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POSTEMERGENCE CRABGRASS CONTROL IN TURFGRASS WITH DITHIOPYR PLUS ADJUVANTS

By

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ABSTRACT

POSTEMERGENCE CRABGRASS CONTROL IN TURFGRASS WITH DITHIOPYR PLUS ADJUVANTS

By

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Field, greenhouse, and laboratory studies were conducted to evaluate the efficacy of dithiopyr plus adjuvants for postemergence crabgrass control. Safety to turfgrasses was investigated and factors involved in the adjuvants' enhancement of dithiopyr activity were studied. Dithiopyr effectively controlled untillered crabgrass in the field, but was ineffective on tillered crabgrass. The primary site of uptake of dithiopyr was through the foliage; thus, adjuvants were evaluated for enhancement of activity. Several adjuvants significantly increased control of 2 to 3- and 3 to 6-tiller crabgrass when compared with dithiopyr alone. Adjuvants enhanced activity by increasing herbicide absorption, translocation, spray retention, and physical placement near the site of action. The relative importance of any factor depended on the adjuvant used.

Chewings fescues were more susceptible to dithiopyr injury than hard or creeping red fescues. Two consecutive annual dithiopyr applications at 1.12 kg ai/ha did not inhibit Kentucky bluegrass rooting. Dithiopyr at 0.42 kg ai/ha was not phytotoxic to Kentucky bluegrass; adjuvants did not increase phytotoxicity.

to Terri,

my best friend and journey companion

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INTRODUCTION

Highly maintained turfgrass is widely recognized as a valuable commodity. The presence of weeds in turfgrass often interferes with the turf's aesthetic or functional purposes. Crabgrass (Digitaria spp.) has been a pernicious weed in lawns in the United States since its introduction as a forage crop in the 19th century. Several species infest the United States, but smooth crabgrass [D. ischaemum (Schreb.) Muhl.] and large crabgrass (D. sanguinalis Scop.) are the most common. Many new herbicides have been developed in the last three decades in an attempt to control these weeds, yet crabgrass control continues to be a challenging problem for turfgrass managers.

Dithiopyr [3,5-pyridinedicarbothioic acid,2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-S,S-dimethylester], a new herbicide from the Monsanto Agricultural Company, has excellent preemergence activity on crabgrass. This product also effectively controls untillered crabgrass when applied postemergence, but is ineffective on tillered crabgrass. If the activity of dithiopyr on tillered crabgrass

could be increased, the total effectiveness of the herbicide would be vastly improved.

Adjuvants are often used to enhance the activity of foliar-applied herbicides; thus, if the site of uptake of dithiopyr applied postemergence to crabgrass is via the foliage, then adjuvants merit investigation. Turfgrass safety is a concern, however, as the addition of adjuvants to a spray solution can increase herbicidal phytotoxicity to desirable crops.

The objectives of this research were: 1) to evaluate the efficacy of dithiopyr for postemergence control of crabgrass, 2) to determine whether adjuvants could be used to enhance postemergence control, 3) to elucidate the factors involved in adjuvants' enhancement of dithiopyr activity, and 4) to evaluate dithiopyr and dithiopyr-adjuvant combinations for safety on turfgrasses.

Chapter 1

EFFICACY OF DITHIOPYR ALONE AND IN COMBINATION WITH ADJUVANTS FOR POSTEMERGENCE CRABGRASS CONTROL

ABSTRACT

Field and greenhouse studies were conducted in 1989 and 1990 to evaluate the efficacy of dithiopyr for postemergence crabgrass control at three growth stages, and to evaluate adjuvants for enhancement of dithiopyr activity on tillered crabgrass. In the 1989 field study, various formulations of dithiopyr gave excellent control of crabgrass when applied at the 2 to 3-leaf growth stage. Control was longer lasting than that provided by single applications of fenoxaprop, fenoxaprop tank-mixed with preemergence herbicides, or quinchlorac. When applied to tillered crabgrass, however, dithiopyr gave virtually no control. In 1990, 95 adjuvants were screened in greenhouse studies in an attempt to identify adjuvants with high potential for enhancing dithiopyr activity on tillered crabgrass. Nearly all adjuvants tested in the greenhouse increased crabgrass control when compared with dithiopyr alone. Ten adjuvants were selected from these screens for evaluation with dithiopyr in the 1990 field study. In comparison with dithiopyr alone, several adjuvants significantly increased crabgrass control when applied to 2 to 3-tiller or 3 to 6-tiller crabgrass. Adjuvants giving

consistent increases in control included Dow Corning X2-5309, Dow Corning 6955-145, CSY-77715512, Pfizer 14636-181-7, Activator 90, Agsco Sunit, Herbimax and X-77. Pfizer M and Dash gave inconsistent control. No adjuvant was clearly superior to the rest; thus, cost and availability may be the deciding factors when selecting an adjuvant to use with dithiopyr. Nomenclature: Dithiopyr, 3,5-pyridinedicarbothioic acid,2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-S,S-dimethylester; fenoxaprop, (±)-2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoic acid; quinchlorac, 3,7-dichloro-8-quinolinecarboxylic acid; crabgrass, *Digitaria* spp. *Additional index words*. Adjuvant screens, tank-mixes.

INTRODUCTION

Crabgrass is a pernicious weed in lawns, gardens and cultivated fields throughout the temperate and tropical regions of the world. Thirteen species infest the United States, but large crabgrass (*D. sanguinalis* Scop.) and smooth crabgrass [*D. ischaemum* (Screb.) Muhl.] are the most common (12). Control of these weeds continues to be a challenging problem for turfgrass managers; consequently, the search for new, more effective herbicides persists.

Dithiopyr is a new preemergence herbicide from the Monsanto Agricultural Company. This compound provides outstanding, season-long preemergence crabgrass control at rates of 0.28 to 0.56 kg ai/ha (1, 5, 6, 7, 8, 13, 18). Excellent safety on Kentucky bluegrass (*Poa pratensis* L.), perennial ryegrass (*Lolium perenne* L.), creeping bentgrass (*Agrostis palustris* Huds.), and zoysiagrass (*Zoysia* spp.) has been reported at rates as high as 1.1 kg ai/ha (1, 4, 8, 9).

In addition to its preemergence activity, dithiopyr gives superior postemergence crabgrass control at 0.56 kg ai/ha or less, if applied before the crabgrass has tillered (1, 4, 6, 8, 9). However, control becomes increasingly more difficult as the crabgrass matures. At the 1-3 tiller growth

stage, rates of 0.84 kg ai/ha or higher are required, while at the 3 to 6-tiller stage, rates of 1.68 kg ai/ha or higher are needed (1, 4, 7, 8, 9, 13). Even at these high rates, control may be marginal.

Improved activity of dithiopyr on tillered crabgrass would increase the versatility and application window of the compound. The use of adjuvants in the spray solution is a potential means of enhancing dithiopyr activity. McWhorter defines adjuvants as materials that facilitate the action of a herbicide or that facilitate or modify characteristics of herbicide formulations or spray solutions (11). Many researchers have reported enhanced weed control when adjuvants were added to the spray solution (2, 3, 10, 15, 16). However, adjuvants do not always increase herbicidal activity; in some cases, control may even be decreased (14, 17). The effectiveness of an adjuvant-herbicide combination depends on the particular adjuvant and herbicide used, and the weed species involved (15, 17, 19). Therefore, screens must be conducted to identify the most efficacious adjuvants for each individual weed control scenario.

The objectives of this research were threefold: 1) to evaluate dithiopyr for postemergence crabgrass control at various crabgrass growth stages in Michigan; 2) to identify

potentially effective adjuvants for use with dithiopyr in the field, and 3) to evaluate adjuvant-herbicide combinations for control of tillered crabgrass in the field.

MATERIALS AND METHODS

1989 Field Study

A field study was conducted during the summer of 1989 to evaluate the efficacy of dithiopyr and other pre- and postemergence herbicides for postemergence crabgrass control at three different growth stages. The research site consisted of a weedy area with a previous history of crabgrass infestation at the Hancock Turfgrass Research Center, East Lansing, Michigan. Glyphosate (1.1 kg ai/ha) was applied in April of 1989 to kill existing vegetation, and the site was overseeded with large crabgrass to supplement the natural population of large and smooth crabgrass. The area was fertilized with 24 kg N/ha in May. Trimec was applied at 3.5 l/ha on 6/14/89 and 8/21/89 to control broadleaf weeds. The plots were mowed as needed to maintain the height at 5 cm. The experimental area was not irrigated, however, rainfall was plentiful during the application period (late May to early July). The soil at the site was an Owosso-Marlette sandy loam complex (Fine-loamy, mixed, mesic, Typic Hapludalfs).

A randomized complete block design was used with three replications. Individual plots measured 1.2 m x 1.8 m. Liquid treatments were applied with a four nozzle boom-CO_2

backpack sprayer delivering 449 L/ha at 0.21 MPa. Granular treatments were weighed and applied with a shaker bottle. All early-postemergence treatments were applied at the 2 to 3-leaf stage on 6/2/89, with the exception of the quinchlorac treatment (1.12 kg ai/ha applied as a late preemergent on 5/23/89), and the DCPA + fenoxaprop treatment (11.8 kg ai/ha DCPA applied as a late preemergent on 5/23/89, and 0.28 kg ai/ha fenoxaprop applied at the 2 to 4-tiller stage on 6/23/89). The mid-postemergence treatments were applied at the 2 to 4-tiller stage on 6/23/89. The late-postemergence treatments were applied at the 4 to 6-tiller stage on 7/7/89. No rainfall occurred for at least 24 hours after the application of all treatments.

Percent crabgrass cover was visually estimated at the time of each treatment application and at two week intervals following application. Data were converted to percent control using the formula:

$$\text{percent control} = [(\text{initial\%} - \text{final\%})/\text{initial\%}]*100$$

Data were transformed by the arcsin transformation and the analysis of variance and LSD multiple range test were performed on the transformed data. Means reported are actual percent control values.

Greenhouse Adjuvant Screens

In April and May of 1990, ninety-five adjuvants were screened in the greenhouse for enhancement of postemergence dithiopyr activity on large crabgrass. For practical reasons, the adjuvants were broken down into subsets of the 95, and twelve separate screening experiments were performed. Most adjuvants were tested three times. Two commonly used adjuvants, X-77 and Herbimax, were included in all twelve experiments as internal standards. Two herbicide-only treatments and two control treatments were also included in all twelve experiments to provide a basis for comparison. Because of a scarcity of material, Dow Corning 8034-150-1 and 8034-150-9 were tested only twice.

A completely randomized design, with four replications per treatment, was used for all screens. Large crabgrass was grown from seed in 355-ml styrofoam cups; on the day of treatment, cups were thinned to one plant each. Plants were treated at the three-leaf stage in the first two sets of screens, and at the two-tiller stage in the third set. Dithiopyr (MON-15151 formulation) was applied to the plants at a rate of 0.03 kg ai/ha. Preliminary dose-response studies indicated that this rate would give approximately 50% control with no adjuvants. Liquid adjuvants were added to the spray

solution at a rate of 0.5% V/V, and dry adjuvants were added at 0.5% W/V. Treatments were applied using a trolley sprayer delivering 163 l/ha at a pressure of 0.21 MPa. Plants were placed in the greenhouse under automatic irrigation, however, no irrigation was applied to the plants for at least 8 hours following treatment. Supplemental lighting provided by metal-halide vapor lamps maintained a 16 hour day length. Plants were fertilized weekly with 50 ml of Peter's 20-20-20 solution, containing 238 ppm N.

Three weeks after treatment, shoot fresh weights were taken. Percent control values were calculated based on the average shoot fresh weights of the control treatments. The data were transformed by the arcsin transformation and the analysis of variance and Tukey's Honestly Significant Difference multiple range test were performed on the transformed data. A scoring system was devised in which an adjuvant received one-half point if it gave significantly greater control than one herbicide-alone treatment in its particular group, and a full point if greater than both. Data reported are the number of points over the number of times the adjuvant was tested (Table 4).

1990 Field Study

A field study was conducted during the spring and summer of 1990 to evaluate the effect of adjuvants on postemergence crabgrass control at three different growth stages with dithiopyr. The research site was in the same general area as the 1989 field study, but in a section that was not treated with preemergence herbicides in 1989. The site was seeded with 49 kg/ha 'Newport' Kentucky bluegrass (Poa pratensis L. cv. Newport) in October of 1989 and was 50-60% established by April of 1990. Large crabgrass was overseeded into the existing turf in April of 1990 to supplement the natural population of smooth and large crabgrass. The area was fertilized with 24 kg N/ha in May. Trimec was applied at 3.5 l/ha on 7/19/90 to control broadleaf weeds. The plots were mowed once or twice weekly to maintain the height at 3.8 cm. Supplemental irrigation was applied as needed to prevent drought stress.

