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Dissipation of spring-applied methiozolin in turfgrass systems

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Research Article

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Abstract

Methiozolin is applied five or more times per year to control annual bluegrass (*Poa annua* L.) in cool, temperate areas, but high market demand in the southern United States and recent registration in Australia has expanded the product's use in variable climates. To better design weed control programs for variable turf types, more information is needed to characterize methiozolin dissipation in different turf systems. Methiozolin was applied biweekly three times to a Kentucky bluegrass (*Poa pratensis* L.) lawn and adjacent bare soil in New Jersey and on 12 hybrid bermudagrass [*Cynodon dactylon* (L.) Pers. × *Cynodon transvaalensis* Burtt Davy] putting greens in Virginia. Soil samples were collected immediately following each application and biweekly for 12 additional weeks. Methiozolin was extracted from each soil sample and analyzed using liquid chromatography with tandem mass spectrometry. Methiozolin was detected only within the top 2 cm of the soil (including verdure), but not below 2 cm, demonstrating its limited vertical mobility. Dissipation was significantly faster in turf-covered soil compared with bare soil. The time required for 50% methiozolin dissipation was 13 and 3.5 d in bare soil and turf-covered soil, respectively. In Virginia, methiozolin dissipation in the 1-m span of three sequential applications differed between years. Methiozolin concentration immediately following the third biweekly application to *C. dactylon* ×*transvaalensis* greens was approximately 105% and 180% of the concentration immediately following the initial application, in 2021 and 2022, respectively. This difference in methiozolin accumulation following three applications was attributed to differential *C. dactylon* ×*transvaalensis* green up during methiozolin treatments each year. Despite differences in posttreatment methiozolin concentration between years, the temporal dissipation rate later into the summer was consistent. Following the final application on *C. dactylon* ×*transvaalensis* greens, methiozolin dissipated 50% and 90% in 14 and 46 d, respectively. These data suggest that methiozolin dissipates more rapidly in turfgrass systems than in bare soil.

Introduction

Methiozolin is a fatty-acid thioesterase–inhibiting herbicide labeled for the selective control of annual grassy weeds in golf course putting greens (Brabham et al. 2021; Koo et al. 2014). In creeping bentgrass (*Agrostis stolonifera* L.) putting greens, methiozolin provides high levels of annual bluegrass (*Poa annua* L.) control through both preemergence and postemergence activity (Askew and McNulty 2014; Flessner et al. 2013; McCullough et al. 2013). Preemergence-only activity of methiozolin in turfgrass systems has not been evaluated in peer-reviewed literature due to the typical application timings of methiozolin for *P. annua* control occurring during fall and spring when *P. annua* is actively growing, which makes the evaluation of preemergence activity difficult to differentiate from postemergence activity (Askew and McNulty 2014).

Persistence of preemergence herbicides in the soil can directly influence weed control throughout the growing season (Bond and Walker 1989; Grey et al. 2007; Mueller et al. 1999). Several factors influence persistence of residual herbicides in soil, including soil pH, temperature, texture, moisture, and organic matter content (Burnside et al. 1969; Harris 1966; Jacques and Harvey 1979; Kwon et al. 2004; Rouchaud et al. 2000; Savage 1978; Stougaard et al. 1990; Szmigielski et al. 2012; Zimdahl and Gwynn 1977; Zimdahl et al. 1984). Residual herbicide concentration in soil can dissipate through processes such as leaching, microbial degradation, and absorption, as well as through sequestration or metabolism by plants. Placement of residual herbicides within the soil column is important for maximum exposure and uptake of the herbicide by weed seedlings in turfgrass systems (Schleicher et al. 1995). Methiozolin's water solubility (3.4 mg L^{-1}) and log K_{ow} value (3.9) indicates that it has a high capacity for retention in the upper portion of the soil (Koo et al. 2010). Further studies by Flessner et al. (2015) confirmed that methiozolin does not readily move within the soil profile and is not likely to leach.

[^{14}C]methiozolin metabolism was evaluated in a dark, controlled laboratory situation by Hwang et al. (2013) on bare-ground sandy clay loam soil from a drained rice paddy field. Results from this study indicated that methiozolin was primarily degraded in the soil via microbial activity. Furthermore, the half-life of methiozolin was reported to be approximately 49 d in this scenario, but experimental conditions were extremely dissimilar to field conditions. Although researchers have cited this 49-d half-life to discuss potential methiozolin length of residual activity (Askew and McNulty 2014; Flessner et al. 2017), it is not indicative of dissipation under field conditions. Studies conducted in Korea indicate methiozolin soil half-life in a putting green system to be approximately 10 d, but no information was given regarding soil type, turf species, or application timing (Jo et al. 2016). The disparity between dissipation of an herbicide in bare soil being relatively slower than a turfgrass system is typical for preemergence herbicides. For example, in cropping systems, pendimethalin half-life was estimated to be around 60 d, but in a Kentucky bluegrass (*Poa pratensis* L.) system, >60% of pendimethalin dissipated within 20 d of application (Stahnke et al. 1991). Differences in herbicide persistence between turfgrass and bare-ground systems are typically attributed to differential soil characteristics. Turfgrass systems generate more soil organic matter than production agriculture or bare-ground systems (Kaye et al. 2005). Organic matter content is highly correlated to microbial population (Kerek et al. 2002; Shi et al. 2006), and microbial organisms are the main driving force for pesticide degradation in soil (Reedich et al. 2017).

