

# Interaction between tolpyralate and atrazine for the control of annual weed species in corn

John C. Flutters<sup>1</sup>, Nader Soltani<sup>2</sup> , Mariano Galla<sup>3</sup>, David C. Hooker<sup>4</sup> ,  
Darren E. Robinson<sup>5</sup> and Peter H. Sikkema<sup>5</sup> 

## Research Article

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### Author for correspondence:

Nader Soltani, Department of Plant Agriculture, University of Guelph, 120 Main Street East, Ridgetown, ON N0P 2C0, Canada.  
Email: [soltanin@uoguelph.ca](mailto:soltanin@uoguelph.ca)

<sup>1</sup>Graduate Student, Department of Plant Agriculture, University of Guelph, Ridgetown, ON, Canada; <sup>2</sup>Adjunct Professor, Department of Plant Agriculture, University of Guelph, Ridgetown, ON, Canada; <sup>3</sup>Product Development and Technical Service Representative, ISK Biosciences Inc., Concord, OH, USA; <sup>4</sup>Associate Professor, Department of Plant Agriculture, University of Guelph, Ridgetown, ON, Canada and <sup>5</sup>Professor, Department of Plant Agriculture, University of Guelph, Ridgetown, ON, Canada

### Abstract

Many studies have documented the interaction between 4-hydroxyphenylpyruvate dioxygenase (HPPD)-inhibiting and photosystem II (PSII)-inhibiting herbicides. Most have focused on the interaction between mesotrione and atrazine, with only a few studies characterizing the nature of the interaction between tolpyralate and atrazine. Therefore, five field experiments were conducted in Ontario, Canada, over a 3-yr period (2019 to 2021) to characterize the interaction between three rates of tolpyralate (15, 30, and 45 g ai ha<sup>-1</sup>) and three rates of atrazine (140, 280, and 560 g ai ha<sup>-1</sup>) for the control of seven annual weed species in corn (*Zea mays* L.). Tolpyralate at 30 or 45 g ha<sup>-1</sup> applied with atrazine at 280 or 560 g ha<sup>-1</sup> controlled velvetleaf (*Abutilon theophrasti* Medik.), redroot pigweed (*Amaranthus retroflexus* L.), common ragweed (*Ambrosia artemisiifolia* L.), common lambsquarters (*Chenopodium album* L.), and wild mustard (*Sinapis arvensis* L.) >90% at 8 wk after application (WAA). Tolpyralate and atrazine were synergistic at each rate combination for the control of *A. theophrasti* at 8 WAA. In contrast, *A. retroflexus* and *S. arvensis* control at 8 WAA was additive with each rate combination. At 8 WAA, *C. album* control was generally additive, but one rate combination was synergistic. *Ambrosia artemisiifolia* control at 8 WAA was synergistic with five rate combinations and additive with the other four. Barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.] control at 8 WAA was additive with seven of the rate combinations and synergistic with two. *Setaria* spp. control at 8 WAA was synergistic with one more rate combination compared with *E. crus-galli*, but the two weed species shared the same synergistic rate combinations. This study concludes that extrapolation or broad classifications of the interaction between tolpyralate and atrazine would be inappropriate, as the interaction can vary due to herbicide rate, weed species, and the response parameter analyzed.

## Introduction

Herbicides that inhibit 4-hydroxyphenylpyruvate dioxygenase (HPPD) and photosystem II (PSII) are complementary with each other and are commonly tank mixed for postemergence weed control in corn (*Zea mays* L.). Inhibition of HPPD halts homogentisic acid formation, which stops the production of plastoquinone and tocopherols in susceptible plants (Pallett et al. 1998; Schulz et al. 1993; Secor 1994; Trebst et al. 2002; Tsegaye et al. 2002). This promotes the degradation of plant cells, because the susceptible plant can no longer quench destructive reactive oxygen species (ROS) with a depleted plastoquinone and tocopherol reserve (Kruk et al. 2005; Pallett et al. 1998; Schulz et al. 1993; Trebst et al. 2002). PSII inhibitors compete with plastoquinone for the Q<sub>B</sub> binding niche on the D1 protein in the photosynthetic electron transport chain, which promotes a buildup of ROS (Hess 2000). The ROS are produced to an amount that overwhelms the quenching capabilities of the carotenoid system and induces lipid peroxidation followed by plant death (Hess 2000). Therefore, when HPPD and PSII inhibitors are tank mixed, the two modes of action work jointly in susceptible plants because (1) the PSII inhibitor binds more efficiently to the D1 protein, because the HPPD inhibitor depletes the plant's plastoquinone; and (2) lipid peroxidation promoted by the PSII inhibitor is amplified, because the HPPD inhibitor stops the production of antioxidants (Abendroth et al. 2006; Armel et al. 2005; Creech et al. 2004; Kim et al. 1999).

Additive, synergistic, or antagonistic interactions can occur between component herbicides in a tank mix (Colby 1967). To characterize the nature of the interaction between two herbicides, Colby's equation is used to compute the expected weed control for a herbicide tank mix (Colby 1967). Additive, synergistic, or antagonistic interactions occur when the observed weed control is equal, greater, or less than expected, respectively (Colby 1967). The interrelationship of the modes of action of HPPD and PSII inhibitors is often credited for documented synergistic

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**Table 1.** Location, year, soil characteristics, corn planting and harvest dates, herbicide application dates, and corn development stages at application for five field trials in Ontario, Canada, in 2019, 2020, and 2021.

Research site	Year	Soil characteristics <sup>a</sup>			Corn planting date	Corn harvest date	Herbicide application information	
		Texture	OM	pH			Application date	Corn development stage
Huron Research Station	2019	Clay loam	3.9	7.8	June 9	n/a <sup>b</sup>	July 5	V5
	2020	Loam	3.6	7.9	May 6	October 26	June 12	V5
	2021	Clay loam	4.4	7.9	April 27	November 9	June 7	V5
Ridgetown Campus	2020	Sandy clay loam	3.1	6.8	May 25	November 5	June 25	V4
	2021	Clay loam	4.1	7.3	May 14	October 1	June 12	V5

<sup>a</sup>Soil cores taken to a depth of 15 cm and subsequent analysis at A&L Canada Laboratories (2136 Jetstream Road, London, ON N5V 3P5, Canada) were used to determine soil characteristics. OM, organic matter.

<sup>b</sup>Corn not harvested in 2019.

interactions between the two groups of herbicides (Abendroth et al. 2006; Armel et al. 2005; Kim et al. 1999). Atrazine is a PSII inhibitor that is commonly tank mixed with an HPPD inhibitor to improve postemergence weed control in corn (Johnson et al. 2002; Metzger et al. 2018; Whaley et al. 2006; Williams et al. 2011). Chahal et al. (2019) observed increased absorption of mesotrione when mesotrione and atrazine were tank mixed and applied to Palmer amaranth (*Amaranthus palmeri* S. Watson), while atrazine absorption, translocation, and metabolism were not affected. This increase in absorption of mesotrione was postulated to be another potential basis of synergy between HPPD and PSII inhibitors, though it has not been observed in all weed species. For example, Armel et al. (2005) found that absorption, translocation, and metabolism of mesotrione were not affected in Canada thistle [*Cirsium arvense* (L.) Scop.] when tank mixed with atrazine. The co-application of atrazine and HPPD-inhibiting herbicides post-emergence has resulted in synergistic improvements in the control of waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer], *A. palmeri*, redroot pigweed (*Amaranthus retroflexus* L.), wild radish (*Raphanus raphanistrum* L.), velvetleaf (*Abutilon theophrasti* Medik.), giant ragweed (*Ambrosia trifida* L.), common cocklebur (*Xanthium strumarium* L.), red morningglory (*Ipomoea coccinea* L.), common lambsquarters (*Chenopodium album* L.), and giant foxtail (*Setaria faberi* Herrm.) (Armel et al. 2007; Hugie et al. 2008; Kohrt and Sprague 2017; Walsh et al. 2012; Woodyard et al. 2009a, 2009b). Additive interactions have also been documented between HPPD-inhibiting herbicides and atrazine for control of *Amaranthus* spp., *A. theophrasti*, *A. trifida*, *C. album*, and *R. raphanistrum* (Hugie et al. 2008; Kohrt and Sprague 2017; Walsh et al. 2012; Willemse et al. 2021; Woodyard et al. 2009a, 2009b).

The classification of the interaction between HPPD inhibitors and atrazine depends on the weed species, weed biotype herbicide-resistance profile, weed height at application, HPPD inhibitor, rate of herbicide used, and assessment timing. Hugie et al. (2008) evaluated eight rates of atrazine tank mixed with a constant rate of mesotrione and seven rates of mesotrione with a constant rate of atrazine to characterize the interaction of the two herbicides on triazine-sensitive and triazine-resistant *A. retroflexus*. The study demonstrated one synergistic interaction on triazine-sensitive *A. retroflexus*, but nine synergistic interactions on triazine-resistant *A. retroflexus* of the 15 combinations of mesotrione and atrazine evaluated (Hugie et al. 2008). Woodyard et al. (2009a) documented that mesotrione at 35 g ai ha<sup>-1</sup> was synergistic with atrazine at 560 g ai ha<sup>-1</sup> at 1 wk after application (WAA), but additive at 4 WAA for *C. album* control; however, the same tank mix was

synergistic at both assessment timings for *A. tuberculatus* and *A. trifida* control. In the same study, mesotrione at 35 and 105 g ai ha<sup>-1</sup> was additive with 280 g ai ha<sup>-1</sup> of atrazine, but synergistic with 560 g ai ha<sup>-1</sup> of atrazine for the control of *A. trifida* at 1 WAA; however, control of *A. tuberculatus* and *C. album* was synergistic at 1 WAA with these rate combinations (Woodyard et al. 2009a). In a study on *A. palmeri* control, mesotrione and topramezone were synergistic with atrazine, while tembotrione and topralate were additive with atrazine for the control of 8-cm *A. palmeri* (Kohrt and Sprague 2017). In the same study, mesotrione and tembotrione were synergistic with atrazine on 15-cm *A. palmeri*, but topralate and topramezone were additive with atrazine (Kohrt and Sprague 2017). A range of factors affects the ability to detect synergy between HPPD inhibitors and atrazine, which adds complexity to the characterization of their interaction.

Much of the peer-reviewed literature has documented the interaction between mesotrione and atrazine; few studies characterized the interaction between topralate and atrazine. It is hypothesized that topralate + atrazine tank mixes synergistically control weeds in corn. The objective of this study was to investigate the interaction between topralate and atrazine using three rates of each herbicide for the control of five annual broad-leaf and two annual grass weed species across a range of response parameters.

