8-1991

Kinetics and Mechanisms of Atrazine Adsorption and Desorption in Soils Under No-Till and Conventional Management

Digital Object Identifier: https://doi.org/10.13023/kwrri.rr.181

V. P. Evangelou
University of Kentucky

W. W. Witt
University of Kentucky

E. Portig
University of Kentucky

Mike Barrett
University of Kentucky

Repository Citation

Evangelou, V. P.; Witt, W. W.; Portig, E.; and Barrett, Mike, "Kinetics and Mechanisms of Atrazine Adsorption and Desorption in Soils Under No-Till and Conventional Management" (1991). *KWRRI Research Reports*. 27.
https://uknowledge.uky.edu/kwrri_reports/27

RESEARCH REPORT NO. 181

KINETICS AND MECHANISMS OF ATRAZINE ADSORPTION AND DESORPTION IN SOILS UNDER NO-TILL AND CONVENTIONAL MANAGEMENT

By

V.P. Evangelou
W.W. Witt
E. Portig

Principal Investigators

Mike Barrett

Consulting Investigator

Department of Agronomy
University of Kentucky

Project Number: G 1564-03 (A-119-KY)

Agreement Number: 14-08-0001-G 1564 (FY 1990)

Period of Project: July 1990 - June 1991

Water Resources Research Institute
University of Kentucky
Lexington, KY 40504

The work upon which this report is based was supported, in part, by funds provided by the United States Department of the Interior, Washington, D.C., as authorized by the Water Resources Research Act of 1984 (Public Law 98-242).

August 1991

Disclaimer

ABSTRACT

Both soils (Maury silt loam and Sadler) exhibited three apparent mechanisms of atrazine adsorption. The first two mechanisms were very rapid (10 minutes) and were assigned to soil-clay surface adsorption reactions via hydrogen bonding. The quantity of atrazine involved in these two reactions for the 0.5 mg/l solution atrazine varied, depending on the soil, from 67 μg/100 g clay to 219 μg/100 g clay. The reason there were two possible atrazine sinks in this range of atrazine adsorption was believed to be the presence of two types of reactive surfaces, the clay inorganic phase and the organic carbon phase. The latter phase exhibited more influence on the Maury silt loam soil than on the Sadler soil, where the Maury silt loam soil contained more organic carbon than the Sadler soil. The third mechanism involved an atrazine condensation mechanism. It was a relatively slow reaction and it appeared to persist for at least 2 hours. This mechanism accounted for about three fourths of the total atrazine adsorbed. After 75 minutes of solution flow the total atrazine adsorbed by the soil clay samples varied from 333 μg/100 g to 710 μg/100 g. Reversibility of the adsorption process was shown to be limited. Approximately one-third of the adsorbed atrazine was desorbed after a 2 hour leaching with 1 mmol L^{-1} $CaCl_2$ solution. The desorption process was shown to be controlled by two types of reactions. A short rapid one and a long extremely slow one (diffusion controlled). The above findings suggest that the amount of atrazine leaching into surface water or groundwater would depend on the amount of time atrazine had to react with the soil. If it rained immediately following atrazine application then most of the atrazine would be carried in the runoff, making water the main mechanism of atrazine movement. If, on the other hand, a significant amount of time passed after atrazine was applied then a much smaller proportion of the applied atrazine would be leached, making soil erosion the main mechanism of atrazine movement. Equations for all these processes have been developed to aid in modeling the movement of atrazine during rain fall events.

DESCRIPTORS: Transport; Adsorption; Desorption; Herbicides; Modeling; Tillage Systems.

IDENTIFIERS: Groundwater; Weed control; Surface water; Pollution; Water quality.

ACKNOWLEDGEMENTS

The principal investigators are grateful to Ms. Libby Reed for the excellent job she did in typing this report.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

(List of Tables Continued)

APPENDIX I

APPENDIX II

(Appendix II Continued)

APPENDIX III

CHAPTER I - INTRODUCTION

Contamination of surface water and groundwater with atrazine, a herbicide commonly used on corn, is a major concern in the state of Kentucky. Approximately, 1.2 million acres of land is under corn production in the state with one third of it under no-till management. Preliminary data by Witt and Sander (1988) of the University of Kentucky show that atrazine (2-chloro-4-ethylamino-6-isopropylaminio-S-trazine) concentration in runoff from corn plots persists above the safe level (3 ppb) up to 100 days after atrazine application. A greater atrazine concentration is present in the runoff of the plots under conventional management than under no-till management. Additionally, EPA (1988) reports that more states experience groundwater contaminated from atrazine than from any other herbicide.

The principal focus of this study is to increase knowledge on kinetics of adsorption/desorption of atrazine from soils under no-till and conventional management. The goal is to improve modeling accuracy of the transport of atrazine to surface water and groundwater. The current approach is to describe atrazine adsorption/desorption from soils through the use of chemical equilibrium models (Leistra, 1986; Donigian Jr. and Carsel, 1987; Wauchope, 1978; Mulkey et al., 1986). In such models, atrazine distribution coefficients (K) are obtained by fitting laboratory adsorption data of atrazine to the Freundlich equation ($x/m = KP^N$) where x/m = adsorption of pesticide per gram of soil, K = distribution coefficient constant and N = empirical constant). There are a number of problems with this approach. First, the Freundlich constants (K, N) represent a chemical equilibrium state. These constants are obtained in the laboratory by allowing 24 hours contact time between water dissolved atrazine and soil suspension (Nkedi-Kizza et al, 1983; Rao and Davison, 1980). However, effective surface and subsurface transport events of atrazine in soils last only a few minutes. Furthermore, for a surface flow on a non-eroding soil (no-till), as well as for the subsurface macropore flow which is found in many Kentucky soils (Phillips and Phillips, 1984), the contact time between moving water and stationary soil with adsorbed atrazine is but a few minutes.

Second, the Freundlich constants (K, N) generated in the laboratory represent atrazine adsorption. In the field environment, however, atrazine concentration in the runoff, is largely regulated by the desorption process. This leads to the frequent use of the Freundlich equation for predicting desorption on the assumption that the Freundlich constants valid for adsorption are equally valid for desorption. This is known not to be true because of the well recognized hysteresis effect (Sparks, 1989; Koskinen et al., 1979). In essence, the adsorption process and desorption process are two distinct processes. It appears that desorption lags far behind adsorption and therefore Freundlich constants of the adsorptions process tend to overestimate the desorption process (Sparks, 1989; Koskinen et al., 1979; Rao and Davison, 1980). Models employing the Freundlich equation tend to overestimate the quantity of a herbicide expected to be transported to a water supply when compared to the quantity of a herbicide that has actually been transported (Leistra, 1986). Due to the above, equilibrium considerations the Freundlich equation has limited use in predicting adsorption/desorption of atrazine in a field environment.

The application of a herbicide such as atrazine onto a field leads to several processes by which the herbicide's transport is influenced. Such processes include: a) adsorption of the herbicide by the solid surface (Leistra, 1986; Wauchope, 1978; Rao and Davison, 1980); b) desorption of the herbicide by the solid surface (Rao and Davison, 1980); c) hydrolysis due to adsorption (Brown and White, 1969; Weber, 1970), and d) degradation (Sparks, 1989; Wauchope, 1978; Leistra, 1986; Rao and Davison, 1980). This proposal deals with the rates at which the herbicide will adsorb and desorb. This kinetic component has been ignored by researchers and those who attempt to model the transport process.

The amount of atrazine that will be transported by surface and subsurface flow will depend on a) the amount of the applied atrazine that is actually in solution and therefore available to the runoff, b) the potential of the atrazine to desorb, c) the rate at which it will desorb, and d) the rate at which it will adsorb onto new surfaces which it encounters during a runoff event.

The desorption process will depend on the mechanism of atrazine adsorption and the potential of the atrazine-surface complex to solvate. The wetting/drying process that a soil surface may undergo after application of the herbicide is expected to have significant impact on the rate of release of atrazine into the runoff.

It is known that clay surfaces tend to be more acid under dry conditions than wet conditions (Mortland, 1968; Mortland and Ramon, 1968). This allows the surface to hydrogen bond with the herbicide at pH values 2-3 units higher than its pKa. In the case of atrazine with a pKa=1.68, the potential of the clay surface to protonate atrazine would play a significant role on atrazine adsorption. Note that normally a herbicide exhibits maximum adsorption with pH at, near or slightly lower than its pKa (Harter and Ahlrichs, 1969). Similar results have been reported by Brown and White (1969). The above adsorption mechanisms also apply to protonated organic matter.

Hydrogen bonding of organic molecules (i.e. atrazine) onto solid surfaces can take place even when the clay surface is saturated with metals. These metals tend to donate a proton to the organic molecule. Therefore, the ability of a surface to adsorb or desorb a herbicide, in addition to functional group make-up, cation exchange capacity, and specific surface, would also depend on cationic make up. This cationic make up is dependent on pH, soil solution composition, and soil solution ionic strength.

The mechanisms of adsorption of atrazine by pure clay minerals and well defined organic material (humic acid, fulvic acid) are well understood (Brown and White, 1969; Weber, 1970; Bailey and White, 1970a). These mechanisms can be classified into two broad categories: 1) physical adsorption and 2) chemical adsorption. The first mechanism implies weak adsorption while the second mechanism implies strong adsorption (Gunther, 1970).

Soil systems are physical and chemical mixtures of clay minerals and organic matter. Because of this, their complexity is enormous and it is hard to predict which of the above two mechanisms predominates in a particular soil system. The proposed research will quantify rates of adsorption and desorption of atrazine from Kentucky soils under no-till and conventional management.

CHAPTER II - RESEARCH PROCEDURES

Two Kentucky soils at two depths (0-5 cm and 5-20 cm) were selected for this study. One soil was the Maury silt loam (fine-silty, mixed, mesic, Typic Paleudalfs) under conventional and no-tillage management. This soil was selected because several other field atrazine leaching studies (Blevins, Barfield, Frye, Witt) have been carried out on it. A rain simulator was employed on this soil to obtain more data on the movement of atrazine. The present study complements the above studies.

The second soil selected was the Sadler (fine-silty, mixed, mesic, Fragiudalfs). This soil is in western Kentucky, also under conventional and no-tillage management.

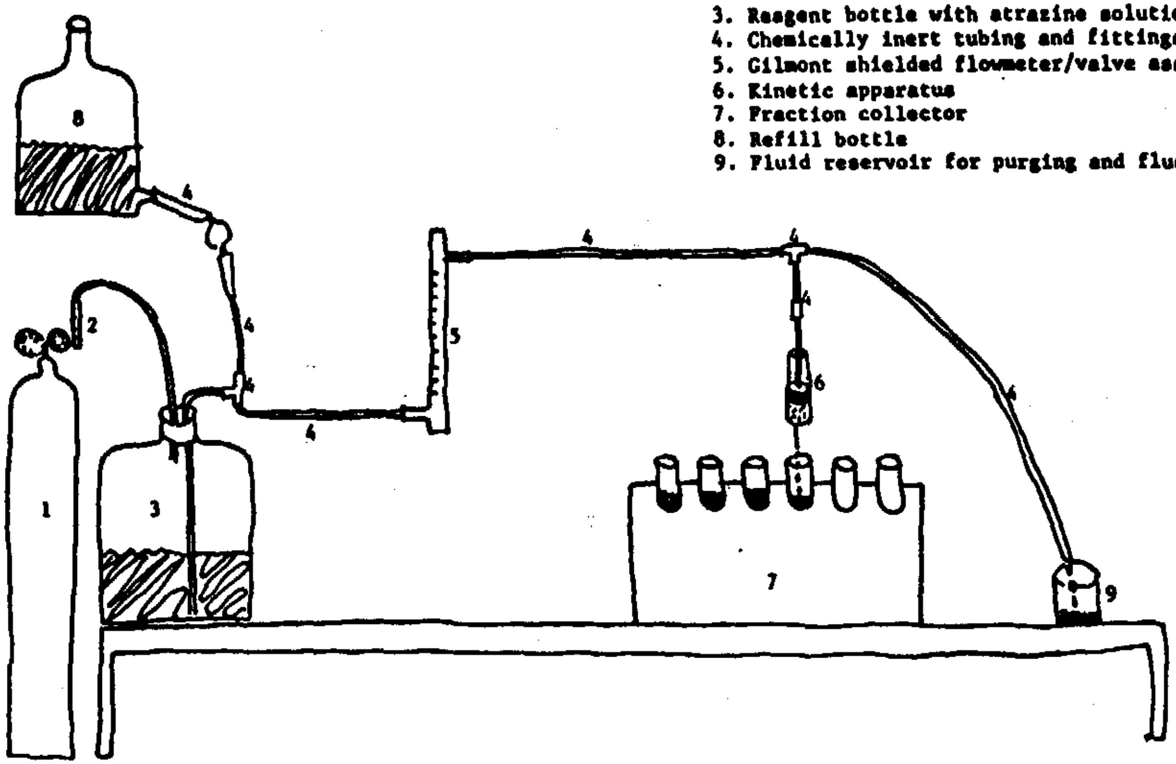
Batch Equilibria

Batch equilibria studies were carried out employing 50 ml test tubes made out of atrazine non-adsorbing material. A 5 or 2.5 or 1 g soil sample was added to each test-tube along with 50 ml adsorbate solution. This adsorbate solution was made out of 1 mmol/l $CaCl_2$ and atrazine varying from zero to 10 mg/l. The latter was spiked with 0.001 μCi/ml of radioactive (^{14}C) atrazine.

The test-tubes were placed on a reciprocal shaker and were shaken for 24 hours. After the 24 hour shaking, the samples were centrifuged and the supernatants were collected for atrazine determination via scintillation counting. Difference between original atrazine concentration minus final atrazine concentration was taken to represent atrazine adsorbed.

Kinetics

The technique employed to evaluate kinetics of atrazine adsorption and desorption was essentially the same with that developed in our laboratory to study cation exchange in soils Lumbanraja, 1991. Some modifications were introduced to accommodate the use of atrazine (Fig. 1). The apparatus consisted of a 6 ml plastic syringe (1 cm in diameter). It served as a soil micro-column or bed-reactor. This syringe was connected via Teflon tubing (0.3 cm inside diameter) to a 2 liter glass container which served as the solution reservoir (0.5 or 0.1 mg/l atrazine plus 1 mmol/l $CaCl_2$ spiked with 0.001 μCi/ml of radioactive (^{14}C) atrazine). The spiked atrazine solution



1. Nitrogen tank
2. Curtis Matheson gas flow regulator
3. Reagent bottle with atrazine solution
4. Chemically inert tubing and fittings
5. Gilmont shielded flowmeter/valve assembly size #1
6. Kinetic apparatus
7. Fraction collector
8. Refill bottle
9. Fluid reservoir for purging and flushing system

Figure 1. Schematic of the gas-pump kinetic apparatus employed for the evaluation of atrazine adsorption/desorption kinetics by Maury silt loam and Sadler soils.

was pumped through the bed-reactor at a flow rate of 0.85 ± 0.05 ml/min employing nitrogen gas pressure as pumping force.

The bed-reactor was prepared as follows: At the bottom of the syringe first a 5 micron stainless steel screen was placed. On top of this filter a mixture of 0.4 g Teflon powder and 0.4 g of soil clay was introduced and on top of this a 0.1 g Teflon powder was added. Aliquots of the flow-through solution were collected at certain time intervals using an Eldex Universal fraction collector.

Analysis of these aliquots for atrazine concentration was carried out by a scintillation counter. Clay separation from each of the soil samples was carried out as follows:

1. Twenty grams of soil were placed in 250 ml centrifuge bottles.
2. The centrifuge bottles, with the soil material, were filled with distilled water and placed on a Eberbach shaker for 0.5 hr.
3. After shaking, the bottles were centrifuged at 750 rpm for 3.5 minutes.
4. After centrifuging, the clay suspension was transferred into fresh centrifuge bottles and centrifuged at 10,000 rpm for 30 minutes.
5. After centrifuging, the supernatant was decanted and the clays were collected.
6. Steps 1 through 5 were repeated 3 or 4 times in order to collect enough clay sample from each soil to carry out the kinetic studies.

<u>Pseudo-First Order Reactions</u>.

Kinetic data of atrazine adsorption were plotted as a pseudo-first order reaction. This was based on the following justification. Consider the case of:

$$\text{Soil} + \text{Atrazine} \dashrightarrow \text{Soil-Atrazine} \qquad [1]$$

The rate of this reaction is expressed as:

$$-\frac{d[\text{Soil-Atrazine}]}{dt} = k_1' \, [\text{Soil}][\text{Atrazine}] \qquad [2]$$

where

$k_1' =$ rate constant.

Considering that atrazine was kept constant (see Materials and Methods)

$$k = k'[\text{Atrazine}] \qquad [3]$$

then

$$-\frac{d[\text{Soil-Atrazine/Soil}]}{dt} = k \qquad [4]$$

Rearranging and introducing integrals and integral limits

$$-\int_{\text{Soil-Atrazine/Soil} = 0}^{\text{Soil-Atrazine/Soil} = 1} d[\text{Soil-Atrazine/Soil}] = k\int_{t=0}^{t=\infty} dt \qquad [5]$$

Solving and taking natural logs on both sides of the equation

$$\ln[\text{Soil-Atrazine/Soil}] = -\,kt \qquad [6]$$

A plot of ln[Soil-Atrazine/Soil] vs. t will produce a linear line with slope k. However, the magnitude of k is conditional. It is dependent on the concentration of atrazine, hence, the plot is referred to as pseudo-first order plot.

CHAPTER III - DATA AND RESULTS

The data in Table 1 show the physical make up of the Maury and Sadler soils. In general, the Maury soil contains more clay and more organic matter than the Sadler soil. Clay and organic matter are two soil constituents that are expected to react with atrazine (Rao et al., 1986; Nkedi-Kizza et al., 1983) because of their high potential to supply atrazine with protons. The data in Table 2 show the surface composition of the two soils. The major difference between these two soils appear to be in the cation exchange capacity (CEC), base saturation, and pH. These major differences appear to play an important role on atrazine adsorption. For example, the CEC could be directly related to atrazine adsortpion by serving as proton donor (Bailey and White, 1964; 1970a,b; Bailey et al., 1968) due to metals occupying exchange sites. Thus, a greater CEC would signify greater atrazine adsorption. Base saturation on the other hand, would be inversely related to atrazine adsorption. Higher base saturation suggests more basic cations and less potential for proton donation to atrazine. The role of pH of soil solution on adsorption is not as apparent (Bailey et al., 1968). The reason for this is that clay surface pH is often 2 to 4 pH units lower than solution pH, depending on the mineral (Harter and Ahlrichs, 1967; 1969). Furthermore, as solution pH decreases, the difference between surface pH and solution pH decreases (Harter and Ahlrichs, 1967).

The data in Table 3 show solution compostion of saturation extracts for the two soils (Maury and Sadler). The role, if any, of soil solution composition to atrazine adsorption is not known. In any case, solution composition determinations for the two soils were made in order to give us some idea on the magnitude of ionic strength to be used in the kinetic and equilibrium experiments.

Table 1. Selected physical properties of Maury silt loam and Sadler soils.

	Sand %	Silt %	Clay %	Organic Matter %	Textural Class
Maury Soil					
Conventional 0-5 cm	5.27	61.55	33.18	4.56±0.22	Silty clay
Conventional 5-20 cm	5.59	61.87	32.53	4.34±0.08	Silty clay
No-till 0-5 cm	6.88	60.49	32.63	7.07±1.03	Silty clay
No-till 5-20	6.38	59.45	34.17	5.11±0.67	Silty clay
Sadler Soil					
Conventional 0-5 cm	4.45	72.86	22.70	2.56±0.24	Silt loam
Conventional 5-20 cm	3.19	73.46	23.35	2.24±0.34	Silt loam
No-till 0-5 cm	3.19	78.96	17.85	5.93±0.11	Silt loam
No-till 5-20 cm	3.19	78.11	18.70	2.66±0.04	Silt loam

Table 2. Exchange phase composition and pH of Maury silt loam and Sadler soils.

	Na	K	Ca	Mg	Mn	Sum of cations	CEC	Base Saturation	pH
	----------	----------	----------	----------	$\mathrm{cmol_c \cdot kg^{-1}}$ soil	----------	----------		
Maury silty loam									
Conventional 0-5 cm	0.035 ±0.002	0.782 ±0.036	6.661 ±1.073	0.604 ±0.074	0.060 ±0.026	8.085 ±1.040	16.49	0.490	5.03 ±0.00
Conventional 5-20 cm	0.039 ±0.003	0.545 ±0.007	7.011 ±1.227	0.627 ±0.068	0.044 ±0.021	8.223 ±1.159	15.70	0.524	5.05 ±0.00
No-till 0-5 cm	0.037 ±0.006	0.978 ±0.032	5.252 ±1.484	0.703 ±0.078	0.083 ±0.019	6.971 ±1.432	18.55	0.376	4.88 ±0.04
No-till 5-20	0.033 ±0.002	0.588 ±0.003	6.100 ±1.110	0.586 ±0.097	0.039 ±0.013	7.307 ±1.012	18.34	0.398	5.06 ±0.02
Sadler									
Conventional 0-5 cm	0.031 ±0.004	0.320 ±0.001	8.807 ±0.474	0.798 ±0.074	0.015 ±0.006	9.962 ±0.405	11.53	0.864	7.02 ±0.02
Conventional 5-20 cm	0.038 ±0.002	0.832 ±0.688	8.670 ±1.484	0.705 ±0.002	0.005 ±0.004	10.246 ±2.169	11.14	0.920	6.77 ±0.08
No-till 0-5 cm	0.038 ±0.006	0.537 ±0.034	7.872 ±1.035	1.100 ±0.138	0.030 ±0.015	9.547 ±0.926	12.53	0.762	6.10 ±0.08
No-till 5-20 cm	0.036 ±0.001	0.185 ±0.004	7.697 ±1.160	0.611 ±0.060	0.013 ±0.010	8.529 ±1.104	10.27	0.830	6.36 ±0.00

Table 3. Saturation extract composition of Maury silt loam and Sadler soils.

	Na	K	Ca	Mg	Mn	Total Cations	EC	P	N	pH
	---------------------- mmol$_c$ L^{-1}					------------------------	dS m^{-1}	---mmol L^{-1}	----	
<u>Maury silty loam</u>										
Conventional 0-5 cm	0.17 ±0.05	0.60 ±0.01	2.69 ±0.95	0.45 ±0.11	0.07 ±0.03	3.92 ±1.11	0.54 ±0.04	0.006 ±0.003	4.46 ±0.89	4.88 ±0.06
Conventional 5-20 cm	0.22 ±0.10	0.37 ±0.01	3.17 ±1.22	0.55 ±0.16	0.06 ±0.02	4.32 ±1.46	0.60 ±0.08	0.005 ±0.002	4.81 ±0.53	4.91 ±0.07
No-till 0-5 cm	0.18 ±0.06	0.72 ±0.03	1.02 ±0.42	0.29 ±0.10	0.05 ±0.02	2.22 ±0.62	0.35 ±0.01	0.010 ±0.006	1.07 ±0.00	4.74 ±0.05
No-till 5-20	0.17 ±0.06	0.26 ±0.01	1.05 ±0.25	0.18 ±0.08	0.02 ±0.01	1.80 ±0.52	0.20 ±0.04	0.005 ±0.002	0.86 ±0.00	4.97 ±0.12
<u>Sadler</u>										
Conventional 0-5 cm	0.21 ±0.07	0.17 ±0.00	3.47 ±1.27	0.52 ±0.14	0.005 ±0.002	4.37 ±1.49	0.51 ±0.07	0.003 ±0.0	1.78 ±0.36	6.92 ±0.23
Conventional 5-20 cm	0.27 ±0.09	0.04 ±0.00	1.79 ±0.65	0.27 ±0.12	0.004 ±0.0	2.38 ±0.85	0.30 ±0.06	0.003 ±0.0	1.25 ±0.18	6.64 ±0.22
No-till 0-5 cm	0.22 ±0.04	0.93 ±0.02	8.31 ±2.37	2.33 ±0.52	0.06 ±0.03	11.80 ±2.89	1.44 ±0.06	0.006 ±0.003	7.14 ±0.0	6.00 ±0.12
No-till 5-20 cm	0.19 ±0.04	0.08 ±0.00	2.19 ±0.55	0.32 ±0.05	0.01 ±0.007	2.80 ±0.63	0.36 ±0.04	0.003 ±0.0	1.29 ±0.14	6.24 ±0.16

Equilibrium Experiments

The data in Fig. 2 show the relationship between adsorbed atrazine by the two soils and atrazine concentration in the solution phase. These data reveal that the Maury silt loam exhibits greater atrazine adsorption potential than the Sadler. This is perhaps due to the higher CEC and organic matter content of the Maury soil (Nkedi-Kizza et al., 1983). Furthermore, the no-till soil samples appear to have greater atrazine adsorption potential than the conventional soil samples. This is also attributed to the greater organic matter content of the no-till soil samples.

