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Impact of simulated rainfall on atrazine wash off from roller crimped and standing cereal rye (*Secale cereale* L.) residue onto the soil

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The combination of soil residual herbicides and cover crops is an integral part of best management practices for herbicide-resistant weeds. However, the interception of soil residual herbicides by cover crop biomass interferes with herbicides reaching the soil, which can lead to lower weed control efficacy and increased selection pressure for herbicide resistance. Once intercepted, these herbicides can only move to the soil with water from rainfall or irrigation. Field trials were conducted in 2022 and 2023 to investigate the effect of cover crop termination strategies (fallow, standing, and roller crimped) and simulated rainfall volumes (0, 4.2, and 8.3 mm simulated over 20 min; equivalent to 0, 12.5, and 25 mm h⁻¹) on atrazine wash off from cereal rye (*Secale cereale* L.) biomass onto the soil. The use of roller crimper resulted in an average of 10% greater ground cover relative to the standing cereal rye. Atrazine interception that was bound to rye biomass reached 29 and 94% in 2022 and 2023, respectively. In 2022, the concentration of atrazine in the soil under roller crimped cereal rye was 9% greater than that under standing cereal rye, after 4.2 mm of rainfall. In 2023, when cereal rye biomass more than doubled, only 6% of the applied atrazine was found under roller crimped cereal rye, after 8.3 mm of rainfall. Cereal rye biomass accumulation negatively impacted the amount of atrazine reaching the soil at the time of application. Although the roller crimped cereal rye reduced the amount of herbicide reaching the soil relative to the standing cereal rye, it also reduced atrazine leaching below the 0–5 cm of soil. In cover cropping systems with high levels of cereal rye biomass (e.g., > 7,000 kg ha⁻¹), more than 8.3 mm of rain are required to wash most of the atrazine off of the biomass.

KEYWORDS

cereal rye, *Secale cereale* L cover crop termination, cover crop residue, soil residual herbicides, herbicide wash off, herbicide leaching, rainfall simulator

Cover crops have been adopted by an increasing number of growers with the intent to improve soil properties and reduce the impact of erosion and nutrient leaching (Acharya et al., 2020). In addition, cover crops can also aid in weed suppression, contributing to an integrated weed management program and reducing the selection pressure for herbicide resistance (Cornelius and Bradley 2017a; DeSimini et al., 2020; Hodgskiss et al., 2020; Loux et al., 2017; Mirsky et al., 2011; Petersen et al., 2023; Pittman et al., 2019; Wallace et al., 2019).

Shoot biomass accumulation is essential when cover crops are used specifically for the suppression of weeds. The longer growing season necessary to produce high amounts of biomass creates significant competition for water, light and nutrients, which can be effective at preventing or reducing the growth of winter annual weeds such as horseweed [*Conyza canadensis* (L.) Cronquist] (Hodgskiss et al., 2020; Wallace et al., 2019; Werle et al., 2017) and early emerging summer annual weeds like giant ragweed (*Ambrosia trifida* L.) (DeSimini et al., 2020). Delayed termination by planting green have been reported to reduce *C. canadensis* biomass by as much as 93% (Schramski et al., 2021). Furthermore, after termination the cover crop residue that remains above the soil creates a physical barrier for weed emergence by preventing light from reaching the soil surface, which can impact weed species that have light-induced seed germination (Teasdale and Mohler, 1993) such as waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer] (Bish et al., 2021). Previous research investigating *A. tuberculatus* suppression with increasing amounts of cover crop residue reported 50% suppression at four weeks after termination with 2,800 kg ha⁻¹ of residue (Pittman et al., 2020). In the same study, 6,610 kg ha⁻¹ of cover crop residue was necessary to achieve the same suppression level through eight weeks after termination (Pittman et al., 2020).

Among the several methods that are available for cover crop termination, chemical termination is the most common and effective (Hill and Sprague, 2021; Teasdale and Rosecrance, 2003). The use of herbicides at cover crop termination is important because cover crops rarely provide adequate weed suppression when used as the sole weed management tool (Alonso-Ayuso et al., 2020; Fernando and Shrestha, 2023). After termination, the amount and uniformity of cover crop residue remaining on the soil surface will determine the potential for weed suppression (Teasdale and Mohler, 2000). In this regard, the use of a roller crimper could be one strategy to increase the ground cover by laying all the plants flat on the soil surface. Roller crimpers have been used for many decades in organic and conventional crop production as the termination strategy for cereal rye (*Secale cereale* L.) cover crop (Davis, 2010; Mirsky et al., 2011; Wallace et al., 2023). Effective termination of cereal rye with roller crimper is only possible if plants have reached the anthesis growth stage (Mirsky et al., 2009). Therefore, the use of a roller crimper in cover cropping systems is, perhaps, one alternative to increase the ground cover and hence weed suppression while using herbicides as the termination strategy.

