

## Research Article

**Cite this article:** Metzger BA, Soltani N, Raeder AJ, Hooker DC, Robinson DE, Sikkema PH (2018) Tolpyralate efficacy: Part 2. Comparison of three Group 27 herbicides applied POST for annual grass and broadleaf weed control in corn. *Weed Technol* 32:707–713. doi: 10.1017/wet.2018.81

Received: 11 May 2018  
Revised: 7 August 2018  
Accepted: 14 August 2018

**Associate Editor:**

David Johnson, Pioneer/DuPont

**Nomenclature:**

Atrazine; mesotrione; tolpyralate; topramezone; barnyardgrass, *Echinochloa crus-galli* (L.) P. Beauv. ECHCG; common lambsquarters, *Chenopodium album* L. CHEAL; common ragweed, *Ambrosia artemisiifolia* L. AMBEL; green foxtail, *Setaria viridis* (L.) P. Beauv. SETVI; ladysthumb, *Persicaria maculosa* Gray. POLPE; Powell amaranth, *Amaranthus powelli* S. Watson AMAPO; redroot pigweed, *Amaranthus retroflexus* L. AMARE; pigweed spp., *Amaranthus* spp., AMASS; velvetleaf, *Abutilon theophrasti* Medik. ABUTH; wild mustard, *Sinapis arvensis* L. SINAR; corn, *Zea mays* L.

**Key words:**

4-hydroxyphenyl-pyruvate dioxygenase; biomass; density; HPPD-inhibiting herbicides; weed control

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# Tolpyralate Efficacy: Part 2. Comparison of Three Group 27 Herbicides Applied POST for Annual Grass and Broadleaf Weed Control in Corn

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**Abstract**

Tolpyralate is a new Group 27 pyrazolone herbicide that inhibits the 4-hydroxyphenyl-pyruvate dioxygenase enzyme. In a study of the biologically effective dose of tolpyralate from 2015 to 2017 in Ontario, Canada, tolpyralate exhibited efficacy on a broader range of species when co-applied with atrazine; however, there is limited published information on the efficacy of tolpyralate and tolpyralate + atrazine relative to mesotrione and topramezone, applied POST with atrazine at label rates, for control of annual grass and broadleaf weeds. In this study, tolpyralate applied alone at 30 g ai ha<sup>-1</sup> provided >90% control of common lambsquarters, velvetleaf, common ragweed, Powell amaranth/redroot pigweed, and green foxtail at 8 weeks after application (WAA). Addition of atrazine was required to achieve >90% control of wild mustard, ladysthumb, and barnyardgrass at 8 WAA. Tolpyralate + atrazine (30 + 1,000 g ai ha<sup>-1</sup>) and topramezone + atrazine (12.5 + 500 g ai ha<sup>-1</sup>) provided similar control at 8 WAA of the eight weed species in this study; however, tolpyralate + atrazine provided >90% control of green foxtail by 1 WAA. Tolpyralate + atrazine provided 18, 68, and 67 percentage points better control of common ragweed, green foxtail, and barnyardgrass, respectively, than mesotrione + atrazine (100 + 280 g ai ha<sup>-1</sup>) at 8 WAA. Overall, tolpyralate + atrazine applied POST provided equivalent or improved control of annual grass and broadleaf weeds compared with mesotrione + atrazine and topramezone + atrazine.

**Introduction**

Herbicides that inhibit the 4-hydroxyphenyl-pyruvate dioxygenase (HPPD) enzyme in susceptible plants represent the most recent herbicide mode of action successfully commercialized for weed management in Ontario, Canada. Although herbicides within the triketone and isoxazole chemical families of HPPD inhibitors have been used in North America for nearly two decades, the registration of topramezone in 2005 marked the first development of the pyrazolone family of HPPD inhibitors (Grossmann and Ehrhardt 2007).

