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HERBICIDE RETENTION AS AFFECTED BY SUGARCANE MULCH RESIDUE

A Thesis

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by
Brian J. Naquin
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ABSTRACT

Best management practices are used by agricultural producers to control or reduce the transport and generation of contaminants to the water resources of the state, ultimately increasing the quality of surface and ground waters. One such practice is residue management used during sugarcane production. The impact of sugarcane residue may have on the retention and release of two herbicides namely; atrazine and metribuzin was the focus of this study is studied.

Adsorption-desorption and transport behavior of herbicides are important processes that influence the amount of herbicide retained by the soil or crop residue and that which is susceptible to runoff or movement within the soil profile. Kinetic batch experiments were used to study the adsorption-desorption behavior of atrazine and metribuzin in sugarcane mulch residue and two surface soils. Atrazine retention was consistently stronger than metribuzin for both sugarcane residue and surface soils. To describe the retention of atrazine and metribuzin by the residue as it ages and across growing seasons, only one value (K_d) was needed for each herbicide, and this value is an order of magnitude greater then those determined for surface soils. Miscible displacement experiments under steady flow conditions were also carried out to examine the mobility of the metribuzin within soils.

In addition field studies quantified the decay of sugarcane residue in the field following combine harvest. Amounts of residue cover varied with the growing season and variety. Half-lives of 126 to 171 days were determined for sugarcane residue as it remains in the field. With residue age mass decreases leaving greater percentages of more recalcitrant residue such as lignin. Fiber analysis identified these changes, there were no obvious relationships between herbicide retention distribution coefficients and percentage of lignin on a mass basis.

CHAPTER 1. INTRODUCTION

1.1 Literature Review

The sugarcane industry is a large part of Louisiana's agricultural economy, with year 2002 production totaling over 1.27 million tons of sugar a year and employing almost 30,000 residents. Louisiana has a great investment in sugarcane with 198,450 hectares planted a year, with operations this large the impacted areas are significant (USDA, 2004). Recently the environmental effects of sugarcane production have been studied with the main concern being the impact it has on surface and ground water resources. Among different agricultural areas, frequencies of detection were positively correlated with nearby agricultural use for atrazine, cyanazine, alachlor, and metolachlor (Barbash et al, 2001). Monitoring by several governmental agencies has shown atrazine exceeding the maximum allowable level for finished drinking water leaving a treatment plant in 34 communities around the nation, one being the Iberville Water District #3 during late winter for several years (EPA, 2003). Solomon (1996) suggests a subset of surface waters, particularly small reservoirs in areas with intensive use of atrazine, may be at greater risk of exposure. This has raised concern about the applied herbicide on some 20,250 hectares of sugarcane in production that drain into this particular Louisiana water district.

Since the Clean Water Act of 1977 the EPA and related agencies have made an effort to reduce contaminant input to surface and groundwater. This act also has requirements to set water quality standards for all contaminants in surface waters including Maximum Contaminant Levels for atrazine 3 μg/L and metribuzin 200 μg/L. Reducing agricultural contaminants has brought best management programs to the forefront of environmental efforts supported by regulating agencies. The focus of these programs, for both regulatory agencies and producers, has been reducing the movement of sediment and agrochemicals off site while not significantly reducing yield.

Residue management (NRCS Code 344) is a best management practice that has shown the potential for reducing offsite movement of chemicals applied to the field. With the introduction of the combine harvester, the practice of non-burning and leaving the plant residue on the soil surface is becoming a common management practice with sugarcane producers. This practice started in the mid to late 1990's and now has been accepted by more than 90% of growers in Louisiana and other parts in the world such as Australia, South Africa and Brazil.

Besides the obvious benefit of increasing organic matter of the surface soil, non-burning can affect the physical and chemical properties of soil over long periods of time. A 59 year sugarcane management study in South Africa suggests that burning cane before harvest results in long term losses of available Ca, K, and P, along with decrease in cation exchange capacity and aggregate stability (Graham et al, 2002). Also in studies in South Africa, Dominy (2002) observed a large decline in soil organic matter and microbial biomass in two soils ranging from sandy to clayey loam. These soils, were exposed to 50 years of pre-harvest burning of sugarcane. In a study in Brazil by Ball-Coelho (1993) involving the pre-harvest burn of the first ratoon crop, 2600 kg of carbon and 17 kg of nitrogen per hectare were lost by convection, while the post-harvest burn resulted in losses of 4800 kg of carbon and 42 kg of nitrogen per hectare. Yadav (1994) in Lucknow, India completed a study with similar results showing losses of organic carbon and available nitrogen due to trash burning when compared with not burning, there was also a reduction in yield. In a nine year study located in Australia, Noble (2003) measured an increase of 4 tons per hectare of organic carbon in soils under a green trash blanket sugarcane harvest when compared to fields which residue was burned. Similar declines were observed with carbon fractions in Australian sugarcane production due to burning trash (Blair, 2000). Trash mulching at 6 tons per hectare led to marginal improvements in shoot population and cane yield over no mulching (Rana et al, 2003). The losses of soil nutrients such as the ones discussed above, over long time periods due to burn management, reveal how the soil can change. These soil nutrient decreases can affect crop production in the future.

For several decades numerous studies have shown strong affinity of applied herbicides to crop residues in comparison to mineral soils. For example, the sorptive capacity of corn residue was 35 to 60 times greater than that for surface soils (Boyd et al, 1990), while in another study wheat straw grown in Oklahoma exhibited a strong affinity for metribuzin (Dao, 1991). Atrazine retained by the corn stalk residue is subject to dissipation or adsorption processes, thus reducing the amount available for wash-off and movement into the soil by the first rain (Sigua et al, 1993). In Louisiana, Selim (2003) has shown that extractable concentrations of atrazine were at least one order of magnitude higher for the sugarcane mulch residue compared with that retained by a Commerce silt loam soil. In the study presented here we will further describe the retention characteristics of the sugarcane residue and the two herbicides described below.

Atrazine and metribuzin are both common herbicides used extensively in sugarcane production. Atrazine garners the most attention because of the low price and effectiveness across crops. Atrazine is a systemic triazine herbicide, which has been registered since 1958 for the control of broadleaf weeds and grasses. At this time it is one of the two most extensively used agricultural pesticides in the United States. Approximately 29-34 million kilograms of active ingredient are applied per year. Annually, 75% of all field corn, 58% of all sorghum, and 76% of all sugarcane grown are treated with atrazine according to the USDA. Atrazine is formulated as a flowable concentrate, a water dispersible granular (dry flowable), and a granular. Maximum application rates for atrazine range from 0.448 kg to 4.48 kg of active ingredient per hectare and may be applied by groundboom sprayer, aircraft, tractor-drawn spreader, rights of way sprayer, low pressure handwand, backpack sprayer, lawn handgun, push-type spreader, and bellygrinder. The number of maximum allowable applications range from 1 to 4 per season or year however specified. Sugarcane herbicide treatments involve both pre and post emergence applications. These are usually at planting (fall), in the spring after emergence, and an additional post-emergence application (layby)(EPA, 2003). After application there are high herbicide concentrations in the top few mm of soil which can lead to high initial runoff concentrations with early rainfall (Southwick et al. 2003).

Though atrazine is the main focus of much research around the world, metribuzin is also of major concern. Using a Commerce soil Kim and Feagley (1998) performed column studies that resulted in metribuzin being readily leached, indicating the potential for groundwater and shallow aquifer contamination. Metribuzin like atrazine is a triazine herbicide that targets grasses and broadleaf weeds. It is a highly soluble (1200 mg/L vs. 29 mg/L) and expensive alternative to atrazine. The higher Maximum Contaminant Level stated above is the primary factor for metribuzin being considered an alternative to atrazine. Metribuzin is also favored because of the smaller environmental foot print it may leave in areas applied. Moorman (1999) observed metribuzin concentrations half of that of atrazine in groundwater after application to corn and soybean fields. Additionally atrazine was detected in over 90% of soil surface samples whereas metribuzin was rarely detected, almost two years after application.

Since the use of combine harvester is a new technology in Louisiana, the effect of leaving sugarcane residues on the soil surface post harvest has not yet been fully explored. Residue management may cause changes in the properties of the chemistry, and microclimate of soil, therefore affecting volatilization, degradation, and uptake of pesticides. Research elsewhere has shown that the organic matter fraction has a significant impact on the sorption of organic chemicals. Shelton (1998) compared a 4-year no-till soil with a 4-year plow-till soil under corn production. The increased organic matter content in the top 0 to 1.5 cm of the no-till resulted in partitioning values that were consistently higher because of increased sorption. Considering sugarcane residue provides more than 90% ground cover at masses greater than 2.68 tons per hectare (Thorburn et al, 2001), this management practice can have a considerable impact on the fate of herbicides in Louisiana soils. Dao (1995) found that under continuos wheat straw cover, no-till soil had elevated organic carbon concentrations in the near-surface zone and showed a two to fivefold increase in metribuzin retention in the 0 to 0.15 m depth. These studies have shown the environmental changes that take place at the soil surface of residue management implemented sites.

Previous studies have also revealed that in the presence of residue cover there is a decrease in net runoff, when compared to no residue, which is the primary goal of residue management. A minimum of 50% reduction in runoff effluent concentrations for atrazine and pendimethalin was realized when the sugarcane mulch residue was not removed (Selim, 2003). In a south Louisiana study atrazine lost 84 to 96% of the seasons losses within the first two rain events of the season (Southwick et al. 2003). Attributed to corn residue cover left on the soil surface, average concentration of atrazine from conventional tillage was about 17% less from no-till (Seta et al, 1993). Dabney (2004) concluded that the resistance of erosion is not only due to the presence of corn residue cover, but also to the improved soil quality resulting from this practice. After conducting studies of herbicide runoff of sugarcane fields, Southwick et al. (2002) noted crop residue management as a possible solution to decreased herbicide contribution to south Louisiana water quality.

Residue cover, commonly known as the trash blanket, causes many changes in field conditions that influence herbicide sorption, desorption or release and eventual fate in the environment. One change includes the age of residue in the field and possible changes to sorptive properties or characteristics. According to Benoit and Preston (2000) when wheat straw was decomposed for six months prior to the introduction of ^{14}C-labelled atrazine, herbicide mineralization was enhanced to 50% of the initial ^{14}C in contrast to 15% of the initial ^{14}C in soil alone and soil amended with fresh straw. Dao (1995) has shown that as wheat straw ages, lignin on mass basis increases resulting in increased sorptive capacity of wheat straw on said mass basis. Similar lignin based studies show measurements of desorption in respective steps indicated that 62% of metribuzin was adsorbed irreversibly and cannot be leached over a period of 24 hours (Ludvík and Zuman, 2000). Other studies have suggested that freshly cut cover crops reduced leaching more than aged corn stalk residue from the previous harvest (Sigua et al, 1993).

The age of residue is not the only important time factor. The amount of time in which the herbicide has been in contact with the environment also plays a roll in its fate. This process is referred to as "aging". According to Lavy et al (1996), there is increasing evidence that shortly after herbicide application dissipation processes occur at different rates. If degradation of atrazine does occur in the subsoil, it starts after a lag phase of five days in an unsaturated zone to more than 25 days in a saturated zone. The disappearance of atrazine is then rapid, with a high mineralization rate. The lag phase is due to the build-up of microbial population (Vanderheyden et al, 1997). With time in the field herbicides bind more strongly, consequently herbicide losses are greatly reduced when runoff events occurred later in the season because of herbicide degradation and binding of herbicide to soil particles (Gaynor et al, 1995). Not only does residue seem to hold the herbicide in the field longer, it may also promote microbial activity. With a relatively high carbon to nitrogen ratio from soybean residue the imbalance of microbial appetite results in the use of herbicide for nitrogen source, resulting in cleavage of nitrogen or sulfur, for metribuzin (Locke and Harper 1991). One study found the proportion of bound residues increased with the total microbial activity after addition of various organic amendments (i.e., glucose, straw, cellulose and humified organic matter) or organic nitrogen forms (i.e., adenine, arginine, albumin, biuret and pyrazine) (Abdelhafid, 2000). A factor influencing increased microbial and chemical degredation is temperature. Savage (1977) stated that the degradation rate of metribuzin was significantly influenced by temperature, with more rapid degradation at 30º C than at 20º C. This can be important as the blanket of residue changes the temperature at the soil surface where the herbicides are bound. In addition photodegradation in the soil surface is accelerated as the percentage of organic matter increases (Konstantinou et al, 2001).

The effect of leaving residue blanket on the soil surface post harvest on the soil organic matter of the top soil surface layer has not been fully investigated in Louisiana soils. Soil organic matter is often considered the dominant sorptive phase for organic contaminants and pesticides in soil-water systems (Sheng et al, 2001; Martin-Neto et al, 2001). Multiple regression of the adsorption constants against selected soil properties indicated that organic matter content was the best single predictor of atrazine adsorption ($r^2 = 0.98$) followed by soil pH ($r^2 = 0.82$) (Jenks et al, 1998). Many different soil types have been studied with the same conclusion, emphasizing the importance of organic matter and related fractions. Citing that the K_d values were strongly and significantly correlated to the organic carbon content ($r^2 = 0.84$), Seybold (1994) concluded that the organic fraction is the most important constituent for adsorption of atrazine in sandy soils that contain small amounts of organic matter and clay. Studies of soils from both Iowa and South Carolina have also reported that the magnitude of atrazine sorption was strongly and positively correlated with soil organic carbon (Novak, 1999). Some research has focused on more specific sorption mechanisms such as organic carbon and humic matter. Piccolo (1998) states that hydrophobic interactions and conformational flexibility in the aliphatic portions of humic matter controlled the adsorption of atrazine in the interior of humic self-associated aggregates and the degree of desorption found both in water and methanol. Sorption-desorption of atrazine and simazine was more hysteretic for humic acid than for montmorillonite, indicating that these herbicides desorb more difficultly from organic matter than from montmorillonite because of the contribution of hydrophobic interactions with humic acid (Celis et al, 1997).

Soil pH also has an influence on the fate of herbicides in the environment, and the addition of crop residue to the soil surface may create a pH shift in the top layer. Studies are consistent in showing the mobility and bioavailability of herbicides in soils is expected to be lower at low pH than at high or neutral pH (Weber, 1993). While pH does have an influence on sorption it is still organic matter that has the greatest impact. Martinezinigo and Almendros (1992) reported the lowest pesticide retention for samples of the soil with the highest pH, where the addition of organic matter led to the greatest enhancements. Again when the various physical, chemical, and biological properties involved with the residue management program are evaluated we have a delicate balance. This balance can be shifted in many different directions. The research presented through this study can certainly contribute to the growing knowledge in this important area of environmental and agricultural relations.

1.2 Objectives

The purpose of this study was to examine the ability of sugarcane mulch residue in reducing non-point source contamination of applied agrochemicals namely atrazine and metribuzin from sugarcane fields, in south Louisiana. To accomplish this goal a number of properties characterizing the relationships between the sugarcane mulch, soil and chemicals were quantified. Overall the objective of this work was to quantify the retention of atrazine and metribuzin by the sugarcane mulch and to characterize their kinetic behavior in soil. Field and laboratory studies carried out to investigate the retention kinetics of atrazine and metribuzin by the mulch residue as well as soils. Multiple residue samples were collected post harvest ranging from 1 day to 212 days from three growing seasons, in order to assess changes in herbicide retention characteristics as a function of the age of the mulch residue as it degrades in the field. Adsorption-desorption studies of herbicide retention by the sugarcane mulch residue were carried out to assess atrazine and metribuzin release behavior and to quantify amounts that are water soluble or readily desorbable herbicide phases over time.

Collectively these studies are a prerequisite to correlate the effectiveness of crop residue remaining on the soil surface, following sugarcane harvest, as a best management practice. Such information is also necessary to predict the ability of residue to retain applied herbicides, buffer losses from runoff, and retard downward movement in the soil profile.

CHAPTER 2. MATERIALS AND METHODS

2.1 Chemicals

Two triazine herbicides were used in this study; namely atrazine (6-chloro-*N*^{2}-ethyl-*N*^{4}-isopropyl-1,3,5-triazine-2,4-diamine) and metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one). A stock solution containing 29.8 mg/L 99.1% pure atrazine was prepared in 0.005 M $CaCl_2$. ^{14}C labeled atrazine with a specific activity of 42.6 µCi/mg was used in this study as a tracer to monitor the extent of atrazine retention by the different residue and soils. This radio-labeled material was provided by Syngenta, Greensboro, NC. Six ^{14}C atrazine spiked atrazine solutions having initial concentrations (C_i) of 2.98, 5, 11, 17, 23 and 29.8 mg/L in 0.005 M $CaCl_2$ aqueous solution were used in our study.