A randomized complete block design was used with three replications. Plot size and treatment application method were the same as in the 1989 field study, except that the spray pressure was increased to 0.28 MPa, giving a spray volume of 533 l/ha. The early-postemergence treatments were applied at the 2 to 3-leaf stage on 6/14/90, the mid-postemergence

treatments at the 2 to 3-tiller stage on 7/10/90, and the late-postemergence treatments at the 3 to 6-tiller stage on 8/1/90. No rainfall occurred for at least 24 hours after the application of all treatments.

Percent crabgrass cover was estimated at 4 and 8 weeks after the early-postemergence treatments, 2, 4 and 9 weeks after the mid-postemergence treatments, and 2, 4 and 6 weeks after the late-postemergence treatments. Percent cover was estimated by placing a 1.2 m x 1.8 m grid, with 112 equally spaced intersections, over each plot and counting the number of times a crabgrass plant occurred under an intersection. Data were converted to percent control based on the average crabgrass cover in the control plots for each replication. Data were transformed by the arcsin transformation and the analysis of variance and LSD multiple range test were performed on the transformed data. Means reported are actual percent control values.

RESULTS AND DISCUSSION

1989 Field Study

Two emulsifiable concentrate formulations of dithiopyr, MON-15104 and MON-15151, and two granular formulations, MON-15111 and MON-15112, provided acceptable (85% or greater) control of 2 to 3-leaf crabgrass, at rates ranging from 0.42-0.84 kg ai/ha, by 4 weeks after treatment (WAT) (Table 1). MON-15104 at 0.56 kg ai/ha was an exception: it provided only 76% control, as compared with 89% for the 0.42 kg ai/ha rate of the same formulation. However, this difference was not statistically significant, and probably is a reflection of the somewhat variable crabgrass infestation levels in the plots early in the season. MON-15175, a granular formulation, did not give acceptable control at 0.42 or 0.56 kg ai/ha. Overall, the sprayable formulations gave slightly greater control than the granular formulations, though differences were not statistically significant.

Dithiopyr exerted its effect on the crabgrass plants more slowly than quinchlorac or the fenoxaprop-dinitroaniline combinations (Table 1). Dithiopyr took 4 weeks to reach peak control levels, while the other compounds typically reached maximum control levels within 2 weeks. Control with all

treatments, except the sequential quinchlorac applications, began to drop by 6 WAT due to late germination and/or regrowth of crabgrass. Single applications of quinchlorac plus surfactant, and fenoxaprop, gave very little control after 6 weeks. Interestingly, quinchlorac without surfactant, applied as a late preemergent, provided significantly greater control after 6 weeks than the single applications of quinchlorac plus surfactant. Perhaps the surfactant, acting as a wetting agent, causes increased movement of the active ingredient through the soil profile, and past the zone of crabgrass germination. Combining fenoxaprop with pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] or Team, a combination of benefin [N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine] and trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine], extended control somewhat over fenoxaprop alone, but control was essentially gone after 8 weeks.

The dithiopyr treatments, particularly the emulsifiable concentrate formulations, had a longer residual control than the other compounds. After 8 weeks, control with the MON-15104 and MON-15151 treatments ranged from 42-75%, which, in most cases, was significantly greater than the single applications of quinchlorac plus surfactant, and the

fenoxaprop treatments. It should be noted that 50% control with these treatments represents fairly low crabgrass levels since initial crabgrass levels in the plots averaged only about 10%. The longer residual control given by dithiopyr is a reflection of its outstanding preemergence activity.

When applied at the 2 to 4-tiller, or the 4 to 6-tiller crabgrass growth stage, dithiopyr (MON-15151) gave essentially no control at rates of 0.42-0.84 kg ai/ha (Tables 2 and 3). By contrast, quinchlorac plus surfactant gave outstanding control of 2 to 4-tiller crabgrass through 8 WAT (Table 2). Fenoxaprop alone, and in combination with pendimethalin, gave outstanding control initially, but control gradually decreased due to regrowth in the plots. Quinchlorac plus surfactant also provided outstanding initial control of 4 to 6-tiller crabgrass, but control decreased over time with regrowth of the crabgrass (Table 3). Fenoxaprop alone did not produce acceptable control of 4 to 6-tiller crabgrass. When combined with pendimethalin, however, 0.39 kg ai/ha of fenoxaprop did give outstanding control at 4 WAT. MSMA (monosodium salt of methylarsonic acid) provided poor control of 2-4 and 4 to 6-tiller crabgrass.

Conclusions drawn from this study are the following: 1) dithiopyr provides effective early-postemergence crabgrass

control at rates as low as 0.42 kg ai/ha; 2) control is longer lasting than that provided by quinchlorac, fenoxaprop, and fenoxaprop combined with pendimethalin or Team; 3) dithiopyr does not give acceptable control of tillered crabgrass.

Greenhouse Adjuvant Screens

The vast majority of the adjuvants tested in the greenhouse increased crabgrass control dramatically over dithiopyr alone. For example, if dithiopyr alone gave 30-40% control, it was not unusual to achieve control levels of greater than 90% when most adjuvants were added to the spray solution (data not shown). No adjuvants resulted in significant decreases in control. Consequently, it was difficult to separate superior adjuvants from inferior ones solely on the basis of percent control values, although some adjuvants did seem to perform consistently better than others on the basis of visual observation. For this reason, we chose Tukey's Honestly Significant Difference multiple range test at p=0.01 for the statistical evaluation, giving us a conservative range test with a high power for detecting differences among treatments. Using the statistical evaluation with the scoring system previously described, we were able to rank the adjuvants (Table 4).

Very slight differences in the sizes of the treated plants between groups resulted in differences in the amount of control provided by the herbicide alone; thus, all adjuvants were not subjected to equally stringent tests. With this in mind, we decided to combine the statistical evaluation with visual observations in order to identify the most efficacious adjuvants.

Our objective was to identify 10 adjuvants, out of the 95 tested, that had high potential for increasing dithiopyr activity on tillered crabgrass in the field, and that included representatives from the various sources at our disposal. A wide representation of adjuvant types was desired because different types may perform dissimilarly under varying environmental conditions. The ten selected for field evaluation (with Table 4 scores in parentheses) were Pfizer 14636-181-7 (3/3), Dash (3/3), Agsco Sunit (3/3), Dow Corning X2-5309 (2.5/3), Dow Corning 6955-145 (2.5/3), CSY-77715512 (2.5/3), Activator 90 (2/3), Pfizer M (2/3), X-77 (7.5/12) and Herbimax (7/12). The first six adjuvants listed were selected due to excellent performance and representation from different sources. Activator 90 and Pfizer M warranted selection despite scoring only 2/3, because they were noticeably superior to other adjuvants in their first two groups.

Herbimax and X-77 are widely used adjuvants, and so were included as standard treatments.

1990 Field Study

The spring and summer of 1990 were cooler than normal; consequently, it was not a favorable year for crabgrass growth. The resulting lack of crabgrass pressure led to greater control with all compounds than in 1989. Particularly notable is the increased control achieved with dithiopyr on tillered crabgrass in 1990 (Tables 6 and 7).

Adding adjuvants to the spray solution did not result in increased crabgrass control with dithiopyr at the 1 to 3-leaf growth stage (Table 5). Dithiopyr alone, at 0.42 kg ai/ha, gave 90% control by four WAT. This result was not unexpected since the early postemergence activity of dithiopyr is well established. All adjuvants, in combination with dithiopyr at the 0.42 kg ai/ha rate, provided 87-90% control, with the exception of Pfizer M, which resulted in only 57% control. This adjuvant seemed to become more effective as the crabgrass matured (Tables 6 and 7).

The level of control provided by the dithiopyr/adjuvant treatments at 4 WAT was similar to that given by fenoxaprop (0.13 and 0.20 kg ai/ha) and fenoxaprop tank-mixed with

pendimethalin (0.09 + 1.68 kg ai/ha). Pendimethalin alone gave poor control (Table 5). Newly germinated crabgrass plants in the plots where fenoxaprop alone was applied caused a decrease in control by 8 WAT, whereas control remained fairly constant with all other treatments, except for the 0.14 kg ai/ha rate of dithiopyr plus Activator 90. For single applications, then, dithiopyr is clearly superior to strictly postemergence products for extended early-postemergence control due to its preemergence activity.

When applied at the 2 to 3-tiller growth stage, several adjuvants, in combination with dithiopyr, gave significantly greater control at 4 WAT than dithiopyr alone (Table 6). These included Dow Corning 6955-145, Dow Corning X2-5309, CSY-77715512, X-77 and Activator 90. Other adjuvants performing well were Agsco Sunit, Herbimax, and Pfizer 14636-181-7. Combining Dash with dithiopyr decreased control slightly in comparison with the herbicide alone, though the difference was not statistically significant. Control with dithiopyr plus the more efficacious adjuvants was similar to that obtained with fenoxaprop (0.20 kg ai/ha) and the sequential MSMA treatment (2.24 + 2.24 kg ai/ha at a 4 week interval). A single application of MSMA resulted in poor control. Ratings taken at the end of the season (9 WAT) revealed that all

treatments had maintained fairly even control, except for fenoxaprop, which decreased from 96% at 4 WAT to 77% at 9 WAT, indicating some regrowth or regermination had occurred in those plots.

The higher crabgrass growth pressure at the 3 to 6-tiller stage resulted in more typical, slow-developing dithiopyr control, taking four weeks to reach maximum control levels (Table 7). All dithiopyr/adjuvant combinations, except dithiopyr at the lower rates of 0.14 and 0.28 kg ai/ha plus Activator 90, gave greater control at 4 WAT than dithiopyr alone; however the differences were not statistically significant. Control with dithiopyr alone dropped from 74% at 4 WAT to 49% at 6 WAT, due to regrowth in those plots. Meanwhile, control with the dithiopyr/adjuvant treatments remained constant, leading to significantly increased control with Dow Corning X2-5309, Pfizer 14636-181-7, CSY-77715512, Herbimax and Dash. Other adjuvants performing well were Pfizer M, Dow Corning 6955-145 and Activator 90.

Lowering the rate of dithiopyr to 0.28 and 0.14 kg ai/ha, in combination with Activator 90, resulted in slight decreases in early-postemergence control compared with the 0.42 kg ai/ha rate of dithiopyr alone (Table 5). The differences in control were more pronounced at 8 WAT,

especially with the lowest rate. However, when applied mid- or late-postemergence, Activator 90 plus dithiopyr at 0.28 kg ai/ha provided greater control (though not statistically different) than dithiopyr alone at 0.42 kg ai/ha. This suggests that a lower rate of dithiopyr, in combination with adjuvants, is probably sufficient to control emerged 1 to 3-leaf plants, but does not provide the residual preemergence activity needed to achieve extended control at the early-postemergence timing.

In summary, this research indicates that effective control of tillered crabgrass is achievable by adding adjuvants to the dithiopyr spray solution. No benefit is gained by using adjuvants in combination with dithiopyr for early-postemergence crabgrass control. All adjuvants performed well, with the exceptions of Pfizer M and Dash, which gave inconsistent control at different growth stages. Based on this research, any of the remaining adjuvants would be a suitable choice for use with dithiopyr on tillered crabgrass. Cost and availability of the compounds may be the determining factor when considering which adjuvant to use. The apparent safety of dithiopyr/adjuvant combinations (discussed in Chapter 2) should make this control strategy a valuable alternative to currently available products.

Table 1. Effect of pre- and postemergence herbicides on early-postemergence crabgrass control.