A lesser studied route of preemergence herbicide dissipation is loss via turfgrass absorption. Many herbicides labeled for preemergence control can be absorbed by turfgrass foliage and roots. For example, metribuzin and mesotrione are important preemergence herbicides in production crops (Armel et al. 2003; Green et al. 1988; McWhorter and Anderson 1976; Mitchell et al. 2001) but are used primarily for postemergence weed control in turf (Brewer et al. 2022). Although organic matter is typically higher in turfgrass systems compared with production crops, both metribuzin and mesotrione are readily absorbed by turfgrass roots and metabolized by turfgrass plants (Brewer et al. 2022; Tate et al. 2019). Methiozolin is similar to the aforementioned herbicides in that it is readily absorbed by turfgrass plants, which may limit its availability to weed species when applied preemergence (Koo et al. 2014; Yu and McCullough 2014).

In preliminary evaluations, methiozolin controlled barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.] in rice 90% at 3 wk after application, but control was ineffective by 6 wk (Norsworthy et al. 2011). Data presented upon the filing of the methiozolin patent indicate that methiozolin can control goosegrass (*Eleusine indica* L. Gaertn) and large crabgrass (*Digitaria sanguinalis* L. Scop.) for at least 4 wk when applied preemergence (Koo and Hwang 2013).

Previous weed efficacy studies and the 2-wk reapplication interval for *P. annua* control on the methiozolin label (Anonymous 2021) suggest that methiozolin may dissipate relatively rapidly in turfgrass systems. Therefore, our objectives were to characterize the dissipation rate of spring-applied methiozolin on hybrid bermudagrass [*Cynodon dactylon* (L.) Pers. × *Cynodon transvaalensis* Burtt Davy] putting greens, and to compare methiozolin persistence when applied to a *P. pratensis* turf versus bare ground. Based on previous literature, we hypothesize that in turfgrass systems, the half-life of methiozolin will be less than in bare-ground scenarios. Additionally, we hypothesize that methiozolin concentrations will be significantly higher in the top 2 cm of the soil profile as opposed to the next 4 cm of the profile.

Materials and Methods

Persistence of Methiozolin Applied to Cynodon dactylon × transvaalensis Putting Greens

Studies were conducted between 2021 and 2022 in Midlothian, VA, at the Independence Golf Club (37.54°N, 77.69°W) to evaluate methiozolin soil persistence when applied to sand-based *C. dactylon* ×*transvaalensis* putting greens. Three biweekly applications of methiozolin (500 g ai ha^{-1}, PoaCure, Moghu Research Center) were carried out according to label recommendations for spring *P. annua* control on 12 putting greens that acted as replications. Each putting green had a sand-based root zone that meets the U.S. Golf Association (USGA) specifications for root zone construction (USGA 2018). Soil pH was 6.5 ± 0.2 and soil organic matter was 1.3 ± 0.4% (Table 1). Putting greens were maintained at 4 mm, and clippings were removed with mowing. Nine replications were conducted in 2021 and three replications were conducted in 2022.

Applications were made to a single 1.8 by 2.4 m plot per replication via a four-nozzle spray boom equipped with TTI 11006 spray tips (TeeJet Technologies, Springfield, IL, 62703, USA), operated at 358 kPa to deliver 374 L ha^{-1}. Applications were made on February 24, March 10, and March 24 in 2021, and March 3, March 17, and March 30 in 2022. Following each application, approximately 6.4 mm of irrigation was applied, according to label recommendations, to wash methiozolin from the foliage. Eight 2.5-cm-diameter soil cores per replicate putting green were collected at each sampling date at each of four random locations distributed across the plot. To prevent error associated with spray pattern overlap, four transects that corresponded to a line directly under the center of each spray nozzle were referenced in each plot. These four transects were parsed into nine positions spaced 20 cm apart along the plot length. At each of the nine assessment dates, a unique and random position was chosen from each of the four transects and two adjacent soil cores were collected. These eight soil cores were divided into two sampling depths that included verdure, thatch layer, and soil above 2 cm below the thatch layer and the soil located from 2 to 8 cm below the thatch layer, yielding two composite soil samples for each replicate putting green at each assessment date.

Soil cores were extracted immediately following trial initiation, immediately following the second spring application, and immediately following the final spring application in order to evaluate the rate of methiozolin accumulation over the course of the spring applications. Cores were then collected at 2, 4, 6, 8, 10, and 12 wk after the final spring application in order to evaluate the dissipation of methiozolin over the course of the summer. Immediately following soil core extraction, samples were stored with ice and transported to Blacksburg, VA (37.22°N, 80.41°W), where they were placed in a freezer and maintained at approximately −20 C until the extraction process began. Previous research demonstrated that methiozolin loss under these conditions after 18 mo was negligible (SJ Koo, personal communication).

In preparation for methiozolin extraction, soil samples were flash frozen with liquid nitrogen, then homogenized using a mortar and pestle. Large particles were removed by passing homogenized soil samples through a 2-mm sieve. A random sample of approximately 10 g of soil from each homogenized soil preparation was collected, weighed, and then placed in an air dryer at 60 C for 72 h until completely dry. Following the drying process, the soil was weighed, and the resulting loss in weight was used to extrapolate gravimetric water content of each sample.

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Table 1. Putting green description of cultivar, age at the time of study initiation, soil pH, and soil organic matter for each putting green evaluated for methiozolin dissipation

Green	Year[a]	Cultivar	Age	Soil pH[b]	Soil organic matter[c]
			yr		%
1	2021	Experimental 'FAES 1302'	4	6.6	1.3
2	2021	'MiniVerde'	4	6.7	1.2
3	2021	'G12'	3	6.7	0.78
4	2021	'TifEagle'	4	6.5	1.4
5	2021	'G12'	4	6.8	1.1
6	2021	'Mach1'	1	6.5	1.3
7	2021	'Tif3D'	4	6.9	1.1
8	2021	Experimental 'JK 110521'	4	6.6	0.74
9	2021	'TifEagle'	4	6.3	1.6
10	2022	'MiniVerde'	5	6.3	1.0
11	2022	'Mach1'	2	6.2	1.0
12	2022	Experimental 'JK 110521'	5	6.2	1.7

[a]Application dates in 2021 were February 24, March 10, and March 24; and in 2022, March 3, 17, and 30.
[b]Putting green soils were built to U.S. Golf Association specifications on all putting greens.
[c]Soil organic matter was measured via loss on ignition from the top 6 cm of soil excluding the verdure and is presented as a percentage of soil dry weight.