Similar to atrazine as discussed above, a stock solution containing 98.9 mg/L, 99% pure unlabeled metribuzin was prepared in 0.005 M $CaCl_2$. ^{14}C labeled metribuzin with a specific activity of 150µCi/mg was used in this study. This radio-labeled material was provided by Bayer Laboratories, Stillwater, Oklahoma. Six ^{14}C metribuzin spiked metribuzin solutions having initial concentrations (C_i) of 2, 10, 20, 40, 70 and 98.9 mg/L in 0.005 M $CaCl_2$ aqueous solution were also prepared for subsequent use in kinetic retention studies.

2.2 Sample Collection of Mulch Residue

Bulk samples of sugarcane residue variety LCP85-384 were collected from field plots at the St. Gabriel Sugarcane Research Station. On October 2, 1999 the sugarcane was planted, in a Sharkey clay soil (very-fine, smectitic, thermic chromic epiaquerts), at 1.8 m row spacing and 200 m in length. Harvesting was carried out on December 8, 2000 for the plantcane, October 22, 2001 for first stubble and November 24, 2002 for second stubble growing season.

A Cameco® (Thibodaux, LA) sugarcane harvester was used for combine harvest. The combine cuts the standing cane stalks into billets, which are directly loaded into wagons for transport to the mill. Extractor fans in the combine harvester separate leaf-material from billets and the plant residue is deposited on the soil surface. This process leaves a blanket of residue on the field post harvest averaging 6.72 tons/ha.

Mulch samples were collected multiple times following combine harvest of the crop, generally at 30 day intervals. The residue was air dried in the laboratory and cut into 1 cm sections for herbicide retention studies. Residue not immediately used was stored at –20 °C for later herbicide retention and transport investigations. The surface layer of the Sharkey clay along with a Commerce silt loam (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts) were also sampled for this study from the St. Gabriel Research Station, located 12 miles south of Baton Rouge, LA.

2.3 Herbicide Adsorption

Adsorption by the sugarcane mulch residue was carried out using the batch equilibration technique. This technique was described in detail by Zhu and Selim (2000) and Selim (2003). Six ^{14}C-atrazine/metribuzin spike samples having initial concentrations (C_i) ranging from 2.98 to 29.8 mg/L for atrazine and from 2 to 98.9 mg/L for metribuzin in 0.005 M $CaCl_2$ were used. Adsorption was initiated by mixing 1 g of dried and cut sugarcane residue with 30 mL of the solutions various herbicide concentrations in a 40 mL Teflon centrifuge tube. Triplicate samples were used. Weights of each component were recorded along with the total combined weight so that a mass balance can be achieved. The mixtures of residue and herbicide solution were kept continuously shaking on a Thermolyne rotator/shaker at 200 rpm. After each specific reaction (sampling) time, the samples were centrifuged at 3500×g for 10 minutes on a Beckman GPR centrifuge (Fullerton, CA) at 25°C.

A 0.5 mL aliquot was sampled from the supernatant at each reaction time ranging from 24 to 504 hours, and deposited into a 7 mL scintillation vial with foil lined cap. The slurries were then weighed, vortex mixed and returned to the shaker after each sampling. The 0.5 mL aliquot was subsequently mixed with 5 mL of scintillation cocktail (Packard Ultima Gold, Meriden, CT) and analyzed using a Packard Tri-Carb 2100TR Liquid Scintillation Analyzer (LS), (Meriden, CT). The amount of pesticide retained by the residue at each reaction time was calculated from the difference in concentrations of the supernatant and that of the initial solution.

2.4 Herbicide Desorption or Release

Desorption of the two herbicides commenced immediately after the last adsorption time step (504 h). Each desorption step was conducted by replacing the supernatant with herbicide free 0.005 M $CaCl_2$ solution and shaking for 24 hours. This was accomplished by centrifuging the slurry at 3500 rpm for 10 minutes. The weight of total solution, residue and tube was recorded in order to keep a mass balance. The supernatant was then decanted leaving only the saturated residue in the tube. The tube and saturated reside was then subsequently weighed. Once weighed, 25 mL of 0.005 M $CaCl_2$ solution was added to each tube. A 0.5 mL sample was taken at each step and herbicide in solution was analyzed using same scintillation technique from adsorption studies. This desorption procedure was repeated for six consecutive steps for a total desorption time of six days.

After the last desorption step the solution was decanted as described above an additional extraction step of the amount of the residual herbicide retained by the residue was made. In this step, the decanted solution was replaced with a 4:1 methanol/water solution and was kept on the shaker for 24 hour as above. This methanol extracting solution is routinely used for herbicide extractions from soil samples from field and laboratory experiments (Johnson and Furman, 1993; Selim et al. 2003)

The amount of herbicide retained by the mulch residue versus time during sorption and desorption was calculated based on mass balance and the change in herbicide concentration in the solution phase.

2.5 Herbicide Adsorption – Desorption by Sugarcane Residue

As stated in the objectives, our primary goal of this study was to quantify the retention of atrazine and metribuzin by the sugarcane mulch and to characterize their kinetic behavior in soil. To achieve this objective, we quantified herbicide retention by the mulch residue following cane harvest using the combine harvester over a 3 successive growing seasons; i.e., for plant cane, and first and second stubbles, respectively. This was carried out during 2000 through 2003 at the St. Gabriel Research Station. The sugarcane variety was LCP85-384 which was planted October 2, 1999 and the soil was Sharkey clay soil which is widely grown to sugarcane in south Louisiana. Residue sampling and sorption-desorption experiments carried out during these three growing seasons are described below.

2.5.1 Plant Cane

The sugarcane was combine harvested on December 8, 2000. Residue samples were collected on January 3, February 7, March 23, and April 27, 2001. Batch equilibration was carried out on the residue from each sampling date. The herbicide reaction times chosen were 24, 48, 136, 336, and 504 hours. The multiple sampling dates were used to investigate the effects of residue aging in the field on herbicide kinetics. Residue ranging from 26 to 140 days in the field were compared.

2.5.2 First Stubble

Residue samples collected following first stubble harvest on were used in 24 hour batch equilibration. Cane harvest was carried out October 22, 2001. A 24 hour equilibration retention for both atrazine and metribuzin was carried out for all samples collected on October 30, November 26, December 20, of 2001, February 22, March 20, May 23, of 2002. This resulted in 24 hour retention values for atrazine and metribuzin on residue ranging in age from 12 to 187 days post harvest.

We also focused on the desorption of both atrazine and metribuzin, for one sampling date namely that of March 20, 2002. The residue sample used had the retention time limited to 24 hour batch equilibration which was subsequently followed by ten consecutive 24 hour desorption steps (10 days) for a total of eleven days. This was carried out in order to quantify the extent of release of each herbicide after equilibrium was reached.

2.5.3 Second Stubble

The second and final stubble of variety LCP85-384 was harvested on November 24, 2002. Residue samples were collected on November 25, December 20, 2002 and January 24, 2003. Batch equilibration studies with reaction times of 8, 24, 48, 136, 336, and 504 hours were carried out followed immediately by six 24 hour desorption steps, using January 24 sample. In addition all sampling dates underwent a 24 hour adsorption study.

2.6 Herbicide Adsorption by Soils

In a separate experiment, atrazine and metribuzin retention by the Sharkey clay surface soil where the sugarcane was grown was measured in a similar fashion as that for the mulch residue. Furthermore, herbicide retention was also carried out on a surface Commerce silt loam soil (fine

Table 2.1. Selected physical and chemical properties of the Sharkey and Commerce soils

Soil	Sand	Silt	Clay	pH	Organic Matter	Cation Exchange Capacity
	---------------%---------------				%	meq/100g
Sharkey	3.0	36	61	6.48	1.41	39.4
Commerce	30	54	16	5.93	1.31	21.8

silty, mixed, nonacid, thermic Aeric Fluvaquents) from an experimental site some 1 Km from the Sharkey plots. The only exception was that in the batch study the soil-to-herbicide solution ratio used was 15 g of air-dried soil (in triplicates) mixed with 30 mL of atrazine or metribuzin solution. The range of input or initial atrazine and metribuzin concentrations (C_i) in 0.005 *M* $CaCl_2$ as the background solution was similar to that used for the mulch residue. Moreover, the reaction times for sorption were 8, 24, 48, 136, 336, and 504 h. Six desorption steps were carried out following the 504 h adsorption step with a total desorption time of six days. Following the sixth step, one further extraction using pure methanol was carried out. The Commerce soil was selected because of recent studies of sugarcane mulch residue and the influence on herbicide runoff (Selim et al., 2003, 2004). Moreover, sugarcane is widely grown on both soils in south Louisiana. Table 2.1 lists soil properties of Commerce and Sharkey soils.

2.7 Residue Decay

To assess the effect of the presence of a surface mulch residue on the retention of herbicides, the rate of decay of the sugarcane residue was quantified. Following plantcane, first stubble and second stubble combine harvest of variety LCP85-384, the sugarcane mulch residue was collected from the surface soil. Also collected was variety HoCP91-555 grown on a Commerce silt loam, for the plantcane and first stubble. The sugarcane residue covers row tops and lies in furrow, and is not uniform throughout the field.

Residue was collected randomly by measuring multiple 1 m^2 areas while all visible leafy residue within each area is collected by hand; billets were not included. Each date 6 – 8 samples were collected to obtain an average for each field. During collection the residue was placed in plastic bags to be weighed. A sub-sample of the residue was transferred to a smaller paper bag and placed in the oven for 24 hours at 55°C. Weights were recorded and moisture was calculated.

Following the first sample collection just after harvest samples were taken roughly on a monthly basis until fields off-barred in the spring. When approaching 200 days post harvest the residue had decayed and mixed with the surface soil through weather events and use of field equipment. Collecting residue past this time proved not practical.

2.8 Fiber Analysis

The sugarcane residue collected for field decay measurements were also used for fiber analysis. This residue was air dried and ground to a powder using a Foss Tecator Cyclotec® 1093 sample mill. The ground residue then placed in glass jars and rolled for homogeneity using a New Brunswick Scientific company RC-41 Rollacell®. The residue from the plantcane and first stubble of both variety LCP85-384 and variety HoCP91-555 was analyzed for neutral detergent fiber (NDF) and acid detergent fiber (ADF) which was carried out at the Louisiana State University Agricultural Center's Southeast Research Station at Franklin, LA.

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). The content of lignin, cellulose and ash was also determined using further steps. Using methods described by Goering and Van Soest (1970) in USDA Agriculture handbook 379, the ADF fraction is additionally dissolved with 72 percent sulfuric acid removing the cellulose. The residue undergoes ashing which leaves the crude lignin fraction including cutin.

2.9 Miscible Displacement Setup

To obtain metribuzin breakthrough curves (BTCs) for various soils and soil and sugarcane residue mixtures, we conducted several miscible displacement experiments under steady state and saturated flow conditions (Selim and Amacher, 1997). To achieve this, plexiglass columns (6.4 cm i.d.) were uniformly packed with air-dried media whether soil alone or a mixture of residue and soil. Full column saturation was achieved by slowly introducing 0.005 M $CaCl_2$ solution at the bottom of the column, where upward flow was maintained and a constant flux was controlled by a piston pump (Figure 2.1). After saturation, each column received approximately one pore volume of tritium (^3H_2O) in 0.005 M $CaCl_2$ used as a tracer solution. This was carried out to obtain the hydrodynamic dispersion of individual soil columns (Selim and Zhu, 2002). Several pore volumes of the background solution (0.005 M $CaCl_2$) was introduced in order to flush the column of the applied tritium.

The herbicide used in all five of the column studies is a ^{14}C-labeled metribuzin solution having a concentration of 100 mg/L. This was the same stock solution used for the batch experiments discussed earlier. To monitor the mobility and retention of metribuzin through the soil column, the effluent flowing from the top of the column was collected using an ISCO Retriever II fraction collector (Model RTRV II). During flow an average of 5.34 mL of effluent was collected every 30 minutes in a 7 mL glass vial. Both tritium and metribuzin samples collected from outflow were analyzed using a liquid scintillation counter which was described earlier. This allowed a defined breakthrough curve for each pulse introduced into the columns. Five column studies were performed in total. The various physical properties for each of the soil columns are listed in Table 2.2. Flow interruption was implemented to maximize the influence of non-equilibrium on metribuzin transport behavior (Murali and Aylmore, 1980; Ma and Selim 2005).

2.9.1 Commerce Soil and Metribuzin

Two columns (hereafter referred to as 13 and 14) each 15-cm in length, containing Commerce silt loam soil received a different sequence and amount of ^{14}C-labeled metribuzin pulse input, interruptions and leaching using $CaCl_2$ background solution. Each column was packed to an average bulk density of 1.18 g/cm^3. Column 13 received a total of 17.7 pore volumes of metribuzin, with a 4 day interruption following 7.9 pore volumes, and 9.8 pore volumes. The mass of the dry packed column and the mass of the column after full saturation was recorded used to determine the solution filled pore spaces, giving a value of one pore volume. After each pulse of metribuzin the flow was stopped or interrupted for a 4 day interruption. Following the last interruption the column was leached out using the 0.005 M $CaCl_2$.

Column 14 three metribuzin pulses were introduced. The metribuzin first pulse of was 5.25 pore volumes followed by 1.87 pore volumes of $CaCl_2$ solution and a 4 day interruption. The second metribuzin pulse of 5.35 pore volumes was followed by 1.64 pore volumes of $CaCl_2$ and a 4 day interruption. The third and final pulse of metribuzin contained 4.82 pore volumes followed by 2.12 pore volumes of $CaCl_2$, we then paused flow for 4 days and leached out.

2.9.2 Soil with Sugarcane Residue

Three plexiglas columns (hereafter referred to as 15, 16 and 17) each 10-cm in length, were uniformly packed with a mixture of soil and sugarcane mulch residue. Approximately 15 g of air dried residue cut into 1 cm sections was mixed with the soil at two depths, 1.5 cm from each end. The residue was collected 153 days after the first stubble harvest of variety LCP85-

384. The two surface soils used in this experiment were: Commerce silt loam (column 16) and Sharkey clay (column 17) (see Table 2.1), in addition one column was packed with reference acid washed sand and sugarcane residue(column 15). The reference sand was used in order to assess the retention of residue in a media with no retention (Selim and Zhu, 2002). Bulk densities of 0.802, 0.845, and 1.15 g/cm^{-3} were recorded for the soil columns packed with Commerce, Sharkey, and sand respectively. The percentage of mulch versus soil on a mass basis averaged 0.0526%. After the tritium pulse described above, each column was subjected to leaching with 0.005 M $CaCl_{2.}$ While the ^{14}C-labeled metribuzin pulse was being introduced into the column an interruption took place. This interruption occurred following pore volumes measuring 3.49, 3.82, and 4.09 for columns 13, 14 and 15 respectively. An interruption of 4 days occurred before the . The sand received 5.00 pore volumes while the commerce passed 3.99 pore volumes and the Sharkey 5.24 for the second pulse. Another 4 day interruption was implemented before the final leaching using 0.005 M herbicide free $CaCl_2$. The average darcy velocity for the three soils was 1.15 cm/h.

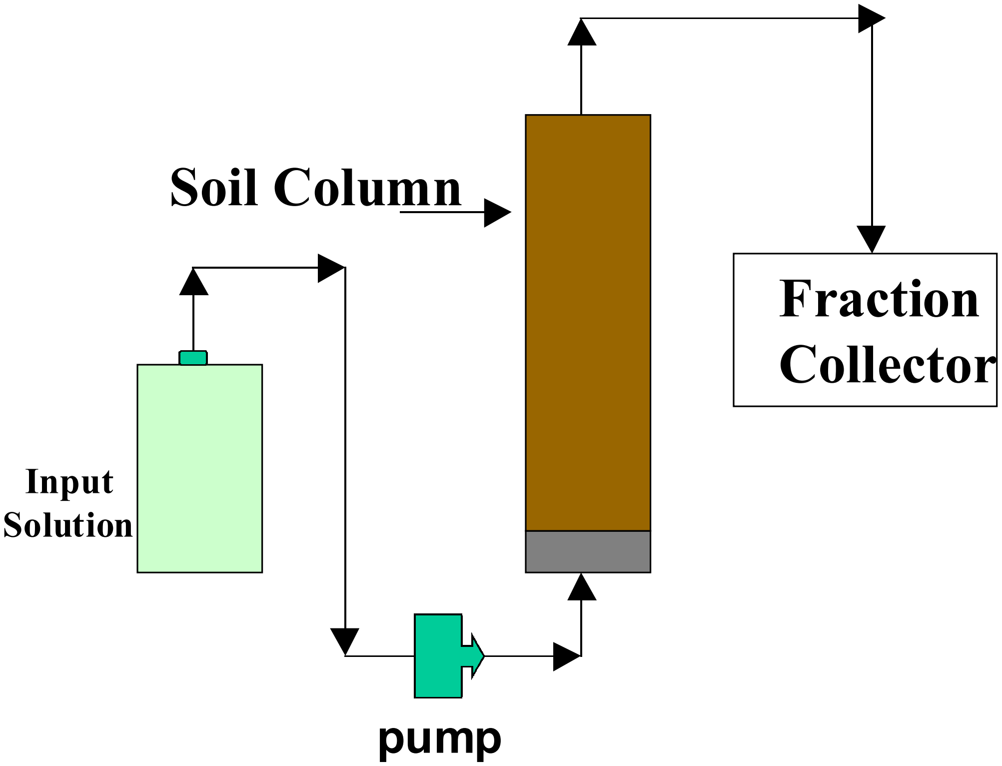

Figure 2.1 Diagram of laboratory setup of miscible displacement experiment equipment.

