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# The influence of winter annual grass litter on herbicide availability

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## Research Article

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## Abstract

Invasive winter annual grass infestations on rangeland accumulate large quantities of litter on the soil surface, as plants senesce yearly and decompose slowly. It has been speculated that winter annual grass litter can adsorb soil-active herbicides and reduce overall performance. Three experiments were conducted from 2017 to 2018 at the Colorado State University Weed Research Laboratory to evaluate interception and subsequent desorption of herbicides applied to litter from three invasive winter annual grass species with simulated rainfall. Imazapic, rimsulfuron, and indaziflam were applied to medusahead [*Taeniatherum caput-medusae* (L.) Nevski], ventenata [*Ventenata dubia* (Leers) Coss.], and downy brome (*Bromus tectorum* L.) litter at two amounts (equivalent to 1,300 and 2,600 kg ha$^{-1}$). Rainfall was simulated at 3, 6, 12, and 24 mm at 0, 1, and 7 d after herbicide application. Herbicide concentration from the collected rainfall was measured using liquid chromatography–tandem mass spectrometry. At 2,600 kg ha$^{-1}$, *B. tectorum* herbicide interception was 84.3%, while *V. dubia* and *T. caput-medusae* averaged 76% herbicide interception. There were no differences in desorption among the three litter types. Simulated rainfall at 0 d after application recovered 100% of the intercepted rimsulfuron and imazapic from *B. tectorum* litter, while recovery decreased to 65% with rainfall at 1 or 7 d after application. Only 54% of indaziflam could be recovered at 0 d, and recovery decreased to 33% when rainfall was applied at 1 or 7 d after application. Applying soil-active herbicides before forecasted rain or tank mixing with a POST herbicide to provide initial control could potentially increase the amount of herbicide reaching the soil and provide more consistent invasive winter annual grass control.

## Introduction

Invasive winter annual grasses present the largest threat to the arid and semiarid ecosystems of western North America (DiTomaso 2000). Winter annual grasses typically germinate in the late summer or fall and overwinter in a semidormant state, resuming growth in early spring and taking advantage of early-season moisture and nutrients before native plant communities break dormancy (Beck 2009). Plants then produce seed and senesce by early summer (Beck 2009). Although fall germination is typical, invasive winter annual grasses are opportunistic and can germinate whenever the growing conditions are favorable (Beck 2009). This opportunistic life cycle and prolific seed production have allowed introduced winter annual grasses to spread through perennial-dominated rangelands (Mack and Pyke 1983). The ecological impacts of winter annual grass invasions include increased fire frequency, altered nutrient cycling, decreased species diversity, and degraded wildlife and pollinator habitat (Corbin and D'Antonio 2004; Knapp 1996; Thill et al. 1984).

Downy brome (*Bromus tectorum* L.) is the most widespread winter annual grass, invading over 22 million ha of rangeland in the United States with an estimated annual spread rate of 14% (Duncan et al. 2004). Since its introduction into North America in the mid-1800s, *B. tectorum* has undergone rapid range expansion, becoming the most dominant and impactful weed in the Intermountain West region (Johnson and Davies 2012; Mack 1981). It has been projected that an additional 31 million ha in the western United States are susceptible to invasion by exotic winter annual grasses (Pellant and Hall 1994).

While *B. tectorum* impacts the most acreage in the western United States (DiTomaso 2000), two other winter annual grasses, medusahead [*Taeniatherum caput-medusae* (L.) Nevski] and ventenata [*Ventenata dubia* (Leers) Coss.], have emerged as major threats to western rangelands (Wallace et al. 2015; Young 1992). *Taeniatherum caput-medusae* was first discovered in the United States in 1887, although populations appear to have remained relatively static until around the 1950s, when it became a major concern for livestock producers (Bovey et al. 1961). It infests more than 2 million ha of rangeland, has low palatability, and can reduce grazing capacity by 80% (Dahl and Tisdale 1975; Hironaka 1961). The invasive winter annual grass *V. dubia* was first reported in Washington in 1952 and spread throughout the Intermountain Pacific Northwest, becoming a major invader in Conservation Reserve Program lands and Palouse grasslands (Wallace et al. 2015). To demonstrate the spread potential of these two relatively new invaders, populations were recently identified for the first time in the Great Plains ecoregion (Sheridan, WY) (USDA-NRCS 2019). Before this discovery it was uncertain whether these species were adapted to the climatic conditions of the Great Plains, but with these recent findings it appears as though, if left unchecked, *T. caput-medusae* and *V. dubia* could potentially become as widespread as *B. tectorum*.

Winter annual grass infestations accumulate large quantities of litter, or thatch, on the soil surface as plants senesce yearly and decompose slowly (Evans and Young 1970). Litter facilitates invasions by promoting winter annual grass germination and suppressing native plants (Evans and Young 1970). Litter accumulation also contributes to increased fire frequency in the western United States by providing a continuous layer of fine fuels, especially in the Great Basin Desert (a region covering nearly all of Nevada, the western half of Utah, and portions of Oregon, Wyoming, Idaho, and California), where historically there was a significant amount of bare soil between plants (Abatzoglou and Kolden 2011; DiTomaso 2000; Knapp 1996). With this continuous fine fuel layer, fire return intervals have decreased from between 60 and 110 yr to less than 5 yr, resulting in displacement of desirable grasses, forbs, and shrubs that are not fire-adapted species (Whisenant 1990).

