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Date August 13, 1987

WEED CONTROL EFFICACY AND PLANT RESIDUE DETERMINATION OF OXYFLUORFEN APPLIED PREEMERGENCE IN TRANSPLANTED BROCCOLI

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

William H. Eaton, Jr.

August 1987

DEDICATION

To my parents,

Bill and Ruth Eaton

and my sister, Annette,

for their love and inspiration.

ACKNOWLEDGMENTS

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ABSTRACT

Field studies were conducted to evaluate the weed control efficacy of the herbicide oxyfluorfen applied preemergence at rates of 0.28, 0.42, 0.56 and 1.12 kg ai/ha in spring and fall transplanted broccoli (Brassica oleracea var. italica L. cv. 'Premium Crop'). Oxyfluorfen at all rates evaluated provided excellent control (90-100%) of redroot pigweed (Amaranthus retroflexus L.), common purslane (Portulaca oleracea L.), turnip (Brassica rapa), goosegrass [Eleusine indica (L.) Gaertn.], and large crabgrass [Digitaria sanquinalis (L.) Scop.]. Oxyfluorfen at rates of 0.56 kg/ha or greater was needed for commercially acceptable control of the annual grass weeds fall panicum (Panicum dichotomiflorum Michx.), giant foxtail (Setaria faberi Herrm.), and Italian ryegrass (Lolium multiflorum Lam.). In one test, crop phytotoxicity and subsequent reduced yields resulted from oxyfluorfen at the highest rate. In all other tests some early crop phytotoxicity was observed among oxyfluorfen treatments, but no reduction in yield occurred. Gas-liquid chromatographic analysis of oxyfluorfen residues was performed on head tissue of plants grown on soil that received the highest rate (1.12 kg/ha) of the herbicide. Neither the parent compound nor any of its metabolites were detected in broccoli head tissue using the accepted analytical method which is sensitive to 0.01 ppm.

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Broccoli (Brassica oleracea var. italica) is one of the few vegetables increasing in popularity in the United States. Recent health awareness trends have made broccoli especially appealing due to its relatively low calorie and high nutrient and fiber content. Broccoli production has doubled since 1970 with much of the increase occurring in the Southeast (3,31). In Tennessee during 1986, approximately 200 acres were grown for fresh market outlets and 300 acres were grown for processing (33).

Broccoli is a labor intensive crop that requires a high level of management. Weed control is one of the many problems confronted in its production. Weeds compete for light, nutrients, water, gases, and space resulting in reduced yields and quality. Weeds also harbor insects and diseases and interfere with harvesting and with application of pesticides and fertilizers. Effective chemical weed control measures can greatly enhance an integrated pest management system making increased and more efficient production possible. By eliminating the need for mechanical cultivation, an efficacious preemergence herbicide could reduce machinery and fuel costs, minimize deleterious effects on soil structure, reduce evaporation, and eliminate the complications of weather and soil restrictions on cultivation.

Few herbicides are currently approved for use in broccoli. Most provide little to no control of many broadleaf weeds as they

are selective for annual grasses. Also, their performance often depends on timely soil incorporation and/or irrigation (18,37,41,43). Nitrofen [2,4-dichloro-1-(nitrophenoxy) benzene] was a selective preemergence herbicide used to control many broadleaf weeds and some grasses in a variety of cole crops until it was withdrawn from the market in 1980 (15,36,38,43). Since that time considerable effort has been made to find a similar broad spectrum herbicide to fill this void. Oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene], an analog of nitrofen, has shown promise in this regard (15,17,18,38,41,43,45).

The objectives of the research conducted in this study were to:

1. Determine the weed control efficacy of oxyfluorfen applied preemergence in spring and fall transplanted broccoli and its effects on yield and quality.

2. Evaluate the reliability of an analytical method for determination of oxyfluorfen residues using broccoli as a substrate.

3. Determine oxyfluorfen residues in the edible portion of transplanted broccoli grown on soil treated with oxyfluorfen at 1.12 kg ai/ha.

PART I

LITERATURE REVIEW

I. OXYFLUORFEN

General Information

Oxyfluorfen is a selective herbicide marketed by Rohm and Haas Company under the trade name Goal®. It is registered for use in certain treefruit, grape and nut crops, artichoke, non-bearing citrus, soybean, cotton, onion, mint, fallowbed, and conifer seedbeds, transplants, and container stock. It is also registered for witchweed [Striga asiatica (L.) Ktze. #[1] STRLU] control in corn in North and South Carolina (5,8).

Applied preemergence or postemergence, oxyfluorfen gives broad spectrum control of many annual broadleaf weeds and grasses at relatively low rates of active ingredient (8,45). It is reported to be 10 times more active than its discontinued analog, nitrofen (25,46). The recommended rate for effective preemergence weed control in soybeans is 0.43 to 0.56 kg/ha (5,8).

Physical and Chemical Properties

Oxyfluorfen is a diphenyl ether compound. Its physical and chemical properties are found in Table I-1 and the structural formula appears in Figure I-1.

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[1]Letters following this symbol are a WSSA-approved computer code from Composite List of Weeds, Weed Sci. 32, Suppl. 2. Available from WSSA, 309 West Clark St., Champaign, IL 61820.

Table I-1. Physical, Chemical, and Toxicological Properties of Oxyfluorfen, DCPA, Napropamide, Bensulide, Trifluralin, and CDEC.

Properties	Herbicides					
	Oxyfluorfen	DCPA	Napropamide	Bensulide	Trifluralin	CDEC
Molecular weight	361.7	332.0	271.4	397.5	335.3	223.8
Physical form[a]	wcs or rbs	wcs	wcs	wcs or cl	os	al
Melting point (°C)	65-80	156	74.8-75.5	34.4	48.5-49	--
Vapor pressure (mm Hg)	$2x10^{-6}$ (25°C)	<0.01 (40°C)	0.1 µm (50°C)	--	$1.1x10^{-4}$ (25°C)	$2.2x10^{-3}$ (200°C)
Specific gravity	1.35 (73°C)	--	--	1.224	--	1.16
Solubility:						
Water	0.1 ppm	0.5 ppm (25°C)	73 ppm	25 ppm (20°C)	<1.0 ppm (27°C)	92 ppm (25°C)
Ethanol	--	--	>1000 g/liter	miscible	$74x10^{3}$(27°C)	soluble
Methanol	--	--	--	--	--	--
Acetone	72.5%	10%	>1000 g/liter	--	$39.5x10^{4}$(27°C)	soluble
LD_{50}[b] (mg/kg)	>5000	>3000	>5000	770	3700	850

[a]wcs = white crystaline solid, cl = clear liquid, os = orange solid, al = amber liquid, rbs = red brown solid.

[b]acute oral toxicity in rats.

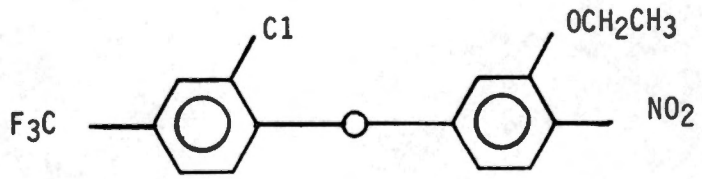


Figure I-1. Structural formula of oxyfluorfen.

Behavior In and On Soils

Oxyfluorfen is strongly adsorbed by soil. It is not readily desorbed, and is highly resistant to leaching. While tests have shown it to be inactivated by muck soils, its bioavailability is affected little by clays (23). These properties contribute to the advantage that its residual activity is not severely diminished by periods of weeks between application and the first wetting (35).

Mode of Action

The mode of action of oxyfluorfen is not completely understood. Although many aspects of plant response are conclusive, its basis of selectivity and primary mechanism of action need further investigation.

Plant Structure and Growth

Oxyfluorfen is considered a contact herbicide that induces cell membrane disruption. This is evidenced by foliar symptoms of watersoaked lesions, followed by necrosis and/or chlorosis (13,30, 34,44). Leaf curling has also been observed with sensitive cole crops (27,38). Susceptible species show rapid injury after herbicide contact, usually within a few hours (13,26,44,45).

Absorption and Translocation

Oxyfluorfen has been shown to be readily absorbed by both roots and shoots of plants with shoot exposure being much more toxic (24,39). This finding is supportive of field studies showing a

diminished effect of the herbicide when mechanically incorporated, possibly reducing herbicide contact in the emerging shoot zone.

In selectivity studies on cabbage using nitrofen, cabbage cultivars with higher wax and cuticle content were found to be more tolerant. From this study it was concluded that differential absorption was the basis of this selectivity (13). However, in tests of oxyfluorfen absorption by greenbean and soybean, it was shown that soybean, a tolerant species, absorbed much more oxyfluorfen than greenbean, a susceptible species (24). Clearly, another mechanism of selectivity is responsible in this case.

Translocation of oxyfluorfen is very limited regardless of the organ of absorption (24,39). It has been suggested that the diminished activity when applied to roots is a result of limited transport to the shoot where light dependent activation could occur (24).

Metabolism

Metabolism of oxyfluorfen is very slow and not extensive. Since plant tissues are injured very rapidly by oxyfluorfen, it is proposed that the rate of metabolism is not great enough to interfere with its herbicidal action (39). Reduction of the $-NO_2$ group on the herbicide molecule to $-NH_2$ and subsequent conjugation with plant constituents have been suggested as metabolic products (13,26,28, 39,44).

Mechanism of Action

Many investigations of the mechanism of action of oxyfluorfen have focused on the plant-light interaction required for its herbicidal activity. It has been established that oxyfluorfen and other ortho- and/or para-substituted diphenyl ethers are inactive in the dark (13,21,22,28,40). It has also been suggested that this requirement for light is different from that of photosynthetic inhibitors such as the substituted ureas and bipyridylium herbicides (22,28,32).

Fadayomi and Warren (22) studied the role of plant pigments in the light induced activity of oxyfluorfen using white and yellow mutants of corn. They found the carotenoid-lacking white mutant to be much more resistant than the yellow mutant, which was as susceptible as a green normal plant. It was proposed that xanthophylls and not chlorophylls must be involved in the photoactivation process.

In subsequent experiments using different wavelengths of light, it was found that light at wavelengths of 565 to 615 nm caused the greatest injury. Since xanthophylls absorb light in the 400 to 440 nm range and oxyfluorfen is known to increase membrane permeability, it was suggested that a xanthophyll-protein complex in the membrane absorbs light in the 565 to 615 nm region thereby causing light activation (40).

Although the precise mechanism of action is not clear, it has been generally proposed that oxyfluorfen forms free radicals by accepting electrons from pigments in the presence of oxygen. The free radicals then cause lipid peroxidation of polyunsaturated

fatty acids in cell membranes, disrupting permeability and leading to the leakage of cellular constituents (26,30,32,34,39,44). Kunert and Boger (29,30) indicated free radical formation was caused by photoreduction due to photosynthetic electron transport whereas Pritchard et al. (32) suggest membrane disruption in light is due to either:

> photooxidation of cell components through interaction with plant pigments, injury due to oxyfluorfen-induced compounds, or interference with a more basic biosynthetic reaction which is required for the prevention of photo-oxidative destruction.

Weed Control

Yih and Swithenbank (45) first described the herbicidal activity of oxyfluorfen in 1975. In greenhouse studies comparing four diphenyl ether compounds, they concluded that oxyfluorfen was 10 times more active than its analog nitrofen. At a 0.25 kg/ha rate, oxyfluorfen demonstrated excellent to complete control (90-100%) of coffeeweed (Sesbania spp.), jimsonweed (Datura stramonium L. # DATST), velvetleaf (Abutilon theophrasti Medik. # ABUTH), and wild carrot (Daucus carota L. # DAUCA) and good control (85%) of common ragweed (Ambrosia artemisiifolia L. # AMBEL). Oxyfluorfen at a rate of 1.0 kg/ha gave complete control (100%) of these weeds. Nitrofen at 1.0 and 4.0 kg/ha was completely ineffective in controlling common ragweed, and with the exception of velvetleaf, did not adequately control any of the other species present.

