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Enhanced Atrazine Degradation: Evidence for Reduced Residual Weed Control and a Method for Identifying Adapted Soils and Predicting Herbicide Persistence

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Soilborne bacteria with novel metabolic abilities have been linked with enhanced atrazine degradation and complaints of reduced residual weed control in soils with an *s*-triazine use history. However, no field study has verified that enhanced degradation reduces atrazine's residual weed control. The objectives of this study were to (1) compare atrazine persistence and prickly sida density in *s*-triazine-adapted and nonadapted field sites at two planting dates; (2) utilize original and published data to construct a diagnostic test for identifying *s*-triazine-adapted soils; and (3) develop and validate an *s*-triazine persistence model based on data generated from the diagnostic test, i.e., mineralization of ring-labeled ^{14}C-*s*-triazine. Atrazine half-life values in *s*-triazine-adapted soil were at least 1.4-fold lower than nonadapted soil and 5-fold lower than historic estimates (60 d). At both planting dates atrazine reduced prickly sida density in the nonadapted soils ($P \leq 0.0091$). Conversely, in the *s*-triazine-adapted soil, prickly sida density was not different between no atrazine PRE and atrazine PRE at the March 15 planting date ($P = 0.1397$). A lack of significance in this contrast signifies that enhanced degradation can reduce atrazine's residual control of sensitive weed species. Analyses of published data indicate that cumulative mineralization in excess of 50% of C_0 after 30 d of incubation is diagnostic for enhanced *s*-triazine degradation. An *s*-triazine persistence model was developed and validated; model predictions for atrazine persistence under field conditions were within the 95% confidence intervals of observed values. Results indicate that enhanced atrazine degradation can decrease the herbicide's persistence and residual activity; however, coupling the diagnostic test with the persistence model could enable weed scientists to identify *s*-triazine-adapted soils, predict herbicide persistence under field conditions, and implement alternative weed control strategies in affected areas if warranted.

Nomenclature: Atrazine; prickly sida, *Sida spinosa* L.

Key words: Simazine, cross-adaptation, persistence model, half-life.

Atrazine is a soil- and (or) foliar-applied, *s*-triazine herbicide that provides residual control of sensitive weeds in corn (*Zea mays* L.), sorghum (*Sorghum bicolor* L.), sugarcane (*Saccharum officinarum* L.), and turf. Effective residual weed control with atrazine depends on its persistence in soil. Historic data indicate that the average atrazine half-life in soil under field conditions is approximately 60 d (Senseman 2007; Wauchope et al. 1992). Atrazine's moderate half-life in soil has been attributed to the halogen and *N*-alkyl substituents, which impede microbial degradation of the *s*-triazine ring (Wackett et al. 2002). However, in the mid-1990s, bacteria able to catabolize atrazine were isolated (Mandelbaum et al. 1995; Radosevich et al. 1995). The genes and enzymes responsible for atrazine catabolism by soil bacteria were subsequently identified and recently have been linked with enhanced *s*-triazine degradation in corn production systems (Figure 1; Krutz et al. 2008a,b).

Enhanced degradation is the phenomenon whereby a soil-applied pesticide is rapidly degraded by a population of microorganisms that have developed the ability to use the pesticide as an energy and/or nutrient source because of previous exposure to it or an analog. Enhanced atrazine degradation has been demonstrated in agricultural soils from around the globe (Barriuso and Houot 1996; Hang et al. 2003; Houot et al. 2000; Ostrofsky et al. 1997; Pussemier et al. 1997; Shaner and Henry 2007; Vanderheyden et al. 1997; Yassir et al. 1999; Zablotowicz et al. 2006). In the United States, observations from Colorado, Hawaii, Louisiana, Mississippi, Tennessee, and Texas indicate shorter residual activity with atrazine in soils with a prior use history (P. Baughman, personal communication; M. D. Poteet, personal communication; L. E. Steckell, personal communication; Shaner and Henry 2007; Viator et al. 2002). It has been postulated that reduced residual weed control with atrazine in these soils was due to enhanced degradation (L. E. Steckell, personal communication; Shaner and Henry 2007; Viator et al. 2002).

Previous research on *s*-triazine-adapted soils indicates that microbial adaptation can occur following one atrazine application (Zablotowicz et al. 2007), and that the phenomenon is likely widespread across the western and southern U.S. corn production regions (Krutz et al. 2008a). Reduced residual weed control with atrazine in *s*-triazine-adapted soils has been confirmed under greenhouse conditions (Krutz et al. 2007), and simazine cross-adaptation has been verified to reduce the herbicides residual weed control under field conditions (Krutz et al. 2008b). However, no study has demonstrated that enhanced degradation decreases atrazine's residual control of sensitive weed species under field conditions. Thus, the objectives of this study were to (1) determine the effects of planting date on atrazine persistence and the control of prickly sida in *s*-triazine-adapted and nonadapted soils; (2) identify a diagnostic tool for determining *s*-triazine-adapted soils; and (3) develop and validate a model for predicting *s*-triazine persistence in adapted soils.

