FIELD DECAY OF SUGARCANE MULCH RESIDUE AND ITS EFFECTS ON METRIBUZIN AND ATRAZINE RETENTION AND RELEASE

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Best management practices such as minimum and no-till are needed in order to minimize soil losses and the movement of applied agricultural chemicals off-site. We are not aware of published research that has been carried out on correlating the effectiveness of sugarcane mulch residue remaining on the soil surface over time, following harvest, on the retention of applied herbicides, leaching losses in the runoff, and their downward movement in the soil profile. In this study, field and laboratory studies were conducted to determine weather-induced changes in sugarcane mulch residue composition. Change in atrazine and metribuzin retention characteristics of the mulch residues as they decay in the field was quantified. A relationship between atrazine and metribuzin retention of the residue and the lignin content on a mass basis of the residue was also quantified.

Field Decay of Mulch Residue

Bulk samples of sugarcane residue (varieties LCP85-384 and CP70-321) were collected from field plots at the St. Gabriel Sugar Research Station. The 384 variety was grown on a Sharkey clay soil, and the 321 variety was grown on a Commerce silt loam. Mulch samples were collected immediately after combine harvesting of the crop. To quantify the rate of decay of the mulch residue, bulk samples were collected over time following harvest. The decay of mulch residue for CP70-321 was monitored following harvest of the third stubble during 1999-2000 only, whereas the LCP85-84 variety was monitored following three successive growing seasons (plantcane, and first and second stubbles) during 2000 to 2003 (see Figure 1). The sugarcane residue was collected randomly within each plot, by measuring 6-8, 1 m^2 areas and collecting all surface mulch within that area. The residue was dried at 55°C for 24 hours and weighed. A portion of dry residue was cut into 1cm sections for batch equilibrium studies, while some of the residue was ground to a powder and mixed for homogeneity as required for fiber analysis

For CP70-321, the amount of mulch on the soil surface decreased from 3.58±0.95 tons/acre on December 17, 1999, to 0.740±0.143 on August 18, 2000. The average yield for CP70-321 was 26.85 tons/acre. For the LCP85-84, average yields for the 2000 and 2001 growing seasons were 31.98 tons/acre and 36.53 tons/acre, respectively. The surface residue decreased from 1.70±0.308 to 0.64±0.239 tons/acre within a four-month period for the 2000 season, and the 2001 season decreased from 2.58±0.642 to 0.870±0.247 tons/acre in five months. Rainfall data shows the 2000 growing season was the third driest on record. This resulted in a lower yield for the plantcane than the first stubble. Such a difference may be attributed to differences in crop variety and yields, soil type, as well as combine setting during harvest.

A rate of residue decay was derived based on simple linear regression where the (negative) slope represents the mass losses per acre over time. For CP70-321 grown on Commerce silt loam, the estimated rate of decay was 0.0105 ± 0.00178 tons/acre/day. Whereas for variety LCP85-384 grown on Sharkey clay, the rates of degradations were of 0.0153 ± 0.00054, 0.0075± 0.00169, 0.0062± 0.00998 tons/acre/day for the three growing seasons (plantcane, first and second stubble), respectively.

Adsorption – Desorption:

Adsorption-desorption by mulch residue was carried out using batch equilibration technique (Zhu and Selim, 2000). Six ^{14}C-atrazine/metribuzin spike samples having initial concentrations (C_i) ranging from 2.98 to 29.8 mg L^{-1} for atrazine and from 2 to 98 mg L^{-1} for metribuzin in 0.005 M $CaCl_2$ solution were used. Adsorption was initiated by mixing 1g of dried and cut sugarcane residue with 30 mL of the various herbicide concentration solutions in a 40-mL Teflon centrifuge tube. The mixtures were shaken for each specific reaction time and centrifuged at 3500 × g for 10 minutes before sampling. A 0.5-mL aliquot was sampled from the supernatant at set reaction times. The mixtures were returned to the shaker after each sampling. The collected samples were analyzed using liquid scintillation counting (LSC).

Desorption commenced immediately after the last adsorption time step (24-h). Each desorption step was conducted by replacing the supernatant with atrazine / metribuzin free 0.005 M $CaCl_2$ solution and shaking for 24 hours. Ten desorption steps were carried out with a total desorption time of 10 days. After the tenth step, two further extractions using pure methanol were carried out. The residue used for desorption studies was from sugarcane variety LCP85-384 grown on Sharkey soil and was collected from the field on March 20, 2002.

