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Field Dissipation of Atrazine and Metribuzin in Organic Soils in Florida

Dennis C. Odero and Dale L. Shaner*

Sugarcane growers have observed reduced residual activity of atrazine on organic soils in the Everglades Agricultural Area (EAA) of south Florida. Field studies were conducted between 2011 and 2012 to determine the rate of dissipation of atrazine at 2.24, 4.48, and 8.96 kg ha^{-1} and metribuzin at 0.56, 1.12, and 2.24 kg ha^{-1} in the top 10 cm of soil in sugarcane fields in the EAA. The bioavailable fraction of atrazine dissipated more rapidly than the total amount of atrazine in the soil. Half-lives of the total and bioavailable fraction of atrazine ranged between 3.9 to 12.1 d and 1.0 to 7.5 d, respectively. Metribuzin dissipated much more slowly than atrazine on organic soils. Similarly, dissipation of the bioavailable fraction of metribuzin was more rapid than was the dissipation of the total amount of metribuzin in the soil. Half-lives of the total and bioavailable fraction of metribuzin ranged between 16.2 and 24.8 d and 6.0 and 14.3 d, respectively. These results indicate that enhanced atrazine degradation occurs on organic soils under field conditions in the EAA, resulting in shorter residual atrazine activity. This implies that metribuzin is a better option for weed control in sugarcane grown on organic soils of the EAA exhibiting enhanced atrazine degradation.
Nomenclature: Atrazine; metribuzin; sugarcane, *Saccharum* spp. hybrids.
Key words: Dissipation, enhanced degradation, organic soil.

Productores de caña de azúcar han observado una actividad residual reducida de atrazine en suelos orgánicos en el Área Agrícola Everglades (EAA) en el sur de Florida. Se realizaron estudios de campo entre 2011 y 2012 para determinar la tasa de disipación de atrazine a 2.24, 4.48, y 8.96 kg ha^{-1} y metribuzin a 0.56, 1.12, y 2.24 kg ha^{-1} en los 10 cm superiores de suelo en campos de caña de azúcar en el EAA. La fracción biodisponible de atrazine se disipó más rápidamente que el total de atrazine en el suelo. La vida media de las fracciones total y biodisponible de atrazine variaron entre 3.9 y 12.1 d y 1.0 y 7.5 d, respectivamente. Metribuzin se disipó mucho más lentamente que atrazine en suelos orgánicos. Similarmente, la disipación de la fracción biodisponible de metribuzin fue más rápida que lo que fue la disipación de la cantidad total de metribuzin en el suelo. La vida media de las fracciones total y biodisponible de metribuzin varió entre 16.2 y 24.8 d y 6.0 y 14.3 d, respectivamente. Estos resultados indican que la degradación acelerada de atrazine ocurre en suelos orgánicos bajo condiciones de campo en el EAA, lo que resulta en una actividad residual de atrazine más corta. Esto implica que metribuzin es una mejor opción para el control de malezas en caña de azúcar sembrada en suelos orgánicos del EAA que exhiben degradación acelerada de atrazine.

Triazine herbicides have an important role in weed management in sugarcane cultivated on approximately 134,000 ha of organic soils in the Everglades Agricultural Area (EAA) of south Florida. Atrazine, the most widely used *s*-triazine herbicide on sugarcane in the EAA is applied PRE or early POST for controlling many broadleaf weeds and certain grasses. In the United States, atrazine is used on > 70% of the sugarcane acreage because it offers consistent performance, low cost, residual weed control, flexibility in time and method of application, compatibility with other herbicides, and crop safety (Smith et al. 2008). The asymmetrical triazine herbicide, metribuzin applied PRE or early POST for controlling annual and broadleaf weeds is also used on sugarcane in the EAA. Metribuzin is used on 19% of sugarcane acreage in the United States (Smith et al. 2008). Sugarcane growers on organic soils of the EAA expect residual weed control following application of these triazine herbicides. Efficacious residual weed control by these triazine herbicides depends on their persistence in soil. Both herbicides have half-lives of up to 60 d under field conditions and relatively low adsorption on most soils (Senseman 2007; Wauchope et al. 1992). However, Florida sugarcane growers have observed reduced residual activity of atrazine on organic soils of the EAA.

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Table 1. Triazine use history of soils used in the studies.[a]

Location	Year	Crop	Triazine use metribuzin (kg ha^{-1}), ametryn (kg ha^{-1})
Main Farm	2010	Fallow period	None
	2009	Sugarcane	1.12, 0.22
	2008	Sugarcane	1.12, 0.67
	2007	Sugarcane	1.12, 0.45
Hillsboro Farm	2010	Sugarcane	1.12, 0.45
	2009	Sugarcane	1.12, 0.22
	2008	Sugarcane	1.12, 0.67
	2007	Sugarcane	1.12, 0.45

[a] Main and Hillsboro farms had continuous atrazine use (4.48 kg ai ha^{-1} atrazine) before 2007 for at least two decades in the sugarcane crop.

