# Modeling the Foliar Behavior of Atrazine with and without Crop Oil Concentrate on Giant Foxtail and the Effect of Tridiphane on the Model Rate Constants

Philip J. McCall,* Lester E. Stafford, Paul S. Zorner, and Patrick D. Gavit

The behavior of atrazine formulated as a 0.48 kg/L solid suspension has been characterized on giant foxtail grass with a compartmental foliar model. Studies were conducted in environmentally controlled chambers. The behavior of the chemical on the plant surface was described by two compartments: a solid compartment and a solution compartment. The atrazine in solution represented that proportion of the total applied chemical readily available for penetration into the leaf. The addition of crop oil concentrate (COC) to the application solution significantly increased the amount of atrazine absorbed by the leaf by apparently solubilizing more atrazine in the available compartment. Typically, 30% of applied chemical penetrated the leaf in the presence of COC, while only 10% penetrated without COC. Model rate constants for atrazine behavior in the presence of COC were determined with and without tridiphane at 12, 20, and 30 °C. The rate of metabolism of atrazine in the plant was decreased significantly in the presence of tridiphane, while little effect on the other rate processes was noted.

## INTRODUCTION

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] is a widely used preemergence herbicide to control annual weeds in corn. Foliar uptake of atrazine has been shown to be an important process for postemergent broadleaf activity (Thompson and Slife, 1970) and a significant factor in the control of giant foxtail (*Setaria faberi*, L.). A review of the literature in this area (Esser et al., 1975) characterizes the foliar behavior of atrazine as exhibiting a slow rate of penetration with limited translocation of the molecule through plants. The penetration rate is enhanced in the presence of oil and under conditions of high humidity or on wet foliage.

The chemical acts by disrupting the normal electron flux through photosystem II (Shimabukuro and Swanson, 1969). Atrazine can be metabolized by several routes in corn or in tolerant weeds such as giant foxtail. Nonenzymic hydrolysis is an important detoxification mechanism in root tissue (Shimabukuro and Swanson, 1969; Shimabukuro et al., 1970; Thompson et al., 1971). N-dealkylation of atrazine also occurs in several plants (Shimabukuro and Swanson, 1969). However, the major metabolic pathway of atrazine in root tissue and in foliage is by conjugation with glutathione catalyzed by glutathione-*s*-transferase (GST) (Frear and Swanson, 1970; Shimabukuro and Swanson, 1969, Shimabukuro et al., 1970). Increasing atrazine rates in the field can overcome the tolerance by overloading the detoxification pathways.

Tridiphane [2-(2,2,2-trichloroethyl)-2-(3,5-dichlorophenyl)oxirane] has been shown to be effective in postemergent control of giant foxtail and crabgrass (Weseloh, 1983). In addition, postemergent treatment combinations of atrazine with tridiphane have been shown to exhibit a synergistic relationship with respect to selective weed control (Bugg and Witt, 1981). It has been hypothesized that tridiphane also interacts with the GST enzyme system that blocks the detoxification of atrazine (Zorner et al., 1983; Lamoureux and Rusness, 1983). This interaction allows for control of grasses at lower rates of atrazine. More recently the synergistic activity of tridiphane has been demonstrated on proso millet (*Panicum miliaceum*) with EPTC and alachlor (Ezra et al., 1985). These herbicides are also known to be detoxified via conjugation with glutathione (shimabukuro et al., 1978).

To study the effect of tridiphane on the behavior of atrazine in grassy weeds, we have utilized a compartmental modeling system that interprets data collected under controlled environmental conditions using a laboratory enviromental chamber. Development of a mathematically based model can provide insight into the interactions of a chemical in the plant and quantitate the sensitivity of the system to external variables such as temperature. The laboratory system also eliminates the environmental variability encountered in the field so that the effects of different application variables can be studied. In a previous study we characterized the behavior of tridiphane when applied with atrazine on giant foxtail (McCall et al., 1985). The rate processes controlling transport and metabolism of tridiphane were described as a function of temperature and spray variables. Tridiphane was characterized by relatively rapid penetration into giant foxtail along with rapid volatility loss into the air. Crop oil concentrate (COC) had a significant effect on increasing the rate of penetration into the plant. The objectives of the studies reported here were to (1) describe a foliar model for atrazine on giant foxtail while characterizing the effect of crop oil concentrate on the surface behavior of the chemical and (2) quantitate differences in the rate of metabolism of atrazine in giant foxtail in the absence and presence of tridiphane under the typical application con dition with crop oil concentrate present in the application solution.