Methiozolin extraction from the soil was conducted using the following methodology: Approximately 2 g of soil was weighed, placed into test tubes, and then homogenized. Ten milliliters of an 80:20 acetonitrile:high-performance liquid chromatography (HPLC) water mixture was added to the soil, homogenized, and then shaken for 30 min using a wrist-action shaker. The soil-containing test tube was then centrifuged for 10 min at 3,000 rpm. Approximately 6 ml of supernatant was transferred to separate test tubes using a 0.45-µm polytetrafluoroethylene (PTFE) syringe filter. The sample was then diluted by adding 990 µl of 50:50 acetonitrile:HPLC water solution to 10 µl of supernatant. One milliliter of the diluted sample was utilized for methiozolin concentration analysis. Methiozolin content was analyzed from the soil extract using HPLC (1290 Infinity, Agilent Technologies, Santa Clara, CA, USA) with a tandem mass spectrometer (6490-triple quadrupole, Agilent Technologies) (LC/MS/MS). The limit of quantitation (LOQ) was 0.025 ppm (on a wet weight basis) and the limit of detection (LOD) was 0.05 ppb (on a soil dry weight basis).

Data included *C. dactylon* ×*transvaalensis* percent visible green coverage and methiozolin concentration over time and were subjected to ANOVA using Proc Mixed SAS v. 9.4 (SAS Institute, Cary, NC, USA) with sums of squares partitioned to account for the effects of sampling time, year, sampling time by year, and replicate nested within year. Data were combined over year if the year by time interaction was insignificant ($P > 0.05$). If sampling time or any interaction with sampling time was significant ($P < 0.05$), then data were subjected to regression analysis to explain trends in the repeated measure over time. *Cynodon dactylon* × *transvaalensis* percent visible green coverage was modeled via a three-parameter Gompertz model using Equation 1:

$$y = ae^{-be^{-kT}} \quad [1]$$

in which y equals the percent *C. dactylon* ×*transvaalensis* green coverage, a equals the asymptote, b equals the displacement along the x axis, k equals the rate of *C. dactylon* ×*transvaalensis* green coverage increase, and T equals time in days.

Methiozolin soil concentrations for all soil cores collected following the final methiozolin application were converted to a percentage of the soil methiozolin concentration measured immediately after the final methiozolin application. These methiozolin concentrations were subjected to nonlinear regression using the exponential decay equation (Equation 2):

$$C_t = C_0 * e^{(-k*t)} \quad [2]$$

where C_t is the percent methiozolin concentration at sampling time t; C_0 is the initial methiozolin concentration at t_0, which was always equal to 100%; k is the estimated rate constant of methiozolin dissipation; and t is time in days. The k values were estimated via PROC NLIN in SAS v. 9.4. Time required, in days, for 50% and 90% dissipation of methiozolin following the final application (D_{50} and D_{90}, respectively) was calculated using Equations 3 and 4, respectively:

$$D_{50} = \left(\frac{\ln(2)}{k}\right) \quad [3]$$

$$D_{90} = \left(\frac{\ln(10)}{k}\right) \quad [4]$$

where D_{50} and D_{90} are time in days for 50% and 90% methiozolin dissipation, respectively, ln is the natural log, and k is the aforementioned predicted rate constant parameter.

Methiozolin soil concentrations for soil cores collected immediately following the second and third applications were converted to a percentage of measured methiozolin immediately following the initial application. Methiozolin concentrations measured in 2021 were subjected to nonlinear regression via the quadratic function with Equation 5:

$$C_t = (a * t^2) + (b * t) + c \quad [5]$$

where C_t is the percent methiozolin concentration at sampling time t, a is an estimated parameter that determines the concavity of the curve, b is an estimated parameter that determines the slope and position of the curve, and c is the y intercept when t is 0. As methiozolin concentrations were calculated as a percent of methiozolin concentration following the initial application, y is set to 100. Due to variability between years in rate of accumulation, methiozolin concentrations measured in 2022 were subjected to linear regression using Equation 6:

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$$y = mx + b \quad [6]$$

where y is the percent methiozolin concentration at sampling time x, m is the slope, and b is the y intercept. To compare methiozolin soil concentration to application rates utilized in previous research, methiozolin concentrations (in ppm) were converted (to g ai ha^{-1}) using the weight and area of each sample in Equation 7.

$$W_m = \left[\frac{\left(\frac{\text{ppm} * W_s}{10^6}\right)}{A_s * 10^8}\right] \quad [7]$$

where W_m is the weight of methiozolin (in g ai ha^{-1}), ppm is methiozolin concentration (in µg), W_s is the weight of the sample (in g), and A_s is the area of the sample (in cm^2).