Atrazine's persistence in soil had been attributed to the halogen, methylthioether, and *N*-alkyl substituents on the *s*-triazine ring, which impeded microbial degradation (Wackett et al. 2002). However, adaptation of bacterial communities able to use atrazine as a C and N source has occurred in soils with repeated atrazine use thereby enabling enhanced degradation (Krutz et al. 2010). *Pseudomonas* sp. strain ADP (Mandelbaum et al. 1995) and *Nocardioides* sp. strain C190 (Topp et al. 2000) able to metabolize and rapidly degrade atrazine have been isolated. The enzymes atrazine chlorohydrolase (AtzA) and triazine hydrolase (TrzN) in *Pseudomonas* sp. strain ADP and *Nocardioides* sp. strain C190, respectively, contribute to microbial hydrolysis of atrazine to the hydroxylated derivative, hydroxyatrazine, the first intermediate in the metabolism of atrazine (de Souza et al. 1996; Topp et al. 2000). Enhanced atrazine degradation has been reported in Colorado, Mississippi, Ohio, and Tennessee on soils with previous atrazine use history (Krutz et al. 2007; Mueller et al. 2010; Ostrofsky et al. 1997; Shaner and Henry 2007; Zablotowicz et al. 2006). Similarly, enhanced atrazine degradation has been reported in Australia, Canada, Europe, and South America in fields with a history of repeated atrazine use (Abdelhafid et al. 2000; Barriuso and Houot 1996; Hang et al. 2003; Houot et al. 2000; Popov et al. 2005; Pussemier et al. 1997; Vanderheyden et al.1997; Yassir et al. 1999).

In the United States, enhanced atrazine degradation has been reported across the full range of sugarcane production areas using laboratory incubation–dissipation studies (Shaner et al. 2010). Atrazine-adapted sugarcane production soils were cross-adapted with ametryn, a similar chloro-*s*-triazine, but not cross-adapted with metribuzin (Shaner et al. 2010), even though the enzyme TrzN has been reported to metabolize *s*-triazines and some asymmetrical compounds (Shapir et al. 2005; Strong et al. 2002). Similarly, Barriuso and Houot (1996) reported atrazine cross-adaptation with simazine, a chloro-*s*-triazine, but not with terbutryn, a thiomethyl-*s*-triazine. Metribuzin dissipates in soil primarily by microbial degradation (Savage 1977; Sharom and Stephenson 1976; Maqueda et al. 2009; Moorman and Harper 1989). Several bacteria and fungi capable of degrading metribuzin have been isolated (Engelhardt and Wallnöfer 1978; Engelhardt et al. 1982; Schilling et al. 1985). The lack of cross-adaptation of atrazine and metribuzin shows that metribuzin could be a viable alternative for use in sugarcane soils with enhanced atrazine degradation. Therefore, the objective of this study was to compare the dissipation of atrazine and metribuzin under field conditions on organic soils in the EAA.

Materials and Methods

Study Location. Field studies were conducted in Belle Glade, FL, at the Glades Sugar Farm Main and Hillsboro Farms between 2011 and 2012 to evaluate field dissipation of atrazine and metribuzin. The experimental fields were planted to sugarcane varieties CP 88–1762 and CP 78–1628 on December 10, 2010, and November 21, 2011, at the Main and Hillsboro Farms, respectively. Both Main and Hillsboro farms' newly planted sugarcane fields (also referred to as *plant cane*) study sites received atrazine at 4.48 kg ai ha^{-1} each year in the sugarcane crop before 2007 for at least two decades (Table 1). Since 2007, both fields have received metribuzin at 1.12 kg ai ha^{-1} and ametryn at 0.224 to 0.67 kg ai ha^{-1} in the sugarcane crop. Soil type at the Main and Hillsboro farms was Dania muck (Euic, hyperthermic, shallow Lithic Haplosaprists) with a pH of 7.3 and 63.5% organic matter at the Main farm and a pH of 7.4 and 77.0% organic matter at Hillsboro farm. Plots were 6.1 m wide by 12 m long at the Main Farm and 3.0 m wide by 7.6 m long at the Hillsboro Farm. The experimental design was a randomized complete block with three and four replications of each treatment at the Main and Hillsboro farms, respectively.

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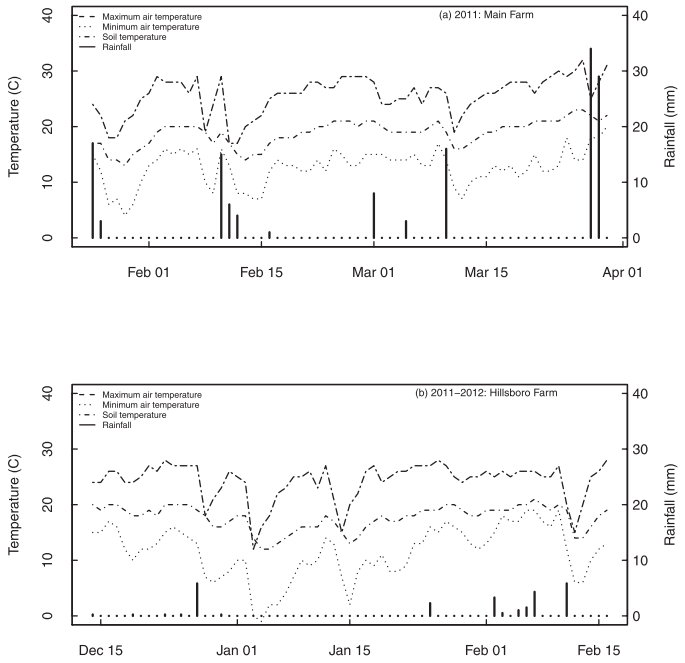

Figure 1. Air temperature, soil temperature, and rainfall during the experiment in 2011 and 2012 (Source: Florida Automated Weather Network; available at http://fawn.ifas.ufl.edu/).