## MATERIALS AND METHODS

**Environmental Chambers.** The environmental chambers used in these studies were designed after a system described by Nash and Beall (1977) and have been described in detail previously (McCall et al., 1985). They are enclosed plate glass chambers that are housed in a temperature-controlled room. Air is drawn through the chambers at approximately 0.8 km/h where polyurethane foam filters are located in the exit ports of the chambers to trap volatile chemical vapors. Plants are placed in the chambers and treated with radiolabeled chemical, and the fate of the chemical is followed in the system. Volatility into the air is quantitated with the foam filters, and pen-

Agricultural Products Department, The Dow Chemical Company, Midland, Michigan 48640.

0021-8561/86/1434-0235$01.50/0 

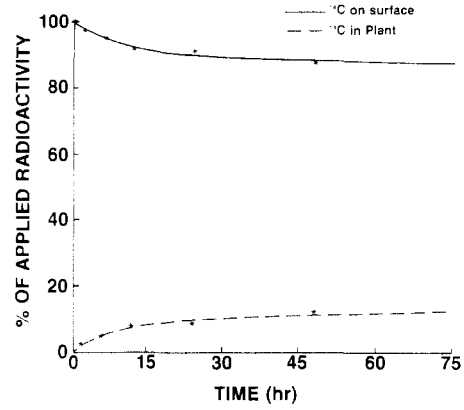


**Figure 1.** Radioactivity on the plant surface and in the plant for $^{14}$C-labeled atrazine applied to giant foxtail grass at 20 °C.

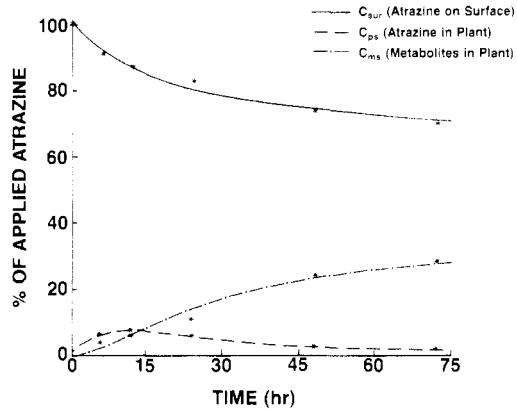


**Figure 2.** Atrazine on the plant surface, in the plant, and as metabolites for $^{14}$C-labeled atrazine applied to giant foxtail grass with crop oil concentrate at 20 °C.

etration and metabolism of the chemical in the leaf are followed by quantitation of chemical residues on the leaf surface and in the leaf over time. Located directly above each chamber are 1000-W G.E. Duroglow Luminaire metal halide lamps. Lights were operated on a 14-h photoperiod. Humidity was not regulated during the experiments; however, normal operating humidities were between 50 and 70%.

**Chemicals.** $^{14}$C-labeled atrazine was purchased from Pathfinder Chemical. Radiochemical purity was greater than 98%. The radiolabeled atrazine was dissolved in acetonitrile and added (10%, v/v) to the commercial atrazine 0.48 kg/L formulation. Specific activity of the final formulation was 0.88 mCi/mmol.

Unlabeled tridiphane was used in conjunction with the labeled atrazine studies as a 0.48 kg/L emulsifiable concentrate.

**Plant Treatments.** Giant foxtail grass was grown in the greenhouse and used at the 2–3 leaf stage of growth. Plants were placed in the temperature-controlled room the night before the beginning of an experiment to acclimate them to the study temperature. Formulations were diluted to simulate field application rates and applied to the plants by syringe in 0.5-$\mu$L drops. Typically, a 1.12 kg/ha application rate of atrazine was employed with a 0.56 kg/ha application rate of tridiphane in a spray volume equivalent to 280 L/ha of water. Crop oil concentrate (COC) was used as an adjuvant in many of the experiments at a rate of application equivalent to 2.3 L/ha. Ten sets of plants, 4 plants/set, were treated with the application solution. Each plant received 5 $\mu$L of the solution equivalent to 10 000 dpm/plant and 20 $\mu$g/plant of atrazine.