Another option to improve a management system that uses herbicides as the cover crop termination strategy is to include soil

residual herbicides in the tank-mixture, which extends the period of weed control during the critical weed-free period. To provide weed control, these herbicides must be incorporated into the soil to be absorbed by the shoots and roots of newly germinated weed seeds. However, herbicide placement becomes a major concern when soil residual herbicides are applied at cover crop termination. In this case, part of the herbicide is intercepted by the plants and only a fraction of what was applied reaches the soil (Nunes et al., 2023b; Whalen et al., 2020). The amount of herbicide interception is directly related to the biomass accumulation, with higher amounts of cover crop biomass intercepting more herbicide (Nunes et al., 2023a). Once the herbicides are intercepted by the cover crop plants, they can only move to the soil with rainfall or irrigation.

In addition to rainfall or irrigation volumes, the chemical properties of the herbicide and the age of the residue are other factors that influence the fate of the soil residual herbicides after interception by the cover crop. Herbicides with higher solubility [low Kow (octanol-water partition coefficient)] have a tendency to be washed off of the residue more easily than those with lower solubility (high Kow) (Khalil et al., 2019). Furthermore, herbicides that were applied onto fresh residue will be washed off more easily than those applied onto aged residue (Dao, 1991; Khalil et al., 2018). In the process of residue decomposition, cellulose molecules are broken down by enzymes, exposing lignin molecules. These lignin molecules are considered sorption sites for herbicides in plant surfaces, whereas cellulose do not have a significant contribution to the sorption of herbicides (Dao, 1991).

Currently there is limited research on the effect of rainfall on herbicide fate in cover cropping systems or crop residue (Banks et al., 1990; Banks and Robinson, 1982; Banks and Robinson, 1984; Banks and Robinson, 1986; Dang et al., 2016; Dao, 1991; Gaston et al., 2001; Ghadiri et al., 1984; Khalil et al., 2018; Khalil et al., 2019; Reddy et al., 1995). Furthermore, the majority of the research was done over two decades ago, using small scale methodologies (e.g., petri dishes or trays with crop residue or soil samples) or even laboratory settings. In this study, our objective was to investigate the fate of atrazine when applied to cereal rye under two termination orientations and assess the wash off of atrazine from the residue to the soil after simulated rainfall. We hypothesize that less atrazine will reach the soil underneath roller crimped cereal rye compared to standing cereal rye at the time of application and that atrazine applied onto roller crimped cereal rye will become more readily available in the soil relative to when applied to standing cereal rye, after one rainfall event.

Materials and methods

Field trials were established in the fall of 2021 and 2022 at the Throckmorton Purdue Agricultural Center (TPAC; 40.29°N, 86.90°W), Lafayette, IN, to determine how much of applied atrazine is intercepted by standing and roller crimped cereal rye and to determine the influence of rainfall volume on the leaching of atrazine from the cereal rye residue onto the soil in adjacent

locations within the same field in both years. The field was previously managed under a corn-soybean rotation in conventional tillage for a minimum of 15 years and was planted to soybean and corn during the 2021 and 2022 growing seasons, respectively. Soil was chiseled and cultivated after cash crop harvest in late September of 2021 and 2022 at 25 cm deep to incorporate the crop residue, eliminate weeds, and provide adequate seed bed for cereal rye planting. On October 1st of 2021 and September 16th of 2022, cereal rye (variety Elbon, Cisco Company, Indianapolis, IN) was planted at 67 kg ha⁻¹ using a no-till drill (John Deere 1590, John Deere Co., Moline, IL) at 19 cm row spacing. Soil samples were taken in March of 2022 and 2023, at 0–10 cm depth to determine the physicochemical properties of the soil (Table 1).