The data in Fig. 3 show the relationship between fraction of added atrazine adsorbed and atrazine added in the solution phase. It is clearly shown that for all soil samples tested, less than 17% of the added atrazine was adsorbed by the soil. This strongly suggests that when atrazine is applied to soil systems, only a small fraction is retained by the soil and thus the likelyhood that this herbicide will be carried by the runoff is great. For this conclusion it is assumed that a 24-hr equilibration period represents distribution of atrazine between soil and soil solution in the actual soil environments. Futhermore, it is also assumed that water moving through the soil does not flow through macropores (Phillips and Phillips, 1984) and thus does not bypass the soil-solution that may be associated with dissolved atrazine.

The data in Figs. 4, 5, 6 and 7 demonstrate the influence of solid to solution ratio on atrazine adsorption by the Maury and Sadler soils. It is clearly shown that only the Sadler soil under conventional management, 0-5 cm depth, (Fig. 6) exhibits atrazine adsorption potential dependency on solid to solution ratio. In other words, the greater the quantity of soil added the greater the quantity of atrazine adsorbed. This behavior suggests that in

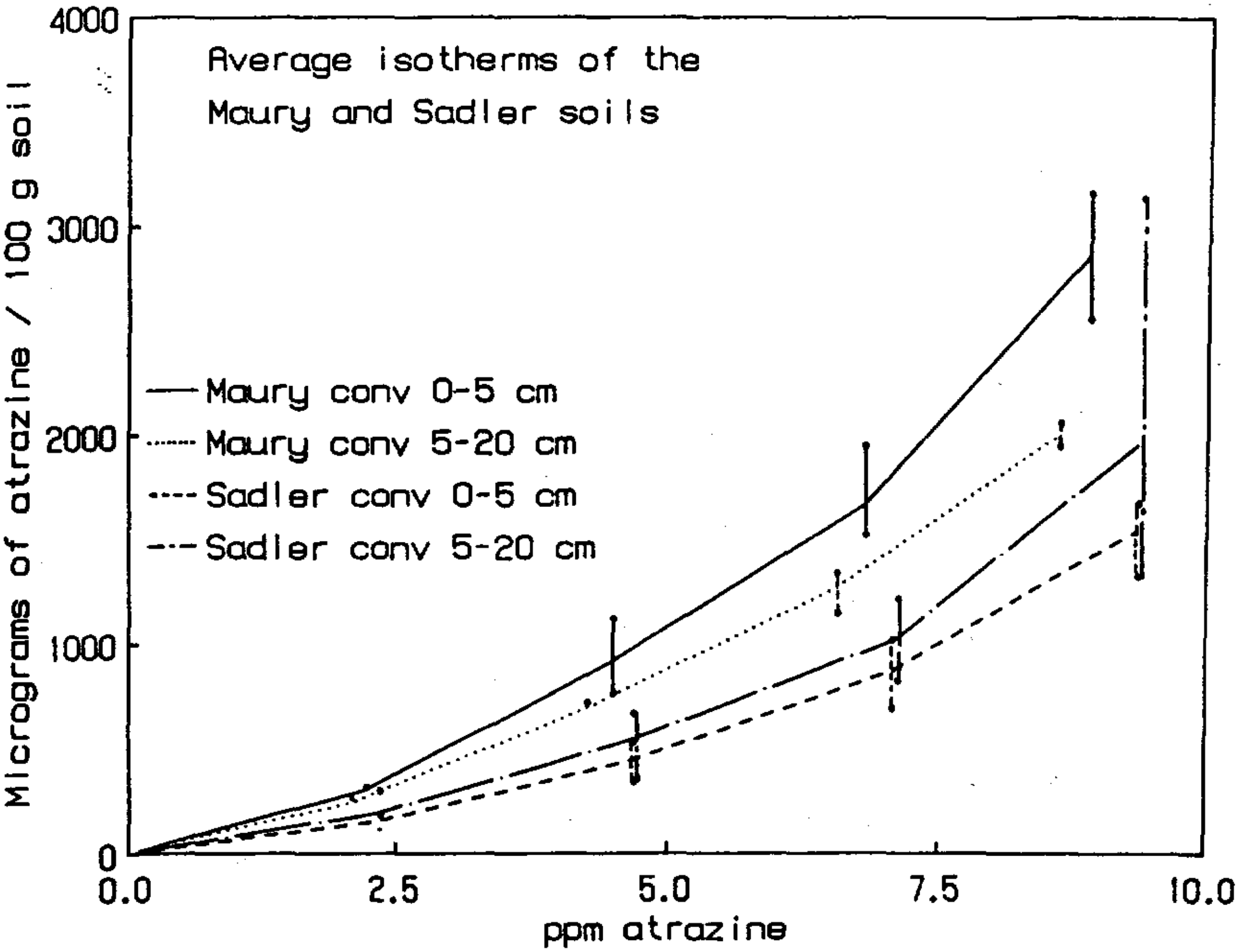


Figure 2. Atrazine adsorption isotherms of Maury silt loam and Sadler soils.

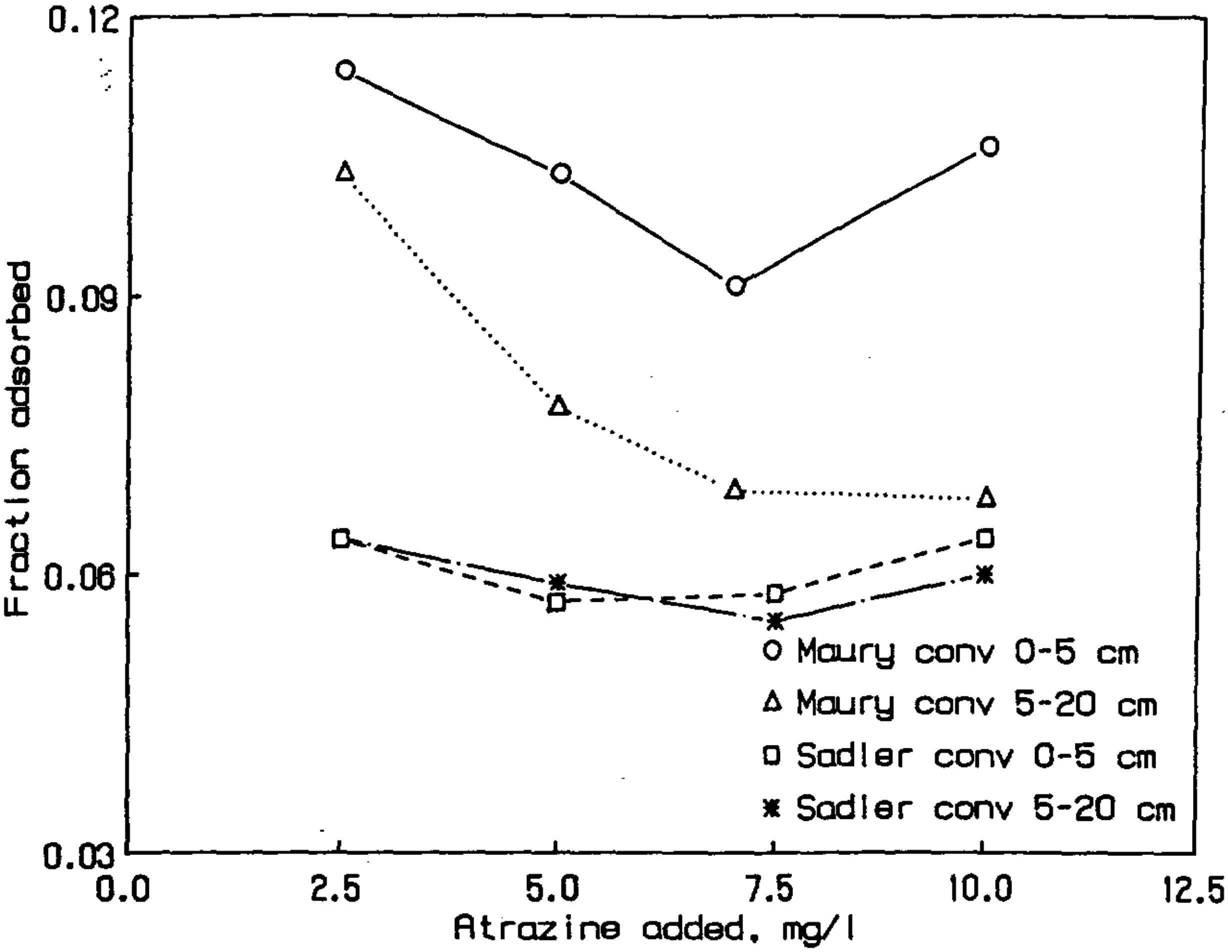


Figure 3. **Fraction of solution added atrazine adsorbed by the surfaces of Maury silt loam and Sadler soil samples.**

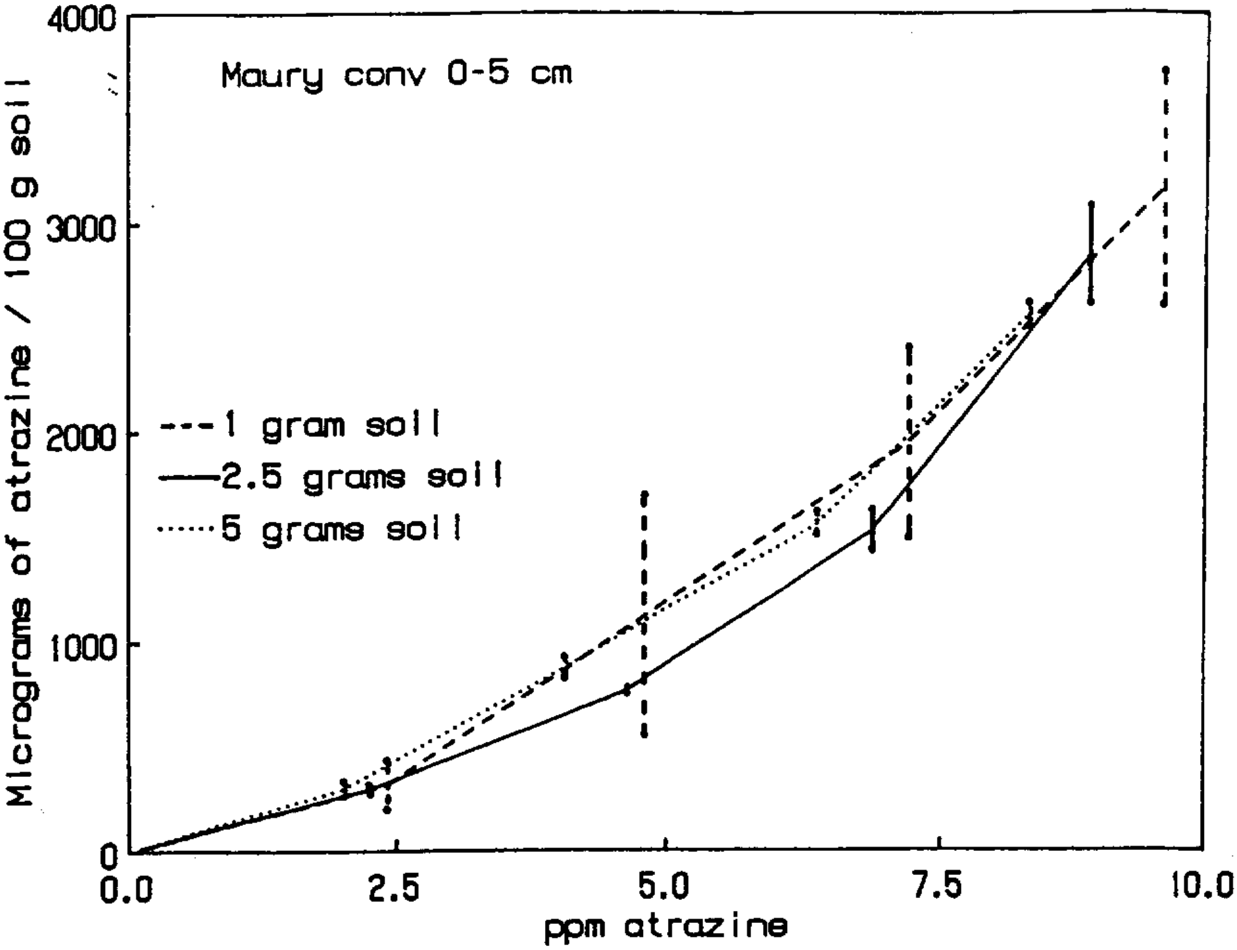


Figure 4. Atrazine adsorption isotherms of Maury silt loam soil, 0-5 cm depth, under various soil to solution ratios.

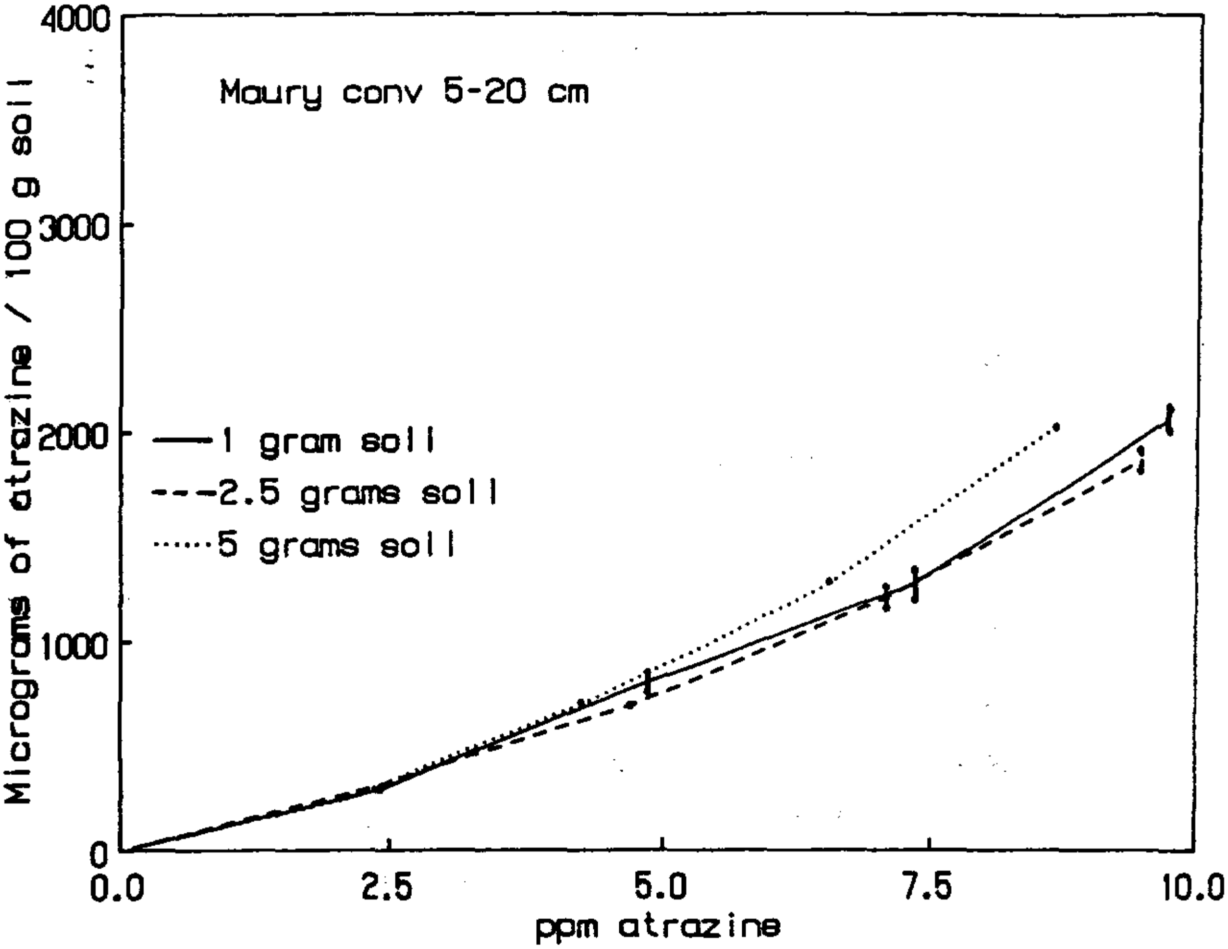


Figure 5. Atrazine adsorption isotherms of Maury silt loam soil, 5-20 cm depth, under various soil to solution ratios.

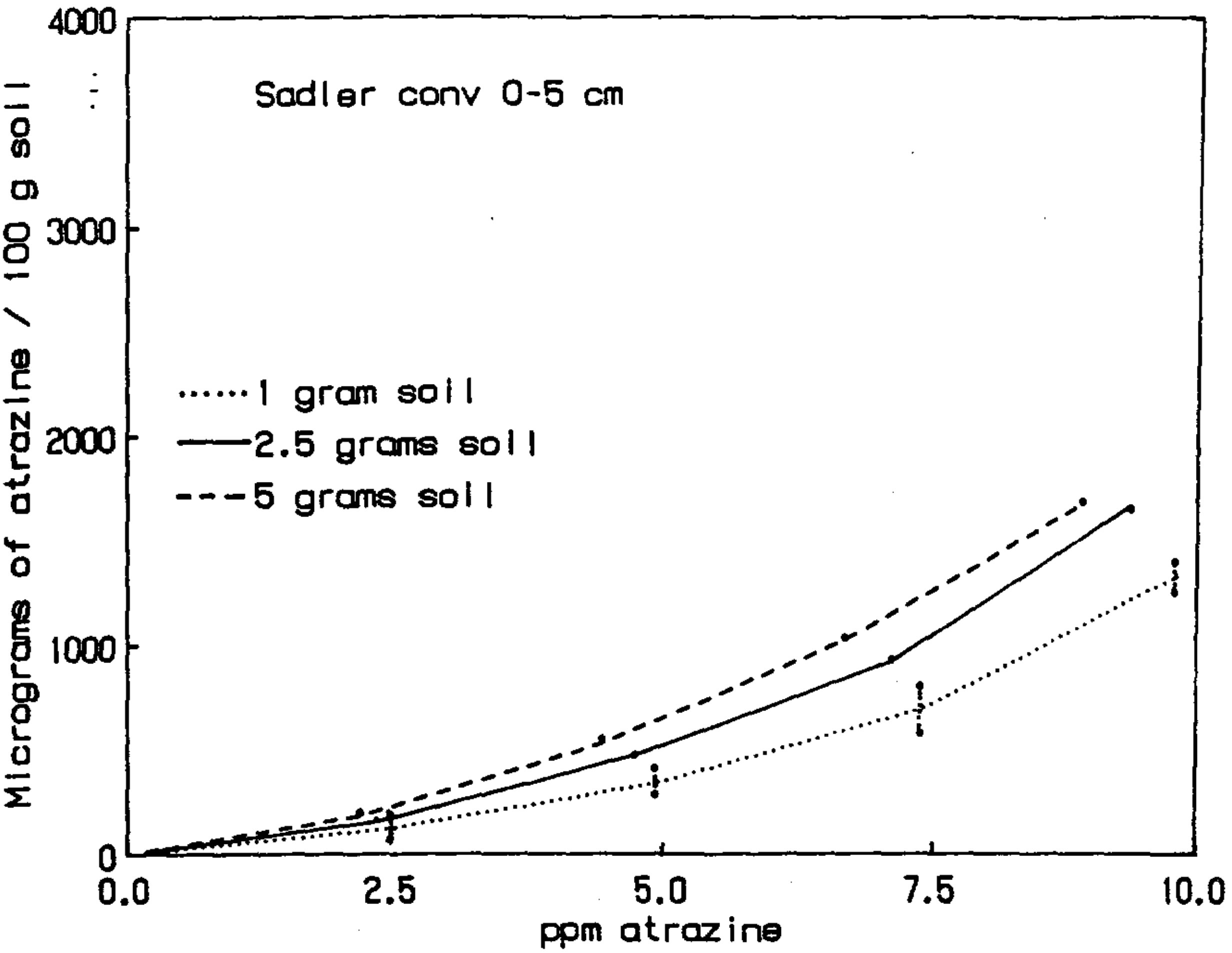


Figure 6. Atrazine adsorption isotherms of Sadler soil, 0-5 cm depth, under various soil to solution ratios.

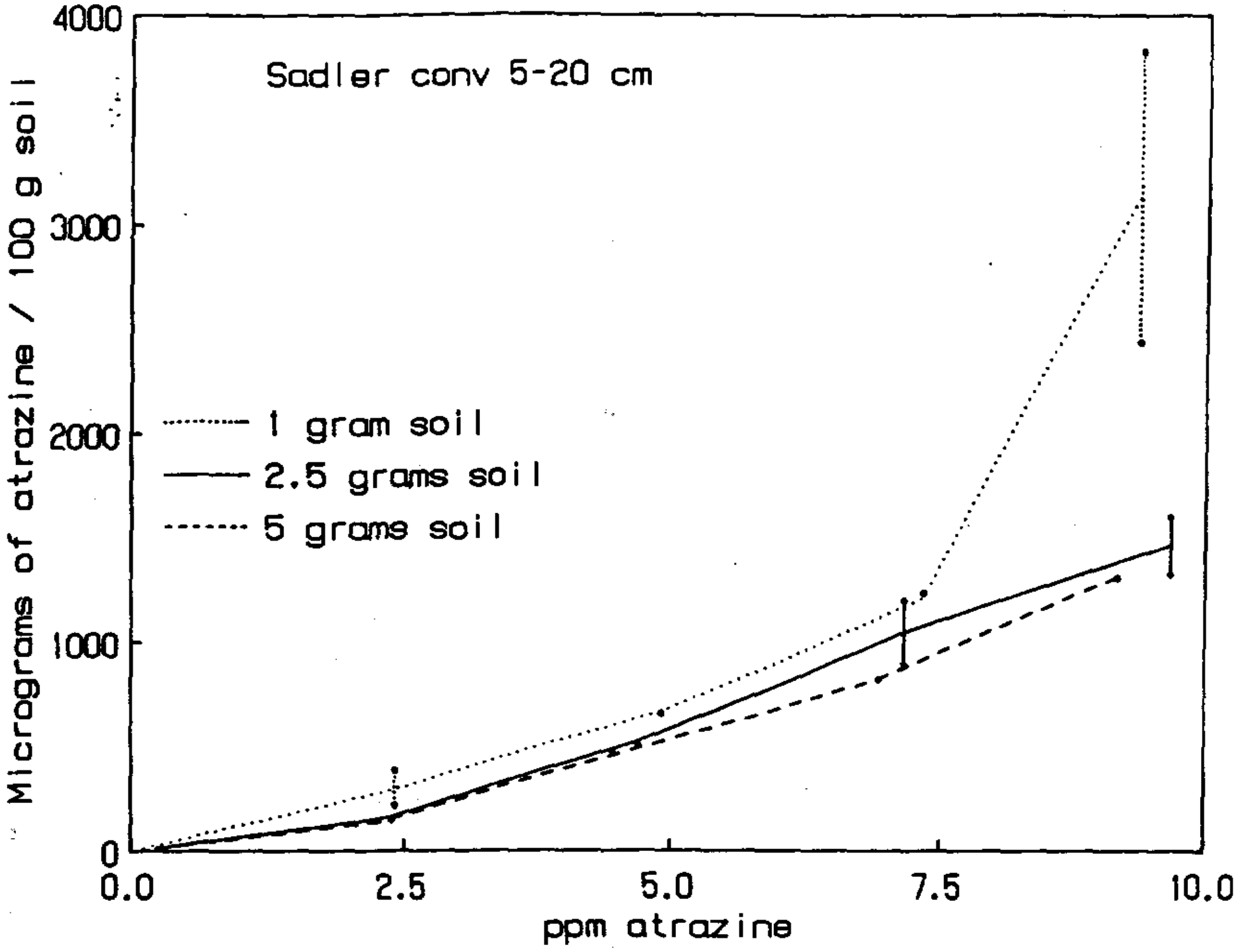


Figure 7. Atrazine adsorption isotherms of Sadler soil, 5-20 cm depth, under various soil to solution ratios.

this particular soil (Sadler, conventional, 0-5 cm depth) adsorption of atrazine is not a surface controlled reaction but rather a reaction controleed by a process analogous to precipitation/dissolution. This kind of behavior is an important consideration when modeling atrazine release to surface runoff during erosion events. Under such conditions, the distribution ratio of atrazine between solution and solid phase changes as the solid to solution ratio changes.