It has been widely speculated that winter annual grass litter, which can exceed 15 cm in thickness, can adsorb soil-active herbicides and reduce overall performance (DiTomaso et al. 2006; Evans and Young 1970; Kessler et al. 2015; Mangold et al. 2013; Monaco et al. 2005). Past studies have reported improved performance with herbicides when litter has been eliminated, although many of these studies have been confounded by the fact that fire was used to remove the litter layer (Davies and Sheley 2011; Kessler et al. 2015; Kyser et al. 2007; Monaco et al. 2005; Sheley et al. 2007). The impacts of winter annual grass litter on soil-active herbicides have only been empirically evaluated in one published study (Kessler et al. 2015). In that study, up to 74.6% of imazapic and tebuthiuron were intercepted when applied over high amounts of *B. tectorum* litter, and only 69% of the intercepted herbicide could be desorbed from the litter with 15 mm of rainfall 7 d after treatment (DAT) (Kessler et al. 2015). That study and several others evaluating crop residues have hypothesized that some irreversible binding to the litter may be occurring. This hypothesis is based on the fact that rainfall is not able to recover 100% of the applied herbicide (Banks and Robinson 1982; Carbonari et al. 2016; Cavenaghi et al. 2007; da Silva 2018; Ghadiri et al. 1984; Kessler et al. 2015).

Herbicide sorption increases with the lipophilic components of litter such as lignin, which increases as a percent of the dry weight as litter decays (Barak et al. 1983; Dao 1991; Van Beinum et al. 2006). A herbicide's chemical properties also influence sorption, with adsorption to organic matter dependent on the herbicide's lipophilic properties (Gennari et al. 1998; Stevenson 1972). Therefore, lipophilic herbicides may adsorb more readily to litter; unfortunately, little is known about differences in adsorption and subsequent desorption from litter with rainfall between water-soluble and water-insoluble herbicides (Barak et al. 1983; Dao 1991).

Imazapic and rimsulfuron, hydrophilic Group 2 herbicides (Shaner 2014), are used for winter annual grass control on rangeland (Kyser et al. 2007, 2013; Mangold et al. 2013; Morris et al. 2016). Both herbicides have PRE residual activity and can provide POST winter annual grass control when applied at the seedling stage (Kyser et al. 2013; Sebastian et al. 2016; Wallace and Prather 2016). Winter annual grass control can be highly variable with imazapic and rimsulfuron, and although selective at low use rates, perennial grass injury can occur (Kyser et al. 2013; Mangold et al. 2013; Sebastian et al. 2016, 2017a).

Indaziflam, a lipophilic Group 29 herbicide, controls winter annual grasses in rangeland and natural areas by inhibiting seedling establishment (Brabham et al. 2014; Sebastian et al. 2017a; Tompkins, 2010). Indaziflam has no significant POST activity (Brabham et al. 2014) but provides much longer (3+ yr) soil residual control compared with imazapic and rimsulfuron (Sebastian et al. 2016, 2017a). This long-term residual control provides an opportunity to start the process of winter annual grass seedbank depletion (Sebastian et al. 2017b). Indaziflam's low water solubility (3.6 mg $L^{-1}$ at pH 7) suggests that its interaction with winter annual grass litter will differ compared with imazapic and rimsulfuron. There are also indications that *V. dubia* and *T. caput-medusae* litter have different physical and chemical properties compared with *B. tectorum* litter (Bovey et al. 1961; Wallace et al. 2015); therefore, the ability to remove herbicide from litter with rainfall could vary between litter types. The objectives of this research were to (1) quantify imazapic, indaziflam, and rimsulfuron, intercepted at two levels of *B. tectorum*, *T. caput-medusae*, and *V. dubia* litter; (2) determine the efficiency of various simulated rainfall events to remove the intercepted herbicide from litter, and (3) determine whether time-dependent binding decreases the amount of herbicide that can be removed from litter by rainfall.

## Materials and Methods

### Litter Collection and Description of Experimental Units

Three separate experiments were conducted to evaluate interception and subsequent desorption with rainfall of herbicides applied to winter annual grass litter. Three winter annual grass litter types were collected in August 2016. *Bromus tectorum* litter was collected from Colorado Parks and Wildlife's Wellington State Wildlife Area in Wellington, CO (40.71°N, 104.95°W); *V. dubia* litter was collected from a Paradise Ridge in Latah County, ID (46.67°N, 116.97°W); and *T. caput-medusae* litter was collected from a natural area in Cache County, UT (41.66°N, 112.08°W). Litter was allowed to dry at room temperature (25 to 28 C) for a minimum of 1 wk before the experiments were conducted. Samples were taken from each litter type and oven-dried at 60 C for 48 h to determine moisture content. After 1 wk of drying at room temperature, moisture content averaged 7% in *B. tectorum* and *V. dubia*, while moisture content averaged 6% in *T. caput-medusae*. Litter was sieved to remove soil, and shoot segments were then cut to 140 mm in length. Each experimental unit consisted of a 150 by 150 by 50 mm glass dish (Pyrex®, Corelle Brands, Rosemont, IL 60018) below a 150 by 150 by 50 mm stainless-steel mesh basket (TWP, Berkeley, CA 94710). The baskets consisted of 0.5-mm stainless-steel mesh with 6.35-mm openings. All experiments were conducted in a complete randomized design with three replicates, and each of the three experiments described in the following sections were repeated.