Plants were sampled at regular intervals. The amount

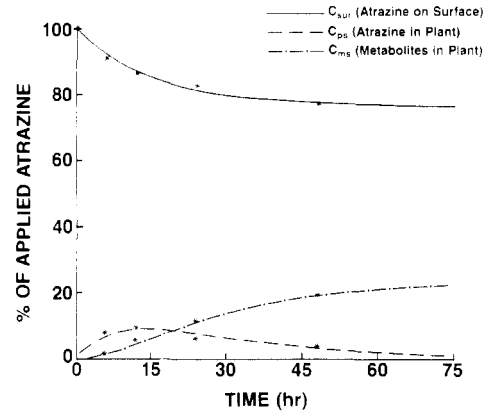


**Figure 3.** Atrazine on the plant surface, in the plant, and as metabolites for $^{14}$C-labeled atrazine applied to giant foxtail grass with crop oil concentrate and tridiphane at 20 °C.

**Table I. Percent of Radioactivity in Plant Extracts as Atrazine**

| | time, h | | | | |
|---|---|---|---|---|---|
| treatment | 6 | 12 | 24 | 48 | 72 |
| | 12 °C | | | | |
| atrazine + COC | 70.5 | | 58.3 | 45.7 | |
| atrazine + COC + tridiphane | 85.0 | | 80.6 | 65.1 | |
| | 20 °C | | | | |
| atrazine + COC | 62.0 | 55.0 | 41.0 | 11.7 | 6.6 |
| atrazine + COC + tridiphane | 83.5 | 73.5 | 48.0 | 25.0 | 14.0 |
| | 30 °C | | | | |
| atrazine + COC | 45.0 | 25.6 | 14.1 | 10.0 | 7.0 |
| atrazine + COC + tridiphane | 55.0 | 44.1 | 28.0 | 28.0 | 23.0 |

of atrazine on the leaf surface, in the plant, and metabolized in the plant was characterized. Preliminary experiments conducted on glass slides demonstrated that insignificant amounts of atrazine volatilized into the air under the conditions employed, so the polyurethane filter plugs were typically not sampled.

**Sample Analysis.** Plants were cut at the soil surface and rinsed twice (5 s each rinse) in 50 mL of methanol. The first rinse typically contained greater than 95% of the radioactivity removed from the surface. The plant rinses were quantitated by liquid scintillation counting by addition of 2 mL of the methanol solutions to 18 mL of Aquasol liquid scintillation cocktail. Samples were counted in a Packard Model 3255 liquid scintillation counter using the external standard method to determine counting efficiency. Characterization of the surface rinses by liquid chromatography showed that atrazine did not break down to other products on the plant surface.

Following rinsing, the plants were homogenized with 10 mL of methanol in a Brinkman Polytron to release the chemical that had penetrated the leaf. Total radioactivity in the soluble fraction of plant homogenate was characterized by removal of the solids by centrifugation and by counting 100 $\mu$L of the extract in 10 mL of Aquasol. The solid residue was combusted in a Harvey Biological Oxidizer where carbon dioxide produced in the combustion was trapped in 15 mL Carbosorb/Permafluor V (2:1, v/v). An additional 5 mL of Permafluor V was added following combustion, and the samples were counted.

The amount of atrazine and its metabolites present in the soluble fraction were determined by liquid chromatography. Typically, 200 $\mu$L of plant extract was injected onto a Waters $\mu$Bondapack C-18 column. The sample was

**Table II. Atrazine Foliar Model Rate Constants as a Function of Temperature with and without Tridiphane[a]**

| treatment | temp, °C | $C_{sf0}$,[b] % | $C_{ss0}$,[c] % | $k_f$, $h^{-1}$ | $k_p$, $h^{-1}$ | $k_m$, $h^{-1}$ |
|---|---|---|---|---|---|---|
| atrazine | 20 | 10 | 90 | 0.0035 ± 0.005[d] | 0.096 ± 0.009 | |
| atrazine + COC | 20 | 22 | 78 | 0.0018 ± 0.0004 | 0.075 ± 0.007 | 0.102 ± 0.011 |
| atrazine + COC + tridiphane | 20 | 22 | 78 | 0.0034 ± 0.0004 | 0.075 ± 0.007 | 0.063 ± 0.009 |
| atrazine + COC | 12 | 22 | 78 | 0.0009 ± 0.0003 | 0.033 ± 0.002 | 0.040 ± 0.005 |
| atrazine + COC + tridiphane | 12 | 22 | 78 | 0.0005 ± 0.0002 | 0.020 ± 0.004 | 0.013 ± 0.003 |
| atrazine + COC | 30 | 22 | 78 | 0.0030 ± 0.0003 | 0.113 ± 0.014 | 0.204 ± 0.037 |
| atrazine + COC + tridiphane | 30 | 22 | 78 | 0.0044 ± 0.0007 | 0.105 + 0.015 | 0.132 ± 0.040 |

