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FATE OF SETHOXYDIM IN PLANTS AND UNDER ABIOTIC CONDITIONS

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ABSTRACT

FATE OF SETHOXYDIM IN PLANTS AND UNDER ABIOTIC CONDITIONS

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The objectives of this research were to: 1) determine the fate or the graminicide sethoxydim in a perennial and an annual grass weed, quackgrass (Agropyron repens (L.) Beauv.) and barnyardgrass (Echinochola crus-galli (L.) Beauv.), and in a perennial and an annual broadleaf crop, alfalfa (Medicago sativa L.) and navybean (Phaseolus vulgaris L.), 2) propose a basis of herbicidal selectivity and 3) determine the stability of sethoxydim under various abiotic condtions.

Greenhouse studies indicated at least a 100 fold difference in tolerance to sethoxydim between the grass and broadleaf species. Photo and thermal transformation of sethoxydim was rapid, within one hour more than 80% of parent sethoxydim was transformed when applied to glass and 95% when dissolved in water. Seven transformation products were resolved by thin layer chromotography (TLC). Two of these compounds, which were more stable than sethoxydim, were phytotoxic to barnyardgrass.

The contribution of soil uptake from postemergence applications of sethoxydim was negligible. Retention of spray solutions on leaves was greatest on navybean and least on alfalfa. Absorption of ^{14}C into leaves was rapid with more than 80% absorbed within 6 hours in all species. Translocation was observed after 1 hour in all species and after 12 hours, ^{14}C was detected in the roots of all species. Navybean

exported the greatest quantity from the treated leaf, 20%, and barnyardgrass the least, 12%. Partitioning of ^{14}C between ethyl acetate-soluble and insoluble fractions was similar among species. TLC analysis of the ethyl acetate fraction resolved nine metabolites. Seven of them co-chromatogaphed with those found from abiotic transformation, including the two previously determined to be phytotoxic to barnyardgrass. There were no qualitative differences in these metabolites between species and quantitative differences were minor.

From the results of these studies, selectivity could not be based on differential retention, absorption, translocation or metabolism. While interspecies differences in herbicidal selectivity are usually based on one of these factors this is not the case in triazine resistant pigweed (Amaranthus sp.) where a modification in a chloroplast protein greatly reduces the herbicide binding and thus photosynthetic electron transport inhibition. It is thus possible that an enzyme(s) in gramineous species is either nonexistent in broadleaf plants or configured sufficiently different so as to greatly reduce the effect os sethoxydim on it. From cytological studies it can be suggested that this enzyme is concentrated in the meristematic zone.

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INTRODUCTION

Until recently there were very few postemergence herbicides active on grasses, dalapon having been one of the most important. Presently, however, there are a growing number of these highly active graminicides, the majority of which have two planer ring systems and a phenoxy side chain. Sethoxydim is differs form these with its cyclohexane based structure. Previously herbicides were applied prophylacticly, in anticipation of expected weed populations. These graninicides are a new type of weed control tool because they are applied to visible weed problems. Now it is possible to establish economic threshold levels for grass weeds and economic models for the most profitable rate of herbicide use.

For a greater understanding of herbicide action selectivity studies are important. These studies describe the differential movement from the leaf surface to the interior of the plant and trace its metabolism. This information is essential if there are antagonistic interactions between pesticides, if selectivity is not apparent under specific environmental conditions or if certain weed biotypes are not controlled.

Studies on abiotic transformations are important for a number of environmental and toxicological reasons, but to the weed scientist an understanding of a rapidly transformed herbicide is necessary to properly interpet and understand its nature within plants.

Sethoxydim is effective in controlling both perennial and annual grass weeds, but there is a difference in the rate of herbicide

necessary to effect economic control between these two groups of weeds. Additionally it is important to kill both underground and above ground plant parts, so studying the fate of sethoxydim in both types of plants would be useful. The objectives of these studies were to: 1) determine the fate of the graminicide, sethoxydim in a perennial and an annual grass weed, quackgrass (Agropyron repens (L.) Beauv.) and barnyardgrass (Echinochola crus-galli (L.) Beauv.), and in a perennial and an annual broadleaf crop, alfalfa (Medicago sativa L.) and navybean (Phaseolus vulgaris L.), 2) propose a basis of herbicidal selectivity and 3) determine the stability of sethoxydim under various abiotic condtions.

Chapter I

SETHOXYDIM, A LITERATURE REVIEW

HISTORY

The compound 2,4-D is considered by many to be the herbicide which ushered in the era of modern weed control. After the initial post-war reports of its usefulness in controlling broadleaf weeds became known, 2,4-D soon came into wide use in small grains performing a task only tediously and laboriously performed previously. It is ironic that, if per chance, chemicals used in those early trials had had another phenoxy between the chlorophenoxy and the acid moiety the revolution in weed control might have started with a broad spectrum graminicide in broadleaf crops. It has taken, however, almost forty years for weed science to put that extra phenoxy ring in and be actively involved in the research of postemergence graminicides. Although sethoxydim is structurally different form the main stream of graminicides it functions similarly.

Sethoxydim was discovered by Miko Sawakl of Fine Chemicals Research Laboratories, Nippon Soda Co. Ltd. and originally patented in 1974 in Japan (52). Sethoxydim, the herbicide, had it's chemical origins as a miticide, benzoximate, discovered in 1968 (33). Slight herbicidal

activity was noted with these hydroxamic acids and extended synthesis resulted in the herbicide alloxydim-sodium. This compound showed selective activity on grasses and was under development by BASF Wyandotte under the code BAS-9021. A common name carbodimedon has also been associated with this compound. Although development was dropped in North America it was continued in Japan and Europe where it is currently marketed under the trade names 'Kusagard' and 'Fervin' (40). In 1981 in Japan sales were valued at 50 Million Yen (49). Continued synthesis of compounds related to alloxydim-sodium resulted in the more potent graminicide sethoxydim. Again BASF Wyandotte conducted the development in North America and now has sethoxydim registered for use in soybean (Glycine max (L.) Merr.) under the trade name 'Poast'. In this review of sethoxydim related literature I would like to cover its herbicidal activity against grasses, soil activity, the effects of herbicide combinations, environment, adjuvants and safeners on activity, physiological responses of treated plants, fate in plants and structure activity relationships of cyclohexane based herbicides.

POSTEMERGENCE HERBICIDAL ACTIVITY

Sethoxydim was recognized by its discovers to have much more activity than alloxydim-sodium (33,40), in paticular,its activity on perennial grasses was much enhanced. The number of grasses controled by sethoxydim is, indeed, very wide. Only rattail fescue (Fescuta myuros L.), red fescue (Fescuta rubra L.), annual bluegrass (Poa annua L.) and hard fescue (Fescuta ovina L.), listed in order of decreasing tolerance, have been reported tolerant to 0.4 kg/ha of sethoxydim. Rattail fescue showed almost no shoot fresh weight reduction by 6.4 kg/ha of sethoxydim (25,26). Postemergent applications of sethoxydim have been proven effective in controlling annual grasses such as yellow foxtail (Setaria lutescens (Weigel) Hubb.), barnyardgrass (Echinochola crus-gall (L.) Beauv.), and perennial grasses like quackgrass (Agropyron repens (L.) Beauv.) and johnsongrass (Sorghum halepense (L.) Pers.) (8,32,41,46). Optimal control is achieved with early postemergence applications (1). In carrots applications 4 weeks after planting at 0.1 kg/ha provided as much control on green foxtail (Setaria faberi (L.) Beauv.) as 0.4 kg/ha 2 weeks later. The use of sublethal rates early, 0.06 kg/ha, did provide good suppression of plant growth. In Arkansas the application rate of 0.67 kg/ha 6 weeks after planting did not provide adequate control of grass weeds (44). In contrast Burdik reported that over a large number of trials there was little difference in grass control between early and late (up to 39

days after planting) treatments with sethoxydim and that yield compared favorably with effective preplant incorporated herbicides (7).

Long term control of quackgrass was achieved with applications of 1.0 kg/ha, again earler applications, at 2 to 3 vs. 4 to 5 leaves, gave greater control (14,55,56). Long term control of quackgrass is dependent on controlling the rhizome system of the plant. One year after application of sethoxydim, 50% of the rhizomes were killed. In another study the number of rhizomes killed in the top 8 cm by sethoxydim was high but a six-fold increase in live buds were found in the 9 to 16 cm depth (55). Increased quackgrass control was obtained by split applications, the use of a non-selective herbicide, glyphosate, or by a timely cultivation (15,33). Cultivations 2 or 7 days after application at 0.8 or 1.2 kg/ha resulted in greater quackgrass control than sethoxydim alone (32,56).

ACTIVITY AND FATE IN SOILS.

Sethoxydim has shown only limited weed control activity when applied to soils for control of annual of perennial grass weeds (6,33,36). A lower level of soil activity has been shown in experiments in the field than in the greenhouse (4,6). Alloxydim exerted most of its activity by foliar uptake but soil uptake was evident and persistence greated than flamprop-isopropyl (28,42). A root bioassay technique was developed which could detect as little as 0.05 ug/g of sethoxydim (27). Concentrations required to effect a 50% inhibition of oat (Avena sativa

L.) root length were in the order of 0.05 ug/g soil. This concentration was similar among the three soil types, sandy loam, clay loam and heavy clay, suggesting that sethoxydim was not strongly adsorbed to the clay or organic colloids (51). Half lives of sethoxydim were determined by 14C techniques to be 12, 12, and 26 days in a sandy loam, clay loam and heavy clay respectively. This persistance did not relate directly to organic matter, pH, or clay content. Root assays of field soil, to which 1.0 kg/ha was applied 1 year previously, indicated less than 0.05 ug/g, or less than 2% of applied sethoxydim remained.

HERBICIDE COMBINATIONS

A weed control program which would use postemergence herbicides as the primary means of control often necessitates tank-mixtures of broadleaf-specific and grass-specific herbicides. Incompatibility between herbicides, whether physical or physiological, will reduce the desirability of such total postemergence programs. Several of the postemergence graminicides, including: sethoxydim, diclofop, haloxyfop nd fluazifop-butyl, exhibited reduced activity when combined with a broadleaf herbicide (11,19,36,41,57,59). Combinations of bentazon, 2,4-DB, chlorambin, MCPA, propanil and in some instances acifluorfen with sethoxydim induced reduced activity to grasses but broadleaf activity remained the same (3,20,41). Tank-mixtures of dalapon, desmedipham, bromoxynil, 2,4-D and TCA with sethoxydim as well as metamitrom with alloxydim showed good grass control (11,24,39,41). This

author is not aware of any reports of increased crop injury of tank-mixtures including sethoxydim. However, with alloxydim severe injury to Gladioli sp. resulted when it was mixed with metoxuron, though gladioli tolerates either chemical applied separately (37).