Adsorption isotherms represent the amount sorbed versus concentration of herbicide in the soil solution. A family of adsorption isotherms for metribuzin by the mulch residue ais shown in Figure 2. Such relationships clearly illustrate metribuzin affinity by the mulch residue as well the extent of retention with time of reactions. Adsorption isotherms are often described by either a linear type model ($S = K_d C$) or nonlinear (Freundlich) type equilibrium model ($S = K_f C^N$), where S is the amount of herbicide sorbed (mg kg^{-1} soil), and C is concentration in the soil solution (mg L^{-1}). The linear parameter K_d (mL g^{-1}) is the distribution coefficient which is widely reported in the literature, K_f is a Freundlich partitioning coefficient (mL g^{-1}), and N is a dimensionless parameter commonly less than unity.

The K_d values for atrazine adsorption by the sugarcane mulch residue increased with reaction times from 15.9 to 23.09 cm^3/g after 24 and 504 hours, respectively (see Table 1). The metribuzin K_d values increased with reaction times from 10.3 to 14.6 cm^3/g after 24 and 504 hours, respectively. These increases are representative of the strong kinetic behavior of atrazine and to a lesser extent, metribuzin adsorption by the sugarcane mulch residue. The adsorption of both atrazine and metribuzin by sugarcane residue was initially rapid and exhibited slower retention after 24 hours of reaction time (see Figure 3). Therefore it is not recommended to rely on 24-K_d values as an estimate for potential sorption of atrazine and metribuzin by the mulch residue.

The K_d values for atrazine and metribuzin discussed above were an order of magnitude higher than that found for soils such as our Commerce silt loam soil. This was expected since organic matter is the principal soil component affecting the adsorption of many herbicides in the soil environment. Specifically, for Commerce soil K_d values for atrazine ranged from 2.095 to 2.352 mL/g after 24 and 384 hours of reaction time, respectively. The corresponding values for metribuzin were 1.18 to 1.52 mL/g after 24 and 384-h of reaction time, respectively. These K_d

values for Commerce soil were measured in our laboratory and clearly exhibit limited kinetic behavior for both atrazine and metribuzin when compared to the mulch residue.

The retention capability of the mulch residue versus time of decay in the field following harvest is depicted in Figure 4. Here we quantified the atrazine and metribuzin retention to find out the changes of adsorption characteristics due to weather-induced changes in the field following harvest. Specifically, the K_d values were measured using 24 hour batch adsorption and for individual mulch samples for two growing season (2000-2001 and 2001-2002). As expected, atrazine retention was much higher than that for metribuzin (Table 2). Striking is that the retention was similar over the two growing seasons and did not change significantly with the time of decay in the field. Such a finding is of significance and implies that only one K_d value is needed to quantify the retention behavior and that such value is nearly time invariant. Such a conclusion is valid for both herbicides. Our results are consistent with those of Dao (1991) for metribuzin adsorption on chopped wheat straw versus time following harvest. The only exception is that a lower retention value was reported from samples obtained immediately after harvest followed by little if any increase in retention over the succeeding five months.

The extent of release or desorption of the herbicides sorbed was also quantified. Following 24 hour adsorption, 10-consecutive 24 hour desorption steps were carried out using successive dilution methods. Metribuzin desorbed an average of 93 ± 3.07% of the original amount adsorbed, all concentrations with the exception of 10mg L^{-1}, recovered over 90% of adsorbed. The desorption of atrazine yielded an average of 87 ± 5.21% of the amount adsorbed after 24 hours of shaking (see Table 3).

Neutral Detergent Fiber during Decay:

The residue from the 2001-2002 sampling dates was analyzed for neutral detergent fiber (NDF) and acid detergent fiber (ADF) and was carried out at the Southeast Research Station. NDF is the fraction of the plant that contains hemicellulose, cellulose and lignin. ADF is the sub-fraction of NDF consisting of mainly lignin and cellulose. The NDF and ADF values are used as indicators of lignin, cellulose, and hemicellulose content of sugarcane residue on a mass basis. Neutral detergent fiber and acid detergent fiber were analyzed using the methods described by Goering and Van Soest (1970), which were modified by excluding decalin. Additionally, 2.0 mL of a 2% (w/v) "-amylase solution and 0.5 g sodium sulfite were added at the beginning of the NDF procedure (Van Soest and Robertson, 1980). A linear relationship between Kd vs ADF was obtained for both atrazine and metribuzin with moderate slopes of 0.19 and 0.11 ml/g, respectively (see Figure 5).

