INVESTIGATIONS ON THE BASIS AND INHERITANCE OF METRIBUZIN TOLERANCE IN WINTER WHEAT

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INTRODUCTION

Each of the parts of this thesis is a separate manuscript to be submitted for publication; Part I in Crop Science, a Crop Science Society of America publication, and Part II in Weed Technology, a Weed Science Society of America publication.

PART I

DIFFERENTIAL METABOLISM OF METRIBUZIN BY TWO WINTER WHEAT CULTIVARS AND THEIR RECIPROCAL CROSSES

Differential Metabolism of Metribuzin by Two Winter Wheat Cultivars and Their Reciprocal Crosses[1]

RANDALL L. RATLIFF, THOMAS F. PEEPER,
EDDIE BASLER, AND HENRY T. NGUYEN[2]

Abstract. Investigations were conducted in the laboratory to determine whether differences in response to metribuzin, 4-amino-6-(1, 1-dimethylethyl)-3- (methylthio)-1,2,4-triazin-5(4H)-one, by two winter wheat (*Triticum aestivum* L.) cultivars, 'TAM W 101' (tolerant) and 'Vona' (susceptible), and their F1 reciprocal crosses are due to differential uptake, translocation, and/or metabolism and to test the hypothesis that metribuzin tolerance is maternally inherited. Twenty-four hours after treatment of wheat seedlings with ^{14}C metribuzin via the nutrient solution, Vona and TAM W 101 X Vona contained more ^{14}C in the leaves than Vona X TAM W 101. However, these differences were not considered to be of major importance in metribuzin tolerance since the leaves of TAM W 101 and Vona did not differ in total ^{14}C content. Relative quantities of metribuzin and the three major metabolites as well as an immobile fraction were determined by liquid scintillation spectrophotometry of ethanol extracted materials separated by developing

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chromatograms in a benzene:chloroform:dioxane (4:3:4) solvent system. No differences between genotypes were observed in the quantity of the three major metabolites in the roots, stem, or leaves. Less metribuzin was recovered from the leaves of TAM W 101 than Vona or TAM W 101 X Vona with 4.32% of the total ^{14}C applied recovered from the leaves of TAM W 101 as metribuzin and 5.84 and 5.98% from the leaves of Vona and TAM W 101 X Vona, respectively. The difference in metribuzin content was inversely proportional to ^{14}C that remained at the origin of thin-layer chromatograms. Most of the ^{14}C remaining at the chromatograms origin was released by base hydrolysis, suggesting a conjugate. In the leaves, TAM W 101 contained 30% more of this fraction than did the other genotypes. In the roots, Vona contained less of the immobile fraction than the other genotypes. The data supports the hypothesis that differential response to metribuzin by TAM W 101 and Vona is due to differential metabolism involving formation of conjugates. It also serves to disprove the hypothesis that metribuzin tolerance is maternally inherited.

<u>Additional index words</u>. Absorption, translocation, inheritance of herbicide tolerance, ^{14}C.

Metribuzin has been used for weed control in soybeans (Glycine max. (L.) Merr.) (14), barley (Hordeum vulgare L.) (13), potatoes (Solanum tuberosum L.) (12), and tomatoes (Lycopersicon esculentum Mill.) (6). Metribuzin is also an effective herbicide for Bromus spp. control in winter wheat but the margin of crop safety is limited (19). Different varieties of these crops have exhibited differences in metribuzin tolerance which in soybeans, potatoes, and tomatoes is reported as being due to differential metribuzin metabolism (6, 7, 10, 11, 12, 13, 16, 19, 20, 23).

Metribuzin detoxification in plants reportedly occurs as a result of metabolism into either the deaminated metabolite (DA) [6-(1,1-dimethylethyl)-3-methylthio-1,2,4-triazine-5(4H)-one] or the diketo metabolite (DK) [4-amino-6-(1,1-dimethylethyl)-1,2,4-triazine-3,5(2H,4H)-dione]. These intermediates are then further metabolized to the deaminated diketo derivative (DADK) [6-(1,1-dimethylethyl)-1,2,4-triazine-3,5(2H,4H)-dione]. DADK is further metabolized by conjugation (1). Other researchers have questioned the significance of these products as *in vivo* plant metabolites and have identified the conjugate in tomato as an N-glucoside conjugate of metribuzin (7). Alternate pathways for metribuzin metabolism in soybeans have been proposed by Frear et al. (8) and Fedtke has reported that the exact pathway of metribuzin metabolism depends on the metribuzin concentration (5). Smith and Wilkerson (20) reported that the major metabolite from metribuzin-tolerant 'Bragg' soybeans was a glucose conjugate. Such conjugates are a common method of herbicide detoxification (9, 17,18, 24, 25).

Inheritance of metribuzin tolerance in tomato (22), soybeans (3), and potatoes (2) has been shown to be controlled by a single nuclear gene. Unlike differential crop tolerance, the mechanism of triazine resistance in some weed species is not based on differential uptake, translocation, or metabolism, but on differential inhibition of the Hill reaction (15). *Brassica campestris* L. inherits this latter type of triazine tolerance uniparentally through the female parent (21). Such inheritance would indicate that the gene for s-triazine resistance is cytoplasmic and thus, in contrast to a nuclear gene, cytoplasmic inheritance could be detected through the use of reciprocal crosses.