Four HPPD inhibitors are available commercially for use in corn in the United States and Canada. These include isoxazoles (isoxaflutole), triketones (mesotrione and tembotrione), and pyrazolones (topramezone) (Health Canada 2018). Tolpyralate is a new pyrazolone herbicide molecule that was registered in 2017 in the United States and Canada, for use in field, pop, seed, and sweet corn (Anonymous 2017). Results from this study presented in a companion manuscript indicate that tolpyralate exhibits strong herbicidal efficacy in field environments (Metzger et al. 2018); however, HPPD inhibitors vary widely in their application timing, use rates, and selectivity (Hawkes 2012; Ontario Ministry of Agriculture, Food and Rural Affairs [OMAFRA] 2016). Mesotrione provides PRE and POST control of several broadleaf weeds, including velvetleaf, common lambsquarters *Amaranthus*, and *Polygonum* spp.; however, control of annual grasses, including green foxtail and barnyardgrass is variable (Crech et al. 2004; OMAFRA 2016). Tembotrione, applied POST, provides control of certain grass weeds, including giant foxtail (*Setaria faberi* Herrm.), witchgrass (*Panicum capillare* L.), and barnyardgrass, in addition to several annual broadleaf weeds (Bollman et al. 2008; Williams et al. 2011). Isoxaflutole is applied PRE or early POST and provides control of grass and broadleaf weeds (Ahrens et al. 2013; Pallet et al. 2001). Conversely, topramezone controls both grass and broadleaf species, but is only applied POST

(Anonymous 2016; Bollman et al. 2008). Similarly, tolpyralate applied POST controls several grass and broadleaf species (Metzger et al. 2018), but is reported to have limited residual activity in soil (Anonymous 2017; Kikugawa et al. 2015). At this time, there is limited published information examining the interspecific selectivity of tolpyralate relative to other HPPD inhibitors.

Due to variation in selectivity and residual control, HPPD inhibitors are commonly applied with other herbicides, such as atrazine, in tank or preformulated mixtures (OMAFRA 2016). Atrazine is a photosystem II (PSII) inhibitor and is one of the most widely used herbicides in corn; it is applied to more than 55% of total corn hectares in the United States (USDA NASS 2015). Atrazine provides broad-spectrum annual broadleaf control, has flexible application timing, and a mode of action that is complementary to that of HPPD inhibitors due to their shared interaction with plastoquinone within PSII (Creech et al. 2004; Hess 2000). Interactions between mesotrione and atrazine are widely reported. For example, a mixture of atrazine and mesotrione improves the control of common ragweed, Palmer amaranth (*Amaranthus palmeri* S. Watson), common cocklebur (*Xanthium strumarium* L.), ivyleaf morningglory (*Ipomoea hederacea* Jacq.), yellow nutsedge (*Cyperus esculentus* L.), redroot pigweed, and velvetleaf compared with mesotrione applied alone (Abendroth et al. 2006; Bollman et al. 2008; Creech et al. 2004; Johnson et al. 2002). Kohrt and Sprague (2017) found that the addition of atrazine to both mesotrione and tembotrione improved control of atrazine-resistant Palmer amaranth biotypes. Stephenson and Bond (2012) reported that the addition of atrazine to isoxaflutole applied POST improved the control of entireleaf morningglory (*Ipomoea hederacea* (L.) Jacq. var *integriuscula* Gray) and Palmer amaranth. Similarly, Bollman et al. (2008) found that the addition of atrazine to topramezone provided better control of common lambsquarters compared with topramezone applied alone.

There have been few studies investigating the benefit of the addition of atrazine to tolpyralate. Tonks et al. (2015) reported that on average, the addition of atrazine to tolpyralate improved control of broadleaf species, including velvetleaf, *Amaranthus* spp., common ragweed, common lambsquarters, and kochia [*Bassia scoparia* (L.) A. J. Scott] at 30 d after application (DAA). However, the difference in control with tolpyralate alone or with atrazine at 30 DAA varied widely by species (Tonks et al. 2015). Kohrt and Sprague (2017) reported similar control of atrazine-resistant Palmer amaranth with tolpyralate alone and tolpyralate plus atrazine.

