ATRAZINE RETENTION BY SUGARCANE RESIDUE AND SOILS

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The primary focus of this investigation was to quantify the reactivity of atrazine with the sugarcane residue and soils. A literature search revealed that no investigations focused on the reactivity of atrazine by the sugarcane residue. The objectives of this study were to (i) determine the adsorption-desorption of atrazine by the sugarcane residue and soils, (ii) to assess the retention of atrazine by sugarcane residue over time following harvest. Specifically, we collected residue samples from sugarcane field experiments following harvest. The sugarcane was grown on two different soils namely; Sharkey clay soil and Commerce soil. We carried out kinetic adsorption experiments to assess the affinity of atrazine by the sugarcane residue and the soils. Such information is necessary in predicting the role of the residue on the mobility and leaching losses of applied agricultural chemicals.

METHODS

Following sugarcane harvest, residue was sampled for several growing seasons over a ten year period (2000-2009). Sugarcane variety LCP85-384 was planted 2 October 1999 on a Sharkey clay soil (very-fine, montmorillonitic nonacid, thermic, vertic Haplaquept) at the LSU AgCenter, St. Gabriel Research Station, St. Gabriel, Louisiana. Sugarcane harvest was carried for three successive growing seasons on December 8, 2000 for plantcane, October 22, 2001 first the ratoon and November 24, 2002 for the second ratoon. The sugarcane residue was collected multiple times following harvest for each of the growing seasons, generally at 30 d intervals (see Table 1 and 2). Residue samples were also collected from two newly adopted varieties during 2002-2009. Specifically, residue was collected from variety HoCP91-555 following harvest of plant cane, first and second ratoons of 6 December 2002, 28 October 2003 and 18 October 2004, respectively. Residue was also collected from L97-128, following harvest of second ratoon (19 November 2008). Both of these varieties were grown on Commerce silt loam soil (fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquept). Additional information is available in Naquin (2005). At each sampling date, a minimum of 8 random samples from two plots were collected. The collected residue was oven dried at 55°C for 24-h and weighed. The dry residue was cut into 1 cm sections for the atrazine retention studies in the laboratory.

Atrazine adsorption by the sugarcane residue was carried using the batch method where radioactive atrazine was used as a tracer to monitor the extent of retention. Six initial atrazine concentrations C_o's (1.80, 2.5, 5.4, 10.3, 20.2, and 30.0 mg L^{-1}) were prepared in 0.005 M $CaCl_2$ solution and spiked with C-14-ring labeled atrazine. Adsorption was initiated by mixing 1g of dried and cut sugarcane residue with 30 mL of the various atrazine solutions in a 40-mL Teflon centrifuge tube. The mixtures were shaken 15 min every hour and centrifuged at 500 × g for 10 minutes after each specific reaction time before sampling. A 0.5-mL aliquot was sampled from the supernatant at reaction times of 6, 24, 48, 96, 168, 336 and 504 hours. The mixtures were subsequently returned to the shaker after each sampling. The collected samples were analyzed using a liquid scintillation counter. For the Commerce and Sharkey soils, atrazine adsorption at several time o reaction was also measured. The batch procedure described above was followed. The only exception is that 3 g soil with 30 mL of the various atrazine solutions was used.

RESULTS AND DISCUSSION

Adsorption isotherms represent the amount sorbed versus concentration of herbicide in solution. The family of isotherms shown in Figure 1 illustrate atrazine affinity by the residue as well as the extent of retention with time of reaction. These isotherms are were described by the linear type model ($S = K_d\ C$), where S is the total amount of herbicide sorbed (mg per kg residue) and C is concentration in solution (mg per L). The linear parameter K_d (mL/g) is the distribution coefficient which is an indication of the extent of atrazine affinity to the sugarcane residue. Based on the results shown in Figure. 1, the K_d values for atrazine adsorption by the residue increased with reaction time. For samples collected in 2003, the K_d values for atrazine adsorption by the residue increased with reaction times from 18.77 to 25.46 cm^3/g after 1- and 21-d, respectively (see Table 1). These increases are representative of the extent of kinetic behavior of atrazine adsorption by the residue. The adsorption of atrazine by sugarcane residue was initially rapid, and exhibited slower retention after 1-d of reaction time.