Williams showed that bentazon reduced absorption of 14C-sethoxydim into the cuticle of german millet Setaria sp and was probably the basis of the antagonism (57). Overcoming antagonisms with bentazon was possible by increasing sethoxydim rates to 0.56 kg/ha or applying the herbicides sequentially, allowing at least 1 hr 30 min between treatments (19,38). The combination treatments of graminicides has only begun to be tested, but it has been shown that the activity if several compounds has been increased by the addition of PP021 (14).

ENVIRONMENT AND ACTIVITY

Soil moisture, rainfall, air and soil temperature, and relative humidity were shown to affect the performance of sethoxydim. Control of johnsongrass was reduced 30% under dry soil conditions when compared to high soil moisture, this difference was not significant when higher rates were used (3). In contrast, little difference in herbicidal activity was shown on the annual grasses, goosegrass (Eleusine indica (L.) Gaertn.), large crabgrass (Digitaria sanguinalis (L.) Scop.) and broadleaf siginalgrass (Brachiaria platyphylla (Grisep.) Nash) between plant grown under low (11%) vs. high (23%) soil moisture (10). Renoylds also indicated no interaction of soil moisture with sethoxydim on annual grasses (47).

Simulated rainfall of less than 2 mm delayed 30 min after application of sethoxydim did not reduce annual grass control, while a 2mm rain withi one hour only reduced control by 17% (12,48). In combination with an oil concentrate a rain free period of 2 hr allowed control equal to that of no rain.

Several investigators reported increased grass injury with sethoxydim at temperature of 30 C (12,48). Conversely, increased soil temperature, from 7 to 21 C, resulted in lower wild oat control (47). relative humidity appeared to interact with temperature so that at lower temperatures lower relative humidities increased control and at higher

temperatures higher relative humidities increased control (12). In a study by Ennis and Ashly it was noted increased sethoxydim activity occured with treatments later in the day, suggesting higher temperatures and relative humidities at the later time of day were the cause (16). From their own data, however, both temperature and humidity were highest at mid-day, it could be suggested that as sethoxydim is unstable in light greater activity at the afternoon time resulted from reduced photobreakdown of the herbicide(34,43).

SPRAY ADJUVANTS

The use of emulsifiable oil adjuvants were effective in increasing sethoxydim's activity to both annual and perennial grass weeds (10,13,32). Cranmer found two oil concentrates 'At Plus 411F' and 'Herbimax' and the surfactant 'Surfel' more effective than two linseed oil derivatives, 'LOMA' and 'LOTM' or a bivert emulsifier 'Bivert' or a mixed surfactant 'X-77' (13).

PROTECTANTS

The use of chemicals to antidote the effect of a herbicide on crops has been proven effective and is commercially in use to protect corn from thiocarbamate and sorghum from acetanilide herbicides. Sethoxydim has been safely and effectively used to control escape grasses in the monocotyledonous crop corn (Zea mays L.), although this was by differential application to the weeds and not by any protective chemical, it does point out the usefulness of a grass killing herbicide in such a crop (39). Two investigators have shown some protection to corn and sorghum (Sorghum bicolor (L.) Moench) with 1,8-naphthalic anhydride, a known seed treatment antidote (22,45). It is interesting to note that although tank-mix combinations of bentazon with sethoxydim resulted in reduced control of yellow foxtail, a greater reduction in injury to wheat (Triticum aestivum L.) and oats (Avena sativa L.) resulted, effectively offering some protection to the two crops (41). Functional systems which give selectivity between monocotyledonous weeds and crops remain to be developed.

PHYSIOLOGICAL RESPONSES

The germination of soybean, sorghum, or yellow foxtail was not

inhibited by concentrations of 10^{-7} M sethoxydim (6). The survival of the the monocot seedlings, however, was reduced by concentrations of 10^{-2} M, soybean tolerated 10^{-2}. A similar pattern of seedling root and hoot elongation inhibition was observed in both susceptible and tolerant grasses by Hosaka et al. (26). Shoot elongation was more sensitive to sethoxydim than root elongation in corn (2).

On intact plants the earlist symptom of sethoxydim injury is a secession of growth, this is followed by leaf chlorosis and a degeneration of the internal meristematic tissue, wilting and necrosis follow (2). The symptoms of alloxydim injury are similar (31).

Inhibition of apparent photosynthesis occurred 24 hours after application of 1% (v/v) sethoxydim in both corn and soybean. The onset of this symptom was more rapid in soybean but recovery occured after 48 hours (17). A reduction in the rate of growth preceded the inhibition of apparent photosynthesis in corn. A reduction in respiration and a concomitant increase in sugars was induced by low rates of sethoxydim (2). Chlorophyll (a+b) content was reduced and anthyocyanin content increased as a result of an application of 0.02 kg/ha of sethoxydim. Alloxydim showed similar effects on the plant pigments but it did not inhibit respiration or apparent photosynthesis (29,50). In studies with isolated soybean cells Hatizios reported that the incorporation of lipid precursors was more sensitive to sethoxydim than the incorporation of photosynthetic, ribonucleic or protein precursors (21). It must be remembered that these studies were conduced on a species highly tolerant to sethoxydim. Alloxydim had no effect on protein synthesis at 10^{-4} M of corn (5).

Cytological and histological investigations have revealed several effects of sethoxydim. One day after application of sethoxydim, necrosis was more severe in two locations of johnsongrass, in the procambium of the 4th to 6th youngest leaf primordia and in the root tip distal from the apex (53). Both cell division and cell elongation were reduced in bermudagrass (Cynodon dactylon (L.) Pers.), mesophyll cells were more affected than bundle sheath cells (9,35). Thylakoids of affected cells retained structural integraty but lost turgidity and the peripheral reticulum was disorganized. Mitochondria had reduced matrix density and internal membrane disorganization. In corn root tips disruption of normal mitotic activity occured, binucleate cells were formed, possibly caused by the observed disruption in cell plate formation and disorientation of daughter cell nuclei (2). The mitotic index was not affected.

FATE IN PLANTS

Rapid absorption of 14C-sethoxydim occured in both johnsongrass and bermudagrass (53,58). This absorption was affected by both temperature and humidity with the greatest absorption at high temperatures and relative humidities. Soybean absorbed sethoxydim more rapidily than johnsongrass. In a study of five monocotyledonous and five dicotyledonous plants absorption of 14C-alloxydim was less than that reported for sethoxydim but after 7 days all species had absorbed from 48 to 78% of applied 14C (54).

Translocation of sethoxydim was evident in both broadleaf and grass species. Johnsongrass translocated more 14C to its roots and rhizomes than soybean but soybean translocated three times as much 14C to apical shoots. Harker reported no significant translocation to sethoxydim to quackgrass roots after 5 days (18). In bermudagrass export of 14C from the treated leaf was increased by high temperature and humidity. This increased export due to environment was similar among shoots above or below treated area and roots (58). Translocation of 14C-alloxydim was similar among broadleaf and grass species with between 19 and 32% of absorbed 14C was translocated. Less than 4% of absorbed 14C was found in the roots of any species (54).

Metabolism of 14C-sethoxydim occurred in both soybean and johnsongrass tissue cultures, three metabolites constituted a large proportion of total 14C (53). These metabolites were similar between species. Alloxydim was metabolized in both wild oat and sugar beet (Beta vulgaris L.), after 7 days 17.8 and 6.2% ,respectively, of total applied 14C was found in the organo-soluble fraction was determined to be alloxydim. Three other metabolites were reported in both species with little qualitative differences between them. These investigators could only attribute part of alloxydim's selectivity to differential metabolism (54). Ishihara reported only 6% of applied 14C-sethoxydim was recovered from whole soybean or sugar beet (30). As only the number 4 posisition on the ring was labled it is possible that this carbon was given off as CO_2 after ring cleavage (23). Several metabolites of sethoxydim were identified, including: a desethoxy, sulfoxide, sulfone and oxazole ring derivatives.

STRUCTURE ACTIVITY RELATIONSHIPS

As mentioned before the synthesis of sethoxydim was realized after herbicidal activity in heterocyclic hydroxamic acid compounds was observed (33). It was noted that an alkoxyaminoalkylidene located between two keto groups on a ring structure exhibited much improved herbicidal activity. In testing a large number of structures several generalizations could be made about herbicidal activity. Hydrogen at R1 is ineffective, n-propyl produces maximum activity while methyl, ethyl, longer chain or branched alkyl, thiol, or halogenated substitutions all decreases activity (Figure 1). At R2 ethyl produces maximum activity while methyl shows weak broadleaf activity and increasing chain length decrease activity to grasses. Relatively high activity is shown when both R3 and R5 are hydrogen or one a methoxy carbonyl group. Certain phenyl substitutions would exhibit selective action between wheat and wild oat. At R4 a wide variety of substituents allow satisfactory herbicidal activity, including isopropyl and dimethyl groups. In exploring sulfur containing groups, however, a ten fold increase in activity was observed. Short chain thioalkyl, halogenated thioalkyl and their sulfone and sulfoxides were among these. When the sulfur was more oxidized there was a tendency toward reduced herbicidal activity to johnsongrass and yellow foxtail (33,34).

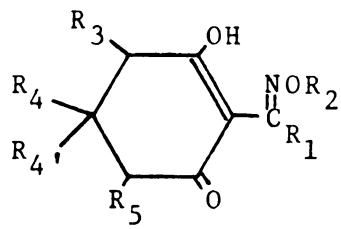

Figure 1. Cyclohexanedione skeleton.

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CHAPTER 2

ABIOTIC TRANSFORMATIONS OF SETHOXYDIM

ABSTRACT

The fate of ^{14}C-sethoxydim [2-[1-(ethoxyimino) butyl]-5-[2-(ethylthio) propyl]-3-hydroxy-2-cyclohexen-1-one] in an aqueous solution and on glass exposed to light was evaluated. Within 1 h more than 80% of the ^{14}C-sethoxydim was transformed to six major products. Quantitatively the transformations were similar for both systems, a single end product constituted the majority of ^{14}C after 72 h. Two transitory compounds were found to be phytotoxic to barnyardgrass [Echinochloa crus-galli (L.) Beauv] and were more stable than sethoxydim. A non-phytotoxic compound isolated and identified by mass spectroscopy was desethoxy-sethoxydim.