The development of wheat varieties with greater tolerance to metribuzin could substantially increase the margin of crop safety and thus the extent to which this herbicide could be used for *Bromus* spp. control. To aid such efforts, this research was undertaken to ascertain the mechanism of differential tolerance and to develop an understanding of the inheritance of metribuzin tolerance in winter wheat.

MATERIALS AND METHODS

Seeds of 'TAM W 101', 'Vona', and their F1 reciprocal crosses were germinated in an aerated water column. Individual seedlings were transplanted into 25 ml vials containing half-strength Hoagland's nutrient solution. Each vial was wrapped with aluminum foil to exclude light. Plants were maintained in a growth chamber with 14 h, 33° C, 300±5 $\mu E \cdot m^{-2} \cdot s^{-1}$ days, and 10 h, 29° C nights. The nutrient solution was changed every 48 h. All treatments were replicated eight times.

Twelve-day-old seedlings were treated with 7.7 μM metribuzin-5-^{14}C (2.678 Ci/M) in the nutrient solution. After 24 hours the plants were removed from the vials, the roots were washed in distilled water for 10 s, and the plants were sectioned into roots, the stem (the area enclosed by the first leaf sheath), and the leaves (the first leaf blade and the portion of the second leaf blade protruding above the collar of the first leaf). After lyophilization and weighing, the plant sections were homogenized in a small glass hand homogenizer using 3 ml of cold 80% ethanol. The ^{14}C in aliquots of the homogenates were quantified by liquid scintillation spectrophotometry as a measure of translocation. A 0.2 ml aliquot of each sample was spotted onto a 0.25 mm thick 20 x 20 cm Silica Gel F-254 thin-layer plate along with known standards of metribuzin, and the metabolites DA, DK, and DADK. Plates were developed in a benzene:chloroform:dioxane (4:3:4, v/v/v) solvent system to separate metribuzin and the metabolites (16). The locations of standards were determined under short-wave UV light (254 nm), and the R_f values for metribuzin,the major metabolites DK, DA, and DADK were 0.88, 0.63, 0.79, and 0.74, respectively.

Areas corresponding to each standard were removed from the plates and analyzed for ^{14}C content by liquid scintillation spectrophotometry. To further identify the nature of the portion of the sample that was immobile on the plate two separate procedures were undertaken. In the first, leaf homogenate samples from both TAM W 101 and Vona were subjected to two-directional chromatography with a much more polar butanol:acetic acid:water (5:1:4) solvent system used as the second solvent system. Additionally, base hydrolysis of the immobile fraction was performed to determine if the ^{14}C was physically incorporated into the plant material or conjugated and not mobile in the non-polar solvent. The plates were developed with the first solvent system, and the immobile ^{14}C was removed from these plates and placed in 1 N NaOH for 1 hour, then centrifuged to recover ^{14}C components in the solid or liquid fractions which were then quantified by liquid scintillation spectrophotometry. The amount of metribuzin and each metabolite present in each plant part is expressed as a percentage of the total ^{14}C-metribuzin applied to the nutrient solution and was calculated by multiplying the total ^{14}C in each plant part by the respective percentage of the metabolites in that plant part. Analysis of variance was conducted to test the significance of genotypic effects, and least significant differences (LSD) were used to compare genotypic means.

RESULTS AND DISCUSSION

Uptake and Translocation. ^{14}C-metribuzin was absorbed and translocated throughout all genotypes within 24 hours with much greater quantities of ^{14}C recovered from the leaves than from the roots or stem (Table 1). Vona and TAM W 101 X Vona accumulated a slightly higher percentage of the applied ^{14}C than did Vona X TAM W 101. Of the total ^{14}C-metribuzin taken up by the plants, 91 to 92 percent was translocated to the foliage and no translocation differences existed among the four genotypes. This would indicate that although differential uptake may occur, uptake and translocation of metribuzin would not be considered to be the primary factor in the differential tolerance observed between TAM W 101 and Vona.

Metabolism. The major differences noted among the four genotypes was in the amount of metribuzin and an unidentified immobile fraction that accumulated in the leaves (Table 2.). There were no differences in the amounts of DK, DADK, or DA found in the leaves, roots, or stems. The leaves of TAM W 101, the tolerant cultivar, contained less metribuzin than the leaves of Vona, the susceptible cultivar, or the TAM W 101 X Vona hybrid. However, TAM W 101 contained more of the immobile fraction than did the other genotypes. This indicates that more metribuzin was being deactivated by metabolism to a conjugate by TAM W 101 than the other wheats.

In the stems, which accumulated much less ^{14}C than the leaves, there were no differences in the quantity of metribuzin present in the four genotypes. However, the stems of TAM W 101 wheat contained significantly more of the immobile fraction than did Vona or the Vona X

TAM W 101 cross. The stems of TAM W 101 X Vona hybrid contained more of the immobile fraction than did Vona.

The roots of the TAM W 101 X Vona cross contained more metribuzin than did the roots of TAM W 101 or the Vona X TAM W 101 cross. The roots of the Vona wheat contained an intermediate amount of metribuzin (0.63 % of the total applied) which was not significantly different in metribuzin content from the other genotypes. However, the quantity of the immobile fraction was lower in the roots of Vona than the other genotypes.

Release of over 80% of the leaf ^{14}C which was immobile on the thin-layer plate was accomplished by base hydrolysis, suggesting that this fraction was a conjugate. This fraction was also mobile in a more polar solvent of butanol:acetic acid: water (4:1:5), suggesting a polar conjugate such as that found in tomato (7) and soybeans (4). These findings also agree with results obtained by Mobay researchers who found that in potatoes the three major metabolites were just intermediary products to conjugation (1).