Following harvest, the amount of residue in the field decreased by an average of 1.34 tons/acre over a five-month period. The percentage of ADF in the mulch increased slightly as time in the field increased. The content of the residue has higher amounts of lignin with a higher adsorption capacity with time. Therefore the residue has the ability, on a mass basis, to adsorb increasing amounts of herbicides with time in the field. However, such an increase is at best modest (see Table 4). This is consistent with metribuzin and lignin relationships described by Dao (1991). Dao (1991) argues that the increase in the percentage of lignin of intact wheat straw is caused by the decay of cellulose. Moreover, he assumed that lignin accounted for most of the sorption sites for metribuzin by the residue. In two separate batch studies, a purified cellulose fraction did not show significant retention of metribuzin or atrazine (Dao, 1991, and Abdelhafid et al. (2000). Increased sorption capacity of decaying straw was thus associated with a decline in cellulose concentration or conversely the lignin enrichment of the straw (Dao, 1991).

REFERENCES

Abdelhafid, R., S. Houot, and E. Barriuso. 2000. Dependence of atrazine degradation on C and N availability in adapted and non-adapted soils. Soil Biology & Biochemistry. 32:389-401.

Dao, T.H. 1991. Field decay of wheat straw and its effects on metribuzin and S-ethyl metribuzin sorption and elution from crop residues. J. Environ. Qual. 20:203-208.

Goering H.K., and Van Soest P.J. 1970. Forage fiber analysis (apparatus, reagents, procedures, and some applications). Agric. Handb. 379. USDA-ARS, U.S. Gov. Print. Office, Washington, D.C.

Van Soest P.J., and Robertson J.B. 1980. Systems of analysis for evaluating fibrous feeds. p. 49-60. *In* W.J. Pigden et al. (ed.) Proc. Int. Workshop on Standardization Anal. Meth. Feeds. Ottawa, Canada. 12-14 Mar. 1979. Unipub., New York.

Zhu, H. and H. M. Selim. 2000. Hysteretic Behavior of Metolachlor Adsorption-Desorption in Soils. Soil Sci. 165:632-645.

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Table 1. Linear and Freundlich model parameters for atrazine and metribuzin adsorption versus retention time by the sugarcane (LCP85-384) mulch residue. The residue was sampled on March 23, 2001.

Atrazine					
Retention	Freundlich Model			Linear Model	
Time (d)	Kf (mL g^{-1})	N	r^2	Kd (mL g^{-1})	r^2
1	19.36 ± 1.82	0.92 ± 0.03	0.997	15.90 ± 0.22	0.987
2	20.01 ± 3.10	0.92 ± 0.02	0.999	16.50 ± 0.16	0.993
7	23.32 ± 3.10	0.89 ± 0.04	0.994	17.65 ± 0.37	0.971
14	25.29 ± 1.62	0.90 ± 0.02	0.999	19.46 ± 0.25	0.989
21	26.55 ± 1.57	0.89 ± 0.01	0.999	20.08 ± 0.26	0.989
Metribuzin					
Retention	Freundlich Model			Linear Model	
Time (d)	Kf (mL g^{-1})	N	r^2	Kd (mL g^{-1})	r^2
1	13.72 ± 2.46	0.94 ± 0.04	0.995	11.20 ± 0.20	0.986
2	17.20 ± 2.78	0.90 ± 0.04	0.995	11.56 ± 0.22	0.984
7	16.94 ± 2.39	0.93 ± 0.03	0.997	12.91 ± 0.20	0.990
14	17.85 ± 2.08	0.92 ± 0.02	0.998	13.47 ± 0.18	0.992
21	17.66 ± 2.20	0.95 ± 0.03	0.997	14.72 ± 0.19	0.993

Table 2. Linear and Freundlich model parameters for atrazine and metribuzin adsorption by the sugarcane (LCP85-384) mulch residue, for different sampling times.