The results presented in the companion manuscript (Metzger et al. 2018) indicate that the addition of atrazine to tolpyralate at a 1:33.3 ratio broadens the spectrum of weed control. Given that tolpyralate is reported to have limited PRE activity (Anonymous 2017), the addition of atrazine may also contribute to improved late-season control of select species; however, there is no published information in this regard. Therefore, the objectives of this study were to examine the effects of atrazine addition to tolpyralate and to compare tolpyralate efficacy in field environments to the efficacy of two other HPPD-inhibiting herbicides currently in use.

## Materials and Methods

### Experimental Methods

The results outlined in this paper describe the results from field studies conducted near Ridgeway and Exeter, Ontario, Canada

from 2015 to 2017, as described in the companion paper (Metzger et al. 2018). A total of six experiments with four replications each were conducted, arranged at each site in a randomized complete block design. Treatments investigated in this paper include tolpyralate applied at 30 g ha<sup>-1</sup>, representing the lowest current label rate (Anonymous 2017), and tolpyralate + atrazine applied at 30 + 1,000 g ha<sup>-1</sup>, representing a 1:33.3 mix ratio. This ratio was determined to be appropriate with consideration of preliminary work conducted by Tonks et al. (2015). Each of these tolpyralate treatments were compared against two current HPPD inhibitors applied at the registered POST label rate for field corn in Canada: mesotrione + atrazine (100 + 280 g ha<sup>-1</sup>) and topamezone + atrazine (12.5 + 500 g ha<sup>-1</sup>). Tolpyralate applications included methylated seed oil (MSO Concentrate<sup>®</sup>; Loveland Products Inc., Loveland, CO, USA) at 0.50% vol/vol plus 28% N urea ammonium nitrate (UAN) at 2.50% vol/vol as adjuvants. Mesotrione applications included a nonionic surfactant (Agral<sup>®</sup> 90; Syngenta Canada Inc., Guelph, ON, Canada) at 0.20% vol/vol, while topamezone treatments included blended surfactant (Merge<sup>®</sup>; BASF Canada Inc., Mississauga, ON, Canada) at 0.50% v/v plus UAN at 1.50% v/v. Treatments were applied when weeds reached 10 cm in height on average, using a four-nozzle handheld sprayer equipped with ULD12002 nozzles (Pentair, New Brighton, MN, USA), calibrated to deliver a 187 L ha<sup>-1</sup> spray volume at 240 kPa.

Visible control was assessed against the nontreated check plots at 1, 2, 4, and 8 WAA, with each species assigned a percent value between 0 and 100, where 0 signifies no control and 100 signifies complete plant death/absence from plots. At 8 WAA, the reduction in density and biomass of each species provided by all treatments was determined by counting and harvesting all plants contained in two 0.5-m<sup>2</sup> quadrats, placed randomly within each plot. Samples were allowed to dry at 60 C, and dry biomass was recorded.

For further information regarding experimental design, location characteristics, and technical methods, readers are referred to the companion manuscript derived from the same field study (Metzger et al. 2018).

### Statistical Analysis

For each of the eight weed species described in the first part of this study (Metzger et al. 2018), visible control data at 1, 2, 4, and 8 WAA, density reduction, and dry biomass reduction (8 WAA) were subjected to a mixed-model variance analysis using the GLIMMIX procedures in SAS v. 9.4 (SAS Institute, Cary, NC). A significance level of  $\alpha = 0.05$  was declared for all tests. Variance was partitioned into random effects of environment (comprising location and year), block nested within environment, and the treatment\*environment interaction, with treatment designated as the fixed effect. The appropriate model was assigned to each parameter based on the distribution and link function that best met assumptions that residuals were normally distributed, homogeneous, and had a mean of zero, as determined with a Shapiro-Wilk test and scatter plots of studentized residuals. Where appropriate, a normal distribution was used. Non-Gaussian data were analyzed using the Laplace method of integral approximation. Visible control data were assigned either a normal distribution with identity link or a beta distribution with a logit or cumulative log link, except for wild mustard control data at 4 WAA, which were arcsine square-root transformed to meet assumptions. Weed density and biomass were analyzed using a normal or lognormal distribution with identity link or a Poisson

or negative binomial distribution with a log link. Least-square means of each parameter were computed on the analysis scale and converted to the data scale using the *ilink* option for all distributions, except lognormal, in which case, data were back transformed using the omega method within PROC GLIMMIX (M. Edwards, personal communication). Least-square means were compared across each of the four treatments using Tukey-Kramer's multiple range test, and letter codes were assigned by specifying the *lines* option in the GLIMMIX procedure.