INTRODUCTION

Sethoxydim is a recently developed postemergence graminicide with a cyclohexone based ring structure. Abiotic transformations of a wide variety of herbicides have been well documented. There are reports of photodegradation in most classes of herbicides including the ureas (2), s-triazines (7,8), benzoic acids (4), dinitroanilines (11) and the bipyridiliums (3). Such factors as altitude and light wavelength have been shown to influence herbicide breakdown and explain differences in activity between geographical locations (6,7). When studying photochemical pesticide transformations the conditions to which a pesticide is exposed can have important effects on breakdown patterns (9). Crosby (1) has suggested that exposure in dry form on glass, in an aqueous solution, and in a neutral organic solvent as the three conditions most relevant to pesticide research. Further enhancing photodecomposition were the presence of certain photosensitizers such as anthraquinone or flavone (5). These compounds have high triplet energy states and act by transferring absorbed light energy to other compounds. All these factors are important in interpreting the degradation of a particular pesticide. Determinations of abiotic transformations occurring with relatively unstable herbicides is prerequisite to the determination and interpretation of the metabolic fate of the herbicide within plants.

The objectives of this study were to examine the transformation of sethoxydim on a neutral glass surface and in water and to determine the phytotoxicity of the transformation products.

MATERIALS AND METHODS

Studies with ^{14}C-sethoxydim in water. All laboratory work was performed using minimal incandescent lighting without exposure to direct fluorescent light or sunlight. All glassware was treated with dimethyldichlorosilane for 3 min then rinsed sequentially with toluene, hexane, and water before drying to reduce sethoxydim adsorption. A solution of 0.0002 µCi/µl was prepared by adding 1.16 µCi of ^{14}C sethoxydim (labeled at the number 4 position on the ring, specific activity 10.3 mCi/mM) to 5.8 ml of distilled water. This resulted in a concentration which was one seventh of saturation [1]. This was then subdivided into 200 ul portions, placed into 6 by 50 mm pyrex test tubes and stoppered with teflon wrapped stoppers. Two treatments were then covered with foil to prevent light exposure, one was kept at -20 C until chromatographed, the other remained with the rest of the tubes in a Rayonet Preparative Photochemical Reactor, type 85 [2]. Light energy density was 63 µE $cm^{-2}sec^{-1}$ at the

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[1] BASF Wyandotte Corporation, Parsippany, N.J., Technical Data Sheet.

[2] The South New England Ultraviolet Co., Middletown, CN.

averaged during the day at 350 $\mu Em^{-2}sec^{-1}$. Daytime temperatures were 25-30 C during the day and 18-22 at night. All treatments were replicated three times and experiments repeated.

Phytotoxicity of transformation products. Our initial work revealed at least ten transformation products of sethoxydim, five of which constituted a major portion of the total. These five separated by TLC with a chloroform:isopropanol (9:1 v/v) solvent system migrated to the following Rf values. 0.52, 0.41, 0.38, 0.13, 0.0. A 10% solution in methanol (v/v) of formulated of sethoxydim left from the previous year was streaked onto five TLC plates and developed, visualized by UV quenching, then scraped into separate funnels. The band corresponding to sethoxydim was also scraped. Each band was eluted with 80 ml of methanol. The volume of these solutions was reduced in vacuo then under nitrogen to 100 µl. To each concentrated solution were added 10 µl each of Aromatic 150 and Makon 10[3] and 700 µl of water. To confirm purity, a 10 µl aliquot was removed from each emulsified extract, applied to a TLC plate, and developed with chloroform:isopropanol (9:1 v/v). It was confirmed that each solution contained a single sethoxydim transformation product. A 20 µl aliquot was placed on the leaf axis

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[3] Solvent and surfactant, respectively, from Stepan Chemical Co., Northfield, IL.

of fifth leaf stage barnyardgrass at 9 pm and these plants placed in the greenhouse. A blank formulation of water, Aromatic 150, and Makon 10 was also applied. After application of the extracts 10µl aliquots were again subjected to TLC as done previously and purity confirmed. Fresh weights of the plants were determined after 14 days. Each treatment was replicated five times with three plants per pot and the experiment was repeated three times.

Transformation product identification. A 1% (v/v) solution of analytical grade sethoxydim in n-hexane was exposed to greenhouse light for 2 days. A sample was removed and was applied to TLC plates. The compound with an Rf of 0.52 was removed, eluted with methanol, and concentrated under nitrogen. After rechecking to determine purity a sample was introduced by direct probe to an HP 5985 electron impact mass spectrometer. The sample was introduced at room temperature then incrementally treated at 25 C/min. Satisfactory spectra were obtained at 1.4 min.

RESULTS AND DISCUSSION

Sethoxydim dissolved in water was found to be unstable at room temperature or kept at -20 C, only 6 and 24% of the parent sethoxydim remained after 72 h. The transformations were increased upon exposure to light (Table 1). Significant phototransformation was evident after 20 min and parent sethoxydim was reduced to less than 2% of the total after 3 h, degradation continued to 30 h.

There were six major transformation products of sethoxydim dissolved in water (Figure 1). Five of these products were transitory and the sixth, which remained at the origin after TLC separation, appeared to be the single end product (Table 2). This product is probably more polar than sethoxydim or the other transformation products as it migrated the least under TLC.

Sethoxydim applied to glass filter disks and not exposed to light was unstable, only 27 and 5% of the parent sethoxydim remained after 0 or 168 h exposure to greenhouse temperatures respectively. Only 19% of the sethoxydim on disks exposed to light remained after 1 h and less than 4% after 24 h (Table 3). The pattern of transformation was similar to that of sethoxydim dissolved in water (Figure 2). A single terminal product was again apparent. One qualitative difference in the transformation of sethoxydim was the presence of compound f upon exposure on glass which was not detected upon exposure in water. Compound b was not detected in the glass system as it was in water. Another qualitative difference was that on glass the transformation products d and e roughly paralleled each other while in water e decreased more rapidly than d. Total recovery of ^{14}C was 99% indicating little loss due to volitility. Evidence of rapid transformation of sethoxydim exposed to light suggested that herbicidal activity resulted from the more stable transformation products. To test this, five of these products were applied to barnyardgrass. Compounds d and e were found to have

significant activity, as did sethoxydim. Since quantitation of individual compounds was not made relative herbicidal potencies were not determined between d, e and sethoxydim. It is relevant, however, that the apparent end product of transformation, h or c and g showed no herbicidal activity.

The mass spectrum of compound c resembled that of the parent sethoxydim (Figure 3b). The molecular ion at m/e 283 was 44 mass units less than sethoxydim (Figure 3a). This can be explained by the loss of the ethoxy side chain. The major ion fragment at m/e 254, 223 and 180 are explained by the loss of an ethyl side chain, a sulfur and a propyl side chain respectively (Figure 4). Isotopic ratio of m/e 283 and 285 as well as m/e 254 and 256 indicate the presence of one sulfur. Compound c had a lower Rf value than sethoxydim, indicating it had greater polarity, and this is consistent with the proposed structure. Additionally, an ethoxy alkyl side chain is important for herbicidal activity, so the loss of this group would explain the lack of activity on barnyardgrass (10).

Sethoxydim was found to be labile in water and on fiber glass both unexposed and exposed to light. Two products were shown to be herbicidally active. A desethoxy-sethoxydim structure was proposed for one of the non-active products, this is consistent with known herbicidal potency.

Table 1. Phototransformation of sethoxydim in water exposed to light[a].

Time	^{14}C Sethoxydim recovered (% of unexposed control)[b]
0 min	100.0 a
5 min	70.1 a
20 min	22.5 b
1 h	5.3 c
3 h	1.7 d
10 h	0.7 e
30 h	0.18 f
72 h	0.24 f

[a]Means with the same letter are not significantly different by Duncan's multiple range test at 5% level of probability.

[b]Control tube was covered and maintained at the same temperature as exposed tubes.

Table 2. Rf values of the transformation products of sethoxydim in water and on fiber glass disks.

Compound Designation	Rf value of transformation products[a]	
	In Water	On Glass
Sethoxydim (a)	0.72	0.72
b	0.60	----
c	0.52	0.52
d	0.41	0.41
e	0.38	0.38
f	----	0.33
g	0.13	0.13
h	0.00	0.00

[a]Solvent system described in materials and methods.

Table 3. Transformation of sethoxydim on fiberglass disks exposed to greenhouse light.

Exposure Time (h)	^{14}C-sethoxydim recovered[a] (% of unexposed control)[b]
0	100.0 a
1	19.0 b
6	9.7 c
12	3.7 c
24	3.8 c
72	1.9 d
168	2.0 d

[a]Means with similar letters are not significantly different by Duncan's multiple range test at 5% level of probability.

[b]Control samples were extracted immediately after application.

Table 4. Phytotoxicity of sethoxydim and transformation products on barnyardgrass.

Treatment	Rf	Fresh weight[a] (% of control)
Untreated	--	100 a
Blank formulation	--	90 a
Sethoxydim (a)	0.72	14 c
c	0.52	91 a
d	0.41	47 b
e	0.38	49 b
g	0.13	96 a
h	0.00	96 a

[a]Means with similar letters are not significantly different by Duncan's multiple range test at 5% level of probability.

Figure 1. Distribution of ^{14}C-sethoxydim and ^{14}C-transformation products in water solution after exposure to light.

14C Distribution (% of total)
Time (min)
14C Distribution (log dpm) LSD .005 = 0.3

Figure 2. Distribution of ^{14}C-sethoxydim and ^{14}C-transformation products on glass exposed to light.