[a] Atrazine was applied at a rate equivalent to 1.12 kg/ha, tridiphane at 0.56 kg/ha, and COC at 2.3 L/ha; spray volume was equivalent to 280 L/ha. [b] Percent of applied atrazine predicted by the model to be in the surface solution compartment at zero time. [c] Percent of atrazine predicted by the model to be in the surface solid compartment at zero time. [d] 95% confidence interval.

eluted with a water/methanol linear gradient from 0 to 100% methanol over 35 min at a flow rate of 1.0 mL/min. The elution solvents were buffered with $NH_4OAc$ at 0.01 M. Fractions of the column eluant were collected at 1-min intervals, diluted with 10 mL of Aquasol, and counted. A profile of the radioactivity was reconstructed to determine the distribution of material in the extract.

## RESULTS AND DISCUSSION

**Model Description.** Development of a suitable foliar model for atrazine employed the same techniques as in our previous work with tridiphane. All transport processes between compartments and transformation rates within compartments were considered to be first order. This assumption was made to simplify the model development and had been shown to give an adequate representation of the behavior of tridiphane in previous studies.

The following model (eq 1) was developed to describe the behavior of atrazine applied on giant foxtail plants,

$$C_{ss} \xrightarrow{k_f} C_{sf} \xrightarrow{k_p} C_{ps} \xrightarrow{k_m} C_{ms} \quad (1)$$

where $C_{ss}$ = amount of atrazine in solid form on the plant surface, $C_{sf}$ = amount of atrazine in solution on the plant surface, $C_{ps}$ = amount of atrazine in the plant, $C_{ms}$ = amount of atrazine metabolites in the plant, $C_{sur} = C_{ss} + C_{sf}$ = total chemical on plant surface, $k_f$ = rate constant for release from solid atrazine, $k_p$ = rate constant for penetration of atrazine into plant, and $k_m$ = rate constant for metabolite formation.

The differential equations for the above mechanism are given in eq 2–4.

$$dC_{sf}/dt = -k_pC_{sf} + k_fC_{ss} \quad (2)$$

$$dC_{ss}/dt = -k_fC_{ss} \quad (3)$$

$$dC_{ps}/dt = k_pC_{sf} - k_{ms}C_{ps} \quad (4)$$

$$dC_{ms}/dt = k_{ms}C_{ps}$$

The equations were solved numerically by a relative least-squares minimization routine with Dow Advanced Continuous Simulation Language (DACSL) on an IBM 370.

The model considers two compartments on the plant surface: one in which the atrazine is in the dissolved form and free to penetrate the surface of the leaf and one in which atrazine exists as a solid that is unavailable for penetration. Atrazine in the solid surface compartment is assumed to be slowly transferred to the solution compartment with rate constant $k_f$. This mechanism provides a means to account for the fact that only a portion of the applied atrazine penetrates the leaf. It also provides for a mechanism to calculate the rate of metabolism in the plant and compare the effect of tridiphane on the metabolic rate. In the model development a reverse rate constant from the solution phase to the solid phase was also considered. This rate constant did not provide a better fit of the data and was therefore not included in the model.