Table 2.2 Soil properties and experimental conditions of individual columns of the miscible displacement experiments.

Note: All columns received 0.005M $CaCl_2$ as background solution, all column i.d. = 6.4 cm. Column 14 underwent 3 pulses resulting in total. pv= pore volume.

Column ID	Soil Name	Soil Weight	Mulch Weight	Column Length	Column Volume	Bulk Density	Pore Volume	Mulch Percent	Darcy Velocity	Metribuzin Recovery	Total Pulse
	(series)	(g)	(g)	(cm)	(cm3)	(g/cm3)	(cm3)	(g/g)	(cm/h)	(%)	(pv)
13	Commerce	589	n/a	15	497.7	1.183	292	n/a	0.98	64	17.7
14	Commerce	587	n/a	15	497.7	1.179	265	n/a	0.92	104	15.4
15	Sand	356	15.61	10	321.5	1.156	148	0.042	1.04	66	8.49
16	Commerce	242	15.89	10	321.5	0.802	210	0.062	1.16	87	7.81
17	Sharkey	257	14.76	10	321.5	0.845	188	0.054	1.24	62	9.33

CHAPTER 3. RESULTS AND DISCUSSION

3.1 Isotherms

Following the laboratory adsorption studies described above, adsorption isotherms were created to represent the amount of herbicide sorbed by the sugarcane residue versus concentration of the herbicide remaining in solution. These relationships clearly illustrate the affinity of atrazine and metribuzin by the mulch residue as well as the extent of retention with time of reactions and age of the mulch.

The relationship between the sugarcane residue and the herbicide is commonly described by an adsorption isotherm. In this study our isotherms were described using either a linear type model, (Selim, 2004)

$$S = K_d C \qquad [1.1]$$

or nonlinear (Freundlich) type equilibrium model, (Selim, 2004)

$$S = K_f C^N \qquad [1.2]$$

where S is the amount of herbicide sorbed (mg/kg soil), C is concentration in the soil solution (mg/L). The linear parameter K_d (mL/g) is the distribution coefficient which is widely reported in the literature, and represents a measure of affinity of the herbicide to the matrix, in this case residue, K_f is a Freundlich partitioning coefficient (mL/g), and N is a dimensionless parameter commonly less than unity.

3.2 Herbicide Adsorption – Desorption by Residue

3.2.1 Plant Cane

The sugarcane residue exhibited increased adsorption with each increase in retention time (see Table 3.1). Although the behavior of adsorption for the two herbicides was described well by both linear and Freundlich models, the N values close to 1.0 clearly indicate that retention can be well described as a linear mechanism. In addition, there was no obvious trend for N versus retention time. In fact, such a finding was consistent for both atrazine and metribuzin as indicated in Tables 3.1 and 3.5. The lack of nonlinear or concentration dependent behavior of the sorption patterns is indicative of the lack of heterogeneity of sorption site energies (Selim and Zhou, 2005). Rather, sorption by mulch residue is best regarded as homogenous or uniform. The linearity of these adsorption isotherms leads to the use of K_d values when describing the affinity of the two herbicides by sugarcane residue. Specifically for atrazine the K_d values increased from 15.90 to 20.08 mL/g after 24 and 504 hours, respectively, while metribuzin increased from 11.20 to 14.72 mL/g after 24 and 504 hours, respectively. The K_d values indicate that the kinetic behavior of metribuzin adsorption by sugarcane residue is not as strong as for atrazine (see Table 3.1). This may be due to the higher solubility of metribuzin. Evaluating K_d values from 24 through 504 hours we see that strong adsorption occurred during early reaction times, and was followed by subsequent slower rates of reactions (see Figures 3.1 and 3.2).

Samples collected post harvest, with ages ranging from 26 to 140 days were compared (see Table 3.2). In the growing seasons, adsorption characteristics were compared to examine the effect each consecutive growing season may have on adsorption of both herbicides for first and second stubble cane. The 24 hour K_d values from each age of residue was compared over time, average K_d values were 16.38 ± 1.30 and 10.70 ± 0.63 mL/g for atrazine and metribuzin respectively. As shown in Figure 3.4 there is no obvious upward trend with time as the residue decays in the field.

3.2.2 First Stubble

The effect of weather-induced changes and natural field degradation of the sugarcane residue on adsorption was investigated based on 24 hour adsorption studies as discussed earlier. The residue was sampled from 12 to 217 days in the field post-harvest (see Table 3.3). As with the plant cane, atrazine retention by the residue from first stubble was much higher than that for

Table 3.1. 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, following Plantcane harvest.

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 3.2. Estimated linear and Freundlich model parameters (with 95% confidence interval) for atrazine and metribuzin adsorption by the sugarcane mulch residue (var. LCP85-384). The residue was sampled at several dates following Plantcane sugarcane harvest of December 8, 2000.

Sampling Date	Age of Residue (days)	Linear Model K_d (mL g^{-1})	Freundlich Model K_f (mL g^{-1})	Freundlich Model N
Atrazine				
03-Jan-01	26	14.99 ± 0.15	18.27 ± 1.11	0.92 ± 0.02
07-Feb-01	61	16.52 ± 0.13	19.48 ± 0.87	0.93 ± 0.01
23-Mar-01	105	15.90 ± 0.22	19.36 ± 1.82	0.92 ± 0.03
27-Apr-01	140	18.09 ± 0.13	20.70 ± 0.97	0.94 ± 0.01
Metribuzin				
03-Jan-01	26	10.00 ± 0.15	13.05 ± 0.80	0.96 ± 0.01
07-Feb-01	61	11.29 ± 0.49	10.11 ± 4.93	1.02 ± 0.12
23-Mar-01	105	11.20 ± 0.20	13.72 ± 2.46	0.94 ± 0.04
27-Apr-01	140	10.36 ± 0.10	13.31 ± 1.18	0.93 ± 0.02

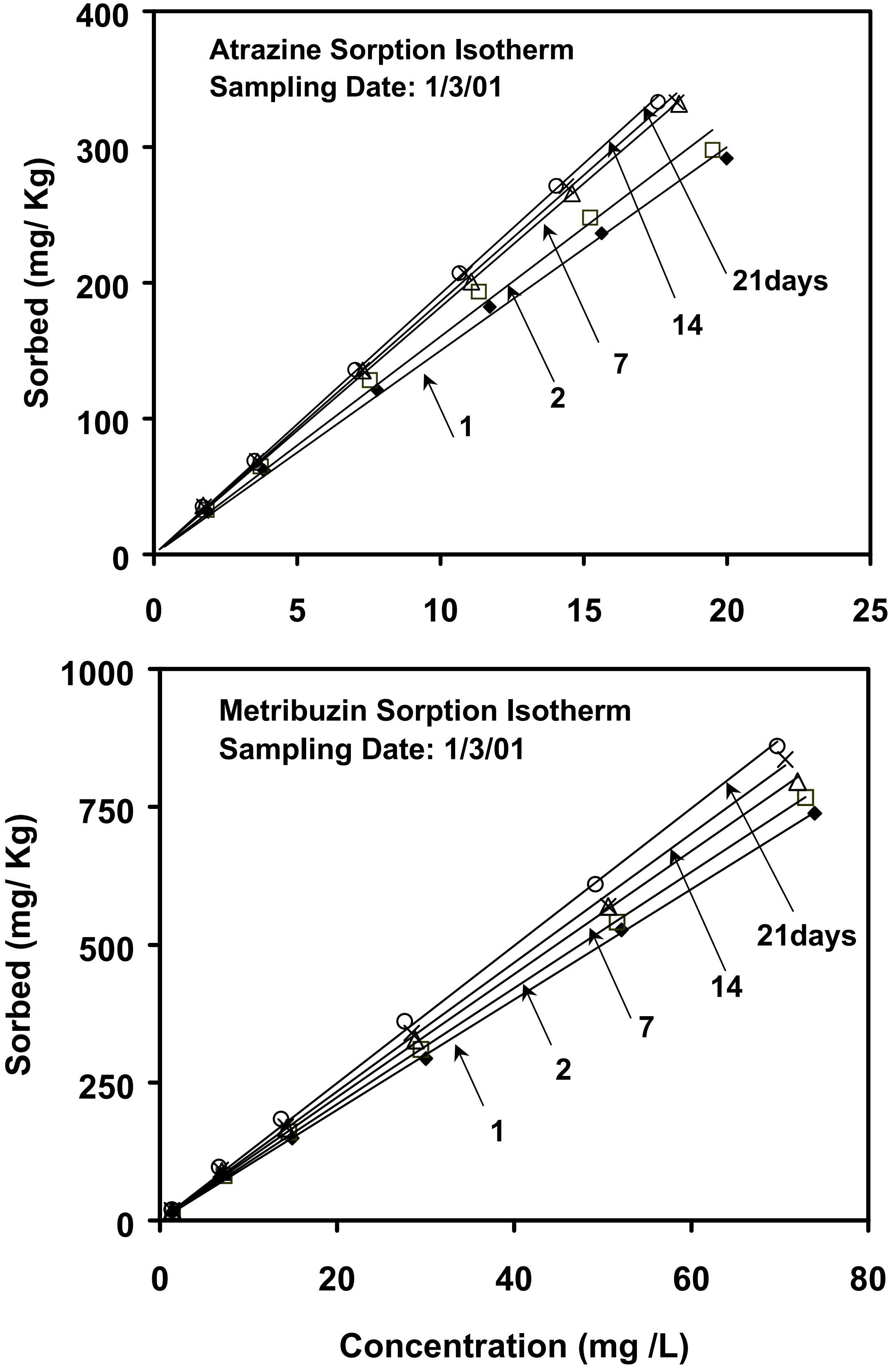

Figure 3.1. Adsorption isotherms for atrazine and metribuzin for sugarcane mulch residue at different reaction times. The residue was sampled following Plantcane harvest on January 3, 2001.

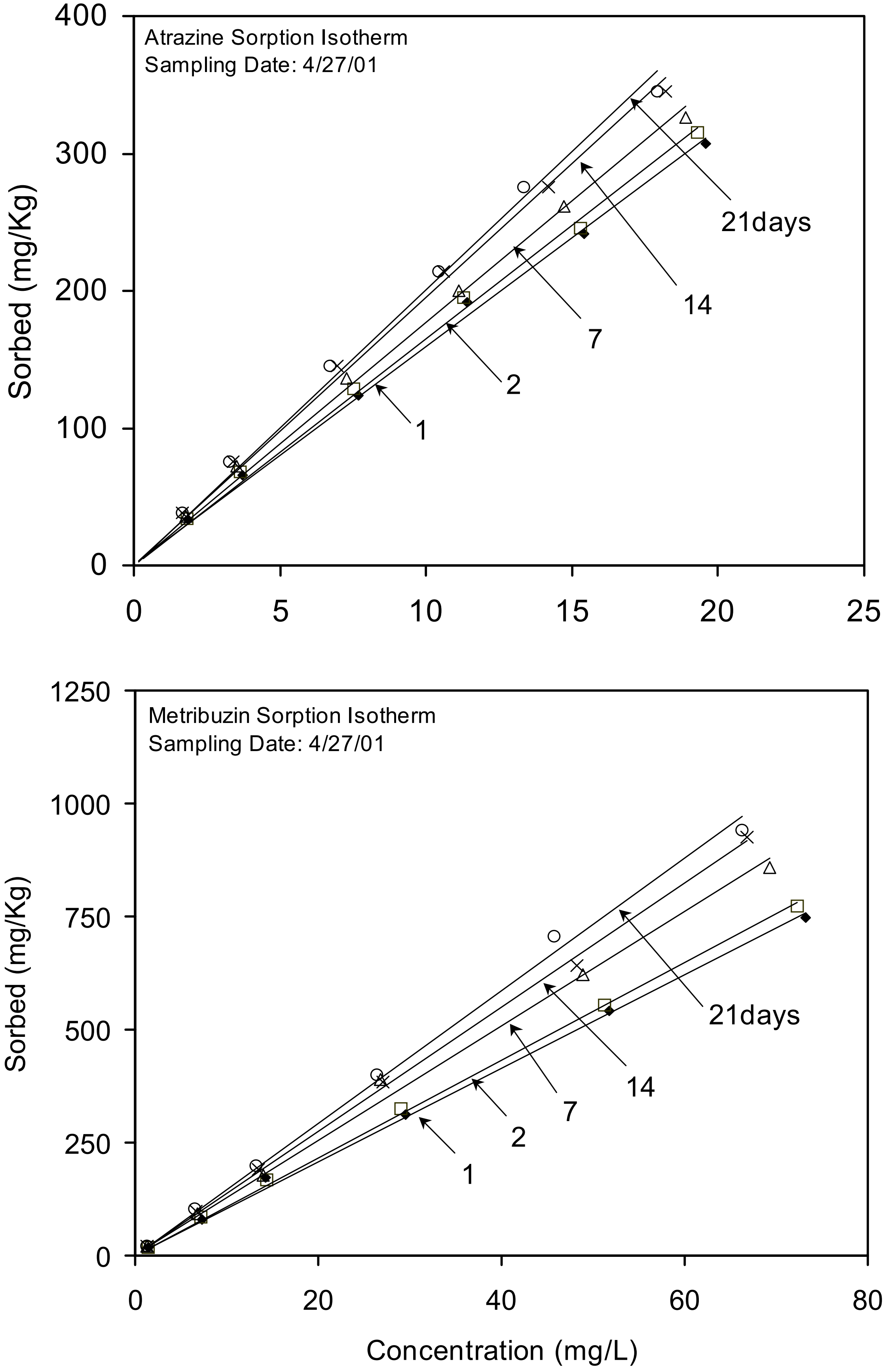

Figure 3.2. Adsorption isotherms for atrazine and metribuzin for sugarcane mulch residue at different reaction times. The residue was sampled following Plantcane harvest on April 27, 2001.

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Table 3.3. Estimated linear and Freundlich model parameters (with 95% confidence interval) for atrazine and metribuzin adsorption by the sugarcane mulch residue. The residue was sampled at several dates following first-stubble sugarcane harvest on October 22, 2001.

Sampling	Age of	Linear Model	Freundlich Model	
Date	Residue (days)	K_d (mL g^{-1})	K_f (mL g^{-1})	N
		Atrazine		
30-Oct-01	12	16.21 ± 0.36	22.62 ± 3.10	0.87 ± 0.05
26-Nov-01	39	14.92± 0.39	18.28 ± 3.51	0.92 ± 0.07
20-Dec-01	63	16.72 ± 0.27	20.67 ± 2.26	0.92 ± 0.04
22-Feb-02	127	15.65 ± 0.16	18.46 ± 1.32	0.93 ± 0.02
20-Mar-02	153	17.18 ± 0.31	22.69 ± 2.63	0.89 ± 0.04
23-May-02	217	15.93 ± 0.18	18.24 ± 1.54	0.94 ± 0.03
		Metribuzin		
30-Oct-01	12	9.23 ± 0.32	10.90 ± 4.02	0.95 ±0.09
26-Nov-01	39	9.47 ± 0.20	8.49 ± 2.12	1.02 ± 0.06
20-Dec-01	63	10.47 ± 0.22	8.76 ± 2.09	1.04 ± 0.05
22-Feb-02	127	11.11 ± 0.04	10.57 ± 0.42	1.01 ± 0.00
20-Mar-02	153	10.07 ± 0.06	11.56 ± 0.67	0.96 ± 0.01
23-May-02	217	10.97 ± 0.06	12.10 ± 0.73	0.97 ± 0.01

metribuzin. For the first stubble, what is interesting is that the retention values are similar to those of the plant cane and did not change significantly with the age of residue. Atrazine had an average K_d value of 16.10 ± 0.79 mL/g while metribuzin averaged 10.22 ± 0.77 mL/g (see Table 3.3). This could suggest that the residue on a mass basis has the same sorption capacities across the growing seasons.

