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Nitrogen-Enhanced Efficacy of Mesotrione and Topramezone for Smooth Crabgrass (*Digitaria ischaemum*) Control

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The herbicides mesotrione and topramezone inhibit 4-hydroxyphenylpyruvate dioxygenase (HPPD) and have efficacy against smooth crabgrass. Research was conducted to determine the impacts of soil-applied nitrogen (N) fertilizer on the effectiveness of single applications of mesotrione and topramezone for postemergence smooth crabgrass control. Field experiments in 2010 and 2011 evaluated the efficacy of mesotrione (280 g a.i. ha^{-1}) and topramezone (9 g a.i. ha^{-1}) for control of multitiller smooth crabgrass subjected to five N fertility treatments (0, 12, 25, 37, or 49 kg N ha^{-1}). Greenhouse experiments evaluated the response of smooth crabgrass to mesotrione (0, 70, 140, 280, 560, and 1,120 g ha^{-1}) and topramezone (0, 4.5, 9, 18, 36, and 72 g ha^{-1}) with 0 or 49 kg N ha^{-1}. Further research evaluated changes in smooth crabgrass leaf tissue pigment concentrations following treatment with mesotrione (280 g ha^{-1}) and topramezone (18 g ha^{-1}) with 0 or 49 kg N ha^{-1}. In field experiments, N increased smooth crabgrass control with mesotrione and topramezone for 8 wk; however, increasing N rate above 25 kg ha^{-1} did not improve control on any rating date. In dose-response experiments, N application reduced I_{50} values for mesotrione and topramezone by 67 and 53%, respectively, 21 d after treatment (DAT). Reductions in aboveground biomass with both herbicides were greater when applied following N treatment as well. In leaf-response experiments, N decreased new leaf chlorophyll and carotenoid concentrations and new leaf production after treatment with topramezone. Future research should investigate whether increased translocation of these herbicides to meristimatic regions contribute to N-enhanced efficacy.

Nomenclature: Mesotrione; smooth crabgrass (*Digitaria ischaemum* Schreb. *ex* Muhl.); topramezone.
Key words: 4-hydroxyphenylpyruvate dioxygenase, carotenoids, chlorophyll, I_{50}, HPPD, nitrogen, turfgrass.

Smooth crabgrass is a problematic weed throughout the United States (Kim et al. 2002). Smooth crabgrass can be selectively controlled by both PRE and POST herbicides (Jagschitz 1970; Troll 1962). Mesotrione and topramezone are inhibitors of HPPD with efficacy against smooth crabgrass in cool-season turfgrass (Beam et al. 2006; Johnson et al. 2008; Jones and Christians 2007; Schönhammer et al. 2006; Willis 2008a,b). Efficacy of mesotrione for smooth crabgrass control varies with growth stage. Giese et al. (2005) reported mesotrione applied at 280 g a.i. ha^{-1} controlled smooth crabgrass 78% at an early POST timing compared to 26% at a late POST timing. Similarly, Dernoeden and Fu (2008) reported greater smooth crabgrass control at the four-leaf to two-tiller stage than the three- to eight-tiller stage from single applications of mesotrione at 280 g ha^{-1}. Increasing the ability of mesotrione and topramezone to control smooth crabgrass at later tiller stages would be beneficial to turfgrass managers.

N fertilization influences the response of weeds to various herbicides. Cathcart et al. (2004) found GR_{50} (the herbicide dose required to reduce biomass by 50%) values increased 3.5-fold for mesotrione against redroot pigweed (*Amaranthus retroflexus* L.) grown under low N compared to high N; however, N status did not influence velvetleaf (*Abulilion theophrasti* Medik.) control with mesotrione. This indicates that plant-N interactions with herbicides are likely species dependent (Cathcart et al. 2004). Brosnan et al. (2010) demonstrated increased control of annual bluegrass (*Poa annua* L.) with flazasulfuron by applying granular N immediately prior to herbicide application. They attributed an increase in control, at least in part, to an increase in flazasulfuron translocation. Dickson et al. (1990) reported activity of fluazifop and glyphosate on oats (*Avena sativa* L. 'Amuri') increased when they were watered with high N as opposed low N solution for 10 d prior to herbicide application. When plants were watered with low N solution 10 d prior to herbicide application and then flushed with a high N solution immediately after herbicide treatment, fluazifop and glyphosate activity was not improved.