Dissipation of Field-applied Methiozolin as Affected by Turfgrass Coverage

A study was conducted from 2014 to 2015 in Frenchtown, NJ (40.54°N, 74.99°W) to evaluate methiozolin dissipation as influenced by the presence or absence of turfgrass coverage. This study was conducted in compliance with Good Laboratory Practices set forth in Title 40, Part 160 of the U.S. Code of Federal Regulations. The trial was arranged as a randomized complete block design with three treatments and three replications. In addition to a nontreated control, treatments included methiozolin applied at 897 g ai ha^{-1} three times at biweekly intervals to *P. pratensis* turf and bare-ground soil. Turfgrass was mown at 8.9 cm throughout the duration of the study. The bare-ground plots were prepared via disk harrowing and were maintained vegetation-free using glyphosate (1.1 kg ai ha^{-1}) as needed throughout the duration of the study. Treated plots measured 6.1 by 16.8 m and were subdivided into 22 1.5 by 3 m subplots to ensure randomization in sample collection. The nontreated plots measured 3 by 9.1 m and were divided into six 1.5 by 3 m subplots. All plots were separated by approximately 30 m to ensure no cross-contamination via drift. The test site soil was a Penn silt loam (fine-loamy, mixed, superactive, mesic Ultic Hapludalfs) with 28%, 51%, and 21% sand, silt, and clay, respectively, with a pH of 6.7 and 2.7% soil organic matter.

Each application was uniformly applied to the treated turf and bare soil plots on May 6, May 20, and June 3, 2014. Applications were made with a tractor-mounted boom sprayer calibrated to deliver 374 L ha^{-1} via TeeJet® AI 11004 nozzles. The initial application to both treated plots was timed to approximate the typical start of herbicide applications in turf in the spring season in New Jersey. Following herbicide application, 2.5 mm of irrigation was administered according to label recommendations. Soil and grass samples in the treated plots were collected for analysis immediately following each application and at 1, 3, 7, 14, 28, 58, 92, 119, 165, and 294 d following the final application. In the nontreated control plot, soil samples were collected 8 d before trial initiation and 7 and 92 d following the final application for use as analytical controls and for procedural recovery samples. All samples were stored frozen until shipment via freezer truck to Ricerca Biosciences, where they were maintained frozen until the time of analysis. Samples of aboveground biomass, 0- to 7.6-cm depth of soil and 7.6- to 15-cm depth of soil were collected from all treated plots at each sampling timing. Aboveground biomass samples were only collected in turf-covered plots. The aboveground samples measured 77 cm^2, and the soil samples measured 7.6 cm in diameter. At each sampling timing in the treated turf plots, five grass samples were taken from each replication by removing all aboveground biomass within a 77-cm^2 area and combined to create a single sample per replication. Likewise, in each sampling timing in the treated turf and bare soil plots, five soil cores were taken from each replication and combined to give a single sample per replication.

The methiozolin from the grass and soil samples was extracted using the methods of Hwang et al. (2013), filtered through 0.45-µm PTFE syringe filters, diluted (if required), and analyzed by LC/MS/MS (SIL-HTA, Shimadzu Scientific Instruments, Kyoto, Japan) equipped with a Phenomenex Luna column (2 mm by 150 mm by 5 µm; Torrance, CA, USA) for methiozolin. The LOQ was 0.01 ppm (on a wet weight basis). The LOD was 0.002 ppm (on a wet weight basis for grass and on a dry weight basis for soil).

Methiozolin dissipation rate and subsequent soil D_{50} and D_{90} values were calculated using Equations 2, 3, and 4, respectively. Methiozolin concentrations, in ppm were converted (to g ai ha^{-1}) using Equation 6. Methiozolin soil D_{50} and D_{90} were subjected to ANOVA using PROC GLM in SAS v. 9.4 with sums of squares partitioned to reflect replicate and treatment effects. Means were separated between turf-covered and bare-ground plots using Fisher's protected LSD at $\alpha = 0.05$.

Results and Discussion

Persistence of Methiozolin Applied to *Cynodon dactylon* × *transvaalensis* Putting Greens

Methiozolin was not detected in soil at the lower soil sampling depth (2 to 8 cm) (data not shown); therefore, all data presented are based on methiozolin concentrations in the upper 2 cm of soil. These results are consistent with other studies evaluating methiozolin movement in soil (Flessner et al. 2015) as well as the chemical properties of methiozolin, such as low water solubility (3.4 mg L^{-1}) and a hydrophobic log K_{ow} (3.9), which indicate limited soil mobility (Koo et al. 2010). In 2021 and 2022, methiozolin concentrations immediately following the initial application were 509 and 482 g ai ha^{-1}, respectively, indicating that application accuracy was within 5% of the targeted application rate (500 g ai ha^{-1}). These values are represented as 100% of initial application for methiozolin concentration following the three applications (Figure 1). However, methiozolin concentrations over time were dependent on year ($P > 0.05$); therefore, the methiozolin concentrations over time are presented separately by year.

The difference in methiozolin accumulation during the treatment period between 2021 and 2022 may be due to *C. dactylon* × *transvaalensis* percent green coverage at the time of trial initiation. In 2021, methiozolin accumulation fit a quadratic model wherein methiozolin accumulated for the first two applications then dissipated between the second and third applications (Figure 1). The final concentration was only slightly higher than the initial concentration, indicating that approximately two applications worth of methiozolin had dissipated in the 28-d span. Increased microbial activity due to increased temperatures may have contributed more rapid methiozolin dissipation. However, it is unlikely that increased dissipation rate can account for the rapid loss of methiozolin within the 14 d between applications. Between the second and third methiozolin applications, *C. dactylon* × *transvaalensis* percent green coverage increased from 0% to approximately 25% (Figure 2). Bermudagrass (*Cynodon* spp.) roots are mostly lost during dormancy and undergo rapid post-dormancy regeneration (DiPaola and Beard 1978). Early-spring meristematic