Using residue collected 153 days after harvest, we performed a 24 hour adsorption study resulting in K_d values of 17.18 ± 0.31 mL/g and 10.07 ± 0.06 mL/g for atrazine and metribuzin respectively. This was followed by ten-consecutive 24 hour desorption steps, as described earlier (see Figure 3.4). As the adsorption studies indicated, sugarcane residue has a stronger affinity for atrazine than for metribuzin. The desorption results also show similar trends (see Table 3.4). The amount of atrazine desorbed averaged 87 ± 5.21% of that adsorbed, while metribuzin desorbed 93 ± 3.07% of the 24 hour adsorption values. Metribuzin desorbed some 90% of that adsorbed for all input concentrations. This could be attributed to metribuzin's solubility of 1200 mg/L while atrazine is at 29 mg/L. Following methanol extraction, the average amount of atrazine that was retained by the residue was only 5.07 ± 2.43% of the initial input, while the amount of metribuzin retained was only 1.89 ± 0.966%.

3.2.3 Second Stubble

Following the harvest of the second stubble, we compared herbicide adsorption characteristics of the mulch residue overtime during the growing seasons. Table 3.5 shows that those K_d values for atrazine adsorption by the sugarcane mulch residue increased with reaction times from 18.77 to 25.46 mL/g after 24 and 504 hours, respectively. For metribuzin, the K_d values increased with reaction times from 10.58 to 14.20 mL/g after 24 and 504 hours, respectively. As

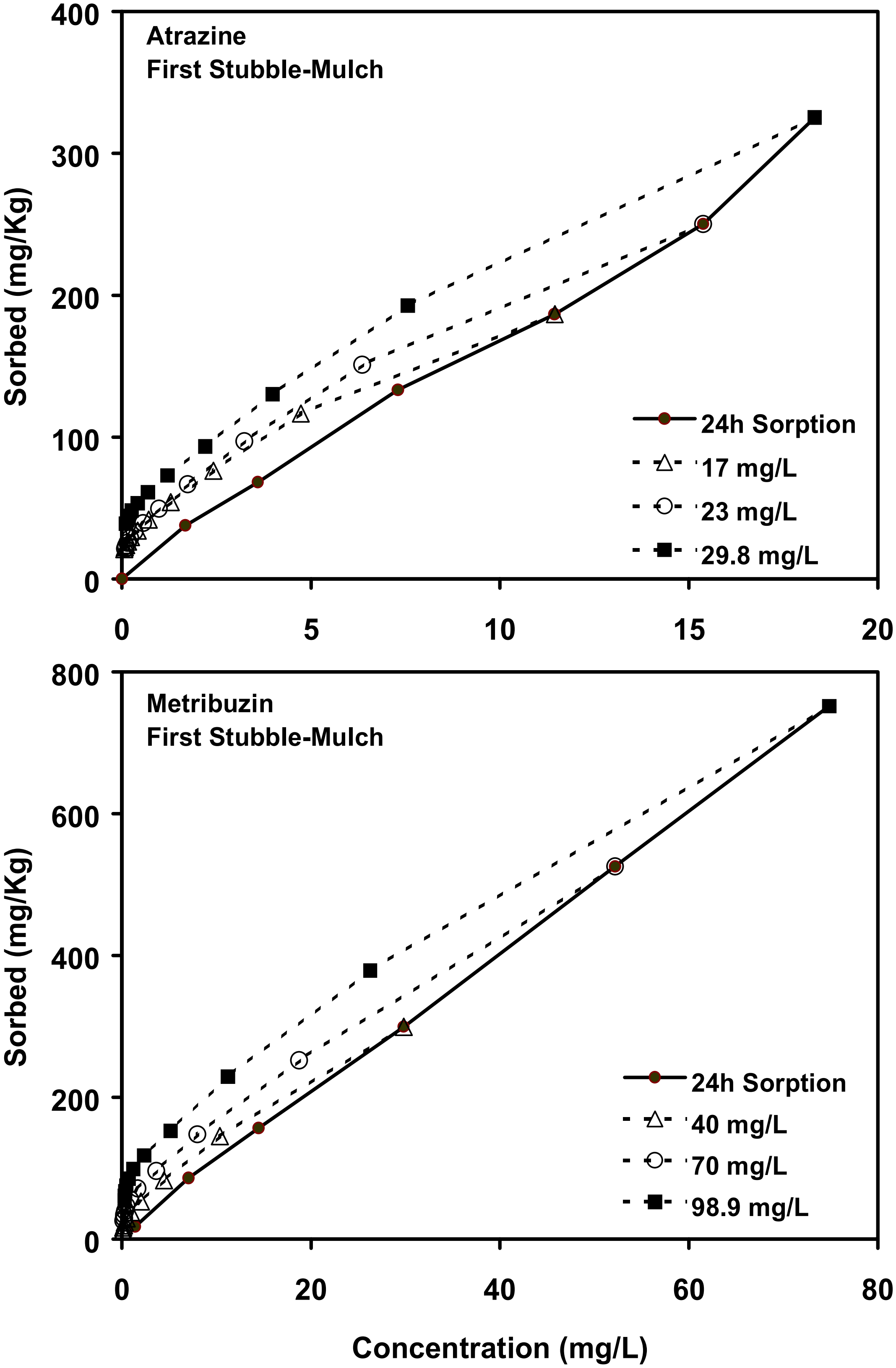

Figure 3.3. Desorption isotherms for atrazine and metribuzin for sugarcane mulch residue subjected to 24 hours of sorption followed by ten 24 hour desorption steps. The residue was samples on March 20, 2002 following second stubble harvest.

Table 3.4. Mass balance of applied atrazine and metribuzin following 24-h adsorption, ten desorptions, and methanol extraction for mulch residue collected 153 d 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
Metribuzin	2.00	17.67	16.05	90.85	2.71	0.37	2.09
	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
Atrazine	2.98	38.20	29.51	77.28	9.71	0.28	9.40
	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

Table 3.5. 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 Jan 24, 2003, following second stubble harvest.

Atrazine

Retention	Freundlich Model			Linear Model	
Time (d)	Kf (mL g^{-1})	N	r^2	Kd (mL g^{-1})	r^2
1	20.67 ± 2.26	0.92 ± 0.04	0.996	18.77 ± 0.58	0.935
2	23.76 ± 4.20	0.89 ± 0.06	0.988	18.04 ± 0.49	0.957
7	27.01 ± 7.60	0.95 ± 0.11	0.989	24.02 ± 0.96	0.916
14	25.12 ± 4.54	0.98 ± 0.07	0.989	24.24 ± 0.60	0.967
21	26.32 ± 4.78	0.98 ± 0.07	0.989	25.46 ± 0.64	0.966

Metribuzin

Retention	Freundlich Model			Linear Model	
Time (d)	Kf (mL g^{-1})	N	r^2	Kd (mL g^{-1})	r^2
1	13.82 ± 0.65	0.91 ± 0.01	0.994	10.58 ± 0.26	0.971
2	18.02 ± 2.49	0.88 ± 0.03	0.993	11.37 ± 0.22	0.985
7	19.28 ± 1.40	0.92 ± 0.01	0.994	13.87 ± 0.15	0.995
14	19.31 ± 1.30	0.92 ± 0.01	0.994	14.03 ± 0.15	0.995
21	19.55 ± 1.29	0.92 ± 0.02	0.994	14.20 ± 0.15	0.995

seen with the plant cane, the adsorption of both atrazine and metribuzin by sugarcane residue of the second stubble was initially rapid, and exhibited slower retention after 24 hours of reaction time. Also similar to the plant cane, the observed increase of K_d values with reaction time, is representative of the strong kinetic behavior of atrazine and to a lesser extent of metribuzin adsorption by the sugarcane mulch residue (see Figure 3.5).

Desorption of both herbicides from the sugarcane residue following 504 hours of adsorption resulted in successive losses in concentration as was the case with the first stubble(see Figure 3.6). This second stubble residue was collected 64 days following harvest. 504 hour K_d values of 25.46 ± 0.64 mL/g and 14.20 ± 0.15 mL/g for atrazine and metribuzin respectively, were determined (see Table 3.5). Following the complete desorption process, retained atrazine was 13.77 ± 3.74% of the initial amount applied and 10.23 ± 0.69% of applied metribuzin was retained (see Table 3.6). Atrazine desorbed some 66.02 ± 4.1% of that applied while 68.10 ± 0.76% of metribuzin applied was desorbed.

Changes of adsorption characteristics due to weather induced changes in the field following harvest were also investigated. The average K_d value was 18.47 ± 2.5 mL/g for atrazine and was 9.91 ± 1.20 mL/g for metribuzin post-harvest of the second stubble (see Table 3.7). These data were compared with results from the previous two growing seasons. Specifically, the K_d values were measured using 24 hour batch adsorption, for the individual mulch samples from three successive growing seasons (plant cane, first stubble and second stubble). The overall herbicide retention did not change significantly with age of residue or the time of decay in the field over the three growing seasons as depicted in Figure 3.4. Again we see that one K_d value for each atrazine and metribuzin across growing seasons and for all ages of residue is sufficient. These data show that an average K_d value could represent the retention

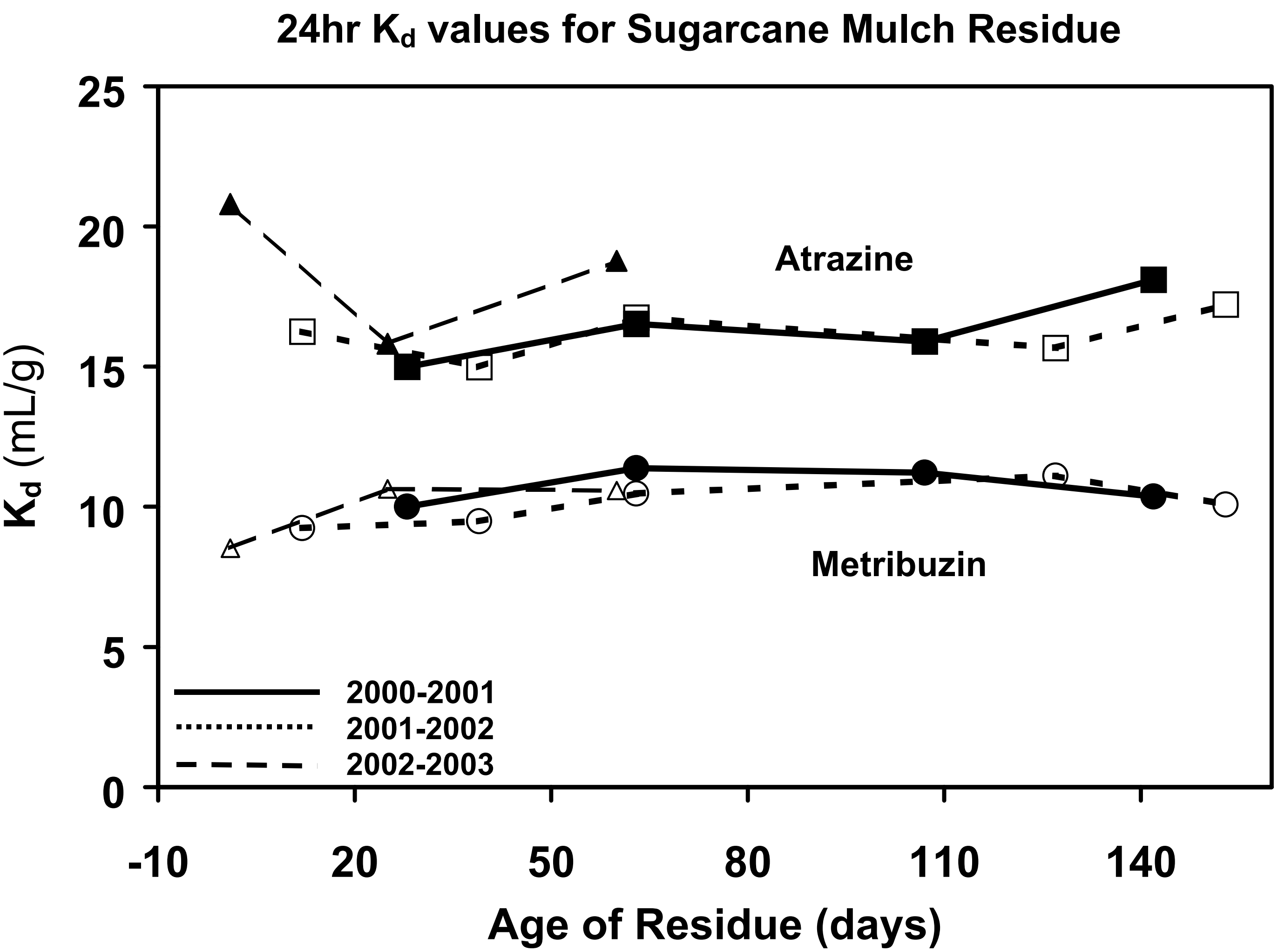

Figure 3.4. Distribution coefficient (K_d) for atrazine and metribuzin by the sugarcane residue versus age of the mulch during for three consecutive growing seasons.

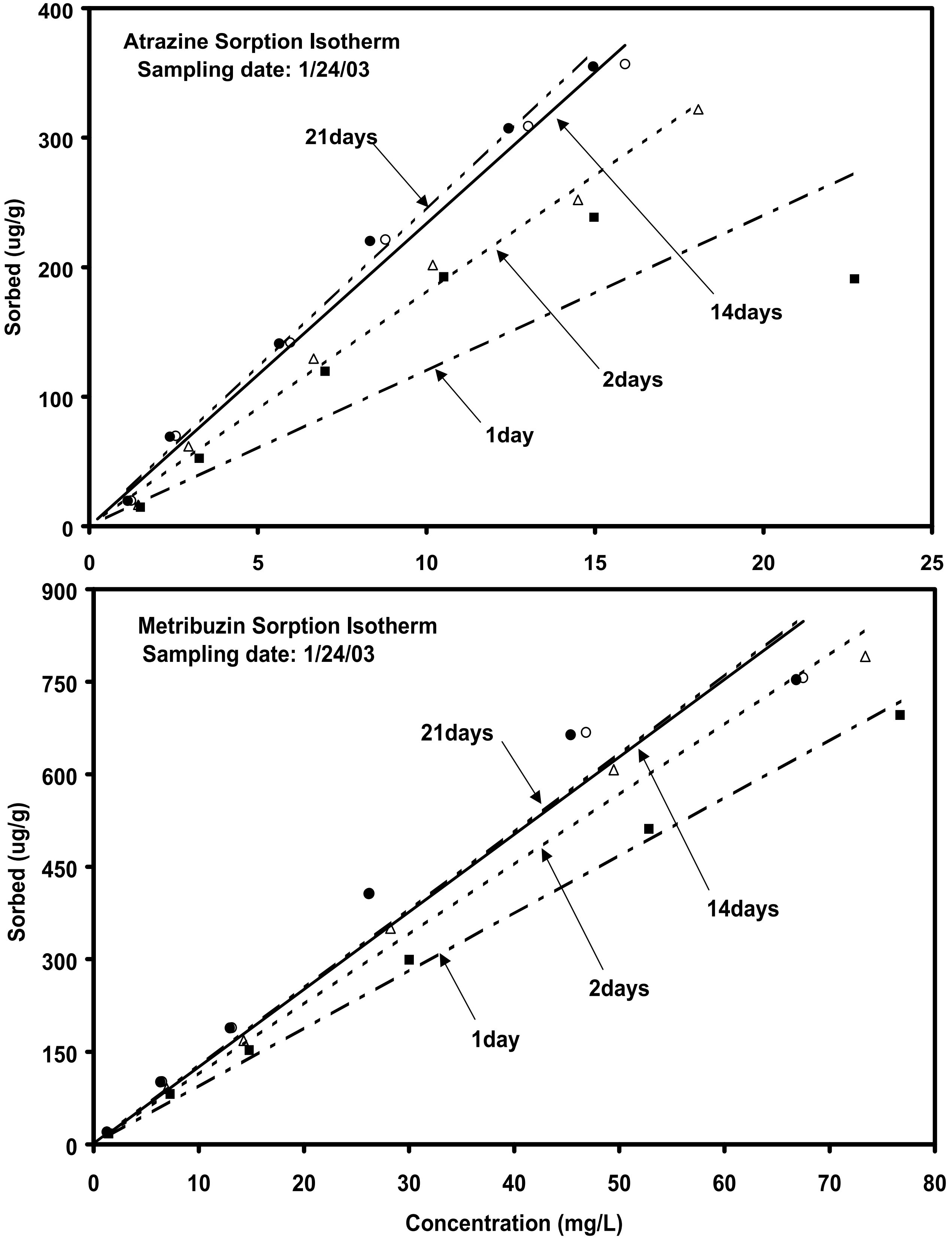

Figure 3.5. Adsorption isotherms for atrazine and metribuzin for sugarcane mulch residue at different reaction times. The residue was samples on January 24, 2003, following second stubble harvest.