Several researchers have conducted field experiments, primarily in the northeastern United States, to compare the weed

control efficacy and tolerance of oxyfluorfen in cole crops to some of the currently registered herbicides. Results of investigations of susceptible weed species have been in general agreement; however, reports of crop tolerance have been inconsistent.

Chitapong et al. (18) reported that oxyfluorfen at 0.28 and 0.43 kg/ha gave better control of common lambsquarters (Chenopodium album L. # CHEAL), redroot pigweed (Amaranthus retroflexus L. # AMARE), common ragweed, and common purslane (Portulaca oleracea L. # POROL) in transplanted broccoli than trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl) benzenamine], DCPA (dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate), or napropamide [N, N-diethyl-2-(1-napthalenyloxy) propanamide]. DCPA was completely ineffective in controlling common lambsquarters and redroot pigweed. The higher rate of oxyfluorfen was needed for acceptable control of the annual grasses, fall panicum (Panicum dichotomiflorum Michx. # PANDI) and large crabgrass [Digitaria sanguinalis (L.) Scop. # DIGSA]. They also reported that soil incorporation of oxyfluorfen greatly diminished its activity.

Vitolo et al. (41) also evaluated these herbicides for weed control in transplanted broccoli. They found that oxyfluorfen at 0.28 to 1.12 kg/ha gave excellent control of common lambsquarters and good control of the grass weeds large crabgrass and fall panicum; however, rates greater than 0.28 kg/ha gave significantly better control of fall panicum. With the exception of the control of fall panicum with trifluralin, control of these weeds with the registered herbicides evaluated was unacceptable.

Warholic and Ramirez (43) compared the same herbicides for control of redroot pigweed and their effect on transplanted broccoli. They reported that oxyfluorfen at 0.56 or 1.12 kg/ha gave almost complete control without crop injury or yield reduction. Napropamide and trifluralin failed to provide acceptable control of this weed species.

In evaluations using oxyfluorfen in transplanted cabbage, Teasdale (38) found no injury at rates up to 1.12 kg/ha. However, in one test some plants displayed "slight speckling and curling of the margins of new leaves" 2 weeks after transplanting. These symptoms were undetectable a few days later and vigor was unaffected. Since these symptoms appeared during hot weather following heavy rain, he suggested that volatilization of oxyfluorfen from the soil surface caused the injury.

In other tests with transplanted cabbage, Bhowmik and McGlew (15) reported substantial injury consisting of bleaching and necrotic leaf spots using oxyfluorfen at rates of 0.43 to 1.12 kg/ha. All plants recovered with time, but delayed maturity caused a decrease in cabbage quality. Excellent control of common lambsquarters, common ragweed, and redroot pigweed was obtained by oxyfluorfen at all rates. Control of fall panicum and large crabgrass was inconsistent with good to excellent control being obtained in one test and unacceptable control in a subsequent study.

Bonanno et al. (17) reported varying degrees of tolerance to oxyfluorfen by transplanted broccoli, cabbage, and cauliflower.

In one test, all three crops were injured at a rate of 1.12 kg/ha. Harvest delays of 3 to 10 days were attributed to oxyfluorfen, although no yield reductions occurred. In another test, cabbage was injured and subsequent yields reduced by oxyfluorfen at rates of 0.42 to 0.56 kg/ha. As was reported earlier by Teasdale (38), they also concluded injury to be caused by oxyfluorfen volatilization; however, they noted that injury and harvest delay did not occur in numerous instances when transplanting did not immediately follow applications.

Determination of Residues

An analytical method for gas-liquid chromatographic determination of total oxyfluorfen residues was developed by Adler et al. (1) in 1978 with minor revisions made by Adler and Hoffman in 1980 (2).

Figure I-2 illustrates how this method chemically converts oxyfluorfen residues to the derivatized compound which is detected and quantitated by chromatographic techniques.

Extraction and cleanup procedures convert the parent compound (Compound I) and reduced metabolites (Compounds II and III) to the corresponding amine (Compound III) by digesting a sample methanol extract with aluminum in aqueous sodium hydroxide. This compound is then partitioned into isooctane using a simultaneous distillation-extraction device (16). A heptofluorobutyric anhydride (HFBA) derivative (Compound IV) is then prepared in order to increase the sensitivity of the chromatograph. The derivative is partially purified

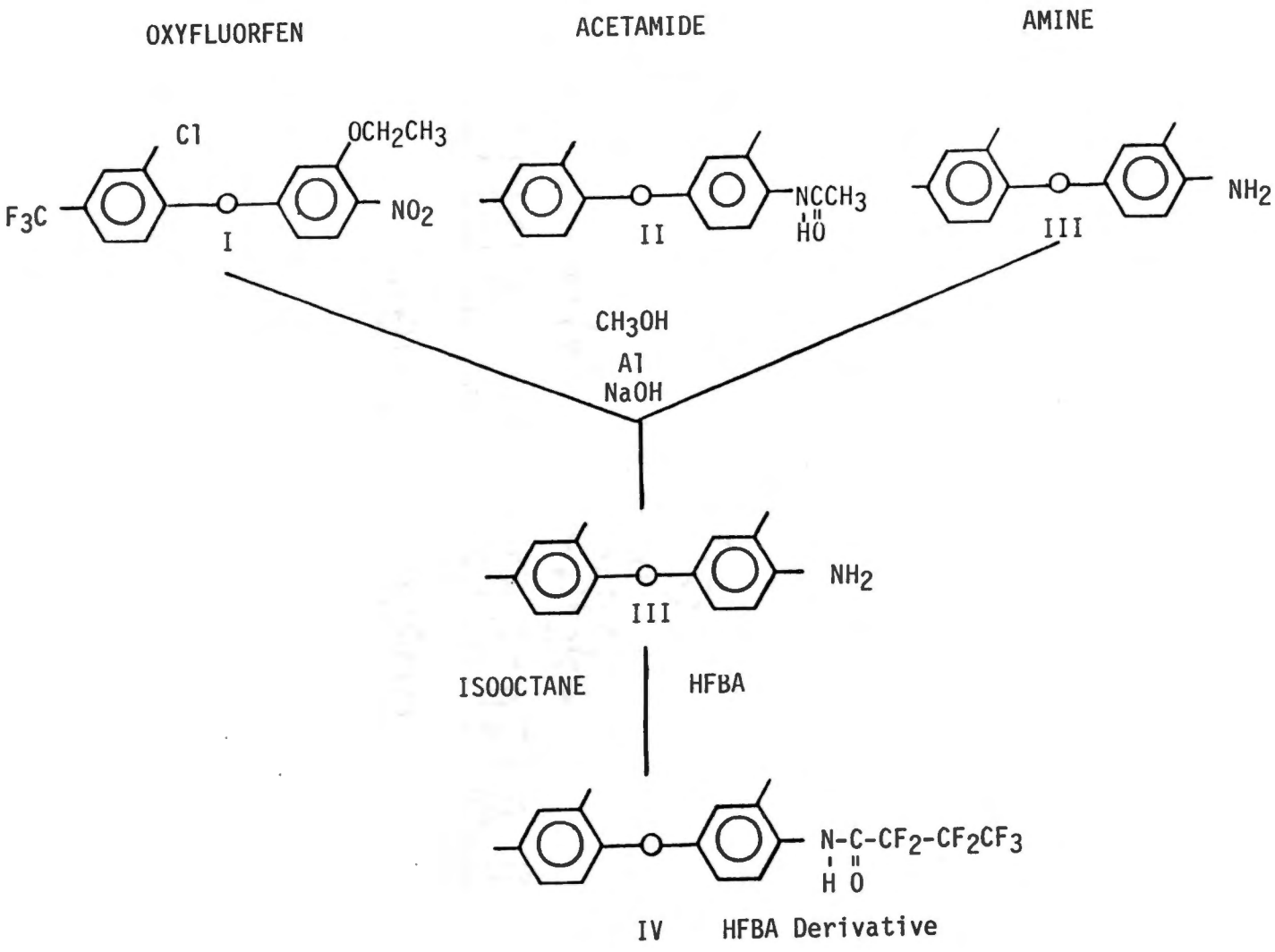


Figure I-2. Chemical conversion of total oxyfluorfen residues to HFBA derivative.

by column chromatography using Florisil and analyzed by electron capture gas-liquid chromatography. The method is described as sensitive to 0.01 parts per million (ppm).

Adler et al. (1,2) validated the method by recovering the derivative (IV) from samples that were fortified with the parent compound (I) prior to the extraction process. Recoveries averaged about 70% for samples fortified to concentrations of 0.01 ppm to 2.40 ppm. Plant samples consisted of soybeans, grapes, peaches, almonds, stonefruits, and corn. There were no reports of the reliability of the method using broccoli or any other cole crop as a substrate.

Past experimental use permits allowed oxyfluorfen usage in broccoli and have established the temporary tolerance concentration at 0.05 ppm (17,19).

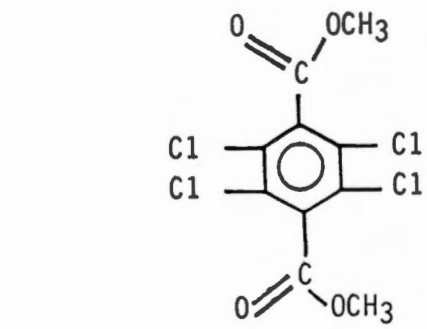
II. A REVIEW OF RESIDUAL HERBICIDES CURRENTLY REGISTERED FOR USE IN BROCCOLI

DCPA

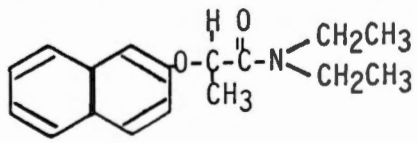
DCPA is a selective herbicide marketed by SDS Biotech under the trade name Dacthal®. It is used to control annual grasses and some annual broadleaf weeds in many vegetable crops, turf, cotton, soybeans and ornamentals (5,6). Susceptible weeds according to the manufacturer include large crabgrass, common lambsquarters, common purslane and carpetweed (Mollugo verticillata L. # MOLVE). Tolerant weeds include common ragweed and smartweed (Polygonum spp.), while redroot pigweed and goosegrass [Eleusine indica (L.) Gaertn. # ELEIN] are considered moderately susceptible (6).

For weed control in transplanted broccoli, DCPA is applied preplant incorporated or directly over the crop preemergence to the weeds. The manufacturer's recommended rate is 5.0 to 11.8 kg/ha depending on soil texture and organic matter content. Adequate rainfall or irrigation is needed within 3 to 5 days after application to insure its effectiveness (5,6,44).

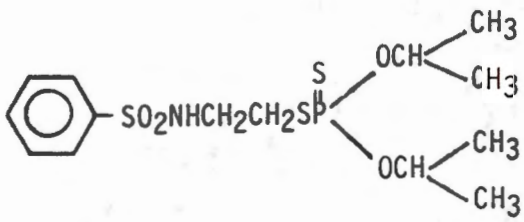
DCPA is classified an arylaliphatic acid, a substituted benzoic or a benzoic in the agricultural chemical literature (13,42,44). The physical and chemical properties of DCPA are found in Table I-1, page 5. Its structural formula appears in Figure I-3.



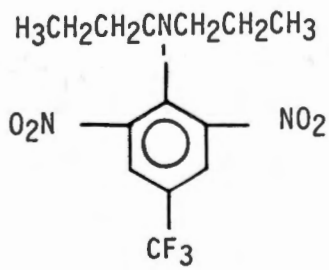
DCPA



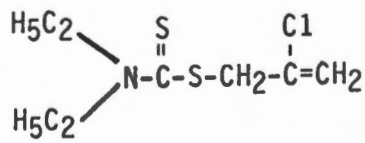
Napropamide



Bensulide



Trifluralin



CDEC

Figure I-3. Structural formulas of DCPA, napropamide, bensulide, trifluralin, and CDEC.