Providing a physiological basis for N-enhanced glyphosate efficacy, Mithila et al. (2008) reported velvetleaf and common lambsquarters (*Chenopodium album* L.) grown under high soil N displayed increased ^{14}C-glyphosate translocation. Mesotrione and topramezone are phloem-translocated to apical meristems and preferentially bleach developing leaves (Goddard et. al. 2010; Grossman and Ehrhardt 2007; Senseman 2007; Weinberg et al. 2003). In N deficient plants, N application increases photoassimilate production, new leaf formation, and leaf area index (Wilson and Brown 1983). Application of N may increase herbicide translocation to shoot meristimatic regions, and increase smooth crabgrass bleached leaf formation, thereby increasing control.

Increased mesotrione and topramezone efficacy using urea ammonium nitrate or other pH-reducing acid adjuvants has been reported (Grossman and Ehrhardt 2007; LiJuan et al. 2011; Wichert and Pastushok 2000; Idziak and Woznica 2008). However, this is likely a result of increased herbicide absorption, especially in a cation-containing spray solution with a neutral to basic pH, as mesotrione and topramezone are weak acids (pK_a 3.12 and 4.06, respectively) (Penner 2000; Senseman 2007). There are no reports of enhanced-efficacy of mesotrione and topramezone when N fertilizer is applied to the soil in quantities that significantly affect plant N status.

We hypothesized that soil-applied N will enhance efficacy of mesotrione and topramezone for multitiller smooth crabgrass control due to greater production of bleached leaf tissue. Research was conducted in 2010 and 2011 at the University of Tennessee to determine the effects of N on the efficacy of mesotrione and topramezone for smooth crabgrass control.

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Table 1. Environmental conditions during experiments evaluating the response of smooth crabgrass in a greenhouse in Knoxville, TN, in 2011. Dose-response experiments A and B were initiated on June 21 and July 7, respectively, in 2011. Leaf-response experiments A and B were initiated on August 1 and 9, respectively, in 2011.

		Air temperature[a]			Relative humidity			PAR[b]		
Experiment	Experimental run	Average	High	Low	Average	High	Low	Minimum peak	Maximum peak	Average 24-h total
		C			%			µmol m^{-2} s^{-1}		mol m^{-2} d^{-1}
Dose-response	A	26	33	20	69	94	47	1,270	1,890	23.6
	B	26	36	19	81	98	45	1,060	1,940	19.3
Leaf-response	A	27	33	23	79	94	49	544	1,618	18.4
	B	25	33	21	76	96	44	738	1,617	18.8

[a] Temperature and relative humidity were recorded every 5 min and averaged for the duration of each experiment; 24-h high and low temperatures were averaged for the duration of each experiment. PAR values were recorded every 15 min. Peak PAR values were determined for each 24-h period; the minimum and maximum of these 24-h peak values were recorded for each experiment. Twenty-four-hour PAR totals were recorded and then averaged for the duration of each experiment.

[b] Abbreviation: PAR, photosynthetically active radiation.

Materials and Methods

Field Experiments. Research was conducted in 2010 and 2011 on a site naturally infested with smooth crabgrass at the East Tennessee Research and Education Center (Knoxville, TN; 35°53≠ N lat). Plots (1.5 by 3.0 m) were established on a Sequatchie loam soil (fine-loamy, siliceous, semiactive, thermic humic Hapludult) measuring 6.2 in soil pH and 2.1% in organic matter content. Field trials were conducted in an area of full sunlight, mowed twice weekly at ~5 cm, and irrigated as needed to prevent wilt. Fertilizer was not applied to the site for 1 yr prior to experiment initiation. At study initiation each year, smooth crabgrass plants had three- to five-tillers and uniformly covered approximately 50% of the site.