Herbicide Treatment Application and Soil Sampling. Treatments consisted of the application of atrazine (Atrazine 4L, Loveland Products, Inc., Greeley, CO 80632) and metribuzin (Metribuzin 75, Loveland) on February 1, 2011, and December 21, 2011, on plant cane fields at the Main and Hillsboro farms, respectively. Atrazine was applied at 2.24, 4.48, and 8.96 kg ha^{-1} and metribuzin at 0.56, 1.12, and 2.24 kg ha^{-1}. These rates are equivalent to 0.5×, 1.0×, and 2.0× labeled use rates of these herbicides in Florida sugarcane (Odero and Dusky 2010). Treatments were applied before sugarcane spiking at both sites. Although the Main Farm site was planted early, before herbicide application, compared with Hillsboro Farm, below-freezing temperature (–2 C) in December 28, 2010, damaged spiking sugarcane, such that there was no new sugarcane regrowth at the time of herbicide treatment application. Weather data during the experiment is presented in Figure 1. At the Main Farm, herbicides were applied with a tractor-mounted sprayer (Lee Spider, LeeAgra Inc., Lubbock, TX 79404) calibrated to deliver 180 L ha^{-1} at 276 kPa with TeeJet TT11002 nozzle tips (Spraying Systems Co., Wheaton, IL 60187). Herbicides were applied with a CO_2-pressurized hand sprayer calibrated to deliver 180 L ha^{-1} at 276 kPa with TeeJet TT11002 nozzle tips at the Hillsboro Farm.

At 7, 14, 21, 28, 35, 42, 49, and 56 d after treatment, soil samples from both locations, comprising four soil cores 3 cm in diameter from the top 10 cm of the soil from the surface were taken randomly from each plot and composited. Soil samples were stored in coolers filled during collection from the field and were subsequently stored at –20 C within an hour before analysis.

Herbicide Extraction and Analysis. Atrazine and metribuzin were extracted using toluene and water extraction methods (Shaner et al. 2007). Toluene extracts 95 to 99% of the herbicide from the soil or the total amount of herbicide in the soil (Shaner and Henry 2007), whereas water extracts 40 to 60% of the herbicide or only the readily bioavailable fraction of the herbicide from the soil (Shaner et al. 2007).

Toluene Extraction and Analysis. Ten grams of soil was placed into a 50-ml glass centrifuge tube with a Teflon-lined cap, and 10 ml of water and 10 ml of water-saturated toluene were added. The tube was shaken horizontally for 2 h on a reciprocating shaker. The samples were removed from the shaker and centrifuged for 20 min at 1,000 × *g*. Two milliliters of the toluene phase were transferred to a 2-ml volumetric container to which 10 µl of a 0.1 mg ml^{-1} butylate internal standard solution was added. Quality control samples were included with each run and showed that the extraction efficiency for atrazine and metribuzin was 93 to 99%. The herbicide concentrations in the toluene phase were analyzed using a gas chromatograph equipped with a mass spectrometer (Shimadzu GC-17A and GCMS QO 5050A, Shimadzu Scientific Instruments, Inc., Columbia, MD 21046) and monitoring the masses for butylate (mass-to-charge ratio [*m*/*z*] 146), metribuzin (*m*/*z* 198), and atrazine (*m*/*z* 200). A RTX-5 column, 30 m by 0.25 mm (Restek Corporation, Bellefonte, PA 16823), was used with a flow of helium (Ultra helium, 5.0, General Air Service and Supply, Fort Collins, CO 80524) at 1 ml min^{-1}. The injection temperature was 250 C, and the detector temperature was 280 C. The program for detecting atrazine and metribuzin was as follows: initial oven temperature was 80 C (hold 2 min), which was ramped at 30 C min^{-1} to 250 C and then held at 250 C for 1.5 min with a run time of 10 min. Under these conditions,