Treatments were arranged in a split plot design and included three rainfall volumes, 0, 4.2, and 8.3 mm as main plots. The two cereal rye management strategies (sub-plots), standing and roller crimped, and a no cover crop (fallow) control were randomized in each main plot and replicated four times for a total of 36 experimental units. Sub-plots were 3 m by 3 m. Glyphosate (Roundup PowerMax[®], Bayer Crop Science, Saint Louis, MO) was applied at 1,740 g ae ha⁻¹ to eliminate cereal rye plants from the no cover crop plots in early March of 2022 and 2023 and again in late April of each year to terminate cereal rye growth at flag leaf stage (Feekes 8) and prevent plants from standing back up after being roller crimped. In addition to the first glyphosate application, in 2023, plots assigned to the no cover crop treatment were rotary tilled (15 cm depth) one week before rainfall simulation to incorporate cereal rye residue when average plant height was approximately 10 cm. Cereal rye plants from the plots assigned to the roller crimper treatment were rolled two days after the second glyphosate application to allow some herbicide translocation through the plants. The roller-crimper was 2.4 m wide, filled with water to increase weight, and rear-mounted on the tractor.

Atrazine (AAtrex 4L[®], Syngenta Crop Protection, Greensboro, NC) was applied at 2,241 g ai ha⁻¹ to the first plot approximately 12 hours after roller crimping the cereal rye. Each plot was sprayed with atrazine precisely 30 minutes prior to the start of rainfall simulation. The interval between herbicide application and start of rainfall simulation was kept constant for each plot during treatments application. All herbicide was applied using a CO₂-pressurized spray boom equipped with eight AIXR 110015 nozzles (TeeJet Spraying Systems Co., Wheaton, IL). Nozzles were spaced 38 cm apart and calibrated to deliver 140 L ha⁻¹ while traveling at 4.8 km h⁻¹ and operating at 165 kPa.

The structure of the rainfall simulator consisted of a “cube” shaped metallic structure measuring 3 m by 3 m at the base and 2.4 m in height (Figure 1). Galvanized pipes (3.17 cm in diameter) were used to assemble the main structure and two oscillating booms (3 m long steel perforated square tubes with 2.54 cm width) at 1 m spacing were mounted across to the top of the simulator. The oscillation was provided by one 12-volt windshield wiper motor (KK International Business Co., Ltd, Shandong, China) connected to both booms and provided a 45° rotation, back and forth. Boom oscillation was necessary to provide variable storm intensities and uniform rainfall across the plots (Blanquies et al., 2003; Bubenzer, 1979; Miller, 1987). One nozzle was mounted to the center of each boom. An air induction, even fan nozzle design was used with an AI9503E nozzle for 4.2-mm and an AI9506E (TeeJet Spraying Systems Co., Wheaton, IL) for 8.3-mm of rainfall, both operating at a constant pressure of 207 kPa. Under this pressure, both nozzles used provided ultra-coarse droplet sizes larger than 665 microns (ANSI/ASABE S572.3 2020), which is slightly smaller than the typical raindrop size [1000 to 2000 microns (AMS, 2012)]. The 4.2 and 8.3-mm of rainfall were simulated for 20 minutes per plot and were equivalent to rainfall intensities of 12.5 and 25 mm hr⁻¹, respectively, both classified as heavy rain (AMS, 2004). To test the uniformity of application, we conducted several catch can tests using 20 rain gages evenly spaced within the simulator area. The nozzles position and angle of oscillation were adjusted to assure a uniform distribution of raindrops across the plot area. Two pneumatic caster wheels (25 cm in diameter) allowed the simulator to be moved to the next plot every 20 minutes.

Cover crop biomass was determined prior to the glyphosate application at the cereal rye flag leaf stage by collecting all aboveground plant material from ten 0.25 m² quadrats. These quadrats were randomly placed within the trial area (cereal rye stand was uniform across the entire trial area), but only in the border allies between plots. The plant material was harvested by cutting the plants at the base (1 cm above soil surface) with scissors. Samples were placed in a forced-air oven at 80 C for 48 hours. Dry weight was recorded and converted to kg ha⁻¹ (Table 2).

Ground cover from each cover crop plot was assessed on the day of atrazine application and rainfall simulation. Two pictures were taken from 1.8 m height, one in the front half of the plot and one in the back half of each plot. Percentage ground cover from each picture was measured by the Canopeo[®] (Canopeo Software, Oklahoma State University, Division of Agricultural Sciences and Natural Resources Soil Physics program, Stillwater, OK) mobile

TABLE 1 Chemical and physical properties of the soil in 2022 and 2023, at 0 to 10 cm depth.

Year	Classification	Ph	OM	CEC	Sand	Silt	Clay	Bulk density
			%	meq 100g ⁻¹	———— % ————			g cm ⁻³
2022	Silt loam	7.2	2.7	11.5	20	55	25	1.21
2023		6.9	2.9	11.4	21	52	27	1.25

OM, organic matter; CEC, cation exchange capacity.