Two herbicides and five N rates were evaluated. Treatments were applied on June 10 in 2010 and May 20 in 2011. At the time of herbicide application, air temperature measured 28 and 32 C in 2010 and 2011, respectively; relative humidity measured 70 and 55% in 2010 and 2011, respectively. Herbicide treatments consisted single applications of mesotrione (Tenacity 4 SC, Syngenta Professional Products, Greensboro, NC) and topramezone (Impact 2.8 SC, Amvac Chemical, Los Angeles, CA) at 280 and 9 g ai ha^{-1}, respectively. Each herbicide included a nonionic surfactant (Activator-90, Loveland Products Inc., Loveland, CO) at 0.25% v/v and was applied using a CO_2-powered sprayer containing four flat-fan nozzles (Teejet 8002 flat fan spray nozzle, Spraying Systems Co., Wheaton, IL) calibrated to deliver 280 L ha^{-1}. Five rates of N (0, 12, 25, 37, or 49 kg ha^{-1}) were applied as granular ammonium sulfate ($21N-0P_2O_5-0K_2O$) to dry leaves and watered in immediately prior to herbicide treatment forming a 2 by 5 factorial treatment design. An untreated control that received no herbicide or fertilizer treatment was also included for comparison.

Smooth crabgrass control was visually evaluated 4 DAT and then weekly from 1 to 8 wk after treatment (WAT) on a 0 (no control) to 100% (complete kill) scale. To assess turfgrass phytotoxicity, these treatments were applied to a weed-free stand of mature 'Coyote II' tall fescue [*Lolium arundinaceum* (Schreb.) S.J. Derbyshire] using the same methodology. Tall fescue injury was visually evaluated weekly until 3 WAT on a 0 (no injury) to 100% (complete kill) scale.

Dose-Response Experiments. Two identical experiments were initiated in 2011 in a greenhouse (Knoxville, TN; 35°57≠ N lat) to establish does-response curves for mesotrione and topramezone with and without N. Environmental conditions in the greenhouse for the duration of these experiments are presented in Table 1. Smooth crabgrass (Smooth crabgrass seed, Herbiseed, New Farm/Mire La West End, U.K.) was seeded into 10-cm diameter pots filled with a Sequatchie loam soil measuring 6.2 in soil pH and 2.1% in organic matter content. This soil was blended with a clay mineral soil amendment in a 3:1 ratio (Turface, Profile Products, LLC, Buffalo Grove, IL). Plants were watered as needed to maximize growth and vigor. Pots were hand-weeded as needed to remove undesired weeds. Pots were hand-thinned to five smooth crabgrass plants at the three- to five-tiller growth stage at application. These five plants were maintained at a 7.5 cm height of cut with scissors prior to treatment.

Herbicide treatments consisted of mesotrione at 0, 70, 140, 280, 560 and 1,120 g ha^{-1} and topramezone at 0, 4.5, 9, 18, 36, and 72 g ha^{-1}. Each herbicide included a nonionic surfactant at 0.25% v/v. Two rates of N (0 or 49 kg ha^{-1}) were also applied, forming a 6 by 2 factorial treatment arrangement. This arrangement allowed for both N-treated and N-withheld controls receiving no herbicides to be included for comparison. Treatments were applied in 2011 on June 21 and July 7 for experimental runs A and B, respectively. Immediately prior to herbicide application, N treatments were soil-applied to each pot using 10 ml of a water solution containing 8.6 g of urea (46N-0P-0K) dissolved in 1 L of water. Herbicide treatments were applied using a CO_2-powered sprayer containing four flat-fan nozzles calibrated to deliver 280 L ha^{-1}. Smooth crabgrass control was visually evaluated at 4, 7, 14, and 21 DAT using a 0 (no control) to 100% (complete kill) scale. Chlorophyll fluorescence (F_v/F_m) was also assessed (OS1-FL, Opti-sciences Inc., Hudson, NH) using methods of Elmore et al. (2011) at 4 and 7 DAT. To provide an additional quantitative measure of smooth crabgrass control, aboveground biomass was harvested from each pot 21 DAT and dried in an oven (Model LR-271C, Greive Corp., Round Lake, IL) at 100 C for 4 d and weighed. Treatment means were expressed as a percent reduction in aboveground biomass of the untreated control for both N-treated and N-withheld plants individually.