Atrazine					
Age	Freundlich Model			Linear Model	
of Residue(d)	Kf (mL g^{-1})	N	r^2	Kd (mL g^{-1})	r^2
12	22.62 ± 3.10	0.87 ± 0.05	0.990	16.21 ± 0.36	0.966
40	18.28 ± 3.51	0.92 ± 0.07	0.989	14.92± 0.39	0.956
63	20.67 ± 2.26	0.92 ± 0.04	0.996	16.72 ± 0.27	0.982
127	18.46 ± 1.32	0.93 ± 0.02	0.999	15.65 ± 0.16	0.993
153	22.69 ± 2.63	0.89 ± 0.04	0.996	17.18 ± 0.31	0.978
187	18.24 ± 1.54	0.94 ± 0.03	0.998	15.93 ± 0.18	0.991
Metribuzin					
Age	Freundlich Model			Linear Model	
of Residue(d)	Kf (mL g^{-1})	N	r^2	Kd (mL g^{-1})	r^2
12	10.90 ± 4.02	0.95 ±0.09	0.980	9.23 ± 0.32	0.951
40	8.49 ± 2.12	1.02 ± 0.06	0.992	9.47 ± 0.20	0.981
63	8.76 ± 2.09	1.04 ± 0.05	0.993	10.47 ± 0.22	0.983
127	10.57 ± 0.42	1.01 ± 0.00	1.000	11.11 ± 0.04	0.999
153	11.56 ± 0.67	0.96 ± 0.01	1.000	10.07 ± 0.06	0.998
187	12.10 ± 0.73	0.97 ± 0.01	0.999	10.97 ± 0.06	0.998

Table 3. Acid detergent fiber (ADF) and neutral detergent fiber (NDF) analysis for sugarcane (LCP85-384) mulch residue at different residue ages.

Age of	Average %*		Kd values (mL/g)	
Residue(d)	ADF**	NDF***	Atrazine	Metribuzin
12	47.410	70.895	16.213	9.239
40	47.850	72.475	14.922	9.916
63	50.475	73.595	16.728	10.876
127	51.695	75.470	15.652	11.111
153	52.920	76.770	17.189	10.077
217	53.975	76.155	15.932	10.977

*ADF and NDF are percentages of total dry mass of residue.
**Acid Detergent Fiber (ADF) includes lignin and cellulose.
***Neutral Detergent Fiber (NDF) includes lignin, cellulose and hemicellulose.

Table 4. Mass balance of applied atrazine and metribuzin following 24 hour adsorption, 10 desorptions, and methanol extraction for mulch residue collected 153 days post-harvest (March 20, 2002).

Herbicide	Initial concentration µg/mL	Total amount absorbed µg/g	Total amount desorbed µg/g	Total amount desorbed % of adsorbed	Total amount retained % of input	Amount of Methanol extracted from residue µg/g	Amount of residual % of input
	2.00	17.67	16.05	90.85	2.71	0.37	2.09
Metribuzin	10.00	86.31	76.19	88.29	3.37	1.62	2.83
	20.00	156.52	148.87	95.13	1.27	3.60	0.67
	40.00	299.32	288.49	96.41	0.90	6.47	0.36
	70.00	525.44	499.63	95.08	1.23	10.93	0.71
	100.00	751.59	696.78	92.71	1.83	17.21	1.25
	2.98	38.20	29.51	77.28	9.71	0.28	9.40
Atrazine	5.96	69.22	62.47	90.26	3.78	0.61	3.44
	11.98	139.61	119.70	85.74	5.54	1.28	5.19
	17.96	195.03	174.03	89.46	3.90	1.41	3.64
	23.95	259.23	237.83	91.76	2.98	2.17	2.68
	29.01	313.68	274.54	87.63	4.50	2.25	4.24