These results indicate that differential varietal tolerance to metribuzin in winter wheat may be associated with a more rapid conjugation of either metribuzin, a metabolite, or both. Although the metabolic products were the same for all genotypes, the amount of ^{14}C metribuzin was lower in the foliage of the tolerant TAM W 101 than in the other genotypes. The differences in quantity of metribuzin recovered from the foliage of the genotypes was inversely related to the quantity of ^{14}C that was conjugated and immobile in the benzene:chloroform:dioxane solvent system. TAM W 101 contained more of this fraction in the shoots

(36%) than the other genotypes (22 to 28%), while in the roots TAM W 101 had a higher quantity of the conjugate (25%) than did Vona (17%).

If metribuzin tolerance was maternally inheritable in winter wheat, the two reciprocal crosses should differ in their ability to metabolize metribuzin. However, in the leaves, both TAM W 101 X Vona and Vona X TAM W 101 metabolized metribuzin in a manner similar to the susceptible Vona. The hybrids differed in the amount of metribuzin present in the roots, however, the hybrids responded the same as their paternal parent. This indicates that metribuzin tolerance is not maternally inherited in winter wheat.

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Table 1. The total uptake and translocation of ^{14}C by wheat seedlings of TAM W 101, Vona, and their reciprocal crosses at 24 h after treatment with ^{14}C-metribuzin.

Genotype	Total ^{14}C uptake	^{14}C translocation to foliage
	(%)¶	
TAM W 101	9.1 ab	91 a
TAM W 101 x Vona	10.4 a	91 a
Vona x TAM W 101	8.2 b	91 a
Vona	10.0 a	92 a

¶Means within a column and one plant part followed by the same letter are not statistically different according to the LSD 0.05. Values for total uptake are expressed as a percent of the total ^{14}C applied to the nutrient solution. Values for translocation are expressed as a percent of the total ^{14}C absorbed.

Table 2. The amount of total ^{14}C, metribuzin, and metabolites in the roots, stems, and leaves of TAM W 101, Vona, and their reciprocal crosses at 24 h after treatment with ^{14}C-metribuzin.

Genotype	Metribuzin	Immobile	DK	DADK	DA
	(% of applied)¶				
Roots					
TAM W 101	0.54 b	0.19 a	0.02 a	0.01 a	0.02 a
TAM W 101 x Vona	0.70 a	0.19 a	0.02 a	0.01 a	0.03 a
Vona x TAM W 101	0.52 b	0.19 a	0.02 a	0.01 a	0.03 a
Vona	0.63 ab	0.14 b	0.02 a	0.01 a	0.03 a
Stem					
TAM W 101	0.62 a	0.32 a	0.02 a	0.01 a	0.02 a
TAM W 101 x Vona	0.61 a	0.27 ab	0.03 a	0.01 a	0.02 a
Vona x TAM W 101	0.52 a	0.23 bc	0.03 a	0.01 a	0.02 a
Vona	0.54 a	0.19 c	0.02 a	0.01 a	0.02 a
Leaves					
TAM W 101	4.32 b	2.62 a	0.22 a	0.08 a	0.18 a
TAM W 101 x Vona	5.98 a	1.98 b	0.28 a	0.08 a	0.18 a
Vona x TAM W 101	4.72 ab	1.42 b	0.18 a	0.06 a	0.12 a
Vona	5.84 a	1.80 b	0.44 a	0.06 a	0.18 a

¶Means within a column and one plant part followed by the same letter are not statistically different according to the LSD 0.05. Values are expressed as a percent of the total ^{14}C applied to the nutrient solution of each plant.

PART II

BROMUS CONTROL IN WINTER WHEAT (TRITICUM AESTIVUM L.) WITH THE ETHYLTHIO ANALOG OF METRIBUZIN

Bromus control in winter wheat (Triticum aestivum L.) with the Ethylthio Analog of Metribuzin[1]

RANDALL L. RATLIFF AND THOMAS F. PEEPER[2]

Abstract. Twenty field experiments were conducted in Oklahoma from 1983 through 1986 to evaluate the ethylthio analog of metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(ethylthio)-1,2,4-triazin-5(4*H*-one] for selective control of cheat (Bromus secalinus L. #[3] BROSE), downy brome (Bromus tectorum L. # BROTE), and rescuegrass (Bromus catharticus Vahl # BROCA) in winter wheat. Bromus spp. control with the ethylthio analog of metribuzin at 0.84 and 1.12 kg/ha applied postemergence before the Bromus sp. tillered was 87 to 100%. Control of tillered Bromus was not as consistent. Dockage reductions and yield increases of wheat occurred in proportion to increases in control. Addition of a surfactant to very early postemergence applications of 0.56 kg/ha increased cheat control but resulted in minor wheat injury. Surfactant use had little or no effect on dockage reduction and yields. Little or no crop injury was evident even with applications on sand and loamy sand soils.

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1. Received for publication.
2. Grad. Res. Asst. and Prof., respectively, Dept. Agron., Okla. State Univ., Stillwater, OK 74078.
3. Letters following this symbol are a WSSA-approved computer code from Composite List of Weeds, Weed Sci. 32, Supp. 2.

Additional index words. BROSE, BROTE, BROCA, BAY SMY 1500, DPX R 7910, as-triazine.