Growth Stage= 2 to 3-leaf		% Crabgrass Control[a]			
Treatment	Rate (kg ai/ha)	2 WAT	4 WAT	6WAT	8 WAT
MON-15104	0.84	57 d-g	100 a	90 ab	75 ab
MON-15151	0.42	48 f-h	98 ab	82 a-e	65 a-c
Fenoxaprop + Team	0.13 + 2.24	98 ab	98 ab	72 a-e	10 de
Quinchlorac + BAS090[c]	0.84 + 2.3 l/ha	100 a	97 ab	97 a	97 a
Quinchlorac + BAS090	0.84 + 2.3 l/ha	98 ab	94 ab	7 hi	0 e
MON-15151	0.56	76 a-f	93 ab	67 a-f	60 a-d
Quinchlorac[b]	1.12	91 a-d	93 ab	86 a-d	54 a-d
Fenoxaprop + Team	0.09 + 2.24	100 a	91 ab	33 e-i	0 e
Fenoxaprop + Pendimethalin	0.09 + 1.68	83 a-e	90 ab	47 b-h	7 de
Fenoxaprop + Pendimethalin	0.13 + 1.68	93 a-c	90 ab	47 c-h	0 e
DCPA[b] + Fenoxaprop[d]	11.8 + 0.28	90 a-d	89 ab	41 b-h	27 de
MON-15112	0.84	58 d-g	89 ab	76 a-e	51 a-d
MON-15104	0.42	78 a-f	89 ab	61 a-g	56 b-d
MON-15111	0.42	60 c-g	87 ab	44 c-h	31 c-e
MON-15112	0.56	45 e-h	85 ab	72 a-e	27 de
Quinchlorac + BAS090[c]	1.12 + 2.3 l/ha	100 a	80 ab	87 a-c	87 ab
Quinchlorac + BAS090	1.12 + 2.3 l/ha	100 a	85 a-c	35 e-i	0 e
Fenoxaprop	0.13	73 b-g	80 a-c	20 f-i	0 e
MON-15104	0.56	54 d-g	76 a-c	72 a-e	42 b-e
Fenoxaprop	0.20	53 e-h	73 bc	0 i	0 e
MON-15175	0.56	17 hi	50 cd	40 d-i	23 de
MON-15175	0.42	33 g-i	33 d	22 g-i	22 de
MSMA	2.24	38 f-h	17 de	0 i	0 e
MSMA[c]	2.24	0 i	0 e	0 i	0 e
CONTROL		0 i	0 e	0 i	0 e
CONTROL		0 i	0 e	0 i	0 e

[a]Means followed by the same letter are not significantly different by LSD at p=0.05

[b]Applied as a late-preemergent on 5/23/89

[c]Treatment repeated after 4 weeks

[d]Applied at 2 to 4-tiller stage on 6/23/89

Table 2. Effect of pre- and postemergence herbicides on mid-postemergence crabgrass control.

Growth Stage= 2 to 4-tillers		% Crabgrass Control[a]			
Treatment	Rate (kg ai/ha)	2 WAT	4 WAT	6 WAT	8 WAT
Quinchlorac + BAS090	0.84 + 2.3 l/ha	98 a	95 a	93 a	88 a
Quinchlorac + BAS090	1.12 + 2.3 l/ha	97 a	93 a	92 a	90 a
Fenoxaprop + Pendimethalin	0.28 + 1.68	93 a	70 ab	50 b	7 b
Fenoxaprop	0.28	93 ab	68 ab	8 cd	0 c
Fenoxaprop + Pendimethalin	0.13 + 1.68	90 ab	47 abc	11 cd	0 c
Fenoxaprop + Pendimethalin	0.20 + 1.68	88 ab	53 bcd	27 c	0 c
Fenoxaprop	0.20	86 ab	20 cde	0 d	0 c
MON-15151	0.84	10 b	10 e	0 d	0 c
MSMA[b]	2.24	6 b	0 e	0 d	0 c
MSMA	2.24	6 b	0 e	0 d	0 c
MON-15151	0.56	0 b	0 e	0 d	0 c
MON-15151	0.42	0 b	0 e	0 d	0 c
CONTROL		0 b	0 e	0 d	0 c
CONTROL		0 b	0 e	0 d	0 c

[a]Means followed by the same letter are not significantly different by LSD at p=0.05

[b]Treatment repeated after 4 weeks

Table 3. Effect of pre- and postemergence herbicides on late-postemergence crabgrass control.

Growth Stage= 4 to 6-tiller		% Crabgrass Control[a]			
Treatment	Rate (kg ai/ha)	2 WAT	4 WAT	6 WAT	8 WAT
Fenoxaprop + Pendimethalin	0.39 + 1.12	70 c	96 a	70 a	67 a
Fenoxaprop + Pendimethalin	0.20 + 1.68	76 bc	82 a	54 a	47 ab
Quinchlorac + BAS090	0.84 + 2.3 l/ha	95 a	81 a	65 a	61 a
Fenoxaprop	0.28	59 c	79 a	52 a	29 abc
Fenoxaprop + Pendimethalin	0.28 + 1.12	72 c	78 a	49 a	33 abc
Fenoxaprop	0.20	70 c	77 a	34 ab	22 abc
Quinchlorac + BAS090	1.12 + 2.3 l/ha	96 ab	74 a	61 a	58 ab
MON-15151	0.84	0 d	26 b	6 bc	8 bc
MSMA	2.24	53 c	18 b	0 c	0 c
MON-15151	0.42	0 d	12 bc	0 c	0 c
MSMA[b]	2.24	20 d	0 c	0 c	0 c
MON-15151	0.56	0 d	0 c	0 c	24 bc
CONTROL		2 d	0 c	0 c	0 c
CONTROL		0 d	0 c	0 c	11 bc

[a]Means followed by same letter are not significantly different by LSD at p=0.05

[b]Treatment repeated after 4 weeks

Table 3. Effect of pre- and postemergence herbicides on late-postemergence crabgrass control.

Growth Stage= 4 to 6-tiller		% Crabgrass Control[a]			
Treatment	Rate (kg ai/ha)	2 WAT	4 WAT	6 WAT	8 WAT
Fenoxaprop + Pendimethalin	0.39 + 1.12	70 c	96 a	70 a	67 a
Fenoxaprop + Pendimethalin	0.20 + 1.68	76 bc	82 a	54 a	47 ab
Quinchlorac + BAS090	0.84 + 2.3 l/ha	95 a	81 a	65 a	61 a
Fenoxaprop	0.28	59 c	79 a	52 a	29 abc
Fenoxaprop + Pendimethalin	0.28 + 1.12	72 c	78 a	49 a	33 abc
Fenoxaprop	0.20	70 c	77 a	34 ab	22 abc
Quinchlorac + BAS090	1.12 + 2.3 l/ha	96 ab	74 a	61 a	58 ab
MON-15151	0.84	0 d	26 b	6 bc	8 bc
MSMA	2.24	53 c	18 b	0 c	0 c
MON-15151	0.42	0 d	12 bc	0 c	0 c
MSMA[b]	2.24	20 d	0 c	0 c	0 c
MON-15151	0.56	0 d	0 c	0 c	24 bc
CONTROL		2 d	0 c	0 c	0 c
CONTROL		0 d	0 c	0 c	11 bc

[a]Means followed by same letter are not significantly different by LSD at p=0.05

[b]Treatment repeated after 4 weeks

Table 4. Greenhouse adjuvant screens with dithiopyr.

Adjuvant	Times better[a]/times tested
Pfizer 14636-181-7	3/3
Dash	3/3
Agsco Sunit	3/3
Frigate	3/3
Dow Corning 8687-12-1	3/3
Dow Corning X2-5309	2.5/3
Dow Corning 6955-145	2.5/3
Dow Corning X2-5177-B	2.5/3
Dow Corning 6736-99	2.5/3
Dow Corning 8687-12-3	2.5/3
Dow Corning 8687-12-9	2.5/3
Dow Corning 8034-150-2	2.5/3
CSY-77715510	2.5/3
CSY-77715512	2.5/3
CSY-77715514	2.5/3
CSY-7771552	2.5/3
CSY-7771553	2.5/3
Dow Corning 8034-150-1	1.5/2
Activator 90	2/3
Pfizer A	2/3
Pfizer B	2/3
Pfizer D	2/3
Pfizer M	2/3
Pfizer 14636-181-2	2/3
Pfizer 14636-181-3	2/3
Pfizer 14636-181-4	2/3
Pfizer 14636-181-6	2/3
Pfizer 14636-181-9	2/3
Dow Corning A	2/3
Dow Corning X2-5177-A	2/3
Dow Corning X2-5152	2/3
Dow Corning X2-5211	2/3

Table 4 (cont'd.).

Adjuvant	Times better[a]/times tested
Dow Corning 6584-14	2/3
CSY-77715515	2/3
CSY-77715516	2/3
CSY-7771551	2/3
CSY-7771554	2/3
CSY-7771559	2/3
Dow Corning 8687-12-2	2/3
Dow Corning 8687-12-8	2/3
Dow Corning 8034-150-3	2/3
Dow Corning 8034-150-6	2/3
X-77	7.5/12
Herbimax	7/12
Pfizer C	1.5/3
Pfizer E	1.5/3
Pfizer L	1.5/3
Pfizer 14636-181-1	1.5/3
Pfizer 14636-181-8	1.5/3
Pfizer 14636-181-11	1.5/3
Dow Corning B	1.5/3
Dow Corning 6584-109	1.5/3
Dow Corning 6584-17	1.5/3
CSY-77715511	1.5/3
Dow Corning 8687-12-7	1.5/3
Dow Corning 8034-150-10	1.5/3
Dow Corning 8034-150-11	1.5/3
Pfizer H	1/3
Pfizer I	1/3
Dow Corning 6584-151	1/3
Dow Corning 6736-30	1/3
Dow Corning 6736-110	1/3
Dow Corning 6736-108	1/3
Dow Corning 8687-12-4	1/3

Table 4 (cont'd.).

Adjuvant	Times better[a]/times tested
Dow Corning 8687-12-5	1/3
Dow Corning 8687-12-6	1/3
Dow Corning 8034-150-4	1/3
Dow Corning 8034-150-5	1/3
Dow Corning 8034-150-7	1/3
Dow Corning 8034-150-12	1/3
Dow Corning 8034-40	1/3
Dow Corning 8687-25-7	1/3
Dow Corning 8034-150-14	1/4
Pfizer 14636-181-5	0.5/3
Triton X-114	0.5/3
Dow Corning 6955-7	0.5/3
Dow Corning 8034-150-15	0.5/3
Dow Corning 8034-85	0.5/3
Dow Corning 8687-25-5	0.5/3
Dow Corning 8034-150-9	0/2
Pfizer F	0/3
Pfizer G	0/3
Pfizer J	0/3
Pfizer K	0/3
Dow Corning 6584-16	0/3
Dow Corning 8034-150-8	0/3
Dow Corning 8034-150-13	0/3
Dow Corning 8687-25-3	0/3
Dow Corning 8687-25-6	0/3
Dow Corning 8687-25-8	0/3
Dow Corning 8687-25-9	0/3
LI700	0/3
Bond	0/3

[a]Significantly better than dithiopyr alone by Tukey's Honestly Significant Difference test at p=0.01

Table 5. Early-postemergence crabgrass control with dithiopyr and adjuvants.

Growth Stage= 1 to 3-leaf		% Crabgrass Control[a]	
Treatment	Rate (kg ai/ha)	4 WAT	8 WAT
Fenoxaprop + Pendimethalin	0.09 + 1.68	97 a	95 a
MON-15104	0.42	90 ab	94 a
MON-15104 + Activator 90	0.42 + 0.5% v/v	90 ab	86 abc
MON-15104 + CSY-77715512	0.42 + 0.5% v/v	90 ab	88 abc
MON-15104 + Dow Corning 6955-145	0.42 + 0.5% v/v	90 ab	90 abc
MON-15104 + Herbimax	0.42 + 0.5% v/v	90 ab	91 abc
MON-15104 + Dash	0.42 + 0.5% v/v	87 ab	95 ab
MON-15104 + X-77	0.42 + 0.5% v/v	87 ab	88 abc
MON-15104 + Agsco Sunit	0.42 + 0.5% v/v	87 ab	94 ab
Fenoxaprop	0.20	87 ab	51 bc
MON-15104 + Pfizer 14636-181-7	0.42 + 0.5% v/v	87 ab	92 ab
MON-15104 + Dow Corning X2-5309	0.42 + 0.5% v/v	87 ab	82 abc
MON-15104 + Activator 90	0.28 + 0.5% v/v	84 ab	75 abc
Fenoxaprop	0.13	82 ab	65 abc
MON-15104 + Activator 90	0.14 + 0.5% v/v	79 ab	50 bc
Pendimethalin	1.68	58 b	50 c
MON-15104 + Pfizer M	0.42 + 0.5% v/v	57 b	62 abc
CONTROL		0 c	0 d

[a]Means followed by the same letter are not significantly different by LSD at p=0.05

Table 6. Mid-postemergence crabgrass control with dithiopyr and adjuvants.