## Materials and Methods

Five field experiments were conducted over three field seasons (2019, 2020, and 2021) at University of Guelph research sites in Ridgetown, ON, Canada (Ridgetown Campus, 42.45°N, 81.88°W) and near Exeter, ON, Canada (Huron Research Station, 43.32°N, 81.50°W) (Table 1). Fields were prepared with conventional tillage practices and fertilization to meet corn requirements before planting. Corn was seeded in rows spaced 75-cm apart to a depth of 5 cm at approximately 85,000 seeds ha<sup>-1</sup>. DKC44-13RIB® (Bayer CropScience Canada, 160 Quarry Boulevard SE, Calgary, AB T2C 3G3, Canada) was planted at the Huron Research Station in 2019. DKC42-04RIB® was planted at the Huron Research Station in 2020 and 2021. DKC42-60RIB® and DKC39-97RIB® were planted at Ridgetown Campus in 2020 and 2021, respectively. Plot length was 10 m at the Huron Research Station and 8 m at the Ridgetown Campus. The plot width was 3 m (4 corn rows). Randomized complete block designs with four blocks in each experiment were used. Details on the five field experiments,

including soil information, corn planting and harvest dates, herbicide application dates, and corn development stage at herbicide application are presented in Table 1.

The treatments were arranged in a two-factor factorial. Factor A included four rates of tolpyralate (Shieldex<sup>®</sup> 400SC herbicide, 400 g ai L<sup>-1</sup>, ISK Biosciences, 740 Auburn Road, Concord, OH 44077, USA): 0, 15, 30, and 45 g ai ha<sup>-1</sup>. The rates of tolpyralate used represent 0.5X, 1X, and 1.5X the lowest label rate (Anonymous 2021). Factor B included four rates of atrazine (AAtrex<sup>®</sup> Liquid 480, 480 g ai L<sup>-1</sup>, Syngenta Canada, 140 Research Lane, Guelph, ON N1G 4Z3, Canada): 0, 140, 280, and 560 g ai ha<sup>-1</sup>. The rates of atrazine used represent 0.25X, 0.5X, and 1X the lowest recommended label rate of atrazine to use with tolpyralate (Anonymous 2021). A CO<sub>2</sub>-powered backpack sprayer was used to administer the herbicide treatments with a spray volume of 200 L ha<sup>-1</sup> at 240 kPa through four ULD120-02 spray nozzles (Pentair, 375 5th Avenue NW, New Brighton, MN 55112, USA) at 50-cm spacing on the spray boom producing a 2-m spray width. Herbicides were applied postemergence when the weed canopy reached 15 cm in height. Depending on the experiment, natural infestations of *A. theophrasti*, *A. retroflexus*, *A. artemisiifolia*, *C. album*, wild mustard (*Sinapis arvensis* L.), *Setaria* spp., and *E. crus-galli* occurred. Experiments contained a heterogeneous population of green foxtail [*Setaria viridis* (L.) P. Beauv.] and *S. faberi*. Therefore, data collection and statistical analysis were conducted on *Setaria* spp. instead of either species individually.

Weed control by species was visually assessed at 2, 4, and 8 WAA as an estimation of the aboveground weed biomass reduction relative to the nontreated control on a percentage scale of 0% to 100%. At 1, 2, and 4 WAA, visible corn injury was evaluated on a 0% to 100% scale; greater values of corn injury indicated greater corn injury. Weed control and corn injury evaluations at 2 WAA were not recorded at the Huron Research Station in 2019. At 8 WAA, the density of each weed species in each plot was determined by counting the number of weeds in two randomly placed 0.5-m<sup>2</sup> quadrats. Concurrent with density determination, the weeds were clipped at the soil surface within the quadrats, sorted by species into paper bags, and placed in a kiln drier so the weed biomass reached constant moisture. Dry biomass for each weed species was then weighed and recorded. A small plot combine was used to harvest the center two corn rows of each plot at corn harvest maturity to obtain grain corn yield weight and harvest moisture. Corn yields were corrected to 15.5% moisture before statistical analysis. Corn yield was not obtained from the Huron Research Station in 2019, because a combination of wet planting conditions and drought during the growing season decimated plots and reduced the relevance of the corn yield as a representation of weed control from the herbicide treatments.

### Statistical Analysis

Response parameters were analyzed using a generalized linear mixed model in SAS v. 9.4 (SAS Institute, 100 SAS Campus Drive, Cary, NC 27513, USA). Variance was partitioned into the fixed effects of tolpyralate (Factor A), atrazine (Factor B), and the interaction between tolpyralate and atrazine. An *F*-test was used to determine the significance of the fixed effects at a significance level of  $\alpha = 0.05$ . Environment (site and year groupings), block within environment, and the interaction of environment with Factors A and B were the random effects. A restricted

log-likelihood test with a type I error set at  $\alpha = 0.05$  was used to determine the significance of random effects. Data for each response parameter were pooled across environments. Control levels of *A. theophrasti*, *A. retroflexus*, *A. artemisiifolia*, *C. album*, and *S. arvensis* at all evaluation timings were arcsine square-root transformed. Data were back-transformed for result presentation when an arcsine square-root transformation was used. All weed density and dry biomass data were analyzed with a lognormal distribution in the GLIMMIX procedure; the omega method of back-transformation (M Edwards, Ontario Agricultural College Statistics Consultant, University of Guelph, personal communication) was used for presentation of results. Barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.] and *Setaria* spp. control and corn yield data were not transformed and were analyzed using a normal distribution. The distributions and transformations chosen were used to best meet the assumptions of the analysis by visual inspection of studentized residual plots and the Shapiro-Wilk statistic. Residuals were assumed to be random, independent of treatment and design effects, homogeneous, and normally distributed about a mean of zero. Least-square means for the main effects (tolpyralate or atrazine) were only compared when there was no statistically significant interaction between the two herbicide factors. When the interaction between tolpyralate and atrazine was significant, the simple effects were discussed. The Tukey-Kramer multiple-range test with type I error set to  $\alpha = 0.05$  was used to distinguish least-square means that were significantly different from one another for simple and main effects.

Each herbicide tank mix had the expected weed control calculated with Colby's equation (Equation 1) by using the observed values for tolpyralate alone (*X*) and atrazine alone (*Y*) in each block.

$$\text{Expected} = (X + Y) - [(X * Y)/100] \quad [1]$$

The modified Colby's equation (Equation 2), which includes the value from the nontreated control (*Z*) within each block, was used to calculate the expected weed density and dry biomass for the herbicide tank mixes.

$$\text{Expected} = [(X * Y)/Z] \quad [2]$$

Two-tailed *t*-tests were used to compare the observed values and calculated expected values for weed control, density, and dry biomass. An additive interaction occurred when observed and expected values were similar. Synergistic or antagonistic interactions occurred when the observed and expected values were significantly different at  $\alpha = 0.05$ ; for presentation of results,  $\alpha = 0.01$  was also noted.

## Results and Discussion

### *Abutilon theophrasti*

*Abutilon theophrasti* results are pooled from two experiments from Ridgetown Campus in 2020 and 2021. The interaction between tolpyralate rate and atrazine rate was significant for *A. theophrasti* control at 2, 4, and 8 WAA, so the effect of every tolpyralate rate was analyzed by every atrazine rate and the effect of every atrazine rate was analyzed by every tolpyralate rate (Table 2). At 2 and 4 WAA, tolpyralate applied alone controlled *A. theophrasti* 16 percentage points more when applied at 45 g ha<sup>-1</sup> than at 15 g ha<sup>-1</sup>; the 30 g ha<sup>-1</sup> rate of tolpyralate controlled *A. theophrasti*

**Table 2.** Least-square means and significance of main effects and interaction for *Abutilon theophrasti* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across two field trials in Ontario, Canada, in 2020 and 2021.

Main effects	Rate	<i>A. theophrasti</i> control			Density	Dry biomass <sup>a</sup>
		2 WAA	4 WAA	8 WAA		
	—g ai ha <sup>-1</sup> —	—%—			—plants m <sup>-2</sup> —	—g m <sup>-2</sup> —
Tolpyralate <sup>b</sup>						
No tank-mix partner	—	16	22	21	2.9	8.7 b
Tolpyralate	15	81	88	90	0.8	0.6 a
Tolpyralate	30	87	93	94	0.5	0.3 a
Tolpyralate	45	91	96	97	0.6	0.3 a
SE		2.7	2.7	2.7	0.2	0.7
Tolpyralate P-value		0.0002	0.0006	0.0015	0.1325	0.0046
Atrazine <sup>b</sup>						
No tank-mix partner	—	41	51	56	1.4	2.0
Atrazine	140	74	82	83	0.9	1.0
Atrazine	280	81	88	88	1.2	1.6
Atrazine	560	83	90	89	1.1	1.5
SE		2.7	2.7	2.7	0.2	0.7
Atrazine P-value		0.0127	0.0016	0.0032	0.2998	0.7837
Interaction						
Tolpyralate × atrazine P-value		0.0317	0.0007	0.0025	0.7547	0.9613

<sup>a</sup>Means within the same main effect and column followed by the same lowercase letter are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate<sup>®</sup>, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

**Table 3.** *Abutilon theophrasti* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across two field trials in Ontario, Canada, in 2020 and 2021.<sup>a</sup>

Herbicide treatment <sup>b</sup>	No tank-mix partner <sup>b</sup>	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Control at 2 WAA					
No tank-mix partner	0 b X	—%—			5.2
Atrazine (140 g ai ha <sup>-1</sup> )	20 a X	56 b Y	64 b YZ	72 b Z	5.4
Atrazine (280 g ai ha <sup>-1</sup> )	27 a Y	78 a Y (65)*	91 a Z (72)**	94 a Z (78)**	5.2
Atrazine (560 g ai ha <sup>-1</sup> )	34 a Y	92 a Z (68)**	94 a Z (74)**	95 a Z (80)**	4.7
SE	2.5	91 a Z (71)**	92 a Z (77)**	97 a Z (82)**	1.9
Control at 4 WAA					
No tank-mix partner	0 c X	67 c Y	78 b YZ	83 b Z	6.0
Atrazine (140 g ai ha <sup>-1</sup> )	29 b X	86 b Y (77)*	95 a YZ (84)**	98 a Z (88)**	5.2
Atrazine (280 g ai ha <sup>-1</sup> )	35 ab Y	95 a Z (79)**	98 a Z (86)**	98 a Z (89)**	4.8
Atrazine (560 g ai ha <sup>-1</sup> )	46 a Y	96 a Z (82)**	96 a Z (88)**	99 a Z (91)**	4.1
SE	3.4	2.5	1.7	1.4	
Control at 8 WAA					
No tank-mix partner	0 b Y	74 b Z	83 b Z	87 b Z	6.5
Atrazine (140 g ai ha <sup>-1</sup> )	29 a Y	89 a Z (81)*	95 a Z (87)**	98 a Z (91)**	5.3
Atrazine (280 g ai ha <sup>-1</sup> )	35 a Y	96 a Z (83)**	98 a Z (89)**	97 a Z (91)**	4.9
Atrazine (560 g ai ha <sup>-1</sup> )	42 a Y	96 a Z (85)**	96 a Z (90)**	99 a Z (93)**	4.4
SE	3.3	2.4	1.7	1.3	
Density					
No tank-mix partner	2.7	1.9	0.6	0.7	0.5
Atrazine (140 g ai ha <sup>-1</sup> )	2.2	0.2 (1.3)	0.8 (0.4)	0.6 (0.3)	0.3
Atrazine (280 g ai ha <sup>-1</sup> )	3.8	0.8 (1.9)	0.4 (0.5)	0.9 (0.3)	0.5
Atrazine (560 g ai ha <sup>-1</sup> )	3.5	0.8 (1.3)	0.5 (0.3)	0.2 (0.5)	0.5
SE	0.6	0.5	0.2	0.2	
Dry biomass					
No tank-mix partner	11.9	0.9	0.1	0.2	1.2
Atrazine (140 g ai ha <sup>-1</sup> )	4.9	0.1 (0.6)	0.4 (0.4)	0.6 (0.2)	1.0
Atrazine (280 g ai ha <sup>-1</sup> )	11.5	0.7 (1.8)	0.1 (1.7)	0.3 (0.0)	1.7
Atrazine (560 g ai ha <sup>-1</sup> )	9.6	0.7 (0.5)	0.4 (0.0)	0.2 (0.2)	1.3
SE	2.1	0.4	0.2	0.2	

<sup>a</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ). Values in parentheses are expected values calculated from Colby's equation. Asterisks indicate significant differences of between observed and expected values based on a two-tailed *t*-test: \* $P < 0.05$ ; \*\* $P < 0.01$ .