Materials and Methods

Site History. The site history for the *s*-triazine-adapted soils utilized in this experiment was previously described (Krutz et al. 2008b; Zablotowicz et al. 2007). Briefly, the soil was a Dundee silt loam (fine-silty, mixed, active, thermic Typic Endoqualf) with pH 6.7, 1.1% organic matter, a CEC of

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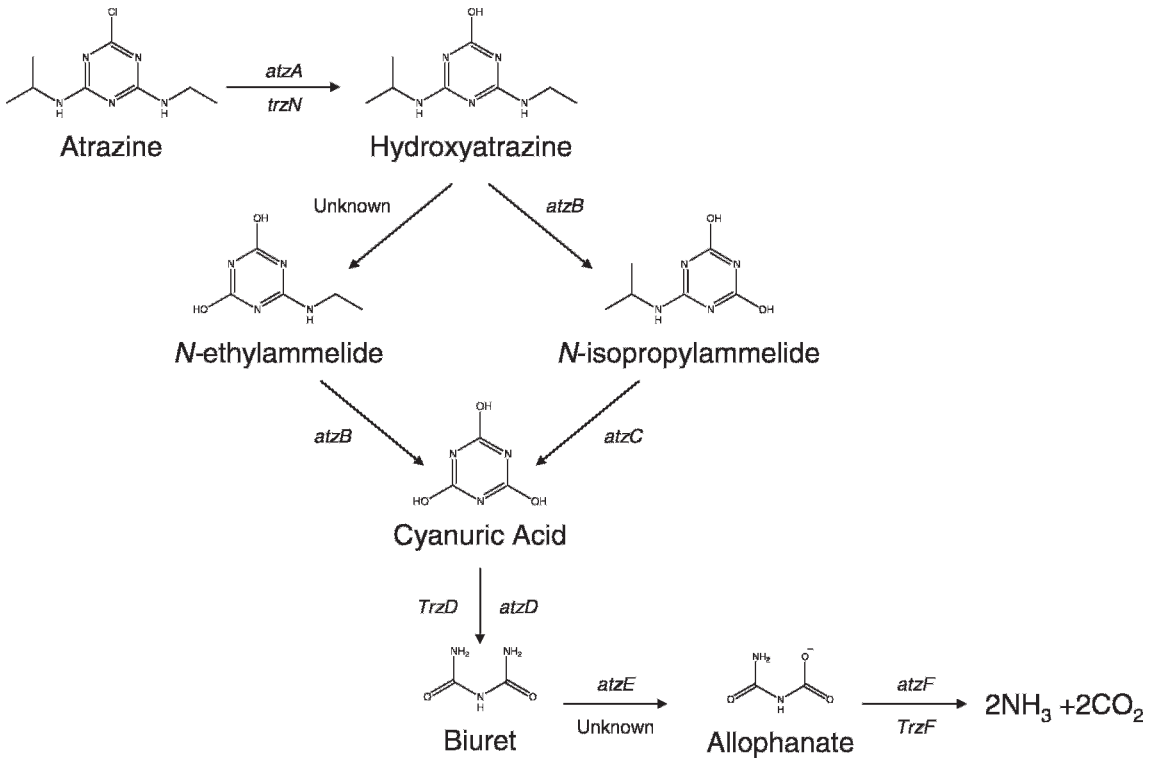

Figure 1. Proposed metabolic pathway responsible for the rapid dissipation of atrazine in *s*-triazine-adapted soils. Abbreviations denote genes coding for the following enzymes: *atzA*, atrazine chlorohydrolase; *trzN*, triazine hydrolase; *atzB*, hydroxyatrazine ethylaminohydrolase; *atzC*, *N*-isopropylammelide isopropylaminohydrolase; *TrzD*, cyanuric acid amidohydrolase; *atzD*, cyanuric acid hydrolase; *atzE*, biuret hydrolase; *atzF*, allophanate hydrolase; and *trzF*, allophanate hydrolase (Boundy-Mills et al. 1997; Cheng et al. 2005; de Souza et al. 1998; Fruchey et al. 2003; Martinez et al. 2001; Mulbry et al. 2002; Sadowsky et al. 1998; Seffernick et al. 2002; Shapir et al. 2002, 2005; Shapir et al. 2006; Smith et al. 2005; Topp 2001).

15 $cmol_c\ kg^{-1}$, and textural fractions of 26% sand, 55% silt, and 19% clay. The field was managed with reduced tillage, planted to corn, and treated with atrazine annually since 2000. The site has exhibited enhanced atrazine degradation since 2001 (Zablotowicz et al. 2007), and bacteria isolated from the adapted soils were positive for the *atzABC* and *trzN* genes (Figure 1; Krutz et al. 2008a). The soil at the nonadapted site utilized in this experiment also was classified as a Dundee silt loam and had similar chemical and physical properties of the *s*-triazine-adapted soil, i.e., pH, organic matter, CEC, and textural fraction. The nonadapted location had been in cotton (*Gossypium hirsutum* L.) or soybean (*Glycine max* L.) production and had no known atrazine exposure history for at least 20 yr.