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### Herbicide Interception

At the *B. tectorum* field site, 1-$m^2$ frames were used to collect three litter samples. Litter was allowed to dry under the same conditions described previously and was then weighed. The average biomass of the three litter samples was equivalent to 2,600 kg $ha^{-1}$, which is consistent with biomass production in high litter sites for all three winter annual grass types (Evans and Young 1970; Kessler et al. 2015; Wallace et al. 2015). Therefore, this biomass was used to simulate high litter conditions, while 50% of the biomass measurement (1,300 kg $ha^{-1}$) was used to simulate low litter conditions. *Bromus tectorum*, *V. dubia*, and *T. caput-medusae* litter was then weighed out into sample sizes of 2.82 g or 5.64 g, which corresponded to the field rate of 1,300 and 2,600 kg $ha^{-1}$, respectively,when adjusted for the size of the mesh basket. Litter was then spread evenly in the metal baskets and placed on top of the glass dishes. Consistent with field-applied concentrations, commercial formulations of imazapic (Plateau® herbicide, BASF, Research Triangle Park, NC 27709), rimsulfuron (Matrix® herbicide, Bayer Crop Science, Research Triangle Park, NC 27709), and indaziflam (Esplanade 200 SC® herbicide, Bayer Crop Science, Research Triangle Park, NC 27709) were applied at 122, 70, and 102 g ai $ha^{-1}$, respectively, over the top of the litter using a Generation III research track sprayer (DeVries Manufacturing, Hollandale, MN 56045) equipped with a TeeJet® 8002 EVS flat-fan spray nozzle (TeeJet Technologies, Springfield, IL 62703) calibrated to deliver 187 L $ha^{-1}$ at 172 kPa. Immediately after herbicide application, dishes were washed with methanol (Millipore Sigma, St Louis, MO 63103) for imazapic and rimsulfuron applications and acetonitrile (Millipore Sigma) for indaziflam applications. These solvents were chosen based on previously developed methods for analysis of these herbicides with liquid chromatography–tandem mass spectrometry (LC-MS/MS) (Demoliner et al. 2010; Pirard et al. 2007; Xu 2008). The methanol and acetonitrile volumes were recorded, and samples were transferred to 15-ml glass tubes (Pyrex® 9826 Culture Tubes, Corning, Corning, NY 14830) and stored at 0 C for analysis. A dish with an empty metal basket was included for all experiments as a control to determine the total quantity of herbicide applied.

#### Leaf Area Quantification

As a follow-up to the herbicide interception experiment, leaf and shoot area differences between *B. tectorum* and *T. caput-medusae* litter were investigated. A leaf area meter (LI-3100, Li-Cor, Lincoln, NE 68504) was used to quantify the leaf area index (LAI) of *B. tectorum* and *T. caput-medusae* litter. Six samples of each litter type weighing 5.64 g were measured by the leaf area meter, and means were calculated.

#### Desorption by Litter Types

To determine herbicide desorption from the three litter types, the litter amount equivalent to 2,600 kg $ha^{-1}$ was spread in the metal baskets and placed over the glass dishes. All three herbicides were applied as previously described to the three litter types. After herbicide application, baskets were removed, and the glass dishes were washed. Baskets were then placed back on the dishes, and 12 mm of simulated cumulative rainfall was immediately applied to half of the experimental units, using the same overhead sprayer previously described equipped with a TeeJet® 8004E nozzle (TeeJet Technologies) at 0.38 m above the experimental unit surface traveling at 0.45 m $s^{-1}$. The research track sprayer simulates rainfall via an automated system that delivers constant pressure (set to 172 kPa) from a hydraulic pump, allowing for simulated rainfall at desired volumes. The system applied 1 mm of rainfall $min^{-1}$ with the conditions described above. The artificial raindrops produced had a median volumetric diameter of 300 μm. The other half of the experimental units were removed from the dishes and stored at 25 to 28 C under laboratory inflorescent light conditions at 200 μmol $m^{-2}$ $s^{-1}$. After 1 d, the remaining treated litter was placed over clean dishes, and 12 mm of simulated rainfall was applied. After the simulated rainfall, the total water volume was recorded for each dish, and an aliquot was taken and stored in a 15-ml glass tube at 0 C.