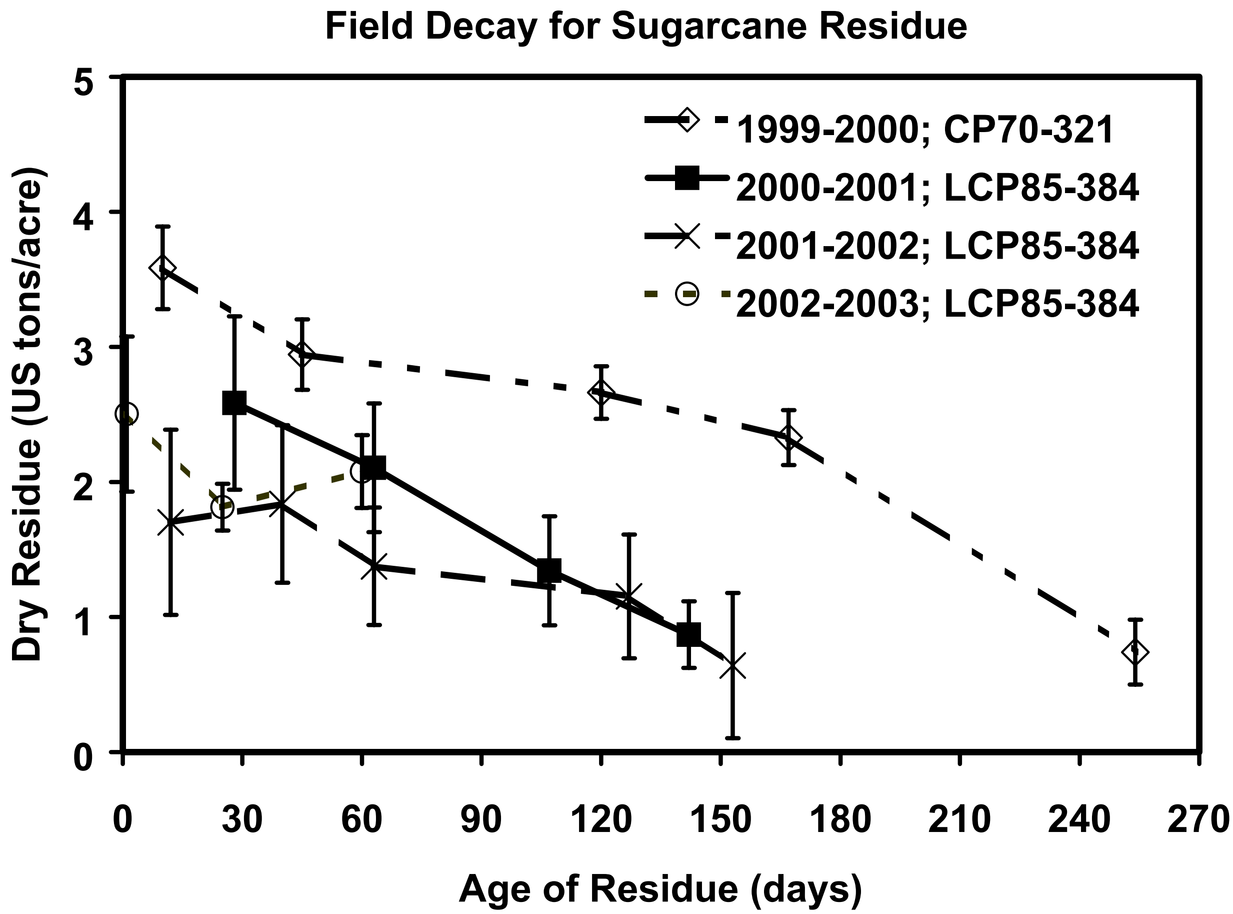

Figure 1. Field decay of sugarcane residue following harvest of CP70-321 and LCP85-384.