DCPA is absorbed from the soil and not by foliage and exhibits its phytotoxicity on germinating seedlings by inhibiting growth of root and shoot tips. It is not translocated nor is it thought to be metabolized in plants. Although its mechanism of action is unknown, DCPA displays properties similar to the phenoxy herbicides by producing auxin type growth effects in plants and by disrupting mitosis (13,26,42).

DCPA has been widely used in transplanted cole crops for many years (18,41,43). It has been reported to be very effective for the control of many annual grasses; however, control of the broadleaf weeds--common lambsquarters, common ragweed, and redroot pigweed--has been inconsistent (14,18,36,37,41,43).

Napropamide

Napropamide is a selective herbicide marketed by Stauffer Chemical Company under the trade name Devrinol®. It is used to control annual grasses and some broadleaf weeds in vegetables, fruits, nuts, citrus, and tobacco. Some of the weeds controlled according to the manufacturer are large crabgrass, foxtails (Setaria spp.), goosegrass, fall panicum, carpetweed, common lambsquarters, redroot pigweed, and common purslane (5,7,44).

For optimum activity in transplanted broccoli, napropamide should be applied preplant incorporated or preemergence followed by sprinkler irrigation. Soil incorporation or irrigation should be performed within 24 hours of application. The recommended rate

is 1.1 to 2.2 kg/ha based on geographic location and soil type (7). Napropamide is currently recommended by The University of Tennessee for control of grasses, pigweed, and common ragweed in cole crops (4). However, reports from other locations have indicated redroot pigweed, common ragweed and common lambsquarters may exhibit tolerance to napropamide (18,37,41,43). Crops not registered for its use cannot be planted within 12 months of the last application.

Napropamide is of the amide class of herbicides. Its physical and chemical properties are found in Table I-1, page 5. The structural formula for napropamide appears in Figure I-3.

Previous work with tomato showed napropamide is readily absorbed by roots and apparently is translocated in the apoplast throughout the stems and leaves. It is readily metabolized to water soluble metabolites, mainly hexose conjugates. In maize, absorption and translocation occurred to a much lesser extent than in tomato (13,26,28).

Although napropamide inhibits the growth and development of roots of grasses, there is no consistent pattern in its mechanism of action.

Bensulide

Bensulide [O,O-bis(1-methylethyl)S-[2-[(phenylsulfonyl) amino] ethyl] phosphorodithioate] is a selective herbicide marketed by Stauffer Chemical Company under the trade name Prefar®. It is used to control annual grasses in many vegetable crops and cotton. Some

of the weeds controlled according to the manufacturer are crabgrasses, foxtails, goosegrass, and fall panicum. In semi-arid areas, bensulide is also active on some broadleaf weeds. Its use is restricted to the Southeast and Southwest (5,9).

In transplanted broccoli, bensulide is applied preemergence or preplant incorporated. It should be applied preemergence only when the crop can be subsurface irrigated immediately after application. Bensulide should not be applied more than once in 12 months and non-registered crops cannot be planted within 18 months of the last application. The recommended rate is 5.6 to 6.7 kg/ha dependent upon soil texture and organic matter content (5,9).

Bensulide is one of the few organophosphate herbicides in use today. Although its mechanism of action is unknown, it acts by inhibiting cell division in root tips and thus interferes with germination and seedling development. It has been shown to be adsorbed onto root surfaces, but only small amounts absorbed into the root with little or no translocation. It is not absorbed by the foliage (13,26,42).

The physical and chemical properties of bensulide are found in Table I-1, page 5. Its structural formula appears in Figure I-3.

Trifluralin

Trifluralin is a selective herbicide marketed by Elanco Products Company under the trade name Treflan®. It is one of the most widely used herbicides in agriculture, controlling many annual

grasses and some broadleaf weeds in a wide variety of crops. Some of the susceptible weeds according to the manufacturer are large crabgrass, fall panicum, giant foxtail (Setaria faberi Herrm. # SETFA), goosegrass, carpetweed, common lambsquarters, redroot pigweed, and common purslane. Common ragweed is listed as a resistant species (5,10).

Trifluralin is applied preplant incorporated. Soil incorporation should be performed immediately after application as trifluralin is subject to volatility and photodecomposition. It does not need rain or irrigation for activation. The rate for use in broccoli is 0.56 to 1.12 kg/ha according to soil type (10). Trifluralin is currently recommended by The University of Tennessee, for control of most annual grasses and pigweeds (Amaranthus spp.) in cole crops (4).

Trifluralin is one of the many dinitroaniline herbicides in use today. Its physical and chemical properties are found in Table I-1, page 5. The structural formula appears in Figure I-3.

Trifluralin appears to be readily absorbed by both roots and shoots of many plants; however, translocation is very limited. Its involved mode of action includes inhibiting development of several hormone induced enzymes, uncoupling oxidative phosphorylation, and increasing nucleic acid synthesis. It is generally reported that trifluralin affects physiological growth processes associated with seed germination and development. This is apparent with trifluralin's classical symptom of inhibition of root growth,

especially lateral roots, accompanied by swelling of roots near the tip (11,13).

CDEC

CDEC (2-chloroallyl diethyldithiocarbamate) is a selective herbicide marketed by Monsanto Company under the trade name Vegadex®. It is registered for control of annual grasses and some broadleaf weeds in various vegetable crops and corn (5,12). CDEC was one of the earlier herbicides used in vegetables; however, it is rarely used today (20).

For use in broccoli, CDEC is applied preplant incorporated or postplant. Overhead irrigation should follow as soon as possible. The recommended rate is 4.5 to 6.7 kg/ha. Because of chemical properties of the compound, it must be transported, transferred, and mixed using closed system equipment (12).

CDEC is a dithiocarbamate herbicide that primarily inhibits the growth of emerging shoots of weeds, especially grasses. It is readily adsorbed, more by shoots than roots, and is translocated mainly in the apoplast system. CDEC alters many metabolic processes, but the primary action may be nucleic acid metabolism and protein synthesis as it inhibits L-leucine incorporation into protein (13,42).

The physical and chemical properties of CDEC are found in Table I-1, page 5. Its structural formula appears in Figure I-3, page 17.

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LITERATURE CITED

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PART II

WEED CONTROL EFFICACY OF PREEMERGENCE APPLIED OXYFLUORFEN IN TRANSPLANTED BROCCOLI

ABSTRACT

Field studies were conducted to evaluate the weed control efficacy of oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene] applied preemergence at rates of 0.28 to 1.12 kg ai/ha in fall and spring transplanted broccoli (Brassica oleracea var. italica L. cv. 'Premium Crop'). Excellent control of redroot pigweed (Amaranthus retroflexus L. #[1] AMARE), common purslane (Portulaca oleracea L. # POROL), turnip (Brassica rapa), goosegrass [Eleusine indica (L.) Gaertn. # ELEIN], and large crabgrass [Digitaria sanguinalis (L.) Scop. # DIGSA] was obtained with oxyfluorfen at all rates. Oxyfluorfen at a rate of 0.42 kg/ha gave good control of common ragweed (Ambrosia artemisiifolia L. # AMBEL) and excellent control of common lambsquarters (Chenopodium album L. # CHEAL). Rates higher than 0.42 kg/ha were required for good control of fall panicum (Panicum dichotomiflorum Michx. # PANDI), giant foxtail (Setaria faberi Herrm. # SETFA), and Italian ryegrass (Lolium multiflorum Lam. # LOLMU). Crop phytotoxicity and subsequent reduced yields resulted from oxyfluorfen at the 1.12 kg/ha rate in one experiment. In all other tests some early crop phytotoxicity was observed, but no reduction in yield or head size occurred.

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[1]Letters following this symbol are a WSSA-approved computer code from Composite List of Weeds, Weed Sci. 32, Suppl. 2. Available from WSSA, 309 W. Clark St., Champaign, IL 61820.

I. INTRODUCTION

Few herbicides are currently registered for use in broccoli. Most provide little control of many broadleaf weeds as they are selective for annual grasses. Also, their effectiveness often depends on timely soil incorporation and/or irrigation. Nitrofen [2,4-dichloro-I-(4-nitrophenoxy) benzene] was used to selectively control broadleaf weeds in cole crops until it was withdrawn from the market in 1980 (1,4). Since that time considerable effort has been made to find potential herbicides that could fill this void. Oxyfluorfen, an analog of nitrofen, has been reported to be more efficacious than several of the registered herbicides providing good to excellent preemergence control of many annual broadleaf and grass weeds (1,2,3, 5,6). However, tolerance of cole crops to oxyfluorfen has varied considerably (1,2,4). The objectives of this research were: 1) to evaluate the weed control efficacy of preemergence applied oxyfluorfen in spring and fall transplanted broccoli and 2) to determine its influence on yield and head size.

II. MATERIALS AND METHODS

Field studies were conducted during the fall of 1985 and the spring of 1986 at The University of Tennessee, Plant Sciences Field Laboratory, Knoxville, TN, and at the Plateau Experiment Station, Crossville, TN. The soil at the Knoxville site was an Etowah silt loam (Typic Paleudult: fine-loamy, siliceous, thermic) with 1.02% total carbon in the top 15.0 cm. The soil at Crossville was a Lily loam (Typic Hapludult: fine-loamy, siliceous, mesic) with 1.37% total carbon.

Plots were three 6.1 m rows, spaced 0.9 m apart. There were 20 plants per row spaced 0.3 m apart within the row. Treatments were arranged in a randomized complete block design and were replicated four times.

The herbicide was pretransplant surface applied to a conventionally prepared seedbed. A CO_2 backpack sprayer was used at 207 kPa pressure with a delivery rate of 190 L/ha.

Four-week-old, greenhouse-grown plants (4 to 5 true leaf stage) of the cultivar 'Premium Crop' were used in all experiments. They were transplanted immediately after herbicide application except during the spring 1986 test at Knoxville in which they were transplanted the following day. Overhead sprinkler irrigation was supplied when necessary during the growing season to achieve a minimum of 2.5 cm precipitation per week.

A moderate natural infestation of annual weeds was present at Knoxville during both seasons. During the fall the predominant weed species were: redroot pigweed, common purslane, large crabgrass, and goosegrass. The same species were predominant in the spring with the addition of common lambsquarters.

Weed populations at Crossville were very high during both seasons including a heavy infestation of Italian ryegrass occurring in the fall. Species observed in the fall were: common ragweed, common lambsquarters, Italian ryegrass, and turnip. The weed species observed in the spring were: redroot pigweed, common lambsquarters, common ragweed, fall panicum, and giant foxtail.

Weed control and crop injury were evaluated at 4 weeks after application and at harvest. For weed control a visual rating scale was used and data are reported as a percentage of control where 0 indicates no effect and 100 indicates complete control. Crop injury data are reported as a percentage reduction in overall growth when visually compared to plants of the cultivated control treatment within the same replication.

Harvests of the main heads from center rows of each plot were made at maturity which occurred approximately 60 days from transplanting. For uniformity, stalks were cut at 15.0 cm from the head apex. Subsamples were measured for stem and head diameters.

Data were subjected to an analysis of variance and means were separated by Duncan's multiple range test at the 5% level of probability.

III. RESULTS AND DISCUSSION

Weed Control

In the fall experiment at Knoxville (data not shown), oxyfluorfen at all rates gave complete (100%) control of the weed species observed. During the spring at this site (Table II-1), excellent control (90-100%) of all weeds was obtained by oxyfluorfen at each rate evaluated.

At Crossville during the fall (Table II-2), oxyfluorfen at the 0.28 kg/ha rate gave acceptable control of all species except Italian ryegrass. At higher rates oxyfluorfen provided good control of this weed and improved control of the other species present. The excellent control of turnip at the lowest rate (0.28 kg/ha) indicates a low potential of this compound for use in direct seeded Brassica crops.