Leaf-Response Experiments. Research was conducted in 2011 in a greenhouse (Knoxville, TN; 35°57′ N lat) to determine the effects of mesotrione and topramezone on leaf tissue production and chlorophyll and carotenoid pigments when applied with and without N. Environmental conditions in the greenhouse during each experimental run are listed in

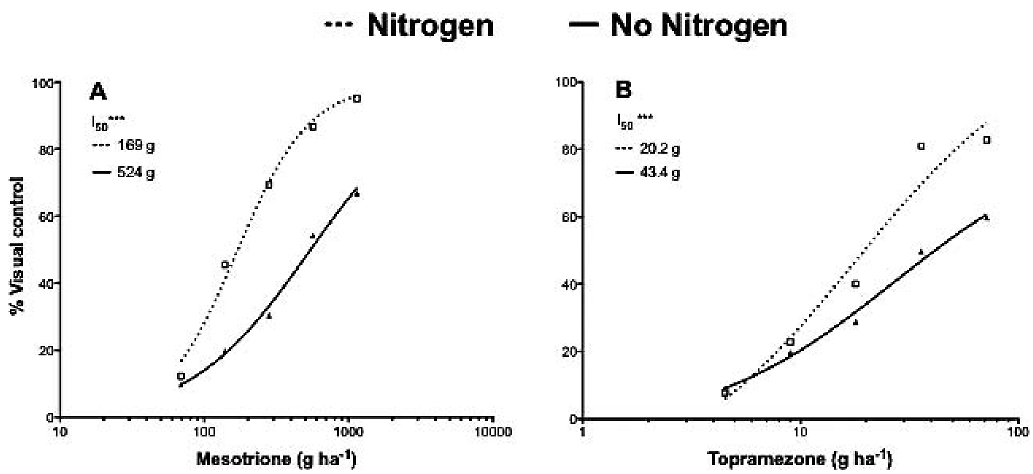

Figure 1. Control of smooth crabgrass in a greenhouse following applications of mesotrione (A) (70, 140, 280, 560, and 1,120 g ha^{-1}) topramezone (B) (4.5, 9, 18, 36, and 72 g ha^{-1}) with and without soil-applied urea (49 kg N ha^{-1}) 21 d after treatment. I_{50} is the rate of herbicide (g ha^{-1}) that controlled smooth crabgrass by 50%. I_{50} values were compared with an *F* test using log-transformed herbicide rates. Untransformed values are presented for clarity. *** indicates significance at the $P \leq 0.001$ level. Data were combined across two experimental runs.

Table 1. Treatments were applied on August 1 and 9, 2011, for experimental runs A and B, respectively.

Smooth crabgrass was seeded into 15-cm diameter pots filled with a Sequatchie loam soil measuring 6.2 in soil pH and 2.1% in organic matter content. This soil was blended with a clay mineral soil amendment in a 3:1 ratio. Plants were clipped weekly to a 10-cm height with scissors. Pots were hand-thinned to contain eight plants at the three- to five-tiller growth stage at study initiation. Prior to herbicide treatment, all leaves (except the bud leaf) of each tiller were marked with a small (< 5 mm length) amount of indelible ink to facilitate future separation of leaves emerged before and after herbicide treatment. Plants were treated with 0 or 49 kg N ha^{-1} and mesotrione (280 g ha^{-1}) or topramezone (18 g ha^{-1}), forming a 2 by 2 factorial treatment arrangement. Both N-treated and N-withheld controls receiving no herbicides were included for comparison. Immediately prior to herbicide application, N treatments were soil-applied to each pot using 20 ml of water solution consisting of 9.7 g of urea (46N-0P-0K) dissolved in 1 L of water. Herbicide treatments were applied with nonionic surfactant (0.25% v/v) and 430 L ha^{-1} of water carrier through a single flat-fan nozzle (Teejet 8004EVS flat fan spray nozzle, Spraying Systems Co.) in a spray chamber (Generation III Research Sprayer, DeVries Manufacturing, Hollandale, MN). Irrigation was withheld for 18 h after treatment application.