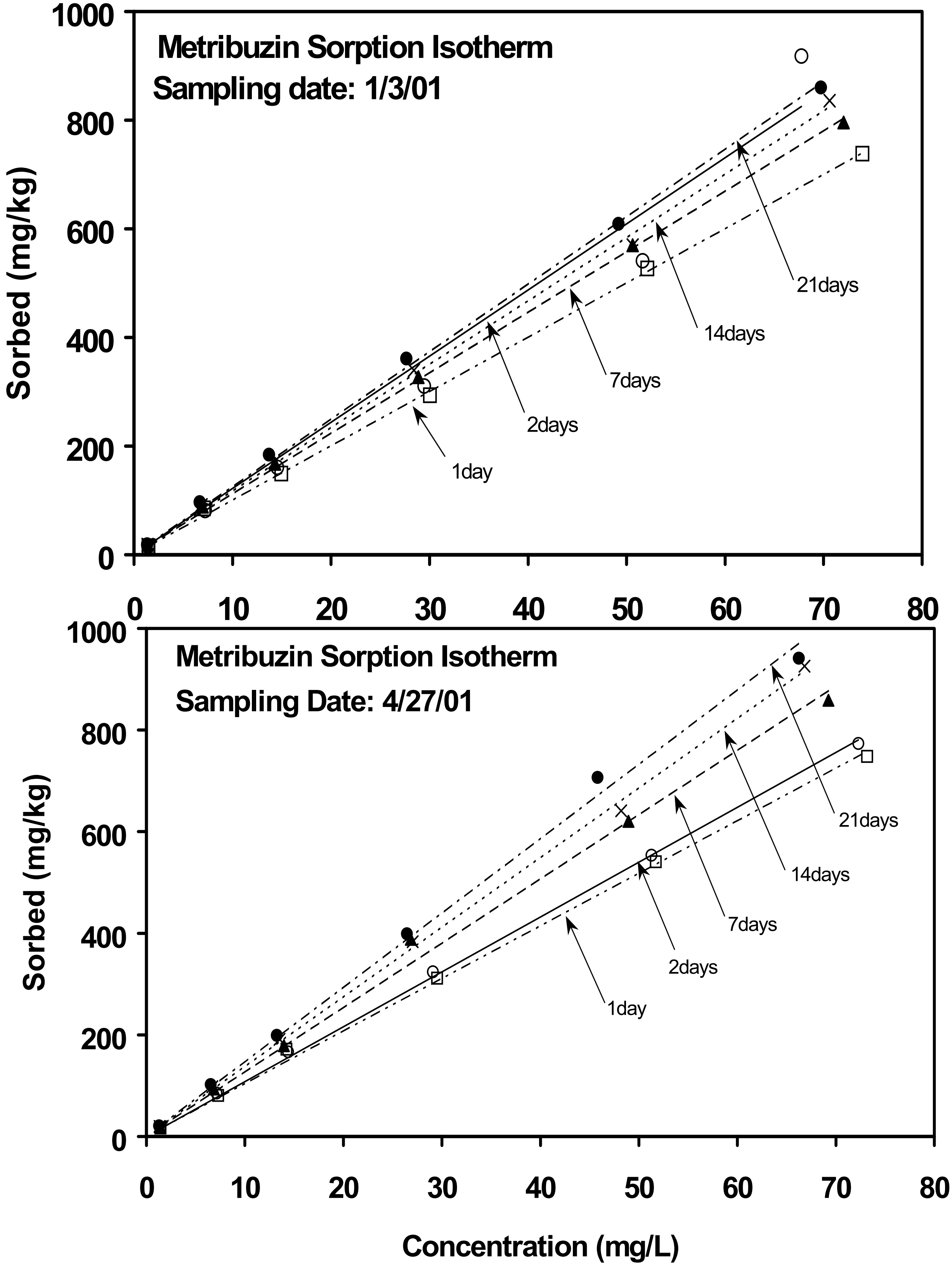

Figure 2. Metribuzin adsorption isotherms by mulch residue sampled on January 3, 2001 and April 27, 2001. The sugarcane (LCP85-384) was harvested on December 8, 2000.