#### Herbicide Desorption of *Bromus tectorum*

The final experiment was conducted to determine herbicide desorption from *B. tectorum* litter at different wait periods and rainfall amounts. The three herbicides were applied to *B. tectorum* litter (2,600 kg $ha^{-1}$), and rainfall was simulated using the previously described procedures. Rainfall was applied cumulatively in amounts of 3, 6, 12, and 24 mm after periods of 0, 1, and 7 d. The experimental units were stored at 25 to 28 C under laboratory inflorescent light conditions for the 1- and 7-d periods. Aliquots were collected and stored in the same manner as previously described until further analysis. The samples from the dishes without litter were diluted 20 times with methanol for imazapic and rimsulfuron samples and acetonitrile for indaziflam samples before filtration.

### Herbicide Quantification

For imazapic and rimsulfuron, the herbicide–methanol and herbicide–water samples were prepared for LC-MS/MS analysis by filtering 1-ml aliquots of each sample through a 0.24-μm membrane syringe filter (VWR International, Radnor, PA 19087) into 1.5-ml autosampler vials (Shimadzu Scientific Instruments, Columbia, MD 21046). For indaziflam, the herbicide–acetonitrile samples from the interception experiment were prepared in the same manner. For the indaziflam–water samples, 80% of the original solution was diluted with 20% acetonitrile, and 1-ml aliquots were filtered through a 0.24-μm membrane syringe filter into 1.5-ml autosampler vials. The samples collected from the dishes without litter were prepared by diluting them 20 times with methanol for imazapic and rimsulfuron applications or acetonitrile for indaziflam applications and using the same filtration process as described earlier. The herbicide concentration in each sample was determined by an LC-MS/MS system (Shimadzu LCMS-8040, Shimadzu Scientific Instruments, Columbia, MD 21046). The LC-MS/MS conditions for each herbicide are listed in Table 1. Five concentrations ranging from 0.01 and 1 μg $ml^{-1}$ were created from analytical standards and included as the calibration curve (rimsulfuron and imazapic, 99.9% purity, Sigma-Aldrich, St Louis, MO 63146; indaziflam, 99.3% purity, Bayer Crop Science).

The herbicide concentration from the samples based on the LC-MS/MS analysis was transformed into mass (μg) by adjusting for the volume recorded from the simulated rainfall. For the interception experiment, the measured herbicide concentrations that passed through the litter were subtracted from the total herbicide applied to the empty dishes to determine the herbicide amount intercepted by the litter. These data were then transformed to a percentage of the total applied herbicide. For the desorption experiments, the concentrations from the simulated rainfall samples were compared against the total herbicide intercepted by the litter in order to calculate percent desorption.

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**Table 1.** Liquid chromatography-tandem mass spectrometry (LC-MS/MS) conditions for rimsulfuron, imazapic, and indaziflam.

| | Herbicides | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Instrument parameters | Rimsulfuron | | | Imazapic | | | Indaziflam | | |
| Ionization mode | ESI+ | | | ESI+ | | | ESI+ | | |
| Column/temperature | Kinetex F5 100 Å column (100 × 4.6 mm; 2.6 µm)[a]; 40 C | | | Kinetex F5 100 Å column (100 × 4.6 mm; 2.6 µm)[a]; 40 C | | | Kinetex F5 100 Å column (100 × 4.6 mm; 2.6 µm)[a]; 40 C | | |
| Solvent A | Water acidified with 0.1% formic acid | | | Water acidified with 0.1% formic acid | | | Water acidified with 0.1% formic acid | | |
| Solvent B | Acetonitrile[b] acidified with 0.1% formic acid[c] | | | Acetonitrile[b] acidified with 0.1% formic acid[c] | | | Acetonitrile[b] acidified with 0.1% formic acid[c] | | |
| Gradient | %B | Flow | Time | %B | Flow | Time | %B | Flow | Time |
| | | ml min$^{-1}$ | min | | ml min$^{-1}$ | min | | ml min$^{-1}$ | min |
| | 50 | 0.4 | 0 | 30 | 0.4 | 0 | 65 | 0.4 | Isocratic |
| | 100 | 0.4 | 4 | 90 | 0.4 | 4 | | | |
| | 100 | 0.4 | 5 | 90 | 0.4 | 6 | | | |
| | 50 | 0.4 | 5.1 | 30 | 0.4 | 6.1 | | | |
| | 50 | 0.4 | 8 | 30 | 0.4 | 8 | | | |
| Injection volume | 1 µl | | | 1 µl | | | 1 µl | | |
| Retention time (min) | 3.23 | | | 3.57 | | | 2.88 | | |

[a]Material source: Phenomenex, Torrance, CA.
[b]Material source: Millipore Sigma, St Louis, MO.
[c]Material source: Thermo Fisher Scientific, Waltham, MA.