Leaves were harvested for pigment quantification 10 DAT. For each pot, leaves from all plants were dissected from stem and sheath tissue and separated into two groups: leaf tissue present at herbicide application (OLD) and leaf tissue produced after herbicide application (NEW). Percent necrosis for both OLD and NEW leaves was determined visually using a 0 (no necrosis) to 100% (complete necrosis) scale. After assessing necrosis, leaf tissue was immediately frozen in liquid N and placed on ice for transfer to storage at −80 C. Prior to pigment extraction, fresh weights of OLD and NEW leaf tissues were determined. Leaf tissue was homogenized in liquid N using a mortar and pestle. A 0.25 g fresh weight leaf tissue sample was then analyzed for carotenoid and chlorophyll pigment concentrations. Leaf tissue pigments were extracted and then quantified through high-pressure liquid chromatography (HPLC) using previously described methods (Brosnan et al. 2011; Kopsell et al. 2007). Pigments are expressed as mg 100 mg fresh weight (FW)$^{-1}$ of smooth crabgrass leaf tissue.

Statistical Analyses. Field experiments were arranged in a randomized complete block design with three replications. Greenhouse experiments were arranged in a completely randomized design with four replications. Model assumptions were tested through residual analysis (Shapiro–Wilk statistic) in SAS (Statistical Analysis Software, Inc., Cary, NC), and no transformations were needed. ANOVA was conducted in SAS with main effects and all possible interactions tested using the appropriate expected mean square values as described by McIntosh (1983). Fisher's protected LSD ($P \leq 0.05$) was used to separate means. Where appropriate, *t* tests conducted in SAS were used to compare two groups of means.

To determine I_{50} values, smooth crabgrass control data from dose-response experiments at 21 DAT were regressed over herbicide dose using a log-logistic model in Prism (Figure 1) (Prism 5.0 for Mac OSX, GraphPad Software, LaJolla, CA):

$$Y = C + ([D - C]/[1 + X/I_{50})^{B}]) \qquad [1]$$

Where *Y* represents smooth crabgrass control, *X* represents the $\log_{10}$ of the herbicide dose applied, *C* is the lower limit for *Y* (i.e., 0% smooth crabgrass control), *D* is the upper limit for *Y* (i.e., 100% smooth crabgrass control), I_{50} is the herbicide dose resulting in 50% control, and *B* is the slope of the line at I_{50} (Seefeldt et al. 1995). Significant differences between I_{50} values of different nitrogen levels were determined using a lack of fit *F* test ($P \leq 0.05$) in Prism. In Figure 2, standard errors calculated in Prism are used as a means of statistical comparison.

Results and Discussion

Field Experiments. Herbicide-by-year interactions were present in smooth crabgrass control data 4 and 7 DAT. However, treatment with N ($P \leq 0.001$) increased smooth crabgrass control with both herbicides each year. At 4 DAT, mesotrione applied without N provided < 10% smooth