Growth Stage= 2 to 3-tillers		% Crabgrass Control[a]		
Treatment	Rate (kg ai/ha)	2 WAT	4 WAT	9 WAT
MON-15104 + Dow Corning 6955-145	0.42 + 0.5% v/v	96 ab	97 a	93 abc
Fenoxaprop	0.20	98 a	96 ab	77 bcd
MON-15104 + CSY-77715512	0.42 + 0.5% v/v	86 abcd	96 ab	98 ab
MON-15104 + Dow Corning X2-5309	0.42 + 0.5% v/v	98 a	96 ab	100 a
MON-15104 + X-77	0.42 + 0.5% v/v	89 abc	94 ab	93 abc
MON-15104 + Activator 90	0.42 + 0.5% v/v	89 ab	92 ab	93 abc
MSMA	2.24 + 2.24	92 ab	93 abc	88 abcd
MON-15104 + Agsco Sunit	0.42 + 0.5% v/v	96 ab	92 abc	95 ab
MON-15104 + Herbimax	0.42 + 0.5% v/v	94 ab	91 abc	87 abcd
MON-15104 + Pfizer 14636-181-7	0.42 + 0.5% v/v	92 ab	89 abc	98 ab
MON-15104 + Activator 90	0.28 + 0.5% v/v	90 ab	86 abcd	84 abc
MON-15104 + Pfizer M	0.42 + 0.5% v/v	94 ab	81 bcd	76 abcd
MON-15104	0.42	73 bcd	72 cd	82 abcd
MON-15104 + Dash	0.42 + 0.5% v/v	61 cd	65 de	59 d
MON-15104 + Activator 90	0.14 + 0.5% v/v	70 bcd	64 de	63 cd
MSMA	2.24	58 d	45 e	64 cd
CONTROL		0 e	0 f	0 e

[a]Means followed by the same letter are not significantly different by LSD at p=0.05

Table 7. Late-postemergence crabgrass control with dithiopyr and adjuvants.

Growth Stage= 3 to 6-tillers		% Crabgrass Control[a]		
Treatment	Rate (kg ai/ha)	2 WAT	4 WAT	6 WAT
Fenoxaprop	0.28	93 a	97 a	98 a
MON-15104 + Dow Corning X2-5309	0.42 + 0.5% v/v	56 abc	90 ab	93 a
MON-15104 + Dash	0.42 + 0.5% v/v	51 abc	83 ab	92 a
MON-15104 + CSY-77715512	0.42 + 0.5% v/v	60 abc	85 ab	90 ab
MON-15104 + Herbimax	0.42 + 0.5% v/v	64 ab	89 ab	90 ab
MON-15104 + Pfizer 14636-181-7	0.42 + 0.5% v/v	63 abc	86 ab	86 ab
MON-15104 + Pfizer M	0.42 + 0.5% v/v	69 ab	90 ab	87 abc
MON-15104 + Dow Corning 6955-145	0.42 + 0.5% v/v	54 abc	88 ab	87 abc
MON-15104 + Activator 90	0.42 + 0.5% v/v	46 abc	83 ab	85 abc
MON-15104 + X-77	0.42 + 0.5% v/v	59 abc	89 ab	80 abc
MON-15104 + Agsco Sunit	0.42 + 0.5% v/v	46 abc	90 ab	80 abc
MON-15104 + Activator 90	0.28 + 0.5% v/v	40 bc	74 bc	74 abc
MON-15104 + Activator 90	0.14 + 0.5% v/v	24 cd	51 c	57 bc
MON-15104	0.42	31 bcd	74 bc	49 c
CONTROL		0 d	0 d	0 d

[a]Means followed by the same letter are not significantly different by LSD at p=0.05

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Chapter 2

SAFETY OF DITHIOPYR TO FINE FESCUES AND KENTUCKY BLUEGRASS AND OF DITHIOPYR-ADJUVANT COMBINATIONS TO KENTUCKY BLUEGRASS

ABSTRACT

Forty-two varieties, representing three fine fescue subspecies, were treated with dithiopyr at rates of 0, 0.42 and 0.84 kg ai/ha in a May 1989 field study. Unacceptable injury occurred only with the high rate. While there were some significant differences in injury among varieties of the same species, dithiopyr was more phytotoxic to the chewings fescues than to the hard or creeping red fescues. In a 1990 field study, Kentucky bluegrass was treated with dithiopyr, at 0.42 kg ai/ha, in combination with ten different adjuvants. Fenoxaprop at 0.20 kg ai/ha was included as a comparison treatment. None of the dithiopyr/adjuvant combinations injured the Kentucky bluegrass, while fenoxaprop resulted in unacceptable injury. In a field study initiated in 1989 on a Kentucky bluegrass turf, two consecutive annual applications of dithiopyr at 0.42, 0.84 and 1.12 kg ai/ha, prodiamine at 0.84 kg ai/ha, pendimethalin at 3.36 kg ai/ha, and oxadiazon at 2.24 and 4.48 kg ai/ha, resulted in no significant reduction of Kentucky bluegrass root dry weight. Nomenclature: Dithiopyr, 3,5-pyridinedicarbothioic acid,2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-S,S-

dimethylester; fenoxaprop, (±)-2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoic acid; prodiamine, 2,6-dinitro-*N*′,*N*′,-dipropyl-6-(trifluoromethyl)-1,3-benzenediamine; pendimethalin, *N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine; oxadiazon, 3-[2,4-dichloro-5-(1-methylethoxy)phenyl]-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2-(3*H*)-one; fine fescue, *Festuca* spp.; chewings fescue, *Festuca rubra* L. ssp. *commutata* Gaud.; hard fescue, *Festuca longifolia* Thuill.; creeping red fescue, *Festuca rubra* L.; Kentucky bluegrass, *Poa pratensis* L.

Additional index words. Herbicide injury, tolerance, crabgrass control, *Digitaria* spp.

INTRODUCTION

Safety to desirable turfgrasses is an integral component of successful crabgrass control with pre- or postemergence herbicides. Injury caused by a particular herbicide may be a function of herbicide rate, turfgrass species, spray additives, or a combination of the above. Consequently, safety of a new herbicide to desirable species must be evaluated over a range of conditions.

Dithiopyr is a new herbicide from the Monsanto Agricultural Company with excellent preemergence and early postemergence crabgrass (<u>Digitaria</u> spp.) activity at rates of 0.28 to 0.56 kg ai/ha (1, 6, 7). Parrish et al. (16) reported no foliar injury from dithiopyr at rates as high as 4.48 kg ai/ha to bermudagrass [<u>Cynodon dactylon</u> (L.)Pers.], St. Augustinegrass [<u>Stenotaphrum secundatum</u> (Walt.)Ktze.], centipedegrass [<u>Eremochloa ophiuroides</u> (Munro.)Hack.], carpetgrass (<u>Axonopus affinis</u> Chase), zoysiagrass (<u>Zoysia</u> spp.), tall fescue (<u>Festuca arundinacea</u> Schreb.), Kentucky bluegrass, perennial ryegrass (<u>Lolium perenne</u> L.), and creeping bentgrass (<u>Agrostis palustris</u> Huds.). However, Brauen et al. (3) observed darkening and thinning of creeping bentgrass when treated with dithiopyr at 2.24 and 4.48 kg ai/ha. At more typical use rates of 0.28 and 0.56 kg ai/ha, these researchers observed no injury. Other researchers have reported safety on creeping bentgrass (1) and zoysiagrass (6) at 1.12 kg ai/ha, and perennial ryegrass (1) and Kentucky bluegrass (10) at 0.84 kg ai/ha. Thinning of the turfs at higher rates was generally the first injury symptom reported. No published information on dithiopyr phytotoxicity to the fine fescues is available. This represents a significant gap in the knowledge base, because these grasses are prone to injury from other pre- and postemergence crabgrass herbicides (5, 11, 17, 21).

Differences sometimes exist in herbicide tolerance among cultivars of a particular species. Bensulide [_O_,_O_-bis(1-methylethyl) _S_-[2-[(phenylsulfonyl)amino] ethyl]phosphorodithioate] and simazine (6-chloro-_N_,_N_′-diethyl-1,3,5-triazine-2,4-diamine) reduced root weight of 'Belair' zoysiagrass (_Zoysia japonica_ Steud.) but not 'Meyer' (9). Bingham (2) reported inhibition of 'Tifgreen' bermudagrass (_C. dactylon_ L. x _C. transvaalensis_ Davy. 'Tifgreen') rooting by siduron [_N_-(2-methylcyclohexyl)-_N_′-phenylurea], bensulide, benefin [_N_-butyl-_N_-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine] and DCPA (dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate); yet Dernoeden et al.

(8) found no inhibition of 'Midiron' bermudagrass by the same herbicides at similar rates. In cases such as these, varietal tests for herbicide tolerance become necessary.

Adding adjuvants to the spray solution can change the selectivity characteristics of a herbicide. While the addition of an adjuvant may increase activity on the target weed, heightened injury to desirable species can be an unwanted side effect. Torello and Jagschitz (19) observed increased injury to desirable turf when surfactants were combined with DCPA. Jagschitz and Sawyer (12) noted injury in one of four Kentucky bluegrass lawns when X-77, a surfactant, was added to 0.84 kg ai/ha dithiopyr. Hurto and Schaber, using the same dithiopyr rate without surfactant, observed no injury to Kentucky bluegrass (10).

Because dithiopyr is a new herbicide, little is known concerning its long term effects on turfgrasses. Research with other preemergence herbicides suggests that long term effects depend on the herbicide and turfgrass species used. Callahan (4) applied siduron, DCPA, bensulide, benefin, bandane (polychlorodicyclopentadiene) and terbutol (2,6-di-*tert*-butyl-*p*-tolyl methylcarbamate) to creeping bentgrass for three consecutive years and found increased injury the third year in comparison with the first. Turgeon et al. (20)

reported increased thatch, decreased root growth, greater leaf spot incidence and higher wilting tendency of Kentucky bluegrass after four consecutive annual applications of calcium arsenate and bandane. Bensulide reduced verdure slightly, while DCPA, benefin and siduron had no ill effects. Johnson (13) reported that zoysiagrass rooting was not inhibited by consecutive annual applications of oxadiazon, bensulide or benefin. In a separate study, he concluded that three consecutive annual applications of bensulide, DCPA, benefin and oxadiazon did not affect the quality of Kentucky bluegrass or bermudagrass (14). Murray et al. (15) observed a decrease in Kentucky bluegrass quality following eight consecutive annual applications of DSMA (disodium salt of methylarsonic acid), but not DCPA, benefin, bensulide, and siduron.

The objectives of this research were threefold: 1) evaluate dithiopyr phytotoxicity on fine fescue types and varieties, 2) determine the effect of adjuvants on dithiopyr phytotoxicity to Kentucky bluegrass, and 3) ascertain whether consecutive annual applications of dithiopyr, prodiamine, pendimethalin or oxadiazon have a deleterious effect on Kentucky bluegrass rooting.

MATERIALS AND METHODS

Three field studies were conducted at the Hancock Turfgrass Research Center, East Lansing, Michigan. The soil at the site is an Owosso-Marlette sandy loam complex (Fine-loamy, mixed, mesic, Typic Hapludalfs). The area was fertilized with 164 kg N/ha in 1989 and 146 kg N/ha in 1990. The turf height was maintained at 4.4 cm. Supplemental irrigation was applied as needed to maintain a high quality turf.

Dithiopyr Injury to Fine Fescues

The fine fescue variety study was initiated on 5/11/89, on a five-year old fine fescue variety trial. The 42 varieties evaluated included 21 chewings, 13 creeping red, and 8 hard fescues. A split plot design with three replications was used, with fine fescue varieties as the main plots, arranged in a randomized complete block design, and dithiopyr rate as the sub plots. The main plots measured 1.2 by 1.8 m, and the sub plots 1.2 by 0.6 m. Dithiopyr, as the MON-15151 formulation, was applied at 0, 0.42 and 0.84 kg ai/ha, using a single-nozzle boom CO_2 backpack sprayer delivering 243 l/ha at 0.21 MPa. The treatments were watered in after 16 hours.

Dithiopyr injury was visually rated at 8 and 12 weeks after treatment (WAT) using a scale of 1-9, with 1 indicating no injury, and 9 indicating complete kill (Table 1). The data were subjected to analysis of variance and means were separated by the Least Significant Difference (LSD) multiple range test. Differences in dithiopyr injury among the three fine fescue subspecies were evaluated by performing orthogonal contrasts (Table 2).

Dithiopyr + Adjuvants Phytotoxicity to Kentucky Bluegrass

The dithiopyr + adjuvants phytotoxicity study was initiated on 6/14/90, on a three year old stand of 'Midnight' Kentucky bluegrass. The experiment was designed as a randomized complete block with three replications. Individual plots measured 1.2 by 1.8 m. Treatments (Table 3) were applied with a four-nozzle boom CO_2 backpack sprayer delivering 533 l/ha at 0.28 MPa. The study received no rainfall or irrigation for at least 24 hours following treatment.

Herbicide injury was rated at 17 and 28 days after treatment (DAT) using a scale of 1-9, with 1 indicating no injury, and 9 indicating complete kill (Table 3). The data were subjected to analysis of variance and treatment means were separated by the LSD multiple range test.