## Results and Discussion

Means comparisons included control at each assessment timing and reduction in density and biomass provided by tolypyralate alone or with atrazine, mesotrione+atrazine, and topramezone+atrazine for the eight weed species discussed in the first part of this study (Metzger et al. 2018). Means comparisons are presented in Tables 1–8.

### Common Lambsquarters

At 1 WAA, tolypyralate controlled common lambsquarters 60%, while the addition of atrazine to tolypyralate improved control to 93% (Table 1). Tolpyralate + atrazine and topramezone + atrazine provided similar control; however, tolypyralate + atrazine provided better control than mesotrione + atrazine. The numerical increase in common lambsquarters control across the four treatments at 1 WAA follows the respective rate of atrazine used with each HPPD inhibitor. However, Woodyard et al. (2009) reported similar control of common lambsquarters with atrazine applied POST at 280 and 560 g ha<sup>-1</sup> 10 DAA, suggesting the differences observed in this study at 1 WAA may be secondary to the rate of atrazine. At 2 WAA,

tolpyralate alone, tolypyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine each provided >90% control of common lambsquarters, and the four treatments were not different from one another. These results did not vary widely from the preliminary results described previously by Tonks et al. (2015), who reported 86% control of common lambsquarters with tolypyralate. Mesotrione + atrazine applied POST at the doses used in this study have previously been reported to provide effective control (93% to 99%) of common lambsquarters (Armel et al. 2003; Whaley et al. 2006; Woodyard et al. 2009). Similarly, Bollman et al. (2008) found that topramezone + atrazine applied POST, following S-metolachlor PRE, provided 100% control of common lambsquarters. At both 4 and 8 WAA, tolypyralate alone provided similar control to tolypyralate + atrazine and both industry-standard HPPD inhibitors; however, the addition of atrazine to tolypyralate led to a greater reduction in common lambsquarters density and biomass than tolypyralate applied alone. Topramezone + atrazine and mesotrione + atrazine provided a similar reduction in density and biomass to tolypyralate applied alone or with atrazine.

### Velvetleaf

At 1 WAA, tolypyralate + atrazine provided better control of velvetleaf than tolypyralate alone; however, at 2, 4, and 8 WAA, no differences were observed between treatments (Table 2). These results suggest that the addition of atrazine to tolypyralate may increase speed of velvetleaf control despite the low biologically effective dose (BED) (3.2 g ai ha<sup>-1</sup>) of tolypyralate for velvetleaf control determined in the first part of this study (Metzger et al. 2018). Speed of weed control may have important physiological implications, with more rapid control ultimately shortening the duration of weed–crop competition. At 4 and 8 WAA, all

**Table 1.** CHEAL-visible control at 1, 2, 4, and 8 wk after application (WAA), density, and biomass of common lambsquarters following treatment with tolypyralate, tolypyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	60 c	91 a	96 a	92 a	0.100 b	0.030 b
Tolpyralate + atrazine	30 + 1000	93 a	100 a	99 a	99 a	0.001 a	0.001 a
Topramezone + atrazine	12.5 + 500	87 ab	99 a	98 a	96 a	0.060 ab	0.003 ab
Mesotrione + atrazine	100 + 280	78 b	94 a	98 a	97 a	0.010 ab	0.007 ab

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .

<sup>b</sup>DM, dry matter.

**Table 2.** ABUTH-visible control at 1, 2, 4, and 8 wk after application (WAA), density, and biomass of velvetleaf following treatment with tolypyralate, tolypyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	81 b	86 a	95 a	98 a	0.0 a	0.0 a
Tolpyralate + atrazine	30 + 1000	93 a	99 a	99 a	99 a	0.0 a	0.0 a
Topramezone + atrazine	12.5 + 500	89 ab	95 a	97 a	99 a	0.0 a	0.0 a
Mesotrione + atrazine	100 + 280	87 ab	98 a	99 a	99 a	0.0 a	0.0 a

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .