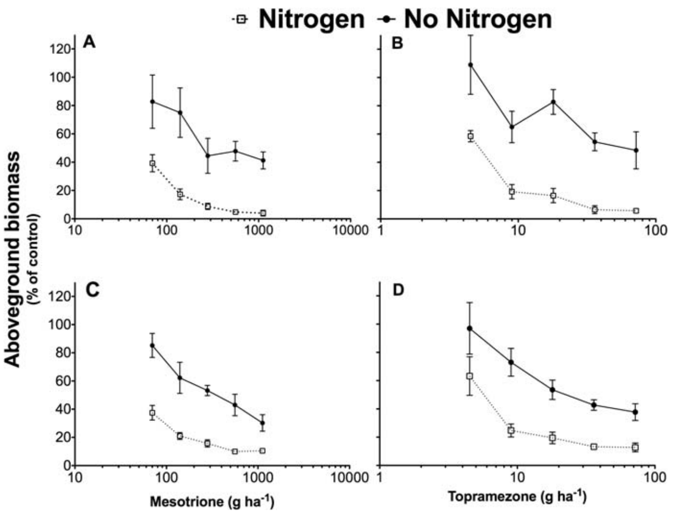

Figure 2. Aboveground smooth crabgrass biomass 21 d after application of mesotrione (in experimental runs 1[A] and 2 [C]) (70, 140, 280, 560, and 1,120 g ha^{-1}) and topramezone (in experimental runs 1[B] and 2 [D]) (4.5, 9, 18, 36, and 72 g ha^{-1}) with and without soil-applied urea (49 kg N ha^{-1}). Biomass reductions for herbicide-treated plants receiving 0 or 49 kg N ha^{-1} are expressed as a percent of the untreated and N-treated controls, respectively. Error bars indicate standard errors.

crabgrass control each year, while application with N (49 kg ha^{-1}) provided 40% control in 2010 and 70% control in 2011. Responses from topramezone applications were similar. By 7 DAT, an application of 49 kg N ha^{-1} improved control of smooth crabgrass with mesotrione and topramezone by 30% each year.

No main effect interactions with year or herbicide were detected in smooth crabgrass control data collected 2 to 8 WAT; therefore, data were combined across years and herbicides (Table 2). On every evaluation date, N application increased smooth crabgrass control with mesotrione and topramezone. While the application of 25 kg N ha^{-1} improved smooth crabgrass control more than 12 kg N ha^{-1} on most dates, no improvements were observed with N rates greater than 25 kg ha^{-1}. These results indicate that N application at rates as low as 12 kg ha^{-1} improve smooth crabgrass control with mesotrione and topramezone, and increasing N application to 25 kg ha^{-1} will further improve control. For example, smooth crabgrass was controlled 30% 7 WAT when herbicide was applied without additional N. An application of N at 12 kg ha^{-1} improved control to 49%, while 25 kg N ha^{-1} further improved control to 67% by 7 WAT. Visual turfgrass injury ranged from 11 to 15% 14 DAT and dissipated by 21 DAT; N rate did not affect injury (data not presented). Turfgrass managers seeking to improve smooth crabgrass control with mesotrione and topramezone should apply N at rates 12 to 25 kg ha^{-1}. Since nitrogen fertility can increase brown patch (Causal agent: *Rhizoctonia solani* Kühn) incidence on tall fescue, turfgrass managers should consider the implications of N fertilization if conditions for brown patch development are favorable (Burpee 1995).

Dose-Response Experiments. Significant herbicide-by-experimental run interactions were detected in smooth crabgrass control and F_v/F_m data collected from 4 to 14 DAT; however, N and herbicide rate increased ($P < 0.001$) smooth crabgrass control 4 to 14 DAT in each experimental run (data not presented). While F_v/F_m decreased with increasing herbicide rate 4 and 7 DAT, N treatment did not affect F_v/F_m (data not presented). Herbicide-by-experimental run interactions were present in aboveground biomass data; thus, data from each run are presented separately. No herbicide-by-experimental run interactions were present in smooth crabgrass control data 21 DAT. Therefore, log-logistic regression analyses were conducted using combined data from both experimental runs.

N application decreased ($P < 0.001$) the amount of mesotrione and topramezone required to control smooth crabgrass by more than 50% (I_{50}) 21 DAT (Figure 1). Mesotrione I_{50} values were reduced by 67% (from 524 to 169 g ha^{-1}) by N application. Topramezone I_{50} values were reduced by 53% (from 43.3 to 20.2 g ha^{-1}) by N application. Similarly, Cathcart et al. (2004) reported N application reduced the amount of mesotrione required to decrease redroot pigweed (*Amaranthus retroflexus* L.)biomass by 50% (GR_{50}) more than 70%.