Field Preparation. As described previously (Krutz et al. 2008b), planting dates were March 15 and April 17, 2006 for both the *s*-triazine-adapted and nonadapted field sites. Pre-emergence (PRE) treatments included (1) no PRE or (2) atrazine at 1,120 g ai ha^{-1}. Post-emergence (POST) treatments included (1) no POST or (2) glyphosate (N-(phosphonomethyl)glycine) applied at 840 g ae ha^{-1} to corn in the V3 to V4 stage corn. Corn, 'Garst 8347 RR', was planted in a conventionally-tilled seedbed at 10 seed m^{-1}, and tefluthrin (2,3,5,6-tetrafluoro-4-methylphenyl)methyl-(1α,3α)-(Z-(±)-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-cyclopropanecarboxylate) was applied in-furrow at 3,700 g ai ha^{-1} at planting. Plots were 6.1 m in length by four rows wide with rows spaced 102 cm apart. PRE and POST herbicides were applied with a CO_2 backpack sprayer calibrated to deliver 127 L ha^{-1} at 207 kPa through 11002 flat-fan nozzles.[1] Prickly sida was seeded at 10 seed m^{-2} prior to planting using a shoulder-mounted rotary spreader. Prickly sida seed were mixed with sand (1 : 1 v/v) to facilitate even distribution from the spreader.

Field Dissipation. The dissipation study was analyzed as a randomized complete block with treatments arranged as a split-plot with twelve replications of each treatment. The whole plot was soil (*s*-triazine-adapted or nonadapted), and the subplot was atrazine PRE application date (March 15 or April 17). From 0 to 42 d after atrazine application, composite soil samples were collected from three locations in each plot to a depth of 5.0 cm. At each location, two samples were collected from within the plant row and two samples were collected from within the furrow between the beds. Composite samples were thoroughly mixed, and a subsample (50 g) was removed for herbicide analysis. Soil samples were stored at −5 C until initiating extractions, typically with 3 d of collection.

Atrazine dissipation data were fitted to Equation 1:

$$C_t = C_0 e^{-kt} \quad [1]$$

where, C_0 is the herbicide concentration in soil in soil at time zero (mg kg^{-1}); k is the first-order rate constant (d^{-1}); and t is time (d). Atrazine half-life ($T_{1/2}$) values were calculated from Equation 2:

$$T_{1/2} = \ln 2/k \quad [2]$$

Herbicide Analysis. *Extraction and concentration*. Soil (50 g) was agitated with methanol + water (8 + 2 by volume,

100 ml) for 24 h and centrifuged for 10 min at 6,000 × g, and the supernatant was removed. The extract was concentrated by rotary evaporation, diluted in water (100 ml) and passed through a C_{18} solid-phase extraction column[2] preconditioned with methanol (4 ml) followed by distilled water (4 ml) under negative pressure. Atrazine was eluted with methanol (2 mL). Terbuthylazine was included as an internal standard.

Quantification. Atrazine was identified and quantified with a Waters 2695 HPLC separations module[3] equipped with a Waters 996 photodiode array detector.[4] The HPLC was fitted with a 2.1-mm diam by 150-mm length Waters symmetry C_{18} column.[5] The mobile phase consisted of acetonitrile + water (4 + 6 by volume), and the flow rate was constant (0.3 ml min^{-1}). Recovery of fortified samples, 1 mg atrazine kg^{-1} soil, was 98.0 ± 4%, and the instrument limit of detection was 0.11 μg ml^{-1} ($n = 8$).

Mineralization Assay. Mineralization of ^{14}C-ring-labeled atrazine was evaluated in biometer flasks as previously described (Krutz et al. 2008b). Briefly, adapted and nonadapted soils (25 g dry weight equivalent) collected from the 0- to 5-cm depth prior to the March 15 and April 17 PRE atrazine applications were fortified with a solution of technical grade atrazine[6] and ring-labeled ^{14}C-atrazine.[7] The initial herbicide concentration was 4 μg g^{-1} and the initial radioactivity was 190 Bq g^{-1}. Biometers were incubated in the dark at 25 C and a gravimetric moisture content of 30%. Cumulative mineralization of ^{14}C-carbon dioxide was fitted to the Gompertz growth equation (Equation 3):

$$y = a \cdot \exp(-\exp(-(t - t_0)/k)) \quad [3]$$

where a is the plateau representing the maximum mineralization (%); t_0, is the abscissa of the inflection point representing the lag phase (d); k is the inverse of the Gompertz mineralization rate constant (d); and t is time (d).

Model Development and Validation. The atrazine persistence model was developed with the March 15 laboratory and field data. A linear model (Equation 4) was used to describe the relationship between the rate constants derived from Equation 3 and the rate constants derived from Equation 1:

$$k_1 = m \cdot k_g + b \quad [4]$$

where k_1 is the predicted first-order rate constant (d^{-1}) derived from Equation 1; m is the slope, 0.19; k_g is the Gompertz mineralization rate constants derived from Equation 3 (d^{-1}), and b is the y intercept, 0.03.