Finally, the data in Fig. 4 through 7 show that adsorption of atrazine by any of the four soil samples tested is not described by a Freundlich isotherm (Bailey et al., 1968; Nkedi-Kizza and Rao, 1987). A Freundlich isotherm is commonly characterized by a rapid initial increase on the adsorption process as the concentration of adsorbate in the solution increases, followed by a rapid decline in adsorption as concentration of the adsorbate (atrazine) in the solution continues to increase (Nkedi-Kizza and Rao, 1987). In this study, the four soils tested show a linear atrazine adsorption response to approximately 5 mg/l solution atrazine, followed by an increase in adsorption as atrazine solution concentration continues to increase. This type of behavior suggests that atrazine adsorption by these soils is not controlled by a surface hydrogen donating process as postualted in the literature (Bailey et al., 1968), but rather it is controlled by a surface catalyzed atrazine condensation (precipitation) reaction. This observation has important ramifications in the release of surface "adsorbed" atrazine. In other words, because atrazine is highly hydrophobic, any atrazine precipitated in the soil solution would be released extremely slowly and consequently could persist for some time. On the other hand, it has been reported in the literature (Armstrong, 1967) that surface adsorbed atrazine hydrolyzes at a rather fast rate, so that atrazine soil adsorption serves as a means of atrazine detoxification.

Kinetics of Atrazine Adsorption/Desorption

The data in Fig. 8 show the dependence of the kinetics of the adsorption of atrazine on its solution concentration. The greater the concentration, the greater are both the total quantity adsorbed and the rate of adsorption. This observation is consistent with surface precipitation phenomena and surface adsorption phenomena induced by proton donation.

The data in Fig. 9, 10, 11 and 12 demonstrate atrazine adsorption behavior kinetics for all eight soil samples tested. These data reveal that kinetics of atrazine adsorption appear to be controlled by two mechanisms distinquished by relative speed. The first mechanism is characterized by rapid speed (lasts approximately 10 minutes) while the second mechanism is characterized by slow speed. The first mechanism is consistent with surface adsorption reactions (Lumbanraja, 1991) while the second mechanism appears to be controlled by other than a surface reaction, perhaps a surface condensation reaction.

The data respresenting the first mechanism were plotted as a first-order reaction. These plots are shown in Fig. 13 through 16. According to these plots, the first mechanism is actually controlled by two atrazine adsorption processes. We postulate that these processes involve two sources of protons. One source may represent the organic soil mineral phase (organic matter) while the second phase may represent the inorganic soil mineral (Rao et al., 1985). This is supported by comparing the plots of Maury silt loam with the plots of Sadler (Fig. 13 vs. Fig. 14). The data in Fig. 13, which represents the Maury

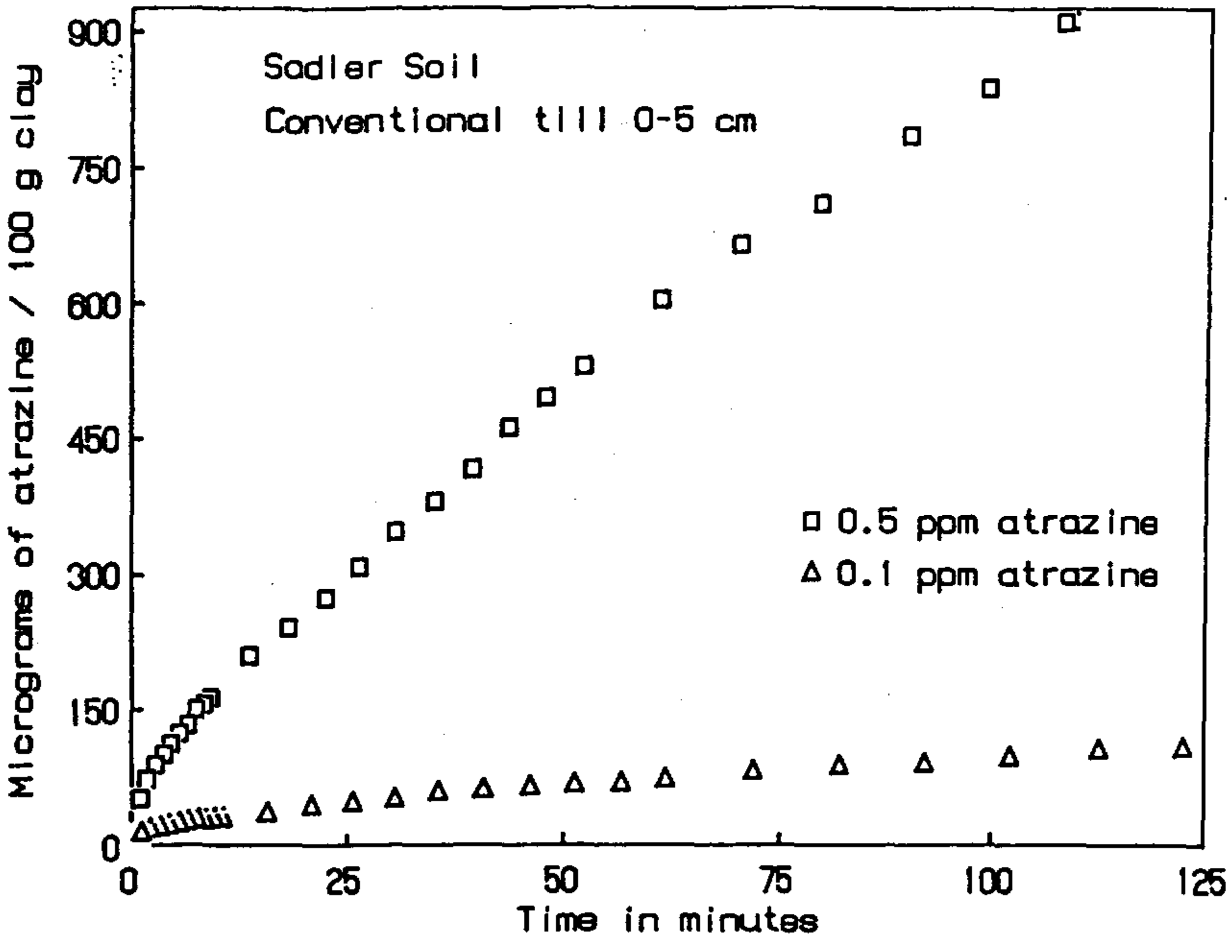


Figure 8. Kinetics of atrazine adsorption at two different solution concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}).

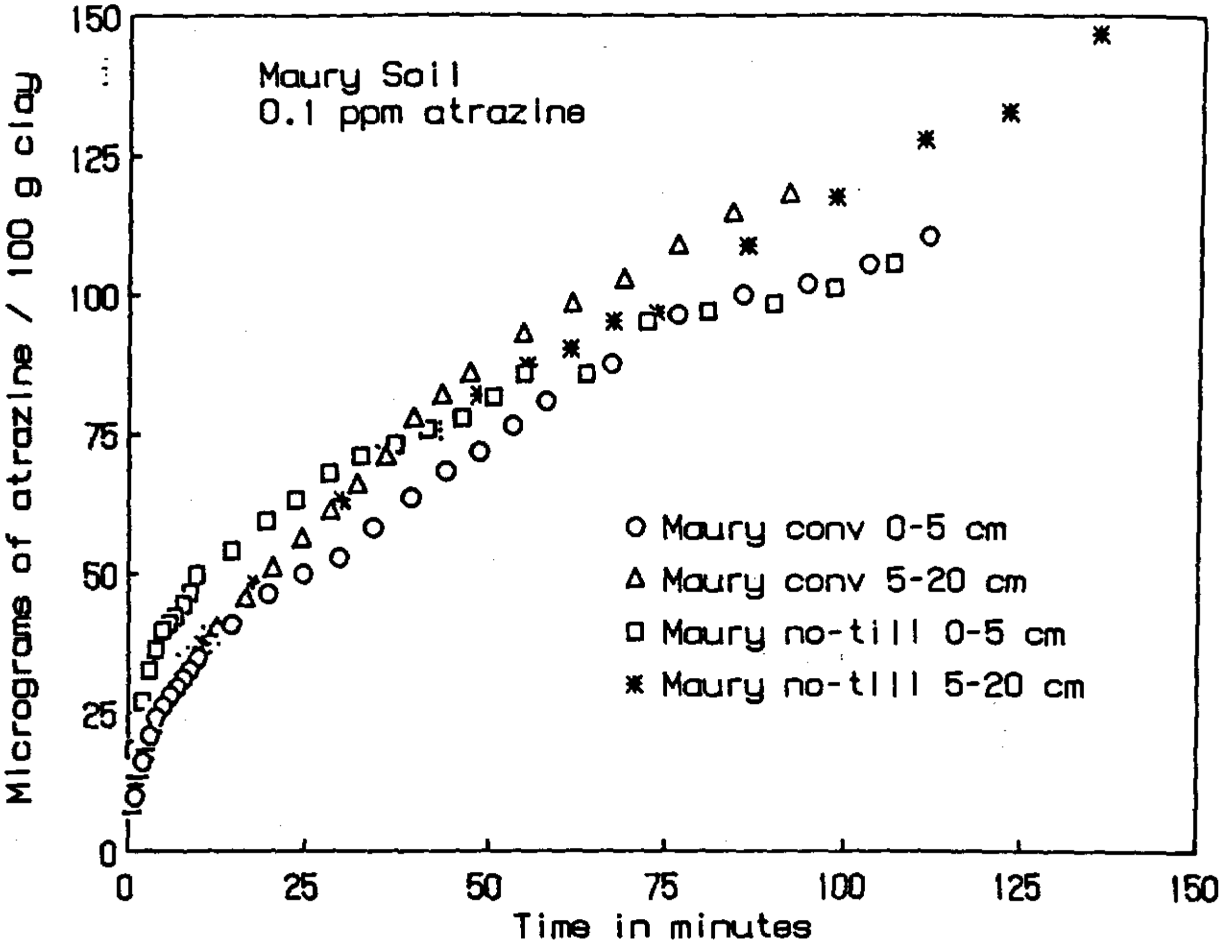


Figure 9. Kinetics of atrazine adsorption at 0.1 mg L^{-1} solution concentration by Maury silt loam soil.

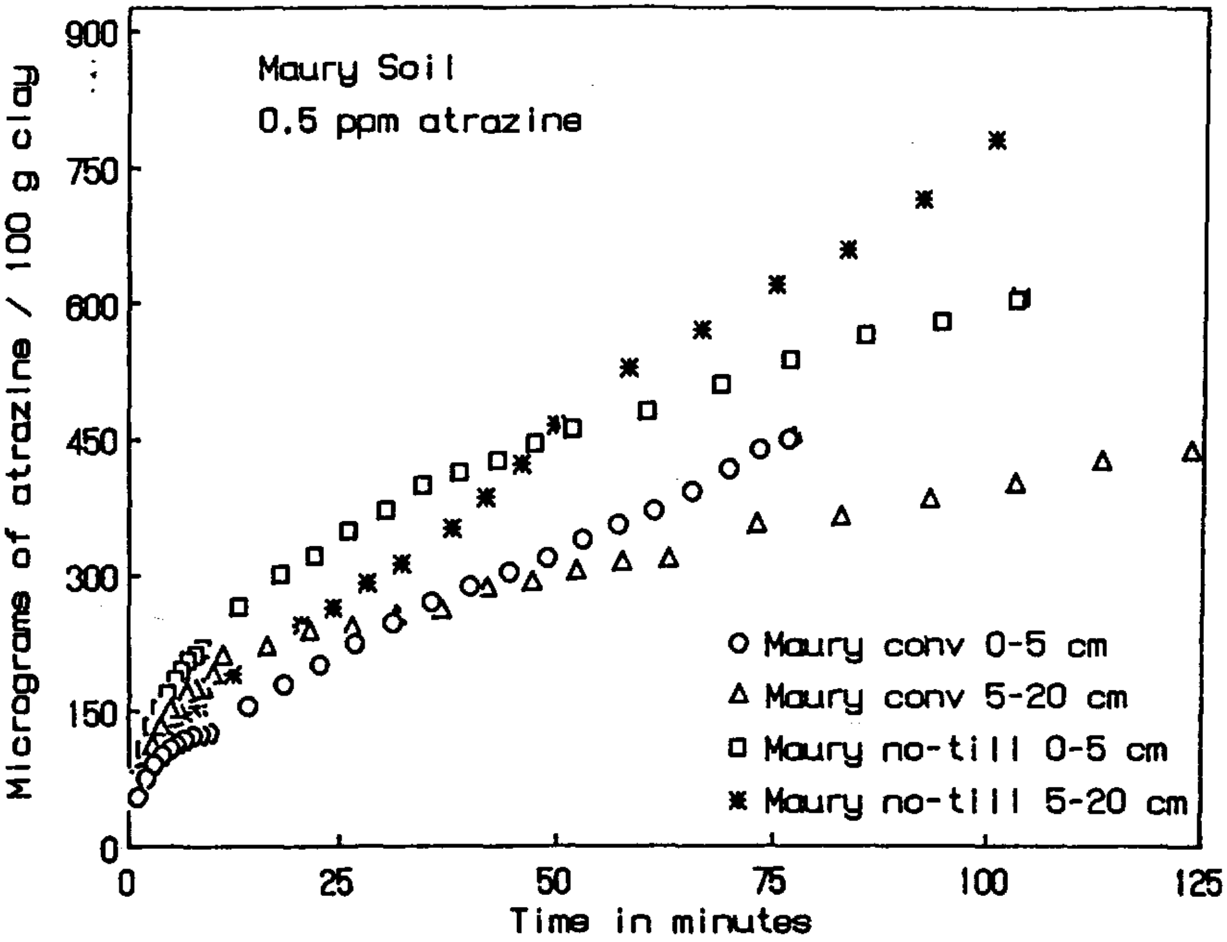


Figure 10. Kinetics of atrazine adsorption at 0.5 mg L^{-1} concentration, by Maury silt loam soil.

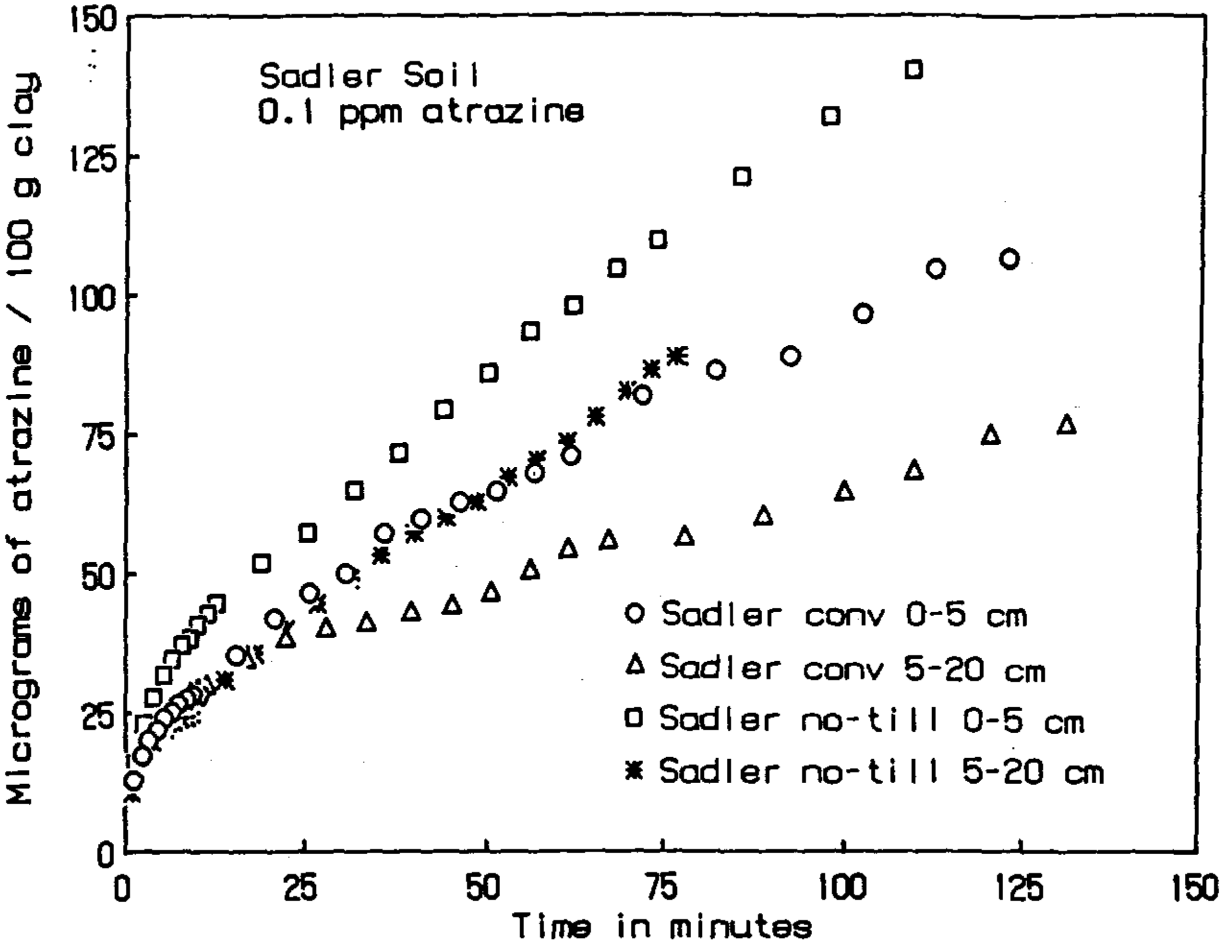


Figure 11. Kinetics of atrazine adsorption at 0.1 mg L^{-1} solution concentration, by Sadler soil.

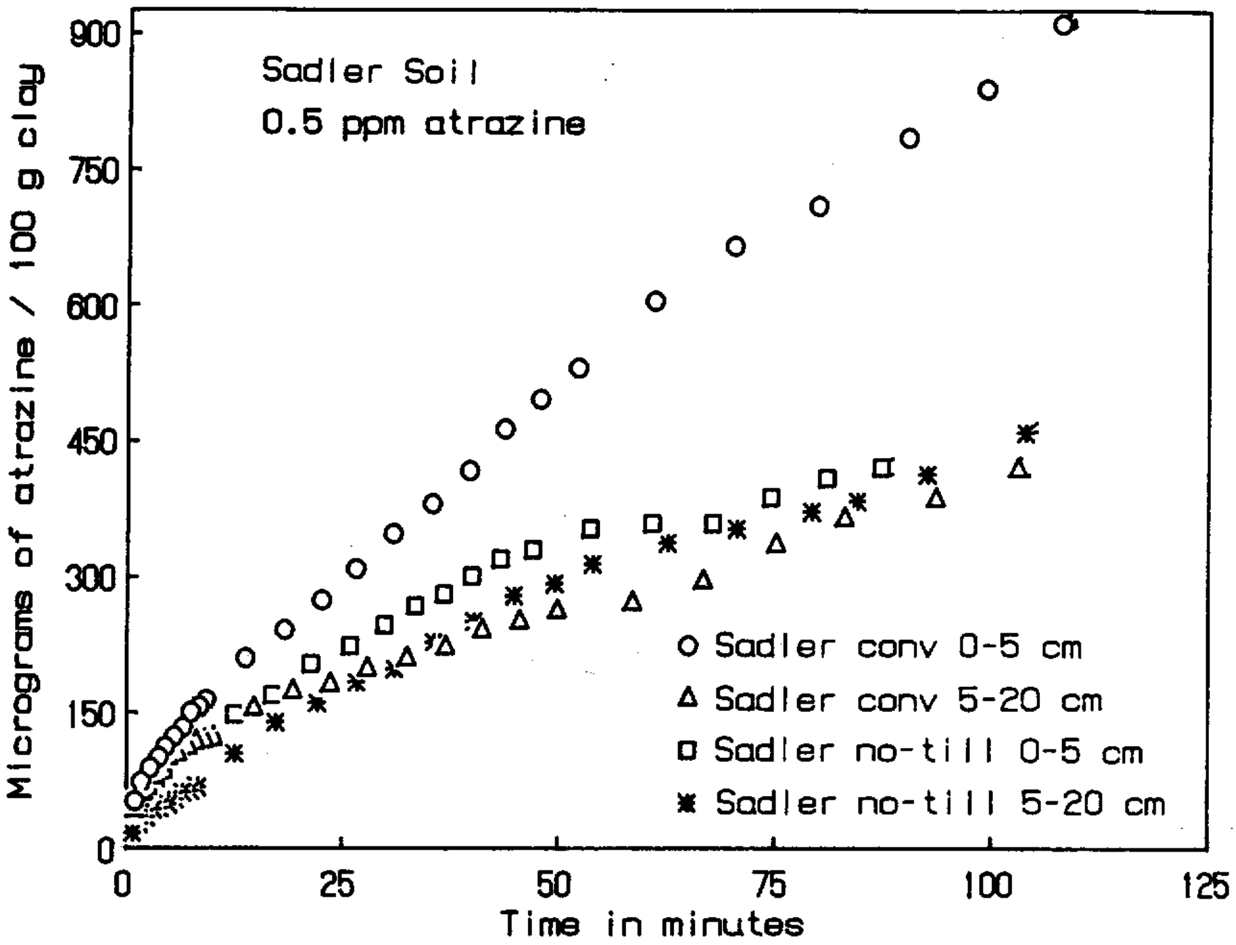


Figure 12. Kinetics of atrazine adsorption at 0.5 mg L^{-1} solution concentration, by Sadler soil.

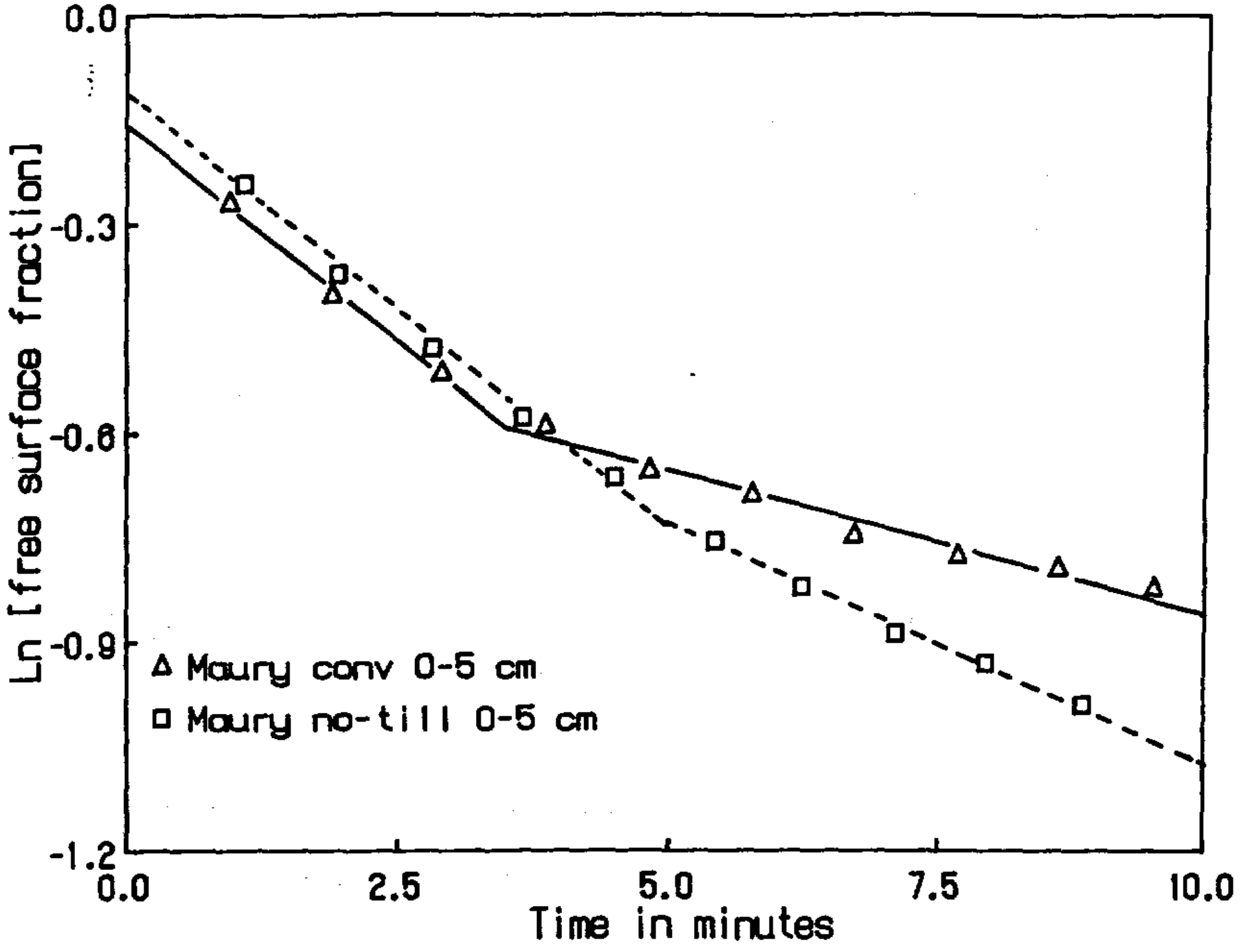


Figure 13. First-order plots of atrazine adsorption at 0.5 mg L^{-1} Maury silt loam soil, at 0-5 depth, under conventional and no-till management.