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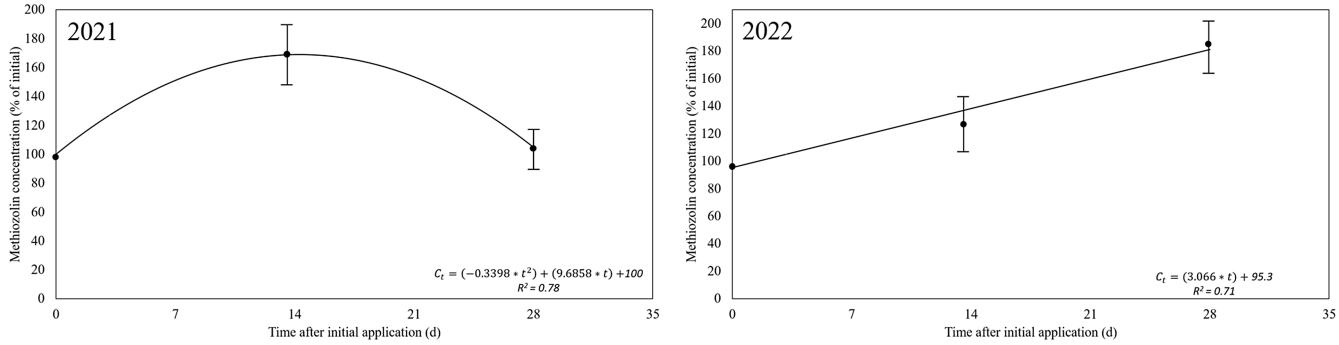

Figure 1. Methiozolin accumulation, as a percent of the measured concentration following the first application, as affected by three biweekly applications of methiozolin at 500 g ai ha^{-1} applied to *Cynodon dactylon* ×*transvaalensis* putting greens in Midlothian, VA, in 2021 and 2022. Methiozolin accumulation data in 2021 were fit to the quadratic function using the equation $C_t = (a * t^2) + (b * t) + c$: where C_t is the percent methiozolin concentration at sampling time t, a is an estimated parameter that determines the concavity of the curve, b is an estimated parameter that determines the slope and position of the curve, and c is the y intercept when t is 0. Methiozolin accumulation data in 2022 were fit to a linear regression using the equation $y = mx + b$: where y is the percent methiozolin concentration at sampling time x, m is the slope, and b is the y intercept.

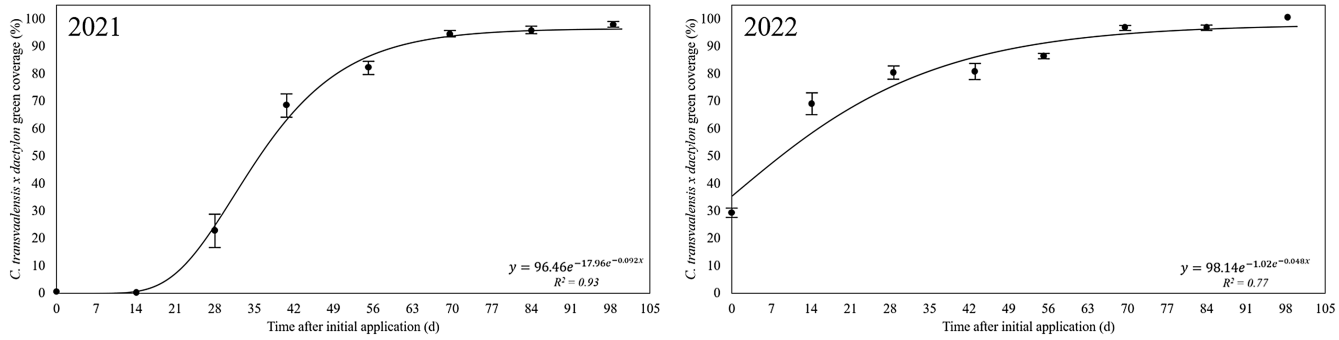

Figure 2. Influence of time, in days, on *Cynodon dactylon* ×*transvaalensis* green coverage in 2021 and 2022. Percent visible green coverage was modeled via a three-parameter Gompertz model using the equation $y = ae^{-be(-kT)}$: in which y equals the percent *C. dactylon* ×*transvaalensis* green coverage, a equals the asymptote, b equals the displacement along the x axis, k equals the rate of *C. dactylon* ×*transvaalensis* green coverage increase, and T equals time in days.

root tissue is highly sensitive to root-absorbed herbicides (Bingham 1967), and methiozolin is readily root absorbed by turfgrass species (Koo et al. 2014; Yu and McCullough 2014). It is plausible that methiozolin was rapidly removed from the system via root uptake and subsequent mowing of the turf with removal of clippings (Yu and McCullough 2014).

Methiozolin accumulation during the treatment period in 2022 was fit to a linear model due to the consistent stepwise accumulation of methiozolin following each application (Figure 1). Due to more frequent usage of putting green covers by golf course personnel during periods of subfreezing temperatures in 2022, *C. dactylon* ×*transvaalensis* percent green coverage was approximately 30% at the time of the initial application in 2022 (Figure 2). It is possible that the initial *C. dactylon* ×*transvaalensis* root regeneration had already occurred before the first treatment in 2022 based on these differences in green turf cover between years. Previous research has shown that *C. dactylon* × *transvaalensis* is more sensitive to methiozolin when treated just before post-dormancy green up compared with midtransition (Peppers and Askew 2023). New root production as *C. dactylon* × *transvaalensis* breaks dormancy may cause increased methiozolin absorption that would account for both the increased injury observed in previous studies and loss of methiozolin concentration in the current study.