In the spring test at Crossville (Table II-3), oxyfluorfen at the lowest rate (0.28 kg/ha) did not adequately control common ragweed or the annual grasses fall panicum and giant foxtail. Control of redroot pigweed and common lambsquarters was commercially acceptable at this rate but was less than that from the three higher rates evaluated. At the 0.42 kg/ha rate it was effective in controlling the broadleaf weeds present; however, oxyfluorfen at rates of 0.56 kg/ha or greater were needed to achieve consistent control of fall panicum and giant foxtail.

Table II-1. Control of Weed Species with Oxyfluorfen Applied Preemergence in Transplanted Broccoli at Knoxville in Spring, 1986.

Treatment	Rate of Application (kg/ha)	Percent Weed Control[a]									
		Redroot pigweed		Common lambsquarters		Common purslane		Large crabgrass		Goosegrass	
		Early	Late	Early	Late	Early	Late	Early	Late	Early	Late
Oxyfluorfen	0.28	98a	100a	97ab	93a	100a	100a	98a	99a	98a	98a
	0.42	98a	100a	94b	93a	100a	100a	97a	100a	98a	100a
	0.56	100a	100a	100a	100a	100a	100a	98a	99a	99a	100a
	1.12	100a	100a	98a	100a	100a	100a	100a	100a	100a	100a
Cultivated control	--	100a	100a	100a	100a	100a	100a	100a	100a	100a	100a
Weedy control	--	0b	0b	0b	0b	0b	0b	0b	0b	0b	0b

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

Table II-2. Control of Weed Species with Oxyfluorfen Applied Preemergence in Transplanted Broccoli at Crossville in Fall, 1985.

Treatment	Rate of Application (kg/ha)	Percent Weed Control[a]							
		Common ragweed		Common lambsquarters		Turnip		Italian ryegrass	
		Early	Late	Early	Late	Early	Late	Early	Late
Oxyfluorfen	0.28	88b	83b	100a	100a	99a	98a	79c	69c
	0.42	97a	86b	98a	96a	100a	98a	89b	84b
	0.56	96a	91ab	100a	100a	98a	94a	83c	74bc
	1.12	100a	100a	100a	100a	99a	100a	98a	97a
Cultivated control	--	100a	100a	100a	100a	100a	100a	100a	100a
Weedy control	--	0c	0c	0b	0b	0b	0b	0d	0d

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

Table II-3. Control of Weed Species with Oxyfluorfen Applied Preemergence in Transplanted Broccoli at Crossville in Spring, 1986.

Treatment	Rate of Application (kg/ha)	Percent Weed Control[a]									
		Redroot pigweed		Common lambsquarters		Common ragweed		Fall panicum		Giant foxtail	
		Early	Late	Early	Late	Early	Late	Early	Late	Early	Late
Oxyfluorfen	0.28	94b	95b	84b	82c	78c	76c	72d	70c	71d	66d
	0.42	100a	100a	92a	94b	88b	90b	85c	78b	85c	85c
	0.56	100a	100a	94a	98ab	96ab	96a	91b	94a	90b	94b
	1.12	100a	100a	98a	100a	99a	100a	99a	100a	100a	100a
Cultivated control	--	100a	100a	100a	100a	100a	100a	100a	100a	100a	100a
Weedy control	--	0c	0c	0c	0d	0d	0d	0e	0d	0e	0e

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

Crop Injury

Evidence of oxyfluorfen phytotoxicity to broccoli was observed in several instances. Within 2 to 4 days after transplanting some plants exhibited various degrees of chlorosis, epinasty, and necrosis. In a few instances, the chlorosis followed the leaf venation. There was a trend toward increased injury, indicated by a greater number of plants with more pronounced symptoms, at the highest rate (1.12 kg/ha). Phytotoxic symptoms were not observed approximately a week after transplanting and leaves that emerged after the symptoms first appeared showed no injury. However, at Knoxville during the fall (Table II-4), several plants subjected to the highest rate did not fully recover and remained stunted throughout the growing season. On two occasions, injury occurred prior to any rainfall or overhead irrigation. This response indicates that injury was not due to the splashing of oxyfluorfen onto the broccoli, but may have been caused by volatilization of the herbicide from the soil surface. This evidence supports the findings of Bonanno et al. (2) and Teasdale (4) who attributed similar phytotoxic symptoms in cole crops to possible volatilization of oxyfluorfen from the soil surface.

Yield

Yields from all treatments were higher in the fall at both locations. These findings concur with current research at The University of Tennessee, Knoxville, which has shown consistently

Table II-4. Effect of Preemergence Applied Oxyfluorfen on Yield, Crop Injury, and Head and Stem Diameter of Transplanted Broccoli at Knoxville in Fall, 1985, and Spring, 1986.[ab]

Treatment	Rate (kg/ha)	Yield		Crop Injury				Stem Diameter		Head Diameter	
				Fall		Spring					
		Fall	Spring	Early	Late	Early	Late	Fall	Spring	Fall	Spring
		MT/ha		Percent		Percent		mm		mm	
Oxyfluorfen	0.28	12.0ab	10.9a	4b	2b	0b	0b	37a	34ab	185a	142a
	0.42	13.2a	9.9a	5b	1b	0b	0b	36a	35ab	190a	155a
	0.56	12.9a	9.9a	5b	2b	0b	0b	38a	36a	190a	148a
	1.12	10.4b	10.2a	21a	12a	4a	2a	34a	34ab	168b	140a
Cultivated control	--	12.1ab	10.1a	0b	0b	0b	0b	37a	34ab	183ab	140a
Weedy control	--	12.1ab	10.4a	4b	8b	0b	0b	38a	33b	183ab	145a

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

[b]Planting dates: August 20 and April 11.

higher broccoli yields of fall crops in cultivar studies at the same locations.

In the fall experiment at Knoxville (Table II-4), oxyfluorfen at the 1.12 kg/ha rate resulted in significantly lower broccoli yields than those of the 0.42 or 0.56 kg/ha rate. Although oxyfluorfen at the 1.12 kg/ha rate resulted in the lowest yield of all treatments, it did not differ significantly from the controls.

At Crossville in the fall (Table II-5), yields from all oxyfluorfen treatments and the cultivated control were higher than the weedy control.

There were no yield differences among treatments during the spring at either location.

Head Size

With the exception of one occurrence there were no indications that oxyfluorfen influenced head or stem diameter (Tables II-4 and II-5). No differences were observed among oxyfluorfen treatments except at the 1.12 kg/ha rate during the fall at Knoxville in which considerable injury slowed growth resulting in smaller plants and heads. Although differences in head and stem diameter existed between oxyfluorfen treatments and controls, no general trend was indicated.

Table II-5. Effect of Preemergence Applied Oxyfluorfen on Yield, Crop Injury, and Head and Stem Diameter of Transplanted Broccoli at Crossville in Fall, 1985, and Spring, 1986.[ab]

Treatment	Rate (kg/ha)	Yield		Crop Injury				Stem Diameter		Head Diameter	
				Fall		Spring					
		Fall	Spring	Early	Late	Early	Late	Fall	Spring	Fall	Spring
		MT/ha		Percent		Percent		mm		mm	
Oxyfluorfen	0.28	10.6a	8.0a	4b	0b	0b	0b	32ab	32ab	163a	135ab
	0.42	11.4a	9.0a	4b	0b	0b	0b	34ab	33a	163a	145a
	0.56	10.9a	8.4a	8ab	1ab	0b	0b	36a	34a	168a	135ab
	1.12	11.3a	8.6a	5b	1ab	5a	4a	35ab	33a	165a	135ab
Cultivated control	--	9.9a	9.0a	0b	0b	0b	0b	36a	32a	170a	122b
Weedy control	--	7.8b	8.4a	14a	5a	0b	0b	31b	33a	165a	132ab

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

[b]Planting dates: August 14 and April 30.

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PART III

RESIDUE DETERMINATION OF PREEMERGENCE APPLIED OXYFLUORFEN IN TRANSPLANTED BROCCOLI

ABSTRACT

Spring and fall transplanted broccoli [Brassica oleracea var. italica L. cv. 'Premium Crop'] grown on soil that had received a 1.12 kg ai/ha preemergence application of oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene] was analyzed by electron-capture, gas-liquid chromatography for residues in head tissue. Validity of the analytical method was demonstrated by recovery of oxyfluorfen residues from samples of broccoli head tissue that had been fortified with the herbicide prior to extraction. Recoveries from fortified samples averaged approximately 75% which is consistent with published results using other substrates. Oxyfluorfen residues were not detected in head tissue from any of the field samples analyzed. The method is sensitive to 0.01 ppm.

I. INTRODUCTION

Since the herbicide nitrofen [2,4-dichloro-1-(4-nitrophenoxy) benzene] was withdrawn from the market in 1980, considerable effort has been made to find a similar herbicide which selectively controls broadleaf weeds in cole crops. Oxyfluorfen, an analog of nitrofen, has shown promise in this regard, providing excellent preemergence control of many annual weeds in cole crops with good crop safety (4,6,7,10,12,13).

Oxyfluorfen is a preemergence or postemergence applied selective herbicide marketed by Rohm and Haas Company under the trade name Goal®. It is registered for use in many economically important crops such as soybeans and cotton as well as for use in orchards and in ornamentals (3). Most susceptible weeds are controlled at relatively low rates of active ingredient; for example, the recommended preemergence rate in soybeans is 0.43 to 0.56 kg/ha (3,14).

The increased use of and dependency upon pesticides in agriculture has resulted in strict federal regulations regarding pesticides and their residues in food (9). Analytical methods and instrumentation now exist that can detect trace amounts of residue such that zero tolerance levels have been established for many pesticides in edible products.

Oxyfluorfen is readily absorbed by plant roots and shoots; however, its subsequent translocation is very limited (8,11).

Therefore, it is unlikely that any internally transported residues would be present in heads of broccoli resulting from a preemergence application of the herbicide.

An analytical method for gas-liquid chromatographic determination of total oxyfluorfen residues was developed by Adler et al. (1) in 1978 with minor revisions made by Adler and Hoffman in 1980 (2). The method chemically converts the parent compound and its reduced metabolites (Figure III-1) to the corresponding amine. The amine is then converted to a heptafluorobutyramide (HFBA) derivative which is analyzed by electron capture gas-liquid chromatography. There were no reports of the method's reliability using a cole crop as a substrate.

The objectives of this research were to: 1) evaluate the performance of the residue method using broccoli as a substrate and 2) to determine oxyfluorfen residues in the head tissue of transplanted broccoli grown on soil that had received an excessive preemergence application of the herbicide.