Preemergence Herbicide Effect on Rooting

This study was initiated on 5/5/89 on an eight year old Kentucky bluegrass sod blend. The study was designed as a randomized complete block with four replications. Individual plots measured 1.2 by 1.8 m. Treatments (Table 4) were applied on 5/5/89 and 5/9/90, except for the 1990 oxadiazon treatments, which were applied on 5/8/90. The oxadiazon treatments were applied with a shaker bottle; all others were applied with a four-nozzle boom CO_2 backpack sprayer, delivering 449 l/ha at 0.21 MPa in 1989, and 533 l/ha at 0.28 MPa in 1990. The treatments were watered in within 48 hours of application.

Root samples were collected from the plots on 6/13 and 6/14/90. A hydraulic coring device was used to remove three randomly chosen samples, each 4 cm in diameter, from each plot. The top 3 cm of the cores was considered the thatch/mat layer and was discarded. The 0-5 cm depths of the remaining cores were then placed in freezer bags and frozen until analysis. Samples were thawed and divided into four subsamples prior to washing the soil from the roots. Initial washing using a hydropneumatic elutriation method (18) removed the bulk of the soil and other debris. The samples were stored in 10% methanol and refrigerated until final washing.

The final washing was performed in the laboratory by agitating the sample, allowing soil particles to settle while removing floating debris with tweezers, then decanting the suspended roots into a fine mesh screen. The root samples were placed in aluminum weigh boats, dried overnight in a convection oven, and dry weights were taken (Table 4). The analysis of variance was then performed on the data.

RESULTS AND DISCUSSION

Dithiopyr Injury to Fine Fescues

The magnitude of dithiopyr injury to the fine fescues was dependent on both the dithiopyr rate and the fine fescue variety. A rating of 3 or greater, on a scale of 1-9, was judged to be unacceptable injury. All 42 varieties had an injury rating of less than 3 at both 8 and 12 WAT, when the dithiopyr rate was 0 or 0.42 kg ai/ha (Table 1). However, at a dithiopyr rate of 0.84 kg ai/ha, 13 varieties showed unacceptable injury 8 WAT. Notably, 12 of the 13 varieties were chewings fescues; the lone non-chewings variety was 'Pennlawn' creeping red fescue. Four varieties, all chewings fescues, still exhibited unacceptable injury 12 WAT.

Orthogonal contrasts confirmed that the chewings fescues were significantly more susceptible to dithiopyr injury through 8 WAT (Table 2). After 12 weeks the turfs had recovered sufficiently so that there were no significant differences among the types. Although an examination of Table 1 seems to suggest that hard fescues are more susceptible to dithiopyr injury than creeping red fescues, the differences were not significant by the LSD multiple range test, and the

contrast indicates no significant difference between the two types (Table 2).

This research suggests that turfgrass managers should refrain from applying dithiopyr to chewings fescues at rates above 0.42 kg ai/ha.

Dithiopyr + Adjuvants Phytotoxicity to Kentucky Bluegrass

This study was conducted on a high quality stand of 'Midnight' Kentucky bluegrass; accordingly, an injury rating of greater than 2, on scale of 1-9, was judged to be unacceptable. None of the dithiopyr/adjuvant treated plots showed any visible injury at 17 or 28 DAT. By contrast, plots treated with fenoxaprop at 0.20 kg ai/ha showed unacceptable injury at both timings.

In conclusion, the dithiopyr/adjuvant combinations and rates used in this study (Table 3), are not phytotoxic to 'Midnight' Kentucky bluegrass. When using these combinations on other Kentucky bluegrass varieties, testing of a small area before full scale usage would be prudent, because of possible varietal differences in dithiopyr phytotoxicity similar to those found with the fine fescues.

Preemergence Herbicide Effect on Rooting

The F-test for treatment effects in the analysis of variance was not significant; thus, two consecutive annual applications of dithiopyr, prodiamine, pendimethalin and oxadiazon at the rates used (Table 4) had no apparent inhibitory effect on Kentucky bluegrass rooting. Despite the lack of significance, it is interesting to note that the control treatment had the highest root dry weight. This study will be continued over the next several years, and it is possible that continued application of these herbicides will result in significant inhibition of rooting.

Table 1. Dithiopyr injury to fine fescue varieties.

		Injury (1-9)[a]					
		8 WAT			12 WAT		
		Rate (kg ai/ha)			Rate (kg ai/ha)		
Variety	Type	0	0.42	0.84	0	0.42	0.84
Weekend	Chewings	1.0	1.3	6.3	1.7	1.7	6.0
Mary	Chewings	2.0	2.0	4.7	2.0	1.0	3.3
Banner	Chewings	1.7	2.7	4.7	1.0	1.7	2.7
Atlanta	Chewings	1.3	1.7	4.3	1.0	2.0	3.7
Magenta	Chewings	1.7	2.3	3.7	1.7	1.3	2.3
Enjoy	Chewings	1.0	1.7	3.7	1.3	1.7	2.7
Ivalo	Chewings	1.7	1.7	3.7	1.3	1.3	1.0
Wilma	Chewings	1.3	1.7	3.3	1.3	1.0	1.0
Tamara	Chewings	1.3	1.3	3.3	1.7	1.3	2.3
Pennlawn	Creeping	1.7	1.3	3.3	1.0	1.0	1.7
Highlight	Chewings	1.3	1.3	3.0	1.0	1.0	1.0
Tatjana	Chewings	1.3	1.7	3.0	1.0	1.0	1.0
Victory	Chewings	1.7	2.0	3.0	1.3	1.0	1.0
Koket	Chewings	1.3	2.0	2.7	1.0	1.0	1.0
Waldorf	Chewings	1.7	1.3	2.7	1.0	1.3	2.3
Center	Chewings	2.3	2.0	2.7	1.0	1.3	1.0
Aurora	Hard	1.7	2.0	2.7	1.0	1.3	1.0
Biljart	Hard	1.3	1.7	2.7	1.0	1.3	1.7
Scaldis	Hard	1.3	1.3	2.3	1.7	1.0	2.3
Checker	Chewings	2.0	2.0	2.3	1.0	1.0	1.0
Waldina	Hard	1.7	1.7	2.3	1.0	1.0	1.0
Barfo 81-225	Hard	2.0	1.3	2.3	1.0	1.0	1.0
Shadow	Chewings	2.0	1.3	2.3	1.0	1.0	1.0
Lovisa	Creeping	2.3	2.3	2.0	1.0	2.3	1.0
Valda	Hard	2.0	2.0	2.0	1.0	1.0	1.0
Wintergreen	Creeping	1.7	2.0	2.0	1.7	2.0	1.3
Jamestown	Chewings	1.0	2.3	2.0	1.0	1.0	1.0
SR3000	Hard	1.7	2.3	2.0	1.0	1.3	1.0
430 CR	Creeping	2.0	1.3	2.0	1.7	1.3	1.0

Table 1 (cont'd.).

		Injury (1-9)[a]					
		---8 WAT---			---12 WAT---		
		---Rate (kg ai/ha)---			---Rate (kg ai/ha)---		
Variety	Type	0	0.42	0.84	0	0.42	0.84
Longfellow	Chewings	2.3	1.0	2.0	1.0	1.0	1.3
Beauty	Chewings	1.7	1.7	2.0	1.3	1.3	3.0
Commodore	Creeping	1.0	1.0	1.7	1.0	1.0	1.0
Reliant	Hard	1.7	1.7	1.7	1.0	1.0	1.0
Ensylva	Creeping	1.0	1.0	1.3	1.0	1.3	1.7
Pernille	Creeping	1.3	1.3	1.3	1.0	1.0	1.0
Ceres	Creeping	2.0	2.0	1.3	1.0	1.0	1.0
Flyer	Creeping	1.3	1.3	1.3	1.0	1.0	1.0
Estica	Creeping	1.3	1.0	1.3	1.0	1.7	1.3
Ruby	Creeping	1.3	1.3	1.0	1.0	1.0	1.0
Boreal	Creeping	1.0	1.0	1.0	1.0	1.0	1.0
Robot	Creeping	1.3	1.0	1.0	1.0	1.0	1.0
Epsom	Chewings	1.0	1.0	1.0	1.0	1.0	1.0
	$LSD_{.05}$	NS	NS	1.8	NS	NS	1.5

[a]1=no injury 9=complete kill; A rating of 3 or greater was considered to be unacceptable injury.

Table 2. Summary of dithiopyr injury to the fine fescue subspecies.

	Injury (1-9)[a]					
	8 WAT			12 WAT		
	Rate (kg ai/A)			Rate (kg ai/A)		
Type	0	0.42	0.84	0	0.42	0.84
Chewings	1.6	1.7	3.2	1.2	1.2	1.9
Creeping	1.5	1.4	1.5	1.1	1.3	1.2
Hard	1.7	1.7	2.2	1.1	1.1	1.2

Contrast	8 WAT	12 WAT
Chewings vs. others	**	NS
Creeping vs. Hard	NS	NS

**Denotes significance at p=0.01

[a]1=no injury 9=complete kill; A rating of 3 or greater was considered to be unacceptable injury.

Table 3. Dithiopyr + adjuvants phytotoxicity to 'Midnight' Kentucky bluegrass.

		Injury (1-9)[a]	
Treatment	Rate (kg ai/A)	17 DAT[b]	28 DAT[b]
MON-15104 + X-77	0.42 + 0.5% v/v	1.0	1.0
MON-15104 + Herbimax	0.42 + 0.5% v/v	1.0	1.0
MON-15104 + CSY-77715512	0.42 + 0.5% v/v	1.0	1.0
MON-15104 + Agsco Sunit	0.42 + 0.5% v/v	1.0	1.0
MON-15104 + Dow Corning 6955-145	0.42 + 0.5% v/v	1.0	1.0
MON-15104	0.42	1.0	1.0
MON-15104 + Pfizer M	0.42 + 0.5% v/v	1.0	1.3
MON-15104 + Activator 90	0.42 + 0.5% v/v	1.0	1.3
MON-15104 + Dow Corning X2-5309	0.42 + 0.5% v/v	1.0	1.3
MON-15104 + Pfizer 14636-181-7	0.42 + 0.5% v/v	1.0	1.3
CONTROL		1.0	1.3
MON-15104 + Dash	0.42 + 0.5% v/v	1.3	1.3
Fenoxaprop	0.20	2.7	3.0
	$LSD_{.05}$:	0.8	0.8

[a]1=no injury 9=complete kill; A rating of greater than 2 was considered to be unacceptable

[b]Days after treatment

Table 4. Effect of preemergence herbicides on rooting of Kentucky bluegrass.

Herbicide	Rate (kg ai/A)	Root dry weight (grams)
CONTROL		1.17
MON-15151 1EC	0.84	1.13
MON-15151 1EC	0.42	1.10
Prodiamine 65WDG	0.84	1.09
MON-15151 1EC	1.12	1.08
Pendimethalin 65WDG	3.36	1.00
Oxadiazon 2G	4.48	0.99
Oxadiazon 2G	2.24	0.98
	$LSD_{.05}$:	NS

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Chapter 3

FACTORS INVOLVED IN THE ADJUVANT ENHANCEMENT OF POSTEMERGENCE CRABGRASS CONTROL WITH DITHIOPYR

ABSTRACT

A greenhouse study was conducted to determine the site of uptake of dithiopyr applied postemergence to large crabgrass. Using barriers to isolate the foliage and the soil, the primary site of uptake was found to be via the foliage. Based on this result, adjuvants were evaluated for enhancement of postemergence crabgrass control with dithiopyr. In previously reported studies, several adjuvants significantly increased control in the field and greenhouse. Further laboratory and greenhouse studies were conducted to elucidate the factors involved in the enhancement of dithiopyr control by nine of these adjuvants. Experiments with ^{14}C-dithiopyr revealed that only two adjuvants significantly increased absorption with the MON-15104 formulation of dithiopyr, giving increases of 5.0-5.4% over the herbicide alone. Seven adjuvants significantly increased absorption with the MON-15151 formulation, giving increases of 6.2-15.2%. Despite the differences in absorption, no adjuvants resulted in increased translocation of the applied herbicide out of the treated leaf, with less than 1% translocated in all cases. However, because of the very low levels of radioactivity detected outside the treated

leaf, these studies may not have been sensitive enough to detect true adjuvant effects on translocation. A greenhouse study in which a single, isolated large crabgrass leaf was treated, indicated that enhancement of dithiopyr activity by adjuvants did involve an effect on translocation, as well as on spray retention, and on the external movement of the spray solution to the apical meristem. Enhancement seems to involve a combination of these three factors plus absorption, with the relative importance of any one factor depending on the particular adjuvant used. A temperature study revealed decreasing absorption, and increasing non-recoverability of dithiopyr, with each 10° C increase in temperature. The percent non-recoverable dithiopyr, believed to represent volatilized herbicide, ranged from 46-55% at 5° C, to 92-95% at 35° C. Volatility losses of this magnitude mitigate any positive adjuvant effects on absorption of dithiopyr. Nomenclature: dithiopyr, 3,5-pyridinedicarbothioic acid,2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-S,S-dimethylester; large crabgrass, *Digitaria sanguinalis* (L.) Scop. #[1] DIGSA.