Equation 5 was adapted to account for temperature effects in the field:

$$k_{1(T)} = \left(0.19k_g + 0.03\right)\left[Q_{10}\left(T - T_{ref}\right)/10\right] \quad [5]$$

where $k_{1\,(T)}$ is the first-order rate constant that accounts for the average soil temperature (C) in the 0- to 10-cm depth; Q_{10} is the factor by which degradation increases when temperature, T, increases by 10 C, 2.0; T_{ref} is the average soil T (C) under field conditions for the reference soil in the 0- to 10-cm depth, 14.4 C. A constant was added to Equation 5 to predict simazine's first-order rate constant under field conditions

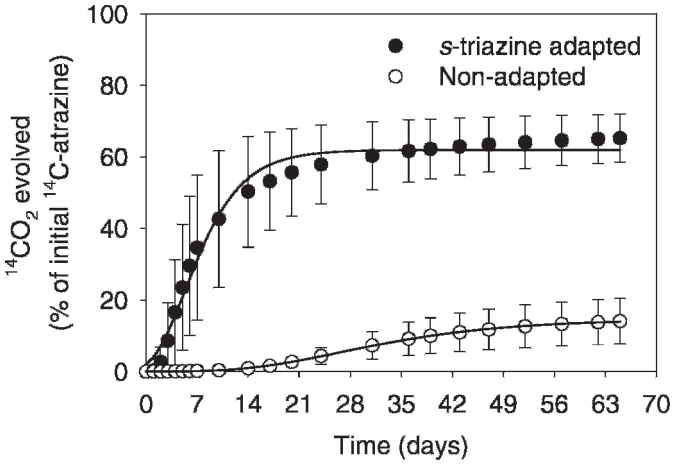

Figure 2. Cumulative ^{14}C-CO_2 evolution from ring-labeled ^{14}C-atrazine applied to *s*-triazine-adapted and nonadapted soils collected prior to the April 17 planting date. Symbols represent the mean of 12 replicates. Error bars indicate one standard deviation and do not appear when smaller than the symbol for the mean. Fitted values, indicated by the smooth line, are the best fit of the modified Gompertz growth model $y = a \cdot \exp(-\exp(-(t-t_0)/k))$ where a is the plateau representing the maximum mineralization (%); t_0, is the abscissa of the inflection point representing the lag phase (d); k is the inverse of the Gompertz mineralization rate constant (d); and t is time (d).

(Equation 6):

$$k_{1(T)} = \left(0.19k_g + 0.03\right)\left(Q_{10}\left(\left(T - T_{ref}\right)/10\right)\right)/b \quad [6]$$

where $b = 1.28$.

Equation 5 was validated for atrazine with independent data by comparing predicted values with the 95% confidence intervals from the observed first-order rate constants from the April 17 planting date. Equation 6 was validated for simazine by comparing predicted values with the 95% confidence intervals from previously reported first-order rate constants (Krutz et al. 2008b).

Evaluating Residual Herbicide Activity. To evaluate residual activity of atrazine, the field study was analyzed as a randomized complete block with a factorial arrangement of treatments. The factorial treatment arrangement consisted of planting date by PRE by POST treatment options. Prickly sida density was evaluated 15, 30, 45, and 60 d after planting (DAP) from a single 1 m^2 plot randomly chosen from between the center two rows of each plot. Prickly sida emerges, develops symptoms, and then dies in response to atrazine before producing a true leaf; therefore, only weeds with one or more true leaf were counted as these were considered to have survived the herbicide treatment. All four rows of each plot were harvested using a combine modified for small plot research. Corn grain yield was adjusted to 15% moisture. Corn yields were higher in the April 17 plating date compared to the March 15 planting date; consequently, corn grain yields were standardized using the average yield of the weed-free treatment (atrazine PRE followed by [fb] glyphosate POST).

Statistics. Data variance was inspected visually by plotting residuals to confirm homogeneity of variance prior to statistical analysis. All analysis was conducted with SAS software. Data were subjected to analysis of variance in SAS[8] using a mixed model approach with replication considered as

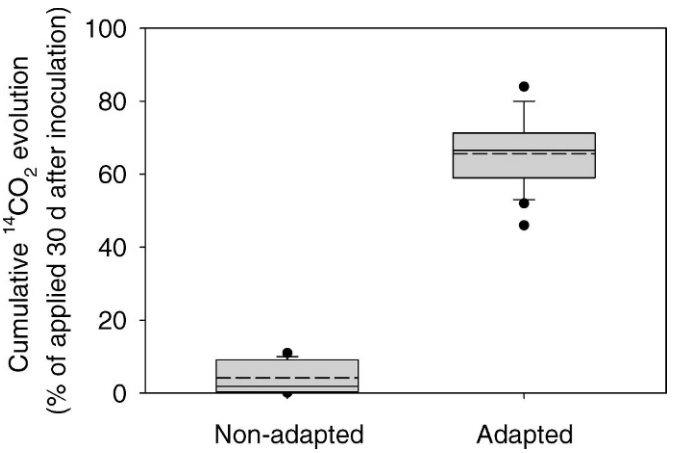

Figure 3. Box plots for cumulative $^{14}CO_2$ evolution of ^{14}C-ring-labeled atrazine 30 d after inoculation in *s*-triazine-adapted and nonadapted soil. Boundary of box closest to zero indicates the 25th percentile, a solid line within the box marks the median, a dashed line within the box delineates the mean, and the boundary of the box farthest from zero indicates the 75th percentile. Error bars above and below the box indicate the 95th and 5th percentile, and solid dots indicate outliers. The number of independent observations is 22 for nonadapted soils and 54 for *s*-triazine-adapted soils (Abdelhafid et al. 2000; Hang et al. 2003, 2005, 2007a,b; Hayar et al. 1997; Krutz et al. 2006, 2008a; Langenbach et al. 2000; Mersie et al. 1999; Mordaunt et al. 2005; Yassir et al. 1999; Zablotowicz et al. 2006).

a random effect, and single degree of freedom contrasts were developed to evaluate prickly sida density between treatments. Mineralization data were fitted to the Gompertz model using SAS NLIN,[8] and 95% confidence intervals were calculated for a, t_0, and k.