INTRODUCTION

The lack of a consistently effective control for *Bromus* spp. is one of the most serious production problems facing many Great Plains winter wheat producers. The most prominent of the *Bromus* spp. in Oklahoma is cheat, however, it is frequently found in association with downy brome, Japanese brome (*Bromus japonicus* Thunb. ex Murr. # BROJA), and rescuegrass. Approximately 1.4 million hectares of Oklahoma wheat are cheat infested (2).

Currently, only metribuzin [4-amino-6-(1,1-dimethylethyl)--3-(methylthio)-1,2,4-triazin-5(4*H*)-one] and triallate [S-(2,3,3-trichloro-2-propenyl) bis(1-methylethyl)carbamothioate] are labeled for cheat control in hard red winter wheat in Oklahoma. However, triallate must be applied preplant incorporated, has a full season grazing restriction, and is recommended on only a few cultivars. Metribuzin, because of differential variety tolerance (4), can currently only be applied to five hard red winter wheat cultivars in Oklahoma. There are also soil pH, textural, and organic matter restrictions associated with metribuzin application that limit its utility. Because of the limitations associated with these two herbicides, more versatile herbicides are needed for selective *Bromus* spp. control in winter wheat. The ethylthio analog of metribuzin (ethyl-metribuzin), also known as 'BAY SMY 1500' or 'DPX R 7910' was synthesized by MoBay Chemical Corp. for evaluation as a *Bromus* spp. control herbicide. It has a lower water solubility than metribuzin (350 ppm[4] versus 1220 ppm) (6). It also has an initial half-life of biological activity that is half that of metribuzin and has less unit activity (5). This research was conducted to evaluate the ethylthio analog of metribuzin for selective Bromus spp. control in winter wheat and to determine the optimum application rate and timing.

METHODS AND MATERIALS

During the 1983-84, 1984-85, and 1985-86 growing seasons, 20 field experiments were conducted at sites selected to provide a wide range of soil textures to evaluate Bromus spp. control with ethyl-metribuzin (Table 1.). The design for each experiment was a randomized complete block with 4 replications except that 3 experiments had 3 replications. Plot size in all experiments was either 2.4 by 6 m or 2.4 by 7.6 m. The dominant Bromus sp. present, its density, the wheat variety seeded and the number of days from herbicide application until at least 0.5 cm of rainfall was received are detailed in Table 2.

Ethyl-metribuzin was applied preplant-incorporated (PPI), preemergence (Zadoks growth stage 00) (7), and postemergence to cheat with 1 to 2 leaves (Zadoks 11 to 12), 2 to 4 leaves (Zadoks 12 to 14), 1 to 2 tillers (Zadoks 20 to 22) and when the cheat had 2 to 5 tillers (Zadoks 22 to 25). Applications of ethyl-metribuzin in combination with a surfactant were made postemergence to cheat with 1 to 2 leaves, 1 to 2 tillers and 2 to 5 tillers. Ethyl-metribuzin was also applied to downy

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[4] Technical Information Sheet - BAY SMY 1500. MoBay Chem. Corp., Kansas City, MO. 6 pp.

brome at Zadoks 11 to 12 and to both downy brome and rescuegrass at Zadoks 20 to 22. Application rates were 0.84, 1.12, and 1.40 kg/ha for the PPI and Zadoks 00 treatments and 0.56, 0.84, and 1.12 kg/ha for the postemergence treatments. Metribuzin tolerant cultivars were used in all experiments because metribuzin was included as a standard treatment at locations with applications at Zadoks 22 to 25. The metribuzin was applied at 0.42 kg/ha at all locations except at P-1 and T-1 which received 0.28 kg/ha. All herbicide treatments were applied with either a compressed air or a compressed nitrogen plot sprayer at a carrier volume of 281 L/ha. Visual Bromus control ratings were made after heading. All plots were harvested with a small plot grain combine which had been adjusted to retain as much Bromus seed as possible with the grain for dockage determinations. Dockage was obtained by cleaning the harvested grain with a small commercial type seed cleaner. Since the combines were adjusted to retain as much weed seed as possible some chaff and straw was collected with the grain. Therefore, in some cases dockage from weed-free plots was as high as 6%. Grain yield was determined after cleaning.

RESULTS AND DISCUSSION

Preplant-incorporated applications. PPI applications of ethyl-metribuzin at rates up to 1.40 kg/ha did not provide over 75% control of cheat at any of 3 locations (Table 3.). Dockage was reduced by over 50% with 1.12 kg/ha of ethyl-metribuzin at both E-1 and E-2 but still remained unacceptably high. Clean grain yield was increased substantially by application of 0.84 and 1.12 kg/ha of ethyl-metribuzin at E-1 with the yield from plots treated with 1.12 kg/ha more than twice that of the check. Yields were more variable at the other two locations with no significant yield increases detected according to the LSD 0.05. Ethyl-metribuzin at 0.84 and 1.12 kg/ha increased wheat yields at K-1.

Preemergence applications. Cheat control obtained with preemergence applications of ethyl-metribuzin appeared less variable than that obtained from PPI applications but none of the treatments provided over 80% control (Table 4.). At E-1 dockage was reduced by application of 0.84 kg/ha, but at the other locations 1.12 kg/ha was required to reduce dockage. The highest herbicide rates used approximately doubled the clean grain yield at E-2 and G-1. There was an even larger yield response at E-1.

Applications at Zadoks 11 to 12. In contrast to the PPI and preemergence treatments, over 90% cheat control was obtained with one or more very early postemergence treatments at each of 5 locations.