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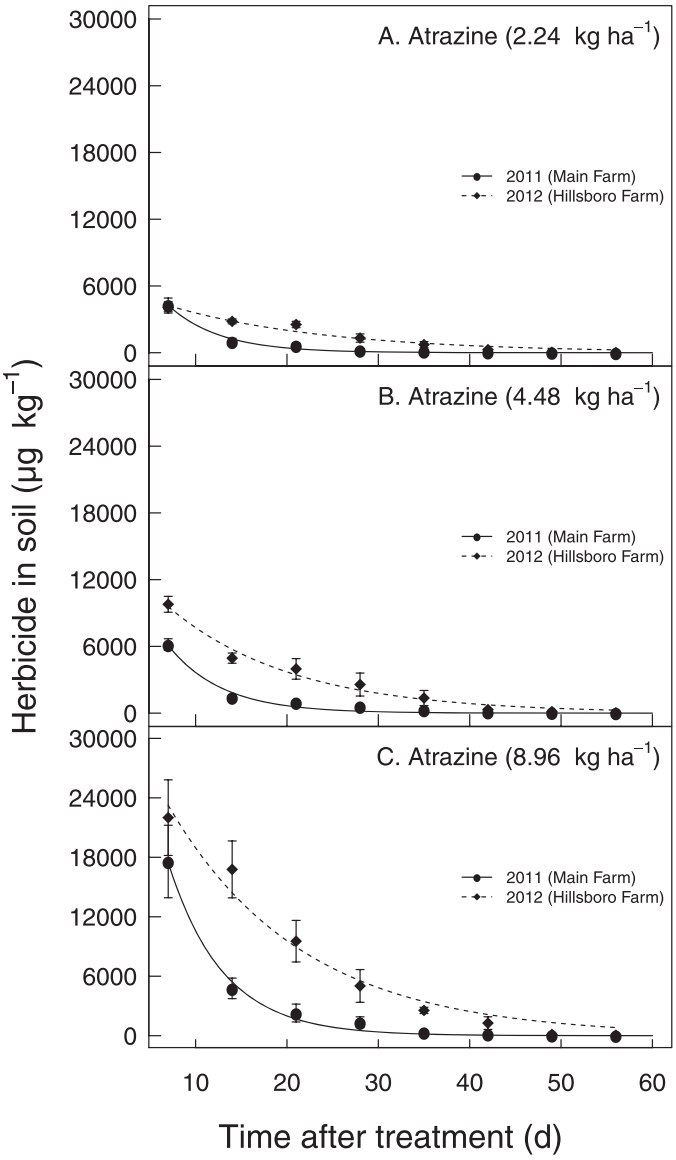

Figure 2. Atrazine dissipation in organic soil in Florida with toluene extraction in 2011 and 2012. Atrazine applied at (A) 2.24, (B) 4.48, and (C) 8.96 kg ha^{-1}. The lines are exponential curves (Equation 1): $Y = 14{,}717.4e^{(t/-5.7)}$ and $Y = 6{,}336.3e^{(t/-17.5)}$ for atrazine at 2.24 kg ha^{-1} in 2011 and 2012, respectively; $Y = 20{,}098.0e^{(t/-5.9)}$ and $Y = 15{,}959.2e^{(t/-13.7)}$ for atrazine at 4.48 kg ha^{-1} in 2011 and 2012, respectively; and $Y = 56{,}242.9e^{(t/-6.0)}$ and $Y = 37{,}482.2e^{(t/-14.7)}$ for atrazine at 8.96 kg ha^{-1} in 2011 and 2012, respectively. Errors bars indicate one standard deviation and do not appear when smaller than the symbol for the mean.

the retention times of butylate, atrazine, and metribuzin were 6.4, 7.7, and 8.3 min, respectively. The limit of quantification was 10 µg kg^{-1}.

$CaCl_2$ Extraction and Analysis. At sampling for the water phase, 10 g of soil was removed and mixed with 10 ml of 0.02 M $CaCl_2$ in a 50-ml glass centrifuge tube and shaken horizontally for 2 h. The tubes were centrifuged at 1,500 × *g* for 10 min, and 700 µl of the supernatant was transferred to a 900-µl centrifuge tube containing a 0.45-µm filter, which was centrifuged at 10,000 × *g* for 10 min. The filtrate was transferred to a vial and analyzed with a high-performance liquid chromatography column equipped with a photodiode array detector (SPD M 10A detector, Shimadzu). Analytes were separated on a C_{18} column (Alltech Econosphere C_{18} column, 5 µm and 150 × 4.6 mm, Alltech Associates, Inc., Deerfield, IL 60015). The mobile phase was acetonitrile to 5 mM ammonium acetate adjusted to pH 5.2 (35 : 65 v/v) and was run isocratically at 50 C at a flow of 1 ml min^{-1}. The injection volume was 100 µl. Metribuzin and atrazine were detected at 240 and 223 nm, respectively, with retention times of 3.5 and 8.7 min, respectively. The limit of detection was 5 µg ml^{-1} ($n = 8$). The dry weight of the soil at each sample was determined, and the results were corrected for dry weight of soil.

Statistical Analysis. Atrazine and metribuzin dissipation were fitted to Equation 1 for each year using the drc package of R software (R version 3.0.2; R Foundation for Statistical Computing, Vienna, Austria) (Ritz and Streibig 2005):

$$Y = Ae^{-t/k} \quad [1]$$

where A is the mass of the herbicide in soil at the first sampling time (µg kg^{-1}), k is the first-order rate constant (d^{-1}), and t is time (d). Half-life ($t_{1/2}$) values for atrazine and metribuzin dissipation were calculated from the model using R software.