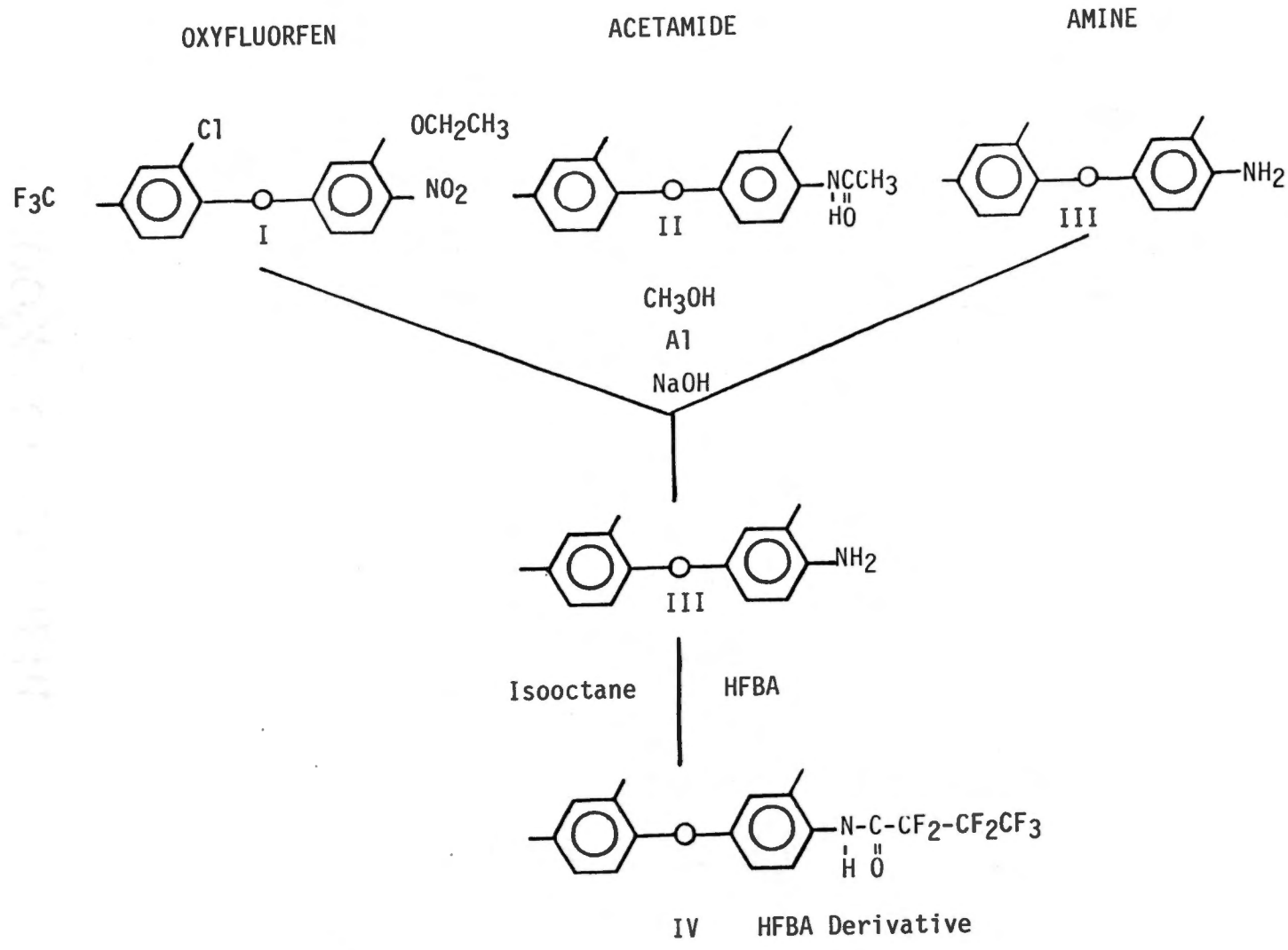

Figure III-1. Chemical conversion of oxyfluorfen and reduced metabolites to HFBA derivative.

II. MATERIALS AND METHODS

Field Production

Field experiments were conducted during the fall of 1985 and spring of 1986 at The University of Tennessee Plant Sciences Field Laboratory, Knoxville, TN, and at the Plateau Experiment Station, Crossville, TN. The soil at Knoxville was an Etowah silt loam (Typic Paleudult: fine-loamy siliceous, thermic) with 1.02% total carbon in the top 15.0 cm. The soil at Crossville was a Lily loam (Typic Hapludult: fine-loamy, siliceous, mesic) with 1.37% total carbon.

The commercial formulation of oxyfluorfen (Goal® 1.6E) was pretransplant surface applied at a rate of 1.12 kg/ha. This rate, which is double the amount needed for acceptable weed control, was used to increase the probability of herbicide contact with the crop.

Greenhouse-grown plants of the cultivar 'Premium Crop' were used in all experiments. They were transplanted immediately after herbicide application except in the spring test at Knoxville in which transplanting was performed the following day.

Sampling and Sample Preparation

Five heads were randomly selected from each plot that had received a 1.12 kg/ha rate of oxyfluorfen and from a non-treated control plot. The heads were immediately frozen in the field at harvest using dry ice. Approximately 5 g of floret and stem tissue

were taken from each of the five heads to give a 25.0 g composite sample per plot for analysis. A total of 20 field samples were tested representing both seasons and locations.

Residue Analysis

Apparatus

Gas chromatograph. Hewlett-Packard 5840A equipped with a ^{63}Ni electron capture detector, a software integrator, and a 183 cm x 2 mm id coiled glass column packed with 4% SE-30/6% OV-210 on 80-100 mesh Gas-Chrom Q. Operating conditions: Argon-methane (95 + 5) at a flow rate of 20 $ml \cdot min^{-1}$; temperatures (°C) - column 190, detector 275, injector 225.

Bleidner apparatus (5). A steam distillation-extraction device equipped with a 6 bulb Allihn condenser for extraction head. The U-tube was filled with equal volumes of water and isooctane. Teflon sleeves were used on all joints.

Reagents

All solvents used were pesticide grade (Burdick and Jackson, Inc.). Florisil (Floridin Co.) 60-100 mesh was heated 24 hours at 135°C, deactivated with 5% water and equilibrated by tumbling 1 hour.

Analytical Standards

The parent compound oxyfluorfen and the derivative standards (95-100% purity) were supplied by Rohm and Haas Company.

Extraction and Cleanup

The extraction and cleanup procedures of Adler and Hoffman (2), described here, were strictly followed:

Preparation of Sample

Dry-blend 25 g of substrate in a Blendor jar for 2 min at low speed. Add 100 ml of conc. HCl-acetonitrile (5:95 v/v), blend for 2 min at low speed, and filter through Whatman No. 3 filter paper with suction. Wash the blender jar with 25 ml of the HCl-acetonitrile, filter, and combine the filtrates. Partition with 100 ml of heptane in a 500 ml separatory funnel. Collect the lower layer and adjust the volume to 125 ml. Evaporate 5 ml of the extract to dryness in a one neck, 1 liter round-bottomed flask using a rotary evaporator (60°C bath). Add 5 ml of methanol and proceed with digestion.

Digestion

To the 5 ml aliquot add two to four boiling chips, 400 ml of 10% aqueous NaOH solution, and 1 g of aluminum granules. Immediately attach the flask to the Bleidner apparatus and begin heating to reflux. Add 75 ml of isooctane and two to four boiling chips to a 250 ml round-bottomed flask attached to the top generator arm of the Bleidner apparatus, and heat to reflux.

Caution: Hydrogen evolution begins immediately. Digestion should proceed in a well-ventilated area.

Allow the digestion to proceed for 18h (overnight), cool to room temperature, remove the generator flask, and cap with a 24/40 ground glass stopper.

Derivatization

To the cooled isooctane extract, add 0.2 ml of heptafluorobutyric anhydride (HFBA), stopper the flask, and shake vigorously. HFBA derivatization should be performed in a well-ventilated area since HFBA is a pungent lachrymator. After 5 min, evaporate to dryness on a rotary evaporator (60°C), dissolve the residue in 10 ml of petroleum ether, and proceed with column cleanup.

Column Chromatography (Column Cleanup)

Pack a 1 x 40 cm column with 7 cm^3 of deactivated Florisil and top with 2-4 ml of sodium sulfate. Pass the petroleum ether solution through the adsorbent and discard the eluate. Add 50 ml of petroleum ether and discard the eluate. Add 60 ml of ethyl ether-petroleum ether (3:97 v/v) and collect the eluate in a 250 ml round-bottomed flask. Carefully evaporate to dryness on a rotary evaporator (60°C bath). Dissolve the residue in an appropriate volume (5 ml minimum) of heptane and proceed with GLC analysis.

Chromatography Analysis

The final volume of the residue containing heptane was recorded for each sample. Sample volumes were in the range of 6 to 9 ml. All chromatograph samples were manually injected 5 µl volumes. Multiple samples of the derivative standard at concentrations of 0.01 to 0.50 ppm were chromatographed to determine the slope of the linear function of the weight of the derivative versus peak area and to establish reliable instrument parameters. Standards of the parent compound were also chromatographed in order to compare peak retention times. Recoveries of oxyfluorfen were determined by the extraction of the derivative from samples of head tissue that had been fortified with the parent compound prior to the extraction. A factor of 0.685 (ratio of molecular weights) was used to convert the weight of the derivative to the weight of the oxyfluorfen parent compound.

The concentration of residue, expressed as oxyfluorfen, was calculated as follows:

$$\text{oxyfluorfen (ppm)} = \frac{\text{ng derivative}}{\mu\text{l injected}} \times \frac{\text{total ml heptane with residue}}{\text{1.0 g sample substrate (i.e., extract dilution factor)}}$$

$$\frac{\text{0.685 g oxyfluorfen}}{\text{1.0 g derivative}} \times \frac{1}{\text{recovery factor}}$$

III. RESULTS AND DISCUSSION

Detection of Standards

The chromatograph response of the concentrations of the derivative standard versus peak area was linear (Figure III-2). Peak retention times for standards of the derivative (Figures III-3 and III-4) and the parent compound (Figure III-5) were approximately 11.8 and 18.3 min, respectively.

Oxyfluorfen Recovery

The method was validated by recovering the oxyfluorfen derivative from broccoli head tissue that had been fortified with the parent compound prior to extraction (Figures III-6 and III-7). The percent recoveries of the range of fortifications are presented in Table III-1. These results are consistent with those of Adler et al. (1,2) whose recoveries averaged approximately 70% while using substrates other than broccoli. Total conversion of parent compound to the derivative probably occurred as no peaks were observed in the 18.3 min retention time vicinity.

Field Sample Analysis

There was no indication of the presence of any oxyfluorfen residues in the 20 composite field samples tested (Figure III-8). Chromatograms of samples from non-treated control plots

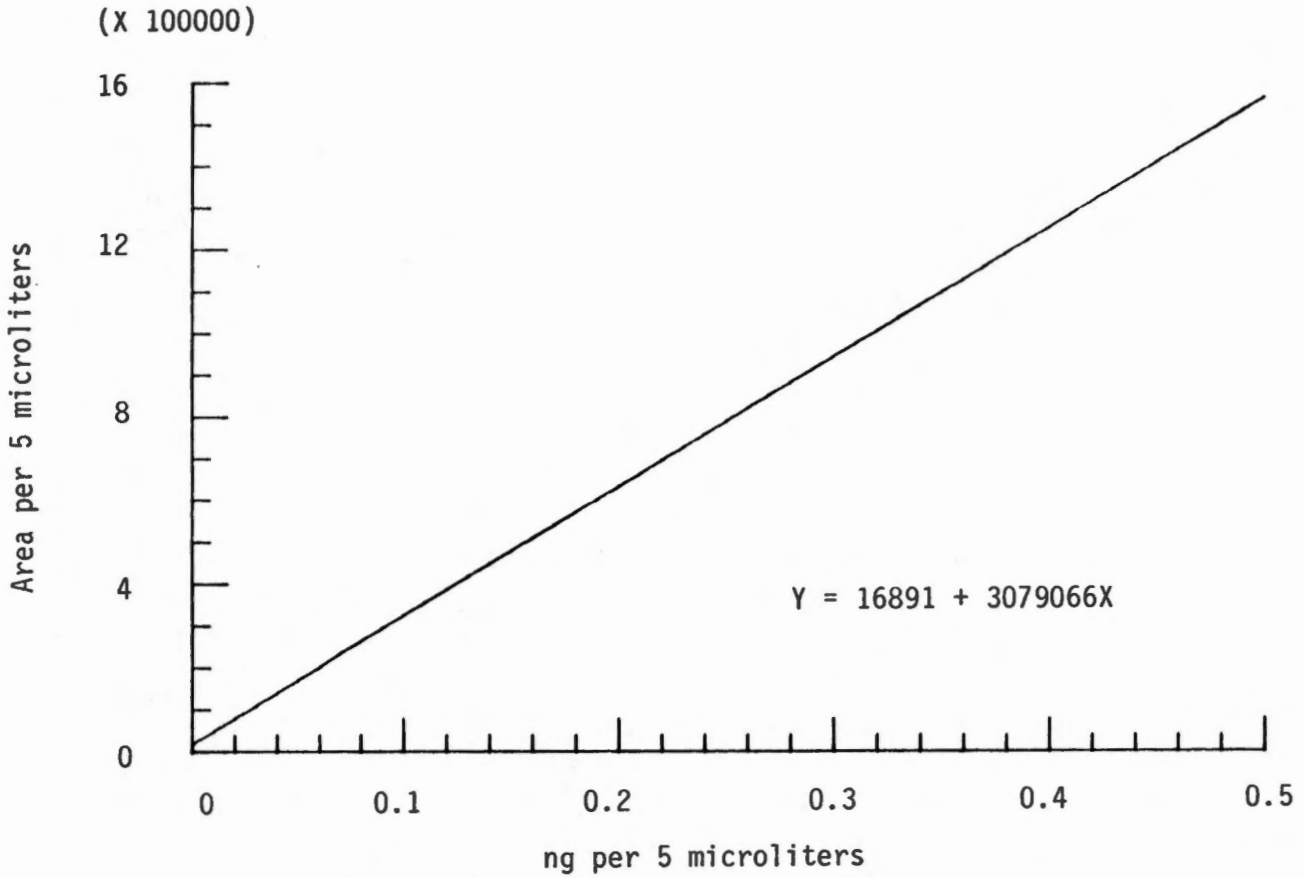

Figure III-2. Regression of chromatogram peak area on weight of HFBA derivative standard per 5 µl heptane injection. R^2=0.998985, Y=peak area, and x=ng HFBA derivative.