Excellent cheat control was obtained at all locations with ethyl-metribuzin at 1.12 kg/ha and at 3 of 5 locations with 0.84 kg/ha (Table 5.). Control with 0.56 kg/ha was variable, with over 90% control obtained only at P-3. The greater cheat control at P-3 could be due to the occurrence of a substantial rainfall within 48 h of application at that location, however, none of the locations went more than 8 days before receiving over 0.5 cm of precipitation. Dockage was reduced over 50% at all locations with all rates except that at P-1 0.56 kg/ha did not significantly reduce dockage. Clean grain yield was increased at all locations with all rates of ethyl-metribuzin. Over fourfold increases in clean grain yield were obtained with 0.84 and 1.12 kg/ha at

P-3. Clean grain yield was more than doubled with all rates at E-1 and with the two higher rates at P-1.

Applications at Zadoks 12 to 14. Delaying herbicide applications until the cheat had up to 4 leaves did not appear to reduce control compared to earlier postemergence treatments. However, excellent cheat control was obtained with 0.56 kg/ha of ethyl-metribuzin at only 2 of 4 locations (Table 6.). Cheat control with 0.84 kg/ha was more consistent than with the lower rate, but performance at P-2 was below average. The poorer control obtained on the Port soil at P-2 was attributed to the soil being saturated at herbicide application.

Excellent cheat control was obtained with 1.12 kg/ha of ethyl-metribuzin at the 3 location that this higher rate was used. Dockage reductions due to cheat control were evident at all locations. All rates of ethyl-metribuzin at T-2 and the higher rates at G-5 reduced dockage to essentially weed free grain. Only 0.56 kg/ha applications at N-2 did not reduce dockage. Yield increases were obtained at all locations except at N-2. However, even at N-2, 0.84 kg/ha increased yield according to the LSD 0.10.

Applications at Zadoks 20 to 22. When ethyl-metribuzin was applied to cheat that had just began to tiller control was relatively poor at 3 of 5 locations (Table 7.). Excellent cheat control was obtained with the two higher rates at P-3 and the high rate at G-5. At P-3 this may be attributed to receiving 4.4 cm of rain within 48 h of application to move the herbicide into the rooting zone whereas the other locations did not receive rain for up to 57 days after treatment. Significant dockage reductions were observed in plots that had received 0.56 kg/ha of ethyl-metribuzin at P-2, P-3, and T-1 indicating that the post-heading visual control ratings that these treatments received were too low.

Dockage reductions were observed at all locations except P-1 when 0.84 kg/ha was applied with the grain from G-5, P-3, and T-1 being essentially free of weed seed. Reductions in dockage were obtained at all locations with the highest rate. At all locations except P-2 application of 0.56 kg/ha increased grain yield even though at P-1 and T-1 the control ratings were very low. This indicates that with relatively heavy weed pressure the visual control ratings on the lower end of the control rating scale may tend to be too low. Yield increases were obtained at all locations with both 0.84 and 1.12 kg/ha with the grain yield more than doubled in several cases.

<u>Applications at Zadoks 22 to 25</u>. Cheat control with ethyl-metribuzin applied to 2 to 5 tiller cheat was substantially less than that obtained from earlier applications (Table 8.). Cheat control was greater with metribuzin than with ethyl-metribuzin at three of the six locations. There was no difference in cheat control between 1.12 kg/ha of ethyl-metribuzin and 0.42 kg/ha of metribuzin at G-2 and 1.12 kg/ha ethyl-metribuzin was superior at T-1 where the metribuzin rate was 0.28 kg/ha. Poor herbicide performance at P-1 and T-1 were probably due to delays of activation by rainfall of 18 and 26 days, respectively.

Ethyl-metribuzin and metribuzin were effective in reducing dockage at 4 of 6 locations. Metribuzin was superior to ethyl-metribuzin in reducing dockage at P-3, while ethyl-metribuzin at 1.12 kg/ha was superior at T-1 where the metribuzin rate was 0.28 kg/ha. Yield increases, while not as large as obtained with earlier treatments, were still evident. The highest rate used of ethyl-metribuzin increased yield at all locations except P-1. There were no differences in yield between the high rate of ethyl-metribuzin and metribuzin.

Effect of surfactant on cheat control. Ethyl-metribuzin was applied to cheat at Zadoks 11 to 12, Zadoks 20 to 22, and Zadoks 22 to 25 with 1/2% v/v of a nonionic surfactant[5] to evaluate the effect on cheat control, wheat injury, dockage and yield (Table 9.). The addition of surfactant increased control of Zadoks 11 to 12 cheat compared to treatments with ethyl-metribuzin alone at E-1 with the low rate and at P-1 with 0.84 kg/ha. Control of Zadoks 20 to 22 cheat was improved by the addition of surfactant only with the high rate at P-1. Addition of the surfactant had no effect on control of Zadoks 22 to 25 cheat. Initial wheat injury, consisting of foliar chlorosis and stunting, was evident with the addition of surfactant to ethyl-metribuzin applications at Zadoks 11 to 12. Significant wheat injury occurred with all rates at E-1 and P-1 and with the high rate at T-1. No wheat injury was observed at the later application stages. Greater dockage reductions due to the addition of the surfactant occurred only with the two higher rates of ethyl-metribuzin applied to Zadoks 22 to 25 cheat at T-1. The addition of a surfactant had no effect on yield at any stage.