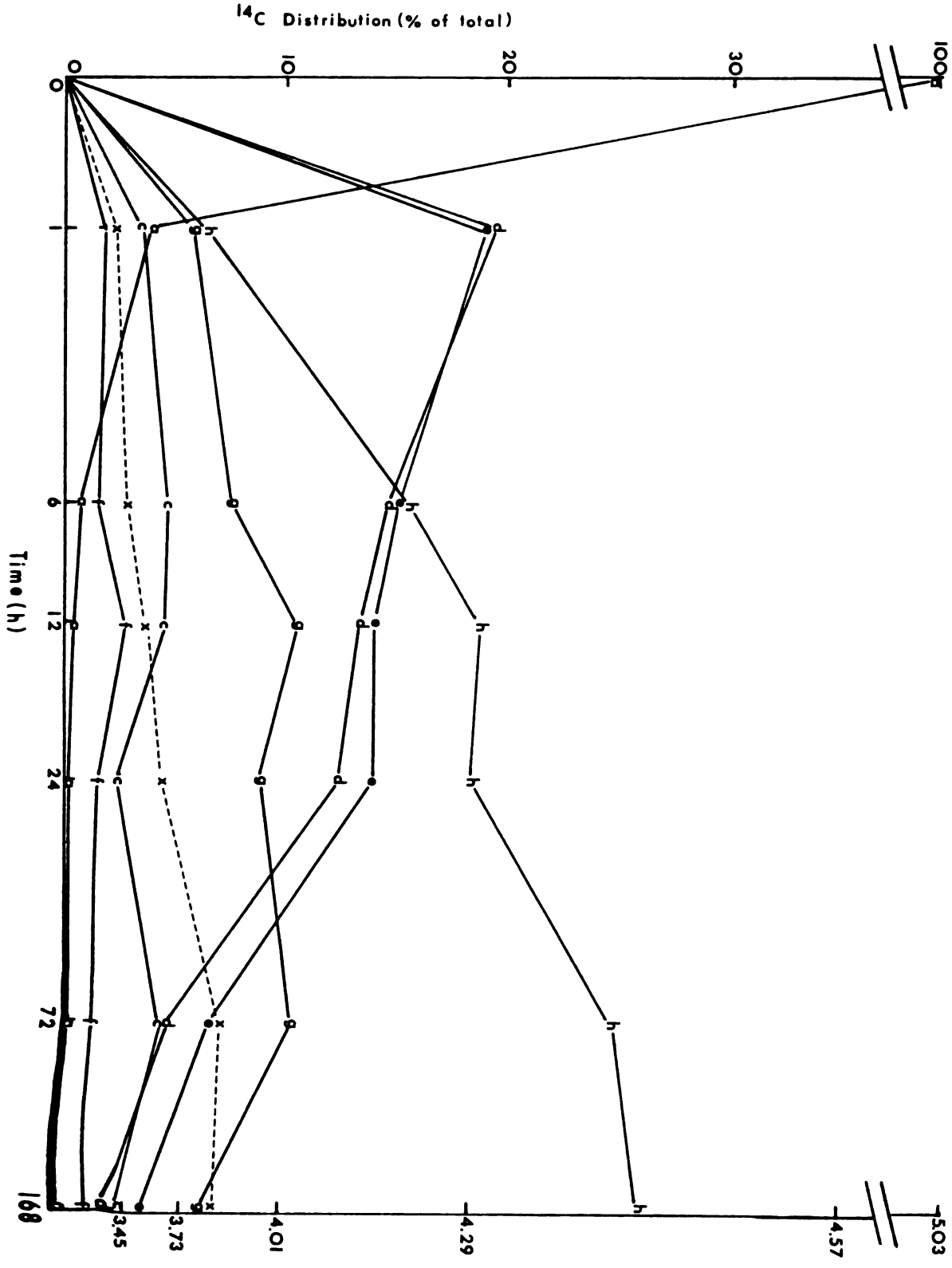
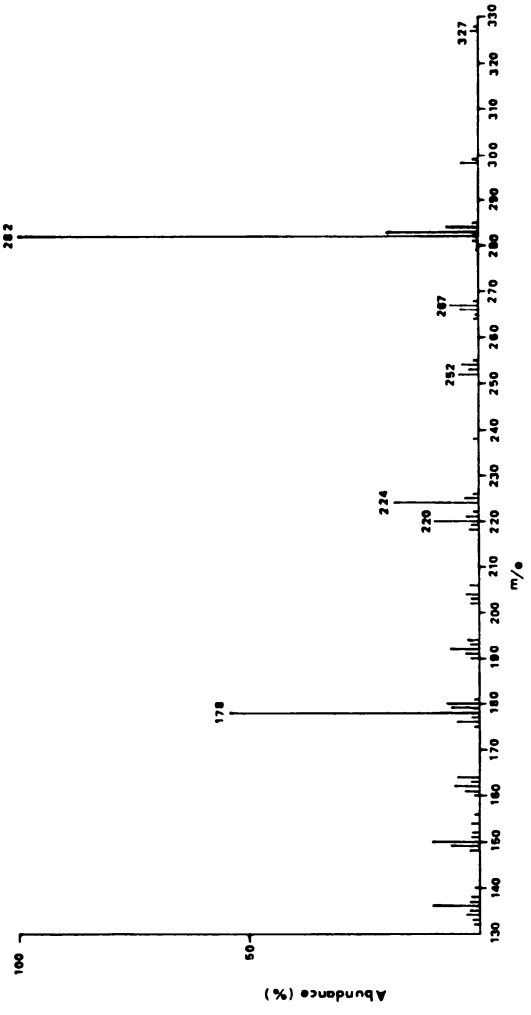

^{14}C Distribution (% of total)
0
10
20
30
100
Time (h)
0
1
6
12
24
72
168
3.45
3.73
4.01
4.29
4.57
5.03
^{14}C Distribution (log dpm)
LSD 0.05 = 0.28

Figure 3. Mass spectra of sethoxydim and product c (below).


Abundance (%)
100
50
282
178
224
220
252
287
327
m/e

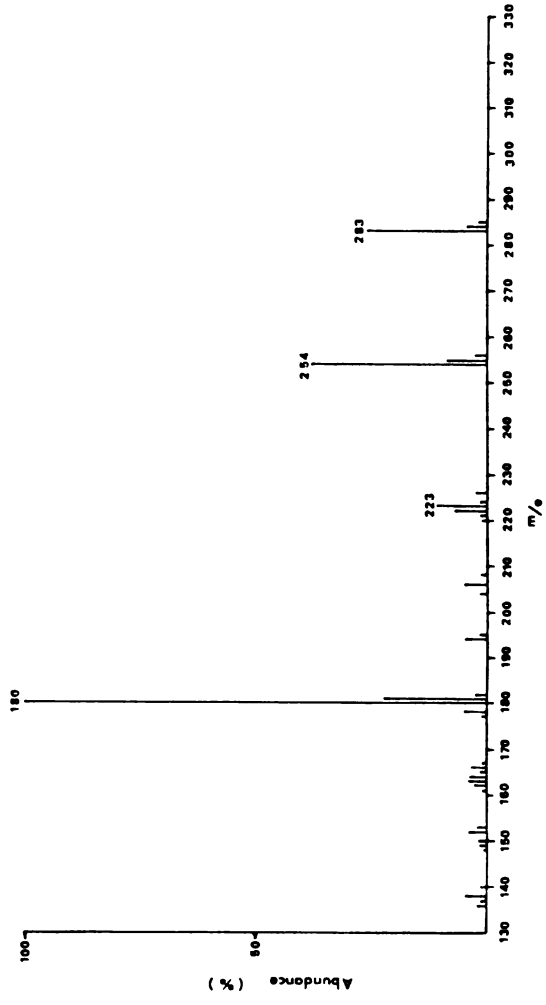
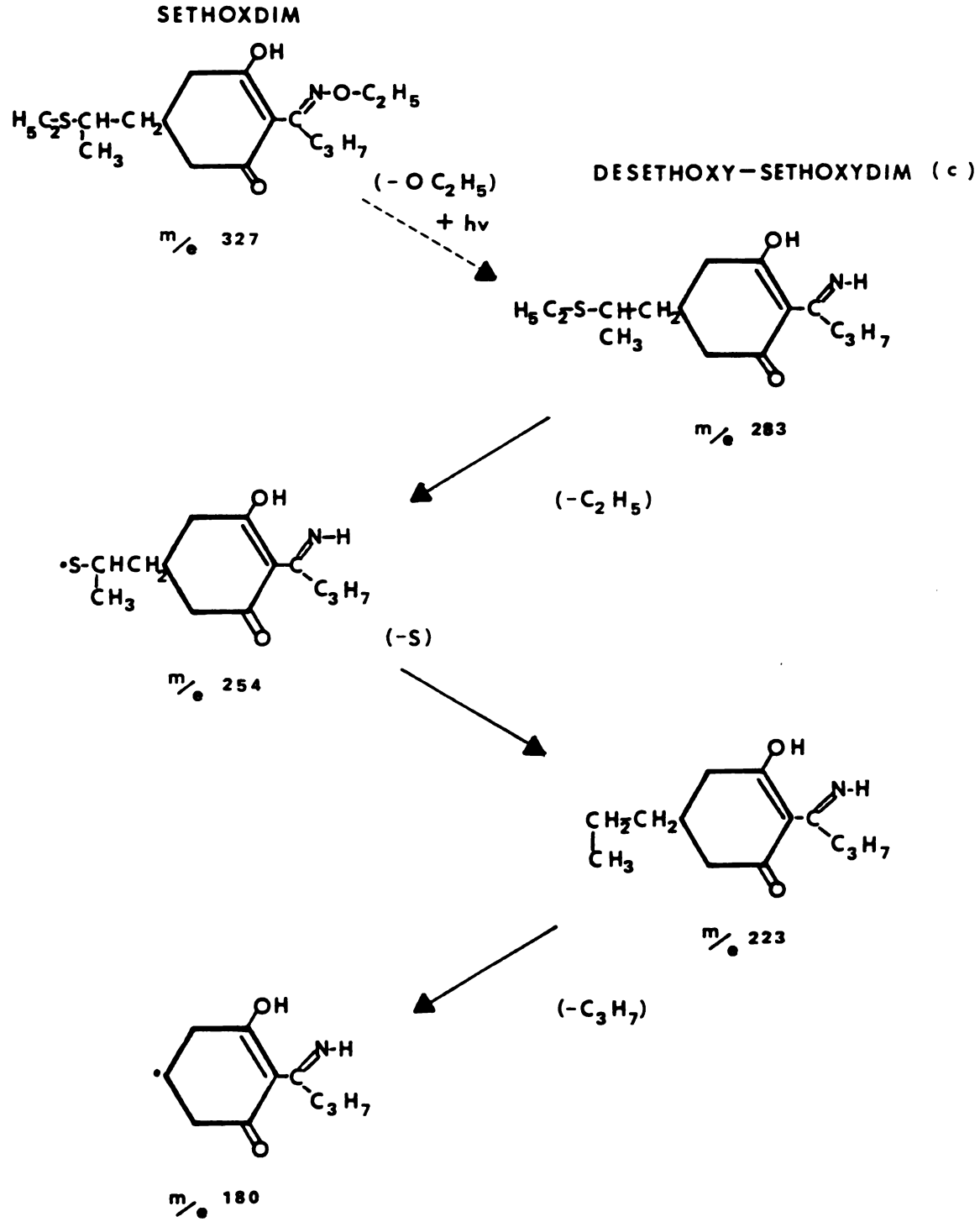

Abundance (%)
100
50
180
223
254
283
m/e

Figure 4. Proposed structure and fragmentation sequence for the molecular ion and majior ion fragments from the mass spectra of the transformation product c.


SETHOXDIM
m/e 327
(- O C2 H5)
+ hv
DESETHOXY-SETHOXYDIM (c)
m/e 283
(-C2 H5)
m/e 254
(-S)
m/e 223
(-C3 H7)
m/e 180

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CHAPTER 3

COMPARISON OF RETENTION, ABSORPTION, TRANSLOCATION, AND DISTRIBUTION OF SETHOXYDIM IN MONOCOTYLEDONOUS VERSUS DICOTYLEDONOUS PLANTS

ABSTRACT

Quackgrass [Agropyron repens (L.) Beauv #[1] AGRRE] and barnyardgrass [Echinochola crus-galli (L.) Beauv # ECHCG] were more than one hundred times more susceptible to sethoxydim [2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohex-1-one] than alfalfa (Medicago sativa L.) or navybean (phaseolus vulgaris L.). Soil uptake of sethoxydim from postemergence applications contributed negligibly to barnyardgrass fresh weight reduction. More than 80% of applied ^{14}C-sethoxydim was absorbed within 6h in all species. Translocation occured in all species with concentrations of ^{14}C in rapidly growing tissues. Initially, most of the ^{14}C partitioned into the ethyl acetate-soluble fraction, this decreased with time with a concomitant increase in the insoluble fraction. Differences in the quantity of ^{14}C in the ethyl acetate-soluble fraction could not account for the observed selectivity.