<sup>b</sup>DM, dry matter.

**Table 3.** AMASS-visible control at 1, 2, 4, and 8 wk after application (WAA), density, and biomass of redroot pigweed/Powell amaranth following treatment with tolpyralate, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	70 b	83 a	92 a	91 a	2.5 b	0.6 b
Tolpyralate + atrazine	30 + 1000	96 a	98 a	98 a	97 a	0.0 a	0.0 a
Topramezone + atrazine	12.5 + 500	83 ab	86 a	86 a	86 a	0.1 ab	0.1 ab
Mesotrione + atrazine	100 + 280	82 ab	84 a	88 a	91 a	0.2 ab	0.1 ab

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .<sup>b</sup>DM, dry matter.**Table 4.** AMBEL-visible control at 1, 2, 4, and 8 wk after application (WAA), density and biomass of common ragweed following treatment with tolpyralate, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	59 c	83 ab	97 a	95 ab	0.20 b	0.03 bc
Tolpyralate + atrazine	30 + 1000	93 a	99 a	100 a	100 a	0.00 a	0.00 a
Topramezone + atrazine	12.5 + 500	80 ab	94 a	96 a	94 ab	0.01 b	0.01 b
Mesotrione + atrazine	100 + 280	67 bc	77 b	80 b	82 b	0.40 b	0.30 c

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .<sup>b</sup>DM, dry matter.**Table 5.** POLPE-visible control at 1, 2, 4, and 8 wk after application (WAA), density, and biomass of ladythumb following treatment with tolpyralate, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	71 a	70 b	72 b	69 b	7.3 b	2.6 a
Tolpyralate + atrazine	30 + 1000	86 a	92 a	94 a	95 a	2.8 ab	0.9 a
Topramezone + atrazine	12.5 + 500	73 a	78 ab	82 ab	82 ab	3.0 ab	0.3 a
Mesotrione + atrazine	100 + 280	71 a	84 ab	92 a	92 ab	2.6 a	0.1 a

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .<sup>b</sup>DM, dry matter.**Table 6.** SINAR-visible control at 1, 2, 4, and 8 wk after application (WAA), density, and biomass of wild mustard following treatment with tolpyralate, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	53 b	59 b	53 b	55 b	27.5 b	62.3 b
Tolpyralate + atrazine	30 + 1000	83 a	99 a	100 a	100 a	0.00 a	0.00 a
Topramezone + atrazine	12.5 + 500	76 ab	99 a	99 a	100 a	0.00 a	0.00 a
Mesotrione + atrazine	100 + 280	73 ab	99 a	100 a	100 a	0.00 a	0.00 a

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .<sup>b</sup>DM, dry matter.

treatments provided  $\geq 95\%$  control of velvetleaf, and there were no differences among treatments with respect to reduction in velvetleaf density or biomass. Similar results were outlined by Tonks et al. (2015), who reported that tolpyralate, tolpyralate + atrazine

and topramezone + atrazine controlled velvetleaf 87%, 94%, and 93%, respectively. Likewise, mesotrione has been found to exhibit excellent foliar activity on velvetleaf (Creech et al. 2004; Johnson and Young 2002).

**Table 7.** SETVI-visible control at 1, 2, 4, and 8 wk after application (WAA), density, and biomass of green foxtail following treatment with tolpyralate, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	72 b	77 a	89 a	91 a	7.4 a	1.2 a
Tolpyralate + atrazine	30 + 1000	90 a	96 a	96 a	93 a	4.9 a	1.3 a
Topramezone + atrazine	12.5 + 500	70 b	84 a	80 a	81 a	16 b	6.1 b
Mesotrione + atrazine	100 + 280	32 c	35 b	33 b	25 b	36 c	51 c

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .

<sup>b</sup>DM, dry matter.