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate<sup>®</sup>, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

similarly to both these rates of tolpyralate at 2 and 4 WAA (Table 3). At 8 WAA, there were no differences among the three rates of tolpyralate for the control of *A. theophrasti* when tolpyralate was applied alone. The three rates of atrazine controlled *A. theophrasti* 20% to 34%, 29% to 46%, and 29% to 42% at 2, 4, and 8 WAA, respectively. There was no difference in *A. theophrasti*

control among atrazine rates at 2 and 8 WAA; at 4 WAA, atrazine controlled *A. theophrasti* 17 percentage points more when applied at 560 g ha<sup>-1</sup> than at 140 g ha<sup>-1</sup>; control with the 280 g ha<sup>-1</sup> rate was intermediate and similar to both. When 140 g ha<sup>-1</sup> of atrazine was tank mixed with tolpyralate, the tolpyralate rates of 30 and 45 g ha<sup>-1</sup> controlled *A. theophrasti* more than the 15 g ha<sup>-1</sup> rate at 2 WAA; the

**Table 4.** Least-square means and significance of main effects and interaction for *Amaranthus retroflexus* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across four field trials in Ontario, Canada, in 2019, 2020, and 2021.

Main effects	Rate	<i>A. retroflexus</i> control			Density <sup>a</sup>	Dry biomass
		2 WAA	4 WAA	8 WAA		
	—g ai ha <sup>-1</sup> —	%			—plants m <sup>-2</sup> —	—g m <sup>-2</sup> —
Tolpyralate <sup>b</sup>						
No tank-mix partner	—	19	27	27	11 c	12.1
Tolpyralate	15	70	85	85	5 b	2.6
Tolpyralate	30	80	91	91	4 ab	1.5
Tolpyralate	45	89	95	96	3 a	0.9
SE		2.0	1.8	1.8	0.7	0.9
Tolpyralate P-value		<0.0001	<0.0001	<0.0001	0.0004	<0.0001
Atrazine <sup>b</sup>						
No tank-mix partner	—	42	58	60	7	4.8
Atrazine	140	68	81	81	5	2.8
Atrazine	280	74	84	84	7	3.7
Atrazine	560	78	87	86	5	2.7
SE		2.0	1.8	1.8	0.7	0.9
Atrazine P-value		0.0010	<0.0001	0.0002	0.1471	0.3611
Interaction						
Tolpyralate × atrazine P-value		0.0002	<0.0001	<0.0001	0.5630	0.0268

<sup>a</sup>Means within the same main effect and column followed by the same lowercase letter are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

45 g ha<sup>-1</sup> rate of tolpyralate was also superior to the 15 g ha<sup>-1</sup> rate at 4 WAA. At 2, 4, and 8 WAA, when the rate of atrazine was 280 or 560 g ha<sup>-1</sup>, the three rates of tolpyralate did not differ in their control of *A. theophrasti*. Likewise, Metzger et al. (2019) found that tolpyralate at 15 g ai ha<sup>-1</sup> tank mixed with atrazine at 500 g ai ha<sup>-1</sup> controlled *A. theophrasti* at 4 WAA similarly to tolpyralate at 30 or 40 g ai ha<sup>-1</sup> tank mixed with 1,000 g ai ha<sup>-1</sup> of atrazine. At 2 and 8 WAA, the addition of atrazine to tolpyralate improved *A. theophrasti* control similarly across all rates of atrazine when the rate of tolpyralate was kept constant. Results at 4 WAA were similar, except when atrazine was tank mixed with the 15 g ha<sup>-1</sup> rate of tolpyralate, the 280 and 560 g ha<sup>-1</sup> rates of atrazine controlled *A. theophrasti* more than the 140 g ha<sup>-1</sup> rate. At 8 WAA, the three rates of tolpyralate did not differ in the control of *A. theophrasti* when applied alone or in combination with the three rates of atrazine when the rate of atrazine was kept constant; the addition of tolpyralate to atrazine at each rate improved the control of *A. theophrasti* at 8 WAA similarly across all rates of tolpyralate when the rate of atrazine was kept constant. Synergism occurred with every tolpyralate + atrazine combination for *A. theophrasti* control at 2, 4, and 8 WAA. Two previous studies also reported synergistic interactions with several mesotrione and atrazine rate combinations applied to *A. theophrasti* (Abendroth et al. 2006; Woodyard et al. 2009b).

The interaction between tolpyralate rate and atrazine rate was not significant for *A. theophrasti* density and dry biomass reduction, so the main effects are presented (Table 2). When averaged across the atrazine rate factor, the three rates of tolpyralate did not differ in their reduction of *A. theophrasti* dry biomass. The dry biomass reduction of *A. theophrasti* was 93% to 97% with tolpyralate when averaged across the atrazine rate factor. The interaction between tolpyralate and atrazine was additive with each rate combination for the density and dry biomass reduction of *A. theophrasti* (Table 3).

### *Amaranthus retroflexus*

*Amaranthus retroflexus* was evaluated in every experiment, except at the Huron Research Station in 2021, so data were pooled from

four field experiments. The interaction between tolpyralate rate and atrazine rate was significant for *A. retroflexus* dry biomass reduction and control at 2, 4, and 8 WAA (Table 4). At 2 and 8 WAA, *A. retroflexus* control with tolpyralate applied alone was greater at the 45 g ha<sup>-1</sup> rate than at the 15 g ha<sup>-1</sup> rate; both of these rates of tolpyralate controlled *A. retroflexus* similarly to the 30 g ha<sup>-1</sup> rate of tolpyralate (Table 5). At 2, 4, and 8 WAA, 560 g ha<sup>-1</sup> of atrazine controlled *A. retroflexus* more than the 140 g ha<sup>-1</sup> rate when atrazine was applied alone; the 280 g ha<sup>-1</sup> rate controlled *A. retroflexus* similarly to both of these rates. Generally, tolpyralate applied at 45 g ha<sup>-1</sup> controlled *A. retroflexus* more than tolpyralate applied at 15 g ha<sup>-1</sup> when the atrazine rate was kept constant, except at 4 and 8 WAA at the atrazine rate of 280 g ha<sup>-1</sup> and at 4 WAA when no atrazine was tank mixed with tolpyralate. At 4 and 8 WAA, tolpyralate applied at a rate of 30 g ha<sup>-1</sup> controlled *A. retroflexus* similarly to the 15 and 45 g ha<sup>-1</sup> rates when the atrazine rate was kept constant. At 2 WAA, the addition of atrazine to tolpyralate improved *A. retroflexus* control similarly across all rates of atrazine when the tolpyralate rate was kept constant. At 4 WAA, only 280 and 560 g ha<sup>-1</sup> of atrazine improved *A. retroflexus* control with 30 and 45 g ha<sup>-1</sup> of tolpyralate, respectively. Similarly, Willemsse et al. (2021) reported that the addition of 560 g ai ha<sup>-1</sup> of atrazine to 30 g ai ha<sup>-1</sup> of tolpyralate did not improve *A. tuberculatus* control at 4 WAA. At 8 WAA, the addition of atrazine to tolpyralate did not improve *A. retroflexus* control. Similarly, the addition of atrazine to tolpyralate did not improve *A. palmeri* control in a previous study (Kohrt and Sprague 2017). Similar to *A. retroflexus* control at 8 WAA, dry biomass reduction of *A. retroflexus* did not improve with the addition of atrazine to tolpyralate when the tolpyralate rate was kept constant. The addition of each rate of tolpyralate to atrazine improved *A. retroflexus* dry biomass reduction similarly at the atrazine rates of 140 and 280 g ha<sup>-1</sup>; however, only the 45 g ha<sup>-1</sup> rate of tolpyralate improved the dry biomass reduction of *A. retroflexus* with the 560 g ha<sup>-1</sup> rate of atrazine.

The interaction between tolpyralate and atrazine for *A. retroflexus* control depended on herbicide rate and evaluation timing. The only synergistic interaction for *A. retroflexus* control across 2, 4, and 8 WAA with 15 g ha<sup>-1</sup> of tolpyralate was with atrazine at a rate of 140 g ha<sup>-1</sup> at 2 WAA; all other interactions with

**Table 5.** *Amaranthus retroflexus* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across four field trials in Ontario, Canada, in 2019, 2020, and 2021.<sup>a</sup>