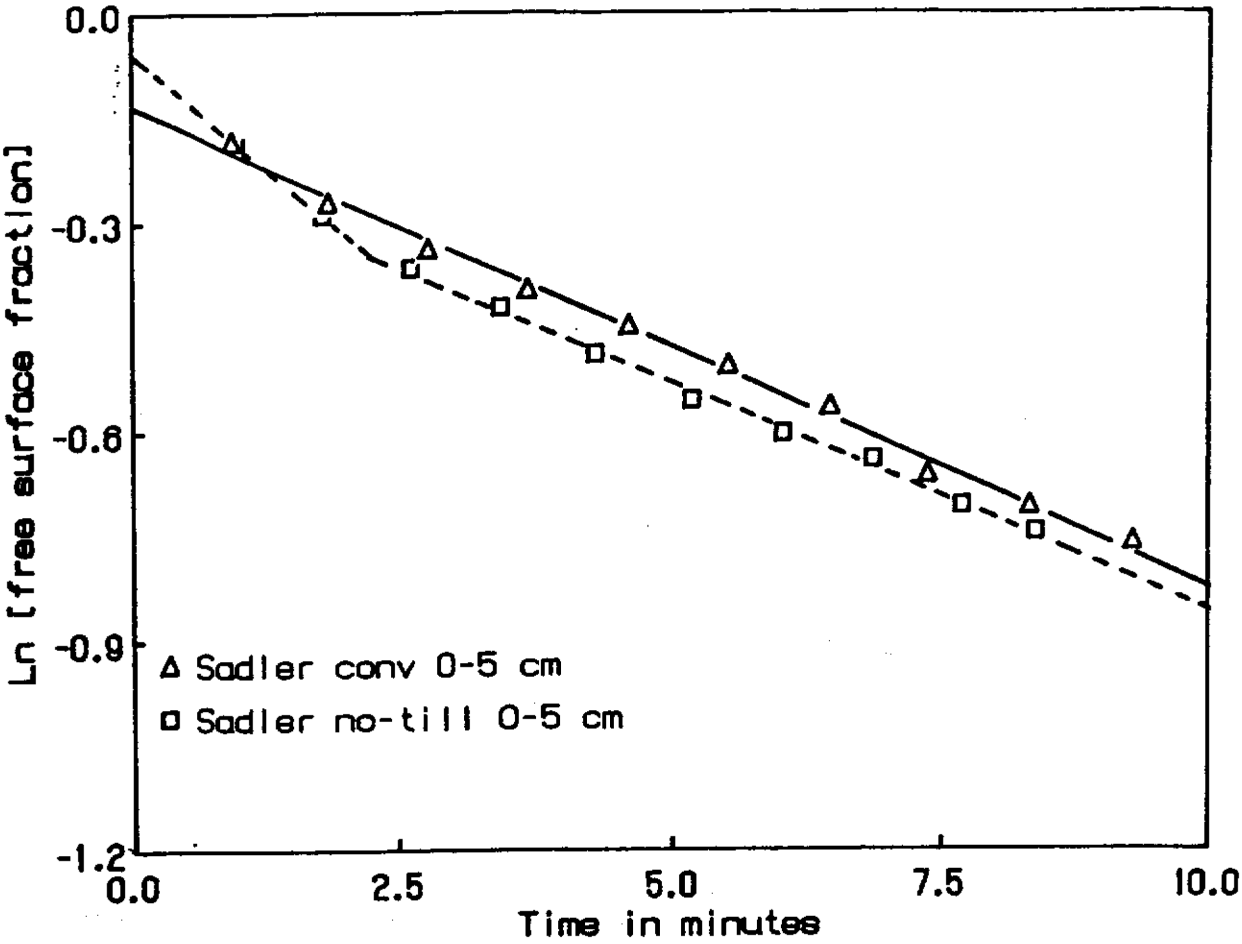


Figure 14. First-order plots of atrazine adsorption at 0.5 mg L^{-1} by Sadler soil, at 0-5 cm depth, under conventional and no-till management.

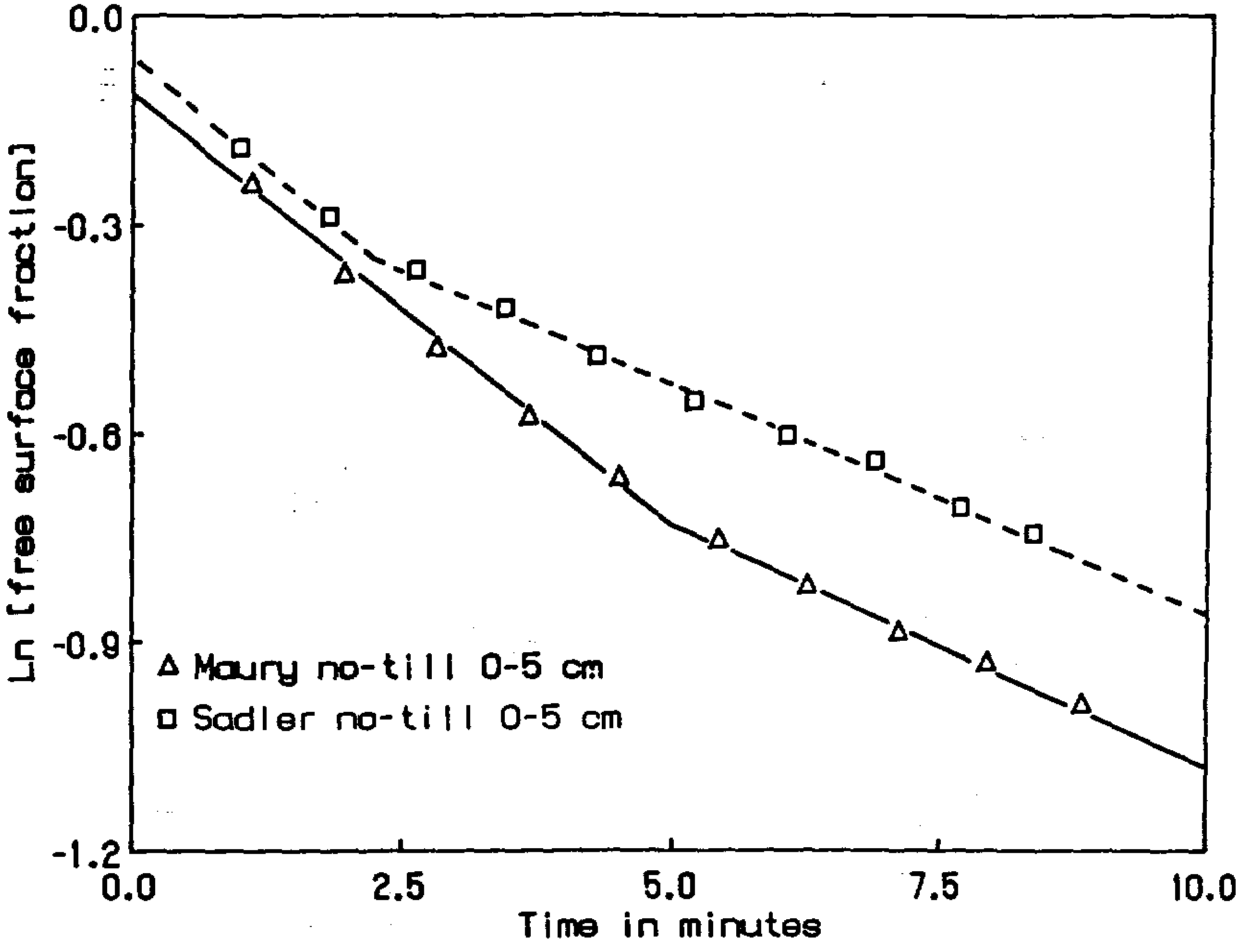


Figure 15. First-order plots of atrazine adsorption at 0.5 mg L^{-1} by Maury silt loam and Sadler soils, at 0-5 cm depth, under no-till management.

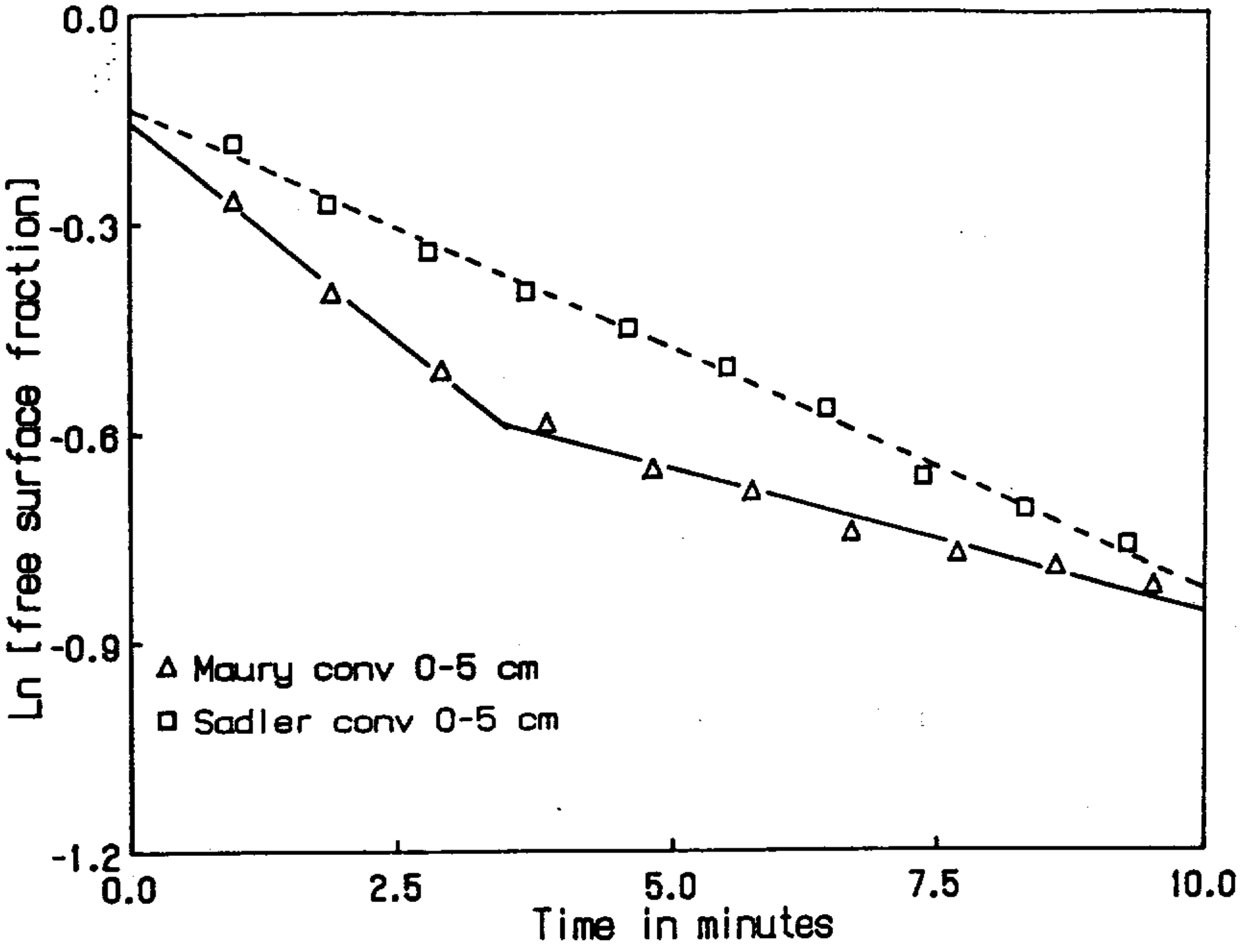


Figure 16. First-order plots of atrazine adsorption at 0.5 mg L^{-1} by Maury silt loam and Sadler soils, at 0-5 cm depth, under conventional management.

under no-till and conventional management, exhibits two distinct slopes. It is postualted that these two slopes represent organic matter surfaces and clay surfaces. On the other hand, Fig. 14 which represents the Sadler soil under no-till and conventional management, exhibits for the most part one slope (conventional one slope; no-till two slopes). Note that a major difference between thee two soils is organic matter content. In general, the Maury soil contains twice as much organic matter as the Sadler soil (Table 1). For a direct comparison with respect to atrazine adsorption between the two soils see Figs. 15 and 16.

The data representing the second mechanism of atrazine adsorption by the soil clay surfaces were treated as zero order reaction. The equations describing the two major mechanisms of atrazine adsorption are summarized in Table 4.

The data in Fig. 17 through Fig. 23 show atrazine adsorption-desorption behavior of all soil samples tested.; It is clearly demonstrated that atrazine adsorption is not a reversible process. Only a small fraction of the atrazine adsorbed can be desorbed. Futhermore, atrazine desorption is a two "rate" process: a rapid rate and a slow rate. From the total quantity of atrazine desorbed, the fast rate represents a larger atrazine fraction. The slow release of adsorbed atrazine may play a very important role in the movement and detoxification of atrazine in natural soils. Atrazine adsorption protects ground-water from being polluted with atrazine and enhances atrazine's detoxification potential.

Table 4. Linear regression equations of first-order and zero-order plots of atrazine adsorption at 0.5 mg L^{-1} by Maury silt loam and Sadler soils.

	Prediction Equation	R^2	Rate Constant	Adsorption Maxima after 75 min.	Adsorption Maxima at the end of k_2
				µg/100 g	
Maury Soil					
Conventional 0-5 cm	$y = 98.652 + 4.557x$	0.997	*$k_0 = 4.56$	439	126
	$y' = -0.157 - 0.125x$	0.994	†$k_1 = 0.12$ min^{-1}		
	$y' = -0.453 - 0.041x$	0.965	‡$k_2 = 0.04$ min^{-1}		
Conventional 5-20 cm	$y = 190.386 + 2.076x$	0.993	$k_0 = 2.08$	365	173
	$y' = -0.121 - 0.158x$	0.995	$k_1 = 0.16$ min^{-1}		
	$y' = -0.948 - 0.022x$	0.957	$k_2 = 0.02$ min^{-1}		
No-till 0-5 cm	$y = 213.710 + 4.969x$	0.985	$k_0 = 4.97$	526	219
	$y' = -0.121 - 0.123x$	0.994	$k_1 = 0.12$ min^{-1}		
	$y' = -0.40 - 0.067x$	0.994	$k_2 = 0.07$ min^{-1}		
No-till 5-20 cm	$y = 89.670 + 7.303x$	0.991	$k_0 = 7.30$	620	148
	$y' = -0.128 - 0.168x$	1.000	$k_1 = 0.17$ min^{-1}		
	$y' = -0.312 - 0.077x$	0.998	$k_2 = 0.08$ min^{-1}		
Sadler Soil					
Conventional 0-5 cm	$y = 90.908 + 8.329x$	0.998	$k_0 = 8.33$	710	164
	$y' = -0.138 - 0.683x$	0.995	$k_1 = 0.68$ min^{-1}		
	------------------	-----	--		
Conventional 5-20 cm	$y = 110.409 + 3.090x$	0.996	$k_0 = 3.09$	333	121
	$y' = -0.122 - 0.131x$	0.996	$k_1 = 0.13$ min^{-1}		
	$y' = -0.460 - 0.051x$	0.970	$k_2 = 0.05$ min^{-1}		
No-till 0-5 cm	$y = 82.508 + 5.424x$	0.995	$k_0 = 5.42$	390	117
	$y' = -0.067 - 0.123x$	1.000	$k_1 = 0.12$ min^{-1}		
	$y' = -0.202 - 0.065x$	0.995	$k_2 = 0.06$ min^{-1}		
No-till 5-20 cm	$y = 46.505 + 5.048x$	0.997	$k_0 = 5.05$	351	67
	$y' = -0.087 - 0.047x$	0.984	$k_1 = 0.05$ min^{-1}		
	------------------	-----	--		

*Denotes zero-order rate constant.

†Denotes first first-order rate constant.

‡Denotes second first-order rate constant.

y' denotes natural log (ln) of clay surface remaining unreactive.

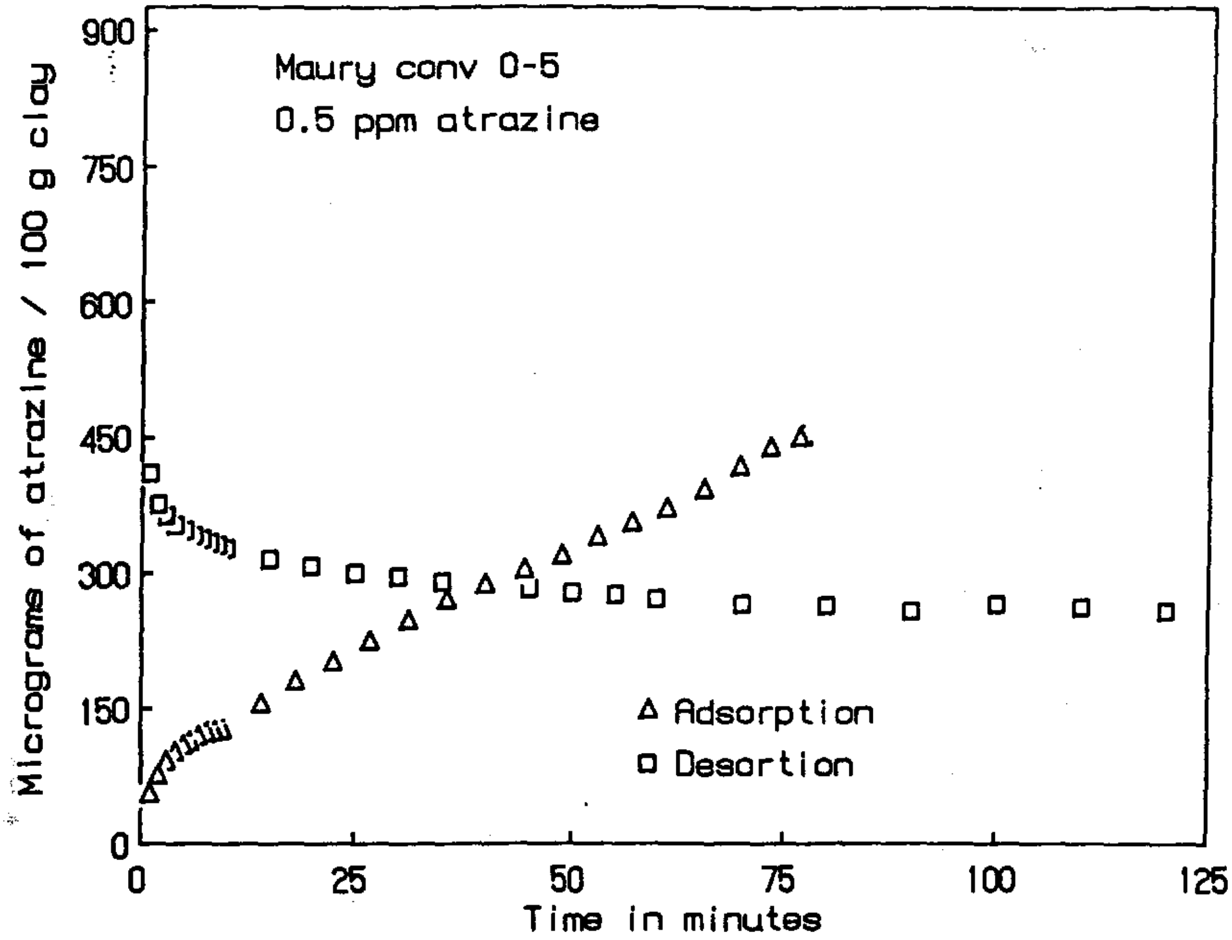


Figure 17. Atrazine adsorption and desorption at 0.5 mg L^{-1} by Maury silt loam soil under conventional management, at 0-5 cm depth.

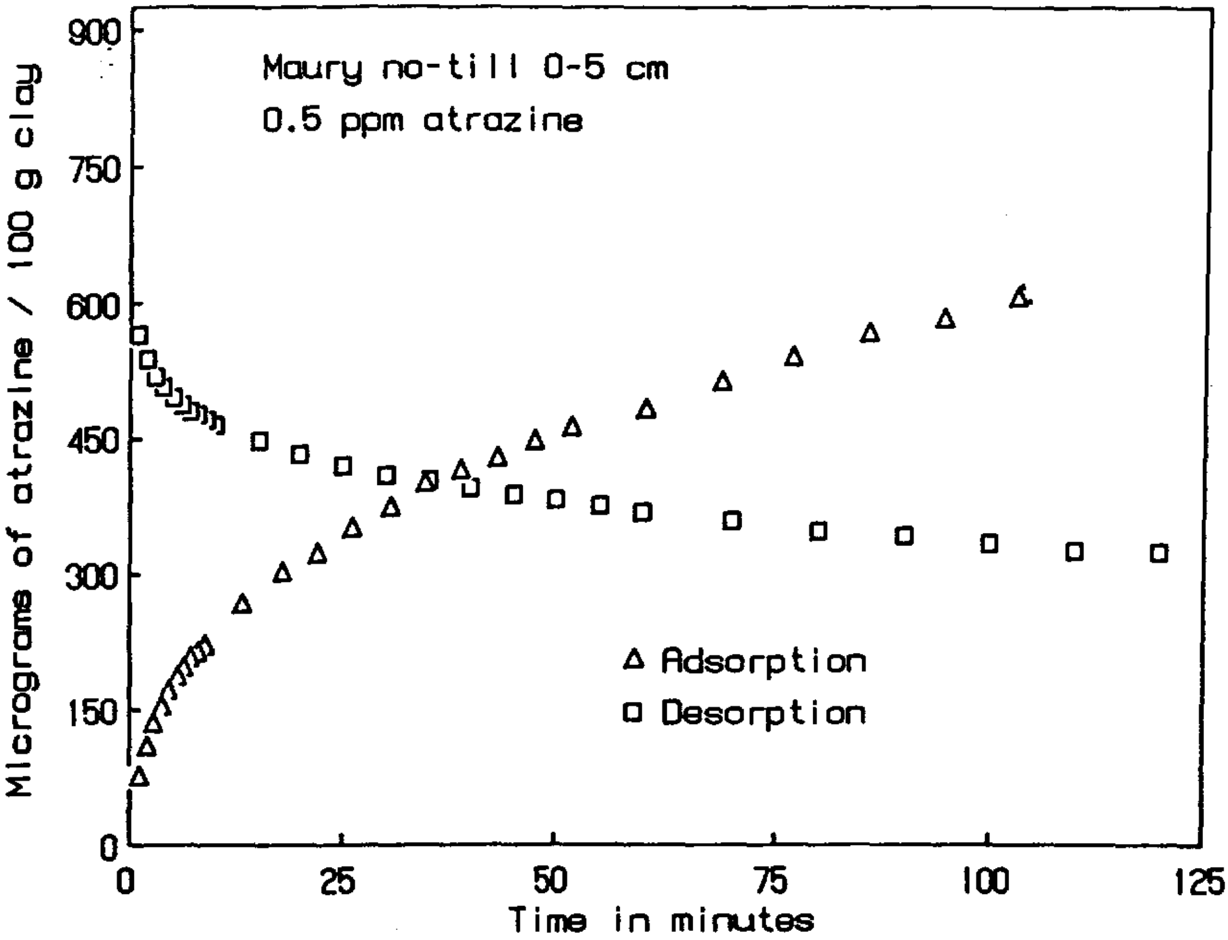


Figure 18. Atrazine adsorption and desorption at 0.5 mg L^{-1} by Maury silt loam soil under no-till management, at 0-5 cm depth.