### *Statistical Analysis*

After failing to reject the null hypothesis of a Levene's test that experimental variances are equal, repeated studies for all three experiments were combined for analysis. Interception data were analyzed in R v. 3.4.3 (R Core Team 2017) using ANOVA, with herbicide, litter type, and litter amount as the factors. Post hoc analysis was performed using the EMMEANS package (Lenth 2018) in R v. 3.4.3 (R Core Team 2017) to obtain comparisons between all pairs of least-squares means with a Tukey-Kramer adjustment ($P < 0.05$). To compare desorption among the three litter types, data were analyzed by herbicide and wait period (0 d and 1 d) using ANOVA, with litter type as the factor in R v. 3.4.3 (R Core Team 2017). For the desorption from *B. tectorum* litter, a model comparison procedure was conducted to determine the best fit for these data. Data were subjected to an asymptotic regression (AR) model, a rectangular hyperbolic model, and linear regression. For each herbicide, best fit was determined by using the procedure outlined by Kniss et al. (2011), which chooses models with lowest bias-corrected Akaike information criterion corrected for small sample size (AICc) value while also considering residual standard errors and AICc ratios between models. The analysis was conducted in R v. 3.4.4 (R Core Team 2017) using the DRM (Ritz and Streibig 2005) and QPCR (Ritz and Spiess 2008) packages. For rimsulfuron and imazapic at all three wait periods (0, 1, and 7 d), as well as indaziflam at 1- and 7-d wait periods, the AR model was chosen as the best fit. The AR equation used to regress rain amount (mm) with percent desorption of intercepted herbicide was:

$$y = A_{\max}X\left\{1 - \exp\left[(\log 0.1)X\left(\frac{r}{r_{80}}\right)\right]\right\} \quad [1]$$

where $y$ is desorption as a percentage of the total intercepted herbicide, $A_{\max}$ is the maximum desorption at large values of $r$, $r$ is rainfall amount, and $r_{80}$ is the rainfall amount required for 80% of maximum desorption to occur. The AR procedure was performed, and parameter estimates of $A_{\max}$ and $r_{80}$ values with standard errors were established. A likelihood ratio test was conducted to compare the parameters statistically among time periods and herbicides. Linear regression was chosen as the best fit for indaziflam data from the 0-d time point, and regression analysis and ANOVA were performed in R v. 3.4.3 (R Core Team 2017).

## Results and Discussion

### *Interception by Litter*

For the interception experiment, herbicide and the interaction of herbicide by litter type were not significant ($P = 0.807$ and $P = 0.1631$, respectively), although there was a difference in interception among the litter types ($P < 0.001$). Therefore, an ANOVA was conducted for all herbicides combined, with litter type and litter amount included as main effects. More herbicide was intercepted by 2,600 kg ha$^{-1}$ of litter compared with 1,300 kg ha$^{-1}$ of litter ($P < 0.001$) across all three litter types (Table 2). *Bromus tectorum* litter also intercepted a higher percent of the herbicide than *T. caput-medusae* and *V. dubia* litter at both litter amounts ($P < 0.001$) (Table 2). At 1,300 kg ha$^{-1}$, *B. tectorum* litter intercepted 69.9 ± 1.1% (mean ± SE) of the herbicide, while *V. dubia* and *T. caput-medusae* litter intercepted 52.5 to 54.0 ± 1.3%. *Bromus tectorum* litter at 2,600 kg ha$^{-1}$ intercepted 84.3 ± 1.0% of the herbicide, while *V. dubia* and *T. caput-medusae* litter averaged 75.5 to 76.4 ± 1.0% interception (Table 2).

The different interception rates for the three litter types at the same weights indicates there may be a difference in the leaf area to weight ratio among the litter types. The mean LAI for *B. tectorum* litter was 540.7 ± 32.4, while the mean LAI for *T. caput-medusae* was 239.0 ± 9.4. The higher LAI potentially explains why *B. tectorum* litter intercepted significantly more herbicide in the experiment, as there was a higher ratio of leaf area to weight compared with *T. caput-medusae.*

Several field studies reported better control with annual grass herbicides in sites where litter had been removed compared with sites with litter (Kessler et al. 2015; Kyser et al. 2007; Monaco et al. 2005; Sheley et al. 2007). Herbicide interception by the litter layer could account for the inconsistent control observed in the field. In

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**Table 2.** Amount of herbicide intercepted by *Bromus tectorum*, *Taeniatherum caput-medusae*, and *Ventenata dubia* litter, as a percentage of total herbicide applied, at two litter amounts (1,300 kg ha$^{-1}$ and 2,600 kg ha$^{-1}$).[a]

| Species | Litter biomass | Interception[b] |
|---|---|---|
| | kg ha$^{-1}$ | % of total herbicide |
| *B. tectorum* | 1,300 | 69.9 ± 1.2 b |
| | 2,600 | 84.3 ± 0.5 d |
| *T. caput-medusae* | 1,300 | 54.0 ± 2.0 a |
| | 2,600 | 76.4 ± 0.7 c |
| *V. dubia* | 1,300 | 52.5 ± 2.0 a |
| | 2,600 | 75.5 ± 0.8 c |

[a]The data for rimsulfuron, imazapic, and indaziflam were combined for ANOVA.
[b]Mean value ± SE (n = 18). Means followed by the same letter are not significantly different at the P < 0.05 level as determined by Tukey's multiple comparison test.

high litter situations, less than 25% of soil-active herbicides may be available immediately after application. The 2,600 kg ha$^{-1}$ litter amount used in this study is based on the biomass present in the site where the *B. tectorum* litter was collected, although past studies have reported litter amounts of more than 8,000 kg ha$^{-1}$ (Evans and Young 1970; Ogle et al. 2003). Kessler et al. (2015) demonstrated herbicide interception increased in a linear relationship as *B. tectorum* litter increased. In the current study, 14% to 24% more herbicide was intercepted by the litter as the amount increased from 1,300 to 2,600 kg ha$^{-1}$ (Table 2); therefore, at very high litter sites, herbicide interception could approach 100%.