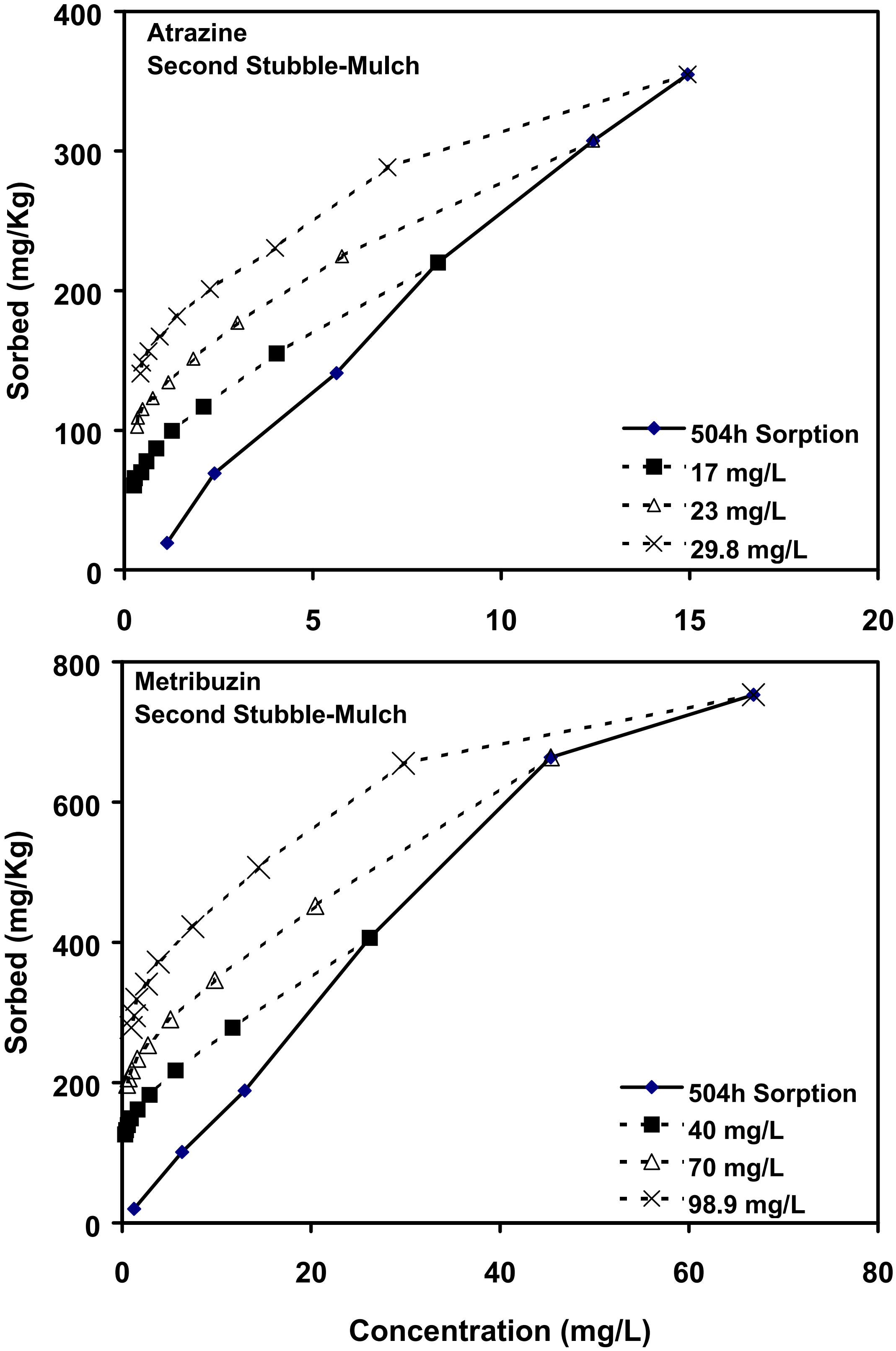

Figure 3.6. Desorption isotherms for atrazine and metribuzin for sugarcane mulch residue subjected to 504 hours of sorption followed by six 24 hour desorption steps. The residue was samples on January 24, 2003, following second stubble harvest.

Table 3.6. Mass balance of applied atrazine and metribuzin following 504-h adsorption, six desorptions, and methanol extraction for mulch residue collected 63 d post-harvest (January 24, 2003).

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
Metribuzin	40.00	406.38	273.99	67.46	11.03	12.35	6.87
	70.00	663.88	457.61	68.95	9.82	20.55	3.67
	100.00	920.65	625.17	67.91	9.85	30.83	7.27
Atrazine	17.90	220.11	154.45	70.19	9.70	26.10	4.09
	23.90	307.34	198.37	65.95	14.56	34.21	9.58
	29.00	384.93	236.39	61.92	17.07	37.50	22.29

Table 3.7. Estimated linear and Freundlich model parameters (with 95% confidence interval) for atrazine and metribuzin adsorption by the sugarcane mulch residue (var. LCP85-384). The residue was sampled at several dates following harvest of second stubble November 24, 2002.

Sampling Date	Age of Residue (days)	Linear Model K_d (mL g^{-1})	Freundlich Model K_f (mL g^{-1})	N
		Atrazine		
25-Nov-02	1	20.82 ± 1.38	22.62 ± 3.10	0.87 ± 0.05
20-Dec-02	25	15.81 ± 1.49	18.28 ± 3.51	0.92 ± 0.07
24-Jan-03	63	18.77 ± 0.58	20.67 ± 2.26	0.92 ± 0.04
		Metribuzin		
25-Nov-02	1	8.52 ± 0.29	9.26 ± 2.39	0.98 ±0.09
20-Dec-02	25	10.63 ± 0.19	11.04 ± 2.21	0.99 ± 0.06
24-Jan-03	63	10.58 ± 0.26	13.82 ± 0.65	0.91 ± 0.05

behavior of the sugarcane residue as it remains in the field. This finding obtained for both atrazine and metribuzin.

3.3 Herbicide Adsorption by Soils

The 24 hour K_d values for atrazine were 2.15 and 1.18 mL/g for Sharkey and Commerce soil, respectively (see Table 3.8). As described earlier the Sharkey clay soil has higher clay content than the Commerce loam soil. Clay is often related to higher adsorption of organics, resulting in higher herbicide retention by the Sharkey soil. The same was true with metribuzin 24 hour K_d values of 1.15 mL/g for Sharkey soil and 0.707 mL/g for Commerce soil. Selim (2004) showed similar results for Sharkey and Commerce soils which were an order of magnitude lower than atrazine and metribuzin K_d values for the mulch residue discussed above (see Figure 3.7). In comparison to the mulch residue, K_d values for both soils clearly exhibited limited kinetic behavior for both atrazine and metribuzin. Since organic matter is the principal soil component affecting the adsorption of many herbicides in the soil environment, this can be expected (Boyd et al. 1990).

3.4 Residue Decay

The amount of mulch residue present on the soil surface, for variety LCP85-384, decreased from 3.80 ± 0.689 to 1.43 ± 0.535 tons/ha within a four-month period for the plantcane season. Following the harvest of the first stubble, the amount of mulch decreased from 5.77 ± 1.43 to 1.94 ± 0.553 tons/ha in five months time. The second stubble harvest resulted in a 5.62 ± 1.28 to 4.65 ± 0.604 tons/ha decrease over a two-month period (Figure 3.8). Due to plowing and other preparations of the field for a new planting the residue was not available to collect beyond two months.

Table 3.8 Estimated linear model parameters for atrazine and metribuzin adsorption by both Commerce and Sharkey surface soils.

	Commerce	Sharkey
Retention Time (days)	Linear Model K_d *(mL g-1)*	
	Atrazine	
0.3	0.829 ± 0.11	1.02 ± 0.26
1	1.11 ± 0.24	2.19 ± 0.23
2	1.17 ± 0.23	2.41 ± 0.27
7	1.30 ± 0.24	2.44 ± 0.24
14	1.22 ± 0.26	2.43 ± 0.25
21	1.14 ± 0.28	2.44 ± 0.27
	Metribuzin	
0.3	0.759 ± 0.22	1.19 ± 0.08
1	0.768 ± 0.06	1.33 ± 0.14
2	0.708 ± 0.06	1.36 ± 0.16
7	0.735 ± 0.07	1.29 ± 0.19
14	0.722 ± 0.07	1.27 ± 0.19
21	0.659 ± 0.07	1.25 ± 0.18

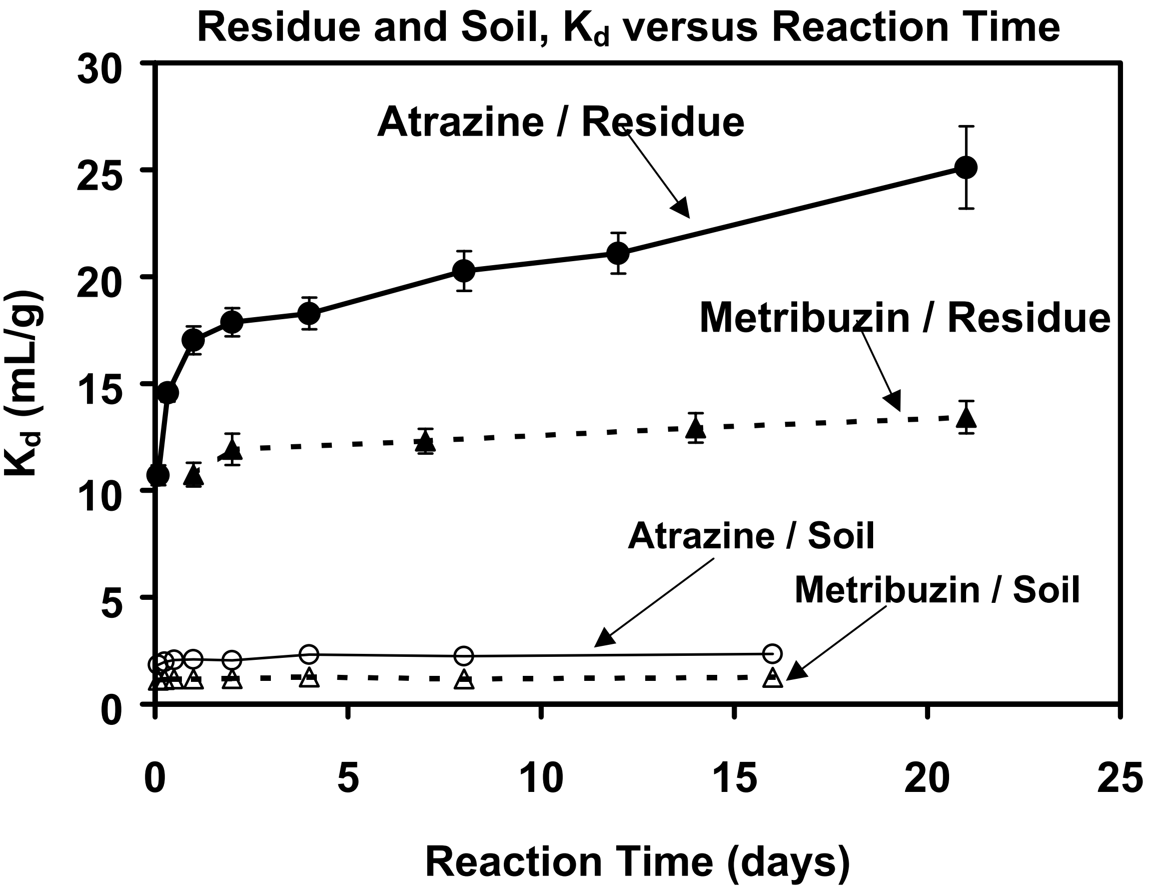

Figure 3.7. Distribution coefficient (K_d) for atrazine and metribuzin by the sugarcane residue and Commerce soils versus reaction times with herbicide.

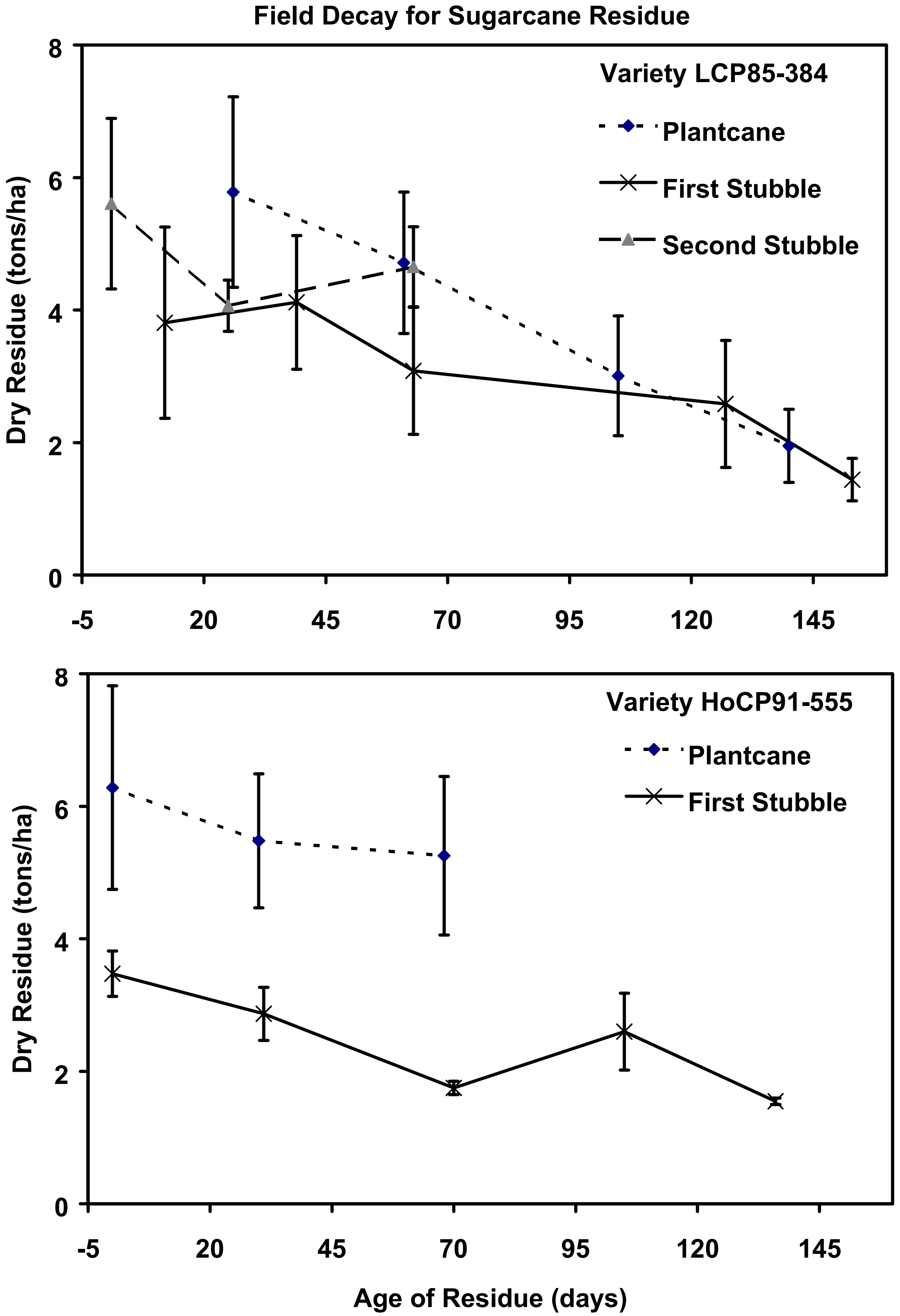

Figure 3.8. Field decay of sugarcane mulch residue following combine harvest of varieties LCP85-384 and HoCP91-555.

Plantcane harvest of variety HoCP91-555 resulted in a decrease from 6.27 ± 1.74 to 5.15 ± 1.19 tons/ha of residue after two months in the field. The limited two month time period for the plantcane harvest was due to heavy rains causing a mixture of residue and mud resulting in collection not being practical. The HoCP91-555 first stubble decayed over a five and a half-month period with residue amounts starting at 3.47 ± 0.342 and ending with 1.54 ± 0.049 tons/ha (Figure 3.8). Such differences may be attributed to differences in the variety and yields, soil type, combine setting during harvest, and other harvest conditions.