Herbicide treatment <sup>b</sup>	No tank-mix partner	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Control at 2 WAA					
No tank-mix partner	0 c X	53 b Y	63 b YZ	76 b Z	4.3
Atrazine (140 g ai ha <sup>-1</sup> )	20 b X	71 a Y (62)**	83 a YZ (71)**	91 a Z (81)	4.1
Atrazine (280 g ai ha <sup>-1</sup> )	34 ab X	76 a Y (69)	88 a Z (76)*	91 a Z (84)	3.6
Atrazine (560 g ai ha <sup>-1</sup> )	42 a X	80 a Y (73)	85 a Y (79)	96 a Z (87)*	3.2
SE	2.7	2.1	1.8	1.6	
Control at 4 WAA					
No tank-mix partner	0 c Y	79 a Z	82 b Z	87 b Z	4.6
Atrazine (140 g ai ha <sup>-1</sup> )	38 b X	83 a Y (85)	93 ab YZ (88)**	96 ab Z (92)*	3.4
Atrazine (280 g ai ha <sup>-1</sup> )	40 ab Y	90 a Z (87)	94 a Z (89)**	96 ab Z (92)*	3.2
Atrazine (560 g ai ha <sup>-1</sup> )	56 a X	89 a Y (89)	93 ab YZ (91)	98 a Z (94)*	2.7
SE	3.3	1.9	1.6	1.1	
Control at 8 WAA					
No tank-mix partner	0 c X	78 a Y	85 a YZ	91 a Z	4.7
Atrazine (140 g ai ha <sup>-1</sup> )	32 b X	82 a Y (85)	92 a YZ (90)	98 a Z (94)	3.5
Atrazine (280 g ai ha <sup>-1</sup> )	42 ab Y	89 a Z (87)	94 a Z (91)	96 a Z (95)	3.1
Atrazine (560 g ai ha <sup>-1</sup> )	57 a X	89 a Y (89)	91 a YZ (93)	98 a Z (96)	2.8
SE	3.3	1.9	1.6	1.3	
Density					
No tank-mix partner	13	7	5	4	1.5
Atrazine (140 g ai ha <sup>-1</sup> )	11	4 (3)	4 (3)	1 (1)	1.2
Atrazine (280 g ai ha <sup>-1</sup> )	11	7 (4)	4 (2)	4 (3)	1.1
Atrazine (560 g ai ha <sup>-1</sup> )	7	6 (7)	5 (3)	2 (1)	1.5
SE	1.7	1.2	1.3	0.6	
Dry biomass					
No tank-mix partner	28.9 b Y	2.0 a Z	1.2 a Z	0.9 a Z	3.3
Atrazine (140 g ai ha <sup>-1</sup> )	10.3 b Y	1.9 a Z (2.6)	1.4 a Z (1.5)	0.4 a Z (0.5)	0.8
Atrazine (280 g ai ha <sup>-1</sup> )	10.7 b Y	2.6 a Z (3.0)	1.5 a Z (1.4)	1.8 a Z (1.4)	0.9
Atrazine (560 g ai ha <sup>-1</sup> )	4.5 a Y	4.8 a YZ (4.1)	1.9 a YZ (1.7)	0.8 a Z (0.8)	0.9
SE	3.2	0.9	0.7	0.4	

<sup>a</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ). Values in parentheses are expected values calculated from Colby's equation. Asterisks indicate significant differences of between observed and expected values based on a two-tailed  $t$ -test: \* $P < 0.05$ ; \*\* $P < 0.01$ .

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

tolpyralate at a rate of 15 g ha<sup>-1</sup> and atrazine were additive at 2, 4, and 8 WAA (Table 5). At 2 and 4 WAA, tolpyralate at a rate of 30 g ha<sup>-1</sup> was synergistic with 140 and 280 g ha<sup>-1</sup> of atrazine but was additive with 560 g ha<sup>-1</sup> of atrazine. Similarly, Willemse et al. (2021) reported additive interactions between tolpyralate at 30 g ai ha<sup>-1</sup> and atrazine at 560 g ai ha<sup>-1</sup> for the control of *A. tuberculatus* at 4 and 8 WAA. The interaction between mesotrione and atrazine for *A. retroflexus* control has been documented to depend on the herbicide rates evaluated, with both additivity and synergism reported (Hugie et al. 2008). Woodyard et al. (2009a) reported synergy between mesotrione and atrazine for *A. tuberculatus* control with mesotrione at 35 or 105 g ai ha<sup>-1</sup> tank mixed with atrazine at 280 or 560 g ai ha<sup>-1</sup> at 4 WAA. Abendroth et al. (2006) reported synergy in one year of a study and additivity in a different year of the same study between mesotrione and atrazine for *A. palmeri* control. Tolpyralate at a rate of 45 g ha<sup>-1</sup> was only synergistic with the 560 g ha<sup>-1</sup> rate of atrazine at 2 WAA, but it was synergistic with all rate rates of atrazine at 4 WAA. The interaction was additive between tolpyralate and atrazine at 8 WAA for *A. retroflexus* control for all rate combinations of tolpyralate and atrazine. Kohrt and Sprague (2017) reported that a combination of tolpyralate and atrazine was generally additive for the control of *A. palmeri* across a range of herbicide rates. This is consistent with the density and dry biomass reduction of *A. retroflexus*, as all interactions between tolpyralate and atrazine were additive for these response parameters. Willemse et al. (2021) also documented additive interactions between tolpyralate at 30 g ai ha<sup>-1</sup> and atrazine at 560 g ai ha<sup>-1</sup> for the density and dry biomass reduction of *A. tuberculatus*.

The interaction between tolpyralate rate and atrazine rate was not significant for the density reduction of *A. retroflexus* (Table 4). When averaged across the atrazine rate factor, 45 g ha<sup>-1</sup> of tolpyralate reduced the density of *A. retroflexus* 73%, which was greater than the 55% reduction by the 15 g ha<sup>-1</sup> rate; the 30 g ha<sup>-1</sup> rate of tolpyralate was similar to both these rates for the density reduction of *A. retroflexus*.

### *Ambrosia artemisiifolia*

*Ambrosia artemisiifolia* was evaluated in each experiment, so results are pooled across five experiments. The interaction between tolpyralate rate and atrazine rate was significant for *A. artemisiifolia* control at 2, 4, and 8 WAA (Table 6). At 2 and 4 WAA, 45 g ha<sup>-1</sup> of tolpyralate controlled *A. artemisiifolia* more than the 30 and 15 g ha<sup>-1</sup> rates (Table 7). At 8 WAA, 45 g ha<sup>-1</sup> of tolpyralate was superior to the 15 g ha<sup>-1</sup> rate for the control of *A. artemisiifolia*, but similar to the 30 g ha<sup>-1</sup> rate. At 2 WAA, 560 g ha<sup>-1</sup> of atrazine controlled *A. artemisiifolia* more than 140 g ha<sup>-1</sup>, but similarly to 280 g ha<sup>-1</sup>. At 4 and 8 WAA, 560 g ha<sup>-1</sup> of atrazine controlled *A. artemisiifolia* more than the other rates of atrazine. At 2, 4, and 8 WAA, 15 g ha<sup>-1</sup> of tolpyralate controlled *A. artemisiifolia* less than 45 g ha<sup>-1</sup> of tolpyralate when tank mixed with 140 g ha<sup>-1</sup> of atrazine. When the atrazine rate was held constant at 560 g ha<sup>-1</sup>, there were no differences in *A. artemisiifolia* control among the three rates of tolpyralate at 2, 4, and 8 WAA. Correspondingly, Metzger et al. (2019) reported that tolpyralate at 15 g ai ha<sup>-1</sup> plus atrazine at 500 g ai ha<sup>-1</sup> controlled *A. artemisiifolia* similarly to tolpyralate at 30 or

**Table 6.** Least-square means and significance of main effects and interaction for *Ambrosia artemisiifolia* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.

Main effects	Rate	<i>A. artemisiifolia</i> control			Density <sup>a</sup>	Dry biomass <sup>a</sup>
		2 WAA	4 WAA	8 WAA		
	—g ai ha <sup>-1</sup> —	%			—plants m <sup>-2</sup> —	—g m <sup>-2</sup> —
Tolpyralate <sup>b</sup>						
No tank-mix partner	—	18	24	24	11 c	52.9 c
Tolpyralate	15	82	88	88	4 b	4.0 b
Tolpyralate	30	89	93	93	3 b	3.1 ab
Tolpyralate	45	93	96	96	2 a	1.5 a
SE		1.9	1.7	1.7	0.5	2.2
Tolpyralate P-value		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Atrazine <sup>b</sup>						
No tank-mix partner	—	44	56	58	6 c	13.1 c
Atrazine	140	74	81	81	4 b	7.5 ab
Atrazine	280	82	85	84	5 bc	13.1 bc
Atrazine	560	87	90	90	3 a	6.0 a
SE		1.9	1.7	1.7	0.5	2.2
Atrazine P-value		<0.0001	<0.0001	<0.0001	0.0022	0.0184
Interaction						
Tolpyralate × atrazine P-value		<0.0001	<0.0001	<0.0001	0.2901	0.7089

<sup>a</sup>Means within the same main effect and column followed by the same lowercase letter are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

**Table 7.** *Ambrosia artemisiifolia* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.<sup>a</sup>

Herbicide treatment <sup>b</sup>	No tank-mix partner	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Control at 2 WAA					
		%			
No tank-mix partner	0 c X	58 c Y	66 b Y	78 b Z	3.9
Atrazine (140 g ai ha <sup>-1</sup> )	19 b X	79 b Y (67)**	92 a Z (73)**	95 a Z (82)**	3.9
Atrazine (280 g ai ha <sup>-1</sup> )	31 ab X	89 ab Y (72)**	94 a YZ (77)**	96 a Z (85)**	3.5
Atrazine (560 g ai ha <sup>-1</sup> )	43 a Y	94 a Z (77)**	95 a Z (81)**	98 a Z (87)**	3.0
SE	2.4	2.0	1.8	1.3	
Control at 4 WAA					
No tank-mix partner	0 c X	73 b Y	79 b Y	89 b Z	4.0
Atrazine (140 g ai ha <sup>-1</sup> )	28 b X	88 a Y (81)**	94 a YZ (85)**	96 ab Z (92)**	3.2
Atrazine (280 g ai ha <sup>-1</sup> )	36 b Y	91 a Z (83)*	96 a Z (86)**	96 ab Z (93)**	3.0
Atrazine (560 g ai ha <sup>-1</sup> )	53 a Y	95 a Z (88)*	97 a Z (90)**	98 a Z (95)**	2.3
SE	2.6	1.5	1.3	0.9	
Control at 8 WAA					
No tank-mix partner	0 c X	76 b Y	83 b YZ	91 b Z	4.1
Atrazine (140 g ai ha <sup>-1</sup> )	28 b X	88 a Y (82)	94 a YZ (88)*	96 ab Z (94)	3.3
Atrazine (280 g ai ha <sup>-1</sup> )	36 b Y	91 a Z (85)	96 a Z (89)**	96 ab Z (94)	3.0
Atrazine (560 g ai ha <sup>-1</sup> )	54 a Y	95 a Z (89)**	96 a Z (92)*	98 a Z (96)**	2.4
SE	2.7	1.6	1.2	0.7	
Density					
		plants m <sup>-2</sup>			
No tank-mix partner	14	5	5	2	1.2
Atrazine (140 g ai ha <sup>-1</sup> )	10	4 (7)	3 (5)	1 (3)	0.7
Atrazine (280 g ai ha <sup>-1</sup> )	12	5 (9)	2 (5)	2 (3)	1.0
Atrazine (560 g ai ha <sup>-1</sup> )	8	1 (8)*	2 (4)	1 (3)	0.7
SE	1.2	1.0	0.6	0.4	
Dry biomass					
		g m <sup>-2</sup>			
No tank-mix partner	69.7	4.3	4.2	2.1	5.5
Atrazine (140 g ai ha <sup>-1</sup> )	47.2	4.4 (8.5)	2.1 (5.9)	0.9 (3.3)	3.7
Atrazine (280 g ai ha <sup>-1</sup> )	60.7	7.1 (9.9)	2.8 (4.5)	3.2 (4.5)	4.6
Atrazine (560 g ai ha <sup>-1</sup> )	34.8	1.6 (9.3)	3.8 (5.4)	0.6 (3.9)*	3.0
SE	6.6	1.3	1.3	0.7	

<sup>a</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ). Values in parentheses are expected values calculated from Colby's equation. Asterisks indicate significant differences of between observed and expected values based on a two-tailed  $t$ -test: \* $P < 0.05$ ; \*\* $P < 0.01$ .