As illustrated in Fig. 2, atrazine isotherms for Commerce soil exhibited modest increase in sorption over time. This is in contrast with the observed extensive kinetics for atrazine retention by the mulch residue shown in Figure 1. For Sharkey soil, similar atrazine adsorption isotherms were obtained where limited increase of sorption was observed over time (Figure not shown). The 24-h K_d values for the Commerce and Sharkey soils were 1.18 and 2.15 cm^3/g, respectively. Thus atrazine K_d values for the mulch residue were an order of magnitude higher than those for the Commerce and Sharkey soils. Other authors measured strong sorption of atrazine by the mulch residue from other crops. Abdelhafid et al. (2000) measured high K_d values for wheat straw compared to soil (15.01 versus 0.77 cm^3/g, respectively). We are not aware of earlier studies where atrazine K_d by sugarcane mulch was measured. In field experiment, Selim et al. (2003) found that the amount of extractable atrazine was 10 to 20 times higher for the sugarcane residue compared with that retained by the underlying (Commerce silt loam) surface soil layer. Therefore, we conclude that results from our laboratory study of the retention kinetics of the mulch residue were consistent with field measurements.

To assess the effect of the age of the residue on atrazine retention, we carried out sorption experiments for residue collected during the 2000-2003 growing season (variety LCP85-384), 2002-2005 growing season (variety HoCP91-555), and 2008-2009 (variety L97-128). The K_d values for the residue are given in Tables 3 and 4 for all the sampling dates during a ten year period (2000-2009). Examination of the measured K_d shows no clear pattern of atrazine retention for the different sampling dates or growing seasons. Based on the review by Alletto et al. (2007), the decay of crop residues influences the interception and retention of pesticides, but in contrasting ways. For example, Sigua et al. (1993) indicated that atrazine retention was enhanced for fresh corn residues, due to a combination of a greater hydrophobicity and a higher sorption capacity of the fresh compared with aged corn residues. In contrast, with metribuzin (Dao, 1991), chlorimuron (Reddy et al., 1995) and cyanazine (Reddy et al., 1997), retention was higher with aged residues. In these cases, the increase in sorption due to aging was attributed to changes in physical chemical composition of the crop residues. Physical alterations of the residues may lead to increases in their external surface area for herbicide sorption compared with fresh residues. On the other hand, degradation may lead to an increase in the lignin/cellulose ratio, resulting in an increase in the sorption of chlorimuron and metribuzin (Dao, 1991; Reddy et al., 1995). Our results indicate that a decreasing or increasing trend of atrazine retention by the sugarcane residue with time of decay was not observed. We conclude that atrazine was strongly sorbed by the sugarcane and its affinity did not indicated decreasing or increasing trends over the growing season. The use of an average retention (K_d) value to represent atrazine retention over an entire growing season is recommended.

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Table 1. Linear and Freundlich model parameters and their standard deviations for atrazine adsorption versus retention time by the sugarcane (LCP85-384) mulch residue. The residue was sampled from Sharkey soil plots on Jan 24, 2003.

Retention	Linear Model	
Time (d)	*Kd (mL g^{-1})*	r^2
1	18.77 ± 0.58	0.935
2	18.04 ± 0.49	0.957
7	24.02 ± 0.96	0.916
14	24.24 ± 0.60	0.967
21	25.46 ± 0.64	0.966

Table 2. Estimated K_d values and their standard deviations for atrazine adsorption by the sugarcane mulch residue (variety LCP85-384). The residue was sampled at several dates following harvest for three growing seasons (2000-2003) on Sharkey clay soil.