Based on simple linear regression, a rate of residue decay was derived where the (negative) slope represents the mass of mulch degradation per hectare over time. For variety LCP85-384 grown on Sharkey clay, the estimated rates of degradations were 20.3 ± 4.25, 16.6 ± 4.25, 13.1 ± 8.73 kg/ha/day for the three growing seasons (plant cane, first and second stubble), respectively. To describe the decay of the mulch for all growing seasons, we employed a regression analysis, which provided a good description suggesting a linear model was appropriate. Furthermore, there was no significant difference of the regression lines and their respective slopes. To estimate the rate of decay we applied a nonlinear regression based on first-order decay. We determined the half-lives for the mulch decay to be in the range of 126 to 171 days.

3.5 Fiber Quantification

The amount of residue in the field, following harvest, decreased by an average of 3.0 tons/ha over a five month time period. The percentage of acid detergent fiber in the leafy residue increased slightly as time in the field increased. With time of decay in the field the content of the residue has greater amounts of lignin with a higher adsorption capacity on a mass basis. This is due to the recalcitrant properties of lignin. Therefore with time in the field, the sugarcane residue has the ability, on a mass basis, to adsorb increasing amounts of herbicides. However, such an

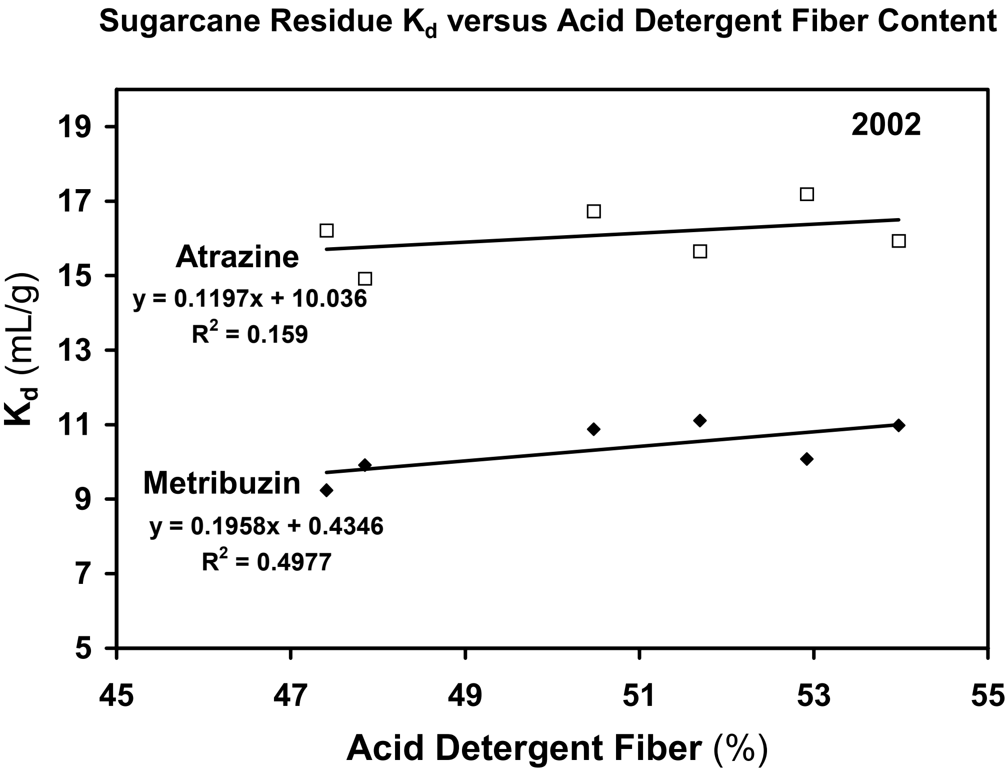

Figure 3.9. Relationship between atrazine and metribuzin K_d for sugarcane mulch residue and acid detergent fiber content for residue collected at different times post harvest.

Table 3.9. Results from Forage fiber analysis of selected sugarcane residue used in retention studies. Analysis preformed by LSU AgCenter Southeast Research Station. Values are percentage on a mass basis.

Soil	Variety	Sampled	Age (d)	ADF	Cellulose	Lignin	Ash
Sharkey	LCP85-384	10/30/01	12	49.46	36.55	8.10	4.81
Sharkey	LCP85-384	11/26/01	40	49.84	34.63	9.45	5.75
Sharkey	LCP85-384	12/20/01	63	54.64	41.40	7.67	5.57
Sharkey	LCP85-384	2/22/02	127	55.05	39.90	9.46	5.70
Sharkey	LCP85-384	3/20/02	153	54.82	38.12	10.91	5.79
Sharkey	LCP85-384	5/23/02	187	53.68	39.36	8.49	5.83
Sharkey	LCP85-384	11/25/02	1	46.59	31.47	6.61	8.51
Sharkey	LCP85-384	12/20/02	26	53.21	34.12	8.34	10.76
Sharkey	LCP85-384	1/24/03	61	54.16	36.45	8.74	8.98
Commerce	HoCP91-555	12/6/02	0	49.67	26.40	7.19	16.09
Commerce	HoCP91-555	1/6/03	31	53.99	33.26	8.31	12.41
Commerce	HoCP91-555	2/14/03	70	58.41	31.71	10.00	16.71
Commerce	HoCP91-555	3/21/03	105	53.83	32.05	9.31	12.48
Commerce	HoCP91-555	4/21/03	136	59.67	29.44	9.88	20.36

increase is at best modest (see Table 3.8). This finding is consistent with metribuzin and lignin relationships using wheat straw explored by Dao (1991). Dao (1991) suggests that an increase in the percentage of lignin of intact wheat straw is due to the decay of cellulose. The purified cellulose fraction did not show significant retention of metribuzin or atrazine. 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). In addition, Dao assumed that the lignin accounted for the majority of sorption sites for metribuzin by the wheat straw.

The fiber analysis data for the sugarcane residue was analyzed for a linear relationship between the K_d values from atrazine and metribuzin adsorption by residue after time in the field and percent acid detergent fiber of the same residue in the field. A simple regression analysis resulted in signifigantly low r^2 values, for K_d versus percent acid detergent fiber. This result was realized for both atrazine and metribuzin, and is clearly exhibited in Figure 3.9. Based on t-test, atrazine and metribuzin p-values were 0.4335 to 0.1174, respectively. Therefore, the respective slopes of the regression lines were not significantly different from 0, respectively, and thus conclude that K_d is independent of the residue age and a single K_d value for metribuzin or atrazine can be used to predict field results.

3.6 Miscible displacement

The breakthrough curves (BTCs) are presented as relative concentration of metribuzin(C/C_o) where C_o is the initial concentration of solution at input, versus relative pore volume (V/V_o) where V_o is the pore volume of the column (cm^3). The concentrations presented here are based on liquid scintillation measurements of the radioactive carbon in the column effluent solution and in turn this does not differentiate between the applied compound (^{14}C - labeled metribuzin) and its degradation products.

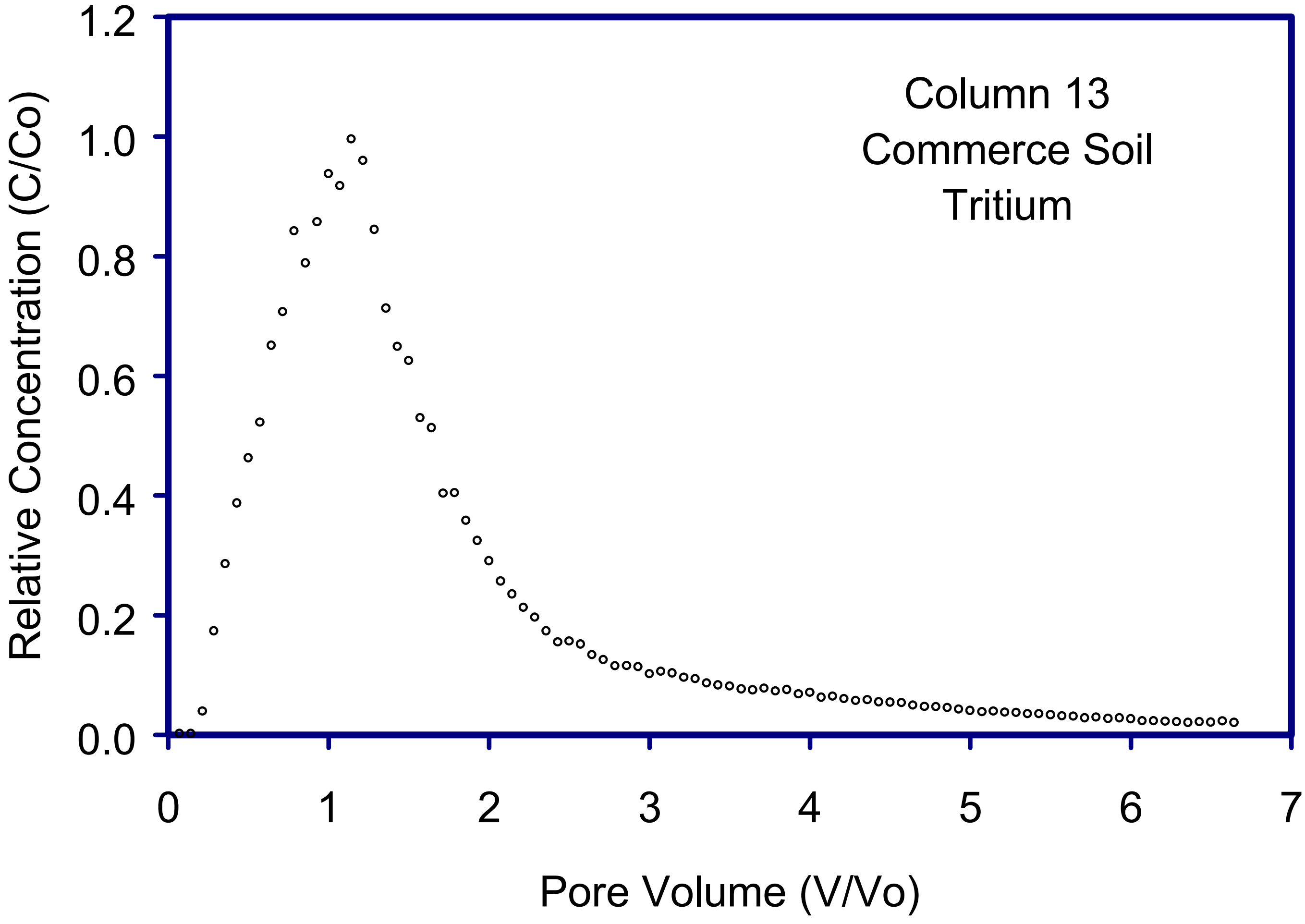

Figure 3.10. Measured tritium breakthrough curve from a 15-cm column packed with Commerce silt loam soil (column 13).

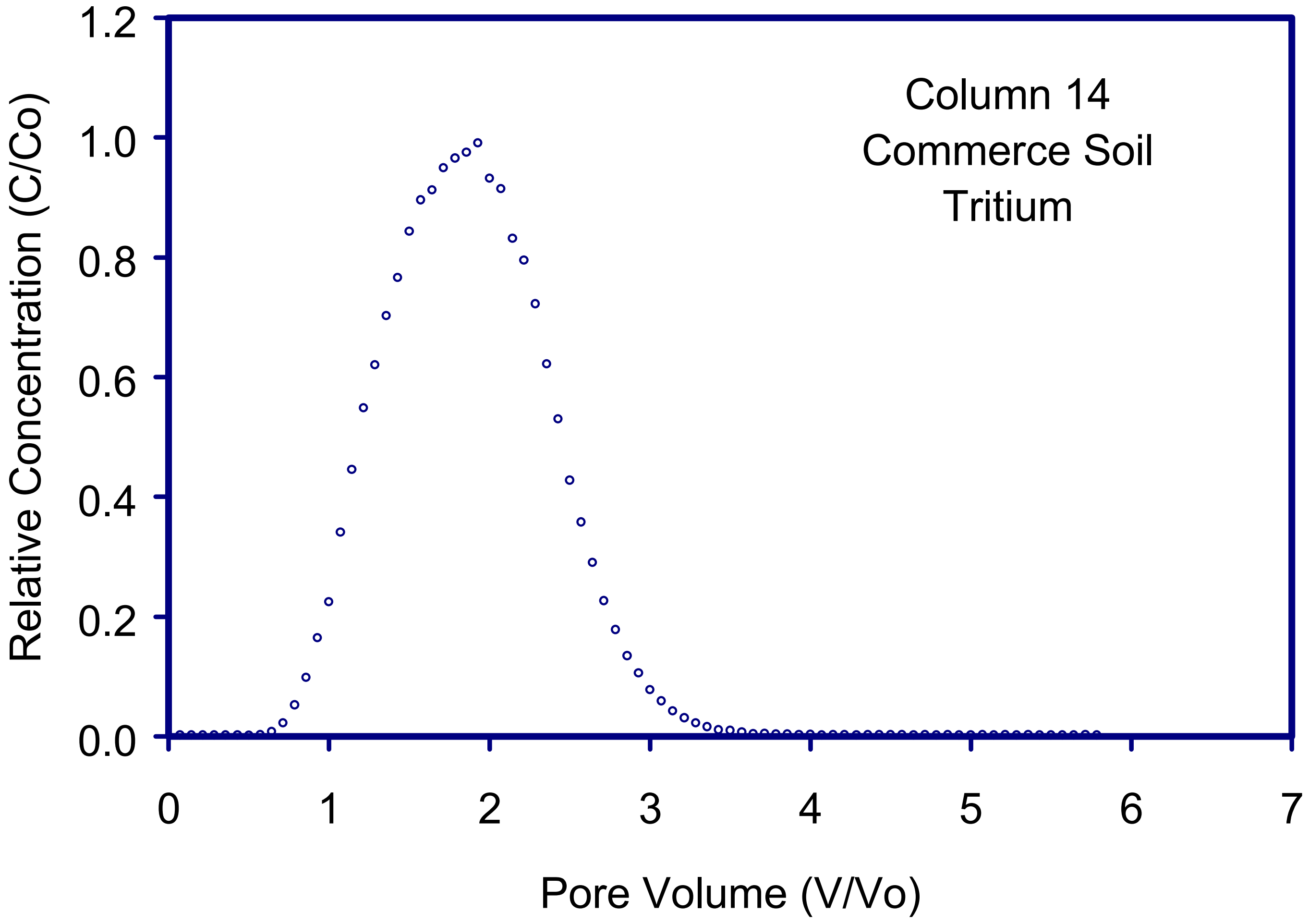

Figure 3.11. Measured tritium breakthrough curve from a 15-cm column packed with Commerce silt loam soil (column 14).