### *Desorption Comparison among Litter Types*

For all three herbicides, total desorption from the three litter types yielded no differences with 12 mm of simulated rainfall at both 0 and 1 d after application (Supplementary Table 1). These data suggest that herbicide desorption is not dependent on litter type. Because *B. tectorum* is more widespread than *T. caput-medusae* and *V. dubia*, we conducted a more in-depth desorption study using only *B. tectorum* litter. This comparison study demonstrates that the desorption study with *B. tectorum* should be applicable to *T. caput-medusae* and *V. dubia* litter.

### *Herbicide Desorption from* Bromus tectorum *Litter*

For herbicide desorption from *B. tectorum* litter, differences were observed among herbicides and wait periods. Overall, rimsulfuron and imazapic behaved similarly in the amount that could be recovered from the litter for each time point. For rimsulfuron, parameter estimates indicated that all the herbicide could be desorbed with rainfall at 0 d, while only 64.6% to 72.3% could be desorbed at 1 and 7 d (Table 3; Figure 1). Based on the $A_{max}$ parameters for imazapic, rainfall is estimated to desorb a maximum of 101.2%, 69.5%, and 66.2% of the herbicide on the litter at 0, 1, and 7 d, respectively (Table 3; Figure 2). A comparison of the $A_{max}$ parameter indicates the higher desorption at 0 d was significant compared with 1 and 7 d for both rimsulfuron and imazapic ($P < 0.001$), while there was not a difference between the $A_{max}$ at 1 and 7 d (rimsulfuron, $P = 0.2478$; imazapic, $P = 0.3972$). The model estimated that for rimsulfuron only, 8.3, 10.9, and 13.1 mm of rainfall would be required to achieve 80% of the total desorption ($r_{80}$) realized at 0, 1, and 7 d, respectively (Table 3). For imazapic, the $r_{80}$ parameters estimated that between 6 to 9 mm of rainfall would be needed to achieve 80% of the total desorption at any time period (Table 3).

Indaziflam desorption at 0 d was linear, and there was a positive correlation between rainfall amount and desorption ($R^2 = 0.96$, $P < 0.001$). At the lowest rainfall amount (3 mm), 9.3 ± 1.1% of

**Table 3.** Parameter estimates describing desorption of rimsulfuron, imazapic, and indaziflam from *Bromus tectorum*, *Taeniatherum caput-medusae*, and *Ventenata dubia* litter after 0, 1, and 7 d with a maximum of 24 mm of simulated rainfall by applying an asymptotic regression model.

| Treatment | Parameter estimate (SE)[a] | | Observed maximum[b] |
|---|---|---|---|
| | $A_{max}$ | $r_{80}$ | |
| Rimsulfuron | | | |
| 0 d | 103 (2.7) | 8 (0.6) | 103 |
| 1 d | 65 (3.3) | 11 (1.4) | 77 |
| 7 d | 72 (5.7) | 13 (2.5) | 71 |
| Imazapic | | | |
| 0 d | 101 (2.3) | 6 (0.4) | 101 |
| 1 d | 70 (3.0) | 8.5 (1.1) | 72 |
| 7 d | 66 (2.4) | 8 (0.8) | 67 |
| Indaziflam[c] | | | |
| 0 d | n/a | n/a | 60 |
| 1 d | 38 (2.3) | 19 (2.4) | 36 |
| 7 d | 41 (4.6) | 24 (4.8) | 36 |

[a]$y = A_{max}X\left\{1 - \exp\left[(\log 0.1)X\left(\frac{r}{r_{80}}\right)\right]\right\}y$, desorption as a percentage of the total intercepted herbicide; $A_{max}$, maximum desorption at large values of $r$; $r$, rainfall amount; $r_{80}$, rainfall amount required for 80% maximum desorption.
[b]Observed maximum indicates the maximum value obtained by any single observation in the study.
[c]Indaziflam at 0 d was fit with linear regression, therefore only the observed maximum is reported.