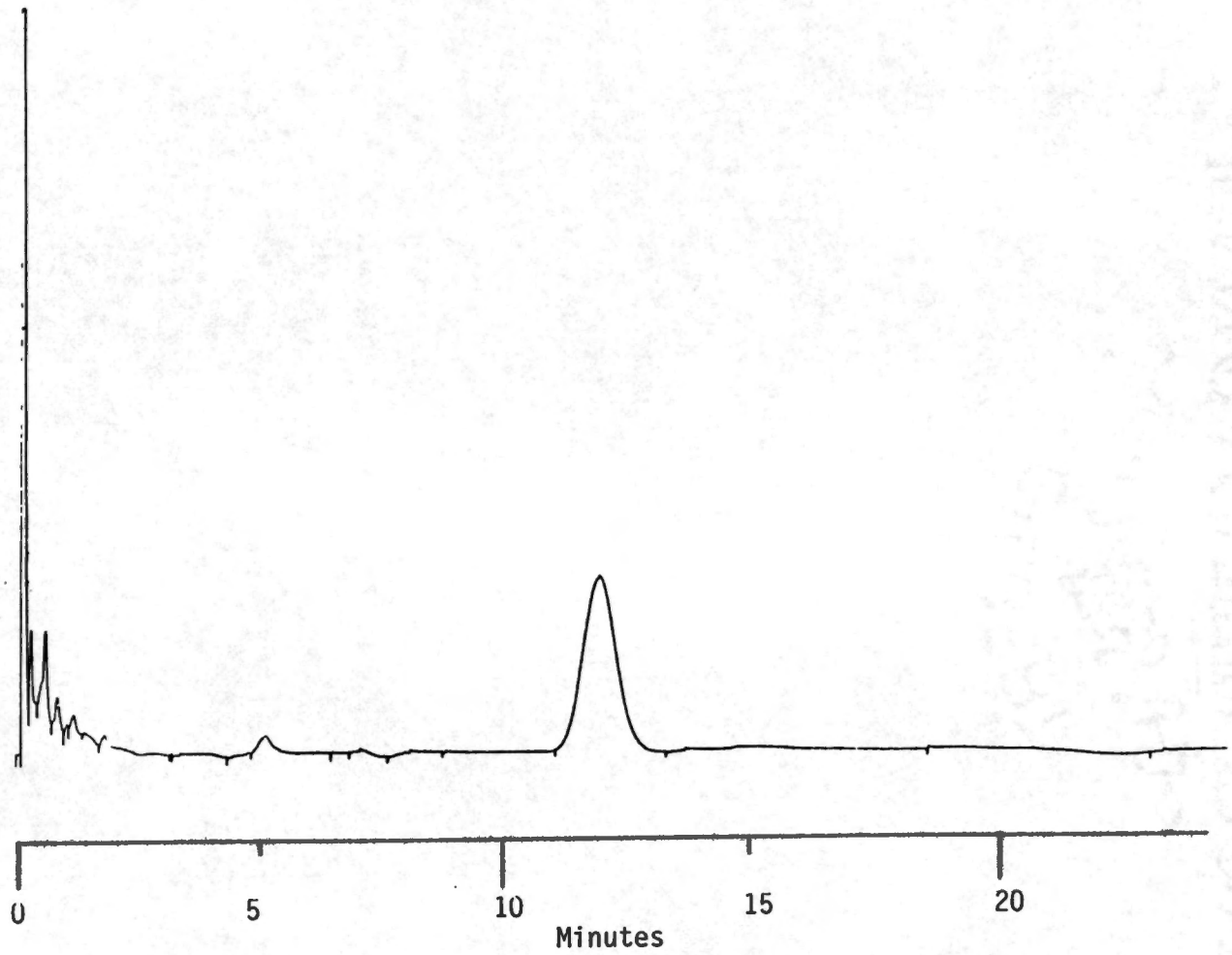

Figure III-3. Representative chromatogram of HFBA derivative standard at a concentration of 0.01 ppm.

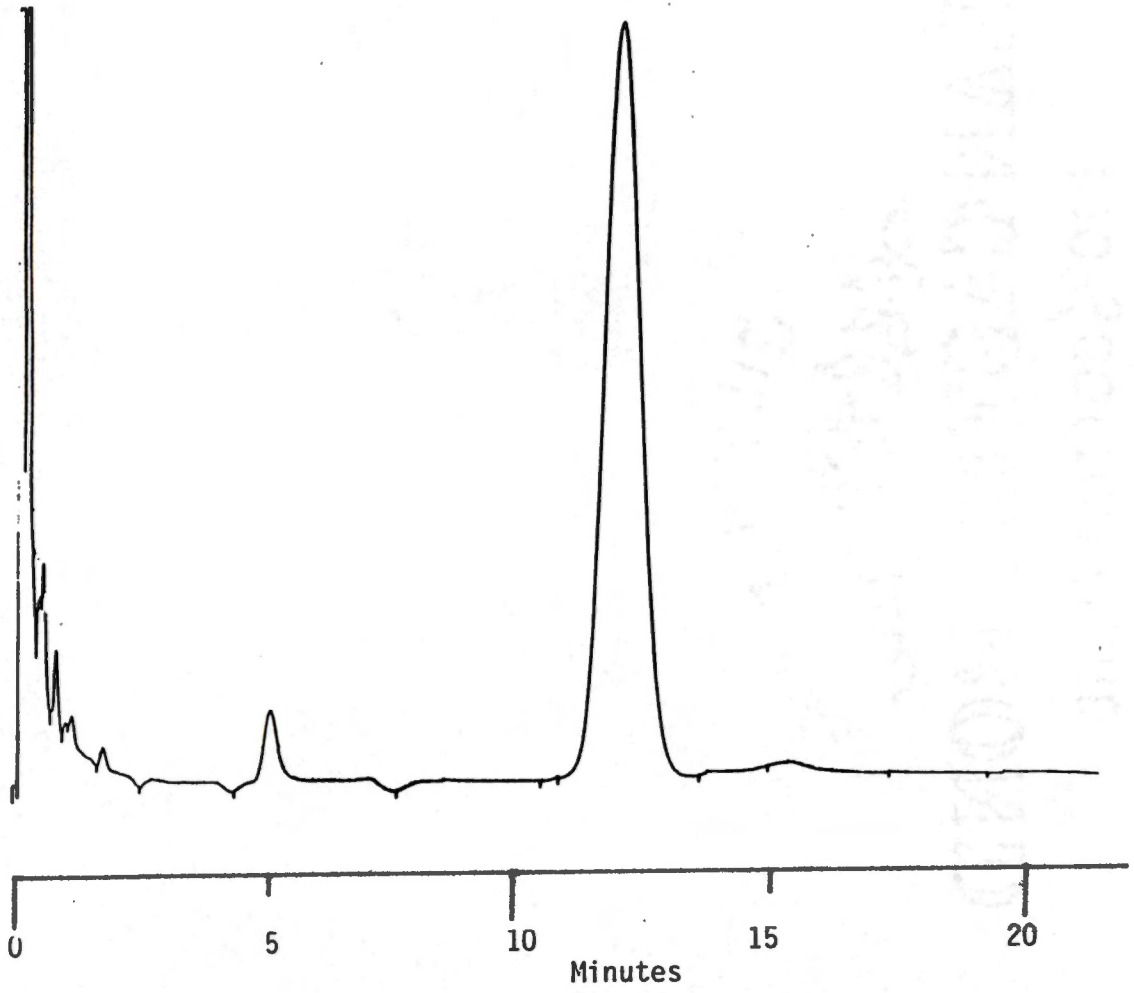

Figure III-4. Representative chromatogram of HFBA derivative standard at a concentration of 0.05 ppm.

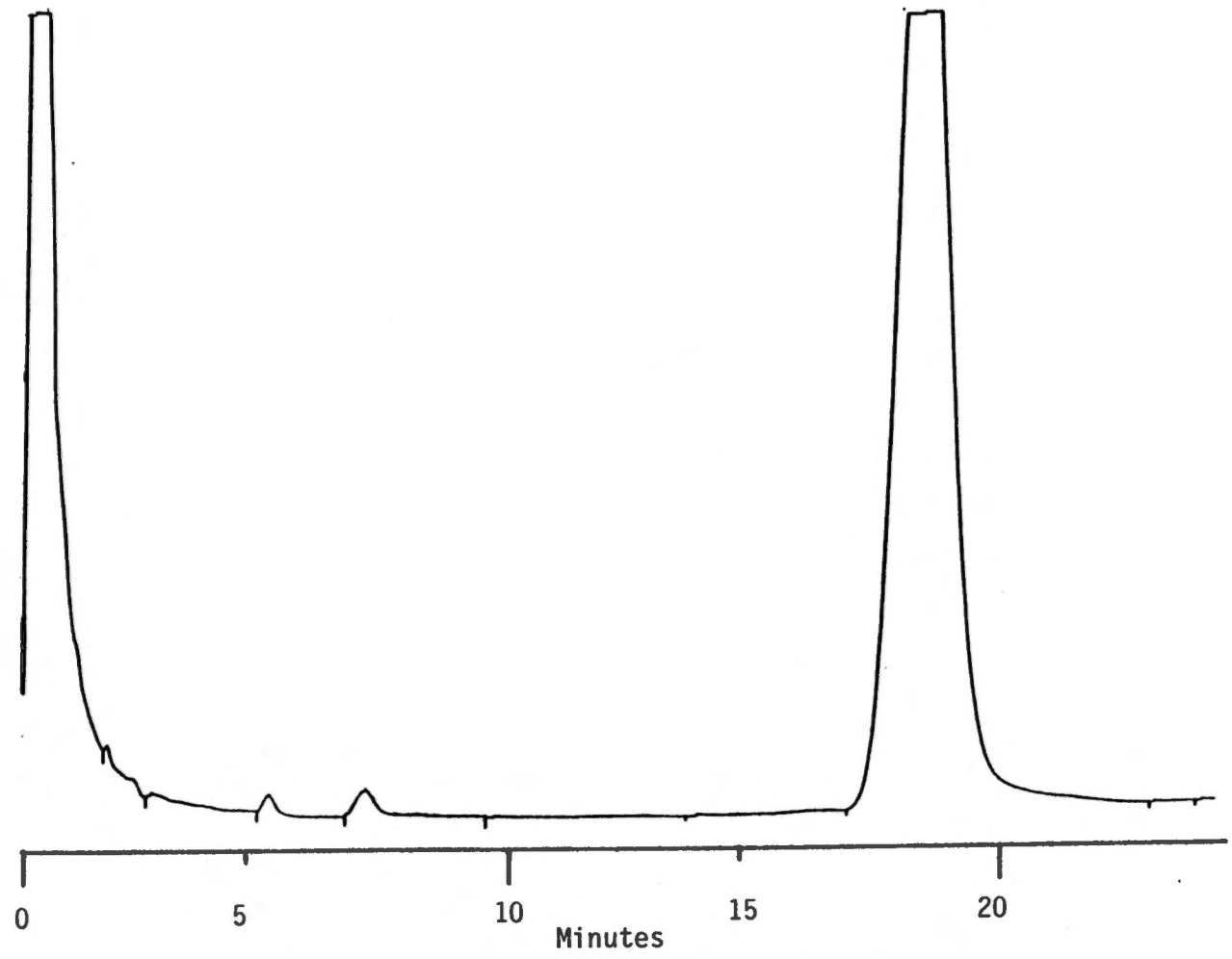

Figure III-5. Representative chromatogram of oxyfluorfen standard at a concentration of 0.10 ppm.