Downy brome control. Excellent control of downy brome in the Zadoks 11 to 12 growth stage was obtained with applications of ethyl-metribuzin at 0.56 to 1.12 kg/ha (Table 10.). Application if 0.84 kg/ha at Zadoks 20

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[5] The surfactant was Triton AG-98, containing alkylarylpolyoxyethylene glycols, produced by Rohm and Haas Co., Philadelphia, PA 19105.

to 22 provided excellent control at U-1. At P-4 1.12 kg/ha did not control downy brome. The lower control obtained at U-2 may be attributable to the lack of activating rainfall for 13 days after treatment. Rainfall occurred within 2 days after application at the other locations. All treatments applied to Zadoks 11 to 12 downy brome significantly reduced dockage. Dockages in the untreated downy brome plots were lower than in the cheat plots due to downy brome maturing and shattering earlier than cheat. At the later application stage the dockage data followed the control ratings with reductions in dockage observed at P-4 and U-1 while no differences were observed at U-2. All Zadoks 11 to 12 treatments increased yield. Applications to Zadoks 20 to 22 downy brome at P-4 and U-1 increased yield but no differences in wheat yield were found at U-2.

Rescuegrass control. Excellent control of rescuegrass was obtained with 0.84 and 1.12 kg/ha of ethyl-metribuzin at each of 2 locations on sandy soil, where rescuegrass is most common (Table 11.). The lowest rate, 0.56 kg/ha, provided enough control at M-2 to reduce dockage and increase grain yield. No dockage reductions were observed at M-1, because the rescuegrass seed shattered before harvest. The rescuegrass density at M-1 was lower than that in M-2. The absence of yield increases in M-1 indicates that relatively high populations of rescuegrass are required to reduce wheat yield. However, that situation may not always be true because at both M-1 and M-2 the wheat was larger than the rescuegrass at the time of treatment, indicating that the wheat had emerged earlier than the weed and thus obtained a competitive advantage.

Applications of ethyl-metribuzin postemergence to cheat, downy brome, and rescuegrass resulted in excellent weed control if applied before the weeds began to tiller. The response from preplant-incorporated and preemergence applications of ethyl-metribuzin was more variable and higher rates were required for effective control. Application of ethyl-metribuzin to cheat, downy brome and rescuegrass at Zadoks 20 to 22 can be effective if prompt activation occurs. Excellent weed control resulted in reduced dockage and increased clean grain yields. Yield responses to the early weed control were greater than to the latter application stages. This response could confirm that early removal in the bromes is as important as in wild oats (Avena fatua L. # AVEFA) in reducing competition (1,3).

Applications of ethyl-metribuzin at up to 1.12 kg/ha did not result in yield reductions at any of the twenty locations. These locations represented a pH range of from 4.9 to 7.4 and textures ranging from a sand to a clay loam. The data indicate that the ethylthio substitution has produced a herbicide which is lower in water solubility, shorter in persistence, and suitable for use on a wider range of soil types than metribuzin.

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Table 1. Crop year and soil characteristics at the 20 experimental locations.

		Soil characteristics					
Location	Year	Classification	Sand	Silt	Clay	OM	pH
			(%)				
E-1	1983-84	Easpur clay loam	42	28	30	1.4	5.4
E-2	1984-85	Easpur sandy clay loam	57	23	21	1.3	5.3
G-1	1983-84	Grant loam	29	45	27	1.7	5.3
G-2	1983-84	Grant silt loam	19	59	23	1.7	5.3
G-3	1983-84	Grant silt loam	19	59	23	1.7	5.3
G-4	1984-85	Grant loam	34	44	24	1.5	4.9
G-5	1985-86	Grant silt loam	25	52	23	0.8	7.4
K-1	1983-84	Kirkland clay loam	34	37	30	1.5	5.7
M-1	1984-85	Meno sand	97	2	1	0.7	5.7
M-2	1985-86	Meno loamy sand	88	2	10	0.7	5.9
N-1	1984-85	Norge clay loam	37	35	29	1.5	5.0
N-2	1984-85	Norge silty clay loam	51	26	24	1.1	4.9
P-1	1983-84	Port clay loam	24	48	29	1.4	5.6
P-2	1984-85	Port loam	29	47	25	1.5	5.3
P-3	1984-85	Port loam	33	44	23	1.0	5.2
P-4	1985-86	Port loam	43	36	21	0.3	6.2
T-1	1983-84	Teller sandy clay loam	50	27	23	1.2	5.3
T-2	1984-85	Teller loam	49	28	23	0.8	7.1
U-1	1985-86	Pulaski loam	48	35	18	0.5	5.6
U-2	1985-86	Pulaski loam	49	32	19	0.7	6.1

Table 2. Wheat variety, weed species, weed population, and days after treatment until the first rainfall (greater than 0.5 cm) was received at the 20 experimental locations.