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1. WSSA approved computer code

INTRODUCTION

Sethoxydim is a cyclohexane derived herbicide effective as a postemergence herbicide for controlling most grasses in dicotyledonous crops (1, 14, 16, 20). Directed postemergence applications of sethoxydim have been reported to be safe and effective for weed control in corn (Zea mays L.) (18). Among the grasses controlled are quackgrass and barnyardgrass (7, 10, 16). Four grasses, annual bluegrass (Poa annua L. # POANN), rattail fescue (Festuca myuros L. # VLPMY), hard fescue (Festuca longifolia Thaill.), and red fescue (Festuca rubra L. # FESRU) are tolerant to rates up to 0.5 kg/ha of sethoxydim (13, 14).

Factors reducing herbicidal activity of sethoxydim are low air temperature (9, 24), high soil temperature (22), and dry soil conditions (3). In each case reduced phytotoxicity can be attributed to environmental stress on the weed. Tank mixtures of sethoxydim with bentazon (3 isopropyl-H-2,1,3-benzothiadiazin-4-(3H)-one 2,2-dioxide), aciflourfen [sodium (5-[2-chloro-4-(triflouromethyl)-phenoxy]-2-nitrobenzoate], and MCPA ([4-chloro-o-tolyl)oxy] acetic acid) have shown decreased control of annual grasses but no decrease in broadleaf weed control (8, 12, 20). Increasing the rate of sethoxydim or splitting the applications overcame the antagonism in most cases. It was reported that bentazon reduced penetration of sethoxydim into the leaf cuticle (28).

Sethoxydim at 1.2 kg/ha gave excellent quackgrass control and increased yields of soybean [Glycine max (L.) Merr.] and potatoes (Solanum tuberosum L.) (16, 27). Rapid translocation of sethoxydim was indicated in studies where a application of sethoxydim followed by a cultivation 1 or 2 days later increased weed control over the herbicide treatment alone or cultivation alone. In a greenhouse study a 24 h exposure of sethoxydim to quackgrass shoots resulted in 100% kill of rhizomes (27).

In laboratory studies a majority of the ^{14}C-sethoxydim was taken up by both Johnsongrass [Sorghum halapense (L.) Pers.# SORHA] and bermudagrass [Cynodon dactylon (L.) Pers. # CYNDA] after 8 days (25, 29). More than 30% was exported from the treated area. Approximately 10% of the ^{14}C was translocated to the roots of johnsongrass after 8 days. Much less was translocated to soybean roots. Conversely, soybean translocated twice as much to the apical leaves. Selectivity studies with alloxydim-sodium (methyl-3-[1-(alloxyimino)butyl]-4-hydroxy-6,6-dimethyl-2-oxocyclohex-3-ene-carboxylate sodium salt), a non-sulfur containing analog of sethoxydim, were conducted on several broadleaf and grass species (26). Absorption and translocation were similar between the two groups of plants. Alloxydim in the organo-soluble phase was found to be three times higher in wild oat [Avena fatua L.# AVEFA] than in sugar beet (Beta vulgaris L.) and this differential metabolism was suggested as a partial basis for selectivity.

The objectives of this research were to examine the differential retention, absorption, translocation, and metabolism of sethoxydim in a perennial grass and broadleaf plant and an annual grass and broadleaf plant to attempt to identify the basis for selectivity.

MATERIALS AND METHODS

General greenhouse procedures. All plants were grown in a potting soil (1:1:1 soil, sand, peat) unless otherwise indicated. Ten-cm diameter 1-L pots were used. Plants were grown under supplemental fluorescent lighting with a 16 h photoperiod. Light energy density was 350 $\mu Em^{-2}sec^{-1}$ at mid-day. Water was applied only to the soil surface after herbicide application in all instances. Temperatures were 25-30C during the day and 18-22C at night. Quackgrass rhizomes were collected from a field near Williamston, Michigan. For the dose-response study five 5-cm rhizome sections were planted 2.5 cm deep. Several navy bean, alfalfa or barnyardgrass seeds were planted and then thinned to two plants per pot for the broadleaf plants and five for barnyardgrass. Quackgrass, barnyardgrass, and navy bean were sprayed at fourth, third, and fourth leaf stages, respectively, the alfalfa plants had 25 cm of regrowth. Spray application was with a link-belt sprayer at 245 KPa pressure with 200 L/ha spray volume. All treatments, including the control, were treated with the oil concentrate Herbimax [2] at 1% (v/v). The treatments were replicated six times and the experiment repeated. Retention of sethoxydim was determined

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[2] Union Carbide Corporation, Research Triangle Park, NC.

using Karmen red dye (2 g/L) and formulated sethoxydim[3] applied with oil concentrate at 1% (v/v) applied at 220 L/ha and 245 KPa (4). Immediately after spraying plants were washed in 300 ml of water. Quantitation of spray solution was determined spectrophotometrically at 640 nm from a standard curve of absorbance vs. µg of sethoxydim. Plants were blotted dry and fresh and dry weights determined. Each treatment was replicated seven times and the experiment repeated. Determination of the relative effect of soil uptake of postemergence applications of sethoxydim was performed on barnyardgrass grown in a sandy loam soil (<1% organic matter) or in sand. Five plants per pot were sprayed with sethoxydim at each herbicide rate, one treatment with the soil surface covered with a 2-cm layer of vermiculite and the other left exposed. After spray application the vermiculite was removed. Differences in fresh weight between treatments with or without vermiculite covering at the same herbicide rate could be attributed to uptake of sethoxydim from the soil. Each treatment was replicated five times and the experiment repeated.

Laboratory procedures with ^{14}C-sethoxydim. Treatment of plant material was similar to that previously described except for quackgrass. A single 125-cm rhizome segment was planted per pot,

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[3] Poast , BASF Wyandotte Corp., Parsippany, N.J.

and as several shoots emerged they were pinched back to three, one large dominant shoot, one immediately adjacent to the first, and a third several centimeters away. All plants were sprayed with formulated sethoxydim at 0.25 kg/ha 30 min prior to treatment with ^{14}C-sethoxydim. As previously reported, sethoxydim is subject to rapid photo and thermal transformation, therefore, preparation of ^{14}C herbicide solution was made immediately prior to herbicide application in a dimly lit room (6) . Uptake of ^{14}C-sethoxydim was determined by applying 0.2 µCi (labelled at the number 4 position on the ring, specific activity 10.3 mCi/mM) in a water suspension of 1.25% (v/v) solvent, Aromatic 150 and 1.25% (v/v) surfactant, Makon 10[4]. Agitation of the mixture established a stable emulsion. A 10-µl drop applied by microsyringe was applied to the adaxil surface of the fourth youngest leaf of quackgrass, the fourth leaf of barnyardgrass, a middle trifoliate leaflet mid-way up the alfalfa plant and the middle trifoliate leaflet of the oldest fully expanded leaf of navybean. Treated leaf sections were washed after 1, 6, 12, 24, 72, and 168 h in 25 ml followed by 5 ml of cold toluene. Aliquots were removed from the combined toluene washes to quantitate unabsorbed ^{14}C. All plants were frozen prior to lyophilization and radioautography or solvent extraction. Extraction was with 50 ml of

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[4] Stephan Chemical Co., Northfield, IL.

cold 80% (v/v) aqueous acetone. The homogenate was filtered through glass fiber discs and the insoluble residue oxidized for ^{14}C quantitation. The acetone was removed under vacuum and ammonium sulfate (0.7g/1g) added to the remaining fluid. To this 50 ml of ethyl acetate was added and and the two phases separated. Aliquots were removed for ^{14}C quantitation by liquid scintillation. Each treatment was replicated four times, with the fourth replication used for radioautography, and the experiment repeated.

RESULTS AND DISCUSSION

Tolerance to foliar application between the four species is as follows: barnyardgrass < quackgrass << navy bean = alfalfa (Table 1). Both alfalfa and navy bean are approximately 100 and 1000-fold more tolerant than quackgrass and barnyardgrass to sethoxydim respectively. Injury to the broad leaf plants was a rapidly ensuing leaf water-soaking followed by necrosis of the leaf tissue. This is not symptomatic of sethoxydim injury to Graminaceae (2). Injury in this case can probably be attributed to the high proportion of solvents and surfactants in the spray solution. These large differences in tolerance are useful in interpreting differential absorption, translocation, and metabolism of sethoxydim.

With fluazifop-butyl[butyl ester of (±)-2-[4-[(5-(trifluoromethyl)-2-pyridinyl)oxy] phenoxy] propanate] between 20 and 70% of the observed activity of postemergence applications could be attributed to soil uptake of the herbicide (17). Root uptake of alloxidim has also been reported (15). However, there was little difference in barnyardgrass fresh weight when sethoxydim was applied only to the foliage and to both the foliage and the soil (Figure 1). The results from barnyardgrass grown in sand, where sethoxydim could move more freely through the soil to the roots, is similar to that of barnyardgrass grown in a sandy loam soil except at very low rates where there appears to be some contribution by soil uptake. This

indicates that the proportion of injury to barnyardgrass from soil uptake of sethoxydim is relatively minor.

Differences in retention of sethoxydim on the leaf surface based on µg/plant or µg/gm tissue could not account for the observed difference in selectivity between broadleaf plants and grasses (Table 2). By all three parameters navy bean retained more sethoxydim than either of the two grasses. Absorption of ^{14}C at 1 h was greater by the two grasses than the two broadleaf plants but after 24 h in all four species was more than 80% of total ^{14}C was absorbed with all species (Table 3). The overall rate of absorption was greatest in barnyardgrass followed by alfalfa with 96 and 90% of ^{14}C absorbed in 6 h respectively. This rapid absorption was consistent with reports on the effectiveness of sethoxydim applied within a few hours of simulated rainfall (9, 24). Differences in absorption among species after 168 h were small.

Translocation 1 h after treatment was observed in all species and after 12 h ^{14}C was detected in the roots of all species (Table 4). Translocation to roots was not observed by Harker and Dekker (10). A maximum of 20% was translocated out of the treated leaf of navybean after 168 h, but this was only 8% greater than barnyardgrass which translocated the least. None of the species translocated greater than 8% of total ^{14}C to the roots, or rhizomes, but the two grasses tended to export more to the roots than the broadleaves. From the radioautography it is evident that ^{14}C moved

to the metabolic sinks (Figure 2). In shoots these sinks were younger developing leaves and floral parts and margins of younger alfalfa leaves. In roots accumulation occurred in the adventitious roots of barnyardgrass and tips of rhizomes that were pinched back.