Additional index words. Site of uptake, surfactants, volatility.

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

INTRODUCTION

Dithiopyr is a new preemergence herbicide from the Monsanto Agricultural Company. This product also effectively controls untillered crabgrass when applied postemergence. Little is known concerning the route of entry of dithiopyr into the crabgrass plant when applied postemergence. Once the route of entry is known, strategies can be explored for enhancing the postemergence activity of dithiopyr.

Herbicides can be taken up by plants through root or shoot tissue (2). If the plant foliage is the primary site of absorption, adjuvants can be used to enhance herbicidal activity. Adjuvants used in postemergence applications to increase the activity of herbicides are classified as activator adjuvants, and include surfactants and oils (6).

According to Holly (3), surfactants may influence herbicidal efficacy by increasing leaf wettability, increasing spray retention, increasing droplet spread, decreasing surface and interfacial tensions, acting as a humectant or co-solvent, or acting as a cuticle solubilizer. Sands and Bachelard (8) found that surfactants increased herbicide uptake by affecting wetting of the leaf surface and dissolving the epicuticular wax. The hydrophilic-lipophilic balance of an adjuvant may

also determine its effectiveness in enhancing herbicidal activity (5).

Many researchers have reported increased absorption of ^{14}C-labeled herbicides when adjuvants were added to the spray solution (1, 8, 9, 11, 12). Adjuvants can also increase the translocation of herbicides (3, 6). McWhorter noted that the most effective surfactants in increasing absorption were not always best in increasing herbicide translocation away from the treated area (6).

Immediately after application, herbicides begin to disappear from the target area through a variety of physical or chemical processes (10). Clearly, a high rate of loss from any process will diminish the positive effects adjuvants may otherwise have on absorption. Volatilization is one process by which herbicides are dissipated. No published information is available regarding losses of dithiopyr by volatilization. According to Nash (7), volatilization losses are influenced by the herbicide vapor pressure, application method, formulation, temperature, relative humidity, wind velocity and target surface roughness. Under unfavorable conditions, losses of herbicide residues may approach 80-90% within a few days (10).

The objectives of this research were: 1) to determine the site of uptake of dithiopyr applied postemergence to

crabgrass, and 2) to evaluate the factors involved in adjuvant enhancement of dithiopyr activity on this weed. The latter objective was pursued by examining adjuvant effects on dithiopyr absorption and translocation, investigating the factors necessary for whole plant control with dithiopyr and adjuvants, and examining the effect of temperature on dithiopyr absorption with adjuvants.

MATERIALS AND METHODS

General procedures for greenhouse experiments

Large crabgrass was grown from seed in 355 ml styrofoam cups. On the day of treatment, cups were thinned to one plant each. Dithiopyr and adjuvant treatments were applied with a trolley sprayer delivering 163 l/ha at 0.21 MPa. Following treatment, plants were placed in the greenhouse under automatic irrigation. Supplemental lighting from metal-halide vapor lamps provided a 16 hour day length. Greenhouse temperature was maintained at 22 $\pm$ 2° C. and relative humidity at 40-75%.

Site of uptake

A two factor randomized complete block design was used with six replications. The factors were dithiopyr (MON-15151) rate and site of application. Crabgrass plants were at the three-leaf stage when treated. The soil in the styrofoam cups was a Spinks sandy loam (mixed, mesic Psammentic Hapludalfs). Dithiopyr rates were 0.01, 0.02, 0.04 and 0.07 kg ai/ha in experiment 1. Two additional rates, 0.14 and 0.28 kg ai/ha, were included in experiment 2. The two experiments were identical in all other respects.

The foliar and soil sites of application were isolated using barriers. A sheet of aluminum foil, placed over the soil and fitted carefully around the base of the crabgrass plant, was used to isolate the foliage. The soil was isolated by carefully folding the crabgrass leaves upwards, along the axis of the stem, and wrapping the plant with a small strip of parafilm. A normally applied treatment (no barriers) was included for comparison purposes, along with two sets of untreated controls. The barriers were removed immediately after treatment and the soil-applied treatments were covered with a 0.5 cm layer of fresh soil to minimize volatilization of the herbicide.

The pots were placed in the greenhouse and irrigation was withheld for eight hours following treatment. After two weeks, shoot fresh weights were taken and the percent of control shoot fresh weight for each treatment was calculated based on the untreated controls. The data were subjected to analysis of variance and the effects of the foliar and soil sites were evaluated by performing orthogonal contrasts.

Leaf isolation

A completely randomized design with six replications was used for these experiments. The large crabgrass plants were

grown in Baccto[2] potting media and were at the three-leaf growth stage when treated.

The second leaf (youngest fully expanded) was isolated for treatment by placing a small, adhesive paper strip, folded at a 90° angle, at the base of the leaf blade. A slit was then cut in a lightweight plastic bag, the leaf was pulled through the slit, and the bag was taped in place. The purpose of the bag was to ensure that only the isolated leaf was contacted by herbicide when sprayed; the purpose of the adhesive paper strip was to prevent the herbicide from running off the treated leaf onto the rest of the plant.

The dithiopyr/adjuvant treatments (Table 4) were applied in the trolley sprayer. The dithiopyr rate was 0.03 kg ai/ha and adjuvants were added at 0.5% v/v. The leaves were allowed to dry before removing the bag, and the plants were placed in the greenhouse. Shoot fresh weights were taken after two weeks, and percent control was calculated based on the shoot fresh weights of the untreated controls. The data were transformed by the arcsin transformation and the analysis of variance and LSD multiple range test were performed on the

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[2]Baccto is a product of Michigan Peat Company, P.O. Box 980129, Houston, TX. 77098.

transformed data. Means reported are the actual percent control values (Tables 4 and 5).

Absorption and translocation

Large crabgrass was grown from seed as described above. Plants were at the four-leaf stage when treated. We encountered great difficulty in forming a stable emulsion with the ^{14}C-dithiopyr; therefore, to accurately determine the radioactivity applied per leaf, it was necessary to prepare a separate spotting solution for each plant. The spotting solutions were made by adding ^{14}C-dithiopyr (specific activity 29.24 mCi/mmole, uniformly ring labeled) to commercially formulated dithiopyr, distilled water and adjuvants, to give a final volume of 10 ul. The dithiopyr formulation was MON-15104 in experiments 1 and 2, and MON-15151 in experiment 3. Each solution contained 12.1 ug dithiopyr, 1.3% of which was ^{14}C-dithiopyr. The effect of adjuvants was examined by adding them to the spotting solution at 0.5% v/v (Tables 1,2 and 3). The spotting solution was equivalent to a dithiopyr spray solution containing 0.28 kg ai/ha at a spray volume of 234 l/ha.

Two microliters of the spotting solution were applied to the center of the adaxial surface, between the midrib and leaf edge, of the youngest fully expanded leaf. The remaining

spotting solution was then transferred into a scintillation vial with five-0.1 ml hexane rinses, covered with 12 ml scintillation cocktail, and radioassayed by liquid scintillation spectrometry. The radioactivity added to the spotting solution, minus the radioactivity in the hexane rinsate, equalled the radioactivity applied to the leaf, and was typically around 0.003 uCi.

The treated plants were placed under fluorescent lighting in the laboratory for 24 h. The laboratory temperature was $21 \pm 2°$ C. The plants were then separated into the treated leaf, parts above, and parts below the treated leaf, excluding roots. After separation, the treated leaf was rinsed with 10 ml acetone to remove any unabsorbed ^{14}C-dithiopyr. Preliminary studies revealed that the 24 h time period allowed maximum absorption and translocation of the herbicide, and that the 10 ml acetone rinse would remove all surface radioactivity. The acetone rinsate was evaporated for 36 h to near dryness, and radioassayed as previously described. Plant parts were frozen until combusted to $^{14}CO_2$ in a biological oxidizer, and the combusted samples were radioassayed.

Percent ^{14}C-dithiopyr absorption was calculated based on the total radioactivity recovered in the plant, and the initial amount applied to the leaf. Percent translocation was calculated based on the radioactivity recovered in plant parts away from the treated leaf, and the initial amount applied to the leaf. No significant difference occurred in translocation to plant parts above or below the treated leaf, so the data were combined for reporting purposes. Percent ^{14}C-dithiopyr not recovered was calculated based on the radioactivity recovered in the plant plus the acetone rinsate, and the initial amount applied.

A randomized complete block design was used with four replications. The data were transformed by the arcsin transformation and the analysis of variance and LSD multiple range tests were performed on the transformed data. Means reported are the untransformed data.

Aside from the different dithiopyr formulation used in experiment 3, all three experiments were identical, except that the experiment 1 plants were kept on the laboratory bench for the 24 h absorption period, while the experiment 2 and 3 plants were kept in a modified fume hood, because of volatility concerns. The fume hood was modified by plugging all lower vents, so that the laboratory air entered the hood only from the front, and was exhausted only at the top of the hood. In this manner, air flow over the treated plants was minimized.

Effect of temperature on ^{14}C-dithiopyr absorption

A two factor randomized complete block design was used with four replications. The factors were post-treatment temperature and adjuvant treatment. Procedures were the same as in the absorption/translocation experiments, except that translocation was not examined, so the treated plant was not separated prior to combustion. Adjuvants used are listed in Table 6. Immediately following treatment, the plants were placed in a growth chamber for the 24 h absorption period. Post-treatment temperatures investigated were 5, 15, 25 and 35° C. Relative humidity in the chamber was maintained at 75 ± 5%. The experiment was repeated, and the data from the two experiments were combined. The arcsin transformation was performed on the data, and the transformed data were subjected to analysis of variance. Means were separated by the LSD multiple range test.

RESULTS AND DISCUSSION

Site of uptake

The herbicidal effect from the foliar-applied treatments closely approximated the effect given by the normally applied treatments, with increasing control as the dithiopyr rate was increased (Figures 1 and 2). By contrast, the soil-applied treatments provided minimal control at all dithiopyr rates.

Orthogonal contrasts between the foliar and soil-applied treatments at each rate revealed highly significant differences at the two high rates, 0.04 and 0.07 kg ai/ha, in experiment 1 (Figure 1). The lowest rate, 0.01 kg ai/ha, was significantly different between the treatments, but this result had little interpretive value because of the varying response to the herbicide at the lowest rates (Figures 1 and 2).

In experiment 2, the overall level of control was lower, possibly because the crabgrass plants were slightly larger when treated. Despite this fact, results were similar to those obtained in experiment 1. Orthogonal contrasts revealed highly significant differences between the foliar and soil-applied treatments at the two highest rates, 0.14 and 0.28 kg ai/ha (Figure 2). The 0.04 kg ai/ha rate was significantly

different between the two treatments, but the 0.07 kg ai/ha rate was not. The lack of significance at the 0.07 kg ai/ha rate was due to a 25% increase in control over the 0.04 kg ai/ha rate by the soil-applied treatments, while the foliar-applied treatments, though still giving far greater control, increased by only 10% over the 0.04 kg ai/ha rate.

These experiments indicate that the primary site of uptake of dithiopyr, applied postemergence to crabgrass, is through the foliage.

Absorption and translocation with MON-15104

In experiment 1, only Dow Corning X2-5309 significantly increased absorption over dithiopyr alone (Table 1), and in experiment 2, only X-77 significantly increased absorption (Table 2). Activator 90, while not significantly different from the herbicide alone, was the only adjuvant to increase absorption by more than 3% in both experiments. No adjuvant significantly decreased absorption in either experiment. Previous field studies, in which the adjuvants were combined with the MON-15104 formulation of dithiopyr, revealed significant increases in crabgrass control with several of the adjuvants, and non-statistically significant increases with the remaining ones (see chapter 1). Therefore, the increased control with adjuvants cannot be explained by an effect on

absorption, with the possible exceptions of Dow Corning X2-5309, X-77 and Activator 90.

Translocation of dithiopyr out of the treated leaf was less than 1% of the applied herbicide in all cases, and was not significantly increased with any of the adjuvant treatments (Tables 1 and 2). This suggests that adjuvants do not affect translocation of dithiopyr in the plant; however, this may be a premature conclusion, because the amount of radioactivity detected outside the treated leaf was nearly always less than twice the background levels. Thus, these experiments may not have been sensitive enough to detect true differences in translocation with the adjuvants.