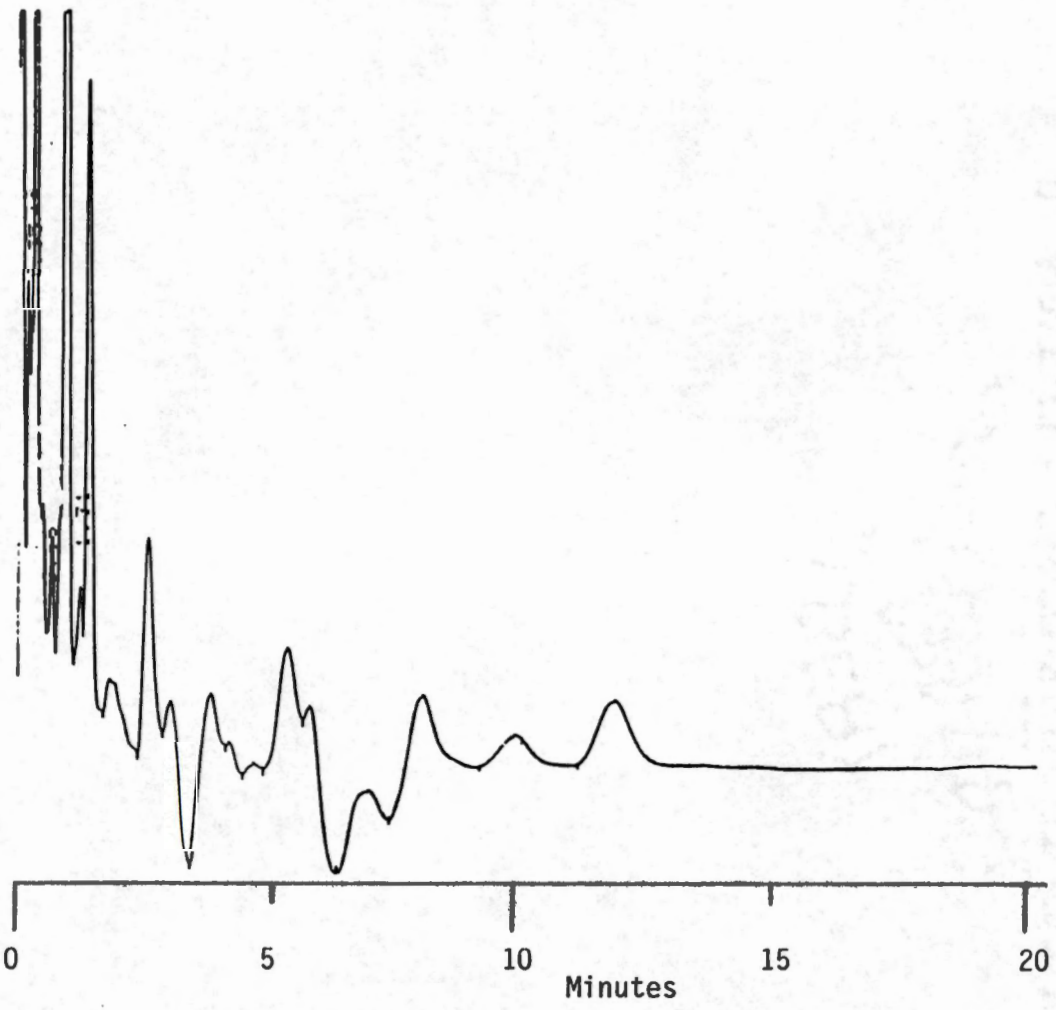

Figure III-6. Representative chromatogram of broccoli head tissue fortified with oxyfluorfen to a concentration of 0.01 ppm prior to extraction process.

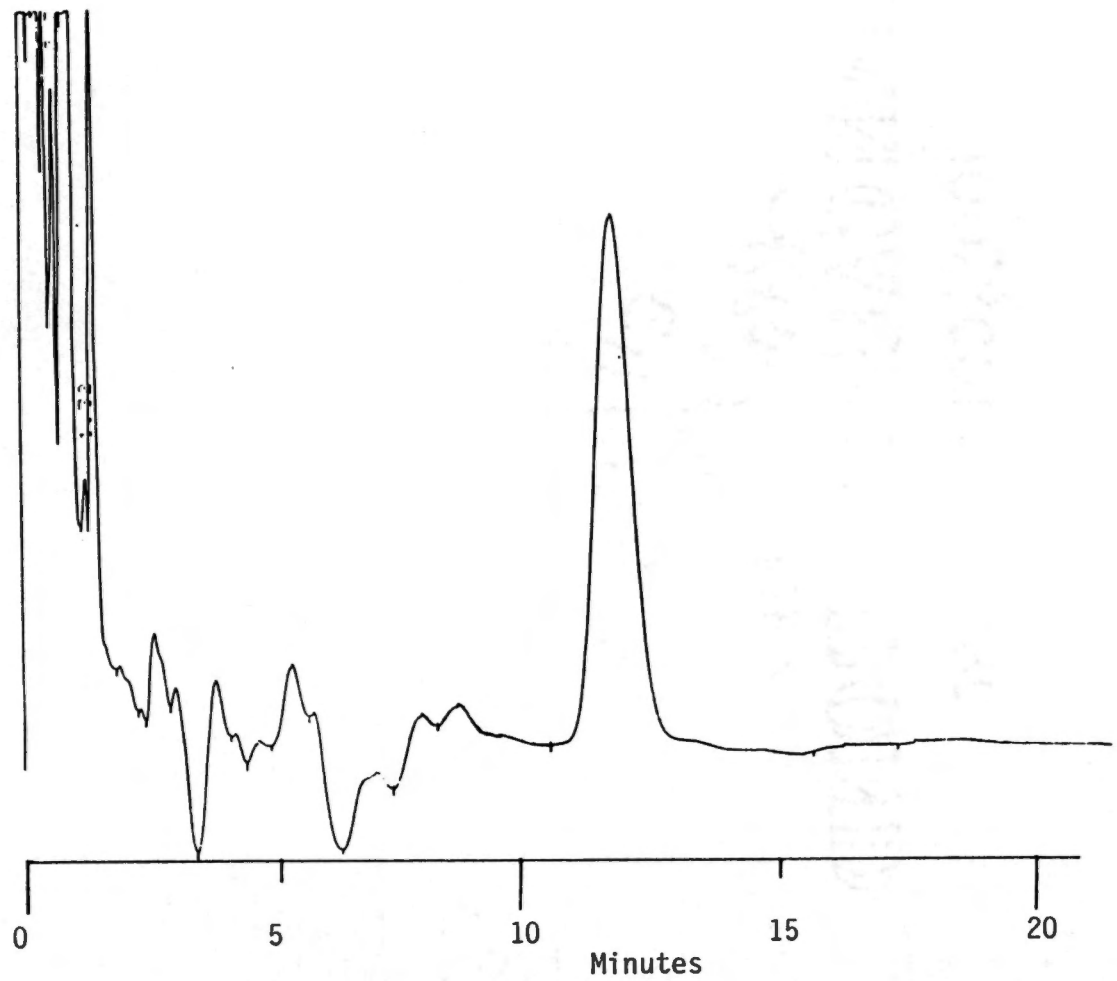

Figure III-7. Representative chromatogram of broccoli head tissue fortified with oxyfluorfen to a concentration of 0.39 ppm prior to extraction process.

Table III-1 Recovery of Oxyfluorfen from Broccoli Head Tissue Fortified with Oxyfluorfen Prior to Extraction Process.

Concentration	Percent Recovery
0.01	59.8
0.04	68.4
0.10	90.6
0.39	80.4
mean	74.8

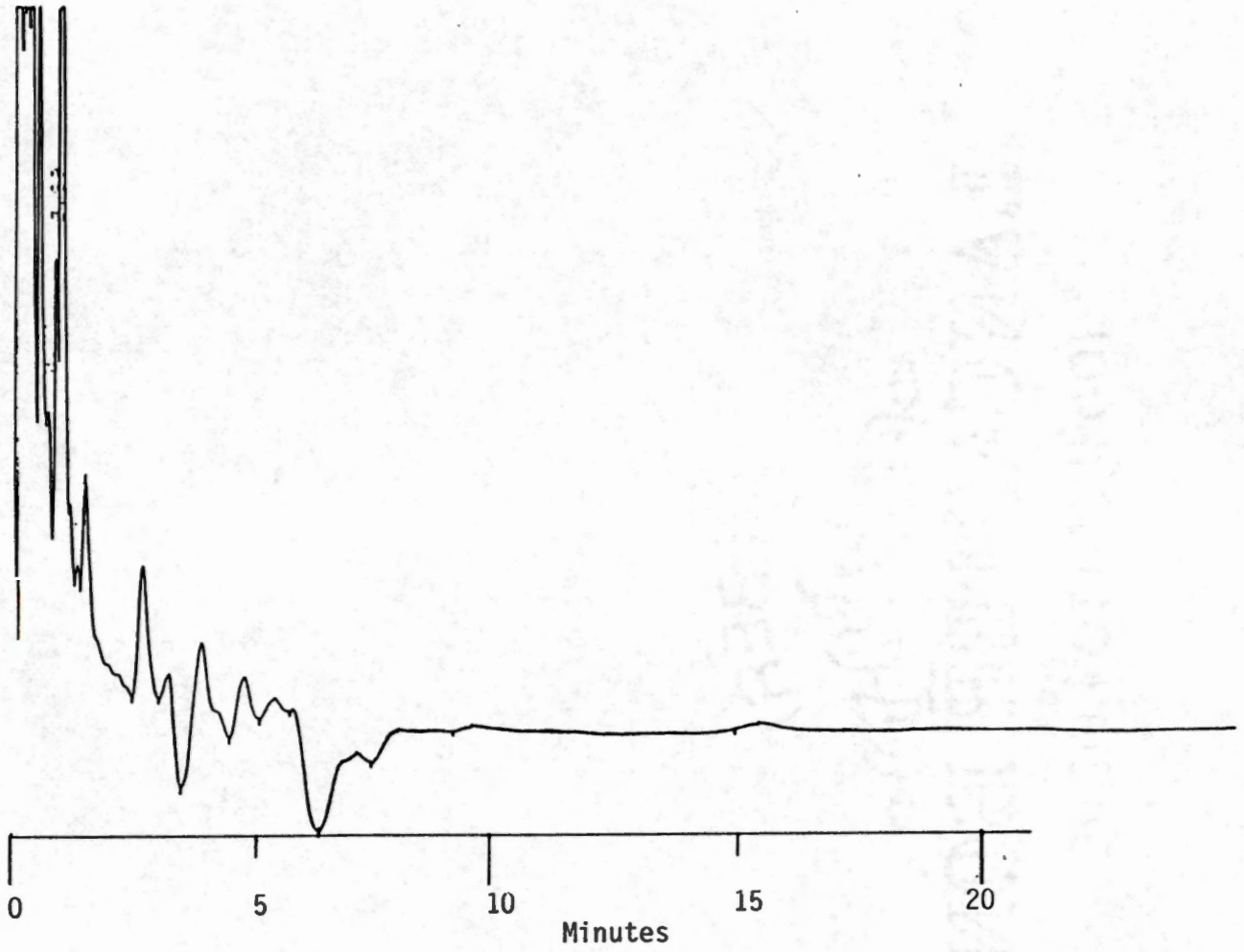

Figure III-8. Representative chromatogram of broccoli head tissue from plants with oxyfluorfen applied preemergence at a rate of 1.12 kg/ha.