Initially the majority of ^{14}C partitioned into the ethylacetate-soluble fraction in all species (Table 5). The proportion of ^{14}C in the ethylacetate-insoluble fraction was similar among quackgrass, barnyardgrass and navy bean at 1 h. In alfalfa it was considerably greater. Over time the ethylacetate-insoluble fraction increased in percent of total in all species. After 168 h the percent of ^{14}C in the ethylacetate-soluble fraction was either similar to, or lower in the two grasses than broadleaf plants. At 168 h, 45, 46, 54 and 58% of the ethylacetate-insoluble fraction was water soluble in quackgrass, barnyardgrass, alfalfa, and navy bean.

A slower rate of decrease of the proportion of ^{14}C as ethylacetate-soluble occurred in the non-treated leaves than in the treated leaves (Table 6). This decrease in ethylacetate-soluble ^{14}C was more pronounced in the grass species than the broad leaf plants. After 72 h the proportion of ethylacetate-soluble ^{14}C was higher in the non-treated leaves than the treated leaves in all species. After 6 h the proportion of ethylacetate-soluble ^{14}C in the roots was greater than that in treated leaf in all species except barnyardgrass. Partitioning of ^{14}C in the treated leaf was similar to that of the whole plant.

A high degree of selectivity by sethoxydim exists between the grass and broadleaf species studied. Absorption of sethoxydim by leaves appears to be the most important absorption pathway in effecting grass weed control. A basis for selectivity due to differential retention, absorption, or translocation cannot be determined from these studies. Any differences in these factors between grass and broadleaf species are either not consistent with, or are not sufficient to explain the high degree of tolerance by broadleaf plants to sethoxydim. There are some indications, however, that the greater susceptibility of barnyardgrass to sethoxydim than quackgrass could be due to a more rapid absorption of the herbicide.

Table 1. Plant fresh weight 14 days after treatment with sethoxydim.

	Plant Fresh Weight[a]			
Rate[b]	Quackgrass	Barnyardgrass	Alfalfa	Navy beans
(kg/hr)	----------(% of control)----------			
0.00	100 a	100 a	100 a	100 a
0.01		64 b		
0.03		26 c		
0.08		10 d		
0.11	70 b			
0.17		6 d		
0.37	24 c			
1.12	32 c		108 a	100 a
3.36	24 c		96 ab	99 a
11.20	17 c		86 b	73 b

[a]Means followed by the same letter within a column are not significantly different from each other at the 5% level as determined by Duncan's multiple range test.

[b]All treatments included oil concentrate at 1% (v/v).

Table 2. Retention of sethoxydim on quackgrass, barnyardgrass, alfalfa and navy bean.

Species	Sethoxydim[a]		
	(µg/plant)	(µg/gm fw)	(µg/gm dw)
Quackgrass	0.13 b	0.32 a	0.30 b
Barnyardgrass	0.36 b	0.19 b	0.32 b
Alfalfa	2.10 a	0.18 b	0.15 c
Navy bean	4.91 a	0.34 a	0.41 a

[a]Means followed by the same letter within a column are not significantly different from each other at the 5% level as determined by Duncan's multiple range test.

Table 3. Absorption of ^{14}C following foliar application to ^{14}C-sethoxydim to quackgrass, barnyardgrass, alfalfa and navybean.

Time	Quackgrass[a]		Barnyardgrass		Alfalfa		Navybean	
	Removed	Absorbed	Removed	Absorbed	Removed	Absorbed	Removed	Absorbed
(h)	(% of total)[b]							
1	42 a	58 b	21 a	79 c	74 a	26 c	65 a	35 e
6	24 ab	76 ab	4 b	96 b	10 b	90 b	50 ab	50 d
12	15 b	85 ab	4 b	96 b	3 c	97 a	36 bc	64 c
24	13 bc	87 ab	4 b	96 b	2 c	98 a	19 c	81 b
72	6 cd	94 a	2 bc	98 ab	1 c	99 a	6 d	94 a
168	7 d	93 a	1 c	99 a	1 c	99 a	2 e	98 a

[a]Means followed by the same letter are not significantly different from each other at the 5% level as determined by Duncan's multiple range test.

[b]Total recovered in or on plant.

Table 4. Translocation of ^{14}C among plant parts after foliar application to quackgrass, barnyardgrass, alfalfa and navybean.

	Quackgrass[a]			Barnyardgrass			Alfalfa			Navybean		
Time	Treated leaf	Untreated leaves	Roots rhizomes	Treated leaf	Untreated leaves	Roots	Treated leaf	Untreated leaves	Roots	Treated leaf	Untreated leaves	Roots
(h)	(% of total)[b]											
1	97 a	2 b	1 b	98 a	2 c	0 b	98 a	1 a	1 ab	94 a	5 bc	1 b
6	92 b	7 ab	1 b	95 a	4 c	1 a	98 a	2 ab	0 b	95 a	3 c	2 b
12	82 c	11 a	7 a	92 b	61 b	2 a	96 a	3 ab	1 ab	89 ab	7 bc	4 a
24	84 c	8 ab	8 a	91 b	7 ab	2 a	95 a	3 b	1 ab	87 b	10 b	3 ab
72	86 c	7 ab	7 a	89 b	9 ab	2 a	92 a	6 b	2 a	87 b	9 bc	4 a
168	84 c	8 ab	8 a	88 b	10 a	2 a	85 b	13 c	1 ab	80 c	17 a	3 ab

[a]Means followed by the same number are not significantly different from each other as determined by Duncan's multiple range test at 5% level of probability.

[b]Total ^{14}C recovered excluding that removed by leaf wash.

Table 5. Partitioning of ^{14}C after foliar application of ^{14}C-sethoxydim to quackgrass, barnyardgrass, alfalfa and navybean.

	Quackgrass[a]		Barnyardgrass		Alfalfa		Navybean	
	Ethyl acetate		Ethyl acetate		Ethyl acetate		Ethyl acetate	
Time	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble
(h)	(% of total)[b]							
1	9 e	91 a	20 c	80 a	44 bcd	56 ab	8 c	92 a
6	24 d	76 b	44 b	56 b	26 d	74 a	14 c	86 a
12	28 d	72 b	48 b	52 b	41 cd	59 ab	38 b	62 b
24	38 c	62 c	45 b	55 b	60 abc	40 bc	30 b	70 b
72	48 b	52 d	79 a	21 c	65 ab	35 bc	51 a	49 c
168	58 a	42 e	82 a	18 c	75 a	25 c	50 a	50 c

[a]Means followed by the same letter are not significantly different from each other at the 5% level as determined by Duncan's multiple range test.

[b]Total ^{14}C recovered within plant.

Table 6. Partitioning of ^{14}C in plant parts after foliar application of ^{14}C-sethoxydim in quackgrass, barnyardgrass, alfalfa and navybean.

Species	Time	Treated leaf[a]		Nontreated leaves		Roots	
		Ethyl acetate		Ethyl acetate		Ethyl acetate	
		Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble
	(h)	(% of total)[b]					
Quackgrass							
	1	8 a	92 a	35 b	65 a	51 a	49 d
	6	23 b	77 b	48 ab	52 ab	29 bc	71 bc
	12	31 c	69 c	36 b	64 a	15 cd	85 ab
	24	40 d	60 d	51 ab	49 ab	14 d	86 a
	72	50 e	60 e	49 ab	51 ab	23 bcd	77 abc
	168	60 f	40 f	67 a	33 b	35 b	65 c
Barnyardgrass							
	1	20 c	80 a	35 b	65 a	42 d	58 a
	6	44 b	56 b	44 b	56 a	46 cd	54 ab
	12	48 b	52 b	53 ab	47 ab	57 c	43 b
	24	46 b	54 b	44 b	56 a	45 d	55 a
	72	81 a	19 c	52 ab	48 ab	73 b	27 c
	168	83 a	17 c	65 a	35 b	86 a	14 d

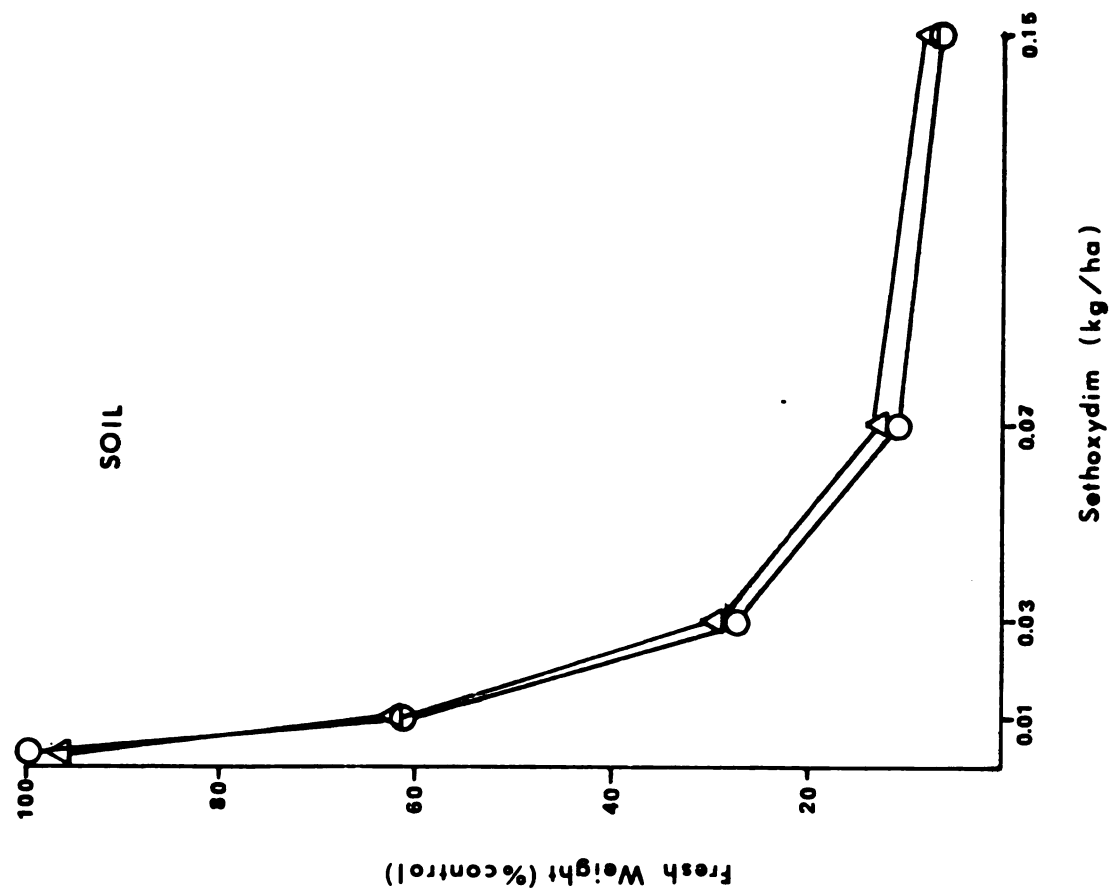
Table 6. Continued.