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

40 g ai ha<sup>-1</sup> plus 1,000 g ai ha<sup>-1</sup> of atrazine at 4 WAA. At 2, 4, and 8 WAA, the addition of atrazine to 15 or 30 g ai ha<sup>-1</sup> of tolpyralate improved the control of *A. artemisiifolia* similarly across all rates of atrazine; however, at 2 WAA, the 140 g ai ha<sup>-1</sup> rate of atrazine improved the control of *A. artemisiifolia* less than the 560 g ai ha<sup>-1</sup>

rate when tank mixed with 15 g ai ha<sup>-1</sup> of tolpyralate. At 2 WAA, each atrazine rate improved *A. artemisiifolia* control when added to 45 g ai ha<sup>-1</sup> of tolpyralate. At 4 and 8 WAA, 560 g ai ha<sup>-1</sup> of atrazine was the only rate of atrazine to improve *A. artemisiifolia* control when tank mixed with 45 g ai ha<sup>-1</sup> of tolpyralate.

**Table 8.** Least-square means and significance of main effects and interaction for *Chenopodium album* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.

Main effects	Rate	<i>C. album</i> control			Density <sup>a</sup>	Dry biomass
		2 WAA	4 WAA	8 WAA		
	—g ai ha <sup>-1</sup> —	%			—plants m <sup>-2</sup> —	—g m <sup>-2</sup> —
Tolpyralate <sup>b</sup>						
No tank-mix partner	—	37	47	49	20 b	25.9
Tolpyralate	15	83	89	89	9 a	7.2
Tolpyralate	30	88	92	91	11 a	7.7
Tolpyralate	45	92	94	94	9 a	6.4
SE		1.7	1.4	1.4	1.1	2.0
Tolpyralate P-value		<0.0001	<0.0001	<0.0001	0.0043	0.0006
Atrazine <sup>b</sup>						
No tank-mix partner	—	44	54	54	18 c	18.9
Atrazine	140	79	86	86	12 b	11.3
Atrazine	280	86	89	89	11 ab	10.9
Atrazine	560	93	96	96	6 a	3.8
SE		1.7	1.4	1.4	1.1	2.0
Atrazine P-value		<0.0001	<0.0001	<0.0001	0.0023	0.0060
Interaction						
Tolpyralate × atrazine P-value		<0.0001	<0.0001	<0.0001	0.2616	0.0002

<sup>a</sup>Means within the same main effect and column followed by the same lowercase letter are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

The interaction between tolpyralate and atrazine changed between evaluation timings and was not consistent among herbicide rates. At 2 and 4 WAA, all rates of tolpyralate and atrazine were synergistic with each other for the control of *A. artemisiifolia* (Table 7). Similarly, Woodyard et al. (2009a) reported that all four mesotrione and atrazine rate combinations evaluated were synergistic for the control of *A. trifida* at 4 WAA. At 8 WAA, the 560 g ha<sup>-1</sup> rate of atrazine was synergistic with each rate of tolpyralate, but the 280 and 140 g ha<sup>-1</sup> rates of atrazine were only synergistic with the 30 g ha<sup>-1</sup> rate of tolpyralate for the control of *A. artemisiifolia*; all other interactions at 8 WAA were additive. Atrazine at 560 g ha<sup>-1</sup> was synergistic with tolpyralate at 15 g ha<sup>-1</sup> for the density reduction of *A. artemisiifolia* and was synergistic with the 30 g ha<sup>-1</sup> rate of tolpyralate for the dry biomass reduction of *A. artemisiifolia*. All other interactions between tolpyralate and atrazine were additive for the density and dry biomass reduction of *A. artemisiifolia*.

The interaction between tolpyralate rate and atrazine rate was not significant for the density and dry biomass reduction of *A. artemisiifolia*, so the main effects are presented (Table 6). Averaged across the atrazine rate factor, tolpyralate at 45 g ha<sup>-1</sup> reduced the density of *A. artemisiifolia* 82%, which was greater than the 64% to 73% reduction by the 15 and 30 g ha<sup>-1</sup> rates of tolpyralate. Averaged across the atrazine rate factor, tolpyralate at 45 g ha<sup>-1</sup> reduced the dry biomass of *A. artemisiifolia* 97%, which was greater than the 92% reduction by the 15 g ha<sup>-1</sup> rate of tolpyralate; the 30 g ha<sup>-1</sup> rate of tolpyralate was similar to both rates of tolpyralate for the dry biomass reduction of *A. artemisiifolia*. Averaged across the tolpyralate rate factor, atrazine at 560 g ha<sup>-1</sup> reduced the density of *A. artemisiifolia* more than the 140 g ha<sup>-1</sup> rate; the 280 g ha<sup>-1</sup> rate did not reduce the density of *A. artemisiifolia* but was similar to the 140 g ha<sup>-1</sup> rate. Averaged across the tolpyralate rate factor, the 140 and 560 g ha<sup>-1</sup> rates of atrazine similarly reduced the dry biomass of *A. artemisiifolia* 43% to 54%.

### *Chenopodium album*

*Chenopodium album* was evaluated in all five experiments, so the results are pooled. The interaction between tolpyralate rate and

atrazine rate was significant for *C. album* control at 2, 4, and 8 WAA and dry biomass reduction (Table 8). At 2, 4, and 8 WAA, the 45 g ha<sup>-1</sup> rate of tolpyralate controlled *C. album* more than the 15 g ha<sup>-1</sup> rate (Table 9). At 2, 4, and 8 WAA, atrazine controlled *C. album* more when applied at 560 g ha<sup>-1</sup> than at 280 or 140 g ha<sup>-1</sup>. The addition of atrazine to 15 g ha<sup>-1</sup> of tolpyralate improved *C. album* control at 4 WAA similarly across all rates of atrazine; however, at 2 and 8 WAA, the 560 g ha<sup>-1</sup> rate was superior to 140 g ha<sup>-1</sup>. At 2, 4, and 8 WAA, with tolpyralate at 30 and 45 g ha<sup>-1</sup>, atrazine improved *C. album* control similarly across all rates of atrazine when the rate of tolpyralate was kept constant. Similarly, Woodyard et al. (2009a) reported that the addition of atrazine to mesotrione improved *C. album* control at 4 WAA. At 2, 4, and 8 WAA, when the rate of atrazine tank mixed with tolpyralate was 560 g ha<sup>-1</sup>, there was no difference among the three rates of tolpyralate for *C. album* control. Metzger et al. (2019) documented that control of *C. album* with tolpyralate at 15 g ai ha<sup>-1</sup> plus atrazine at 500 g ai ha<sup>-1</sup> was similar to tolpyralate at 30 or 40 g ai ha<sup>-1</sup> plus 1,000 g ai ha<sup>-1</sup> of atrazine at 2 and 4 WAA. At 2 and 8 WAA, the 45 g ha<sup>-1</sup> rate of tolpyralate controlled *C. album* more than the 15 g ha<sup>-1</sup> rate of tolpyralate when tank mixed with 280 g ha<sup>-1</sup> of atrazine. At 2 WAA, the 30 and 45 g ha<sup>-1</sup> rates of tolpyralate provided better control than the 15 g ha<sup>-1</sup> rate of tolpyralate when paired with atrazine at a rate of 140 g ha<sup>-1</sup>, but by 4 and 8 WAA there were no differences between the three rates of tolpyralate. The dry biomass reduction of *C. album* was similar across all rates of tolpyralate when applied alone and when tank mixed with atrazine when the rate of atrazine was kept constant. The addition of atrazine to any rate of tolpyralate did not improve the dry biomass reduction of *C. album*, except with the addition of 560 g ha<sup>-1</sup> of atrazine to 45 g ha<sup>-1</sup> of tolpyralate. When applied alone, atrazine at a rate of 560 g ha<sup>-1</sup> reduced the dry biomass of *C. album* more than the 140 g ha<sup>-1</sup> rate. The dry biomass reduction of *C. album* with atrazine at a rate of 140 g ha<sup>-1</sup> was improved by adding tolpyralate; however, the addition of tolpyralate to the 280 or 560 g ha<sup>-1</sup> rates of atrazine did not improve the dry biomass reduction of *C. album*.

At 2 WAA, the interaction between tolpyralate and atrazine was additive with tolpyralate at 15 g ha<sup>-1</sup> plus atrazine at 140 g ha<sup>-1</sup> and with tolpyralate at 30 or 45 g ha<sup>-1</sup> plus atrazine at 560 g ha<sup>-1</sup>; all

**Table 9.** *C. album* (*Chenopodium album*) control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.<sup>a</sup>

Herbicide treatment <sup>b</sup>	No tank-mix partner	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Control at 2 WAA					
No tank-mix partner	0 c X	58 c Y	67 b Y	77 b Z	3.9
Atrazine (140 g ai ha <sup>-1</sup> )	42 b X	82 b Y (76)	91 a Z (81)**	93 a Z (87)*	2.8
Atrazine (280 g ai ha <sup>-1</sup> )	55 b X	89 ab Y (82)*	94 a YZ (85)**	95 a Z (90)*	2.3
Atrazine (560 g ai ha <sup>-1</sup> )	77 a Y	96 a Z (90)*	96 a Z (92)	97 a Z (94)	1.5
SE	3.7	2.1	1.7	1.4	
Control at 4 WAA					
No tank-mix partner	0 c X	71 b Y	79 b YZ	85 b Z	3.9
Atrazine (140 g ai ha <sup>-1</sup> )	55 b Y	90 a Z (87)	93 a Z (90)	95 a Z (93)	2.2
Atrazine (280 g ai ha <sup>-1</sup> )	67 b Y	92 a Z (90)	95 a Z (93)	96 a Z (95)	1.8
Atrazine (560 g ai ha <sup>-1</sup> )	87 a Y	97 a Z (96)	97 a Z (97)	98 a Z (98)	0.9
SE	3.8	1.5	1.3	1.0	
Control at 8 WAA					
No tank-mix partner	0 c X	72 c Y	79 b Z	85 b Z	3.9
Atrazine (140 g ai ha <sup>-1</sup> )	59 b Y	91 b Z (88)*	92 a Z (92)	94 a Z (94)	2.1
Atrazine (280 g ai ha <sup>-1</sup> )	69 b X	92 ab Y (91)	94 a YZ (94)	96 a Z (95)	1.8
Atrazine (560 g ai ha <sup>-1</sup> )	90 a Y	97 a Z (97)	96 a Z (98)	98 a Z (99)	0.8
SE	3.9	1.5	1.3	0.9	
Density					
No tank-mix partner	33	11	16	16	2.6
Atrazine (140 g ai ha <sup>-1</sup> )	20	10 (7)	11 (9)	9 (9)	2.0
Atrazine (280 g ai ha <sup>-1</sup> )	18	10 (6)	9 (8)	9 (9)	2.4
Atrazine (560 g ai ha <sup>-1</sup> )	8	5 (3)	8 (4)	4 (4)	1.7
SE	2.6	1.6	2.0	2.4	
Dry biomass					
No tank-mix partner	87.1 c Y	8.5 a Z	7.7 a Z	8.8 b Z	4.9
Atrazine (140 g ai ha <sup>-1</sup> )	23.7 b Y	9.5 a Z (5.1)	10.0 a Z (4.0)**	6.8 ab Z (4.7)	4.3
Atrazine (280 g ai ha <sup>-1</sup> )	18.4 ab Z	10.1 a Z (4.6)	10.7 a Z (4.3)	7.4 ab Z (4.9)	4.1
Atrazine (560 g ai ha <sup>-1</sup> )	4.6 a Z	3.1 a Z (1.2)	4.3 a Z (1.1)**	3.5 a Z (1.1)	1.9
SE	5.8	2.9	3.4	2.7	

<sup>a</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ). Values in parentheses are expected values calculated from Colby's equation. Asterisks indicate significant differences of between observed and expected values based on a two-tailed  $t$ -test: \* $P < 0.05$ ; \*\* $P < 0.01$ .