FIGURE 1

Rainfall simulator structure. 3 x 3 x 2.4 m (width, length, height). Plastic tarp was used to minimize wind disturbance inside the simulator. Caster wheels allowed the simulator to be moved from one plot to another without stopping the rainfall simulation.

device application (adjustment value set at 1.07 - default) that calculated the fractional green canopy cover based on the ratios of red to green, blue to green, and excess green index (Patrignani and Ochsner, 2015) (Table 2).

The amount of atrazine that was intercepted by cereal rye plants was determined by collecting eight plants from each plot after the rainfall simulation and once the plants were dry. The time between rainfall simulation and sample collection varied from one year to another because of differences in environmental conditions (air temperature, relative humidity, wind speed, and solar radiation). Plant material was harvested by cutting the plants at the base (1 cm above soil surface) with scissors. All samples from one plot were combined to form one composite sample and placed in a paper bag

(to prevent condensation) that was kept at ambient temperature and in the dark. Within 60 days of sampling, all plant material collected from one plot was ground and homogenized using the UDY cyclone sample mill (UDY Corporation, Fort Collins, CO, USA) to obtain particles ≤ 1 mm in size. All material used to handle the samples and the interior blades from the grinder were cleaned with a 50% acetone solution before processing each sample. Samples were then placed in 15 ml tubes for storage. A 0.5 g (± 0.01) subsample was transferred to a 15 ml tube where two ml of double deionized water, 4 ml of acetonitrile, 10 μ l of an isotopically labeled internal standard containing atrazine, and anhydrous salts of magnesium sulfate (1.2 g) and sodium acetate (0.3 g) were added. The tubes were then agitated for 30 sec with a Mini vortex mixer

TABLE 2 Average cereal rye biomass for the trial area and ground cover from each cereal rye management strategy, in 2022 and 2023.

Year	Average cereal rye biomass	Cereal rye management	Ground cover	
	kg ha ⁻¹		%	
2022	3,591	Roller crimped	74	a ¹
		Standing	58	b
2023	7,726	Roller crimped	94	a
		Standing	89	b

¹Numbers followed by the same letter within year are not significantly different according to Fisher's protected LSD ($P \leq 0.05$).

(VWR, Radnor, PA) and shaken for 5 min at 800 rpm with a Geno/Grinder 2010 (SPEX sample prep, Metuchen, NJ). The 15 ml tubes were then centrifuged at 2,500 rpm for 10 min. One ml of the supernatant was transferred into dispersive solid phase extraction tubes (part no: 5982-5321; Agilent technologies, Santa Clara, CA) that were shaken for 5 min at 800 rpm with a Geno/Grinder 2010 (SPEX sample prep, Metuchen, NJ) then centrifuged at 4,000 rpm for 5 min. The supernatant was transferred into a 15-ml tube and placed in a speed vacuum (SC250EXP; ThermoFisher Scientific, Waltham, MA) to dry overnight. The dried pellet that formed at the bottom of the 15 ml tube was re-suspended with 150 μ l of acetonitrile and the tube was agitated with a Mini vortex until the pellet was dissolved. The 15 ml tubes were then centrifuged at 4,000 rpm for 5 min and the supernatant transferred to 96-well microplates (NuncTM low-binding 96-well polypropylene, ThermoFisher Scientific, Waltham, MA) prior to the analysis in the ultra-high performance liquid chromatography (UHPLC).

The concentration of atrazine in the soil was determined by collecting ten soil cores (2 cm in diameter by 5 cm deep) per plot, once the water had drained through the soil surface (no more than 1.5 hours after rainfall simulation). All soil cores taken in one plot were combined to form one composite sample and were kept in a cooler with ice during sampling. The 30 cm border on both sides and the center 60 cm (walking path during herbicide spray) of each plot were not used to collect samples. Soil samples were sieved (2 mm) within 24 hours of collection to remove debris, homogenize, and then transferred to the -20 C freezer for storage. A 50% acetone solution was used to clean the sieve after each sample processing, thus, preventing herbicide contamination from one sample to another. No more than six months after sampling, a 3-g (± 0.01) subsample of wet soil was transferred from each composite sample into a 50-ml tube. The exact weight of each sample was recorded and later used to calculate the dry weight based on the moisture content from each composite sample. The moisture content was determined from a 5-g subsample of wet soil from each composite sample that was placed in a forced-air oven at 105 C for 24 hours. Fifteen ml of double deionized water, 15 ml of acetonitrile (1% formic acid), and 10 μ l of an isotopically labeled internal standard containing atrazine