Season	Sampling Date	Age of Residue	Atrazine K_d
		(days)	(mL g^{-1})
2000-2001	4-Jan-01	26	14.99 ± 0.15
	7-Feb-01	61	16.52 ± 0.13
	23-Mar-01	105	15.90 ± 0.22
	27-Apr-01	140	18.09 ± 0.13
2001-2002	30-Oct-01	12	16.21 ± 0.36
	26-Nov-01	39	14.92± 0.39
	20-Dec-01	63	16.72 ± 0.27
	22-Feb-02	127	15.65 ± 0.16
	20-Mar-02	153	17.18 ± 0.31
	23-May-02	217	15.93 ± 0.18
2002-2003	4-Dec-02	12	20.82 ± 1.38
	2-Jan-03	39	15.81 ± 1.49
	24-Jan-03	63	18.77 ± 0.58

Table 3. Estimated Kd values (with 95% confidence interval) for atrazine adsorption by the sugarcane mulch residue (variety HoCP91-555) for 2002-2005 growing seasons and variety 128-L97 growing season on Commerce silt loam soil.

Growing Season	Sampling Date	Age of Residue	Atrazine K_d
		(days)	(mL g^{-1})
2002-2003	6-Dec-02	1	14.06±0.23
	6-Jan-03	30	15.54±0.57
	14-Feb-03	68	13.45±0.40
2003-2004	29-Oct-03	1	14.82±0.40
	4-Dec-04	37	18.20±0.61
	27-Jan-04	90	18.34±0.25
	2-Mar-04	128	19.51±0.99
	5-Apr-04	160	15.14±0.63
2004-2005	28-Oct-04	3	18.83±0.69
	3-Dec-04	45	15.26±0.51
	26-Jan-05	98	15.44±0.48
2008-2009	7-Nov-08	4	17.39±0.72
	8-Dec-08	37	18.69±1.43
	8-Jan-09	68	17.47±0.99
	4-Feb-09	105	16.82±0.62
	6-Mar-09	136	19.16±0.61