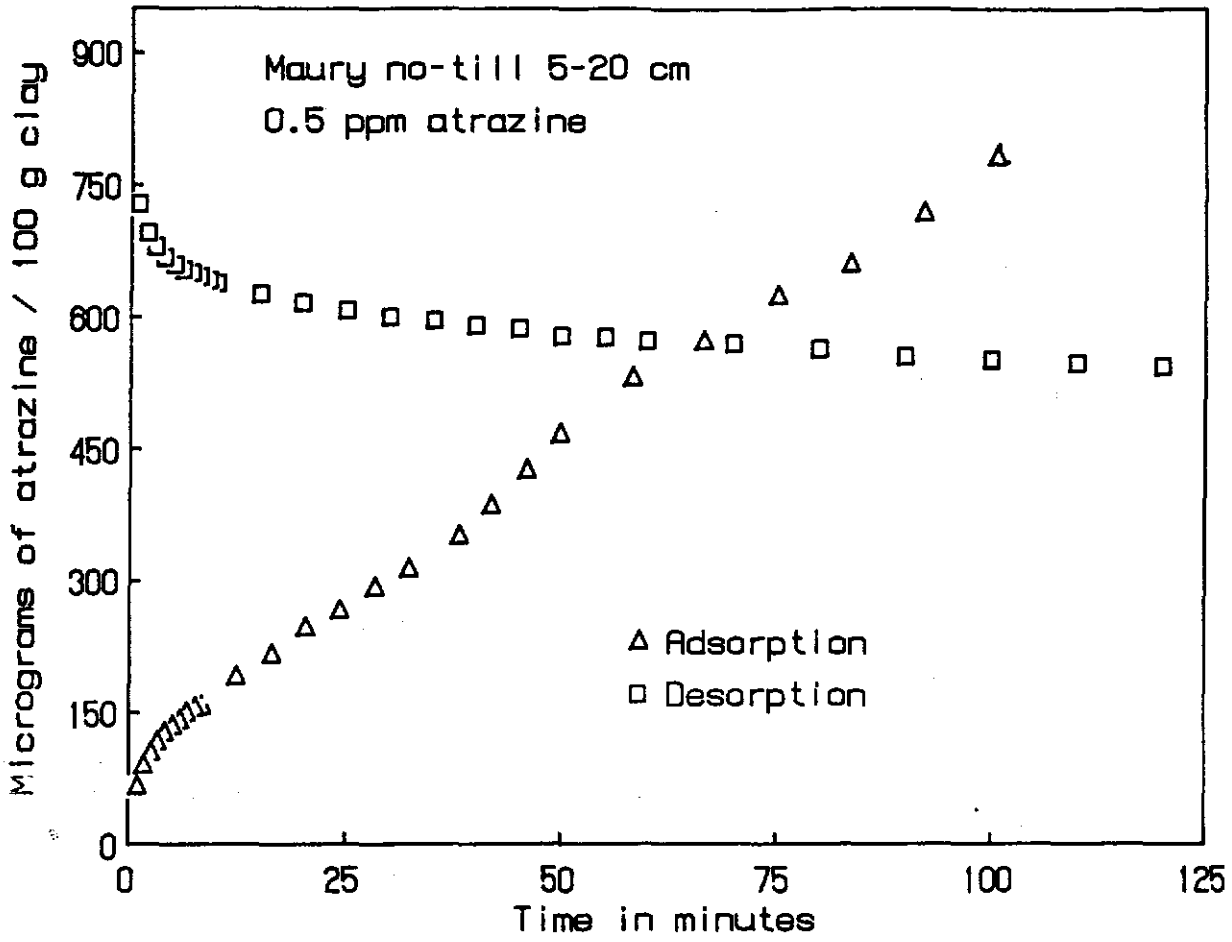


Figure 19. Atrazine adsorption and desorption at 0.5 mg L^{-1} by Maury silt loam soil under no-till management, at 5-20 cm depth.

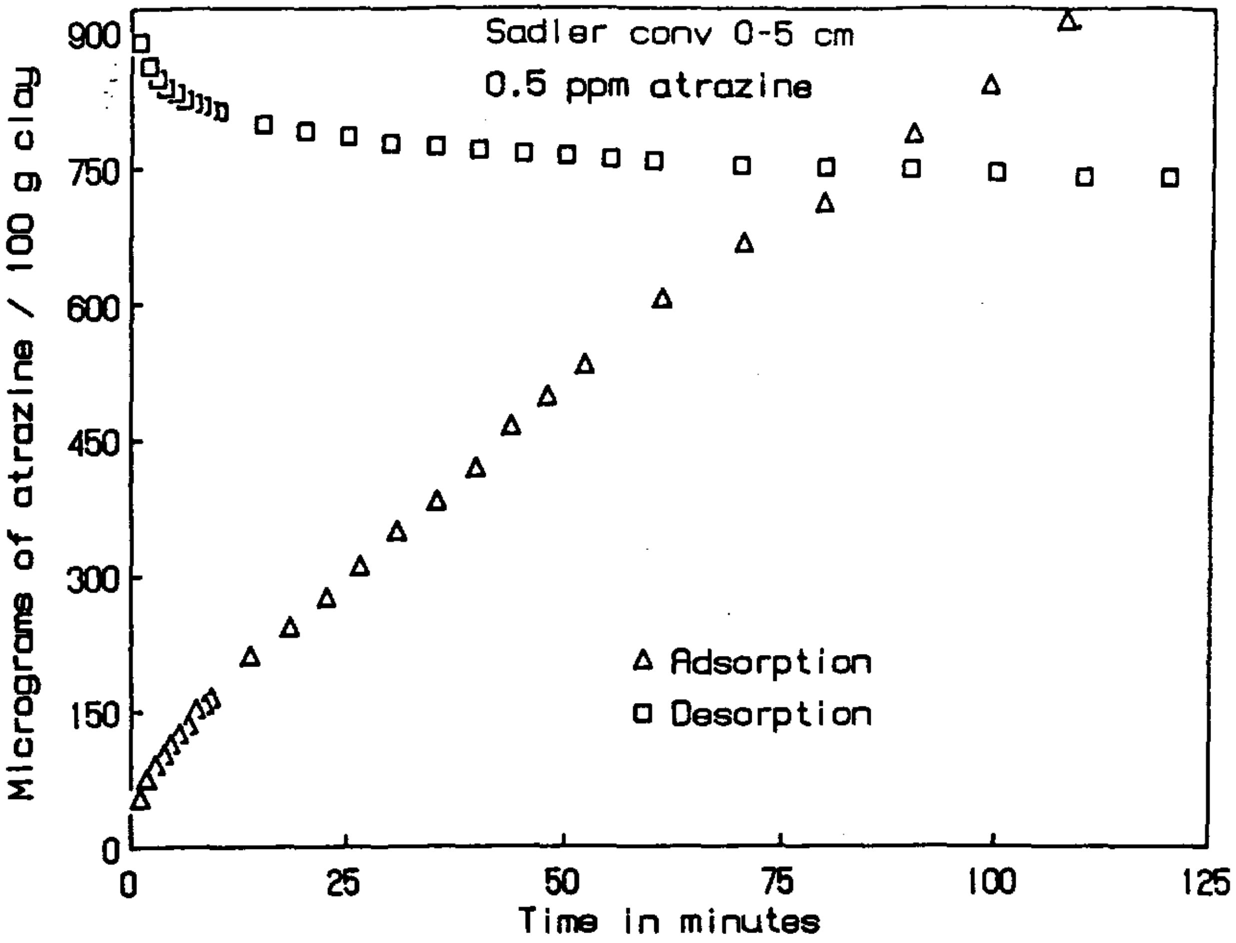


Figure 20. Atrazine adsorption and desorption at 0.5 mg L^{-1} by Sadler soil under conventional management, at 0-5 cm depth.

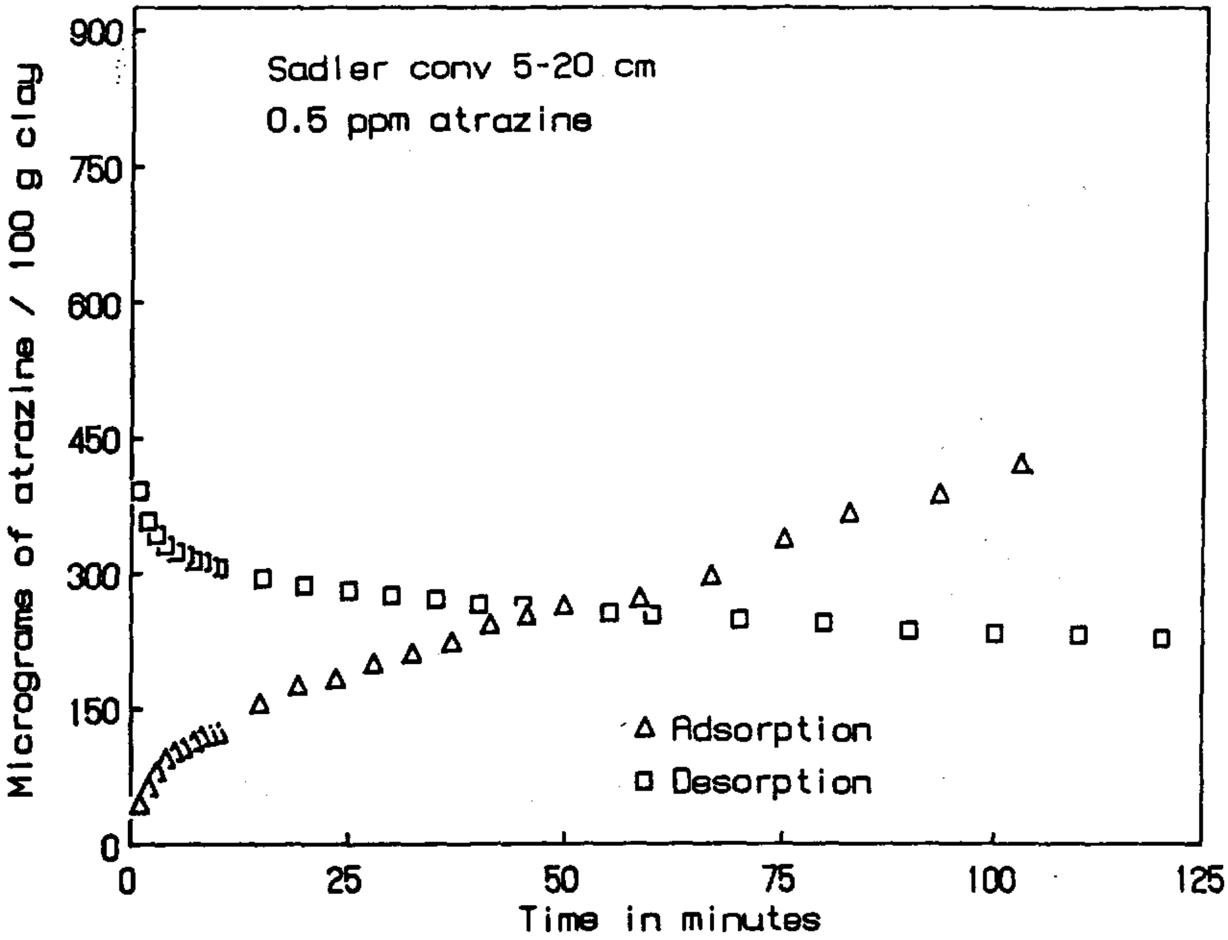


Figure 21. Atrazine adsorption and desorption at 0.5 mg L^{-1} by Sadler soil under conventional management, at 5-20 cm depth.

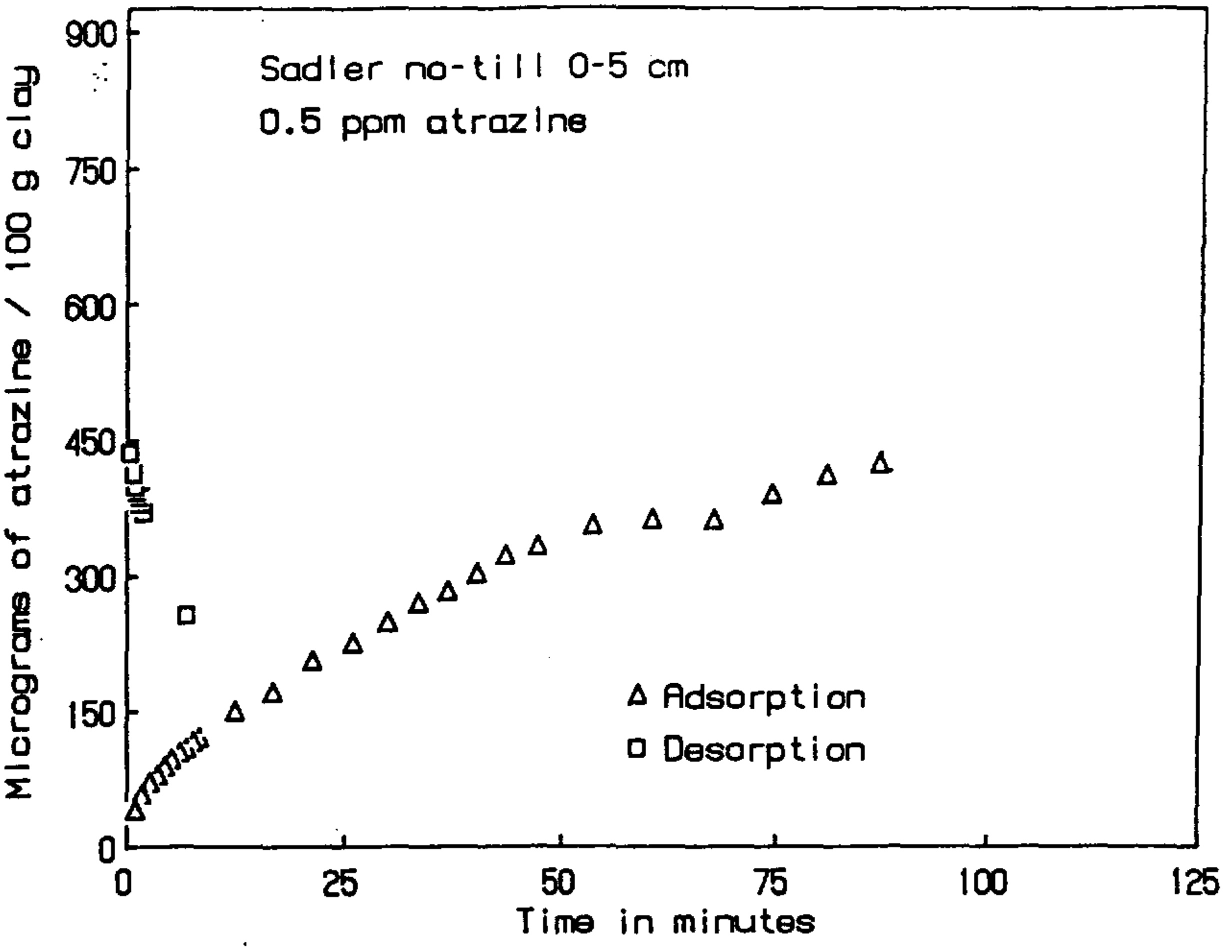


Figure 22. Atrazine adsorption and desorption at 0.5 mg L^{-1} by Sadler soil under no-till management, at 0-5 cm depth.

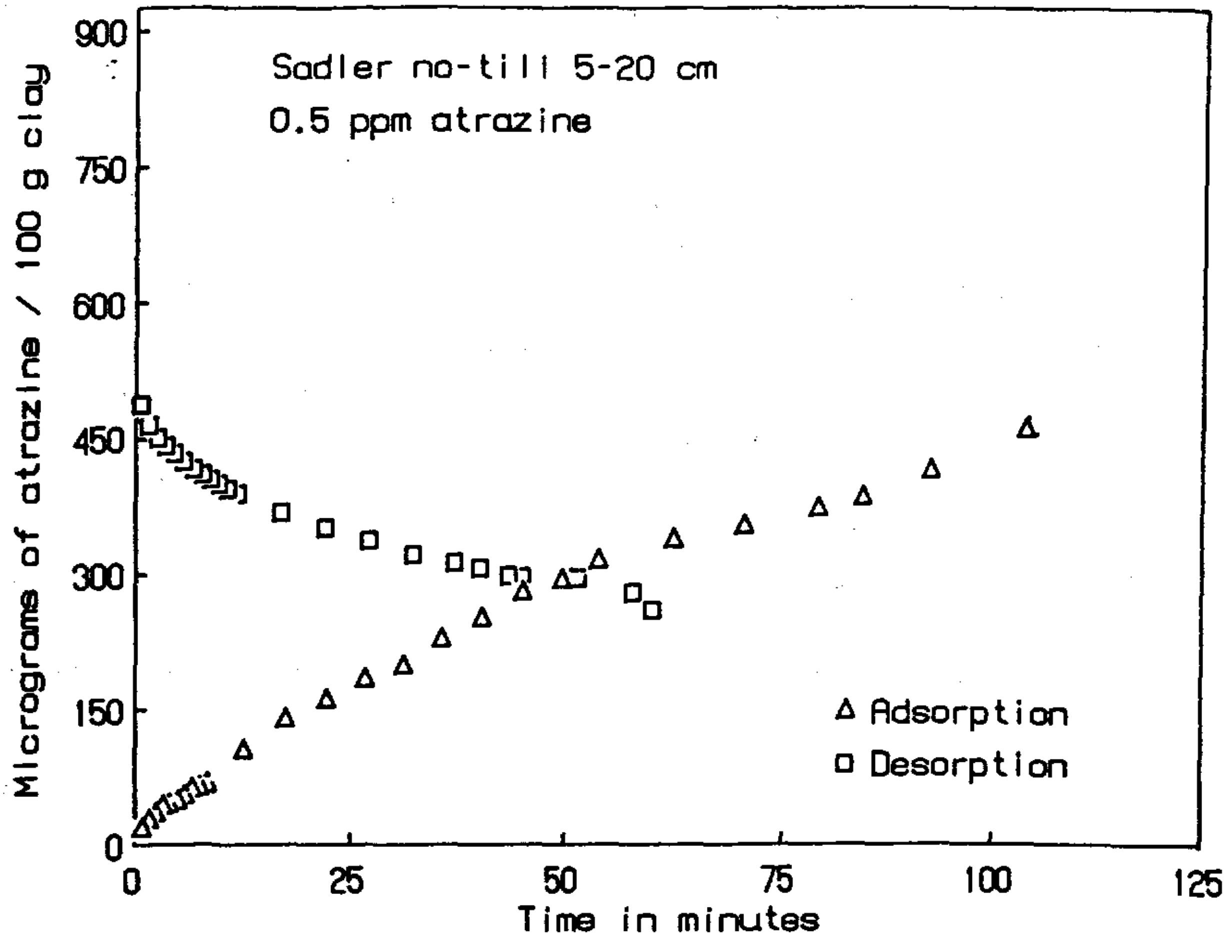


Figure 23. Atrazine adsorption and desorption at 0.5 mg L^{-1} by Sadler soil, under no-till manmagement, at 5-20 cm depth.

CHAPTER IV - CONCLUSIONS

The overall results of this project demonstrate that atrazine adsorption by soils involve hydrogen bonding as well as soil-surface catalyzed precipitation. The quantity of atrazine adsorbed by hydrogen donation in the soils tested appears to be very small in comparison to that "adsorbed" by surface condensation (precipitation). The atrazine adsorption process, for all practical purposes, appears to be an irreversible process. The relative slow kinetics of atrazine adsorption has important ramification in the management of applied atrazine. The data suggest that because it takes a significant amount of time for atrazine to move to the solid phase of the soil, the quantity of applied atrazine to be leached during a rain event would depend on the amount of time atrazine had to react with the soil, the intensity of rainfall, and the type of water flow in the soil (macropore vs. micropore vs. surface flow).. Careful field experimentation is needed in natural soils to test both the implications of all these mechanisms dealing with atrazine movement, as well as atrazine detoxification due to hydrolysis induced by soil surface adsorption.

NOMENCLATURE

$\mathrm{cmol_c\ kg^{-1}}$	milliequivalents per 100 g of soil
$\mathrm{dS\ m^{-1}}$	electrical conductivity of solution
$\mathrm{mmol_c\ L^{-1}}$	milliequivalents per litter solution
$\mathrm{min^{-1}}$	first-order rate constant (1 over minutes)

APPENDIX I

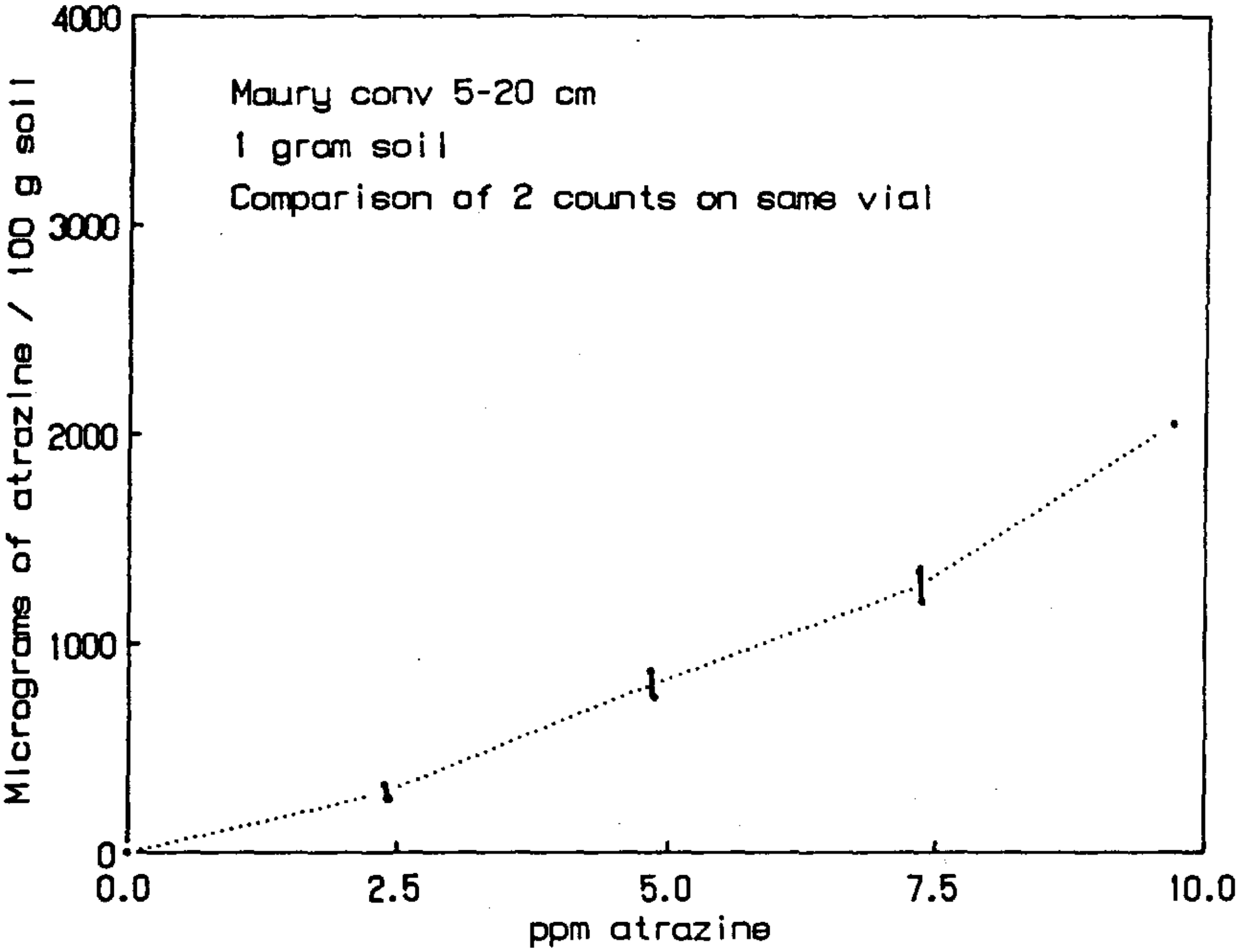


Figure 1. Influence of number of counts on atrazine adsorption isotherms.