(Figure III-9) were not discernible from those of treated plots.

This evidence supports the presumption that broccoli grown on soil that has been treated with preemergence applied oxyfluorfen is free from the presence of oxyfluorfen residues in the harvested product.

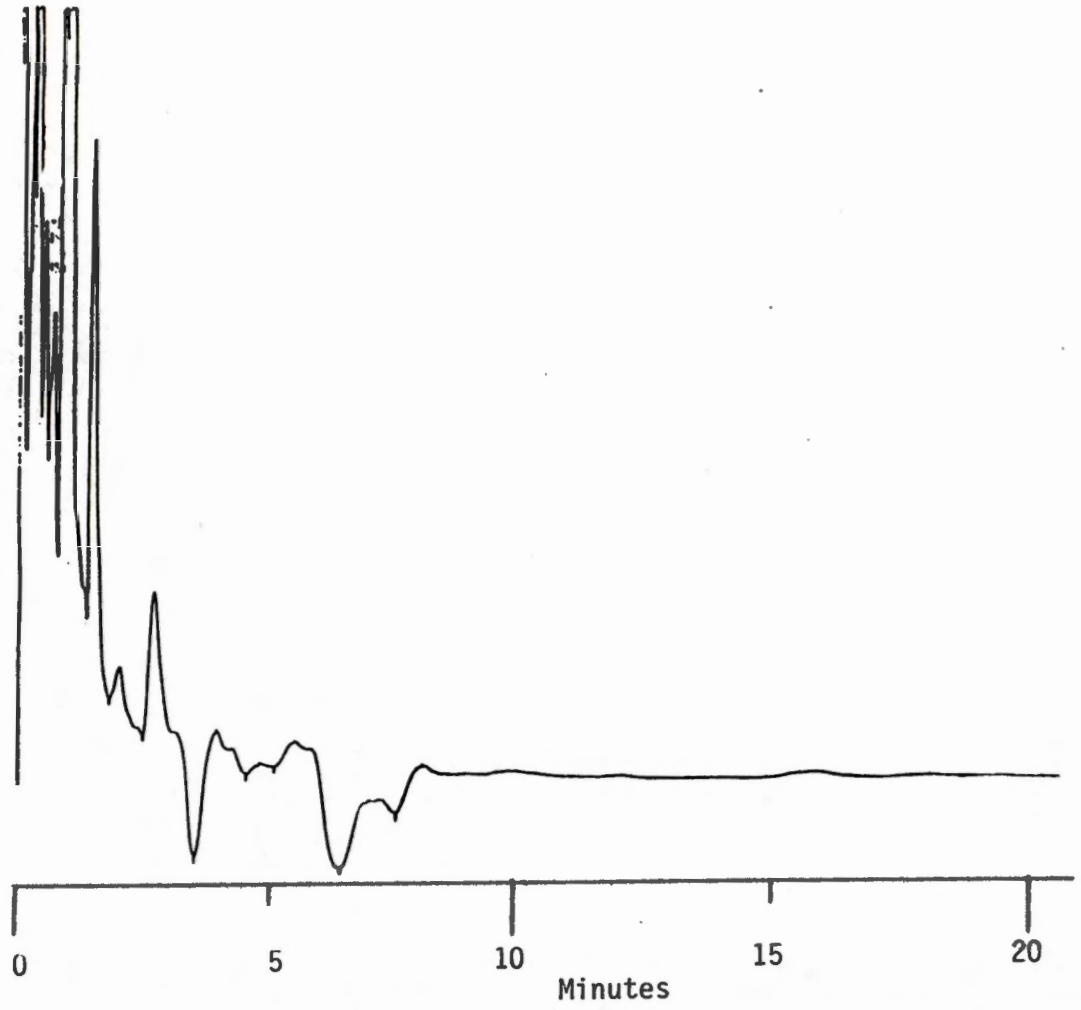

Figure III-9. Representative chromatogram of broccoli head tissue from plants of non-treated control field plots.

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LITERATURE CITED

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Table A-1. Daily Precipitation Received at Plant Sciences Field Laboratory, Knoxville, TN, in Fall, 1985, and Spring, 1986.[a]

	1985			1986		
Day	August	September	October	April	May	June
1	21.25		4.00			
2	26.75		25.00			1.25
3			9.00			
4			13.75			12.25
5			2.00			
6	10.00					
7	1.00			0.75		
8	1.75			17.50	1.25	
9				2.50		4.00
10						6.25
11						
12					0.25	1.75
13						
14					2.50	
15			1.00	1.00		
16			2.50			
17	35.75					
18	6.00					
19					2.50	
20					5.00	
21			10.75	12.50		
22			1.00	4.00		
23	1.75	6.50	17.25		14.25	
24	29.50				13.25	
25	0.75				7.00	
26		4.25				
27	26.25		3.50		15.50	
28					4.25	2.00
29				10.25	3.50	
30						12.50
31	9.25		0.10			

[a]Reported in millimeters.

Table A-2. Daily Maximum and Minimum Temperatures (°C) at Plant Sciences Field Laboratory, Knoxville, TN, in Fall, 1985, and Spring, 1986.[a]

	1985						1986					
	August		September		October		April		May		June	
Day	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
1	31	22	28	16	29	8	28	7	29	20	29	16
2	28	19	31	16	16	9	28	8	29	6	29	18
3	27	16	32	17	17	9	27	8	29	6	30	18
4	29	16	31	17	20	14	29	9	18	0	28	18
5	28	17	32	18	26	9	28	9	24	6	26	17
6	28	17	32	19	19	2	28	10	28	8	29	18
7	24	19	27	17	18	2	27	12	29	16	30	20
8	27	20	31	18	21	2	27	14	30	14	32	23
9	30	19	33	18	25	4	20	6	29	11	24	20
10	32	19	32	18	28	9	12	0	30	11	30	20
11	32	18	32	19	28	10	18	0	27	16	30	21
12	33	19	29	14	28	11	22	2	27	16	30	21
13	34	19	24	14	29	13	23	5	25	17	30	17
14	34	19	23	17	27	14	26	7	25	10	29	17
15	33	18	23	5	28	16	26	12	30	14	30	17
16	32	18	24	7	24	13	20	5	28	16	32	17
17	27	20	26	7	24	9	20	3	29	14	32	17
18	23	19	27	8	27	9	10	5	31	16	32	14
19	30	18	28	9	28	12	22	4	27	16	32	13
20	32	18	29	10	28	12	26	8	26	13	32	13
21	30	19	29	10	28	18	26	9	21	9	33	19
22	27	13	29	15	22	15	14	4	20	6	33	16
23	27	14	30	13	21	15	13	-3	23	9	33	16
24	23	17	29	16	19	16	16	-2	18	9	34	21
25	22	18	23	7	20	16	23	4	27	14	33	16
26	27	18	28	7	24	9	29	10	24	16	32	13
27	27	18	24	10	24	10	32	11	24	18	34	17
28	27	18	20	4	18	12	32	11	28	18	34	19
29	30	17	24	4	24	13	26	9	27	18	35	23
30	31	17	26	7	18	8	26	8	28	18	33	22
31	29	16			18	12			29	16		

[a]Recorded at 1.5 m above soil surface.

Table A-3. Daily Precipitation Received at Plateau Experiment Station, Crossville, TN, in Fall, 1985, and Spring, 1986.[a]

	1985			1986		
Day	August	September	October	April	May	June
1	4.00		90.00			
2	6.00		17.25			4.00
3			1.50			
4			2.00			10.50
5		6.75	0.75			2.25
6	11.50	3.00		1.25		
7	7.75	1.75		7.00		0.75
8	7.00			10.25		3.50
9						
10						18.00
11						0.50
12						2.00
13					1.50	
14						
15			4.00	2.00		
16	0.75		0.75			
17	72.75					
18	6.25					
19					1.25	
20				1.50	9.50	
21	1.25		1.75	12.00		
22			0.25	5.50		
23	3.00				19.75	
24	0.50	6.25			2.75	
25	8.50				9.50	
26	11.25	19.75			1.00	
27		12.00			38.00	
28			4.00		73.25	
29				6.00	2.50	5.00
30			1.25			0.25
31	9.25		3.00			

[a]Reported in millimeters.

Table A-4. Daily Maximum and Minimum Temperatures (°C) at Plateau Experiment Station, Crossville, TN, in Fall, 1985, and Spring, 1986.[a]

	1985						1986					
	August		September		October		April		May		June	
Day	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
1	30	19	27	16	22	7	26	10	28	10	27	14
2	28	16	27	16	9	6	24	10	22	7	28	16
3	24	16	28	17	11	7	24	10	18	2	27	15
4	27	16	27	17	17	8	26	13	16	2	26	16
5	26	14	29	14	22	4	25	13	23	4	22	16
6	23	16	28	19	16	1	25	13	26	15	26	17
7	21	17	26	17	15	1	23	12	27	14	27	17
8	22	18	29	17	18	2	24	13	29	13	28	20
9	28	17	30	17	20	9	20	3	28	12	29	19
10	29	17	29	17	24	12	10	0	28	11	29	18
11	30	17	29	18	26	11	14	2	27	13	27	19
12	31	18	27	13	27	11	18	4	24	13	28	19
13	30	20	22	9	27	16	21	7	22	15	26	14
14	29	18	20	7	26	14	23	9	27	15	25	13
15	29	19	18	6	27	17	22	4	27	16	28	16
16	27	18	22	6	21	10	16	0	24	16	27	14
17	24	19	23	7	22	10	7	2	27	16	29	15
18	22	18	24	8	24	10	8	2	28	18	28	11
19	28	16	26	8	24	15	22	7	21	15	26	13
20	30	18	26	10	26	13	24	11	19	10	29	16
21	27	18	27	10	26	15	16	6	17	4	30	18
22	25	13	27	12	22	14	12	0	17	4	32	16
23	24	15	26	13	20	14	9	-4	21	8	32	17
24	22	16	20	12	18	16	15	0	21	12	32	19
25	22	16	19	7	22	15	23	10	26	14	29	14
26	24	16	24	9	20	9	27	11	22	14	28	13
27	24	14	18	7	22	11	29	14	20	16	30	13
28	26	15	17	3	18	13	29	12	22	17	32	18
29	28	15	20	5	22	13	20	6	22	17	31	20
30	29	17	8	-1	16	9	23	9	27	15	28	18
31	27	13			18	10			28	16		

[a]Recorded at 1.5 m above soil surface.

VITA

William H. Eaton, Jr., was born in Goodlettsville, Tennessee, in 1954. He received a Bachelor of Science degree in Agriculture with high honors from The University of Tennessee, Knoxville, in 1984. During his graduate program he was employed as a teaching and research assistant with the Plant and Soil Science Department at The University of Tennessee, Knoxville. He completed the requirements for a Master of Science degree with a major in Plant and Soil Science in August of 1987.