N application also enhanced aboveground biomass reductions with all rates of mesotrione and topramezone (Figure 2). When applied with N in the first experimental run, mesotrione at 70 g ha^{-1} reduced aboveground biomass 61%, while mesotrione rates of 280, 560, and 1,120 g ha^{-1} were required to achieve a similar reduction when N was withheld. The 1,120 g ha^{-1} rate of mesotrione reduced aboveground biomass 96% when applied with N but only 59% when N was withheld. Similar responses were observed in the second experimental run with mesotrione. In both experimental runs, topramezone at ≥ 9 g ha^{-1} reduced aboveground biomass 75 to 94% when applied with N compared to 17 to 62% when N was withheld. Data from dose-response experiments indicate that soil-applied N at

Table 2. Percent control of smooth crabgrass 2 to 8 WAT with mesotrione (280 g ha^{-1}) or topramezone (9 g ha^{-1}) in combination with N (nitrogen) at 0, 12, 25, 37, or 49 kg ha^{-1} in 2010 and 2011. Herbicides were applied with a nonionic surfactant at 0.25% v/v on June 10, 2010, and May 20, 2011. Data are combined across years and herbicides.

	Smooth crabgrass control													
Nitrogen[a]	2 WAT[b]		3 WAT		4 WAT		5 WAT		6 WAT		7 WAT		8 WAT	
——kg ha^{-1}——	%													
0	55	c[c]	59	c	53	c	51	b	47	b	30	c	39	b
12	73	b	74	b	65	b	60	b	58	ab	49	b	50	ab
25	86	a	86	a	82	a	77	a	69	a	67	a	67	a
37	91	a	89	a	84	a	82	a	69	a	61	ab	61	a
49	86	a	81	ab	79	a	79	a	67	a	62	ab	56	ab

[a] Nitrogen was applied as granular ammonium sulfate (21-0-0) and watered in prior to herbicide application.
[b] Abbreviation: WAT, weeks after treatment.
[c] Means followed by the same letter are not significantly different as determined by Fisher's protected LSD test ($P \leq 0.05$).

Table 3. Leaf weight, number, and necrosis of smooth crabgrass leaves emerged before (OLD) and 10 d after (NEW) treatment with the combination of mesotrione (280 g ha^{-1}) or topramezone (18 g ha^{-1}) and 0 or 49 kg N ha^{-1}. Means are comprised of 8 observations.

Herbicide	N[b]	Leaf weight NEW		Leaf weight OLD	Leaf number NEW	Leaf number OLD	Leaf necrosis[a] NEW		Leaf necrosis[a] OLD	
	kg ha^{-1}	%			#		g			
Mesotrione	0	0.71	ab[c]	0.55	67	60	28	b	4	b
	49	0.59	b	0.43	62	55	43	a	12	a
Topramezone	0	0.84	a	0.53	67	53	10	c	4	b
	49	0.61	b	0.45	57	51	34	ab	16	a

[a] Necrosis was visually evaluated on a 0% (no necrosis) to 100% (complete necrosis) scale.

[b] Nitrogen was soil-applied as urea (46-0-0) solution.

[c] Means followed by the same letter are not significantly different as determined by Fisher's protected LSD test ($P \leq 0.05$).

49 kg ha^{-1} enhances the activity of mesotrione and topramezone at a variety of herbicide rates on three- to five-tiller smooth crabgrass.

Leaf-Response Experiments. *Leaf Number, Weight and Necrosis*. Main effect interactions with experimental run were not significant; therefore, data from each experimental run were pooled. Applied N affected smooth crabgrass growth in these studies. The number of NEW leaves averaged 106 and 178 per pot for control plants receiving 0 and 49 kg N ha^{-1}, respectively. Similarly, NEW fresh leaf weights measured 2.1 and 3.6 g for control plants receiving 0 and 49 kg N ha^{-1}, respectively. Nitrogen did not affect the number or weight of OLD leaves present on non- or herbicide-treated plants (Table 3). Nitrogen had no effect on the number of NEW leaves produced after herbicide treatment as well. However, N treatment did reduce the weight of NEW leaf tissue in topramezone-treated plants. Treatment with N also increased necrosis of OLD and NEW leaves following mesotrione and topramezone application. Nitrogen increased leaf necrosis of mesotrione-treated plants by 8 and 15% for OLD and NEW leaves, respectively. Similarly, N increased leaf necrosis of topramezone-treated plants by 12 and 24% for OLD and NEW leaves, respectively.