Results

Mineralization Assay. Analysis of variance conducted on the cumulative mineralization data from soils collected prior to the April 17 planting date indicated that the soil by time interaction was significant ($P = 0.0001$). From 4 d after study inception until termination, atrazine mineralization was at least 4.6-fold higher in *s*-triazine-adapted than nonadapted soils (Figure 2). It is important to note that cumulative mineralization of ring-labeled ^{14}C atrazine in the *s*-triazine-adapted soils exceeded 50% of C_0 after 30 d of incubation, which is indicative of *s*-triazine-adapted soils (Figure 3). Conversely, mineralization of ring-labeled ^{14}C atrazine in the nonadapted soils did not exceed 20% of C_0 after 30 d of incubation, which is typical for nonadapted soils. Nonlinear regression analysis indicated that the lag phase was 5-fold shorter and the mineralization rate constant 2.9-fold higher in the *s*-triazine-adapted soils compared to nonadapted soil (Table 1), which was similar to the mineralization kinetics of ring labeled ^{14}C-simazine in *s*-triazine-adapted and nonadapted soils (Krutz et al. 2008b).

Field Persistence. For atrazine persistence under field conditions, the soil by time interaction was significant ($P = 0.0002$). Within both *s*-triazine-adapted and nonadapted soils, atrazine half-life values were at least 2.3-fold lower at the April 17 than the March 15 planting date (Figure 4; Table 2). A similar trend was noted in a companion study where simazine half-life values pooled over *s*-triazine-adapted and nonadapted soils were 2.4-fold lower at the April 17 planting date compared to the March 15 planting date (Krutz et al. 2008b). Decreased *s*-triazine persistence at the later planting date was attributed to a temperature effect. For example, average soil temperatures for the 0- to 10-cm depth for the March 15 and April 17 planting dates were 14.4 and 24.2 C, respectively. A 1.8- to 2.8-fold decrease in half-life values between planting dates is in agreement with projected Q_{10} effects on *s*-triazine persistence (Krutz et al. 2008a). Additionally, atrazine half-life values were at least 1.4-fold lower in *s*-triazine-adapted than nonadapted soils, regardless of planting date. This observation is consistent with earlier reports from Mississippi and Colorado where atrazine and/or simazine persistence were at least 1.4-fold lower in *s*-triazine-adapted soils relative to nonadapted soils (Krutz et al. 2007, 2008b; Shaner and Henry 2007). In this experiment, reduced atrazine persistence in the *s*-triazine-adapted soil was expected in that the soil had been treated with atrazine since 2000; it began exhibiting enhanced atrazine degradation in 2001, and contained bacterial isolates positive for the atz*ABC* and trz*N* genes (Krutz et al. 2007, 2008a; Zablotowicz et al. 2007).

Model Development and Validation. The mineralization rate constants from the March 15 planting date were positively correlated with the March 15 first-order rate constants, which were fitted with Equation 4 (Figure 5). In an attempt to predict atrazine field persistence at the April 17 planting date using companion laboratory mineralization data, Equation 4 was adjusted to account for Q_{10} effects, i.e., Equation 5. Using the April 17 mineralization data and the appropriate Q_{10} adjustment, the predicted first-order rate constants generated with Equation 5 were within the 95% confidence intervals of the observed values, regardless of *s*-triazine use history (Figure 6). Equation 5 was then applied to previously published simazine data (Krutz et al. 2008b), but the model overpredicted the observed first-order rate constants. A constant was applied to Equation 5 that accounted for the model's inability to predict simazine persistence under field conditions, i.e., Equation 6. The predicted first-order rate constants for simazine generated from Equation 6 were within the 95% confidence intervals of the observed values, regardless of planting date or *s*-triazine use history (Figure 6).

Residual Atrazine Activity in *s*-Triazine-Adapted and Nonadapted Soils. A differential effect of atrazine on prickly sida density was observed between *s*-triazine-adapted and

Table 1. Gompertz growth model estimates for atrazine in *s*-triazine-adapted and nonadapted soils for the April 17 planting date at Stoneville, MS in 2006.

Soil	a (Maximum evolved)	k (Reciprocal of the rate constant)	t_0 (Lag-phase)	r^2
	%	d		
Adapted	61.94 (60.45–63.42)[a]	4.36 (3.71–5.02)	5.38 (4.97–5.79)	0.99
Nonadapted	14.66 (10.04–19.28)	12.78 (2.29–23.26)	26.68 (19.14–34.22)	0.99

[a] Numbers in parentheses indicate 95% confidence intervals as estimated by SAS NLIN.