Methiozolin dissipation trends following the final application were consistent between years and were pooled over years. Methiozolin D_{50} and D_{90} were 13.6 and 45.5 d, respectively (Table 2). Methiozolin rapidly dissipated in the first 4 wk following the final application, with approximately 80% of the initial methiozolin concentration dissipating within 28 d after the final application (Figure 3). These results predictably differ from dissipation rates observed by Hwang et al. (2013) in work characterizing the primary mechanism of degradation, where 80%

Table 2. Estimated time required, in days, for 50% and 90% dissipation of methiozolin following the final of three methiozolin applications at 500 g ai ha^{-1} (D_{50} and D_{90}, respectively) in *Cynodon dactylon* ×*transvaalensis* putting greens in Midlothian, VA, and a bare-ground and *Poa pratensis* turf-covered soil in Frenchtown, NJ

Soil cover	Location[a]	D_{50}[b]	D_{90}
		d	
Cynodon dactylon × *transvaalensis*	Virginia	14 —	46 —
Bare ground	New Jersey	13 a[c]	45 a
Poa pratensis	New Jersey	3.5 b	11 b

[a]The soil at the Virginia location met U.S. Golf Association putting green specifications with soil pH and organic matter ranging from 6.2 to 6.9 and 0.78% to 1.7%, respectively. The soil in the New Jersey trial location was a Penn silt loam (fine-loamy, mixed, superactive, mesic Ultic Hapludalfs) with 28%, 51%, and 21% sand, silt, and clay, respectively, with a pH of 6.7 and 2.7% soil organic matter.
[b]Methiozolin dissipation was modeled using the exponential decay equation: $C_t = C_0 * e^{(-k * t)}$, in which C_t is the percent methiozolin concentration at sampling time t; C_0 is the initial methiozolin concentration at t_0, which was always equal to 100%; k is the estimated rate constant of methiozolin dissipation; and t is time in days.
[c]Letters following means indicate significant difference between means within a given dissipation percent.

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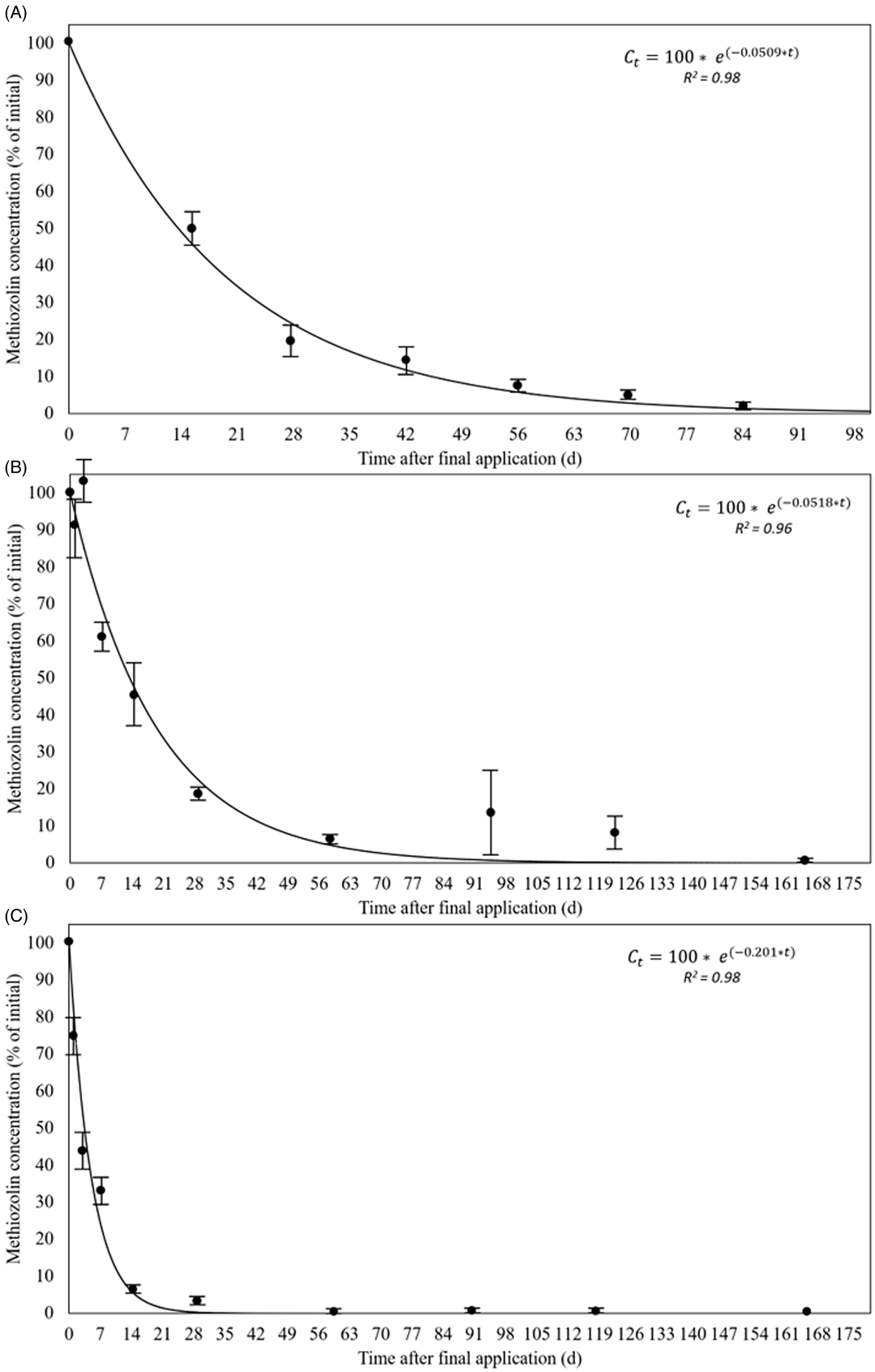

Figure 3. Influence of time, in days, on percent methiozolin dissipation following the third biweekly methiozolin application made to *Cynodon dactylon* ×*transvaalensis* putting greens in Midlothian, VA, in 2021 and 2022 (A), a bare-ground soil (B), and soil covered by *Poa pratensis* turf (C) in Frenchtown, NJ. All dissipation curves were modeled using the exponential decay equation $C_t = C_0 * e^{(-k*t)}$: where C_t is the percent methiozolin concentration at sampling time t; C_0 is the initial methiozolin concentration at t_0, which was always equal to 100%; k is the estimated rate constant of methiozolin dissipation; and t is time in days. The soil at location A met U.S. Golf Association putting green specifications with soil pH and organic matter ranging 6.2 to 6.9 and 0.78% to 1.7%, respectively; the soil at locations B and C was a Penn silt loam (fine-loamy, mixed, superactive, mesic Ultic Hapludalfs) with 28%, 51%, and 21% sand, silt, and clay, respectively, with a pH of 6.7 and 2.7% soil organic matter.