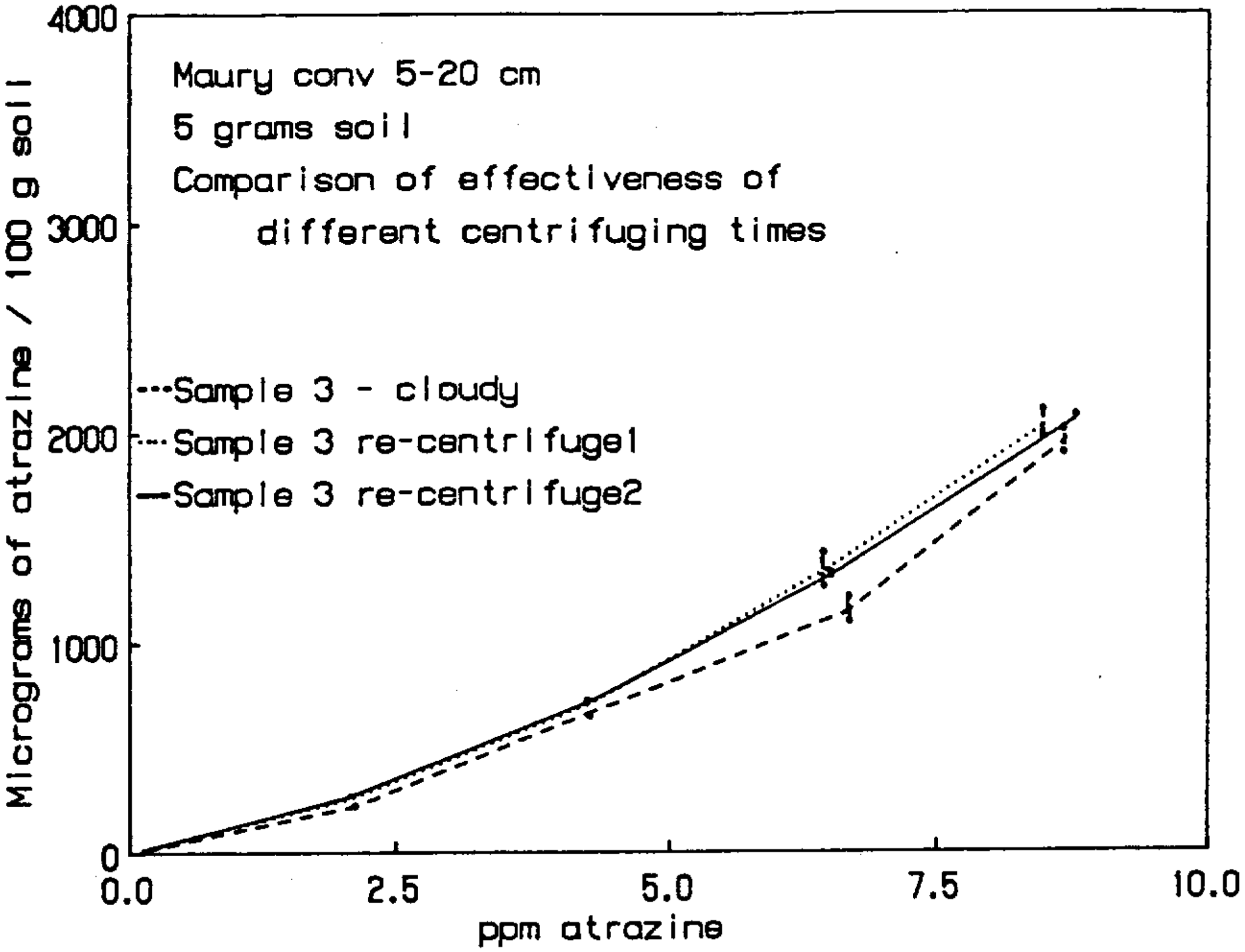


Figure 2. Influence of centrifuging of soil/solution suspensions on atrazine adsorption isotherms.

APPENDIX II

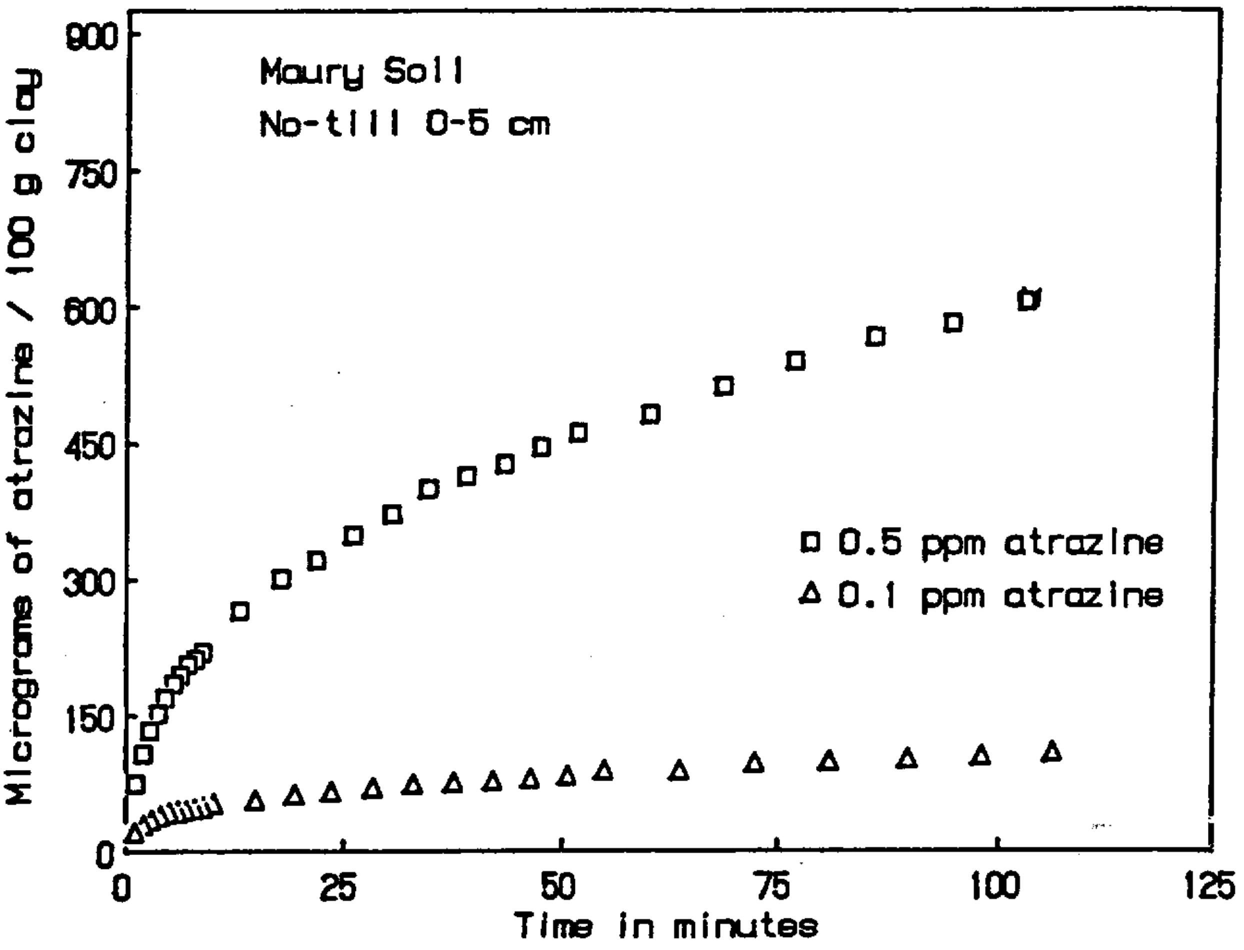


Figure 1. Kinetics of atrazine adsorption at two different concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}) by Maury silt loam at 0-5 cm depth, under no-till management.

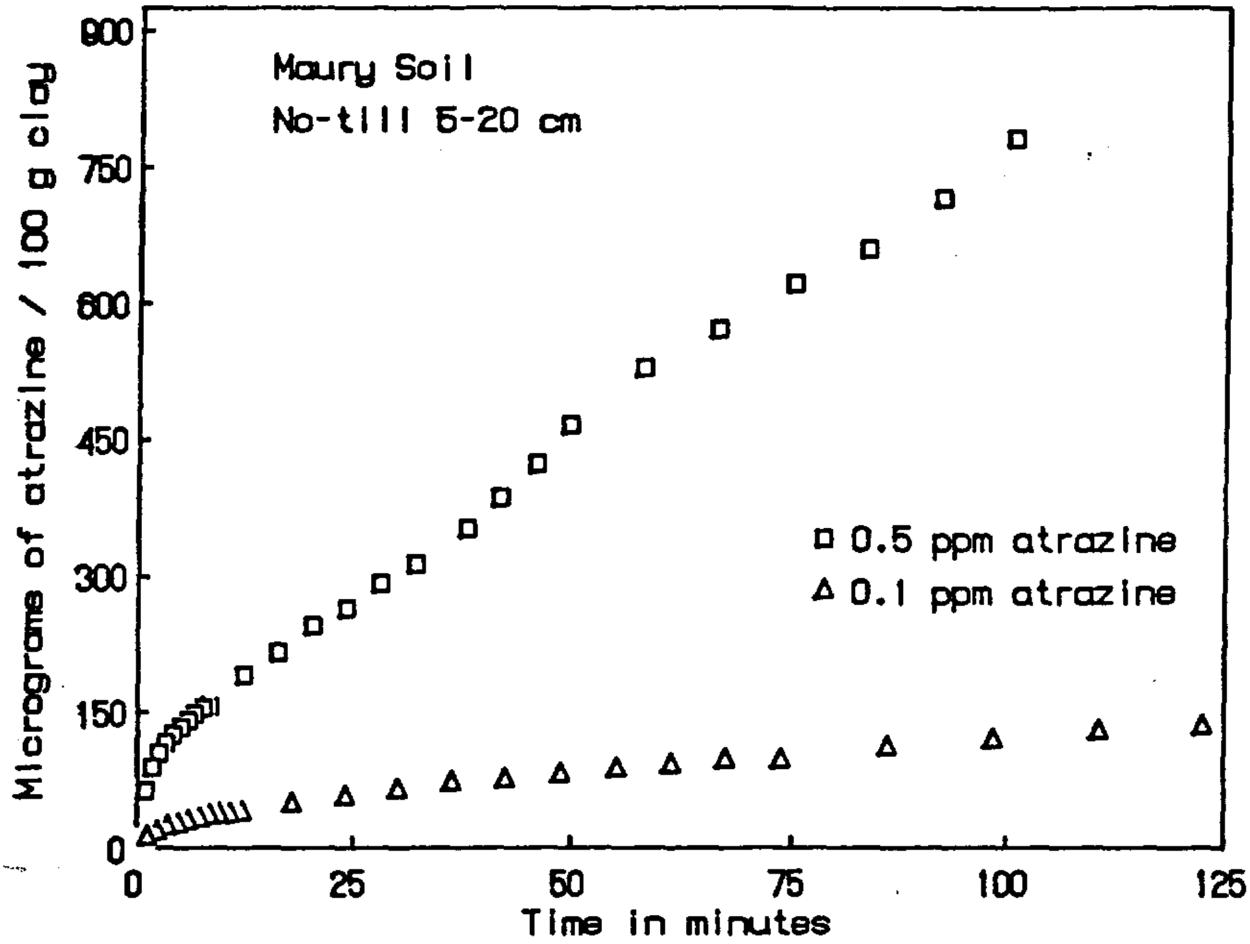


Figure 2. Kinetics of atrazine adsorption at two different concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}) by Maury silt loam at 5-20 cm depth, under no-till management.

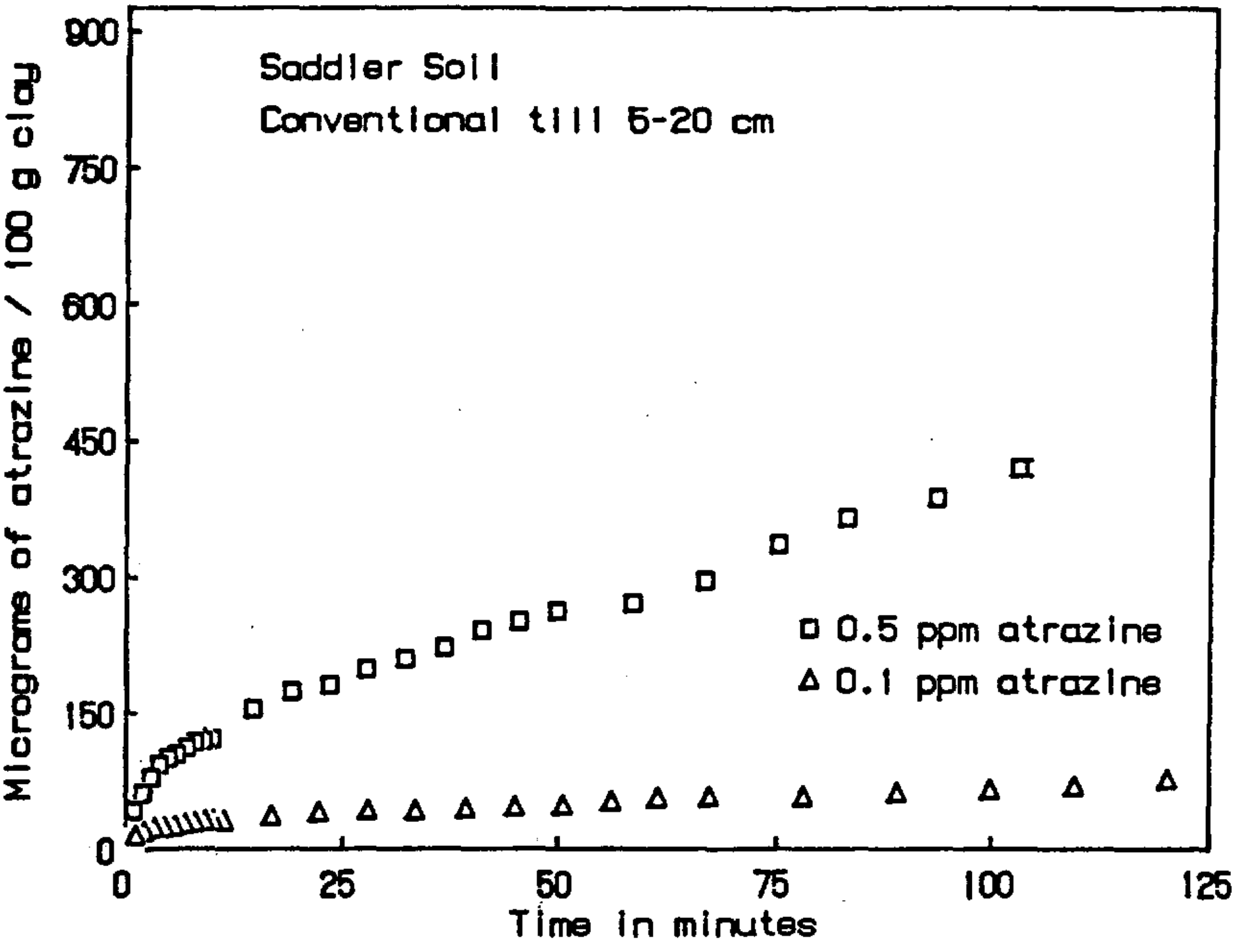


Figure 3. Kinetics of atrazine adsorption at two different concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}) by Sadler soil at 5-20 cm depth, under conventional management.

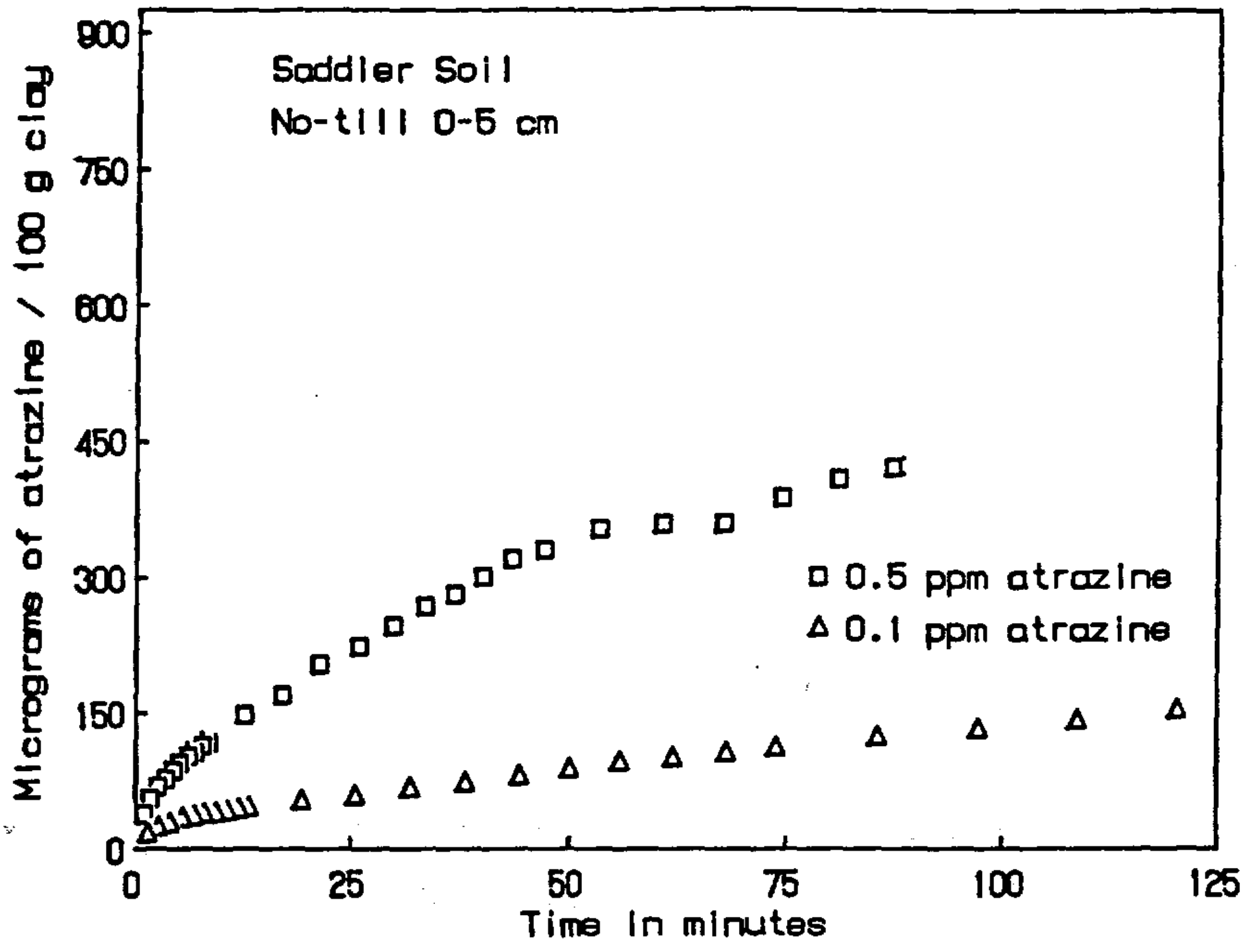


Figure 4. Kinetics of atrazine adsorption at two different concentrations ($0.5\ mg\ L^{-1}$ vs. $0.1\ mg\ L^{-1}$) by Sadler soil at 0-5 cm depth, under no-till management.

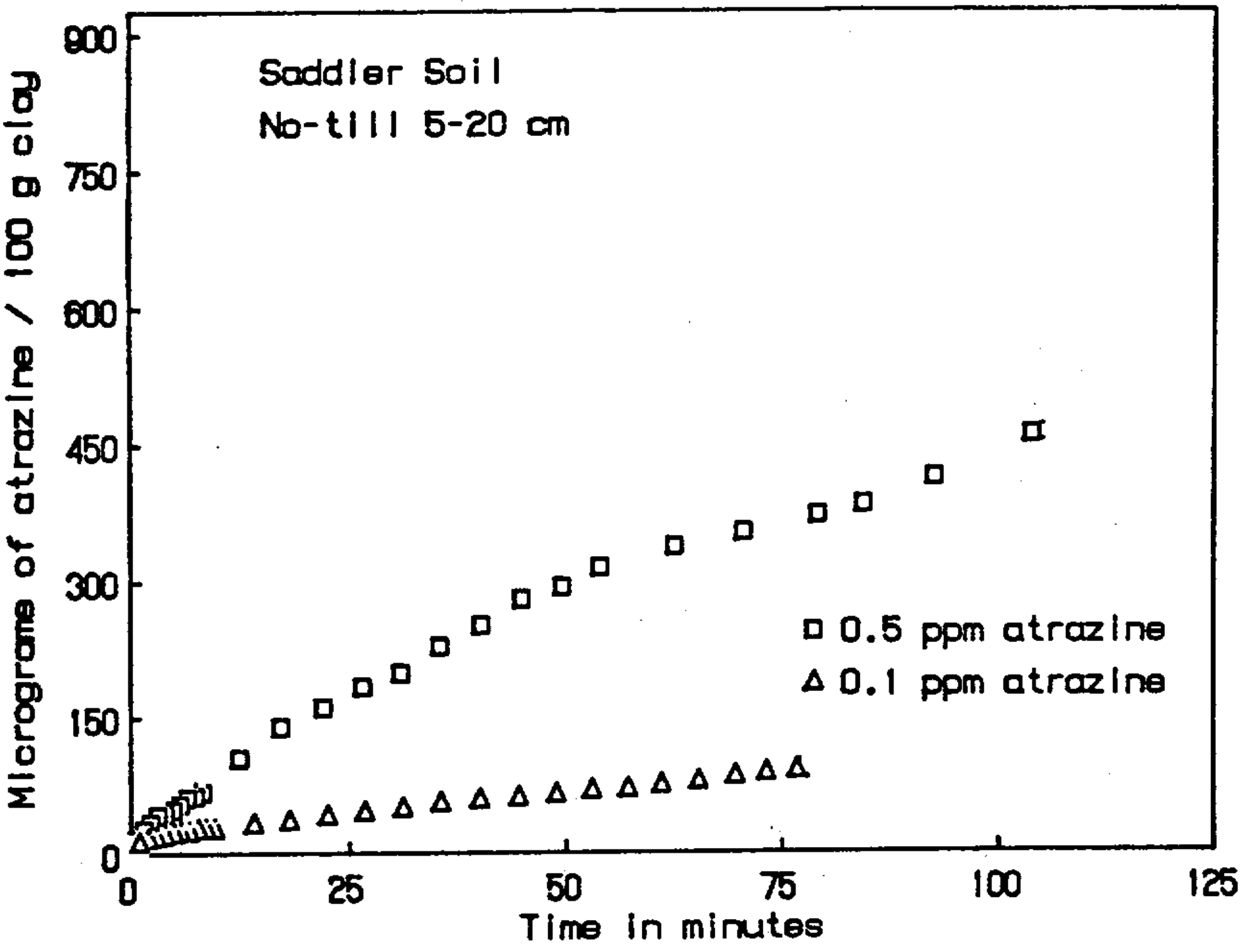


Figure 5. Kinetics of atrazine adsorption at two different concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}) by Sadler soil at 5-20 cm depth, under no-till management.