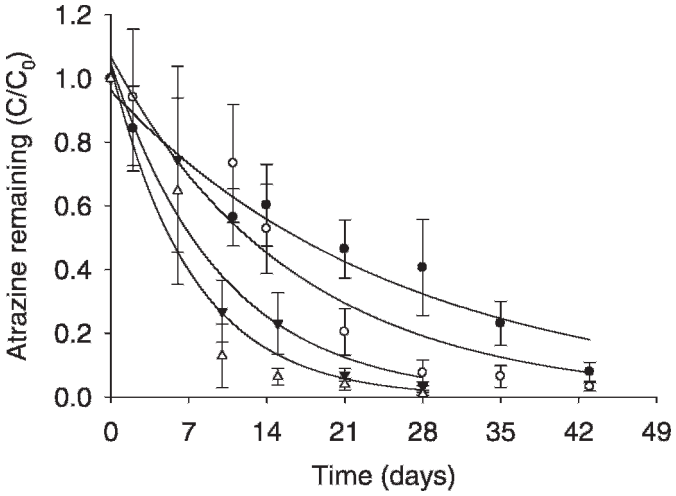

Figure 4. Atrazine dissipation kinetics in *s*-triazine-adapted and nonadapted soils at the March 15 and April 17 planting dates. Symbols represent the mean of twelve replicates for each of the following treatments: nonadapted March 15 (closed circles), *s*-triazine-adapted March 15 (open circles), nonadapted April 17 (closed inverted triangles), *s*-triazine-adapted April 17 (open triangles). Error bars indicate one standard deviation and do not appear when smaller than the symbol for the mean. Smooth lines represent the best fit of the first-order kinetics mode $C_t = C_0 e^{-kt}$ where C_0 is the herbicide concentration in soil at time zero (mg kg^{-1}); k is the first-order rate constant (d^{-1}); and t is time (d).

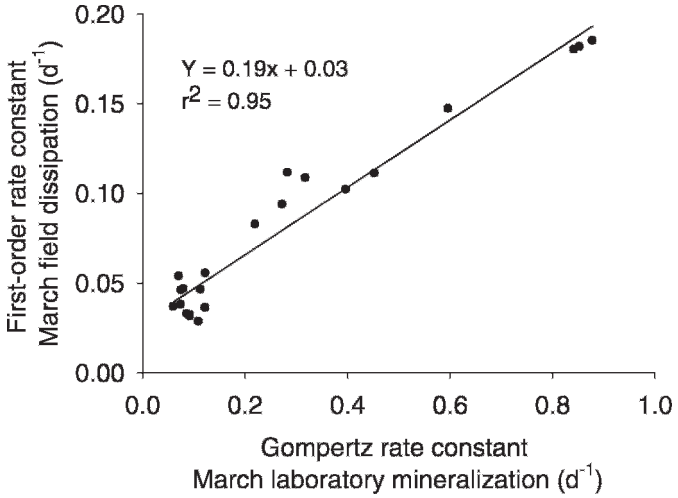

Figure 5. Relationship between the March 15 first-order dissipation rate constants and Gompertz mineralization rate constant. Symbols represent independent replicates from *s*-triazine-adapted and nonadapted soils.

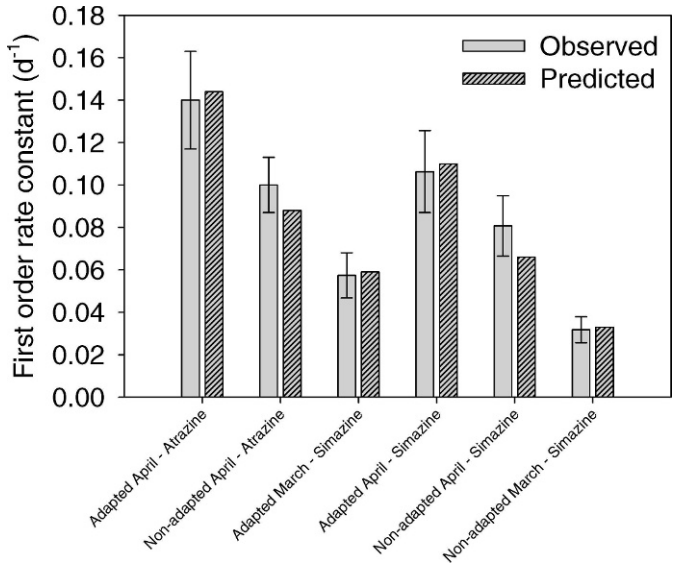

Figure 6. Measured vs. predicted first-order rate constants for atrazine and simazine based on the proposed empirical persistence models.

nonadapted soils at the March 15 planting date. Prickly sida density in the nonadapted soils was 4.8-fold lower in atrazine PRE compared with no atrazine PRE ($P = 0.0012$; Table 3). Reduced prickly sida density in the atrazine PRE treatment was expected, because the weed typically is controlled by the herbicide (Parker et al. 2006; Tharp and Kells 1999). Conversely, the contrast between no atrazine PRE and atrazine PRE was not significant in the *s*-triazine-adapted soils ($P = 0.1397$). A lack of significance in this contrast indicates that atrazine had no herbicidal effect on prickly sida density in the *s*-triazine-adapted soils. These trends were not evident at the April 17 planting date when the contrast of no atrazine PRE vs. atrazine PRE was significant at the $P \leq 0.0091$ level, regardless of *s*-triazine use history. Prickly sida control with atrazine in the *s*-triazine-adapted soils at the April 17 planting date was likely obtained because the later application date synchronized with prickly sida emergence and herbicide concentrations above the phytotoxic threshold. In a companion study, simazine PRE at the March 15 and April 17 planting dates reduced prickly sida density at least 5.4-fold compared with the no simazine PRE treatment (Krutz et al. 2008b). In the *s*-triazine-adapted soils, prickly sida densities were not statistically different between simazine PRE and no simazine PRE, regardless of planting date. The authors concluded that there is potential for cross-adaptation among *s*-triazine herbicides resulting in reduced residual weed control. Combined, these studies demonstrate that enhanced degradation can decrease atrazine's residual control of prickly sida. Yet, under the conditions of this experiment, the economic significance of enhanced atrazine degradation was minimal, because there was no observed corn grain yield loss in *s*-triazine-adapted soils, regardless of planting date (Table 4).