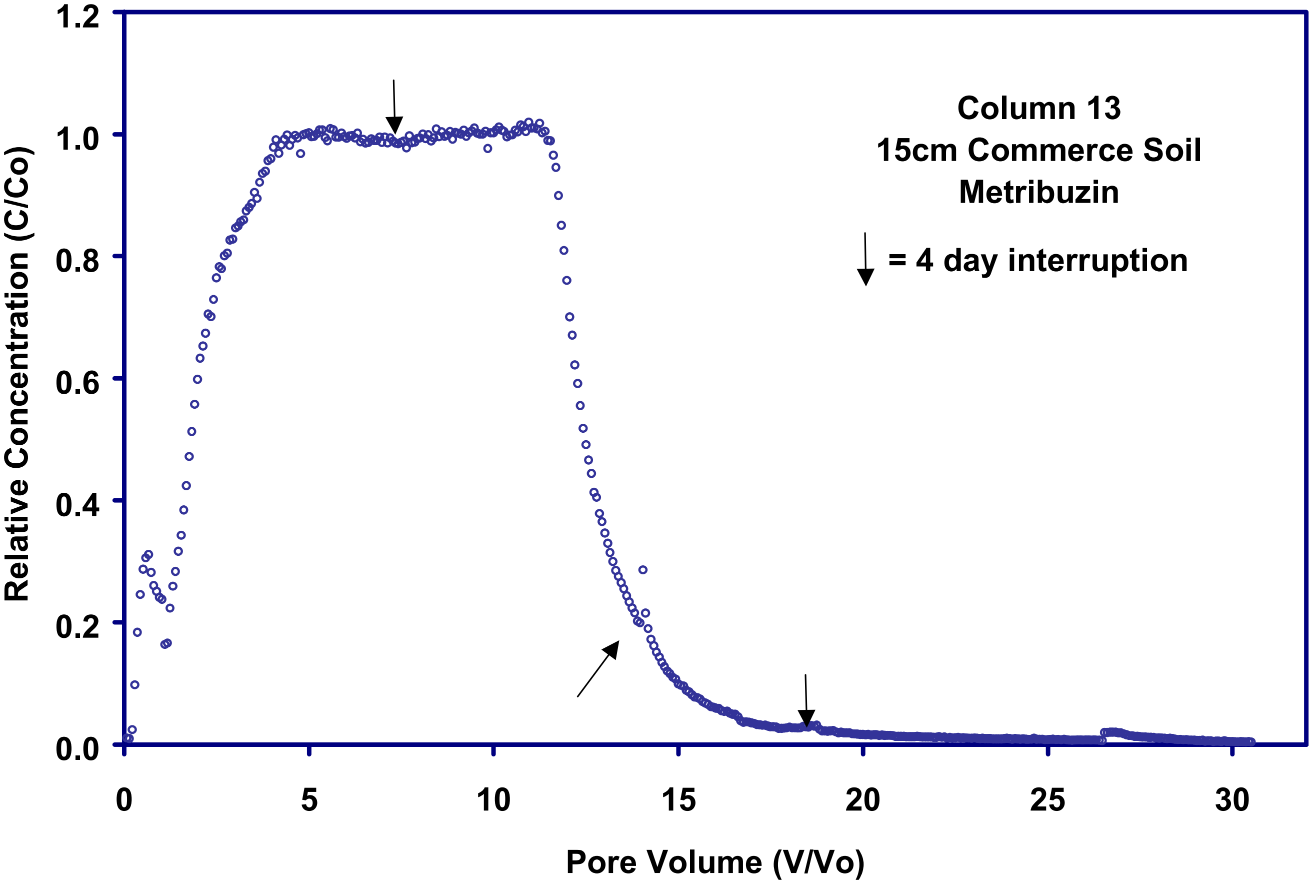

Figure 3.12. Measured metribuzin breakthrough curve from a 15-cm column packed with Commerce silt loam soil. (column 13). Arrows indicate 4 day flow interruption.

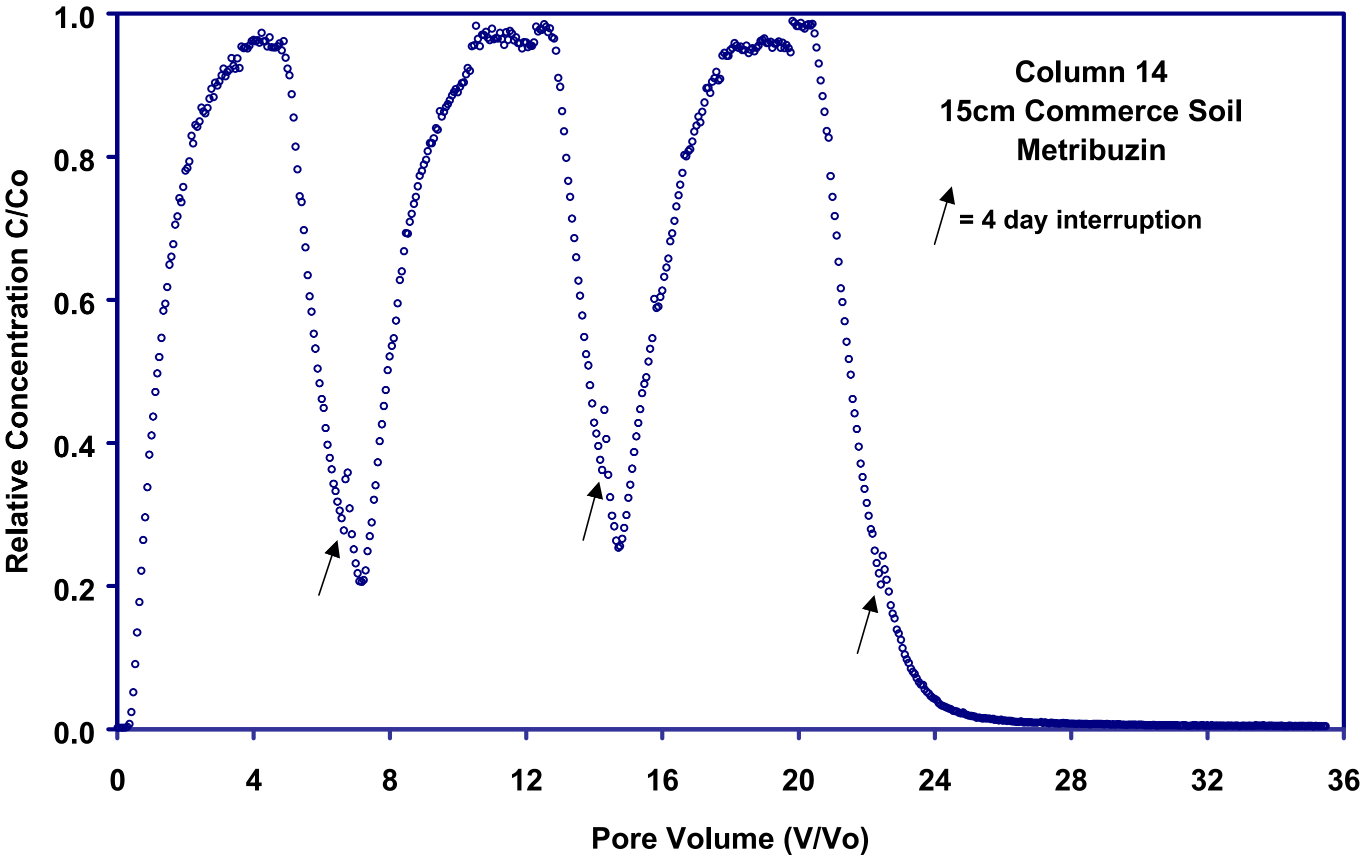

Figure 3.13. Measured metribuzin breakthrough curve from a 15-cm column packed with Commerce silt loam soil. (column 14). Arrows indicate 4 day flow interruption.

The time of arrival (or number of pore volumes) of the BTC is expressive of the extent of mobility of metribuzin in each soil column and thus in the commerce soil. The desorption side of the BTCs show the release of tritium and metribuzin in the effluent from the soil columns. Flow interruption provides an experimental condition to understand the non-equilibrium phenomena associated with retention and release during the transport of chemicals (Murali and Aylmore, 1980).

3.6.1 Commerce Soil

The column 13 with commerce soil passed 1.14 pore volumes of tritium for C/Co to 0.99, while for column 14 tritium moved 1.92 pore volumes to reach 0.99 (see Figures 3.10 and 3.11). Peak maximum for metribuzin occurred after 4.41 and 4.24 pore volumes for Columns 13 and 14 respectively (see Figures 3.12 and 3.13). Breakthrough times for the non-reactive tritium tracer was significantly faster than for any of the metribuzin peak arrivals. This is expected due to adsorption of metribuzin by the soil matrix as opposed to the relatively free flowing non-reactive tritium. Metribuzin peak arrival times were very similar for both 15-cm columns with average relative concentration C/Co of 0.98 at an average of 4.33 pore volumes. After 17.7 pore volumes of metribuzin in column 13, 0.30 relative concentration was released for every pore volume of metribuzin free 0.005 M $CaCl_2$ solution, once leaching began. Desorption of metribuzin from Column 14 with three separate pulses averaged 39.6% drop in relative concentration over a pore volume of 0.005 M $CaCl_2$ when leaching each separate pulse. These data may be referred to during further studies involving sugarcane residue and commerce soil.

3.6.2 Soil and Residue

Earlier batch results indicated that sugarcane residue have significantly greater adsorption capacity for metribuzin than soil alone on a mass basis (i.e., per gram or kilogram). The three columns packed with soil plus residue mixtures are designed to quantify retardation of metribuzin transport in the presence of residue in the soil. Tritium peak reached a C/Co = 0.99 of relative concentration for the sand and residue mixture (column 15) while only 0.67 and 0.65 for Commerce (column 16) and Sharkey with residue (column 17) respectively (see Figures 3.14 to 3.15). The non-uniform pore structure and possibly slower movement through the columns may have influenced tritium flow in the soils as compared to uniform sand. The 15-cm columns 13 and 14 had tritium peak maxima C/Co of 0.99 relative concentration where the 10-cm column 16 with residue present peak C/Co of 0.67, with extensive tailing.

Metribuzin effluent following the first pulse of 3.49 and 4.09 pore volumes, resulted in peaks reaching C/Co of 0.84 to 0.89 for Commerce and Sharkey soils respectively (see Figures 3.17 and 3.18). All three columns reached their respective metribuzin peaks almost 3 pore volumes later than the initial tritium pulse. This can be attributed to the adsorption of metribuzin to soil particles and sugarcane residue. The BTCs of the columns 13 and 14 occurred around one pore volume later than the Commerce and residue mixture. The greater peak arrival times for the columns without residue may be attributed to the 5-cm difference in column length, also the bulk density differences.

The two 4 day interruptions applied to each soil column were used to assess the effect of equilibrium on the retention and release of metribuzin under saturated conditions. With all three soils, concentration of effluent decreased once flow was resumed after the first 4 day interruption. Possibly due to incomplete adsorption within the column pore spaces, with some sorption sites remain available during flow interruption, i.e., diffusion to such sites is the controlling mechanism, this allowed time for adsorption and available sites to be occupied. Conversely following the second interruption there was an increase in concentration of effluent of almost 20% of that applied for Commerce and Sharkey, this is indicated by arrows in Figures

3.16 to 3.18. This may be due to release of metribuzin at equilibrium. Hence available sorption sites were limited and kinetic reaction is dominant. Unlike columns 15 and 16 the acid washed sand lacked any sharp increases in the amount of metribuzin recovered following the second 4 day interruption.

Overall amounts of metribuzin recovery were 66 and 62% of total metribuzin applied for the columns 15 and 17 respectively. The ability to have recovery values of sand and Sharkey soils so similar expresses the impact of residue on metribuzin retention. Metribuzin release was slowest with Sharkey soil followed by Commerce then sand. The rate of release for sharkey soil was steeper than that of sand once leaching began. This release may have been revealing of the amount of metribuzin initially sorbed by Sharkey soil and residue as opposed to sand.

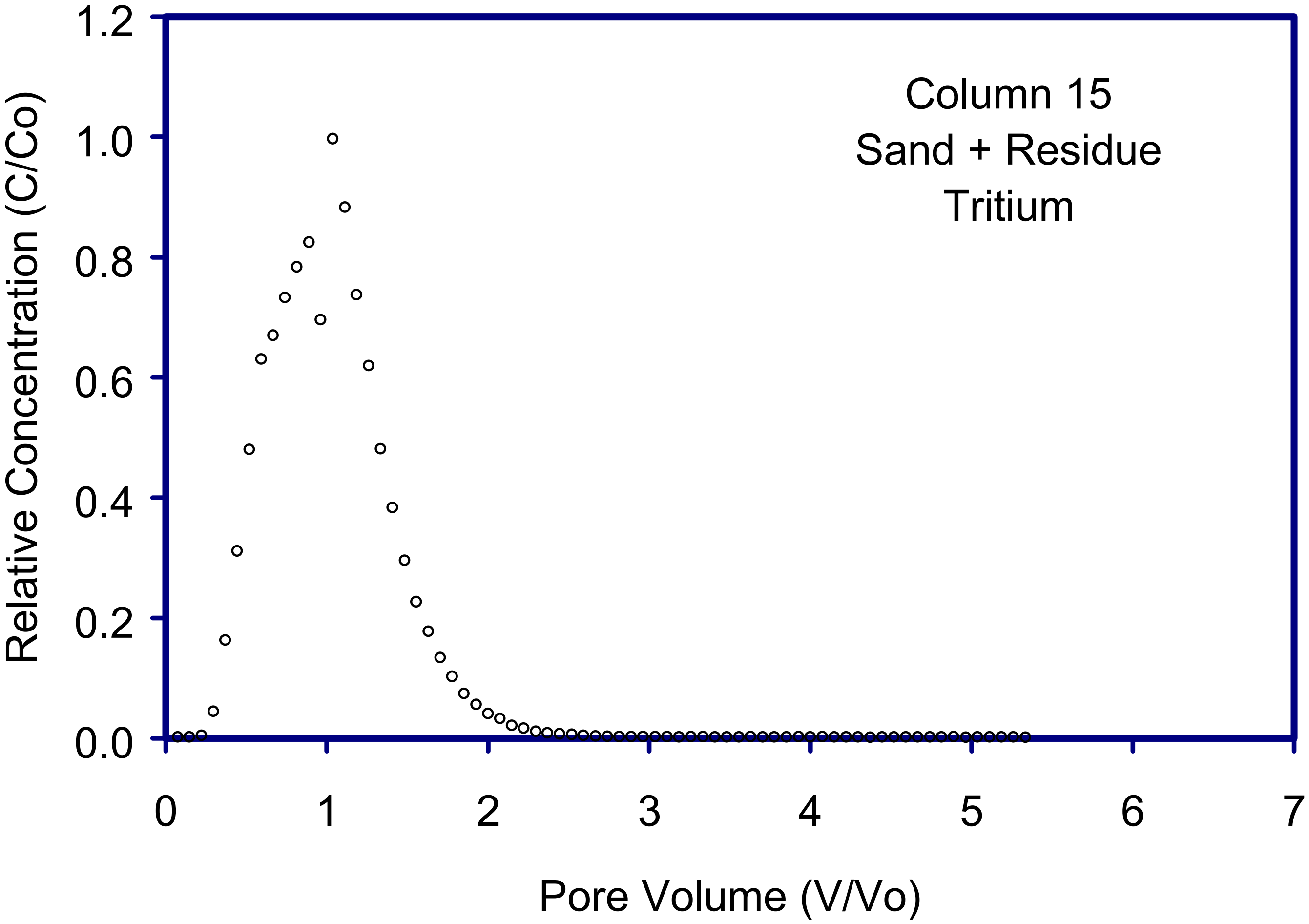

Figure 3.14. Measured tritium breakthrough curve from a 10-cm column packed with sugarcane residue and acid washed sand.(column 15)

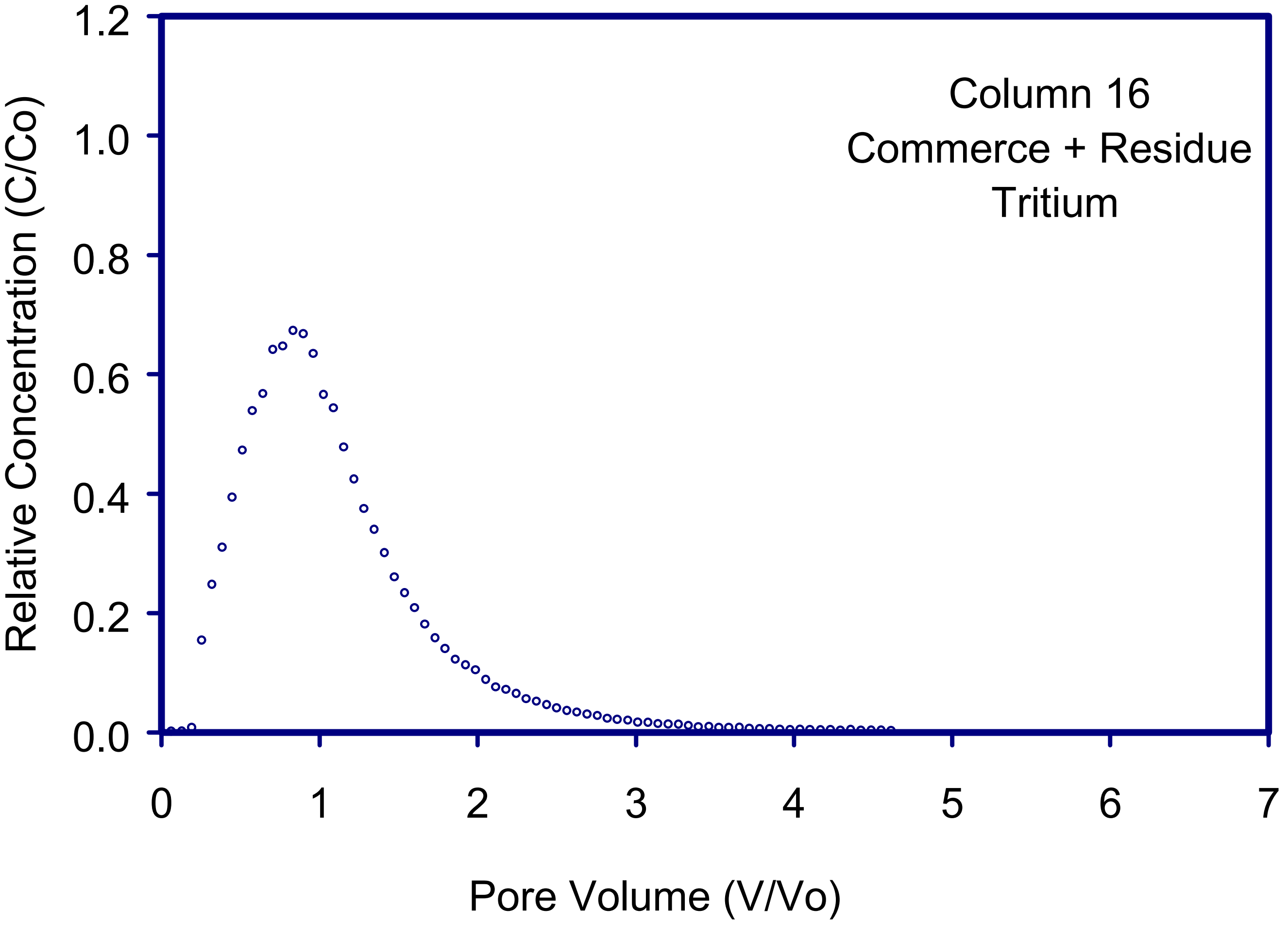

Figure 3.15. Measured tritium breakthrough curve from a 10-cm column packed with sugarcane residue and Commerce silt loam soil.(column 16)