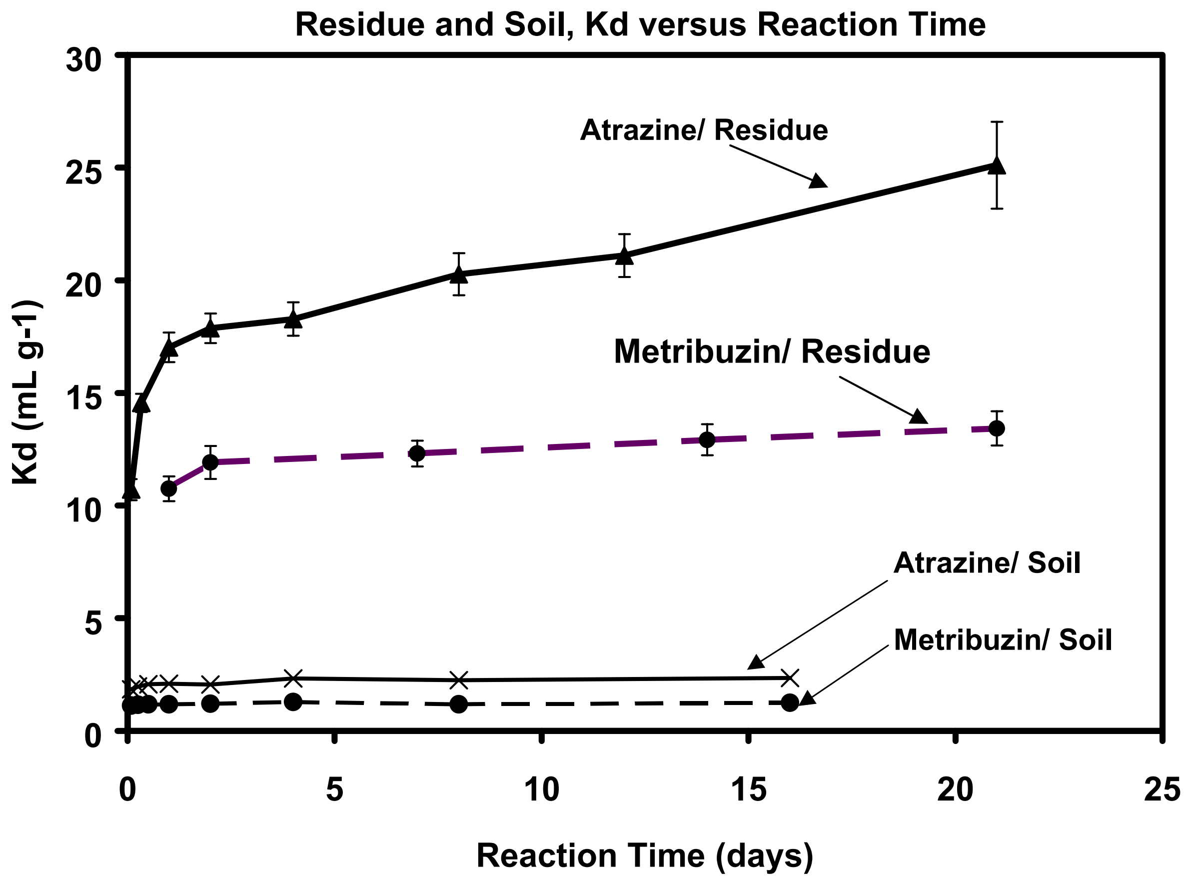

Figure 3. Measured atrazine and metribuzin distribution coefficient (Kd) versus reaction time during adsorption for sugarcane (LCP85-384) mulch residue and Commerce silt loam. Error bars represent one standard deviation.