**Table 8.** ECHCG-visible control at 1, 2, 4, and 8 wk after application (WAA), density, and biomass of barnyardgrass following treatment with tolpyralate, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine in field studies conducted in Ontario, Canada, in 2015, 2016, and 2017.<sup>a</sup>

Treatment	Dose (g ai ha <sup>-1</sup> )	1 WAA	2 WAA	4 WAA	8 WAA	Density (no. m <sup>-2</sup> )	Biomass (g DM m <sup>-2</sup> ) <sup>b</sup>
Tolpyralate	30	76 a	82 ab	86 a	84 ab	14 a	3.6 a
Tolpyralate + atrazine	30 + 1000	86 a	97 a	97 a	93 a	4.0 a	0.7 a
Topramezone + atrazine	12.5 + 500	74 a	74 b	81 a	79 ab	9.9 a	3.0 a
Mesotrione + atrazine	100 + 280	44 b	31 c	27 b	26 b	9.7 a	6.3 a

<sup>a</sup>Means followed by the same letter within columns are not significantly different according to Tukey-Kramer multiple range test  $\alpha = 0.05$ .

<sup>b</sup>DM, dry matter.

### Pigweed Species

Similar to common lambsquarters and velvetleaf, differences were observed among treatments in control of pigweed species (*Amaranthus* spp.) at 1 WAA but not at later assessment timings. The addition of atrazine to tolpyralate provided 96% control of pigweed species at 1 WAA, which was superior to tolpyralate applied alone, but not different from either mesotrione + atrazine or topramezone + atrazine (Table 3). Tolpyralate alone provided equivalent control of pigweed species compared with tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine at 2, 4, and 8 WAA. Tolpyralate + atrazine provided a greater reduction in pigweed density and biomass than tolpyralate alone, but results were similar to both topramezone + atrazine and mesotrione + atrazine. Similar activity with these HPPD inhibitors has been reported in other *Amaranthus* spp. (Hugie et al. 2008; Kohrt and Sprague 2017; Tonks et al. 2015; Woodyard et al. 2009). Kohrt and Sprague (2017) observed no difference in control of atrazine-resistant Palmer amaranth with tolpyralate (40 g ai ha<sup>-1</sup>) compared with tolpyralate + atrazine (40 + 560 g ai ha<sup>-1</sup>). Similarly, Armel et al. (2003) found that mesotrione (105 g ai ha<sup>-1</sup>) with or without atrazine (560 g ai ha<sup>-1</sup>) controlled smooth pigweed (*Amaranthus hybridus* L.) 99%. Tonks et al. (2015) reported an average of 89% control of *Amaranthus* spp. including Palmer amaranth, redroot pigweed, and waterhemp [*Amaranthus tuberculatus* (Moq.) J.D. Sauer] with tolpyralate (30 g ai ha<sup>-1</sup>). Thus, consistent with results obtained in the BED study (Metzger et al. 2018), tolpyralate exhibits high activity on *Amaranthus* spp.

### Common Ragweed

At 1 WAA, there was a greater range in common ragweed control than in other broadleaf species. Tolpyralate + atrazine

provided 34 percentage points better control than tolpyralate alone and 26 percentage points better control than mesotrione + atrazine, but results were not significantly different from topramezone + atrazine (Table 4). Control with mesotrione + atrazine was similar to tolpyralate alone and topramezone + atrazine treatments. At 2 WAA, tolpyralate and tolpyralate + atrazine provided similar control of common ragweed. Tolpyralate + atrazine and topramezone + atrazine provided similar control of common ragweed, which was greater than mesotrione + atrazine. At 4 WAA, tolpyralate, tolpyralate + atrazine, and topramezone + atrazine each provided better common ragweed control than mesotrione + atrazine. Previous research has shown variable control of common ragweed with mesotrione, but improved control when co-applied with atrazine (Armel et al. 2003; Bollman et al. 2008; Whaley et al. 2006). At 8 WAA, tolpyralate + atrazine controlled common ragweed 100%, which was equivalent to tolpyralate alone and topramezone + atrazine control and greater than mesotrione + atrazine control. It is possible that poorer control of common ragweed with mesotrione + atrazine at 8 WAA may be reflective of the comparatively lower rate of atrazine applied. However, tolpyralate alone provided 95% control of common ragweed in this study when no atrazine was applied, suggesting that the observed differences can be attributed to the HPPD inhibitors. Additionally, tolpyralate alone provided an equivalent reduction in common ragweed density and biomass compared with topramezone + atrazine and mesotrione + atrazine treatments. In contrast, there was a greater decrease in common ragweed density and biomass with tolpyralate + atrazine compared with other treatments. Therefore, the addition of atrazine to tolpyralate provided no significant benefit in visible control at 2, 4, and 8 WAA, but it provided more complete weed necrosis at 8 WAA, contributing to a greater reduction in common ragweed density and biomass compared with all other treatments. Similarly, the results from

