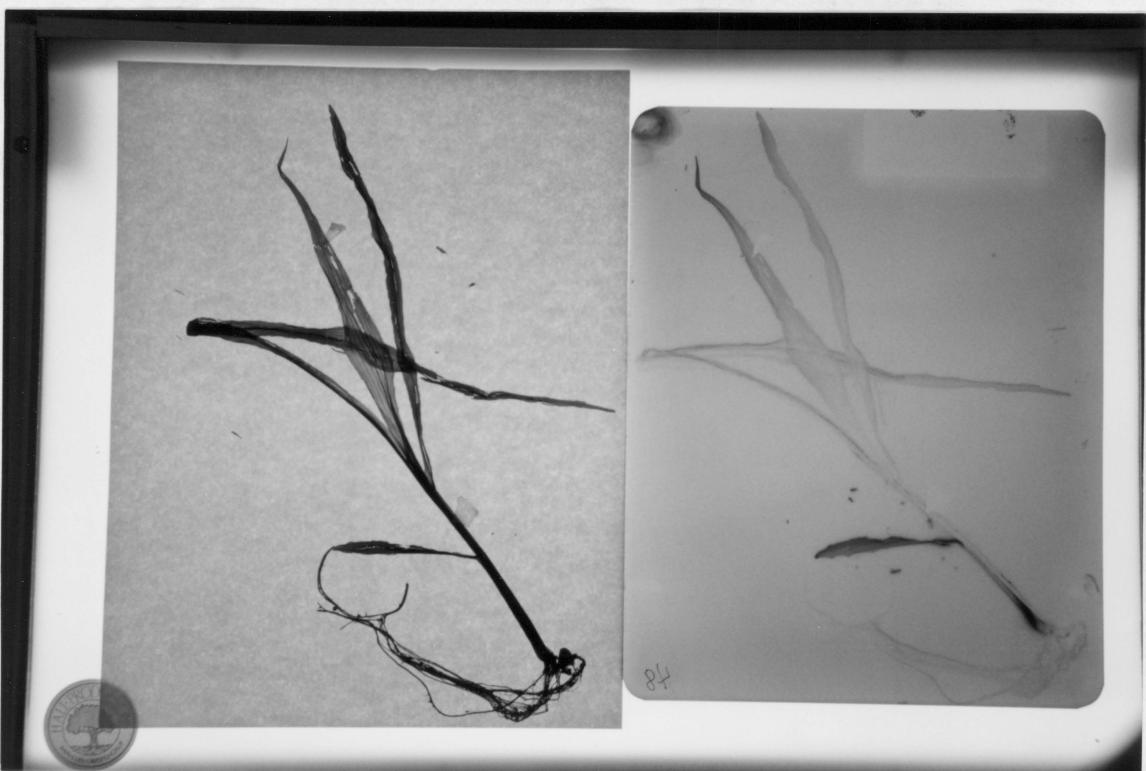


Figure 2. Distribution of foliar absorbed ^{14}C -SC-0051 in corn seedlings 48 h after application.



Figure 3. Distribution of root absorbed ^{14}C -SC-0051 in soybean seedlings 48 h after application.



Figure 4. Distribution of foliar absorbed ^{14}C -SC-0051 in soybean seedlings 48 h after application.

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VI. SUMMARY AND CONCLUSIONS

This research examined SC-0051 and SC-0774, two experimental compounds of undisclosed chemistry, as potential new herbicides for use in conventional and no-till corn in Virginia. Field studies were conducted evaluating various rates of these herbicides alone and in combination with other, currently available herbicides for weed control and corn response. SC-0051 controlled many broadleaf weed species when applied preemergence or postemergence in corn and was particularly effective in controlling common lambsquarters and common ragweed. SC-0051, however, failed to adequately control smooth pigweed. SC-0051 did not injure corn in any of these studies. SC-0774 applied preemergence was effective in controlling large crabgrass in no-till corn but failed to provide adequate control of other grass or broadleaf weeds in these studies. SC-0774 injured corn in some studies but not severely enough to cause yield reductions. While neither SC-0051 nor SC-0774, applied alone, provided adequate weed control, combinations of the two provided broad-spectrum weed control and yields comparable to atrazine plus metolachlor treatments. Combinations of SC-0051 and atrazine, applied preemergence or postemergence provided excellent broad-spectrum weed control and high yields. Because of the high activity of

SC-0051 on common lambsquarters, this treatment might provide a useful alternative for the control of triazine resistant common lambsquarters.

Field and laboratory studies were conducted which examined the effect of soil pH on the mobility and persistence of SC-0774 and SC-0051 sandy loam soils. These studies showed that the mobility of SC-0774 in soil in the field was greater in high pH soil (pH near 6) than in low pH soil (pH near 4). This was supported by soil column studies which showed that the mobility of both SC-0774 and SC-0051 in soil increased with increasing pH. SC-0774 residues remained high enough in low pH soil to bleach large crabgrass 24 weeks after application. In contrast, SC-0774 residues were detectable for only 10 weeks in high pH soils. Similarly, yellow nutsedge showed bleaching symptoms 13 months after application of SC-0774 in low pH soils but was not bleached in identical treatments in high pH soils. This information is important considering current concerns about pesticide movement into ground water. Much of the corn grown in Virginia and throughout the corn belt is planted in soils with a pH above 6. These studies show that the potential for leaching of SC-0774 and SC-0051 into ground water is significant at this high pH. These studies also show that in low pH soils, the potential for carryover of SC-0774 and SC-0051 increases which could restrict crop rotation options.

This family of herbicides kills plants by reducing pigment levels, causing susceptible plants to turn white (bleached) and ultimately die of starvation. Studies were conducted to examine the molecular mechanism of the bleaching action of SC-0051. These studies showed that SC-0051 inhibited the biosynthesis of carotenoids while causing an accumulation in the carotenoid precursor phytoene. This herbicide also caused an accumulation of an unidentified pigment. The absorption spectra of the unidentified pigment is similar to that of phytoene, indicating that it is probably structurally similar. These data indicate that the mechanism of SC-0051 action is the inhibition of phytoene desaturase activity, causing an accumulation of phytoene in bleached tissue.

Studies were conducted to investigate the basis for the selectivity of SC-0051 in tolerant corn seedlings versus susceptible soybean seedlings. These studies showed that the uptake of radiolabelled SC-0051 into the roots and foliage was similar in corn and soybeans. However, SC-0051 accumulated in the actively growing areas of the susceptible soybean seedlings more than it did in tolerant corn seedlings. This suggests that differential response of plants to this herbicide may be the result of its differential translocation in plant species. The role of differential metabolism in the selectivity of this herbicide may also be important and needs to be addressed in future

investigations.

The effectiveness of SC-0051 on a wide range of broadleaf weed species, combined with its preemergence and post-emergence safety to corn make it a potentially useful new herbicide for use in Virginia. The potential for crop injury combined with the limited weed control provided by SC-0774, are viewed as serious disadvantages for the use of this herbicide in corn production in Virginia. The use of products from this family of herbicides will require a consideration of soil pH to prevent problems of injury to crops planted in rotation, or to avoid leaching into ground water.

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