The percent of the applied herbicide that was not recovered ranged from 65-77% in experiment 1 (Table 1), and 64-78% in experiment 2 (Table 2). This almost certainly represents loss by volatilization, because the root system is the only other possible sink for the non-recovered herbicide, and translocation out of the treated leaf was less than 1%. Volatility losses of this magnitude in 24 h will certainly mitigate any adjuvant effects on absorption. The decreased absorption effect of Dow Corning X2-5309 in experiment 2 may be related to increased volatility of this adjuvant/herbicide

combination in the fume hood versus on the laboratory bench (Tables 1 and 2).

Absorption and translocation with MON-15151

When added to the MON-15151 formulation of dithiopyr, all adjuvants except Agsco Sunit and Dash significantly increased absorption over MON-15151 alone (Table 3). Notably, the MON-15104 formulation also significantly increased absorption over MON-15151.

Despite the increased absorption, none of the adjuvants had a significant effect on the amount of herbicide translocated out of the treated leaf, which was less than 1% in all cases (Table 3). It is important to note that, as with the MON-15104 formulation, the radioactivity detected outside the treated leaf was nearly always less than twice the background levels. Thus, this experiment may not have been sensitive enough to detect true differences in translocation with adjuvants, and the conclusion that adjuvants have no effect on translocation may be premature. Previous greenhouse studies, in which these adjuvants were added to the MON-15151 formulation, resulted in significantly increased control with all the adjuvants (see chapter 1). The fact that Agsco Sunit and Dash did not significantly increase absorption of ^{14}C-dithiopyr suggests that other factors besides absorption

are involved in the adjuvants' enhancement of dithiopyr activity in the greenhouse.

The percent of the applied herbicide that was not recovered ranged from 52-78% (Table 3). It is interesting to note that a lower value here (meaning greater recovery) did not always relate to greater absorption. Some of the adjuvants seemed to decrease volatilization of the herbicide, but rather than leading to greater absorption, much of the herbicide simply remained on the leaf surface. This particularly seems to be the case with Pfizer 14636-181-7, Agsco Sunit and Dash.

Leaf isolation

The site of action of dithiopyr is believed to be the apical meristem, where it functions as a mitotic inhibitor[3]. Therefore, dithiopyr must reach the apical meristem in toxic quantities for effective control to occur. This experiment was designed to test the hypothesis that adjuvants enhance crabgrass control by increasing the external movement of the spray solution down the plant, so that the active ingredient is placed near the apical meristem.

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[3]J. E. Kaufman, Monsanto Agricultural Co., personal communication.

Because the spray solution was prevented from moving off the treated leaf externally, the achievement of control levels as high as 77% in experiment 1 (Table 4), and 61% in experiment 2 (Table 5), indicates that, with some adjuvants, enough herbicide is being translocated to the apical meristem to exert a toxic effect on the plant. In light of the fact that less than 1% of the applied herbicide was translocated out of the treated leaf in the absorption/translocation experiments, it seems that very low levels of dithiopyr at the site of action are necessary to exert a toxic effect.

Several of the adjuvants increased control significantly over dithiopyr alone (MON-15151 formulation) in experiment 1 (Table 4). Interestingly, these were not necessarily the same adjuvants that were most effective in increasing absorption in absorption/translocation experiment 3, in which the MON-15151 formulation of dithiopyr was also used. This suggests that there may be differences in spray retention among treatments, because any adjuvant effects on spray retention in the absorption/translocation experiments were effectively bypassed by placing the spray solution on the leaf with a microsyringe.

Even with differences in spray retention among adjuvants, however, it seems probable that adjuvant effects on translocation are more important in achieving control. Pfizer

M, Pfizer 14636-181-7 and Agsco Sunit gave the best control in both leaf isolation experiments (Tables 4 and 5), yet were among the poorest adjuvants in increasing absorption (Table 3). Even if an effect on spray retention caused a 50% increase in absorption with these adjuvants, they still would not equal the absorption achieved with X-77 and Activator 90 (Table 3). It is quite possible that some adjuvants are enhancing dithiopyr absorption into the cuticle, but are causing the herbicide molecules to be bound there, preventing further penetration into the symplast.

Several of the adjuvants, particularly the two Dow Corning products, gave no greater control than dithiopyr alone (Table 4), despite dramatically increasing control in previous greenhouse experiments where the whole plant was treated (see chapter 1). This result confirmed our hypothesis that these adjuvants were enhancing control by increasing movement of the spray solution down the plant so the active ingredient was physically placed near the apical meristem. Experience in working with the two Dow Corning adjuvants, both organo-silicone based compounds, showed that they decreased the surface tension of the spray solution more than any other adjuvant, as judged by the droplet spread on the leaf.

None of the adjuvants were significantly different from dithiopyr alone in experiment 2 (Table 5), though the trend was similar to experiment 1, in that the same three adjuvants gave the best control, and the two Dow Corning adjuvants gave the worst. For reasons that are not clear, the crabgrass plants grew less vigorously in experiment 2, resulting in control plants nearly half the size of those in experiment 1, and, consequently, less separation of the treatments. However, the results of this experiment further confirm the physical placement hypothesis.

In summary, these experiments indicate that the adjuvant enhancement of dithiopyr activity on crabgrass is related to effects on absorption, translocation, spray retention and the physical placement of the active ingredient near the apical meristem. Enhancement seems to be a combination of the four factors, and the importance of any one factor depends on the particular adjuvant used.

The conclusion that adjuvants affect dithiopyr translocation contradicts the results from the ^{14}C-dithiopyr absorption/translocation experiments in which no differences in translocation were found. As stated previously, very little dithiopyr is apparently needed at the site of action; consequently, the ^{14}C-dithiopyr translocation experiments were

probably not sensitive enough to detect true differences in translocation. Because of their apparent ability to detect translocation differences, the leaf isolation experiments would seem to be superior to ^{14}C-dithiopyr screens for selecting adjuvants to enhance dithiopyr control of crabgrass. However, the leaf isolation experiments are tedious to perform, and their exclusive use for adjuvant selection would preclude selection of adjuvants which increase control primarily by enhancing physical placement of dithiopyr near the apical meristem, such as Dow Corning X2-5309 and Dow Corning 6955-145. Consequently, the most reliable screening method for selecting superior adjuvants, as well as the least expensive, appears to be greenhouse screens with whole crabgrass plants. This screening method needs to be made more stringent, however, to facilitate separation of superior adjuvants from inferior ones. A more stringent test could be achieved by treating larger, tillered crabgrass plants, or by simulating an actual turf situation, perhaps by mixing perennial ryegrass (Lolium perenne L.) with crabgrass, in which the turf foliage would intercept some herbicide that might otherwise reach the crabgrass apical meristem.

Effect of temperature on ^{14}C-dithiopyr absorption

The regression equation for the relationship between dithiopyr absorption and temperature was significant at p=0.001, and the association was strong, as indicated by the r^2 value of 0.87 (Figure 3). The mean absorption was 32.4, 20.1, 11.6 and 5.1% at 5, 15, 25 and 35° C, respectively. Similarly, the regression equation for the relationship between non-recoverability of dithiopyr and temperature was significant at p=0.001 and the association was strong, with an r^2 value of 0.92 (Figure 4). The mean percent not recovered was 50, 71, 86 and 94% at 5, 15, 25 and 35° C, respectively.

Non-recoverable dithiopyr, as stated previously, almost certainly represents volatilized herbicide, and this supposition is strengthened by the increasing loss at higher temperatures.

As shown by the orthogonal contrast in table 6, Dow Corning X2-5309 significantly increased absorption over the other adjuvants and dithiopyr alone. Though the Dow Corning X2-5309 treatment had the highest absorption at each temperature, the effect was decreased at 25 and 35° C, leading to a significant interaction between the adjuvant effect and temperature in the analysis of variance (not shown). This decreased effect at higher temperatures can be directly

attributed to the increased volatility of the herbicide, thereby giving the adjuvant less opportunity to enhance absorption.

Though volatility increased, and absorption decreased, for each individual treatment as the temperature was raised, it was not necessarily true that the adjuvant giving the least volatility was most effective in increasing absorption. This is evidenced by the fact that Dow Corning X2-5309 had the highest volatility at the 5° C temperature, but also had the highest absorption. Comparing orthogonal contrasts reveals that the X-77 treatment had significantly ($p=0.001$) less volatility than dithiopyr alone (Table 7), but did not give significantly more absorption (Table 6). Thus, comparing volatility at different temperatures for an individual adjuvant provides a good indication of its relative effectiveness at each temperature, but the same is not true of volatility comparisons made among different adjuvants at the same temperature.

Based on the results of this experiment, turfgrass managers would be wise to apply dithiopyr, with or without adjuvants, at times when volatilization will be at a minimum. Applications during the early morning hours, when soil and air

temperatures are at a minimum, are recommended. Applications during the heat of the day should be strictly avoided.

Table 1. Effect of adjuvants on absorption and translocation of ^{14}C-dithiopyr (MON-15104) - Experiment 1.

Adjuvant	% Absorbed[a]	% Translocated[a]	% Not recovered[a]
Dow Corning X2-5309	23.1 a	0.7 a	70 bc
Activator 90	21.5 ab	0.5 ab	65 c
X-77	20.1 abc	0.4 b	70 bc
Agsco Sunit	18.8 bcd	0.5 ab	70 bc
Dow Corning 6955-145	18.3 bcd	0.7 a	77 a
none	18.1 bcde	0.5 ab	73 ab
Pfizer M	16.9 cde	0.4 b	74 ab
Herbimax	16.4 cde	0.5 ab	74 ab
Pfizer 14636-181-7	16.0 de	0.3 bc	69 bc
Dash	14.5 e	0.2 c	77 a

[a]Means followed by the same letter are not significantly different by LSD at p=0.05.

Table 2. Effect of adjuvants on absorption and translocation of ^{14}C-dithiopyr (MON-15104) - Experiment 2.

Adjuvant	% Absorbed[a]	% Translocated[a]	% Not recovered[a]
X-77	20.3 a	0.3 ab	69 cd
Activator 90	20.2 ab	0.2 b	65 d
Dash	16.2 abc	0.3 ab	70 bcd
Pfizer M	16.1 abc	0.2 b	75 abc
Dow Corning 6955-145	16.0 abc	0.3 ab	76 ab
Dow Corning X2-5309	15.5 abc	0.2 b	78 a
none	14.9 bc	0.4 a	76 ab
Herbimax	13.1 c	0.2 b	77 a
Agsco Sunit	13.0 c	0.3 ab	75 abc
Pfizer 14636-181-7	11.5 c	0.2 b	64 d

[a]Means followed by the same letter are not significantly different by LSD at p=0.05.

Table 3. Effect of adjuvants on absorption and translocation of ^{14}C-dithiopyr (MON-15151) - Experiment 3.

Adjuvant	% Absorbed[a]	% Translocated[a]	% Not recovered[a]
X-77	22.4 a	0.3 a	60 cde
Activator 90	21.7 a	0.2 a	64 cd
Dow Corning 6955-145	19.1 ab	0.3 a	76 ab
Pfizer M	18.6 abc	0.2 a	69 bc
Herbimax	17.4 abc	0.1 b	77 ab
Dow Corning X2-5309	15.8 bc	0.3 a	78 a
MON-15104 only	15.7 bc	0.2 a	76 ab
Pfizer 14636-181-7	13.4 cd	0.1 b	52 e
Agsco Sunit	10.4 de	0.2 a	64 cd
Dash	9.8 de	0.2 a	59 de
MON-15151 only	7.2 e	0.2 a	77 ab

[a]Means followed by the same letter are not significantly different by LSD at p=0.05.

Table 4. Treatment of an isolated crabgrass leaf with dithiopyr (MON-15151) and adjuvants - Experiment 1.

Adjuvant	% Control[a]
Pfizer M	77 a
Agsco Sunit	72 ab
Pfizer 14636-181-7	70 ab
Herbimax	66 abc
X-77	63 abc
Activator 90	59 bcd
Dash	51 cd
none	44 de
Dow Corning X2-5309	41 de
Dow Corning 6955-145	28 e

[a]Means followed by the same letter are not significantly different by LSD at p=0.05.

Table 5. Treatment of an isolated crabgrass leaf with dithiopyr (MON-15151) and adjuvants - Experiment 2.

Adjuvant	% Control[a]
Pfizer 14636-181-7	61 a
Pfizer M	55 ab
Agsco Sunit	52 abc
none	40 abcd
Dash	38 abcd
Activator 90	30 abcd
Herbimax	29 abcd
X-77	27 bcd
Dow Corning 6955-145	28 cd
Dow Corning X2-5309	4 d

[a]Means followed by the same letter are not significantly different by LSD at p=0.05.