this study suggest that treatments with atrazine at 500 or 1,000 g ha<sup>-1</sup> provided a greater numerical decrease in common ragweed density than tolpyralate alone or mesotrione + atrazine. Therefore, it is likely that these higher rates of atrazine contributed to better residual control of late-emerging seedlings, which were counted during harvests, but contributed little to biomass measurements. Overall, the results from this study are similar to those of Tonks et al. (2015), who reported 89% and 95% control of common ragweed with tolpyralate and tolpyralate + atrazine, respectively.

### Ladysthumb

There was considerable variation in control of ladysthumb observed with all treatments, potentially due to interspecific competition within plots that could have prevented thorough spray coverage of ladysthumb foliage in the lower part of the weed canopy. At 1 WAA, all treatments provided equivalent control; however, treatment separation was present at later assessment timings. Consistent with findings described in the first part of this study (Metzger et al. 2018), the addition of atrazine to tolpyralate improved ladysthumb control at 2, 4, and 8 WAA (Table 5). At 2, 4, and 8 WAA, topramezone + atrazine provided control which was similar to tolpyralate alone, tolpyralate + atrazine, and mesotrione + atrazine. At 4 WAA, mesotrione + atrazine provided better ladysthumb control than tolpyralate alone; however, by 8 WAA, control with both treatments was equivalent. At 8 WAA, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine all provided similar control of ladysthumb. Mesotrione + atrazine reduced ladysthumb density more than tolpyralate alone; however, all treatments provided a similar reduction in biomass. Previous research has not investigated tolpyralate efficacy on this species; however, in agreement with relatively higher BED values outlined in the first part of this study (Metzger et al. 2018), ladysthumb appears to exhibit greater tolerance to tolpyralate than other broadleaf species, including common lambsquarters, velvetleaf, pigweed species, and common ragweed. These results suggest that the addition of atrazine is necessary to achieve adequate control (>80%) of this species. Comparable findings have been reported by Rahman et al. (2013), who found that the addition of atrazine to topramezone was required for control of another *Polygonum* species, prostrate knotweed [*Polygonum aviculare* (L.)].

### Wild Mustard

Consistent with findings presented previously (Metzger et al. 2018), wild mustard showed high tolerance to tolpyralate. At 1 WAA, bleaching symptoms were visible on wild mustard plants across all treatments; however, tolpyralate + atrazine provided better control than tolpyralate alone (Table 6). At 1 WAA, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine provided similar control of wild mustard. At 2, 4, and 8 WAA, tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine controlled wild mustard  $\geq 99\%$ , which was better than tolpyralate applied alone. Similarly, density and dry weight were reduced to zero with tolpyralate + atrazine, topramezone + atrazine, and mesotrione + atrazine. Consistent with these results, atrazine applied alone POST is reported to have excellent efficacy on wild mustard (OMAFRA 2016), suggesting there may be little benefit to inclusion of the HPPD inhibitor. However, mesotrione applied POST has been reported to control wild

mustard (Cornes 2005). Because atrazine was not applied alone in this study, distinctions cannot be made between the relative wild mustard control provided by atrazine versus the respective HPPD inhibitor.