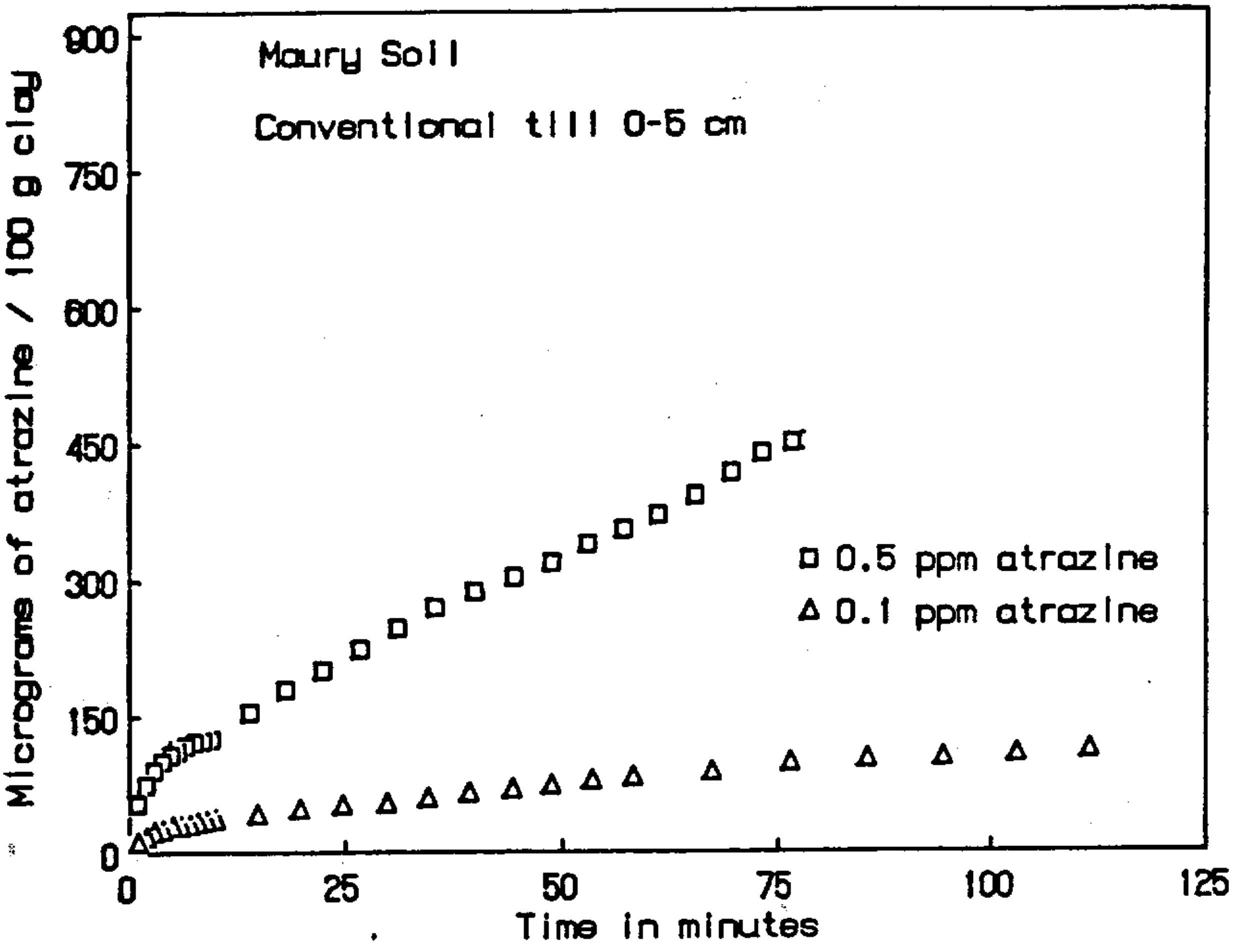


Figure 6. Kinetics of atrazine adsorption at two different concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}) by Maury silt loam at 0-5 cm depth, under conventional management.

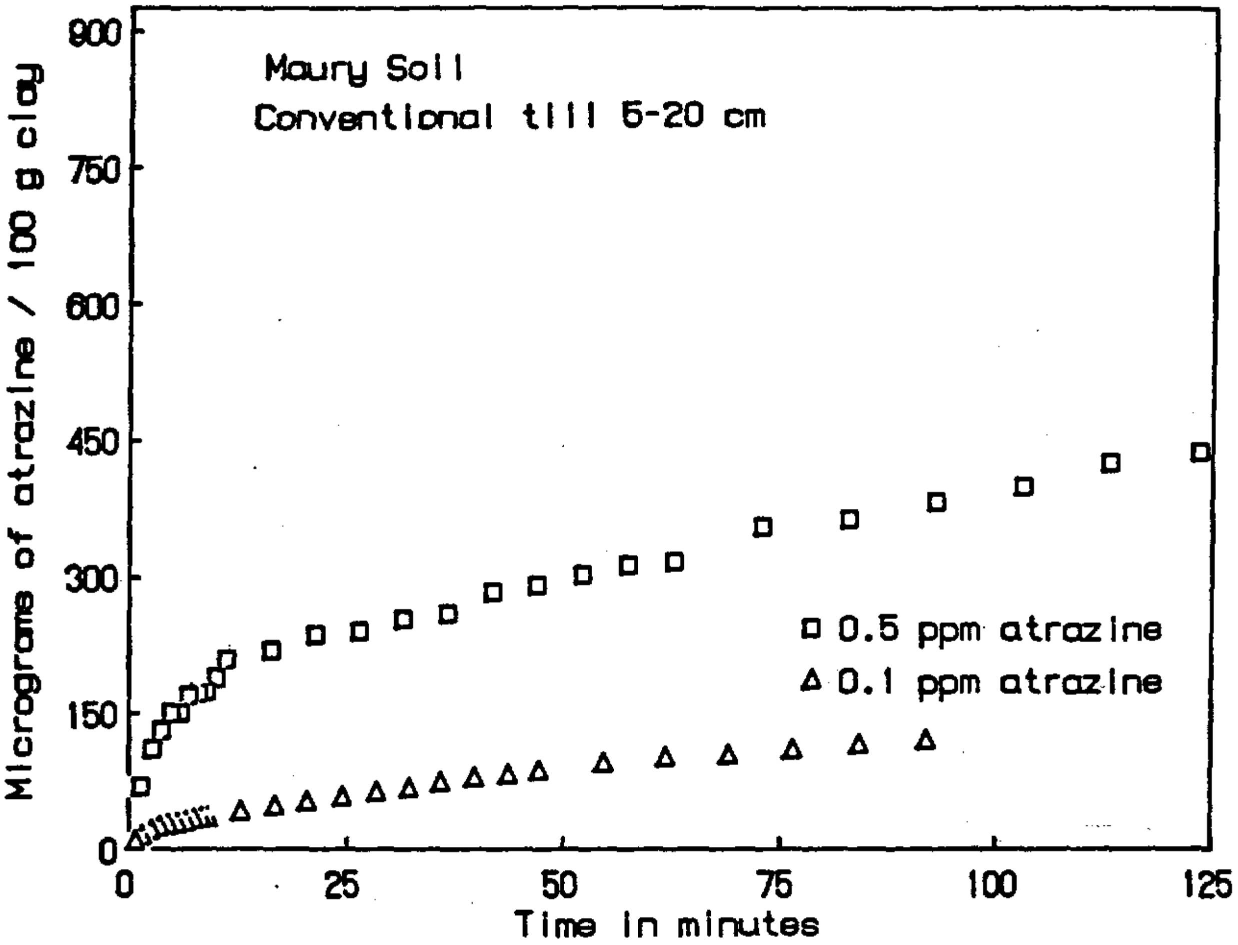


Figure 7. Kinetics of atrazine adsorption at two different concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}) by Maury silt loam at 5-20 cm depth, under conventional management.

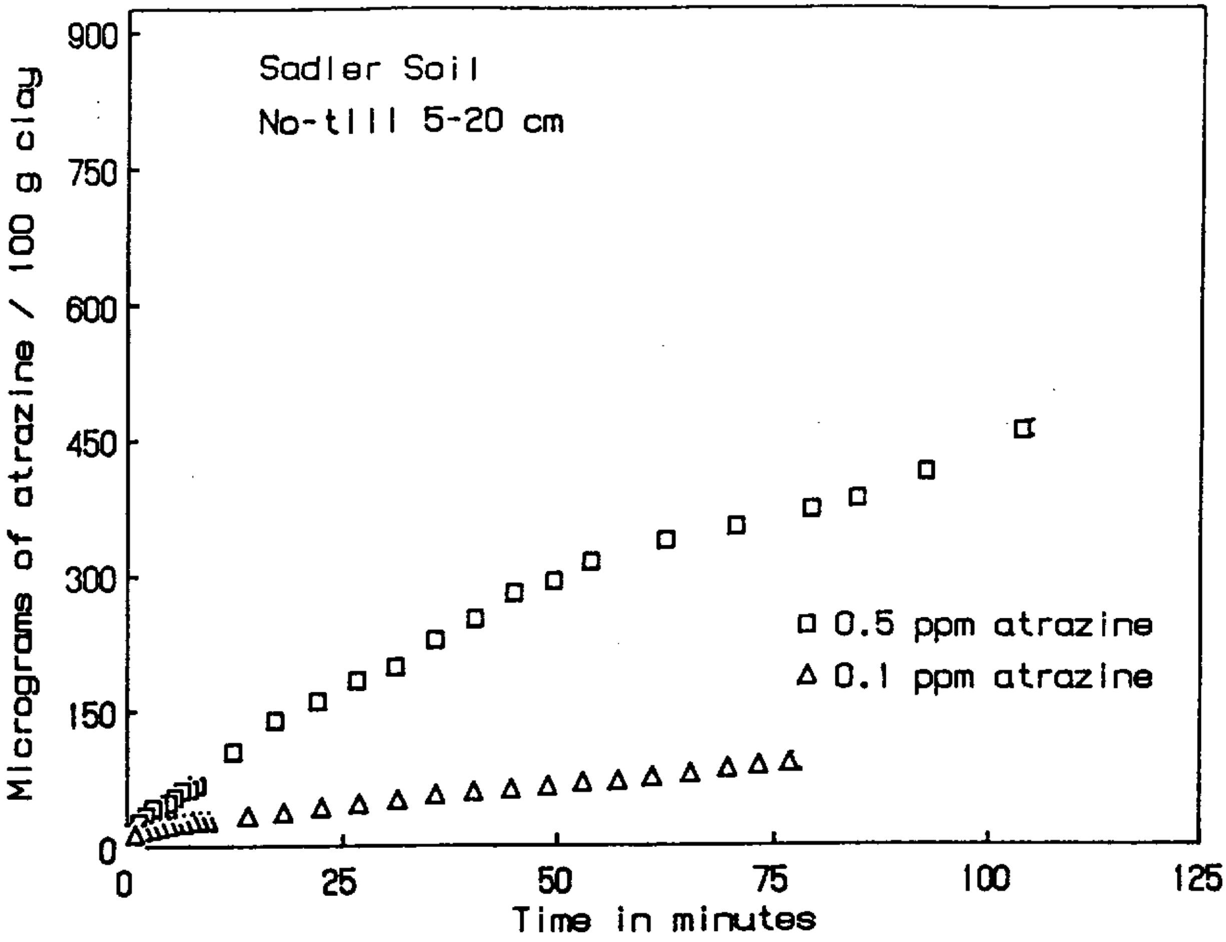


Figure 8. Kinetics of atrazine adsorption at two different concentrations (0.5 mg L^{-1} vs. 0.1 mg L^{-1}) by Sadler soil at 5-20 cm depth, under no-till management.

APPENDIX III

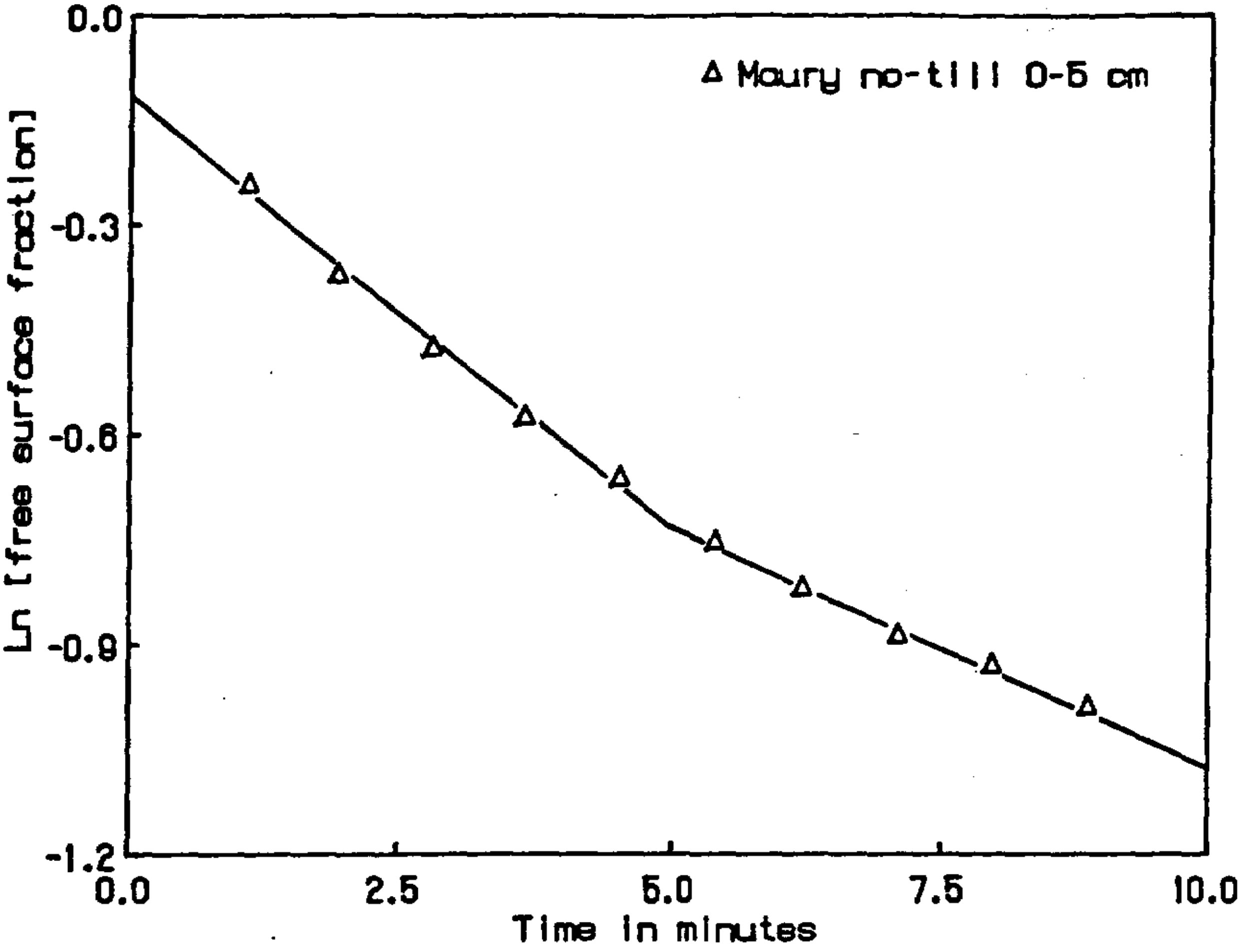


Figure 1. First-order plot of atrazine adsorption by Maury silt loam at 0-5 cm depth, under no-till management.

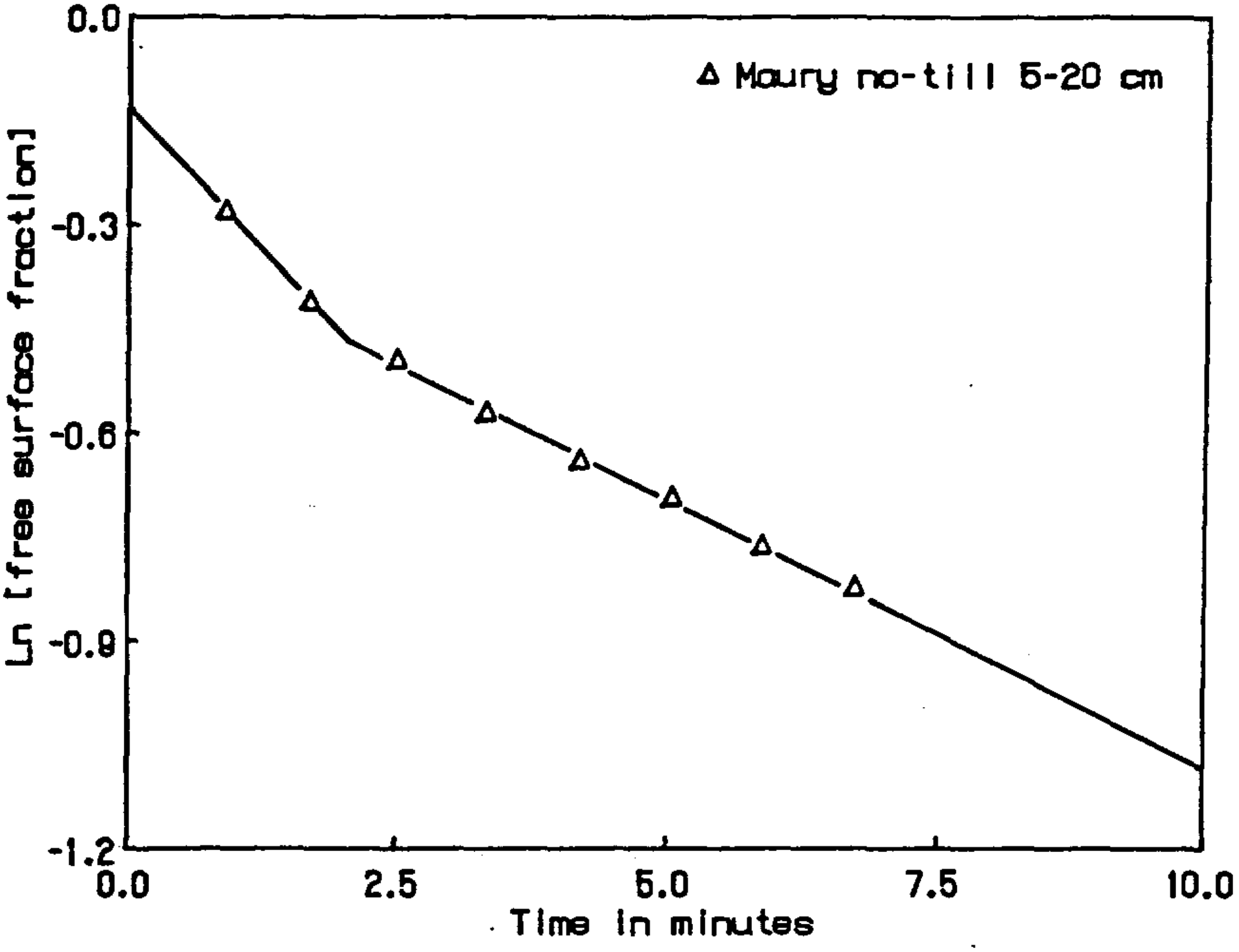


Figure 2. First-order plot of atrazine adsorption by Maury silt loam at 5-20 cm depth, under no-till management.

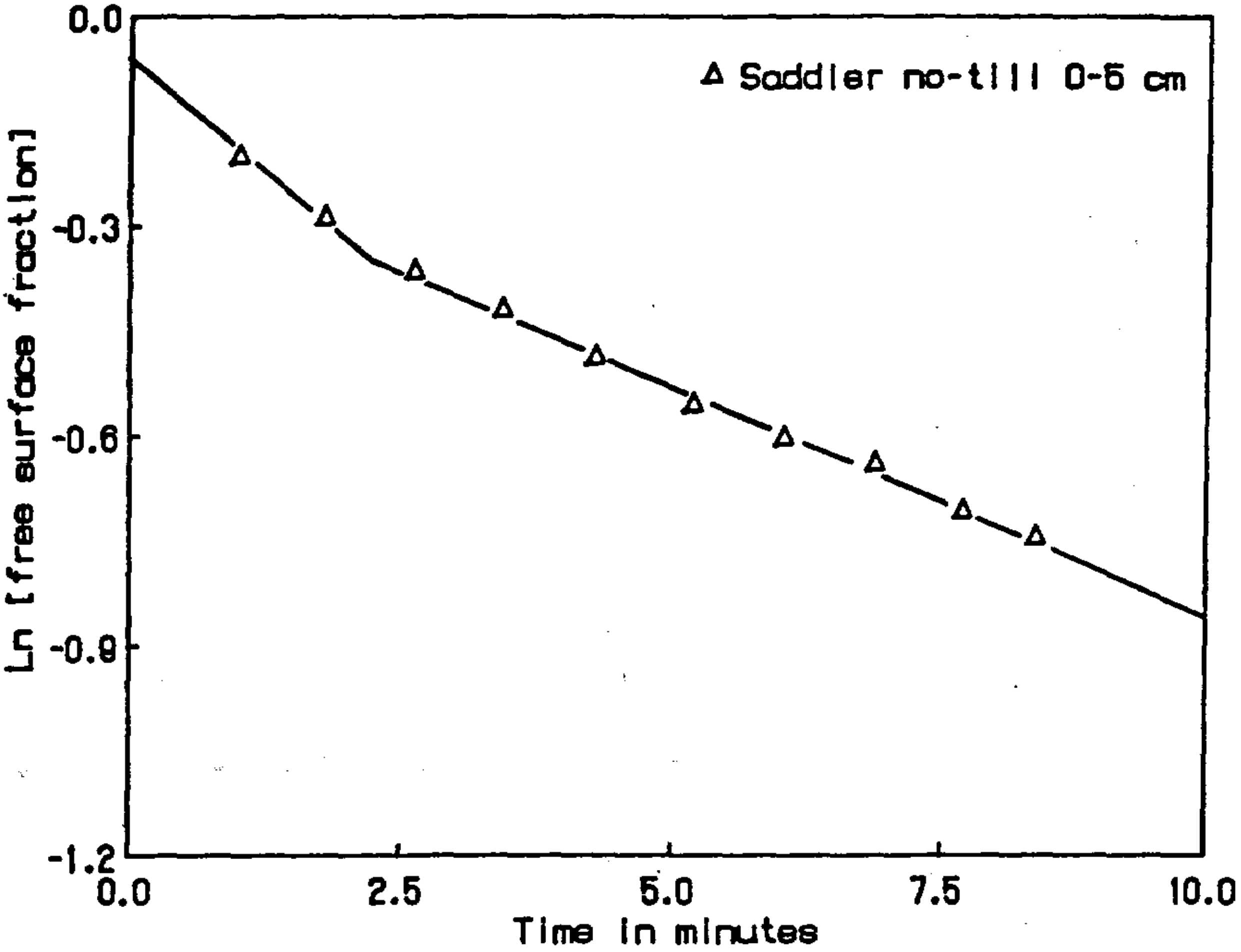


Figure 3. First-order plot of atrazine adsorption by Sadler at 0-5 cm depth under no-till management.

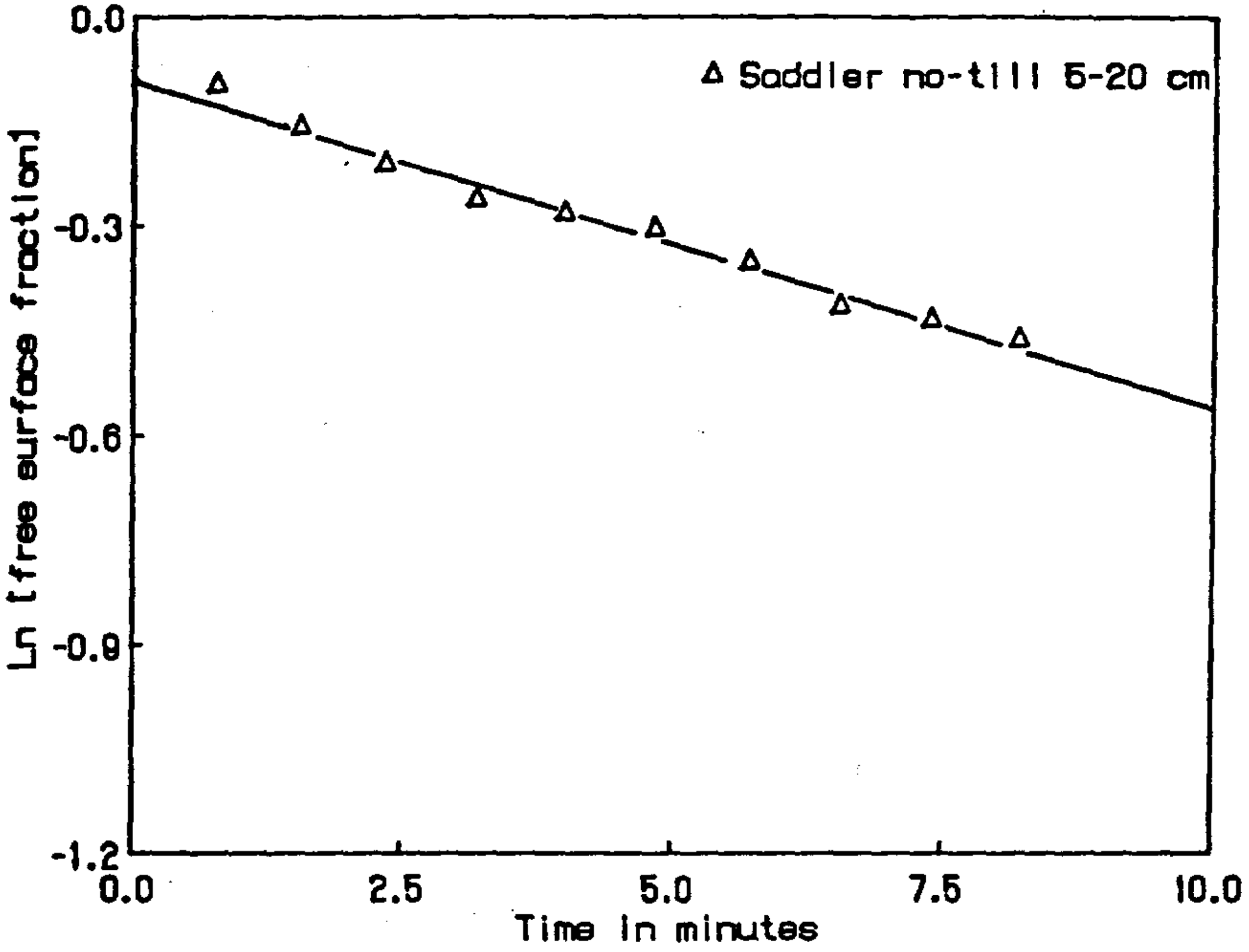


Figure 4. First-order plot of atrazine adsorption by Sadler at 5-20 cm depth, under no-till management.