Data for atrazine applied to giant foxtail at 20 °C at a rate equivalent to 1.12 kg/ha without and with COC at 2.3 L/ha are plotted in Figures 1 and 2, respectively. It can be seen that the model gives a reasonable fit of the data and that COC has a dramatic effect on the amount of atrazine penetrating the leaf. In the absence of COC, approximately 12% of the applied atrazine penetrates the leaf. Metabolism was not characterized here because of the low levels of $^{14}C$ in the plants, and the primary interest was the effect of COC on penetration. When COC is present, 30% of the atrazine penetrates in the first 24–48 h following application, represented by the sum of the atrazine and metabolites in Figure 2. In both cases, penetration of atrazine slows dramatically after this time because the transfer rate from the solid compartment is very slow. In addition to fitting the rate constants for the model, the initial amounts in each of the surface compartments ($C_{ss0}$, $C_{sf0}$) can also be calculated since these are also unknowns. The predicted values for $C_{ss0}$ and $C_{sf0}$ are 90% and 10% without COC and 78% and 22% with COC, which supports the assumption that when COC is present more atrazine is solubilized on the plant surface. The rate of penetration without COC was 0.096/h and 0.076/h with COC. The rates are nearly the same, as would be expected according to the mechanism proposed by the model where the rate constants are independent of the amount of atrazine in a given compartment.

**Effect of Tridiphane on Atrazine Model Rate Constants.** The effect of tridiphane on the metabolism of atrazine in giant foxtail was studied at three temperatures: 12, 20, 30 °C. Tridiphane was added at a rate equivalent to 0.56 kg/ha to the spray solution containing atrazine and COC at 1.12 kg/ha and 2.3 L/ha, respectively. Plants were treated with and without tridiphane and the rate constants calculated by the model. An example of the effect of tridiphane on atrazine behavior at 20 °C is shown in Figure 3 and can be compared with Figure 2 where no tridiphane was present. The behavior on the surface is essentially the same where in both cases approximately 30% of the applied atrazine penetrated the plant after 2 days. In the study with no tridiphane, greater amounts of metabolites were formed and less atrazine accumulated in the plants. Examination of the percent of the total $^{14}C$ in the plant extracts as atrazine (Table I) demonstrates that more atrazine is conserved in the treatments that included tridiphane.

The rate constants for all three temperatures are summarized in Table II. All the rate constants were observed to increase as temperature increased, which is the typical expected kinetic behavior. The rate of release from the solid compartment ($k_f$) is much smaller than the rate of penetration from the solution compartment ($k_p$), which follows from the observed very slow penetration of atrazine after the initial period of absorption. The rate constants

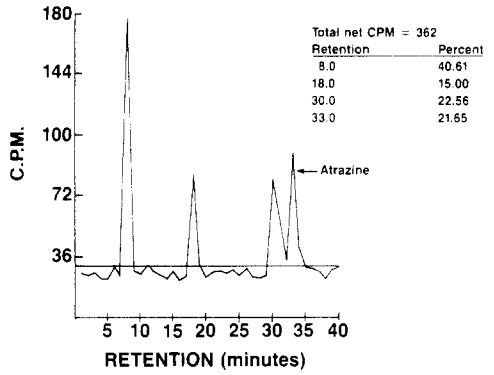


**Figure 4.** HPLC radioactivity profile of 24-h plant extract of giant foxtail grass treated with $^{14}C$-labeled atrazine without tridiphane at 20 °C.

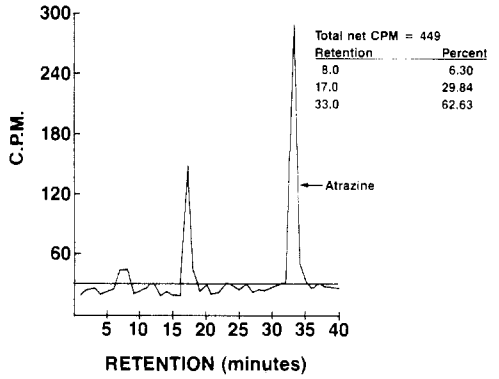


**Figure 5.** HPLC radioactivity profile of 24-h plant extract of giant foxtail grass treated with $^{14}C$-labeled atrazine with tridiphane present at 20 °C.

for penetration are similar with and without tridiphane at each temperature, demonstrating that tridiphane has little effect on the penetration of atrazine. The rates of metabolism at each temperature are, however, significantly reduced when tridiphane is present. This behavior supports the hypothesis that the biological synergistic behavior observed with treatment combinations of atrazine and tridiphane is a result of differential metabolism of atrazine in the plant.