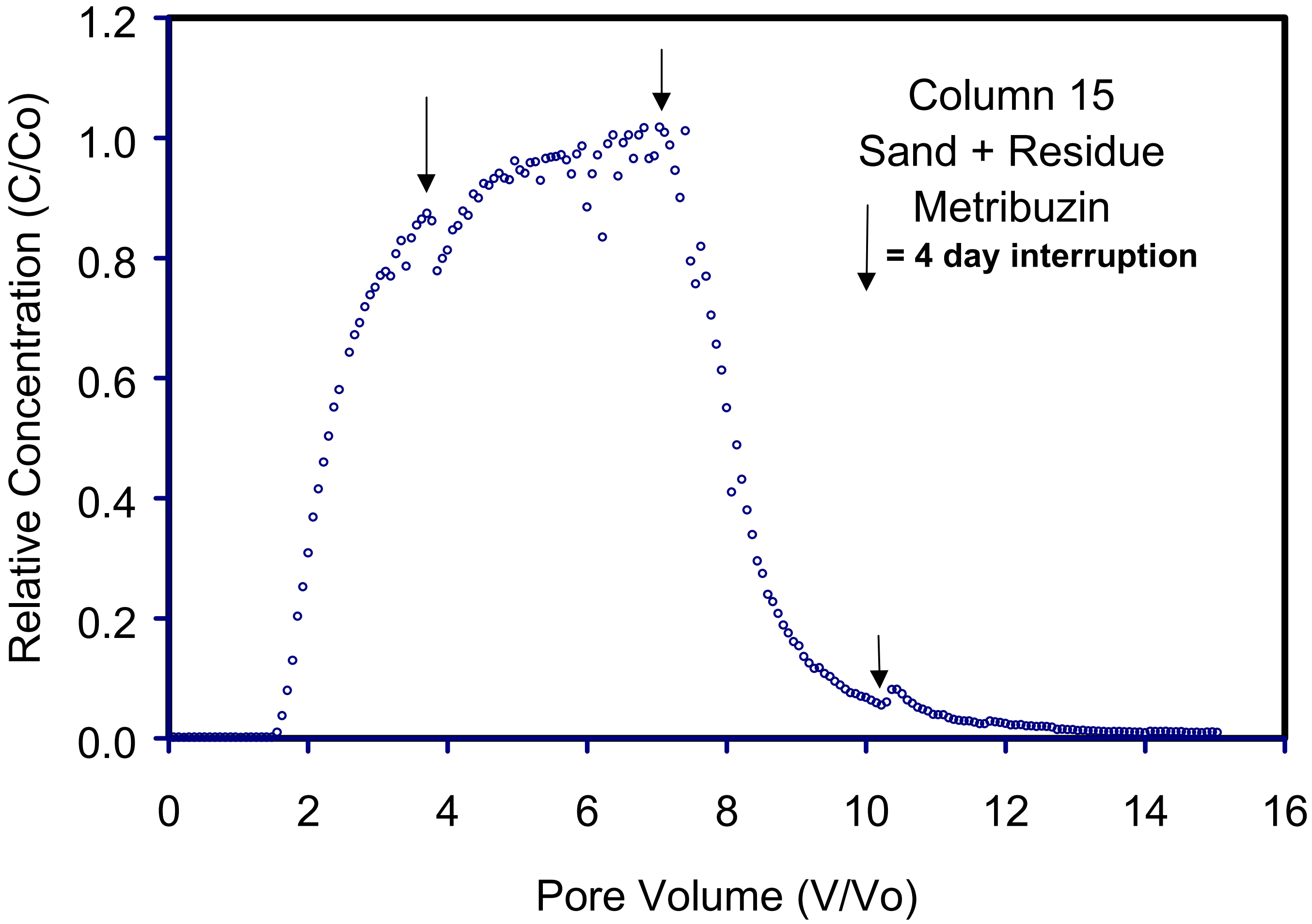

Figure 3.16. Measured metribuzin breakthrough curve from a 10-cm column packed with sugarcane residue and acid washed sand (column 15). Arrows indicate 4 day flow interruption.

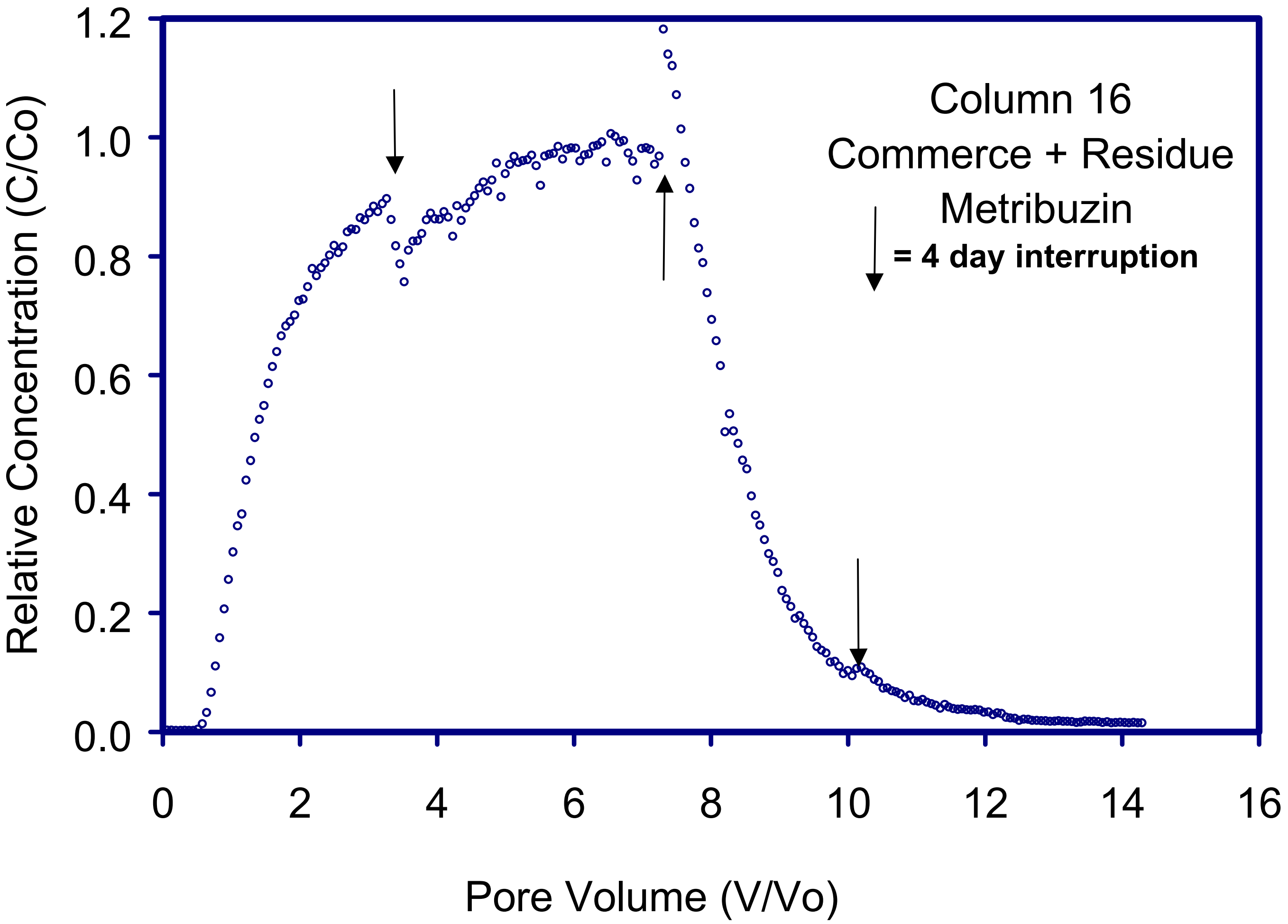

Figure 3.17. Measured metribuzin breakthrough curve from a 10-cm column packed with sugarcane residue and Commerce silt loam soil (column 16). Arrows indicate 4 day flow interruption.

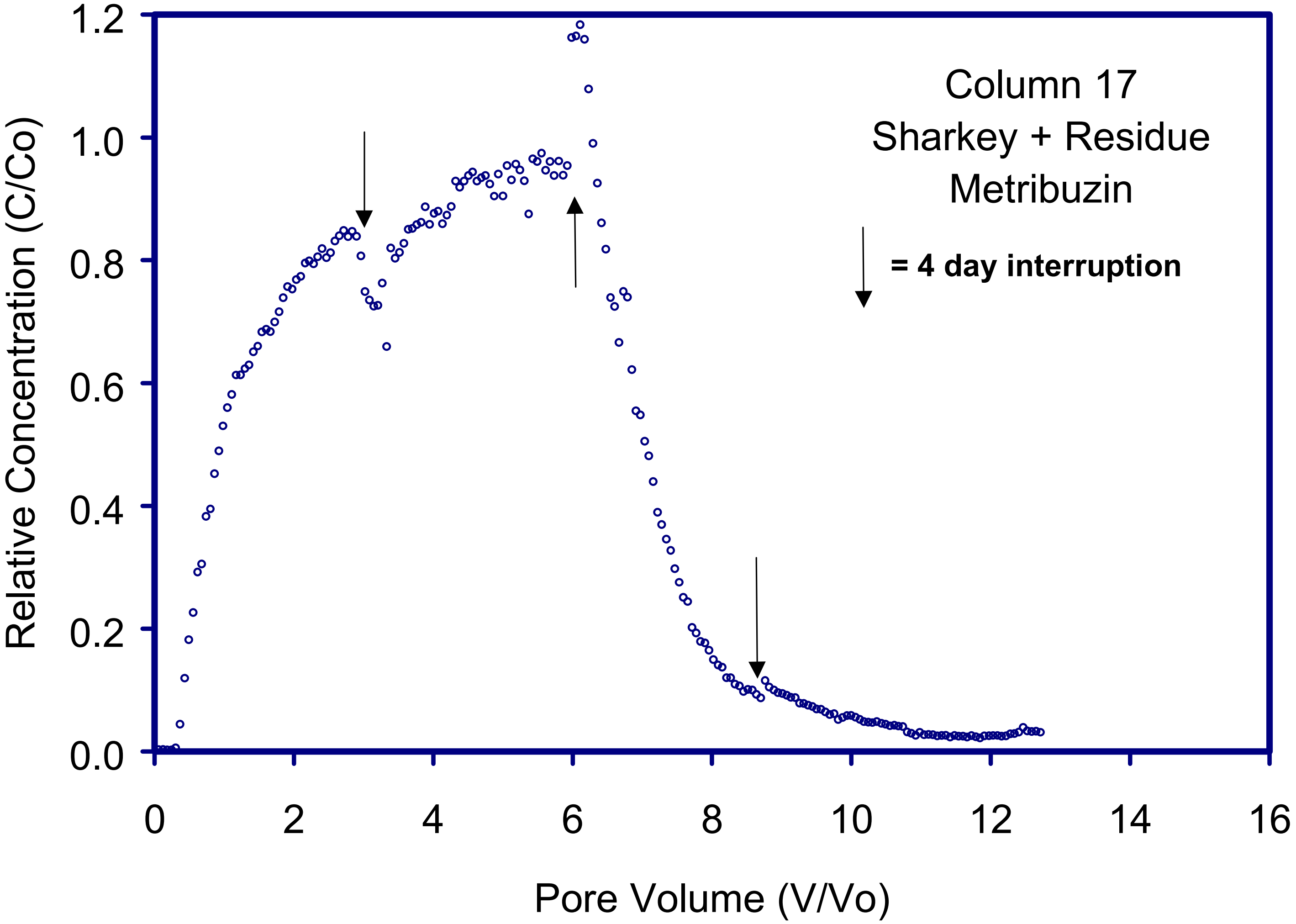

Figure 3.18. Measured metribuzin breakthrough curve from a 10-cm column packed with sugarcane residue and Sharkey clay soil (column 17). Arrows indicate 4 day flow interruption.

CHAPTER 4. CONCLUSIONS

Following the analysis of all experimental studies carried out in this work several conclusions can be made. The linear relationships between the amount of herbicide sorbed and the concentration in solution, can be explained by the presence of homogenous or uniform sorption properties of the sugarcane residue. When comparing herbicides we found consistently that the K_d values indicate that the kinetic behavior of metribuzin adsorption by sugarcane residue is not as strong as that for atrazine. During batch studies, adsorption by the residue was initially rapid, and then exhibited slower retention after 24 hours of reaction time for both herbicides. K_d values were compared across 2002 through 2004 growing seasons and at varying stages of residue decay. The overall herbicide retention did not change significantly with the age of the residue or the time of decay in the field over three growing seasons. The desorption studies verified that atrazine is more strongly sorbed than metribuzin, i.e., the mulch exhibited stronger retention for atrazine than metribuzin. Based on comparison across growing seasons of two desorption studies, one would conclude that with longer incubation times, hysterisis is more pronounced. Such a finding is consistent with Ma et al. (1993) for atrazine desorption on a Sharkey soil. Furthermore, based on all adsorption results presented here metribuzin has a greater capacity for leaching and wash off than that for atrazine.

The soil retention of herbicides is consistent with results and conclusions from field experiments on Commerce soil of Selim et al. (2003). They observed that the mulch residue intercepted significant amounts of applied herbicides. This is of great importance when considering the impact of residue management on the runoff of applied herbicides. Without the residue cover, the soil is much weaker at sorbing the herbicides, hence allowing for offsite movement. Transport studies revealed residue has a rate limiting effect on the transport of metribuzin through Commerce soil.

Sugarcane residue decay in the field was quantified for plantcane, first stubble and second stubble. The rates of decay were not significantly different over all three growing seasons. The calculated half-lives of 126-171 days for the mulch decay indicate a substantial presence for the protection of the soil surface in the months following harvest. Lignin analysis on a percent mass basis indicated no significant changes as the residue decayed in the field. Moreover, lignin analysis data and the corresponding K_d values also showed no obvious linear relationship. Again this emphasizes the need for only one K_d value across growing seasons and age of residue lying in the field post-harvest.

The overall conclusion of laboratory and field studies is that the mulch residue can sorb an amount of atrazine and metribuzin significantly greater than that of the mineral soil. By implementing residue management practices, the potential benefits of keeping atrazine and metribuzin from entering surface waters below maximum containment levels should be greatly increased. Continued research is required to assess the impact of residue management practices and weigh the environmental benefits with sugarcane production costs. Research is underway to evaluate the impact residue management practices have on sugarcane emergence and crop yield.

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VITA

Brian Naquin was born in Plano, TX on February 7, 1978 to Ronald and Wanda Naquin and welcomed home by sisters Ronda and Amy. Soon his family moved to Baton Rouge, Louisiana, there he spent the next years of his life schooling and enjoying south Louisiana. Following graduation from high school he enrolled at the University of Louisiana at Lafayette, there he completed his Bachelors degree in Environmental and Sustainable Resources. Also while in Lafayette he happened upon the love of his life the former Summer Lynn Perault. Following graduation from ULL, he was accepted by Louisiana State University, Graduate School on behalf of Dr. H. M. Selim, of the Department of Agronomy and Environmental Management, to work towards a Master's degree. During his time at LSU, Brian had the opportunity to study with and under many great people. Also during this time he was engaged and married to his love, Summer. Currently Brian is a Research Associate with the LSU AgCenter and a candidate for a Master of Science degree in the spring of 2005.