were added to the 50 ml tube containing the 3-g soil sample. The tube was agitated for 30 seconds with a Mini vortex mixer (VWR, Radnor, PA). Once agitation was complete, anhydrous salts of magnesium sulfate (6 g) and sodium acetate (1.5 g) were added followed by another agitation of 30 seconds. Tubes were then transferred to the Geno/Grinder 2010 (SPEX sample prep, Metuchen, NJ) and shaken for 2 min at 800 rpm and then centrifuged at 2500 rpm for 10 minutes. Twelve ml of the supernatant were transferred into 15 ml dispersive solid phase extraction tubes (part no: 5982-5158; Agilent technologies, Santa Clara, CA) that were then shaken for 2 minutes at 800 rpm on the Geno/Grinder 2010 and then centrifuged at 4,000 rpm for 5 min. The supernatant was transferred into 15 ml tubes and dried overnight in a speed vacuum (SC250EXP; ThermoFisher Scientific, Waltham, MA). The dried pellet was re-suspended with 150 μ l of acetonitrile and the tube was agitated with a Mini vortex mixer until the pellet was dissolved. The 15-ml tubes were then centrifuged at 4,000 rpm for 5 min and the supernatant transferred to 96-well microplates (NuncTM low-binding 96-well polypropylene, ThermoFisher Scientific, Waltham, MA) prior to the analysis in the UHPLC. The expected concentration of atrazine in the soil for each year was calculated based on the bulk density of the soil, which allowed the calculation of the total soil weight for the 0–5 cm depth. Given the atrazine application rate of 2,241 g ai ha⁻¹ and soil weight, we were able to calculate the expected concentration of atrazine (i.e., assuming complete incorporation of the herbicide) in ppm for each year of the study. The expected concentration of atrazine in the 0–5 cm soil depth was 3.6 and 3.7 ppm in 2022 and 2023, respectively. The atrazine interception was then calculated as the percentage difference between the expected concentration and the actual concentration of atrazine measured in the soil samples.

The concentration of atrazine (ppb) in the plant and soil samples was determined using the QuEChERS (Quick-Easy-Cheap-Effective-Rugged-Safe) method as previously described by (Olaya-Arenas and Kaplan, 2019) with modifications. All samples were analyzed in an Agilent 1290 Infinity II UHPLC with a 6470 triple quadrupole mass spectrometry and a EclipsePlus C18 RRHD 1.8 μ m, 2.1x50mm column (Agilent technologies, Santa Clara, CA) at the Bindley Bioscience Center at Purdue University. Recoveries from fortified untreated soil samples indicated that recovery was 113% for atrazine.

All data were subjected to an Analysis of Variance (ANOVA) using the PROC GLIMMIX procedure in SAS 9.4. There was a significant treatment by year interaction for the ground cover and atrazine concentration in the cereal rye plants and soil. Therefore, results were presented separately by year. Cover crop management and rainfall volumes were considered fixed and replication as random effects. Assumptions of normality and homogeneity of variance were evaluated by visual assessment of residual plots. Data was log transformed when needed. However, original mean values are presented. Means were separated using Fisher's protected LSD ($\alpha = 0.05$).

TABLE 3 Atrazine concentration in the soil (0 to 5 cm depth), leached from the sampling zone, and intercepted by cereal rye, in 2022 and 2023.

Year	Cereal rye management	Rainfall	Atrazine in the soil ¹		Variation in atrazine concentration after rainfall ²	Interception ³
		mm	ppm		ppm	%
2022	Standing	0	2.89	ab ⁴		22
		4.2	2.89	ab	0	
		8.3	1.95	b	-0.94	
	Roller crimped	0	2.62	ab		29
		4.2	3.24	ab	0.62	
		8.3	2.21	ab	-1.03	
	Fallow	0	2.94	ab		
		4.2	3.52	a	0.58	
		8.3	2.53	ab	-0.99	
2023	Standing	0	0.73	c		79
		4.2	0.99	bc	0.26	
		8.3	0.53	c	-0.46	
	Roller crimped	0	0.21	d		94
		4.2	0.49	c	0.28	
		8.3	0.20	d	-0.29	
	Fallow	0	1.83	a		
		4.2	2.10	a	0.27	
		8.3	1.54	ab	-0.56	

¹Atrazine concentration in the soil (0 to 5 cm depth) measured through UHPLC analysis.