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

other interactions were synergistic at 2 WAA (Table 9). At 4 WAA, the interaction between tolpyralate and atrazine was additive across all rates of either herbicide. In contrast, Woodyard et al. (2009a) reported that several rate combinations of mesotrione and atrazine were synergistic for the control of *C. album* at 4 WAA. At 8 WAA, one synergistic interaction between tolpyralate and atrazine occurred, and it was at the lowest rates of both herbicides; the rest of the interactions were additive at 8 WAA. The density reduction of *C. album* was additive with each rate combination of tolpyralate and atrazine. The dry biomass reduction of *C. album* was antagonistic with tolpyralate at 30 g ha<sup>-1</sup> plus atrazine at 140 or 560 g ha<sup>-1</sup> but was additive with all other rate combinations of tolpyralate and atrazine. It is difficult to explain the antagonistic response between tolpyralate and atrazine for the dry biomass reduction of *C. album*; however, previous studies have reported antagonistic interactions between tolpyralate and atrazine for the control of *A. tuberculatus* and *A. palmeri* (Kohrt and Sprague 2017; Willemse et al. 2021). Walsh et al. (2012) reported antagonism for the biomass reduction of *R. raphanistrum* with three rate combinations of mesotrione and atrazine, while reporting either additive or synergistic responses for survival of *R. raphanistrum* with the same rate combinations. In other studies, one rate combination of mesotrione and atrazine was antagonistic for the biomass reduction of *A. theophrasti* and two were antagonistic for *A. retroflexus* biomass reduction of the numerous rate combinations evaluated (Hugie et al. 2008; Woodyard et al. 2009b).

The interaction between tolpyralate rate and atrazine rate was not significant for the density reduction of *C. album*, so the main

effects are presented (Table 8). Averaged across the atrazine factor, tolpyralate at 15, 30, and 45 g ha<sup>-1</sup> reduced the density of *C. album* 45% to 55%. Averaged across the tolpyralate factor, atrazine at 560 g ha<sup>-1</sup> reduced the density of *C. album* 67%, which was greater than the density reduction of 33% by atrazine at a rate of 140 g ha<sup>-1</sup>.

### *Sinapis arvensis*

*Sinapis arvensis* results were pooled across three field experiments at the Huron Research Station in 2019, 2020, and 2021. The interaction between tolpyralate and atrazine rate was significant for the control of *S. arvensis* at 2, 4, and 8 WAA (Table 10). At 2, 4, and 8 WAA, tolpyralate controlled *S. arvensis* more when applied at 45 g ha<sup>-1</sup> than at 15 g ha<sup>-1</sup>; the 30 g ha<sup>-1</sup> rate of tolpyralate was similar to the two other rates for *S. arvensis* control (Table 11). At 2, 4, and 8 WAA, 560 g ha<sup>-1</sup> of atrazine controlled *S. arvensis* more than 140 g ha<sup>-1</sup>; *S. arvensis* control with atrazine at 280 g ha<sup>-1</sup> was intermediate and similar to control with 140 g ha<sup>-1</sup> and 560 g ha<sup>-1</sup>. At 2, 4, and 8 WAA, the addition of atrazine to tolpyralate improved *S. arvensis* control similarly across all rates of atrazine when the tolpyralate rate was held constant. Likewise, Metzger et al. (2018) reported that the addition of 1,000 g ai ha<sup>-1</sup> of atrazine to tolpyralate at 30 g ai ha<sup>-1</sup> improved *S. arvensis* control at 2, 4, and 8 WAA. At 2 WAA, the addition of tolpyralate improved the control of *S. arvensis* similarly when added to atrazine across all rates of tolpyralate when the rate of atrazine was kept constant. At 4 WAA, the addition of tolpyralate improved the control of *S. arvensis* with atrazine at 140 g ha<sup>-1</sup> similarly across all rates

**Table 10.** Least-square means and significance of main effects and interaction for *Sinapis arvensis* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across three field trials in Ontario, Canada, in 2019, 2020, and 2021.

Main effects	Rate	<i>S. arvensis</i> control			Density	Dry biomass <sup>a</sup>
		2 WAA	4 WAA	8 WAA		
	—g ai ha <sup>-1</sup> —	%			—plants m <sup>-2</sup> —	—g m <sup>-2</sup> —
Tolpyralate <sup>b</sup>						
No tank-mix partner	—	43	50	58	50	21.6
Tolpyralate	15	71	70	78	33	12.7
Tolpyralate	30	78	77	84	39	13.3
Tolpyralate	45	84	82	88	41	9.6
SE		2.7	2.0	2.1	3.4	2.0
Tolpyralate P-value		0.0012	0.0005	0.0004	0.2518	0.0506
Atrazine <sup>b</sup>						
No tank-mix partner	—	18	22	25	78	55.8 b
Atrazine	140	78	78	86	36	7.6 a
Atrazine	280	84	83	91	26	6.0 a
Atrazine	560	91	91	95	13	2.3 a
SE		2.7	2.0	2.1	3.4	2.0
Atrazine P-value		0.0043	<0.0001	<0.0001	0.0718	0.0118
Interaction						
Tolpyralate × atrazine P-value		0.0307	<0.0001	<0.0001	0.6189	0.5692

<sup>a</sup>Means within the same main effect and column followed by the same lowercase letter are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

**Table 11.** *Sinapis arvensis* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across three field trials in Ontario, Canada, in 2019, 2020, and 2021.<sup>a</sup>

Herbicide treatment <sup>b</sup>	No tank-mix partner	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Control at 2 WAA					
		%			
No tank-mix partner	0 c X	20 b Y	30 b YZ	43 b Z	3.0
Atrazine (140 g ai ha <sup>-1</sup> )	52 b Y	80 a Z (62)**	86 a Z (67)**	90 a Z (73)**	3.2
Atrazine (280 g ai ha <sup>-1</sup> )	68 ab Y	85 a Z (75)**	90 a Z (78)**	91 a Z (82)**	2.3
Atrazine (560 g ai ha <sup>-1</sup> )	79 a Y	92 a Z (83)**	94 a Z (85)**	96 a Z (88)**	1.9
SE	5.6	5.3	4.8	3.9	
Control at 4 WAA					
No tank-mix partner	0 c X	25 b Y	36 b YZ	48 b Z	2.7
Atrazine (140 g ai ha <sup>-1</sup> )	61 b Y	79 a Z (71)	82 a Z (75)	86 a Z (80)	2.1
Atrazine (280 g ai ha <sup>-1</sup> )	74 ab Y	82 a YZ (81)	87 a YZ (84)	89 a Z (87)	1.6
Atrazine (560 g ai ha <sup>-1</sup> )	87 a Z	88 a Z (90)	92 a Z (92)	95 a Z (93)	1.3
SE	4.9	3.9	3.4	2.9	
Control at 8 WAA					
No tank-mix partner	0 c X	30 b Y	42 b YZ	51 b Z	3.0
Atrazine (140 g ai ha <sup>-1</sup> )	74 b Y	87 a YZ (82)	88 a Z (85)	93 a Z (88)	1.7
Atrazine (280 g ai ha <sup>-1</sup> )	83 ab Y	88 a YZ (88)	95 a Z (90)	95 a Z (92)	1.3
Atrazine (560 g ai ha <sup>-1</sup> )	92 a Z	96 a Z (94)	96 a Z (95)	98 a Z (96)	0.9
SE	5.4	3.9	3.3	2.9	
Density					
		plants m <sup>-2</sup>			
No tank-mix partner	85	62	92	76	7.9
Atrazine (140 g ai ha <sup>-1</sup> )	51	38 (27)	28 (35)	35 (33)	6.7
Atrazine (280 g ai ha <sup>-1</sup> )	30	20 (20)	22 (29)	38 (29)	4.1
Atrazine (560 g ai ha <sup>-1</sup> )	12	16 (8)	21 (3)	9 (7)	5.3
SE	7.7	6.0	6.9	6.7	
Dry biomass					
		g m <sup>-2</sup>			
No tank-mix partner	74.6	66.7	55.2	33.1	4.8
Atrazine (140 g ai ha <sup>-1</sup> )	14.2	5.7 (10.6)	8.0 (6.9)	4.5 (5.2)	2.5
Atrazine (280 g ai ha <sup>-1</sup> )	7.9	5.8 (5.1)	4.9 (3.9)	5.8 (3.4)	0.8
Atrazine (560 g ai ha <sup>-1</sup> )	2.4	2.4 (1.8)	3.0 (1.0)	1.9 (1.0)	0.8
SE	4.9	4.3	3.9	2.4	

<sup>a</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ). Values in parentheses are expected values calculated from Colby's equation. Asterisks indicate significant differences of between observed and expected values based on a two-tailed  $t$ -test: \*\* $P < 0.01$ .

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

of tolpyralate; however, only the 45 g ha<sup>-1</sup> rate improved the control of *S. arvensis* when tank mixed with atrazine at 280 g ha<sup>-1</sup>, and no rates of tolpyralate improved the control of *S. arvensis* with atrazine at 560 g ha<sup>-1</sup> at 4 WAA. At 8 WAA, the addition of 30 or 45 g ha<sup>-1</sup> of tolpyralate improved the control of *S. arvensis* when tank mixed with atrazine at 140 or 280 g ha<sup>-1</sup>. At 8 WAA,

the addition of tolpyralate did not improve *S. arvensis* control when added to 560 g ha<sup>-1</sup> of atrazine.

The interaction between tolpyralate and atrazine for *S. arvensis* control at 2 WAA was synergistic for each rate combination of tolpyralate and atrazine (Table 11). At 4 and 8 WAA, the interaction between tolpyralate and atrazine changed to additive for each

**Table 12.** Least-square means and significance of main effects and interaction for *Echinochloa crus-galli* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.