Table 2. Degradation rate constants (k) and half-life values for atrazine in *s*-triazine-adapted and nonadapted soils at the March 15 and April 17 planting dates at Stoneville, MS in 2006.

Planting date	Soil	k	$T_{1/2}$	r^2
		d^{-1}	d	
March 15	*s*-Triazine-adapted	0.06 (0.054–0.069)[a]	11.6 (10.1–12.8)	0.94
	Nonadapted	0.04 (0.034–0.044)	17.3 (15.8–20.4)	0.96
April 15	*s*-Triazine-adapted	0.14 (0.117–0.157)	5.0 (4.4–5.9)	0.93
	Nonadapted	0.10 (0.087–0.115)	6.9 (6.0–7.9)	0.94

[a] Values in parenthesis indicate 95% confidence intervals as estimated by SAS NLIN.

Table 3. Interaction of planting date, soil, and herbicide treatment on prickly sida density in a corn study conducted at Stoneville, MS in 2006.

Planting date	Soil[a]	Atrazine[b] PRE	Glyphosate[c] POST	Prickly sida density
				plants m^{-2} (SE)
March 15	*s*-triazine-adapted	−	−	3.5 (0.8)
		−	+	1.0 (0.5)
		+	−	6.0 (2.7)
		+	+	0.3 (0.2)
	Nonadapted	−	−	5.7 (1.0)
		−	+	0.2 (0.2)
		+	−	1.2 (0.6)
		+	+	1.3 (0.3)
April 17	*s*-triazine-adapted	−	−	6.7 (2.2)
		−	+	4.0 (1.7)
		+	−	1.0 (0.6)
		+	+	0.8 (0.4)
	Nonadapted	−	−	3.7 (0.7)
		−	+	3.2 (2.0)
		+	−	0.0 (0.0)
		+	+	0.5 (0.5)

[a] The *s*-triazine-adapted soil had been treated with atrazine since 2000, has exhibited enhanced atrazine degradation since 2001, and was positive for the *atzABC* and *trzN* genes. The nonadapted soil has no known atrazine exposure history for at least 20 yr.
[b] Atrazine pre-emergence (PRE) included no PRE (−) or atrazine at 1,120 g ai ha^{-1} (+).
[c] Glyphosate postemergence (POST) included no POST (−) or glyphosate at 840 g ae ha^{-1} (+).

Discussion

Prior to the discovery of bacteria able to catabolize *s*-triazine herbicides (Mandelbaum et al. 1995; Radosevich et al. 1995), the weed science community widely accepted that the average atrazine half-life in soil was approximately 60 d. This assertion is founded on atrazine persistence estimates published in the Herbicide Handbook (Senseman 2007), Wauchope's review of the literature (Wauchope et al. 1992), and U.S. Environmental Protection Agency documents (US EPA 2006). An examination of atrazine persistence data published prior to 1995 indicates that an average atrazine half-life of 60 d in soil was justified (Figure 7). Yet, the data contained herein coupled with other reports imply that atrazine persistence under field and laboratory conditions is lower in *s*-triazine-adapted compared to nonadapted soils (Figure 7). For example, a laboratory study revealed that atrazine persistence in Colorado and Mississippi adapted soils was 13-fold lower than nonadapted soil, 10-fold lower than Wauchope's estimate, and 18-fold lower than U.S. EPA's estimate (Krutz et al. 2008a). Previous publications from Colorado and Mississippi indicate a similar trend for atrazine and simazine persistence in *s*-triazine-adapted soils under field conditions (Krutz et al. 2007, 2008b; Shaner et al. 2007).

From an agronomic perspective, the prickly sida data coupled with the report of simazine cross-adaptation demonstrate that reduced herbicide persistence in *s*-triazine-adapted soils can result in decreased residual weed control (Krutz et al. 2008b). Based on atrazine mineralization kinetics, laboratory dissipation experiments, and probing for atz*ABC* and trz*N* genes, it also is likely that soils exhibiting enhanced *s*-triazine degradation are widespread across the western and southern U.S. corn production regions (Krutz et al. 2008a). Thus, it is possible that complaints of poor residual weed control with atrazine in *s*-triazine history soils in Colorado, Hawaii, Louisiana, Mississippi, Tennessee, and

Table 4. Interaction of planting date, soil, and herbicide treatment on corn yield and corn yield expressed as a percent of the weed-free treatment in Stoneville, MS in 2006.