Results and Discussion

The total amount of atrazine in the soil dissipated rapidly both years at all rates (Figure 2). However, dissipation was more rapid in 2011 than it was in 2012. The $t_{1/2}$ of the total amount of atrazine in the soil ranged from 3.9 to 4.1 d in 2011 and 9.5 to 12.1 d in 2012 (Table 2). Similarly, the readily bioavailable fraction of atrazine dissipated rapidly both years at all rates (Figure 3). Similar to the total amount of atrazine in the soil, dissipation of the bioavailable fraction of atrazine was more rapid in 2011 than it was in 2012. The $t_{1/2}$ of the bioavailable fraction of atrazine in the soil ranged

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Table 2. Half-lives ($t_{1/2}$) for atrazine and metribuzin with standard error in parenthesis on organic sugarcane fields in Florida between 2011 and 2012.

			$t_{1/2}$[a]	
		Herbicide rate	2011	2012
Herbicide	Extractant	kg ai ha^{-1}	d (±SE)	
Atrazine	Toluene	2.24	3.9 (0.6)	12.1 (1.2)
		4.48	4.1 (0.4)	9.5 (1.0)
		8.96	4.1 (0.7)	10.2 (1.1)
	Water	2.24	1.0 (1.2)	5.4 (1.1)
		4.48	1.0 (1.5)	6.0 (1.0)
		8.96	1.9 (0.6)	7.5 (1.1)
Metribuzin	Toluene	0.56	23.5 (4.7)	16.2 (1.6)
		1.12	24.8 (3.0)	18.6 (1.3)
		2.24	24.8 (3.1)	20.0 (2.4)
	Water	0.56	7.3 (1.4)	6.0 (1.9)
		1.12	11.0 (1.2)	8.9 (1.1)
		2.24	14.3 (1.5)	8.5 (1.0)

[a] Half-life of each herbicide was calculated from Equation 1.

from 1.0 to 1.9 d in 2011 and 5.4 to 7.5 d in 2012 (Table 2). Overall, the bioavailable fraction of atrazine dissipated more rapidly than the total amount in the soil in both years. The $t_{1/2}$ values of atrazine under field conditions in our study were much lower than the average of 60 d (Senseman 2007; Wauchope et al. 1992). The short persistence of atrazine under field conditions in these organic soils with a history of previous atrazine use indicated enhanced atrazine degradation. Enhanced atrazine degradation in these organic soils could also be related to ametryn use. Atrazine degradation has been shown to be highly correlated to ametryn degradation because of cross-adaptation of these chloro-*s*-triazines (Shaner et al. 2010). The hydrolysis of the methylthio group of these herbicides to corresponding hydroxyatrazine products is also catabolized by the enzyme TrzN (Krutz et al. 2010; Topp et al. 2000). Shaner et al. (2010) conducted a laboratory incubation dissipation study using soils collected from sugarcane production regions in the United States, including Florida, with previous atrazine use, which also indicated enhanced atrazine degradation. In their study, the $t_{1/2}$ of the bioavailable fraction of atrazine on organic soils from Florida was 1.2 and 3.1 d for fields treated with atrazine at 4.5 and 9.0 kg ha^{-1}, respectively, within 3 mo. In the same study, the $t_{1/2}$ of atrazine in fallow and noncropland fields that did not receive any atrazine was 6.9 and 6.1 d, respectively. In the present study, the $t_{1/2}$ of the bioavailable atrazine at similar rates under field conditions was 1.0 and 6.0 d at 4.48 kg ha^{-1} atrazine in 2011 and 2012, respectively, and 1.9 and 7.5 d at 8.96 kg ha^{-1} atrazine in 2011 and 2012, respectively. The contrasting difference between years in the present study may be due to differences