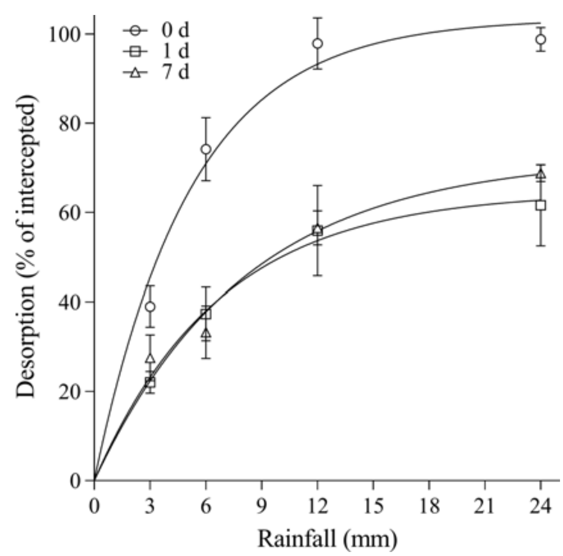


**Figure 1.** Rimsulfuron desorption from *Bromus tectorum* litter as a function of the amount of simulated rainfall after 0, 1, and 7 d expressed as a percentage of total herbicide intercepted. Data points are the means of replications with bars indicating the standard error of the mean ($n = 6$): 0 d: $y = 103.45X\left\{1 - \exp\left[(\log 0.1)X\left(\frac{24}{8.35}\right)\right]\right\}$; 1 d: $y = 64.58X\left\{1 - \exp\left[(\log 0.1)X\left(\frac{24}{10.87}\right)\right]\right\}$; 7d: $y = 72.31X\left\{1 - \exp\left[(\log 0.1)X\left(\frac{24}{13.06}\right)\right]\right\}$.

the intercepted herbicide was removed from the litter, while 53.7 ± 1.9% was desorbed with the highest rainfall amount (24 mm) (Figure 3). Although this relationship was linear, it would eventually become asymptotic as it reaches the maximum amount that can be desorbed from the litter. The 1- and 7-d wait periods fit an asymptotic curve, and the AR model estimated $A_{max}$ values of 37.7% and 40.9% desorption, respectively. Comparison of the $A_{max}$ indicated no difference between the two time points ($P = 0.54$) (Table 3; Figure 3). The $r_{80}$ parameters indicated that 19 and 24 mm of rainfall are required to achieve 80% of the maximum

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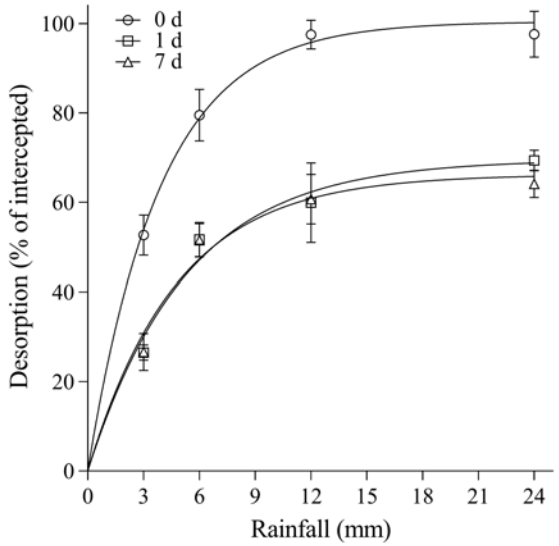


**Figure 2.** Imazapic desorption from *Bromus tectorum* litter as a function of the amount of simulated rainfall after 0, 1, and 7 d expressed as a percentage of total herbicide intercepted. Data points are the means of replications with bars indicating the standard error of the mean ($n$ = 6): 0 d: $y = 101.19X\{1 - \exp[(\log 0.1)X(\frac{24}{6.39})]\}$; 1 d: $y = 69.53X\{1 - \exp[(\log 0.1)X(\frac{24}{8.54})]\}$; 7d: $y = 66.22X\{1 - \exp[(\log 0.1)X(\frac{24}{7.69})]\}$.

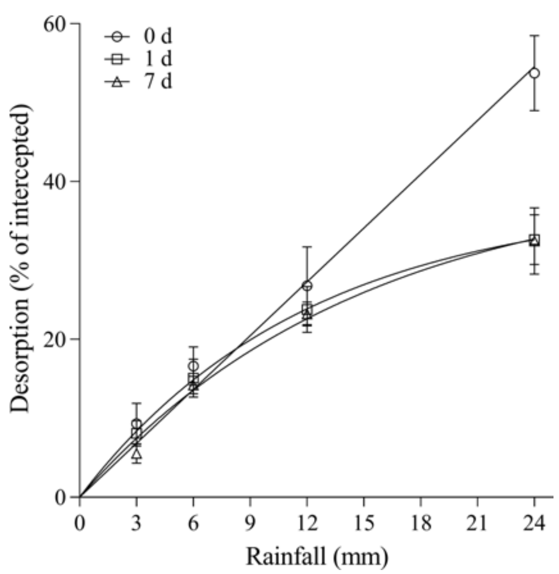


**Figure 3.** Indaziflam desorption from *Bromus tectorum* litter as a function of the amount of simulated rainfall after 0, 1, and 7 d expressed as a percentage of total herbicide intercepted. Data points are the means of replications with bars indicating the standard error of the mean ($n = 6$): 0 d: $y = 2.27x$, $R^2 = 0.94$; 1 d: $y = 37.72X\{1 - \exp[(\log 0.1)X(\frac{24}{19.29})]\}$; 7d: $y = 40.89X\{1 - \exp[(\log 0.1)X(\frac{24}{23.99})]\}$.

desorption at 1 and 7 d, respectively. Although 0-d data could not be directly compared with 1 and 7 d using the $A_{max}$ value, the fact that these data presented as linear instead of asymptotic demonstrates there were differences in desorption with rainfall at 0 d compared with the other wait periods.