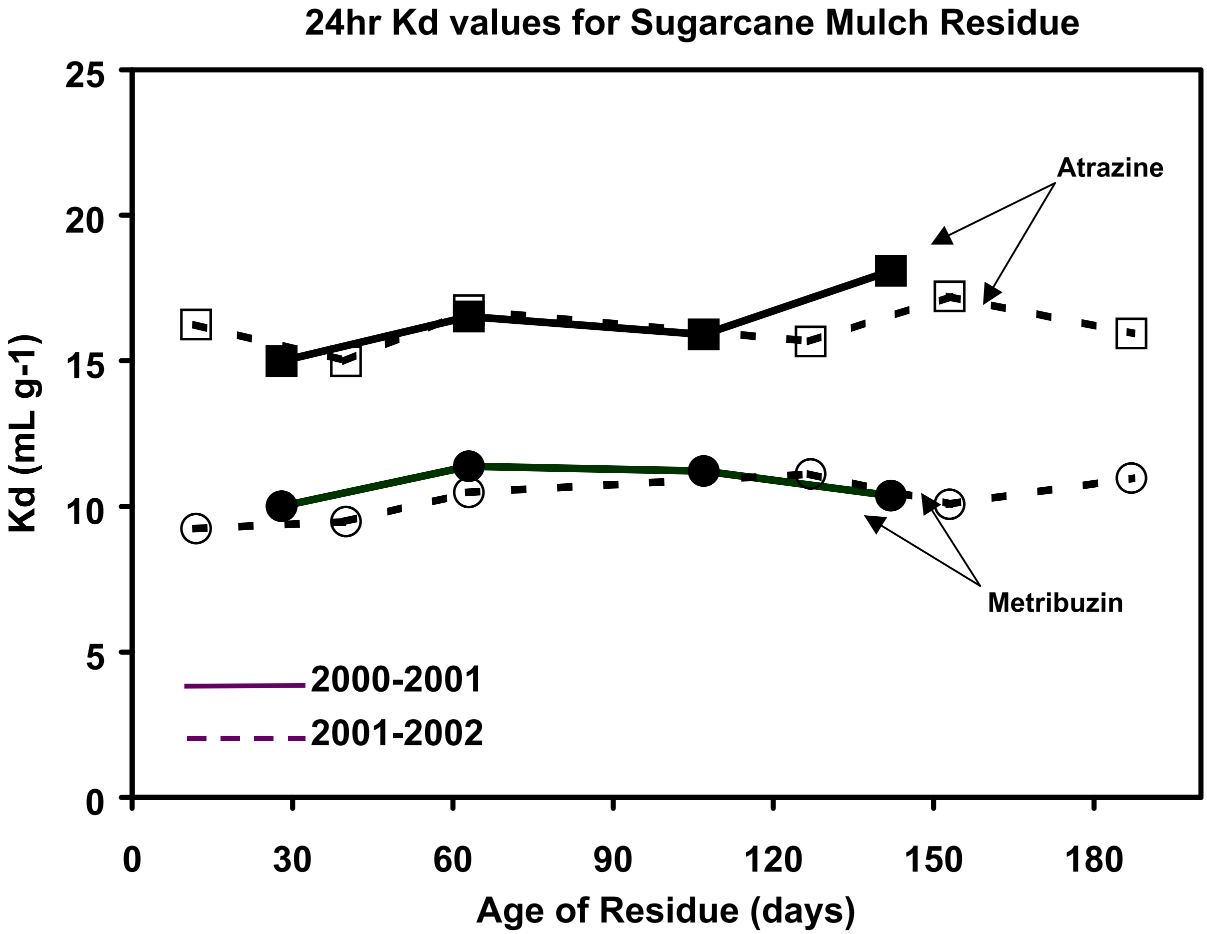

Figure 4. Values of the distribution coefficient (Kd) after 24 hours sorption for atrazine and metribuzin for 2001 and 2002 sugarcane residue (LCP85-384) versus residue age.

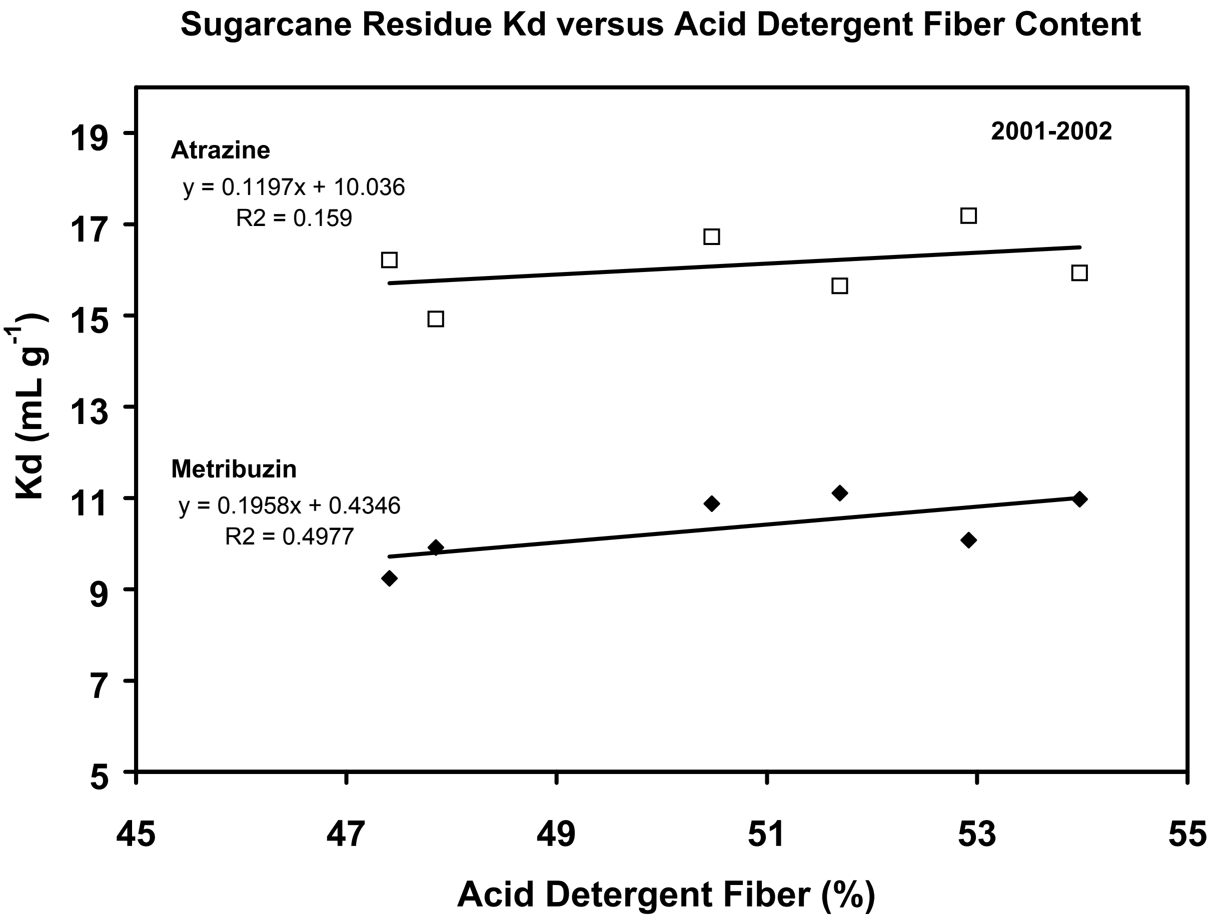

Figure 5. Relationship between atrazine and metribuzin Kd for sugarcane residue (LCP85-384) and acid detergent fiber content at different sampling dates (see Table 3).