Modeling of the fate of metabolites was not performed, nor were they identified in this study. All metabolites in the soluble fraction of the plant homogenate, together with the radioactivity in the insoluble fraction, were grouped together and considered as the total metabolite pool produced from atrazine in the plant. Therefore, different pathways of metabolite production were not distinguished. For example, whether atrazine detoxification was occurring by a series of sequential steps or by several parallel pathways was not carefully studied. Examples of radioactivity profiles in the 24-h plant extracts from the 20 °C studies with and without tridiphane are shown in Figures 4 and 5. When tridiphane is present, two peaks disappeared from the chromatogram, suggesting parallel pathways are acting in the system under the conditions of our experiment. The decrease in the rate of metabolism at each temperature, Table II, is a reflection of this phenomenon. The overall rate of atrazine metabolism is reduced because one route of metabolism appears to have been blocked. Potentially, the metabolic pathway inhibited could be glutathione-*s*-transferase as suggested by other workers. Without identification of metabolites formed, this datum is inconclusive with respect to which pathway of detoxification is inhibited. However, the intent of the study, to demonstrate a quantitative difference in the rate of metabolism of atrazine in the presence of tridiphane, has been shown.

Other models could have been postulated to describe the behavior of atrazine in this foliar system; however, we have attempted to describe the simplest model that could characterize the data. The model selected was based upon goodness of fit to the data, as well as incorporating processes that physically appeared reasonable. The model clearly shows that the surface behavior of the atrazine formulation limits the penetration of the chemical. In a field situation, it is clear that the first good rainfall will wash the remaining atrazine from the plant surface. Therefore, a 24–48-h period (the time when most of the atrazine is absorbed through the leaf) without rain would be required for optimal foliar penetration of atrazine. Tridiphane is adsorbed much faster with optimal levels reached in the plant within a few hours under normal conditions (McCall et al., 1985) and is, therefore, much less susceptible to washoff.

Temperature has a significant effect on the rate processes characterized. Under constantly changing temperatures in the field, the rate constants can be expected to vary accordingly. The impact this had on biological efficacy has not been addressed in these studies. The rate of detoxification of atrazine was reduced in the presence of tridiphane at all temperatures; however, an optimal temperature regime was not identified.

**Registry No.** Atrazine, 1912-24-9; tridiphane, 58138-08-2.

## LITERATURE CITED

Bugg, M. E.; Witt, W. W. *Abstr., Weed Sci. Soc. Amer.* **1981**, *47*, 23.

Esser, H. D.; Dupris, G.; Ebert, E; Marco, G.; Ebert, E. In "Herbicides Chemistry, Degradation and Mode of Action"; 2nd ed.; Kearney, P. C., Kaufman, D. D., Eds.; Marcel Dekker: New York, 1976; Vol. I, Chapter 2.

Ezra, G.; Deckker, J. H.; Stephenson, G. R. *Weed Sci.* **1985**, *33*, 287.

Frear, D. S.; Swanson, H. R. *Photochemistry* **1970**, *9*, 2133.

Lamoureux, G. L.; Rusness, D. G. "Abstracts of Papers", 186th National Meeting of the American Chemical Society, Washington, DC, Fall 1983; American Chemical Society: Washington, DC, 1983; PEST 115.

McCall, P. J.; Stafford, L. E.; Gavit, P. D. *J. Agric. Food. Chem.*, preceding paper in this issue.

Nash, R. G.; Beall, M. L., Jr. In "Terrestrial Microcosms and Environmental Chemistry"; Gillett, J. W., Wyatt, J., Eds; Orgon State University: Corvallis, OR, 1977; p 86.

Shimabukuro, R. H.; Swanson, H. R. *J. Agric. Food. Chem.* **1969**, *17*, 199.

Shimabukuro, R. H.; Swanson, H. R.; Walsh, W. C. *Plant Physiol.* **1970**, *46*, 103.

Thompson, L.; Houghton, J. M.; Slife, F. W.; Butler, H. J. *Weed Sci.* **1971**, *19*, 409.

Thompson, L., Jr.; Slife, F. W. *Weed Sci.* **1969**, *17*, 251.

Thompson, L., Jr.; Slife, F. W. *Weed Sci.* **1970**, *18*, 349.

Weseloh, J. W. *Proc.—North Centr. Weed Control Conf.* **1983**, *38*, 120.

Zorner, P. S.; Stafford, L. E.; McCall, P. J. *Proc.—North Centr. Weed Control Conf.* **1983**, *38*, 109.

Received for review June 10, 1985. Accepted December 26, 1985.