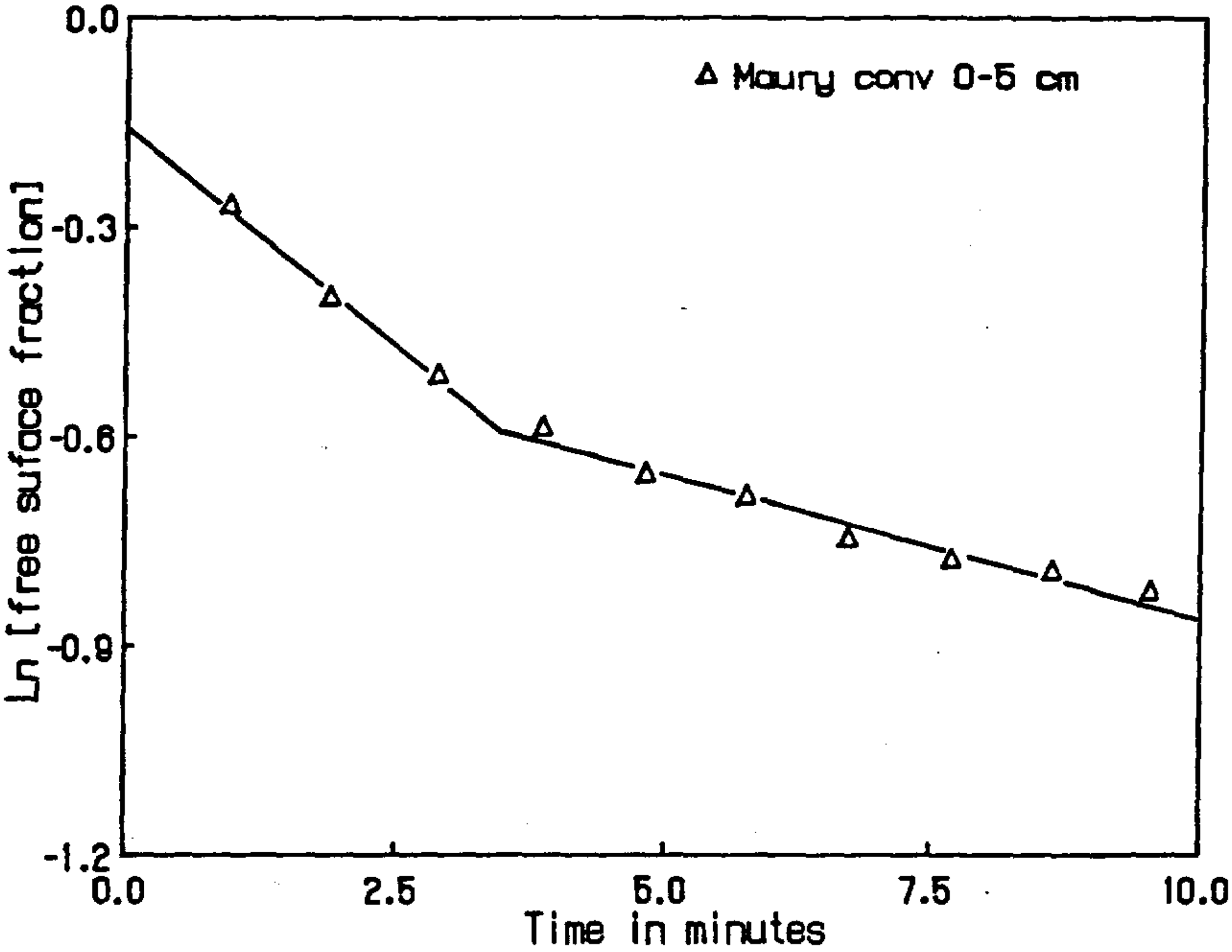


Figure 5. First-order plot of atrazine adsorption by Maury silt loam at 0-5 cm depth, under conventional management.

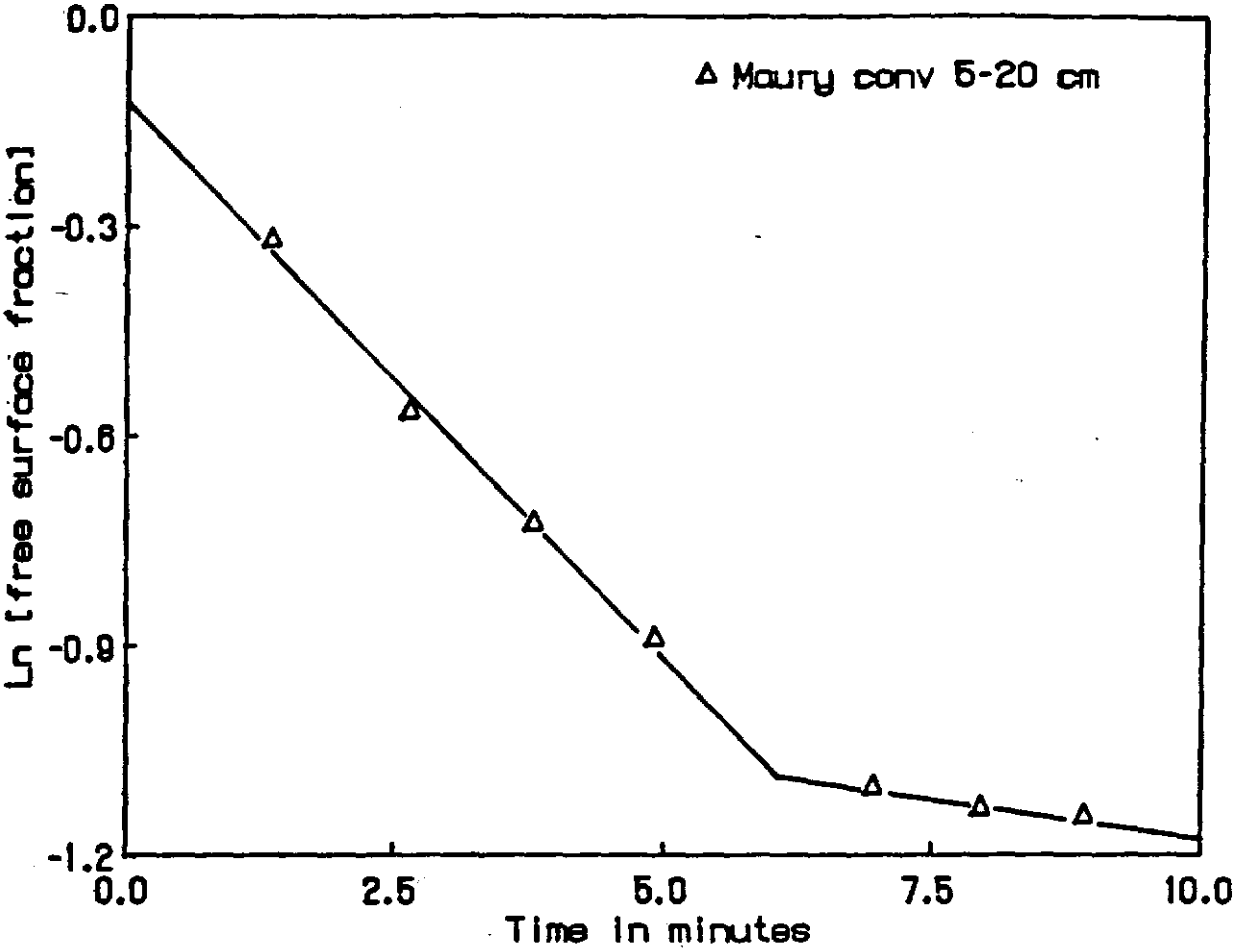


Figure 6. First-order plot of atrazine adsorption by Maury silt loam at 5-20 cm depth, under conventional management.

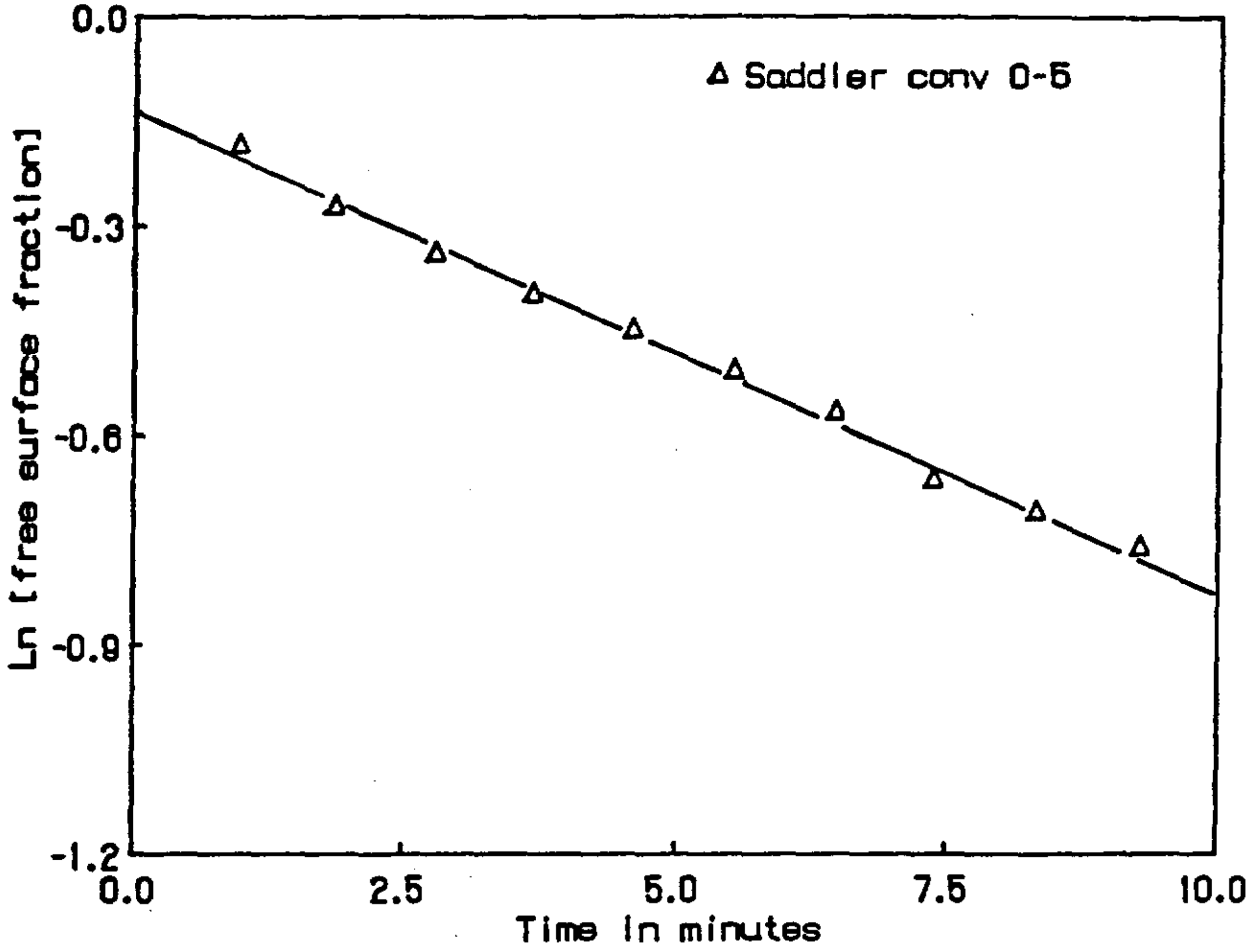


Figure 7. First-order plot of atrazine adsorption by Sadler at 0-5 cm depth, under conventional management.

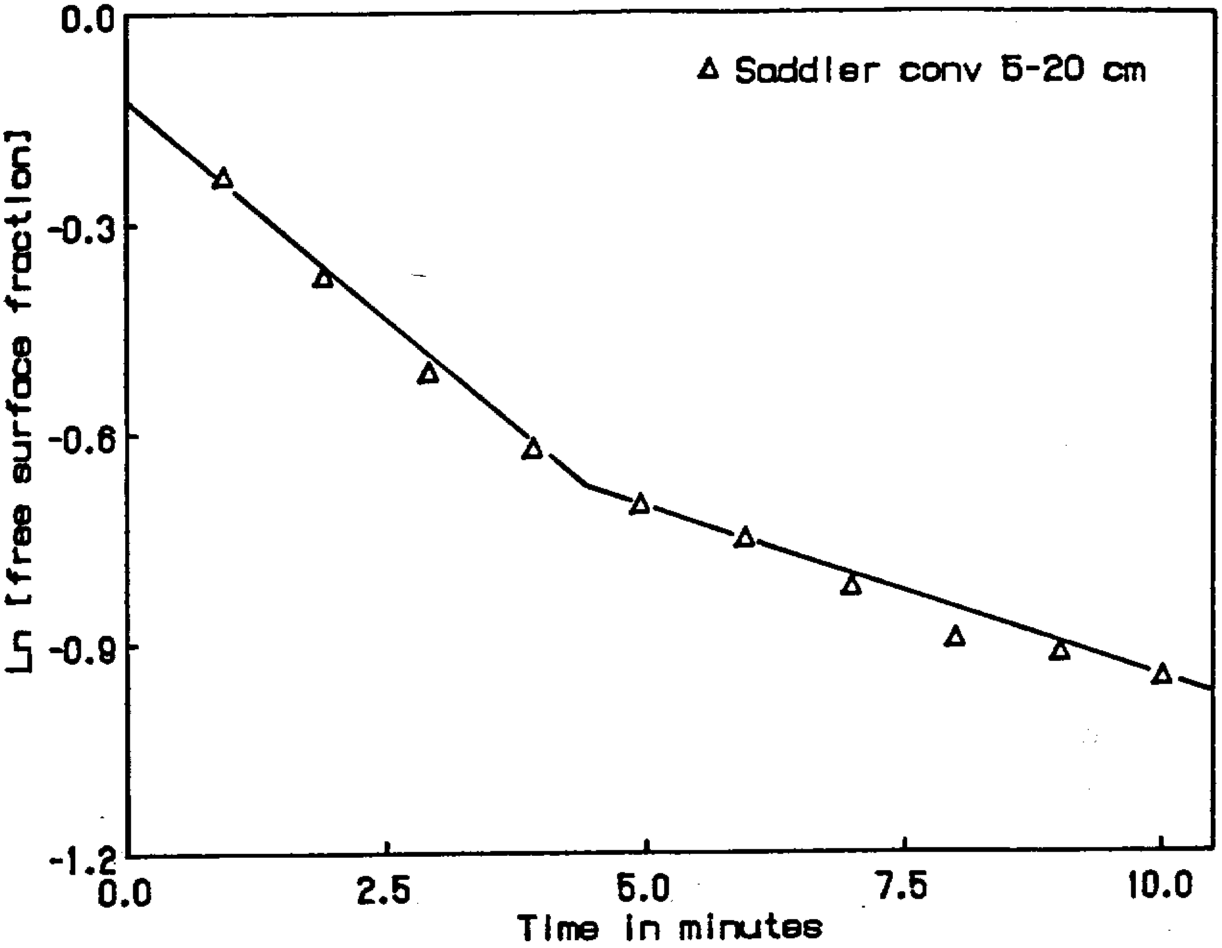


Figure 8. First-order plot of atrazine adsorption by Sadler soil at 5-20 cm depth, under conventional management.

REFERENCES

Armstrong, D.E. 1967. Atrazine hydrolysis in soil. Soil Sci. Soc. Amer. Proc., Vol. 31, pp. 61-66.

Bailey, G.W. and J.L. White. 1964. Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. Agricultural and Food Chemistry, Vol. 12, pp. 324-331.

Bailey, G.W., and J.L. White. 1970a. Factors influencing the adsorption, desorption, and movement of pesticides in soil. F.A. Gunther and J.D. Gunther (Edit.) Springer-Verlag, New York.

Bailey, G.W. and J.L. White. 1970b. Herbicides: a compilation of their physical, chemical, and biological properties. Residue Reviews, Vol. 10, pp. 97-121.

Bailey, G.W., J.L. White, and T. Rothberg. 1968. Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. Soil Sci. Soc. Amer. Proc., Vol. 32, pp. 222-234.

Blevins, R.L., G.W. Thomas, M.S. Smith, W.W. Frye, and P.L. Cornelius. 1983. Changes in soil properties after 10 years continuous non-tilled and conventionally tilled corn. Soil Tillage Res. 3:135-146.

Bohn, H., B. McNeal, and G. O'Connor. 1985. Soil Chemistry. 2nd Edition. John Wiley and Sons, New York, NY.

Brown, C.B. and J.L. White. 1969. Reactions of 12 s-Triazines with soil clays. Soil Sci. Soc. Amer. Proc., Vol. 33, pp. 863-867.

Davidson, J.M., P.S.C. Rao, and P. Nkedi-Kizza. 1983. Physical processes influencing water and solute transport in soils. In Chemical Mobility and Reactivity in Soil Systems, Chapter 3.

Donigian, Jr., A.D., and R.F. Carsel. 1987. Modeling the impact of conservation tillage practices on pesticide concentrations in ground and surface waters. Env. Toxic. and Chem. 6:241-250.

Elprince, A.M., A.P. Vanselow, and G. Sposito. 1980. Heterovalent, ternary cation exchange equilibria: NH_4^+-Ba^{2+}-La^{3+} exchange on montmorillonite. Soil Sci. Soc. Am. J., Vol. 44, pp. 964-968.

Environmental Protection Agency. 1988. Environmental News. Pesticides in ground water data base, 1988 Interim report. Office of Public Affairs. (1-177).

Evangelou, V.P. 1989. Mechanisms regulating ammonia bonding with various crystalline salts and their field implications. Soil Sci. Soc. Am. J. (In Press).

Evangelou, V.P. 1990. Influence of water chemistry on suspended solids in coal-mine sedimentation ponds. J. Environ. Qual. 19:428-434.

Gunther, F.A. (Ed.). 1970. Residue Reviews: The triazine herbicides. Springer-Verlag, New York.

Harter, R.D. and J.L. Ahlrichs. 1969. Effect of acidity on reactions of organic acids and amines with montmorillonite clay surfaces. Soil Sci. Soc. Amer. Proc. 33:859-862.

Harter, R.D. and J.L. Ahlrichs. 1967. Determination of clay surface acidity by infrared spectroscopy. Soil Sci. Soc. Amer. Proc., Vol. 31, pp. 30-33.

Johanson, R.C., J.C. Imhoff, and H.H. Davis, Jr. 1980. User's manual for hydrological simulation program-Fortran (HSPF). U.S. Environmental Protection Agency, Athens, GA. EPA-600/9-80-015.

Koskinen, W.C., G.A. O'Connor, and H.H. Cheng. 1979. Characterization of hysteresis in the desorption of 2,4,5-T from soils. Soil Sci. Soc. Am. J. 43:871-874.

Leistra, M. 1986. Modeling the behavior of organic chemicals in soil and ground water. Pestic. Sci. 17:256-264.

Lumbanraja, J. 1991. Bianry and ternary K-NH_4-Ca exchange equilibria, kinetics and spectroscopic evidence of cation-soil mineral surface interactions. Ph.D. dissertation, University of Kentucky, Agronomy Department, Lexington, KY.

Mortland, M.M. 1968. Protonation of compounds on clay mineral surfaces; 9th Int. Congr. Soil Sci. Vol. I, 691-699.

Mortland, M.M., and K.V. Ramon. 1968. Surface acidity of smectites in relation to hydration, exchangeable cation and structure. Clays and Clay Min. 16:393-398.

Mulkey, L.A., R.F. Carsel, and C.N. Smith. 1986. Development, testing, and applications of nonpoint source models for evaluation of pesticides risk to the environment. In Agricultural Nonpoint Source Pollution: Model Selection and Application. A. Giorgini and F. Zingales (Eds.) Elsevier, New York, pp. 383-397.

Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby. 1985. Influence of organic cosolvents on sorption of hydrophobic organic chemicals by soils. Environmental Science & Technology, Vol. 19, Pages 975-979.

Nkedi-Kizza, P. and P.S.C. Rao. 1987. Effect of soil particle size on nonsingularity of pesticide sorption isotherms. Submitted to Environmental Science & Technology.

Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby. 1987. The influence of organic co-solvents on leaching of hydrophobic organic chemicals (HOC) through soils. Submitted to: Environmental Science & Technology.

Nkedi-Kizza, P., P.S.C. Rao, and J.W. Johnson. 1983. Adsorption of diuron and 2,4,5-T on soil particle size separates. J. Environ. Qual. 12:195-197.

Ogram, A.V., R.E. Jessup, L.T. Ou, and P.S.C. Rao. 1985. Effects of sorption on biological degradation rates of (2,4-Dichlorophenoxy)acetic acid in soils. Applied and Environmental Microbiology. p. 582-587.

Phillips, R.E. and S.H. Phillips, Editors. 1984. No-tillage Agriculture: Principles and Practices. Van Nostrand Reinhold Co., New York, NY.

Rao, P.S.C., A.G. Hornsby, D.P. Kilcrease, and P. Nkedi-Kizza. 1985. Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation. J. Environ. Qual., Vol. 14, no. 3, pp 376-383.

Rao, P.S.C., and J.M. Davison. 1980. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models. In "Environmental Impact of Nonpoint Source Pollution" (M.R. Overcash and J. M. Davidson, eds.), pp. 23-67. Ann Arbor Sci. Publ., Ann Arbor, Michigan.

Russell, J.D., M. Cruz, J.L. White, G.W. Bailey, W.R. Payne, Jr., J.D. Pope, Jr., and J.I. Teasley. 1968. Mode of a chemical degradation of s-triazines by montmorillonite. Science, Vol. 19, pp. 1340-1342.

Shainberg, I., J.D. Oster, and J.D. Wood. 1980. Sodium/calcium exchange in montmorillonite and illite suspensions. Soil Sci. Soc. Am. J. 44:960-964.

Sparks, D.L. 1989. Kinetics of soil chemical processes. Academic Press, Inc. New York.

Sparks, D.L., and P.M. Jardine. 1981. Thermodynamics of potassium exchange in soil using a kinetic approach. Soil Sci. Soc. Am. J. 45:1094-1099.

Tahoun, S.A. and M.M. Mortland. 1966. Complexes of montmorillonite with primary, secondary, and tertiary amides: I. Protonation of amides on the surface of montmorillonite. Soil Science, Vol. 102, pp. 248-254.

Wauchope, R.D. 1978. The pesticide content of surface water draining from agricultural fields - A review. J. Env. Qual. 7;459-472.

Weber, J.B. 1970. Mechanisms of adsorption of s-triazines by clay colloids and factors affecting plant availability. In Residue Reviews, F.H. Gunther and J.D. Gunter. (Edit.) Springer-Verlag, New York.

Witt, W.W., and K.W. Sander. 1988. Potential of surface water contamination from three triazine herbicides. Water Resources Research Institute, University of Kentucky, Lexington, KY.