For rimsulfuron and imazapic, 12 mm of rainfall was sufficient to achieve maximum desorption at all time points. Although nearly all the herbicide was recovered when rainfall was received immediately after application (0 d), more than 30% of the intercepted herbicide could not be desorbed from the litter with 24 mm of rainfall at 1 and 7 d after application (Table 3; Figures 1 and 2). For indaziflam, desorption continued to increase between the 12- and 24-mm rainfall amounts, although only 53.7 ± 1.9% could be desorbed from the litter, even with immediate rainfall (0 d). Recovery rates went down to an average of 32.6 ± 1.1% by 1 and 7 d after application (Table 3; Figure 3). Interestingly, for all three herbicides, there were no differences in maximum desorption if rainfall was received 1 or 7 d after application.

The amount of herbicide recovered from the litter decreases as time without rainfall increases, implying irreversible binding to litter may be occurring (Carbonari et al. 2016; da Silva 2018; Kessler et al. 2015; Tofoli et al. 2009). Johnson et al. (2000) determined adsorption of imazethapyr to soil was time dependent, with a rapid, initial adsorption phase occurring in the first 1 to 4 d following application, and adsorption becoming stronger over time. This time-dependent binding may be occurring as herbicides bind to the lipophilic litter components. For example, only 69.5% of imazapic and 59.5% of tebuthiuron could be recovered with 15 mm of rainfall at 7 d after application to *B. tectorum* litter (Kessler et al. 2015). Between 15% and 25% of the imazapic and tebuthiuron could not be desorbed from the litter with methanol extraction (Kessler et al. 2015). In our study, there was a 30% to 40% decrease in herbicide recovery when rainfall was delayed for 1 d after application, although there was no additional decrease in recovery from 1 to 7 d. Other studies have demonstrated that herbicide recovery continues to decrease as time without rainfall increases from 1 to 60 DAT (Carbonari et al. 2016; Cavenaghi et al. 2007; Tofoli et al. 2009).

The recovery rate for indaziflam was approximately half that for rimsulfuron and imazapic at all three time points, suggesting that the amount of herbicide that can be desorbed from the litter with rainfall is dependent on the physical and chemical characteristics of the herbicide. Rimsulfuron and imazapic are both highly water-soluble herbicides, with log $K_{ow}$ (octanol–water partition coefficient) values of −1.47 and 0.393, respectively (Shaner 2014), while indaziflam is lipophilic, with a log $K_{ow}$ of 2.8 (Tompkins 2010). Because lipophilicity increases adsorption to organic matter for most herbicides, the lipophilic nature of indaziflam appears to increase its adsorption to litter (Barak et al. 1983; Cox et al. 2000; Hance 1965).

Inconsistencies in winter annual grass control provided by soil-active herbicides have been reported (Kyser et al. 2013; Mangold et al. 2013; Sebastian et al. 2016, 2017a; Shinn and Thill 2004). These inconsistencies may be due to the amount of litter present at a site and how soon rainfall occurs after herbicide application. This information is critical for land managers using soil-active herbicides, especially in high litter sites. Applying herbicides before forecasted rain could potentially improve herbicide performance, as maximum desorption from the litter may be attained with as little as 12 mm of rainfall. Another option for land managers is to combine soil-active herbicides with a POST herbicide, such as glyphosate, and apply herbicides during native species dormancy, while winter annual grasses are in a semidormant state (Sebastian et al. 2017a). This combination would provide immediate, POST winter annual grass control and allow time for precipitation events to desorb the soil-active herbicide from the residue, providing PRE control of seeds germinating from the soil seedbank.

Additionally, land managers could consider using the higher labeled rates of effective herbicides under high litter situations. This may increase the amount of active ingredient reaching the soil immediately after application and with subsequent rainfall events.

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Even though a large percentage of the herbicide may be bound to the litter layer, long-term control with indaziflam has been consistently achieved with very low rates (44 to 102 g ai $ha^{-1}$) in high litter sites, outperforming the hydrophilic herbicides imazapic and rimsulfuron (Sebastian et al. 2016, 2017a). This suggests that although interception and adsorption of indaziflam occurs, this herbicide is highly active when incorporated into the soil profile via rainfall. Future research should evaluate the relationship between litter degradation and release of the adsorbed herbicide back into the soil profile. For herbicides like imazapic and rimsulfuron, which photodegrade, this may not be significant; however, indaziflam has limited photodegradation and could be released and activated into the soil profile as litter naturally degrades over time. Research has suggested that herbicides may be released from the litter in active form as it decays, providing a slow release of the herbicide back to the soil and extending control (Dao 1991); however, additional research is needed to determine impacts of litter decay for indaziflam.

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**Supplementary material.** To view supplementary material for this article, please visit https://doi.org/10.1017/wsc.2019.45.

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