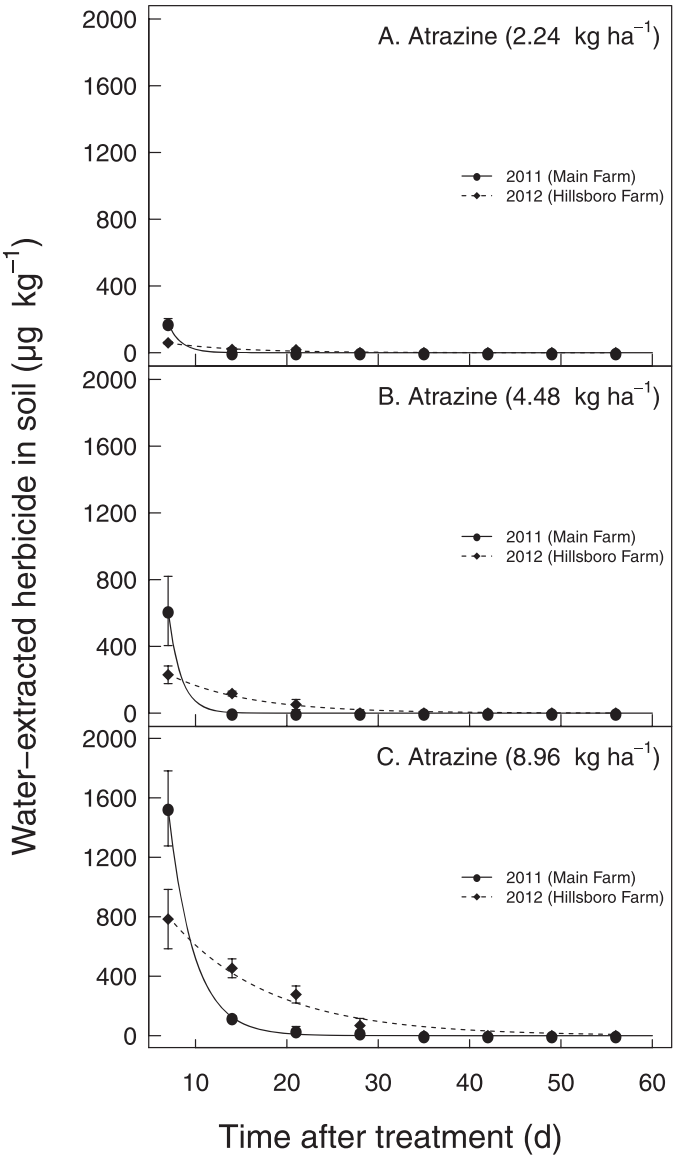

Figure 3. Atrazine dissipation in organic soil in Florida with water extraction in 2011 and 2012. Atrazine applied at (A) 2.24, (B) 4.48, and (C) 8.96 kg ha^{-1}. The lines are exponential curves (Equation 1): $Y = 25{,}934.0e^{(t/-1.4)}$ and $Y = 144.4e^{(t/-7.7)}$ for atrazine at 2.24 kg ha^{-1} in 2011 and 2012, respectively; $Y = 92{,}047.1e^{(t/-1.4)}$ and $Y = 523.7e^{(t/-8.7)}$ for atrazine at 4.48 kg ha^{-1} in 2011 and 2012, respectively; and $Y = 18{,}668.0e^{(t/-2.8)}$ and $Y = 1{,}532.8e^{(t/-10.8)}$ for atrazine at 8.96 kg ha^{-1} in 2011 and 2012, respectively. Errors bars indicate one standard deviation and do not appear when smaller than the symbol for the mean.

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in precipitation at the Main Farm in 2011 compared with Hillsboro Farm in 2012 (Figure 1) because both study sites had similar triazine use history in previous sugarcane crops (Table 1). Atrazine's persistence in soil has been reported to vary depending on soil moisture (Krutz et al. 2008). The $t_{1/2}$ of the bioavailable fraction of atrazine under field conditions in corn (*Zea mays* L.) fields with a history of atrazine use has been reported to be < 10 d (Krutz et al. 2007). Dissipation of atrazine under field conditions in corn is similar to what was found in the present study. However, the use rate of atrazine in corn is between 1.1 to 2.2 kg ha^{-1} (Senseman 2007), compared with 4.5 to 9.0 kg ha^{-1} on sugarcane on organic soils in the EAA. This shows rapid dissipation of atrazine at higher use rates in sugarcane on these organic soils.

Organic soils of the EAA are characterized by organic matter content of up to 85% (Wright and Hanlon 2009). The organic matter content in the present study was between 63.5 and 77.0%. Microbial adaptation for enhanced atrazine degradation has been reported in soils with organic matter content of up to 46% (Krutz et al. 2010). Several researchers have reported limited effect of organic matter on atrazine degradation (Briceño et al. 2010; Goux et al. 2003; Shapir and Mandelbaum 1997). Shapir and Mandelbaum (1997) reported that high organic matter content in the upper soil level did not result in a sorption-related decrease in degradation rates of atrazine, but the limiting factor for atrazine degradation was the absence of adopted atrazine-degrading microorganisms. This suggests that degradation of atrazine in the organic soils of the EAA was probably not sorption-related. In addition, atrazine is moderately adsorbed to soil, with an average organic carbon adsorption coefficient (K_{oc}) value of 100 mL g^{-1} (Senseman 2007).

Enhanced degradation of atrazine is correlated with soil pH (Barriuso and Houot 1996; Vanderheyden et al.1997; Zablotowicz et al. 2006). Soil pH is considered a key factor driving microbial diversity and processes in agroecosystems (Wakelin et al. 2008). Increasing soil pH supports higher bacterial biomass and enzymatic expression, which in turn helps bacterial communities to adapt and develop gene–enzyme systems for enhanced degradation of pesticides (Singh et al. 2003). Several studies have also shown an increase in soil bacterial biomass and enzymatic activities with increase in soil pH (Bardgett and Leemans 1995; Zelles et al. 1990). In contrast, the spectrum of fungal species has been shown to decline with increasing soil pH (Zelles et al. 1990). Soil pH levels ranging from 5.1 to 8.6 have been reported for *s*-triazine–adapted soils, with 90% of the soils having a pH between 5.8 and 8.1 (Krutz et al. 2010). The organic soils in our study were characterized by pH of 7.3 and 7.4, which probably contributed to rapid degradation of atrazine because soil bacterial diversity and richness is maximal at neutral pH (Krutz et al. 2010). Mueller et al. (2010) also reported rapid atrazine dissipation in soils with pH of 5.5 or greater under Tennessee field conditions. Similarly Goux et al. (2003), reported an immediate strong increase in atrazine biodegradation at soil pH > 7. Results of these studies are contrary to the report by Senseman (2007), who found that persistence of atrazine was increased by higher soil pH as well as by cool, dry conditions. The Senseman (2007) report is based on the premise that atrazine adsorption increases at lower pH.