Main effects	Rate	<i>E. crus-galli</i> control <sup>a</sup>			Density	Dry biomass
		2 WAA	4 WAA	8 WAA		
	—g ai ha <sup>-1</sup> —	—%—			—plants m <sup>-2</sup> —	—g m <sup>-2</sup> —
Tolpyralate <sup>b</sup>						
No tank-mix partner	—	3	2 b	2 b	115	223.3
Tolpyralate	15	59	53 a	58 a	96	89.9
Tolpyralate	30	65	60 a	66 a	94	96.6
Tolpyralate	45	72	67 a	70 a	107	94.5
SE		1.9	1.7	1.8	12.1	13.7
Tolpyralate P-value		<0.0001	<0.0001	<0.0001	0.2929	0.0654
Atrazine <sup>b</sup>						
No tank-mix partner	—	42	41 b	44 b	116	158.1
Atrazine	140	49	45 ab	49 ab	101	129.5
Atrazine	280	53	47 a	50 a	140	115.5
Atrazine	560	55	49 a	53 a	67	95.4
SE		1.9	1.7	1.8	12.1	13.7
Atrazine P-value		0.0002	0.0140	0.0234	0.1079	0.2637
Interaction						
Tolpyralate × atrazine P-value		<0.0001	0.8744	0.4162	0.0607	0.1886

<sup>a</sup>Means within the same main effect and column followed by the same lowercase letter are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

rate combination of tolpyralate and atrazine. Similarly, the density and dry biomass reduction of *S. arvensis* was additive between all rate combinations of tolpyralate and atrazine.

The interaction between tolpyralate rate and atrazine rate was not significant for the density and dry biomass reduction of *S. arvensis*, so the main effects are presented (Table 10). Averaged across the tolpyralate factor, atrazine at 140, 280, and 560 g ha<sup>-1</sup> reduced the dry biomass of *S. arvensis* by 86% to 96%.

### *Echinochloa crus-galli*

*Echinochloa crus-galli* results are pooled from five field experiments. The interaction between tolpyralate rate and atrazine rate was significant for the control of *E. crus-galli* at 2 WAA (Table 12). At 2 WAA, the addition of tolpyralate to atrazine improved *E. crus-galli* control with all rates of atrazine (Table 13). The 45 g ha<sup>-1</sup> rate of tolpyralate controlled *E. crus-galli* more than the 15 g ha<sup>-1</sup> rate when applied alone or with atrazine at 140 g ha<sup>-1</sup> at 2 WAA. When tank mixed with atrazine at 280 or 560 g ha<sup>-1</sup>, the three rates of tolpyralate did not differ in the control of *E. crus-galli* when the rate of atrazine was kept constant at 2 WAA. Metzger et al. (2019) reported that tolpyralate at 30 and 40 g ai ha<sup>-1</sup> controlled *E. crus-galli* similarly when tank mixed with a constant rate of 1,000 g ai ha<sup>-1</sup> of atrazine at 2 WAA. At 2 WAA, the addition of atrazine to tolpyralate improved the control of *E. crus-galli* across all rates of atrazine. At 2 WAA, the addition of 560 g ha<sup>-1</sup> of atrazine improved the control of *E. crus-galli* more than the 140 g ha<sup>-1</sup> rate when added to tolpyralate at 15 or 30 g ha<sup>-1</sup>. At 2 WAA, the three rates of atrazine did not differ for the improvement of *E. crus-galli* control with tolpyralate at 45 g ha<sup>-1</sup>.

The interaction between tolpyralate rate and atrazine rate was not significant for *E. crus-galli* control at 4 and 8 WAA, density reduction, and dry biomass reduction (Table 12). Averaged across the atrazine rate factor, tolpyralate at 15, 30, and 45 g ha<sup>-1</sup> controlled *E. crus-galli* similarly at 4 and 8 WAA. Averaged across the tolpyralate rate factor, the addition of atrazine at 140 g ha<sup>-1</sup> did not improve *E. crus-galli* control, but the 280 and 560 g ha<sup>-1</sup> rates similarly improved *E. crus-galli* control at 4 and 8 WAA.

The interaction between tolpyralate and atrazine on *E. crus-galli* varied among response parameters (Table 13). At 2 WAA, each rate combination of tolpyralate and atrazine was synergistic. At 4 WAA, tolpyralate at 30 g ha<sup>-1</sup> was synergistic with atrazine at 280 g ha<sup>-1</sup>, while tolpyralate at 45 g ha<sup>-1</sup> was synergistic with atrazine at 280 and 560 g ha<sup>-1</sup> for *E. crus-galli* control; all other interactions were additive at 4 WAA. At 8 WAA, tolpyralate at 15 g ha<sup>-1</sup> was synergistic with atrazine at 560 g ha<sup>-1</sup>, while tolpyralate at 45 g ha<sup>-1</sup> was synergistic with atrazine at 280 g ha<sup>-1</sup>; the rest of the interactions were additive between tolpyralate and atrazine at 8 WAA. The density reduction of *E. crus-galli* was antagonistic between atrazine at 140 g ha<sup>-1</sup> and tolpyralate at 30 or 45 g ha<sup>-1</sup> but synergistic between atrazine at 560 g ha<sup>-1</sup> and tolpyralate at 45 g ha<sup>-1</sup>; all other interactions were additive between tolpyralate and atrazine for density reduction of *E. crus-galli*. The interaction between tolpyralate and atrazine for the dry biomass reduction of *E. crus-galli* was additive with all rate combinations, except for the synergistic tank mixes of tolpyralate at 45 g ha<sup>-1</sup> plus atrazine at 280 or 560 g ha<sup>-1</sup>.

### *Setaria* spp.

*Setaria* spp. results are pooled from five field experiments. The interaction between tolpyralate and atrazine was significant for the control of *Setaria* spp. at 2 WAA (Table 14). At 2 WAA, the addition of tolpyralate to atrazine improved *Setaria* spp. control across all rates of tolpyralate (Table 15). At 2 WAA, tolpyralate at 45 g ha<sup>-1</sup> controlled *Setaria* spp. more than tolpyralate at 15 g ha<sup>-1</sup> when applied alone or when co-applied with atrazine at 140 or 280 g ha<sup>-1</sup>. When tank mixed with atrazine at 560 g ha<sup>-1</sup>, all three rates of tolpyralate controlled *Setaria* spp. similarly at 2 WAA. Correspondingly, Metzger et al. (2019) reported that tolpyralate at 30 and 40 g ai ha<sup>-1</sup> controlled *S. viridis* similarly when tank mixed with 1,000 g ai ha<sup>-1</sup> of atrazine at 2 WAA. When the rate of tolpyralate was held constant, the addition of atrazine at 560 g ha<sup>-1</sup> improved the control of *Setaria* spp. more than the addition of 140 g ha<sup>-1</sup> of atrazine.

The interaction between tolpyralate and atrazine was not significant for *Setaria* spp. control at 4 and 8 WAA, density

**Table 13.** *Echinochloa crus-galli* control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.<sup>a</sup>

Herbicide treatment <sup>b</sup>	No tank-mix partner	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Control at 2 WAA					
No tank-mix partner	0 a X	48 c Y	54 c YZ	65 b Z	3.5
Atrazine (140 g ai ha <sup>-1</sup> )	2 a X	58 b Y (50)**	64 b YZ (55)**	72 a Z (66)**	3.7
Atrazine (280 g ai ha <sup>-1</sup> )	4 a Y	62 ab Z (51)**	69 ab Z (56)**	75 a Z (67)**	3.8
Atrazine (560 g ai ha <sup>-1</sup> )	5 a Y	67 a Z (51)**	72 a Z (56)**	77 a Z (67)**	3.9
SE	0.4	1.8	1.7	1.5	
Control at 4 WAA					
No tank-mix partner	0	47	54	62	3.3
Atrazine (140 g ai ha <sup>-1</sup> )	2	52 (48)	60 (55)	66 (63)	3.4
Atrazine (280 g ai ha <sup>-1</sup> )	2	55 (49)	62 (55)*	69 (63)*	3.5
Atrazine (560 g ai ha <sup>-1</sup> )	5	58 (50)	64 (57)	69 (64)*	3.6
SE	0.5	2.3	2.3	2.2	
Control at 8 WAA					
No tank-mix partner	0	50	62	66	3.7
Atrazine (140 g ai ha <sup>-1</sup> )	3	57 (51)	64 (63)	71 (66)	3.6
Atrazine (280 g ai ha <sup>-1</sup> )	2	61 (51)	67 (62)	73 (66)*	3.7
Atrazine (560 g ai ha <sup>-1</sup> )	6	63 (52)*	70 (64)	72 (68)	3.8
SE	0.8	2.5	2.4	2.3	
Density					
No tank-mix partner	160	136	70	167	27.9
Atrazine (140 g ai ha <sup>-1</sup> )	91	87 (77)	204 (36)**	88 (74)*	23.1
Atrazine (280 g ai ha <sup>-1</sup> )	109	173 (106)	156 (49)	205 (77)	26.5
Atrazine (560 g ai ha <sup>-1</sup> )	150	62 (175)	43 (73)	50 (97)*	17.9
SE	23.8	23.8	25.8	24.8	
Dry biomass					
No tank-mix partner	228.0	205.9	105.5	175.5	33.4
Atrazine (140 g ai ha <sup>-1</sup> )	298.4	114.7 (314.9)	137.5 (128.9)	92.5 (223.8)	29.8
Atrazine (280 g ai ha <sup>-1</sup> )	160.7	72.4 (193.8)	188.1 (85.6)	93.5 (105.5)*	19.1
Atrazine (560 g ai ha <sup>-1</sup> )	351.5	57.9 (638.2)	47.5 (170.6)	64.9 (186.1)*	25.2
SE	39.9	21.6	19.5	18.2	

<sup>a</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ). Values in parentheses are expected values calculated from Colby's equation. Asterisks indicate significant differences of between observed and expected values based on a two-tailed  $t$ -test: \* $P < 0.05$ ; \*\* $P < 0.01$ .

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

**Table 14.** Least-square means and significance of main effects and interaction for *Setaria* spp. control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.