²Amount of atrazine being washed-off from the residue into the soil and/or leaching below the top 5 cm of soil. Positive numbers mean atrazine moving from the cereal rye residue into the soil. Negative numbers mean a net negative movement of atrazine in the top 5 cm of soil (i.e., there was more atrazine leaching below the 0–5 cm of soil than atrazine being washed-off from the residue to the soil).

³Percentage difference between the expected concentrations (3.6 and 3.7 ppm in 2022 and 2023, respectively) and the actual concentration of atrazine measured in the soil samples.

⁴Numbers followed by the same letter within a year are not significantly different according to Fisher's protected LSD ($P \leq 0.05$).

Results and discussion

Cereal rye biomass and ground cover

Total cereal rye biomass increased 2.2-fold in the spring of 2023 compared to 2022 (Table 2). The use of roller crimper provided between 5 to 16% greater ground cover compared to the cereal rye that was left standing (Table 2). Although the cereal rye biomass more than doubled from 2022 to 2023, the use of roller crimper provided only a 5% increase in ground cover relative to the standing cereal rye in 2023. The benefits of additional ground cover from using a roller crimper were more evident under moderate amounts of cereal rye biomass. In 2022, when the cereal rye accumulated 3,591 kg ha⁻¹ of biomass, the use of roller crimper resulted in 16% greater ground cover compared to the standing cereal rye. This suggests that under moderate amounts of biomass the use of a roller crimper can increase the ground cover and hence weed suppression by reducing light penetration through the residue (Teasdale and Mohler, 2000). In general, as biomass increases, the differences in ground cover between standing and roller crimped cereal rye are reduced.

Atrazine concentration in the soil

The expected concentration of atrazine in the soil (0–5 cm) based on the application rate of 2,241 g ai ha⁻¹ was 3.6 and 3.7 ppm in 2022 and 2023, respectively. When cereal rye biomass increased from 3,591 kg ha⁻¹ in 2022 to 7,726 kg ha⁻¹ in 2023 (Table 2), atrazine interception also increased from an average of 26% in 2022 to an average of 87% in 2023, relative to the expected concentration of atrazine in the soil for each year (Table 3). Previous research by Crutchfield et al. (1986) reported that metolachlor interception ranged from 67 to 88% in the presence of 3,400 to 6,800 kg ha⁻¹ of wheat straw. In addition to biomass accumulation, ground cover was also a limiting factor to the increased interception of atrazine by cereal rye residue. In 2023, the combination of high biomass accumulation and use of roller crimper resulted in 94% of ground cover and 94% interception of atrazine by the cereal rye residue (Tables 2 and 3). In a recent study, Nunes et al. (2023b) observed up to a 12-fold reduction in spray coverage underneath 12,200 kg ha⁻¹ of roller crimped cereal rye compared to a no cover crop control.

In 2022, after the simulation of 4.2 mm of rain, 0.62 ppm of the atrazine was washed off from the roller crimped cereal rye into the soil (Table 3). Conversely, atrazine concentration remained the same (2.89 ppm) in the soil of plots with standing cereal rye even after 4.2 mm of rainfall, in 2022. This result corroborates the hypothesis that the atrazine that is sprayed onto a roller crimped cereal rye would be more readily available in the soil relative to when sprayed onto a standing cereal rye, after rainfall. We suggest that the proximity of the residue with the soil surface and the increased direct contact of the plants with the soil facilitates the movement of the herbicide with rainfall onto the soil.

Nearly complete incorporation of atrazine was achieved in 2022 after 4.2 mm of rainfall, in the fallow plots. However, the concentration of atrazine in the soil without cereal rye cover crop was reduced by 28% when the rainfall volume increased from 4.2 to 8.3 mm. Although not statistically significant, these data shows that 8.3 mm of rainfall was enough to induce the leaching of almost one third of the applied atrazine below the sampling zone (5 cm) in the fallow plots. Similarly, the concentration of atrazine in the soil was reduced by 0.94 and 1.03 ppm (33 and 32%) when 8.3 mm of rainfall were simulated onto the standing and roller crimped cereal rye, respectively, in comparison to the simulation of 4.2 mm (Table 3). Thus, indicating a net-negative flow of atrazine within the upper 5 cm of soil – there was more atrazine leaching below the sampling zone than atrazine being washed out from the residue onto the soil. In 2022, the presence of 3,591 kg ha⁻¹ of cereal rye biomass (standing or roller crimped) did not reduce atrazine leaching below the top 5 cm of soil in comparison to the fallow treatment, after 8.3 mm of rainfall. However, these results should not be extrapolated to increased risks of atrazine leaching to the ground water, considering that soil samples were taken only at the 0–5 cm depth. Nevertheless, reduced concentrations of atrazine near the soil surface can reduce the weed control efficacy. A similar effect was observed in a study conducted by Krutz et al. (2007) in fields where enhanced degradation of atrazine was an issue. These authors observed 50% reduced persistence of atrazine and greater fresh weight