Planting date	Soil[a]	Atrazine[b] PRE	Glyphosate[c] POST	Yield (SE)	Yield (SE)
				kg ha^{-1}	% weed-free
March 15	*s*-Triazine-adapted	−	−	10,350 (260)	105 (3)
		−	+	10,190 (240)	103 (2)
		+	−	9,960 (310)	101 (3)
		+	+	10,020 (110)	101 (1)
	Nonadapted	−	−	9,180 (380)	103 (4)
		−	+	8,880 (210)	99 (2)
		+	−	9,080 (340)	102 (4)
		+	+	8,950 (180)	100 (2)
April 17	*s*-Triazine-adapted	−	−	9,320 (230)	99 (2)
		−	+	9,690 (100)	103 (1)
		+	−	9,660 (170)	102 (2)
		+	+	9,640 (130)	102 (1)
	Nonadapted	−	−	11,530 (140)	99 (1)
		−	+	11,340 (150)	98 (1)
		+	−	11,690 (240)	101 (2)
		+	+	11,840 (280)	102 (2)

[a] The *s*-triazine-adapted soil had been treated with atrazine since 2000, has exhibited enhanced atrazine degradation since 2001, and was positive for the *atzABC* and *trzN* genes. The nonadapted soil has no known atrazine exposure history for at least 20 yr.
[b] Atrazine pre-emergence (PRE) included no PRE (−) or atrazine at 1,120 g ai ha^{-1} (+).
[c] Glyphosate postemergence (POST) included no POST (−) or glyphosate at 840 g ae ha^{-1} (+).

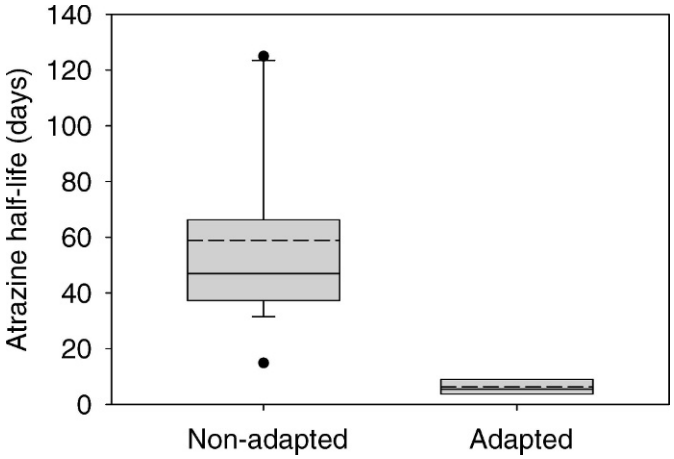

Figure 7. Box plot of reported atrazine half-life values generated under field conditions for *s*-triazine-adapted and nonadapted soils. Boundary of box closest to zero indicates the 25th percentile, a solid line within the box marks the median, a dashed line within the box delineates the mean, and the boundary of the box farthest from zero indicates the 75th percentile. Error bars above and below the box indicate the 95th and 5th percentile, and solid dots indicate outliers. The number of observations was 20 for nonadapted and seven for adapted soils (Bacci et al. 1989; Frank et al. 1991; Gish et al. 1991, 1994; Khan et al. 1981; Krutz et al. 2007; Ng et al. 1995; Shaner and Henry 2007; Sorenson et al. 1994; Winkelmann and Klaine 1991; Workman et al. 1995).

Texas are due to enhanced degradation and not *s*-triazine resistant weed biotypes, improper application techniques, or lack of activation. This signifies that a diagnostic laboratory method that allows one to identify *s*-triazine-adapted soils would be beneficial.

Mineralization of ring-labeled ^{14}C-atrazine might be used as a diagnostic test for identifying *s*-triazine-adapted soils and predicting herbicides persistence under field conditions. Prior to bacteria developing the metabolic pathway depicted in Figure 1, cumulative mineralization of ring-labeled ^{14}C-atrazine after 30 d of incubation under optimal temperature and moisture levels did not exceeded 20% of C_0 (Figure 3). In contrast, cumulative mineralization of ring-labeled ^{14}C-atrazine after 30 d of incubation in *s*-triazine-adapted soils typically exceeds 50% of C_0 when incubated at optimal temperature and moisture levels (Figure 3). It is important to note that the analysis contained in Figure 3 encompasses 52 independent observations from North America, South America, and Europe. These data demonstrate that cumulative mineralization of ring-labeled ^{14}C-atrazine in excess of 50% of C_0 after 30 d of incubation under optimal temperature and moisture levels is indicative of enhanced *s*-triazine degradation and should be considered as diagnostic for adapted soils. Moreover, Equation 5 and Equation 6 reveal the potential to predict atrazine and simazine persistence under field conditions, respectively, using mineralization data generated from the proposed diagnostic test. Coupling the diagnostic test with the persistence model(s) will aid in identifying *s*-triazine-adapted soils, predicting herbicide persistence under field conditions, and implementing alternative weed control programs in affected hectarage as warranted.

Sources of Materials

[1] Teejet 11002 flat fan nozzles, Spraying Systems Co., North Ave., Wheaton, IL.

[2] C_{18} solid phase extraction column, Bakerbond, J. T. Baker, Phillipsburg, NJ.

[3] Waters 2695 HPLC separations module, Waters Inc., Milford, MA.

[4] Waters 996 photodiode array detector, Waters Inc., Milford, MA.

[5] 2.1-mm diam by 150-mm length Waters symmetry C_{18} column, Waters, Inc., Milford, MA.

[6] Technical grade atrazine, 99% purity, Chemservice, Lancaster PA.

[7] Ring-labeled ^{14}C-atrazine, 115 μCi mmol^{-1} specific activity, 94% radiological purity, Sigma Chemical Co., St. Louis, MO.

[8] SAS Institute, Inc., Cary, NC.

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