Main effects	Rate	<i>Setaria</i> spp. control <sup>a</sup>			Density <sup>a</sup>	Dry biomass <sup>a</sup>
		2 WAA	4 WAA	8 WAA		
	—g ai ha <sup>-1</sup> —	%			—plants m <sup>-2</sup> —	—g m <sup>-2</sup> —
Tolpyralate <sup>b</sup>						
No tank-mix partner	—	2	1 c	0 c	78 b	119.8 b
Tolpyralate	15	62	58 b	61 b	49 a	18.2 a
Tolpyralate	30	68	66 ab	69 ab	38 a	17.2 a
Tolpyralate	45	75	72 a	76 a	28 a	13.0 a
SE		2.0	1.8	1.9	2.8	4.4
Tolpyralate P-value		<0.0001	<0.0001	<0.0001	0.0044	0.0008
Atrazine <sup>b</sup>						
No tank-mix partner	—	44	46	48	53	29.5
Atrazine	140	51	48	51	50	36.7
Atrazine	280	54	50	53	43	34.3
Atrazine	560	57	53	54	49	43.1
SE		2.0	1.8	1.9	2.8	4.4
Atrazine P-value		<0.0001	0.0780	0.1097	0.9035	0.3433
Interaction						
Tolpyralate × atrazine P-value		<0.0001	0.2271	0.1331	0.8754	0.9110

<sup>a</sup>Means within the same main effect and column followed by the same lowercase letter are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

reduction, and dry biomass reduction (Table 14). Averaged across the atrazine rate factor, tolpyralate at 45 g ha<sup>-1</sup> controlled *Setaria* spp. more than the 15 g ha<sup>-1</sup> rate at 4 and 8 WAA; the 30 g ha<sup>-1</sup> rate of tolpyralate was intermediate and similar to the other two rates of tolpyralate. The density and dry biomass

reduction of *Setaria* spp. was similar among all three rates of tolpyralate when averaged across the atrazine rate factor. Tolpyralate at 15, 30, and 45 g ha<sup>-1</sup> reduced the *Setaria* spp. density 37% to 64% and the dry biomass 85% to 89% when averaged across the atrazine rate factor.

**Table 15.** *Setaria* spp. control at 2, 4, and 8 wk after application (WAA), density, and dry biomass in corn after the application of tolpyralate, atrazine, and tolpyralate + atrazine across five field trials in Ontario, Canada, in 2019, 2020, and 2021.<sup>a</sup>

Herbicide treatment <sup>b</sup>	No tank-mix partner	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Control at 2 WAA					
No tank-mix partner	0 a X	53 c Y	57 c YZ	68 c Z	3.6
Atrazine (140 g ai ha <sup>-1</sup> )	1 a X	61 b Y (53)**	68 b YZ (57)**	75 b Z (68)**	3.9
Atrazine (280 g ai ha <sup>-1</sup> )	2 a X	65 ab Y (54)**	73 ab YZ (58)**	78 ab Z (69)**	4.0
Atrazine (560 g ai ha <sup>-1</sup> )	4 a Y	69 a Z (54)**	75 a Z (58)**	81 a Z (69)**	4.1
SE	0.3	1.6	1.6	1.4	
Control at 4 WAA					
No tank-mix partner	0	54	60	69	3.4
Atrazine (140 g ai ha <sup>-1</sup> )	0	58 (54)	66 (60)	70 (69)	3.6
Atrazine (280 g ai ha <sup>-1</sup> )	0	59 (54)	66 (60)	75 (69)*	3.7
Atrazine (560 g ai ha <sup>-1</sup> )	2	63 (55)*	72 (60)**	73 (70)	3.7
SE	0.6	2.1	2.0	1.8	
Control at 8 WAA					
No tank-mix partner	0	56	65	72	3.7
Atrazine (140 g ai ha <sup>-1</sup> )	0	61 (56)	69 (65)	75 (72)	3.8
Atrazine (280 g ai ha <sup>-1</sup> )	0	61 (56)	70 (65)	79 (72)**	3.9
Atrazine (560 g ai ha <sup>-1</sup> )	0	66 (56)*	73 (65)*	78 (72)	3.9
SE	0.0	2.2	2.1	1.8	
Density					
No tank-mix partner	83	53	39.9	35	6.7
Atrazine (140 g ai ha <sup>-1</sup> )	74	52 (58)	50 (45)	26 (36)	5.4
Atrazine (280 g ai ha <sup>-1</sup> )	73	46 (61)	30 (41)	25 (41)	5.5
Atrazine (560 g ai ha <sup>-1</sup> )	82	47 (56)	37 (44)	30 (42)	4.8
SE	6.8	5.2	4.6	3.9	
Dry biomass					
No tank-mix partner	104.8	14.7	14.5	10.7	8.5
Atrazine (140 g ai ha <sup>-1</sup> )	121.6	17.7 (25.5)	23.6 (25.3)	12.1 (20.9)	8.1
Atrazine (280 g ai ha <sup>-1</sup> )	118.9	16.9 (31.9)	16.6 (22.6)	12.4 (20.9)	8.6
Atrazine (560 g ai ha <sup>-1</sup> )	140.9	24.9 (36.4)	16.5 (33.9)	18.7 (30.1)	10.0
SE	13.2	2.2	3.4	2.0	

<sup>a</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ). <sup>c</sup>Values in parentheses are expected values calculated from Colby's equation. Asterisks indicate significant differences of between observed and expected values based on a two-tailed  $t$ -test: \* $P < 0.05$ ; \*\* $P < 0.01$ .

<sup>b</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate<sup>®</sup>, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

The interaction between tolpyralate and atrazine was synergistic at all rate combinations of tolpyralate and atrazine for the control of *Setaria* spp. at 2 WAA (Table 15). In a comparable study, *S. faberi* control was synergistic at 2 WAA with mesotrione and atrazine tank mixes (Armel et al. 2007). At 4 and 8 WAA, the interaction between tolpyralate and atrazine was generally additive, except tolpyralate at 15 and 30 g ha<sup>-1</sup>, which were synergistic with atrazine at 560 g ha<sup>-1</sup>, and tolpyralate at 45 g ha<sup>-1</sup>, which was synergistic with atrazine at 280 g ha<sup>-1</sup>. The interaction between tolpyralate and atrazine for the density and dry biomass reduction of *Setaria* spp. was additive for each rate combination of tolpyralate and atrazine.

### Corn Injury and Grain Yield

Corn injury was transient, as it was  $\leq 2\%$ ,  $\leq 1\%$ , and 0% at 1, 2, and 4 WAA, respectively (data not presented). Other studies have also reported low corn injury with tolpyralate, atrazine, and tolpyralate + atrazine (Kohrt and Sprague 2017; Willemse et al. 2021).

The interaction between tolpyralate and atrazine rate was significant for corn yield (Table 16). There were no differences in corn yield among the three rates of tolpyralate when applied alone or with atrazine when the atrazine rate was held constant (Table 17). Reduced weed interference with tolpyralate applied alone improved corn yield 82% to 102% compared with the nontreated control. Reduced weed interference with atrazine at 140 g ha<sup>-1</sup> improved corn yield 24% compared with the nontreated control, while the use of the 280 or 560 g ha<sup>-1</sup> rates of atrazine resulted in corn yield that was 49% to 55% greater compared with

**Table 16.** Least-square means and significance of main effects and interaction for corn grain yield after the application of tolpyralate, atrazine, and tolpyralate + atrazine across four field trials in Ontario, Canada, in 2020 and 2021.

Main effects	Corn grain yield	
	—g ai ha <sup>-1</sup> —	—kg ha <sup>-1</sup> —
Tolpyralate <sup>a</sup>		
No tank-mix partner	—	6,500
Tolpyralate	15	10,200
Tolpyralate	30	10,200
Tolpyralate	45	10,400
SE		210
Tolpyralate P-value		<0.0001
Atrazine <sup>a</sup>		
No tank-mix partner	—	8,300
Atrazine	140	9,300
Atrazine	280	9,700
Atrazine	560	10,000
SE		210
Atrazine P-value		<0.0001
Interaction		
Tolpyralate × atrazine P-value		0.0425

<sup>a</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate<sup>®</sup>, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

the nontreated control. Reduced weed interference with the addition of tolpyralate at each rate to atrazine improved corn yield similarly across all rates of tolpyralate when the atrazine rate was held constant. Reduced weed interference with the addition of atrazine to tolpyralate at 15 g ha<sup>-1</sup> improved corn yield similarly across all rates of atrazine. The addition of 280 or 560 g ha<sup>-1</sup> of atrazine to 30 g ha<sup>-1</sup> of tolpyralate increased corn yield, while

**Table 17.** Corn grain yield after the application of tolpyralate, atrazine, and tolpyralate + atrazine across four field trials in Ontario, Canada, in 2020 and 2021.

Herbicide treatment <sup>a</sup>	No tank-mix partner <sup>b</sup>	Tolpyralate (15 g ai ha <sup>-1</sup> )	Tolpyralate (30 g ai ha <sup>-1</sup> )	Tolpyralate (45 g ai ha <sup>-1</sup> )	SE
Corn grain yield	kg ha <sup>-1</sup>				b
No tank-mix partner	4,900 c Y	8,900 b Z	9,400 b Z	9,900 a Z	440
Atrazine (140 g ai ha <sup>-1</sup> )	6,100 b Y	10,500 a Z	10,000 ab Z	10,600 a Z	450
Atrazine (280 g ai ha <sup>-1</sup> )	7,300 a Y	10,500 a Z	10,500 a Z	10,300 a Z	400
Atrazine (560 g ai ha <sup>-1</sup> )	7,600 a Y	10,900 a Z	10,800 a Z	10,700 a Z	390
SE	330	410	390	350	

<sup>a</sup>Each herbicide treatment included methylated seed oil (MSO Concentrate®, Loveland Products, 3005 Rocky Mountain Avenue, Loveland, CO 80538, USA) at 0.5% v/v.

<sup>b</sup>Means followed by the same lowercase letter within the same column and response parameter or means followed by the same uppercase letter within a row are not statistically different according to the Tukey-Kramer multiple-range test ( $P < 0.05$ ).

the addition of 140 g ha<sup>-1</sup> of atrazine did not. The addition of atrazine to tolpyralate at 45 g ha<sup>-1</sup> did not increase corn yield compared with tolpyralate at 45 g ha<sup>-1</sup> applied alone.

In summary, this study provides comprehensive documentation of the interaction between tolpyralate and atrazine across a range of herbicide rates for the control of seven annual weed species. The interaction between the two herbicides depended on the response parameter, herbicide rate, and the weed species; however, a few general conclusions can be made on the control of the weed species at 8 WAA. The interaction between tolpyralate and atrazine was synergistic for the control of *A. theophrasti* for each rate combination. In contrast, *A. retroflexus* and *S. arvensis* control was additive with each rate combination. The interaction between tolpyralate and atrazine was mainly additive for *C. album* control, with only one synergistic interaction documented among the nine rate combinations. *A. artemisiifolia* displayed five synergistic interactions and four additive interactions between tolpyralate and atrazine of the nine rate combinations. *E. crus-galli* and *Setaria* spp. had two and three synergistic interactions, respectively, between tolpyralate and atrazine with the rest of the interactions being additive. Therefore, the interaction between tolpyralate and atrazine cannot be extrapolated, as it depends on several factors. Future studies should document the interaction between tolpyralate and atrazine on several other weed species and with other rate combinations on the species evaluated in this study. Additionally, future work should characterize the interaction between other HPPD- and PSII-inhibiting herbicides. Studies should be conducted to determine whether absorption, translocation, or metabolism of tolpyralate and atrazine are affected in tolpyralate + atrazine tank mixes to better understand the nature of the interaction between tolpyralate and atrazine on several weed species.

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