Location	Wheat Variety	Weed	Weed Population	Treatment Stage[a]					
				PPI	Pre	VEP	EP	ET	T
			pl/m^2	-------- days until rainfall --------					
E-1	TAM W 101	cheat	1075	12	12	8	—	—	—
E-2	TAM 105	cheat	430	8	8	—	—	—	—
G-1	TAM 105	cheat	860	—	17	—	—	—	—
G-2	TAM W 101	cheat	430	—	—	—	—	—	2
G-3	TAM W 101	cheat	376	—	—	—	—	—	2
G-4	TAM W 101	cheat	538	—	—	—	—	—	8
G-5	TAM 105	cheat	1075	—	—	—	15	57	—
K-1	TAM W 101	cheat	4300	12	—	—	—	—	—
M-1	TAM W 101	rescuegrass	430	—	—	—	—	8	—
M-2	TAM 105	rescuegrass	914	—	—	—	—	15	—
N-1	TAM 105	cheat	1600	—	—	6	12	—	—
N-2	TAM 105	cheat	1300	—	—	—	5	—	—
P-1	TAM 105	cheat	807	—	—	3	—	7	18
P-2	TAM 105	cheat	1076	—	—	—	11	6	—
P-3	TAM W 101	cheat	970	—	—	2	—	2	9
P-4	TAM W 101	downy brome	2150	—	—	—	—	2	—
T-1	TAM W 101	cheat	807	—	—	5	—	10	26
T-2	TAM W 101	cheat	860	—	—	—	5	—	—
U-1	TAM W 101	downy brome	1076	—	—	8	—	2	—
U-2	TAM 105	downy brome	1300	—	—	1	—	13	—

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[a] PPI=preplant incorporated, Pre=Zadoks growth stage 00, VEP=Zadoks stage 11 to 12, EP=Zadoks stage 12 to 14, ET=Zadoks stage 20 to 22, T=Zadoks stage 22 to 25. A — indicates that no herbicide treatments were applied at the indicated growth stage.

Table 3. Effect of PPI applications of ethyl-metribuzin at three locations on cheat control, dockage, and clean grain yield.

	Cheat control				Dockage				Clean grain yield			
	Rate (kg/ha)											
Loc.	0	0.84	1.12	1.40	0	0.84	1.12	1.40	0	0.84	1.12	1.40
	(%)[a]								(kg/ha)			
E-1	0b	41a	54a	----	40.4a	21.8b	14.6c	----	1110c	2179b	2724a	----
E-2	0g	70h	54h	75h	39.4g	41.2g	15.9h	15.7h	1358gh	1089g	1964h	1708gh
K-1	0t	53r	36r	21s	16.9r	13.6r	9.0r	10.1r	1453r	2408r	2192r	1903r

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[a] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

Table 4. Effect of preemergence (Zadoks 00) applications of ethyl-metribuzin at three locations on cheat control, dockage and clean grain yield.

	Cheat control				Dockage				Clean grain yield			
	Rate (kg/ha)											
Loc.	0	0.84	1.12	1.40	0	0.84	1.12	1.40	0	0.84	1.12	1.40
	(%)[a]								(kg/ha)			
E-1	0b	69a	88a	—	40.4a	14.7b	13.0b	—	1110b	2710a	2858a	—
E-2	0g	63f	55f	62f	39.4f	29.8fg	14.8gh	10.6h	1358g	1600g	2031fg	2589f
G-1	0t	39s	70r	80r	11.2r	9.7rs	5.3s	7.7rs	1520t	2401s	3046r	3013r

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[a] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

Table 5. Effect of very early postemergence (Zadoks 11 to 12) applications of ethyl-metribuzin at five locations on cheat control, dockage and clean grain yield.

	Cheat control				Dockage				Clean grain yield			
	Rate (kg/ha)											
Loc.	0	0.56	0.84	1.12	0	0.56	0.84	1.12	0	0.56	0.84	1.12
	(%)^a								(kg/ha)			
E-1	0c	77b	94ab	99a	40.5a	12.1b	8.0b	7.4b	1110c	2777b	3241a	3114ab
N-1	0g	---	98f	---	33.9f	----	9.0g	---	1991g	----	3342f	----
P-1	0t	28s	44s	91r	31.0r	19.8rs	12.2s	7.8s	1614s	3141r	3470r	3822r
P-3	0b	97a	100a	100a	30.4a	4.5b	3.1b	2.7b	820b	3044a	3722a	3353a
T-1	0h	66g	87fg	95f	13.6f	6.1g	3.7g	3.9g	2032g	2542f	2636f	2871f

[a] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

Table 6. Effect of early postemergence applications (Zadoks 12 to 14) of ethyl-metribuzin at five locations on cheat control, dockage and clean grain yield.

	Cheat control				Dockage				Clean grain yield			
	Rate (kg/ha)											
Loc.	0	0.56	0.84	1.12	0	0.56	0.84	1.12	0	0.56	0.84	1.12
	(%)[a]								(kg/ha)			
G-5	0c	70b	95a	96a	29.1a	8.6b	3.9b	5.1b	859b	1501a	1759a	1860a
N-1	0g	—	97f	—	33.9f	—	10.9g	—	1991g	—	3389f	—
N-2	0t	70s	93r	—	25.0r	17.7rs	12.0s	—	1520r	1621r	1997r	—
P-2	0d	20c	65b	94a	37.1a	18.7b	11.5bc	7.4c	1076c	1863b	2266ab	2535a
T-2	0g	100f	100f	100f	14.5f	3.7g	2.6g	2.4g	1762g	2563f	3093f	2694f

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[a] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

Table 7. Effect of early tillering (Zadoks 20 to 22) applications of ethyl-metribuzin at five locations on cheat control, dockage and clean grain yield.