of the weed species tested when this herbicide was applied once a year in a continuous corn system, in comparison to the application to a field without history of atrazine use.

The concentration of atrazine in the soil of fallow plots were substantially lower in 2023 in comparison to 2022 (Table 3). The use of a rotary till one week before atrazine application and rainfall simulation increased the soil-water infiltration rate within the 0–15 cm depth which, most likely, contributed to a greater leaching of atrazine below the sampling zone in 2023. With 7,726 kg ha⁻¹ of cereal rye biomass in 2023, the concentration of atrazine in the soil of plots with standing or roller crimped cereal rye did not reach more than 0.99 and 0.49 ppm, respectively (28 and 14% of the expected concentration in the soil) (Table 3). Similar results were reported by other authors showing reduced concentrations of residual herbicide in the soil with increasing amounts of cover crop or wheat biomass (Banks and Robinson, 1982, Banks and Robinson, 1986 ; Khalil et al., 2018, Khalil et al., 2020; Whalen et al., 2020). By delaying the termination of cover crops in two weeks and therefore, accumulating more biomass, Whalen et al. (2020) observed a reduction of approximately 57% in the concentration of sulfentrazone in the soil. The reduced concentrations of residual herbicides in the soil can contribute to the selection pressure for herbicide-resistant weed biotypes (Busi et al., 2012; Neve and Powles, 2005). Busi et al. (2012) subjected three generations of a multiple-resistance *Lolium rigidum* population to low doses of pyroxasulfone and observed more than 30% survival when plants were sprayed with a dose equivalent to 240 g ai ha⁻¹ (2.4-fold the label rate). These authors concluded that only the full rates of pyroxasulfone would provide adequate weed control.

Atrazine concentration in cereal rye plants

The concentration of atrazine in standing and roller crimped cereal rye were similar at the no rainfall control and after 4.2 mm of simulated rainfall, in 2022 (Figure 2). In the same year, after the simulation of 8.3

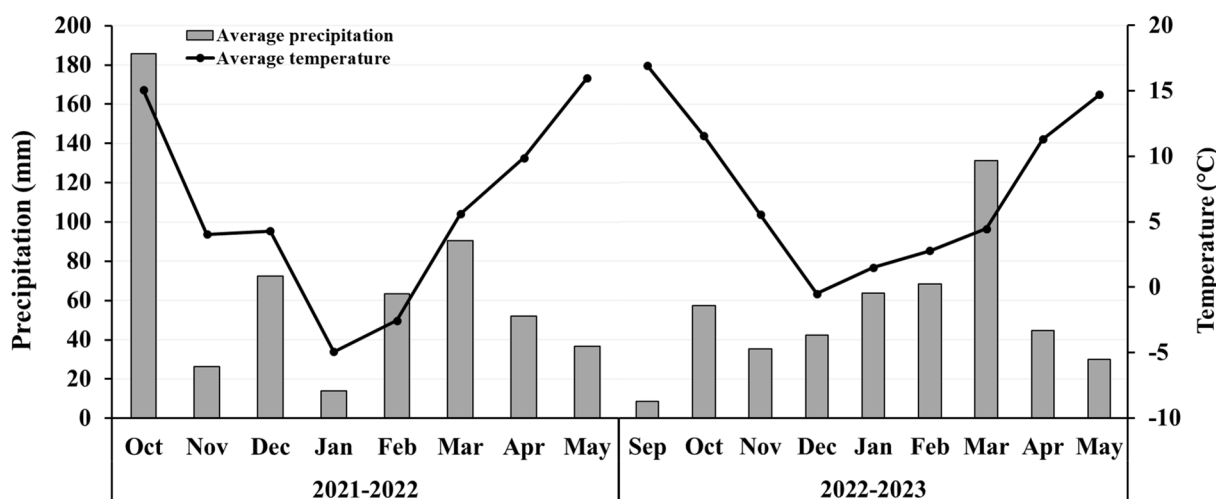


FIGURE 2
Monthly average temperature and total precipitation during the two cereal rye growing seasons.