Dissipation of the total amount of metribuzin in soil increased over time for all rates both years (Figure 4). The $t_{1/2}$ of the total amount of metribuzin in the soil ranged from 23.5 to 24.8 d in 2011 and 16.2 to 20.0 d in 2012 (Table 2). Similarly, dissipation of readily bioavailable fraction of metribuzin increased over time at all rates both years (Figure 5). The $t_{1/2}$ of the bioavailable fraction of metribuzin in the soil ranged from 7.3 to 14.3 d in 2011 and 6.0 to 8.9 d in 2012 (Table 2). The $t_{1/2}$ of metribuzin in laboratory incubation studies of organic soils of the EAA was 6.6 to 11.9 d (Shaner et al. 2010). Dissipation of the bioavailable fraction of metribuzin on organic soils in our present study was 6 to 14 d, compared with a range of 30 to 60 d during the growing season (Senseman 2007). The present and previous studies (Shaner et al. 2010) show that persistence of metribuzin on organic soils of the EAA was probably not increased by sorption of the herbicide to organic matter. Metribuzin is weakly sorbed to soil with an average K_{oc} of 60 mL g^{-1} (Senseman 2007). However, sorption of metribuzin has been reported to increase with soil organic matter (Majumdar and Singh 2007). The organic soils in the present study had pH slightly above neutral. There is a direct relationship between metribuzin degradation and soil pH (Maqueda et al. 2009). Degradation of metribuzin is lowest in soils with low pH exhibiting weak bioactivity (Maqueda

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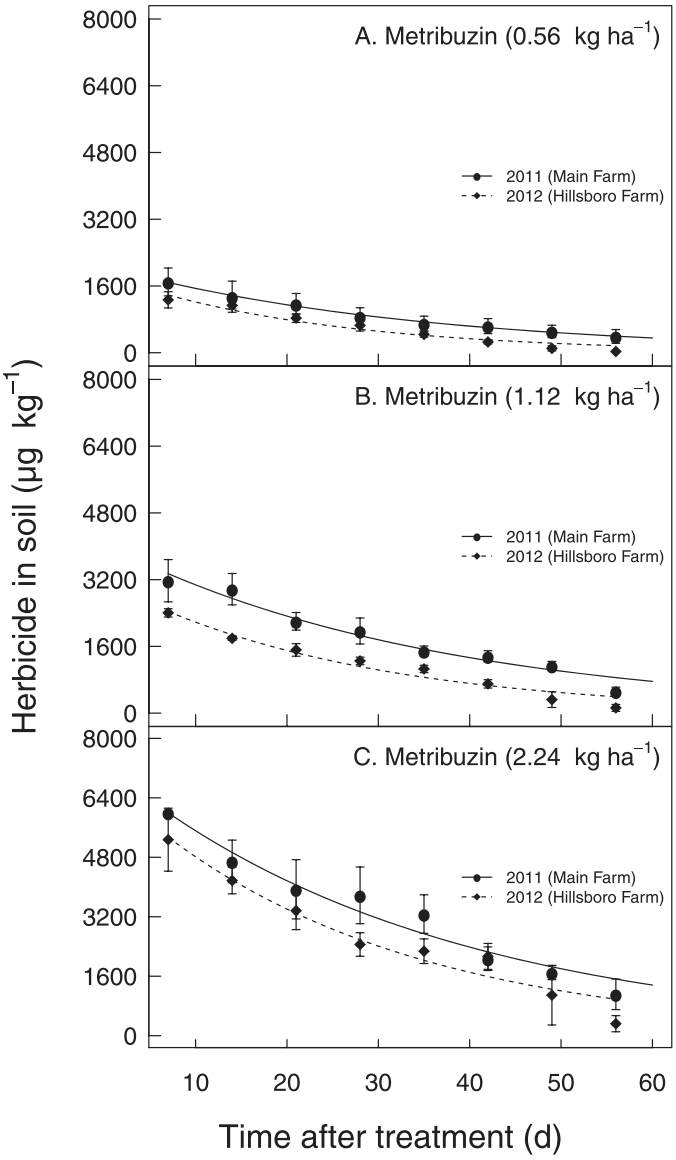

Figure 4. Metribuzin dissipation in organic soil in Florida with toluene extraction in 2011 and 2012. Metribuzin applied at (A) 0.56, (B) 1.12, and (C) 2.24 kg ha^{-1}. The lines are exponential curves (Equation 1): $Y = 2{,}070.6e^{(t/-34.0)}$ and $Y = 1{,}867.9e^{(t/-23.3)}$ for metribuzin at 0.56 kg ha^{-1} in 2011 and 2012, respectively; $Y = 4{,}065.0e^{(t/-35.8)}$ and $Y = 3{,}165.7e^{(t/-26.8)}$ for metribuzin at 1.12 kg ha^{-1} in 2011 and 2012, respectively; and $Y = 7{,}292.9e^{(t/-35.8)}$ and $Y = 6{,}802.7e^{(t/-28.9)}$ for metribuzin at 2.24 kg ha^{-1} in 2011 and 2012, respectively. Errors bars indicate one standard deviation and do not appear when smaller than the symbol for the mean.