	Cheat control				Dockage				Clean grain yield			
	Rate (kg/ha)											
Loc.	0	0.56	0.84	1.12	0	0.56	0.84	1.12	0	0.56	0.84	1.12
	(%)[a]								(kg/ha)			
G-5	0b	63a	88a	93a	29.1a	14.0ab	5.0a	5.8a	859b	1356a	1372a	1581a
P-1	0h	0h	24g	68f	31.0f	18.8fg	13.6fg	5.5g	1614h	2831fg	2650g	3544f
P-2	0r	0r	34s	50s	37.1r	27.2s	17.9st	15.9t	1076s	1486rs	1749r	1755r
P-3	0d	70c	93b	100a	32.0a	6.7b	5.9bc	3.0c	820c	2192b	3127ab	3416a
T-1	0h	11gh	30g	60f	13.6f	8.2g	4.9gh	3.8h	2031g	2508f	2589f	2845f

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[a] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

Table 8. Effect of tillered (Zadoks 22 to 25) applications of ethyl-metribuzin and metribuzin at six locations on cheat control, dockage and clean grain yield.[a]

	Cheat control					Dockage					Clean grain yield				
	Rate (kg/ha)														
Loc.	0	0.56	0.84	1.12	Met.	0	0.56	0.84	1.12	Met.	0	0.56	0.84	1.12	Met.
	(%)[b]										(kg/ha)				
G-2	0b	0b	11b	36a	40a	23.9a	19.9a	11.7b	9.7b	11.7b	1567c	1997bc	2246ab	2575a	2683a
G-3	0g	--	--	21f	36f	13.8f	----	----	14.6f	8.4f	1776g	----	----	2387f	2744f
G-4	0t	--	75s	--	99r	37.1r	----	8.3s	----	7.5s	847s	----	1829r	----	1472r
P-1	0b	0b	1b	9b	33a	31.0a	32.3a	25.6a	20.7a	17.3a	1614b	1567b	2051b	2394ab	2986a
P-3	0h	--	25g	35g	100f	32.0f	----	15.3g	14.7g	3.9h	820t	----	1674st	2260rs	3369r
T-1	0c	3b	20b	43a	11b	13.6a	7.2c	8.6bc	8.0c	11.8ab	2031b	2528a	2747a	2697a	2367ab

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[a] Metribuzin rate was 0.42 kg/ha at all locations except P-1 and T-1 where it was 0.28 kg/ha.

[b] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

Table 9. Effect of the addition of surfactant on applications of ethyl-metribuzin on cheat control, dockage and clean grain yield.

	Cheat control			Wheat Injury			Dockage			Clean grain yield		
	Rate (kg/ha)											
Loc.	0.56	0.84	1.12	0.56	0.84	1.12	0.56	0.84	1.12	0.56	0.84	1.12
	(%)[a]									(kg/ha)		
Zadoks growth stage 11 to 12												
E-1	19*	3	—	13*	25*	—	-4.2	5.3	—	189	-302	—
P-1	22	25*	2	9*	8*	20*	3.2	1.4	2.1	-317	-497	72
T-1	-2	1	-9	0	3	11*	-0.5	1.1	1.6	141	390	210
Zadoks growth stage 20 to 22												
P-1	0	-18	42*	0	0	0	8.8	6.1	6.5	807	121	289
T-1	-2	-19	5	5	0	1	-2.8	1.3	0.5	54	-276	-1
Zadoks growth stage 22 to 25												
G-2	4	4	-16	0	0	0	-7.8	-1.3	-0.3	203	27	-94
P-1	3	4	-4	0	0	0	4.3	2.7	12.7	-27	-175	-659
T-1	12	10	12	0	0	0	-2.4	-3.9*	-4.7*	290	-238	13

[a] Data presented is the increase or decrease in the parameter measured as a result of the addition of surfactant. Values followed by an asterisk are significantly different from the same treatment without the surfactant according to the LSD 0.05.

Table 10. Effect of applications of ethyl-metribuzin at three locations on downy brome control, dockage, and clean grain yield.

	Downy brome control				Dockage				Clean grain yield			
	Rate (kg/ha)											
Loc.	0	0.56	0.84	1.12	0	0.56	0.84	1.12	0	0.56	0.84	1.12
	(%)[a]								(kg/ha)			
Zadoks 11 to 12												
U-1	0b	91a	100a	100a	6.1a	2.4b	4.1b	2.5b	2098b	2819a	2614a	2796a
U-2	0g	88f	89f	93f	12.0f	5.0g	4.9g	4.2g	1260g	2208f	2025f	2297f
Zadoks 20 to 22												
P-4	0s	--	68r	90r	26.2r	---	7.8s	6.4s	886s	----	1174r	1189r
U-1	0b	--	91a	98a	6.1a	---	3.3b	3.4b	2098b	----	2720a	2535a
U-2	0g	--	64f	43f	12.0f	---	9.0f	9.6f	1260f	----	1427f	1380f

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[a] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

Table 11. Effect of applications of ethyl-metribuzin to rescuegrass at Zadoks growth stage 20 to 22 at two locations on rescuegrass control, dockage, and clean grain yield.

	Rescuegrass control				Dockage				Clean grain yield			
					Rate (kg/ha)							
Loc.	0	0.56	0.84	1.12	0	0.56	0.84	1.12	0	0.56	0.84	1.12
	(%)[a]								(kg/ha)			
M-1	0c	65b	97a	99a	6.5a	3.9a	4.3a	3.4a	1749ab	1794ab	1479b	1869a
M-2	0g	81f	97f	96f	18.5f	2.8g	2.6g	2.7g	711g	1246f	1115f	1061f

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[a] Means within each row and parameter followed by the same letter are not statistically different according to the LSD 0.05.

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VITA

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Doctor of Philosophy

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