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Table 3. Average methiozolin concentration (in g ai ha^{-1}) extracted from *Cynodon dactylon* ×*transvaalensis* putting greens in Midlothian, VA, and bare-ground soil and *Poa pratensis* in Frenchtown, NJ, in samples collected immediately following biweekly methiozolin applications

Days after trial initiation	Methiozolin concentration				
	Cynodon dactylon × *transvaalensis*[a]		Bare ground[b]	*Poa pratensis*	
	2021	2022	Soil	Foliage	Soil
			g ai ha^{-1}		
0	509	482	1,039	650	387
14	818	633	1,317	958	389
28	491	910	1,715	678	478

[a]The targeted methiozolin application rate in *C. dactylon* ×*transvaalensis* was 500 g ai ha^{-1}.
[b]The targeted methiozolin application rate to bare soil and *P. pratensis* turf was 897 g ai ha^{-1}.

methiozolin dissipation required approximately 90 d. On greens of unreported turf species in Korea, 50% methiozolin dissipation similarly required approximately 10 d (Jo et al. 2016).

Although dissipation rates were similar between 2021 and 2022, the methiozolin concentration immediately following the third application was approximately 490 and 910 g ai ha^{-1} in 2021 and 2022, respectively (Table 3). This result can be attributed to the differential accumulation trends between the 2 yr. Based on the results of greenhouse rate response screens, methiozolin controls *P. annua* 90% when applied at approximately 45 g ai ha^{-1} preemergence (Koo et al. 2014). In 2021 and 2022, methiozolin dissipated to below this effective rate at 56 and 70 d after the final application, respectively (data not shown). These data suggest that methiozolin may offer appreciable preemergence *P. annua* control in *C. dactylon* ×*transvaalensis* putting greens. Additionally, this length of residual activity on *P. annua* may be prolonged if methiozolin is applied in the fall due to less microbial activity during the winter months. However, no peer-reviewed literature exists regarding methiozolin preemergence *P. annua* control in *Cynodon* spp. turf systems.

Dissipation of Field-applied Methiozolin as Affected by Turfgrass Coverage

Similar to results in Virginia putting greens, methiozolin was not detected below the 0- to 7.6-cm sampling depth (data not shown) in the New Jersey lawn turf or bare ground. In the turf-covered and bare-ground soil, methiozolin concentrations immediately following the initial application were 387 and 1,039 g ai ha^{-1}, respectively (Table 3). This variability in soil methiozolin concentration was due to 650 g ai ha^{-1} of methiozolin being retained by the foliage despite postapplication irrigation (Table 3). Averaged across all applications, 64% of applied methiozolin was retained by the foliage, while 36% was recovered in the soil. Methiozolin application placement studies indicate that methiozolin most efficiently controls *P. annua* when applied to soil only or to the foliage plus the soil (Brosnan et al. 2013; Flessner et al. 2013). This foliar retention of methiozolin may contribute to an apparent differential postemergence *P. annua* control as affected by mowing height. When comparing studies that were conducted at different mowing heights, methiozolin applied twice at 1.5 kg ai ha^{-1} controlled *P. annua* 85% in a perennial ryegrass (*Lolium perenne* L.) lawn managed at 3.81 cm in preliminary work by McNulty and Askew (2011). Conversely, just one-third of this methiozolin rate applied twice in a similar manner was needed to control *P. annua* approximately 80% on an *A. stolonifera* putting green maintained at 3.2 mm (Brosnan et al. 2013). Additionally, higher rates of methiozolin are required to effectively control *P. annua* at mowing heights greater than that typical of golf course putting greens according to the methiozolin product label (Anonymous 2021).

Methiozolin dissipation rate was significantly higher in *P. pratensis*–covered soil relative to bare-ground soil (Figure 3). In bare-ground soil, methiozolin D_{50} and D_{90} were 13.4 and 45.5 d, respectively (Table 3). Conversely, in *P. pratensis*–covered soil, methiozolin D_{50} and D_{90} were 3.5 and 11.4 d, respectively. These results are consistent with previously reported research regarding pesticide dissipation in turfgrass systems. In a direct comparison study, cyproconazole half-life was 12 d in *A. stolonifera* turf and 129 d in bare-ground soil (Gardner et al. 2000). Horst et al. (1996) observed shorter half-lives in turf of metalaxyl, pendimethalin, chlorpyrifos, and isazofos than typically reported in bare-ground systems. These differential dissipation rates were attributed to the thatch layer found in turfgrass systems, where pesticides are likely to be retained (Horst et al. 1996; Stahnke et al. 1991) and microbial activity is generally heightened (Gold et al. 1988). It is reasonable to attribute quicker methiozolin dissipation in turf-covered versus bare-ground soil to heightened microbial activity in the turf-covered soil. This is consistent with the findings of Hwang et al. (2013), wherein methiozolin was only degraded via aerobic microbial populations and not in anaerobic conditions. However, removal via turfgrass uptake, as has been demonstrated by others (Yu and McCullough 2014) may also have contributed to the rapid removal of methiozolin from the soil.