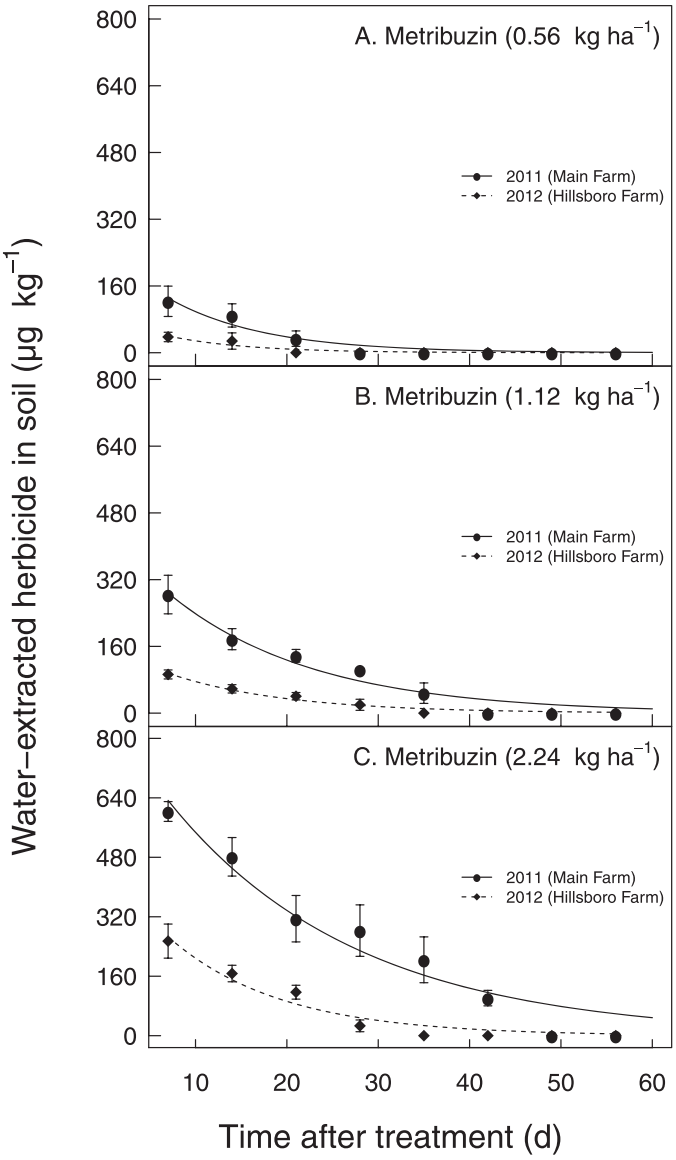

Figure 5. Metribuzin dissipation in organic soil in Florida with water extraction in 2011 and 2012. Metribuzin applied at (A) 0.56, (B) 1.12, and (C) 2.24 kg ha^{-1}. The lines are exponential curves (Equation 1): $Y = 255.4e^{(t/-10.5)}$ and $Y = 90.1e^{(t/-8.7)}$ for metribuzin at 0.56 kg ha^{-1} in 2011 and 2012, respectively; $Y = 447.5e^{(t/-15.9)}$ and $Y = 165.0e^{(t/-12.8)}$ for metribuzin at 1.12 kg ha^{-1} in 2011 and 2012, respectively; and $Y = 888.8e^{(t/-20.6)}$ and $Y = 470.4e^{(t/-12.3)}$ for metribuzin at 2.24 kg ha^{-1} in 2011 and 2012, respectively. Errors bars indicate one standard deviation and do not appear when smaller than the symbol for the mean.

et al. 2009). Several studies have demonstrated the influence of soil pH on microbial biomass and pesticide degradation rate (Bardgett and Leemans 1995; Wakelin et al. 2008; Zelles et al. 1990). Dissipation of metribuzin observed in our study was most likely attributed to soil pH and the presence of adapted metribuzin-degrading microorganisms in these high organic-matter soils because both experimental fields had a history of metribuzin use before initiation of the studies.

Overall, atrazine dissipated more rapidly than metribuzin did under field conditions in organic

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soils of the EAA. Atrazine $t_{1/2}$ values in these *s*-triazine-adapted organic sugarcane soils were up to 60-fold lower than previous estimates of 60 d under field conditions depending on atrazine rate and use history. This implies that residual weed control by PRE atrazine in sugarcane grown in the EAA is up to 60-fold lower in these *s*-triazine-adapted soils. However, the nonsymmetrical triazine herbicide metribuzin had relatively longer $t_{1/2}$ values under field conditions at the labeled use rate for sugarcane in the EAA than atrazine did, implying that metribuzin is the better alternative for PRE weed control in sugarcane grown on organic soils of the EAA exhibiting enhanced atrazine degradation.

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