Table 6. Effect of temperature on dithiopyr uptake with adjuvants.

	% Uptake				
	Adjuvant				
Temp. (^{o}C)	Dash	Dow Corning X2-5309	Agsco Sunit	X-77	No adjuvant
5	31.6	39.0	32.6	31.9	31.1
15	17.0	28.6	17.3	20.1	17.5
25	10.5	16.1	10.9	10.8	9.9
35	4.5	6.4	4.2	5.9	4.5
Mean:	15.9	22.5	16.3	17.2	15.7
Contrast					
X2-5309 vs. rest			***		
X-77 vs. no adjuvant			NS		

*, **, *** Denote significance at p=0.05, 0.01 and 0.001, respectively.

Table 7. Effect of temperature on non-recoverability of dithiopyr with adjuvants.

	% Not recovered				
	Adjuvant				
Temp. (^{o}C)	Dash	Dow Corning X2-5309	Agsco Sunit	X-77	no adjuvant
5	49	55	49	46	52
15	76	67	70	67	73
25	88	82	87	86	89
35	95	92	95	93	95
Mean:	77	74	75	73	77
Contrast					
X2-5309 vs. rest			*		
X-77 vs. no adjuvant			***		

*, *** Denote significance at the p=0.05 and 0.001 levels, respectively.

Figure 1. Effect of site of application of dithiopyr on large crabgrass control-- Experiment 1.

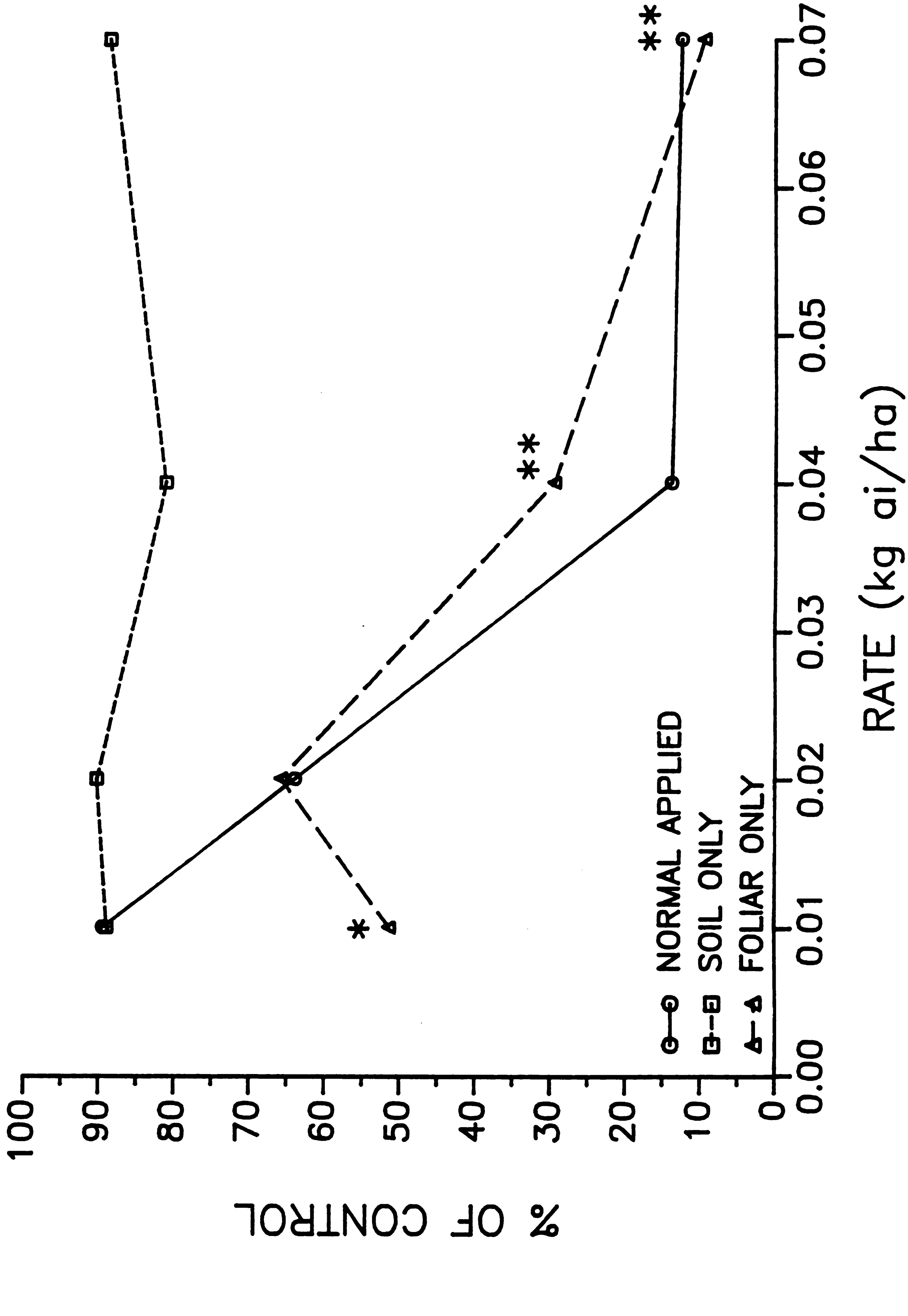
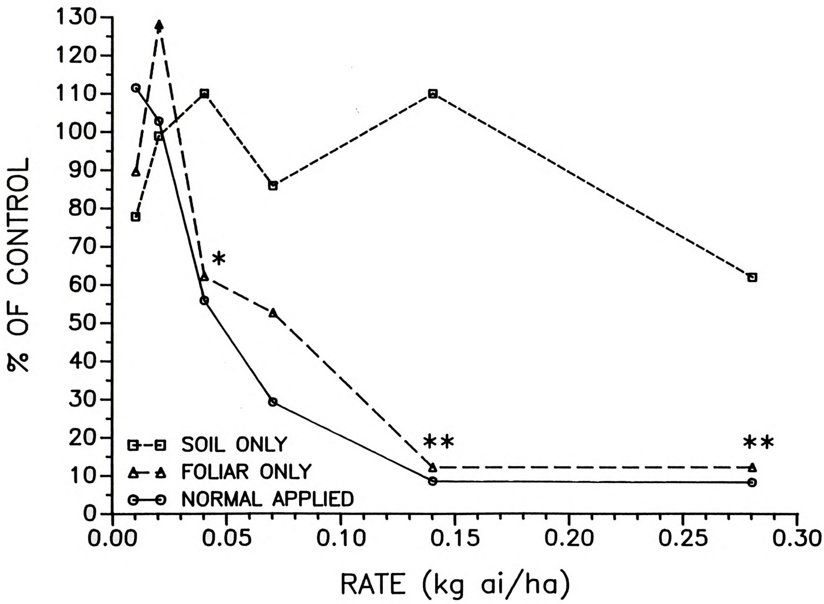

% OF CONTROL
100
90
80
70
60
50
40
30
20
10
0
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
RATE (kg ai/ha)
NORMAL APPLIED
SOIL ONLY
FOLIAR ONLY
*
**
**

Figure 2. Effect of site of application of dithiopyr on large crabgrass control-- Experiment 2.



% OF CONTROL
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.00
0.05
0.10
0.15
0.20
0.25
0.30
RATE (kg ai/ha)
SOIL ONLY
FOLIAR ONLY
NORMAL APPLIED
*
**
**

Figure 3. Effect of temperature on absorption of ^{14}C-dithiopyr alone and in combination with adjuvants.

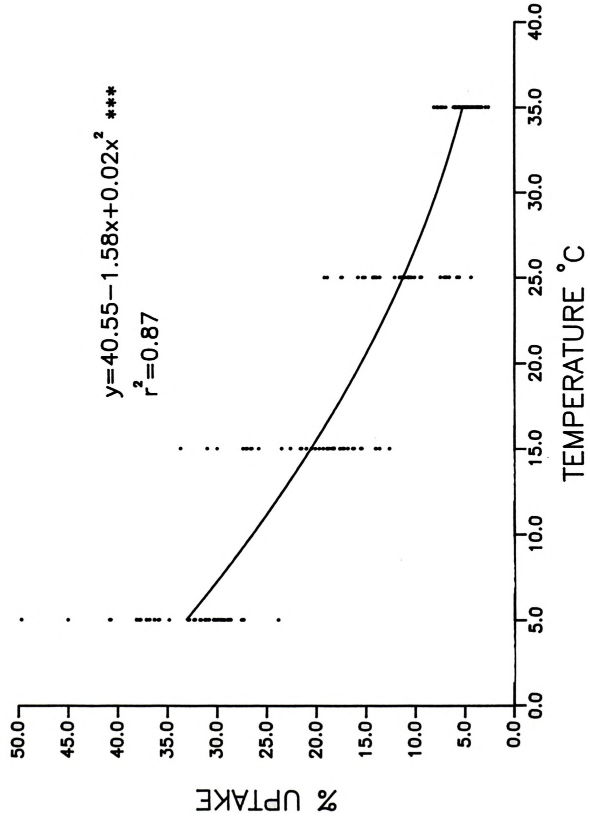
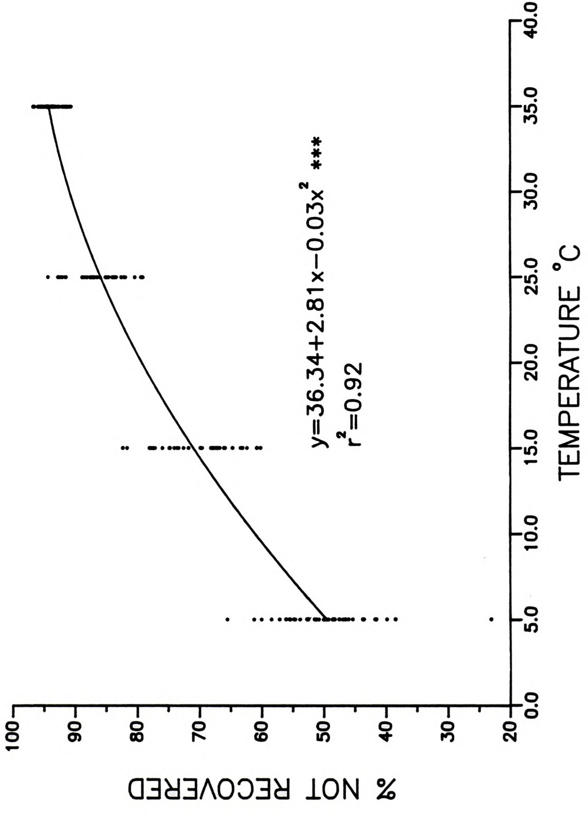

y=40.55−1.58x+0.02x^2 ***
r^2=0.87
TEMPERATURE °C
% UPTAKE
0.0 5.0 10.0 15.0 20.0 25.0 30.0 35.0 40.0
0.0 5.0 10.0 15.0 20.0 25.0 30.0 35.0 40.0 45.0 50.0

Figure 4. Effect of temperature on non-recoverability of ^{14}C-dithiopyr alone and in combination with adjuvants.



$y=36.34+2.81x-0.03x^2$ ***
$r^2=0.92$
% NOT RECOVERED
TEMPERATURE °C
100
90
80
70
60
50
40
30
20
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0

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APPENDIX

APPENDIX

INFORMATION ON THE CHEMICAL COMPOSITION OF SELECTED ADJUVANTS

Table A1. Chemical composition of the ten adjuvants used in field, laboratory, and greenhouse experiments.

Adjuvant	Composition	Manufacturer
Activator 90	a mixture of alkyl polyoxyethylene ether, free fatty acids, and isopropanol	Loveland Industries, Inc., Greeley, CO
Agsco Sunit	methylated vegetable oil and surfactant	Agsco, Inc., Grand Forks, ND
CSY-77715512	experimental vegetable oil-based adjuvant	
Dash	commercial, proprietary adjuvant (composition unknown)	BASF Corp., Research Triangle, NC
Dow Corning X2-5309 (Dow Corning product Sylgard 309)	organo-silicone based adjuvant	Dow Corning Corp., Midland, MI
Dow Corning 6955-145	organo-silicone based adjuvant	Dow Corning Corp., Midland, MI
Herbimax	a mixture of paraffin base petroleum oil, and mono and diesters of hydroxypoly oxyethylene	Loveland Industries, Inc., Greeley, CO
Pfizer M	experimental adjuvant (composition unknown)	Pfizer Inc., Groton, CT
Pfizer 14636-181-7	experimental adjuvant (composition unknown)	Pfizer Inc., Groton, CT
X-77	a mixture of alkylaryl polyoxyethylene glycols, free fatty acids, and isopropanol	Chevron Chem. Co., San Francisco, CA