Species	Time	Treated leaf[a]		Nontreated leaves		Roots	
		Ethyl acetate		Ethyl acetate		Ethyl acetate	
		Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble
	(h)	(% of total)[b]					
Alfalfa							
	1	44 bc	56 ab	49 a	51 a	61 a	39 b
	6	27 c	73 a	44 a	56 a	47 ab	53 ab
	12	41 bc	59 ab	49 a	51 a	37 b	63 a
	24	61 ab	39 bc	36 a	64 a	33 b	67 a
	72	68 a	32 c	39 a	61 a	38 b	62 a
	168	72 a	28 c	52 a	58 a	50 ab	50 ab
Navybean							
	1	6 c	94 a	41 a	59 a	47 a	53 ab
	6	12 c	88 a	47 a	53 a	40 ab	60 ab
	12	39 b	61 b	26 a	74 a	26 ab	74 ab
	24	30 b	70 b	32 a	68 a	20 b	80 a
	72	53 a	47 c	42 a	58 a	30 ab	70 ab
	168	53 a	47 c	40 a	60 a	49 a	51 b

[a]Means followed by the same letter within a column and species are not significantly different from each other at the 5% level as determined by Duncan's multiple range test.

[b]Total recovered within plant part.

Figure 1. Barnyardgrass fresh weight 14 days after post-emergence applications of sethoxydim with and without soil covered with vermiculite.


SOIL
Fresh Weight (%control)
100
80
60
40
20
0.01
0.03
0.07
0.15
Sethoxydim (kg/ha)

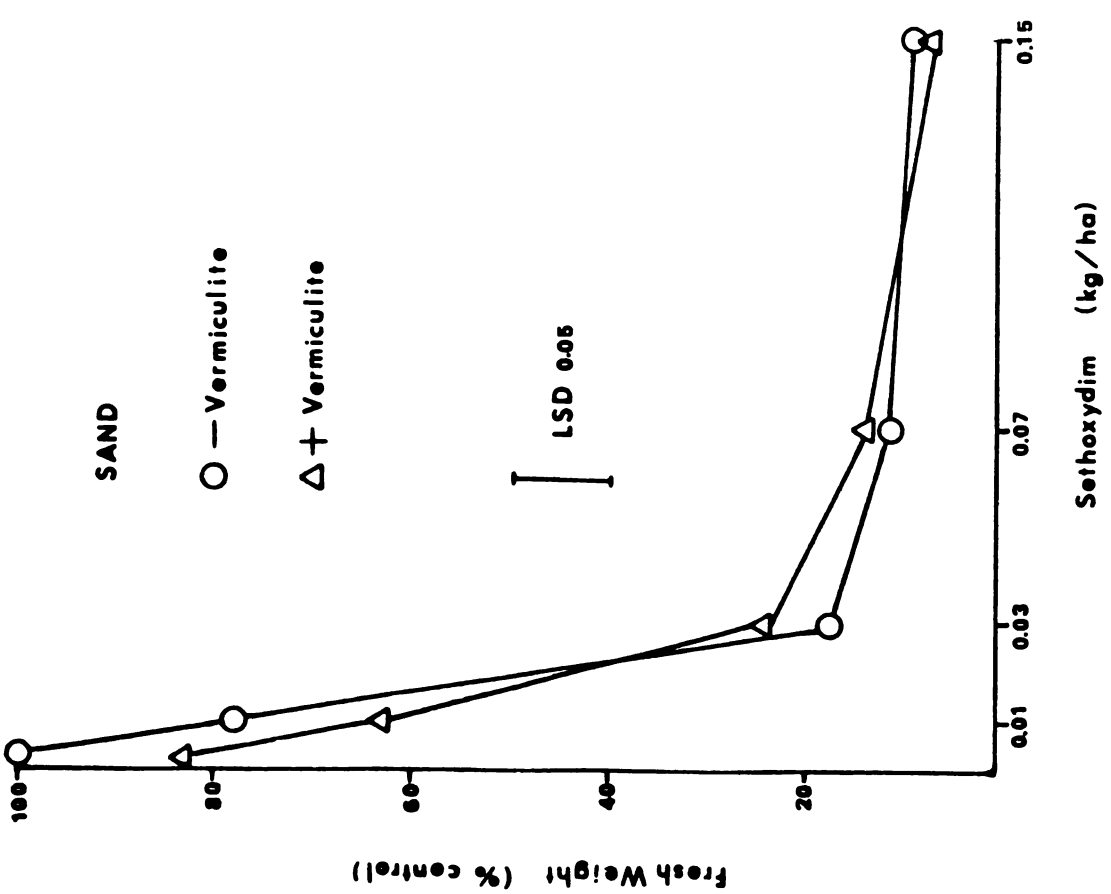

SAND
○ — Vermiculite
Δ + Vermiculite
LSD 0.05
Fresh Weight (% control)
100
80
60
40
20
0.01
0.03
0.07
0.15
Sethoxydim (kg/ha)

Figure 2. Radioautographs of quackgrass and alfalfa 24 h after application of ^{14}C-sethoxydim.

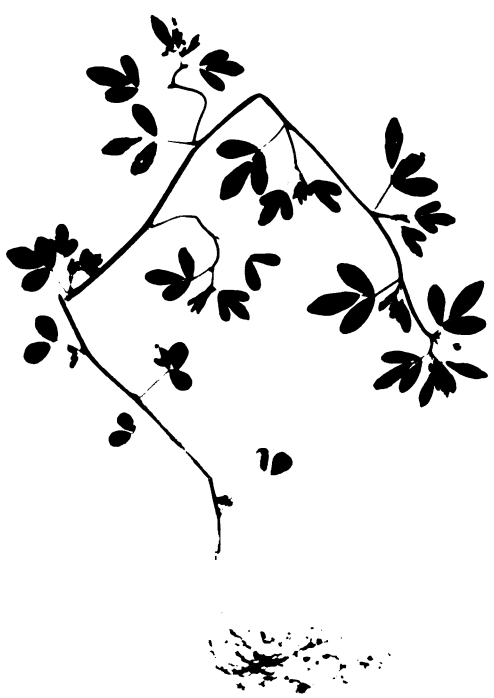


Figure 3. Radioautographs of barnyardgrass and navy bean 24 h after application of ^{14}C-sethoxydim.

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CHAPTER 4

SETHOXYDIM METABOLISM IN MONOCOTYLEDONOUS AND DICOTYLEDONOUS PLANTS

ABSTRACT

Sethoxydim [2-(1-ethoxyimino)butyl0-5-(ethylthio)propyl)-3-hydroxy-2-cyclohexen-1-one] was rapidly metabolized by quackgrass [Agropyron repens (L.) Beauv. # AGRRE], barnyardgrass [Echinochola crus-galli (L.) Beauv. # ECHCG], alfalfa (Medicago sativa L.) and navybean (Phaseolus vulgaris L.), with 46, 27, 38 and 46% remaining after 1 h application respectively and less than 2% after 24h in all species. Nine metabolites were observed, seven of which co-chromatographed with photo and thermal products of sethoxydim. Two metabolites, previously shown to be phytotoxic to barnyardgrass, contained the majority of ^{14}C 24 h after application. Quantitative or qualitative differences in metabolism could not account for the observed selectivity.

INTRODUCTION

The herbicide sethoxydim is registered for grass control in dicotyledonous crops such as soybean (7). Visual symptoms of sethoxydim injury include a cessation in plant growth (1,6), chlorosis of younger expanding leaves, increases in anthocyanin pigments followed by extensive leaf necrosis. Histological studies in johnsongrass [Sorghum halepence (L.) Pers. # SORHA] revealed localized neucrotic zones in the apical region 1 day after application and extensive collapse of cells at the base of the youngest leaf primondia 3 days after application (3). Although the mitotic index of corn [Zea mays (L.)] was not affected, binucleate cells, an absence of cell walls, and disorientation of daughter nuclei were observed (1). In bermudagrass [Cynodon dactylodon (L.) Pers. # CYNDA] thylacoids and mitochondria of mesophyll cells were affected (4). These symptoms were similar to those for alloxydim-sodium [sodium salt of 2-(1-allyloxyaminobutylidene)-5,5-dimethyl-4-methoxycarbonylcyclohexane-1,3-dione], a non-sulfur containing analog of sethoxydim (7,10). Respiratory activity of corn roots was highly sensitive to sethoxydim (1), chlorophyll a + b decreased, and anthocyanin content increased after an application of 0.02 kg/ha. Treatments with less than 1% (w/w) did not inhibit apparent photosynthesis of corn but did cause a transient inhibition in

soybean [Glycine max (L.) Merr.], higher concentrations caused irreversible inhibition in corn (5). Translocation of ^{14}C-fructose was inhibited 75% in johnsongrass by an application of 1.1 kg/ha (13).

Sethoxydim is rapidly absorbed by johnsongrass, bermudagrass, and soybean and translocation occurs in all species (3,11,12). Three metabolites were reported in both johnsongrass and soybean. Both alloxydim-soduim and sethoxydim are photo and thermally labile the desethoxy and oxazole derivatives are formed, but all these compounds show only weak herbicidal activity (2,8,9). For maximum activity on grasses, an alkoxyaminoalkylidene moiety must exist between two keto groups of cyclohexane ring (8). Further enhancement of activity can be made with various substitutions at the number 5 position. High postemergence activity is exhibited on intact grasses by alkylthioalkyl, arylthioalkyl, alkylsulfonealkyl, or alkylsulfoxidealkyl derivatives (9). However, the sulfone and sulfoxides of sethoxydim derivatives showed reduced graminicidal activity in comparison with sethoxydim.

The objectives of this research were to determine the extent of sethodyxim metabolism in grasses and dicotyledonous crop plants and to determine if metabolism contributed to the basis of selectivity.

MATERIALS AND METHODS

Quackgrass rhizomes were collected from a field near Williamston, Michigan. From one vigorously growing plant, single

125 cm rhizome sections were planted 2.5 cm deep in a 1-L pot of potting mix (1:1:1 sand:soil:peat). Barnyardgrass, alfalfa, and navybean seed were planted in the same mix and then thinned to single uniform plants. Alfalfa was cut and allowed to regrow once before treatment. Plants were grown under supplemental flourescent lighting with a mid-day photon flux density of 350 $\mu Em^{-2}sec^{-1}$. Greenhouse temperatures were 25-30 C during the day and 18-22 C at night.