Methiozolin D_{50} and D_{90} were numerically similar between applications made to *C. dactylon* ×*transvaalensis* putting greens and the bare-ground study in New Jersey (Table 2). This may be attributed to differential application timings and temperatures following application. Final methiozolin applications were applied in late March for the study conducted in Virginia. In New Jersey, the final methiozolin application was administered on June 3. Average temperatures varied widely between the two locations due to the timing of applications. Average daily temperature for the first 14 d following the final application (the approximate D_{50} for each location) was 12 and 20 C in Virginia and New Jersey, respectively (Figure 4). Additionally, the average daily temperature for the first 45 d following the final application was 15 and 22 C in Virginia and New Jersey, respectively (Figure 4). Increases in temperature are known to speed herbicide dissipation in soil (Zimdahl and Gwynn 1977; Zimdahl et al. 1984). Furthermore, the bare-ground soil in New Jersey had a higher organic matter content than the putting green soil in Virginia. This higher organic matter content may have contributed to higher populations of methiozolin-degrading microbial organisms (Hwang et al. 2013; Kerek et al. 2002; Reedich et al. 2017; Shi et al. 2006). However, no statistical comparisons can be made between the dissipation rates in the two studies.

Results from these studies align with previously conducted research regarding the depth of methiozolin within the soil following application. Based on the results of the studies conducted on *C. dactylon* ×*transvaalensis* putting greens, we can conclude that methiozolin does not appreciably move below 2 cm below the thatch layer in golf course putting greens. This methiozolin placement in the soil is seemingly ideal for preemergence control of small-seeded grassy weeds; however, annual grassy weeds such as

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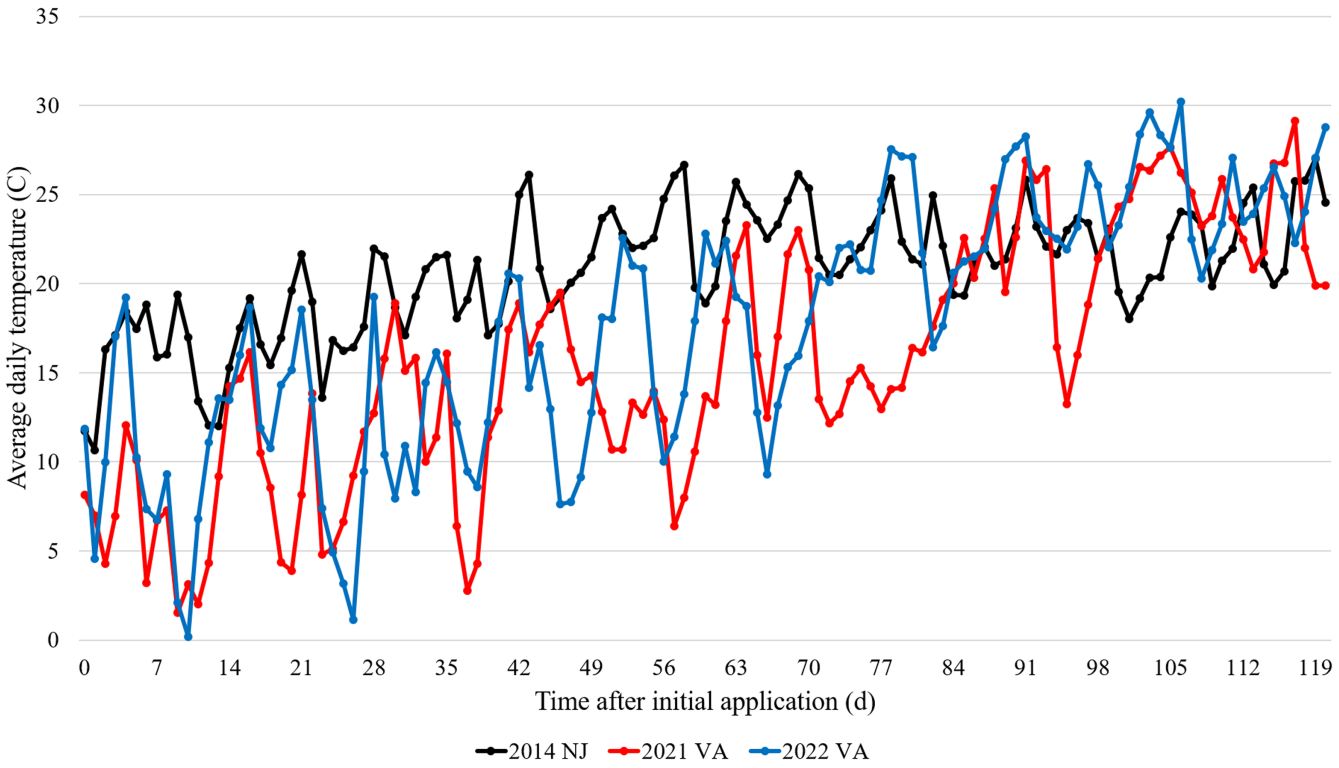

Figure 4. Average daily temperature at each study location as affected by time after study initiation. Studies were initiated on May 6, 2014, February 23, 2021, and March 3, 2022, for the New Jersey, Virginia 2021, and Virginia 2022 studies, respectively.

D. sanguinalis and *E. indica* can emerge from depths of up to 8 cm (Benvenuti et al. 2001; Chauhan and Johnson 2008; Hoyle et al. 2013). It is unclear how preemergence efficacy of methiozolin may be affected by seedling emergence depth. Based on the results from the study comparing methiozolin dissipation in turf versus bare-ground systems, we can conclude that methiozolin dissipates more rapidly in *P. pratensis* turf systems compared with bare-ground systems. Due to the rapid dissipation rate of methiozolin in turfgrass systems, future research should evaluate residual preemergence efficacy of methiozolin in turfgrass systems.

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