Leaf Tissue Chlorophyll and Carotenoid Concentration. As was observed by Goddard et al. (2010), mesotrione and topramezone preferentially bleached newer leaves formed after herbicide application; carotenoid and chlorophyll pigment concentrations in NEW leaves were lower than those in OLD leaves after treatment with mesotrione and topramezone ($P < 0.001$) (Table 4).

N application did not affect total chlorophyll, total xanthophyll, or lutein concentrations in OLD leaves of herbicide-treated plants. Nitrogen decreased total chlorophyll, total xanthophyll, and lutein concentrations in NEW leaf tissue in topramezone-treated plants by approximately 50%. Chlorophyll and carotenoid pigment concentrations in NEW leaves of mesotrione-treated plants were not affected by N. While not statistically significant, this trend was observed in necrosis data as N treatment increased necrosis by only 15% in mesotrione-treated plants and 24% in topramezone-treated plants. This could be attributed to greater activity of mesotrione as compared to topramezone at rates selected for this experiment. NEW leaf pigment concentrations and necrosis in N-withheld plants treated with mesotrione were similar to those of N-treated topramezone plants, suggesting herbicidal activity of these treatments were similar. Mesotrione alone may have caused near-threshold reduction in pigments, reducing the ability of N to cause further reductions. Moreover, immature (new) shoot tissues have lower pigment concentrations than fully mature shoot tissues (Lefsrud et al. 2007). Lower pigment concentrations present in immature tissues, combined with greater tissue necrosis, may have contributed to pigment responses following mesotrione treatment in the current study.

Concentrations of the carotenoid precursor phytoene in NEW leaves of herbicide-treated plants measured 0.26 mg 100 g FW^{-1}. This indicates observed reductions in carotenoid pigment concentrations are likely due to a lack of phytoene desaturase, a symptom of HPPD-inhibiting herbicide application (Kopsell et al. 2010; Mayonado et al. 1989). Phytoene concentrations did not differ between mesotrione and topramezone and was not affected by N treatment. Phytoene was not detected in OLD leaves of herbicide-treated plants or in NEW or OLD leaves of nonherbicide-treated plants.

Leaf-response data indicate N application does not enhance efficacy of mesotrione and topramezone by increasing bleached leaf production. Rather, carotenoid and chlorophyll

Table 4. Total chlorophyll (chlorophyll $a + b$), lutein, and total xanthophyll cycle (antheraxanthin + violaxanthin + zeaxanthin) pigment concentrations in smooth crabgrass leaves emerged before (OLD) and 10 d after (NEW) treatment with the combination of mesotrione (280 g ha^{-1}) or topramezone (18 g ha^{-1}) and 0 or 49 kg N ha^{-1}. Means are comprised of eight observations.

Herbicide	N[a]	Total chlorophyll NEW[b]	Total chlorophyll OLD	Total xanthophyll cycle NEW	Total xanthophyll cycle OLD	Lutein NEW	Lutein OLD
	kg ha^{-1}	mg 100 g FW^{-1}					
Mesotrione	0	27.6 b[c]	130.7	2.5 b	9.9	2.3 b	2.3
	49	22.9 b	126.7	1.9 b	8.5	2.0 b	2.0
Topramezone	0	48.0 a	144.7	4.6 a	9.7	3.9 a	3.9
	49	24.9 b	138.2	2.3 b	8.3	2.0 b	2.0

[a] Nitrogen was applied as urea (46-0-0) solution.

[b] Abbreviations: NEW, new leaf tissue after herbicide application; OLD, leaf tissue present when herbicides were applied; NS, nonsignificant; FW, fresh weight.

[c] Means followed by the same letter are not significantly different as determined by Fisher's protected LSD test ($P \leq 0.05$).

pigment data suggest efficacy enhancement may be caused by an increase in the activity of these herbicides in shoot meristems. Future research should investigate whether N fertility status increases phloem translocation of these herbicides to shoot meristems due to increased photoassimilate production, as was reported by Mithila et al. (2008) with glyphosate. Increased translocation has been attributed to N-enhanced efficacy of flazasulfuron as well (Brosnan et al. 2010). Comparisons of different water-soluble N sources and their application method, as well as the timing of N application relative to herbicide treatment are also warranted and would have implications for turfgrass managers.

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