Prior to application of ^{14}C-sethoxydim all plants were sprayed with 0.25 kg/ha of formulated sethoxydim[1]. A water emulsion containing 0.2 µCi ^{14}C-sethoxydim (labelled in the number 4 position, specific activity 10.3 mCi/mM), 1.25% (v/v) solvent Aromatic 150 and 1.25% (v/v) surfactant, Makon 10[2] in 10 µl was applied to each plant. The ^{14}C-herbicide was applied to the adaxil side of the fourth leaf of eight-leaf stage quackgrass, on the fourth leaf of five-leaf stage barnyardgrass, on the middle trifoliolate leaflet of 25 cm tall alfalfa and on the middle trifoliolate leaflet of the second leaf of four-leaf stage navy bean. After 1, 6, 12, 24, 72, and 168 h treated leaves were excised, washed with 30 ml of cold toluene and frozen at -20C. All

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[1] Poast BASF Wyandotte Corp., Parsippany, NJ.

[2] Stephan Chemical Co., Northfield, IL.

extraction procedures and chromotography were performed under reduced lighting without direct flourescent light or sunlight exposure, and procedures were completed within 3 days of freezing. Extraction was with 50 ml of cold 80% (v/v) aquous acetone. After extraction the acetone was removed under vacuum and ammonium sulfate (0.7 g/1 g fluid) and 50 ml of ethyl acetate were added to the remaining fluid. The ethyl acetate fraction was then separated, reduced under nitrogen to 0.4 ml, and 100 µl applied to silica gel TLC plates. TLC plates were developed in chloroform:isopropanol (9:1 v/v) and ^{14}C-containing areas located by radioautography. These spots were scraped into scintillation vials into which 1 ml of water was added and shaken for 5 min, scintillation fluid added and samples counted. Co-chromatography with photo and thermal transformation products was made using a combined sample of ^{14}C-sethoxydin exposed to light on glass and in water. Each treatment was replicated three times and the experiment repeated, data presented here are the results of both experiments.

RESULTS AND DISCUSSION

After 1 hour, more than 50% of the sethoxydim was degraded in all species, this degradation continued and after 24 h less than 2% of the parent compound remained (Table 1.). Nine metabolites were separated by TLC, no qualitative differences were detected between species. A number of plant metabolites co-chromotographed with compounds previously reported to form in abiotic system (2) (Table

2). However, two plant metabolites were evident which did not occur when sethoxydin was exposed to light on glass or dissolved in water. As sethoxydin disappeared rapidly, one or more metabolites may have contributed to observed phytotoxicity. Other studies have indicated that metabolites 4 and 5 were phytotoxic to barnyardgrass (2), while 3, 9, 10 were not. This would indicate that metabolites 4 and 5 were transformed in a sequence either prior to that of 3, 9 and 10 or along an alternate pathway.

There were minor quantitative differences in the distribution of ^{14}C between species. In barnyardgrass metabolite 2 was more prevalent than in other species as was metabolite 9 in quackgrass (Table 3). More striking are the similarities across species. In all four plants, metabolites 4 and 5 were the major ^{14}C-products up to 24 h after treatment, after which, metabolites 9 and 10 contained the majority of ^{14}C. These latter metabolites appear to be end products of the primary metabolism. From their elution sequence they also appear to be more polar than the bioactive compounds.

The results of these studies indicate rapid degradation of sethoxydim occurs in both grasses and dicotyledonous crop plants. Whether this represented absorption of photo and thermal products or metabolism by the plant is uncertain. Two of these compounds, previously determined to be phytotoxic, were detected in similar quantities in all species. Distribution of other products was also

similar among species and differences could not account for observed selectivity.

TABLE 1. Metabolism of ^{14}C-sethoxydim by quackgrass, barnyardgrass, alfalfa and navy bean.

	Sethoxydim[a]			
Time	Quackgrass	Barnyardgrass	Alfalfa	Navy bean
(h)	----------(% of total)----------			
1	46.1 a	27.4 a	38.0 a	46.0 a
6	7.0 b	0.6 b	2.5 b	11.6 b
12	1.6 c	0.5 b	0.7 b	6.0 bc
24	1.1 c	0.8 b	0.6 b	1.6 c
72	0.6 c	0.6 b	1.0 b	0.7 c
168	0.6 c	2.1 b	0.8 b	0.8 c

[a]Means within a column followed by the same letter are not significantly different from each other at the 5% level as determined by Duncan's multiple range test.

[b]Percent of total of the ethyl acetate-soluble fraction.

Table 2. Rf values of compounds separated by TLC extracted from plants and formed after photo and thermal transformation.

	Metabolite designations	Plant transformation Products	Abiotic transformation ^{14}C-products[a]
		---------(R_f)---------	
Sethoxydim	1	0.72	0.72
	2	0.60	0.60
Desethoxy-sethoxydim	3	0.52	0.52
	4	0.41	0.41
	5	0.38	0.38
	6	0.33	0.33
	7	0.29	--
	8	0.25	--
	9	0.13	0.13
	10	0.00	0.00

[a]Solvent system described in materials and methods.

Table 3. Distribution of ^{14}C-sethoxydim and ^{14}C-metabolites extracted from quackgrass, barnyardgrass, alfalfa, and navybean[a].

Metabolite designation	Time (h)[b] 1	6	12	24	72	168
	----------(% of total)[a]----------					
	Quackgrass					
1	46.1a	7.0b	1.6c	1.1c	0.6c	0.6c
2	3./bc	2.5c	3.5ab	5.1a	4.5a	2.7c
3	1.5c	1.1c	1.7c	3.5b	4.4ab	5.4a
4	16.9abc	29.9a	25.5ab	12.9bc	9.1bc	3.8c
5	17.7bc	29.5a	27.2a	24.2ab	12.6cd	5.6d
6	4.9b	3.6b	7.4ab	11.0a	6.7b	7.7ab
7	1.2d	4.3c	4.4c	6.4ab	5.1bc	6.9a
8	0.6d	2.0c	2.6bc	3.4b	5.2a	4.6a
9	2.4e	7.0d	11.4c	15.9b	20.6a	16.5b
10	5.0d	12.9c	14.7c	16.5c	30.5b	46.2a
	Barnyardgrass					
1	27.4a	0.6b	0.5b	0.8b	0.6b	2.1b
2	3.9b	6.0b	8.3a	9.2a	8.3a	10.0a
3	1.3bc	1.1c	1.7bc	2.0b	2.9a	2.8a
4	19.6a	24.3a	27.8a	19.0b	4.1b	3.8b
5	28.0b	38.1a	26.4b	23.9a	8.0c	5.3c

Table 3. Continued.

Metabolite designation	Time (h)[b] 1	6	12	24	72	168
	(% of total)[a]					
6	1.3c	3.3c	6.4b	7.8b	11.6a	12.8a
7	1.1d	1.6cd	2.3c	3.3b	4.4a	3.9ab
8	1.3c	1.9c	1.9c	2.2bc	3.3a	3.0ab
9	5.8d	6.4cd	8.2bc	9.6b	12.0a	9.1b
10	10.3c	16.7bc	16.5bc	22.4b	44.9a	47.1a
	Alfalfa					
1	38.0a	2.5b	0.7b	0.6b	1.0b	0.8b
2	2.5ab	1.2b	2.3ab	3.3a	3.6a	2.6a
3	1.6b	0.9b	0.9b	1.7b	4.1a	4.6b
4	18.9b	32.8a	25.7b	23.2b	7.5c	4.4c
5	25.8c	33.0a	31.4ab	27.7bc	8.7d	4.6d
6	0.8d	3.7bc	3.3c	4.2bc	5.6a	4.6ab
7	4.9a	3.0a	6.8a	3.7a	6.6a	7.5a
8	0.6c	1.1c	1.7c	1.6c	5.0b	8.4a
9	1.9d	6.9c	8.8bc	6.6c	10.1ab	11.8a
10	5.0d	14.9c	18.3c	27.5b	47.7a	50.8a
	Navybean					
1	46.0a	11.6b	6.0bc	1.6c	0.7c	0.8c
2	8.3a	3.7b	2.7b	3.0b	4.2b	2.9b

Table 3. Continued.

Metabolite designation	Time (h)[b] 1	6	12	24	72	168
	(% of total)[a]					
3	1.3a	1.3a	1.3a	1.4a	1.9a	1.7a
4	14.1c	21.1b	28.7a	26.4ab	7.0d	5.2d
5	23.7c	40.0a	32.9b	29.1bc	16.5d	11.1d
6	1.8d	2.6cd	3.1c	3.0c	4.6b	6.7a
7	0.7d	1.0cd	1.5c	2.9b	2.4b	3.6a
8	0.7d	2.0bc	1.6cd	2.7bc	3.0b	4.8a
9	1.2d	3.9c	4.7c	6.4bc	9.6a	7.9ab
10	2.3d	12.8c	17.5bc	23.4b	50.2a	55.5a

[a]Means within a line followed by the same letter are not significantly different from each other at the 5% level as determined by Duncan's multiple range test.

[b]Percent of total of ethyl acetate-soluble fraction.

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CHAPTER 5

SUMMARY AND CONCLUSIONS

In spite of the rapidity of degradation of sethoxydim it has proven to be a highly effective postemergence graminicide. Under non-biological conditions its disappearance is significant after a matter of minutes. In both susceptible and tolerant plants disappearance is similarly rapid. Although this is a desirable trait from a environmental stand point, normally it is detrimental to optimum herbicidal efficacy. It would not appear so in the case of sethoxydim. It's activity can probably be attributed to more stable yet phytotoxic transformation products that were detected after both abiotic exposure and apparent plant metabolism. If there were ways of reducing breakdown from the environment an increase in activity might be realized. This is commonly done with pyrethrum type insecticides, it is enzymatic inhibition in this case. But there still may be possibilities to combine sunscreens, anti-oxidants or other reaction inhibiting compounds with sethoxydim to increase activity.

There are few differences among species in the retention, absorption, translocation or metabolism of sethxoydim which would account for the magnitude of difference in selectivity. There is, indeed, a surprising similarity in metabolism among plants which react so differently to this chemical. Although a basis for selectivity can normally be attributed to one of the aformentioned factors for most chemicals, the story is becoming less clear with the postemergence graminicides.

Although this work did not address any differences in polar metabolites

or conjugates, there have been inter-family differences reported with the graminicide diclofop-methyl. These qualitative differences result in tolerance differences of one order of magnitude. Tolerance differences of two to three orders of magnitude suggest other mechanisms. This author would speculate to say that there exist differing enzyme systems between the two groups of plants which either do not exist in the tolerant group or are configured sufficiently differently so as to limit herbicide binding, and thus activity.

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