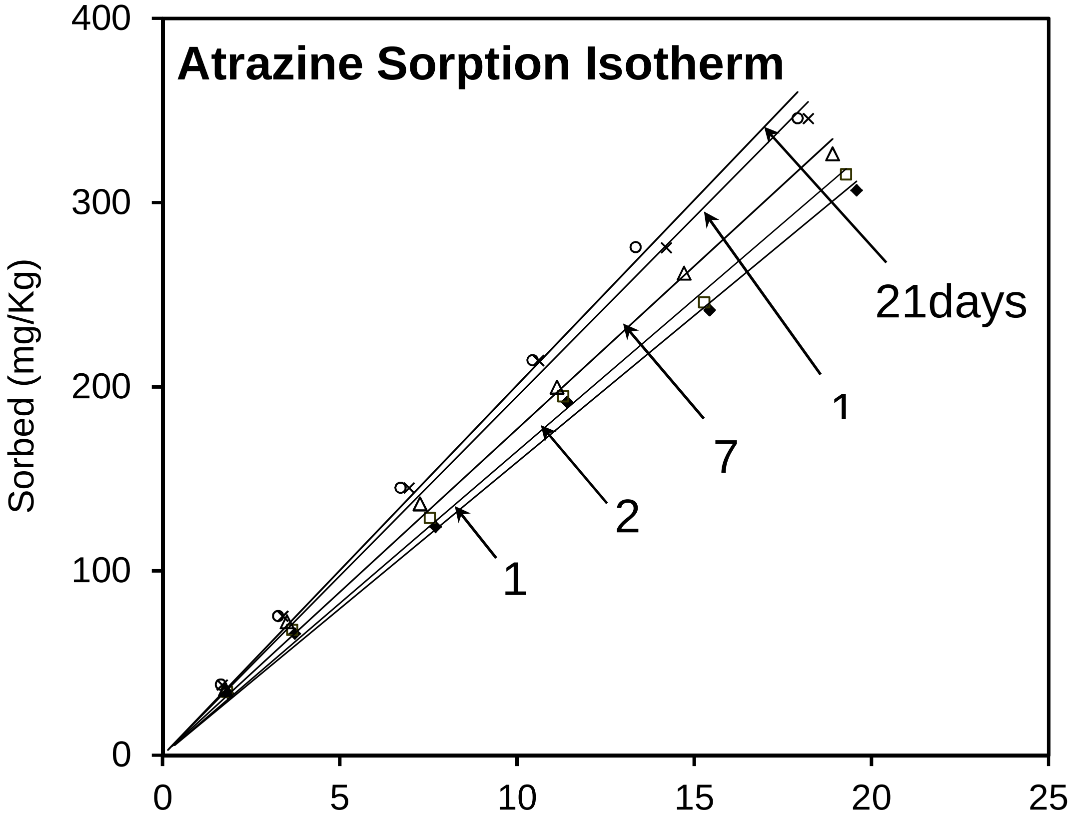

Figure 1. Adsorption isotherms for atrazine by sugarcane mulch residue at different reaction times. The sugarcane was grown on Sharkey clay soil. Solid lines are predictions using a linear model.

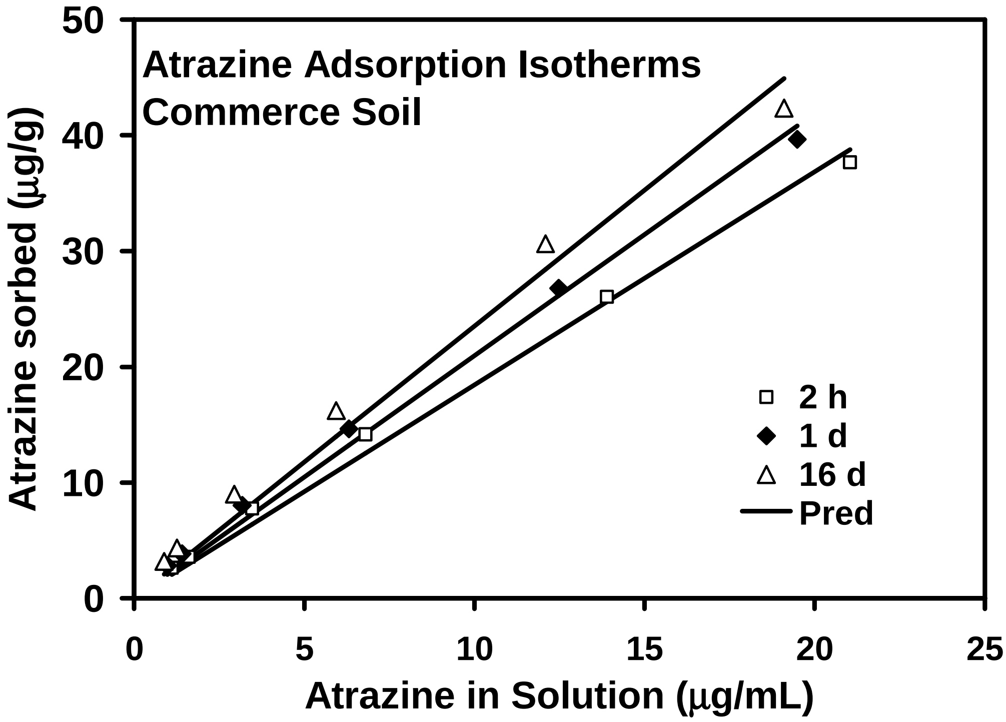

Fig. 3. Adsorption isotherms for atrazine by Commerce soil for 2 h, 1-d and 16-d reaction time. Solid lines are predictions using a linear model.