### Green Foxtail

At 1 WAA, tolpyralate + atrazine was the most efficacious treatment for control of green foxtail. Control of green foxtail with tolpyralate was similar when applied alone or in combination with atrazine at most assessment timings; however, at 1 WAA, tolpyralate + atrazine provided 18 percentage points better control than tolpyralate alone (Table 7). Tolpyralate + atrazine also provided better green foxtail control than topramezone + atrazine and mesotrione + atrazine. At 2, 4, and 8 WAA, tolpyralate applied alone or in combination with atrazine and topramezone + atrazine provided better control of green foxtail than mesotrione + atrazine. These results are consistent with those reported in the literature, which have documented poor control of *Setaria* spp. with mesotrione (Armel et al. 2003; Creech et al. 2004; Kaastra et al. 2008), but acceptable control with topramezone (Bollman et al. 2008; Grossmann and Ehrhardt 2007; Kaastra et al. 2008; Whaley et al. 2006). Reduction in green foxtail density and biomass was equivalent with tolpyralate applied alone or with atrazine and was greater than with topramezone + atrazine and mesotrione + atrazine. Results from the first part of this study (Metzger et al. 2018) determined the BED of tolpyralate in green foxtail to be 29.6 g ai ha<sup>-1</sup> 8 WAA when applied alone. Thus, the dose of 30 g ai ha<sup>-1</sup> examined in this analysis is likely to diminish any contribution to green foxtail control provided by atrazine; however, control data collected at 1 WAA suggest that atrazine may improve speed of green foxtail control with tolpyralate.

### Barnyardgrass

Control of barnyardgrass followed trends similar to green foxtail control but was more variable with all treatments. Tolpyralate alone or with the addition of atrazine provided similar control at all assessment timings (Table 8). At 1 WAA, tolpyralate + atrazine and topramezone + atrazine provided similar barnyardgrass control, while mesotrione + atrazine provided poorer control. In agreement with these results, mesotrione + atrazine has not been found to provide adequate control of barnyardgrass in Ontario in previous studies (OMAFRA 2016). In contrast, both Creech et al. (2004) and De Cauwer et al. (2012) found that mesotrione provided complete barnyardgrass control; however, those studies were conducted in a greenhouse environment. At 2 WAA, tolpyralate + atrazine provided better control of barnyardgrass than topramezone + atrazine and mesotrione + atrazine. Topramezone has previously been reported to control barnyardgrass at doses similar to those used in this study (De Cauwer et al. 2012). At 4 and 8 WAA, tolpyralate alone and tolpyralate + atrazine provided similar barnyardgrass control. No statistically significant difference was observed among treatments in barnyardgrass density or biomass at 8 WAA; however, the numerical differences across treatments may have biological significance.

### Conclusions

The addition of atrazine to tolpyralate improved the control of ladysthumb and wild mustard, while there was no improvement in control of common lambsquarters, velvetleaf, pigweed

species, common ragweed, green foxtail, or barnyardgrass compared with tolpyralate applied alone. Tolpyralate + atrazine and topramezone + atrazine provided equivalent control of common lambsquarters, velvetleaf, pigweed species, common ragweed, ladysthumb, wild mustard, green foxtail, and barnyardgrass 8 WAA. Tolpyralate + atrazine and mesotrione + atrazine provided equivalent control of common lambsquarters, velvetleaf, pigweed species, ladysthumb, and wild mustard; in contrast, tolpyralate + atrazine provided better control of common ragweed, green foxtail, and barnyardgrass than mesotrione + atrazine. The co-application of tolpyralate with atrazine at the 1:33.3 ratio used in this study resulted in more rapid control of all species compared with tolpyralate alone, with the exception of ladysthumb and barnyardgrass. Additionally, the rate of atrazine used with tolpyralate in this study may have contributed to extended residual control of late-emerging weed seedlings, particularly in the case of common ragweed. However, it is unclear what ratio of tolpyralate to atrazine is required for these effects to occur. Future research on the optimal ratio of atrazine to use in combination with tolpyralate would help to maximize weed control and reduce the selection pressure for resistance to a single herbicide mechanism of action, while minimizing environmental loading of herbicides.

**Acknowledgments.** The authors thank Christy Shropshire and Todd Cowan for their technical contributions to this study. Funding for this project was provided in part by the Grain Farmers of Ontario and through the Growing Forward (GF 2) program administered by the Agricultural Adaptation Council (AAC) and by ISK Biosciences Inc. No conflicts of interest have been declared.

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