mm of rainfall, atrazine concentration in the roller crimped cereal rye was 2-fold greater than that in standing cereal rye. The multi-layered residue created with the use of the roller crimper results in more opportunity for atrazine to become sorbed and desorbed since one molecule of the herbicide will likely be intercepted by residue from multiple plants prior to reaching the soil surface (i.e., the movement of the molecule will be vertically and laterally on the way to the soil surface). This sorption-desorption reaction reduces the rate at which atrazine moves from the residue onto the soil.

In 2023, atrazine concentration in the roller crimped residue was 134, 112, and 139% higher than in the standing cereal rye plants after 0, 4.2, and 8.3 mm of simulated rainfall, respectively (Figure 2). These higher concentrations in the roller crimped residue were expected due to the increase in biomass (2.2-fold increase) and ground cover (20% increase) compared to 2022 (Table 2). The concentration of atrazine in the soil underneath the roller crimped residue after 8.3 mm of rainfall was equivalent to only 6% of the atrazine applied, as opposed to the 60% in 2022. We conclude therefore that, under excessive biomass accumulation ($> 7,700 \text{ kg ha}^{-1}$), 8.3 mm of rainfall may represent only a fraction of what would actually be needed to wash off the majority of the atrazine from the residue onto the soil.

The use of roller crimper resulted in greater ground cover relative to the standing cereal rye in both years of the study. In the presence of moderate amounts of cereal rye biomass ($3,591 \text{ kg ha}^{-1}$), atrazine interception reached 29%. However, after 4.2 mm of simulated rainfall, 78 and 87% of the applied atrazine was incorporated into the upper 5 cm of soil underneath standing and roller crimped cereal rye, respectively. In 2023, when cereal rye biomass increased to $7,726 \text{ kg ha}^{-1}$, up to 94% of the applied atrazine was intercepted. Under this excessive amount of biomass accumulation, 4.2 mm were not enough to incorporate more than 28 and 14% of the applied atrazine into the 0–5 cm of soil underneath standing and roller crimped cereal rye, respectively. In 2022 and 2023, 8.3 mm of rainfall were enough to wash off some of the atrazine from the residue, incorporate into the top 5 cm of soil, and also leach some of it below the sampling zone.

Previous research have demonstrated the benefits from using residual herbicide at cover crop termination (Cornelius and Bradley, 2017b; Whalen et al., 2020; Wiggins et al., 2016). Although moderate amounts of cereal rye biomass reduced atrazine concentration in the soil by up to 29% at the time of application, the amount of the herbicide that reached the soil would likely result in some level of weed suppression, giving that residual herbicides are normally applied at doses much higher than the necessary to kill susceptible weed biotypes. Furthermore, after 4.2 mm of rainfall, 90% of the applied atrazine was recovered in the top 5-cm of soil underneath roller crimped cereal rye residue. However, data from this study shows that significant losses of atrazine can happen if there is an excessive accumulation of cereal rye biomass and not enough rainfall to move the herbicide intercepted by the residue onto the soil. In 2023, the presence of more than $7,700 \text{ kg ha}^{-1}$ of cereal rye biomass reduced atrazine concentration in the soil by up to 94%, which would likely result in unacceptable weed

control efficacy from the herbicide. Furthermore, a single rainfall event equivalent to 25 mm h^{-1} was not enough to wash more than 6% of the atrazine off of the cereal rye residue onto the soil.

In this respect, it is important that future research focuses on investigating the effect of multiple rainfall events on the fate of atrazine when applied at cereal rye termination. In high-residue cover cropping systems, herbicides with higher water solubility are one alternative to increase the chances that the herbicide will be incorporated into the soil after a rainfall event. Based on the results presented, we recommend that soil residual herbicides should be applied at the early termination of cereal rye (e.g., two weeks prior to cash crop planting). Thus, minimizing biomass accumulation and hence herbicide interception, while increasing the chances that most of the herbicide will be washed off of the residue after a single rainfall event.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

LM: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. SA: Conceptualization, Supervision, Writing – review & editing. EK: Conceptualization, Supervision, Writing – review & editing. BY: Conceptualization, Supervision, Writing – review & editing. WJ: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing.

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Conflict of interest

Author LM was employed by the company Corteva Agriscience LLC.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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