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TRANSPORT OF IMAZETHAPYR IN UNDISTURBED SOIL COLUMNS AS RELATED TO IMAZETHAPYR PERSISTENCE IN SOIL SOLUTION

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

James David O'Dell

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ABSTRACT

The soil fate and transport of imazethapyr [(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazole-2-yl]-5-ethyl-3-pyridinecarboxylic acid] was evaluated in soil solution and undisturbed column leaching studies. Soil solution studies provided information as to the diffusion-controlled fate of imazethapyr and column leaching indicated the relative magnitude of diffuse versus channelized flow to the vertical transport of imazethapyr through the soil profile.

Laboratory experiments were conducted to determine the effects of application rate, wheat (Triticum aestivum L.) straw addition, and incubation time on the concentration of imazethapyr in soil solution. Field-moist loam (clayey, kaolinitic, thermic Typic Hapludult) Ap horizon was amended with finely ground wheat straw at rates of 0 and 2 g kg^{-1} and imazethapyr was applied at rates of 0, 31, 62, and 124 μg kg^{-1}. Soil solution was obtained by vacuum displacement at times of 0, 1, 2, 4, 8, and 16 days after application and analyzed to determine liquid-phase imazethapyr concentration. The concentration of imazethapyr in solution decreased exponentially as a function of time, and tended to be higher in solution from the straw-amended samples. Variation in K_d as a function of equilibration time may have been a consequence of diffusion-limited movement of imazethapyr into

micropores. For days 0 to 8, the K_d tended to be lower for straw-amended versus unamended soil, perhaps as a consequence of competitive exclusion of imazethapyr by straw for sorption sites in the soil solid phase.

A tractor-mounted core sampler was constructed to obtain large undisturbed soil columns for a leaching study. An 89 000 N hydraulic cylinder was used to push a steel sampling cylinder containing schedule 40 PVC pipe into the soil. The hydraulic cylinder was then retracted to pull the pipe and enclosed soil from the ground, with the soil separating evenly at the bottom of the column. Columns 30 cm in diameter were taken to a depth of 68 cm, with compaction observed to be less than three percent.

Undisturbed soil columns were mounted vertically in the laboratory and deionized water applied at a rate of approximately 90 mL h^{-1}. After two weeks of wetting, a tension of -0.5 kPa was applied to the bottom of one column, while another column was subjected to a tension of -2 kPa. A 25 mL pulse of 100 mmol L^{-1} Br^- and 0.518 mmol L^{-1} imazethapyr was applied to the surface of each column. Leachate was collected as a function of time and analyzed to determine Br^- and imazethapyr concentrations. Breakthrough curves were asymmetrical and characterized by rapid appearance of both solutes in the column effluent, with maximum concentrations occurring well ahead of one pore volume of the column. Breakthrough curves were analyzed with the one-dimensional

convection-dispersion equation to determine transport parameters and predict the elution of the solutes. The first-order decay constant for imazethapyr in soil solution was useful in predicting the breakthrough of imazethapyr after determining transport parameters from the Br^- data, but distribution coefficients predicted by the model were lower than those determined from soil solution.

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CHAPTER I

INTRODUCTION

As of December 1988, 46 different pesticide residues have been detected in the groundwater of 26 states as a result of normal agricultural use (USEPA, 1988). This has led the Environmental Protection Agency to require that pesticide manufacturers provide information regarding the potential leachability of chemicals currently registered or seeking registration. Monitoring wells have been used to trace pesticide movement in field environments, but other methods are needed to evaluate pesticide leachability before groundwater contamination occurs.

Knowledge concerning pesticide partitioning between the soil solid and liquid phase, especially regarding the rate of adsorption onto the solid phase, may be useful in determining pesticide mobility. Batch equilibration techniques are useful for estimating solute distribution between solid and solution phases, but the high solution to soil ratios normally used may result in unrealistic distribution coefficients. Distribution coefficients performed at moisture contents closer to those found in the field may provide data more representative of field environments, but the small quantity of solution recovered from the soil requires that analytical methods be suited to small volumes of solution.

In addition to determining the distribution of a chemical between solid and solution phases, an understanding of water movement in the field is needed to estimate the percentage of soil water which is active in solute transport. In well developed soils, preferential flow of water may occur around structural units and through larger pores such as worm channels. Solutes moving through the soil by this type of flow contact relatively few of the soil particles as compared to solutes moving by diffuse flow. Therefore, the probability of adsorption is decreased and the chemical may be leached deep into the profile before substantial adsorption occurs.

Studies of chemical mobility have been performed on columns of disturbed and undisturbed soil. Disturbed columns are preferred for their ease of use and the uniformity of results provided. Undisturbed columns, however, may provide information which is more closely related to solute movement under field conditions. When sieved soil is packed into a column, the total porosity can be controlled but the pore size distribution is often more uniform than in an undisturbed soil. As a result, more of the soil water is active in the transport process. This diffuse flow allows the solute to contact more soil particles, thus increasing the probability of adsorption.

Experiments with undisturbed columns are limited by the difficulty of securing columns large enough to obtain a representative sample. The use of undisturbed soil columns

in chemical leaching studies is further complicated by difficulties in the interpretation and modeling of systems exhibiting heterogeneous pore size distributions.

The objectives of this study were to determine the persistence of imazethapyr in soil solution as affected by application rate and the addition of wheat straw. After obtaining large undisturbed soil columns, the mobility of imazethapyr was assessed relative to that of bromide, a non-reactive reference tracer. Data from the soil solution persistence study was then evaluated as a predictor of imazethapyr movement in undisturbed soil columns.

CHAPTER II

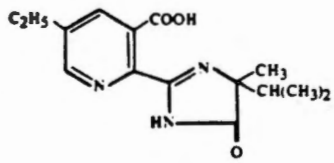
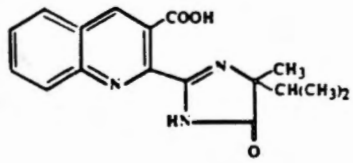
SOIL SOLUTION PERSISTENCE OF IMAZETHAPYR AS AFFECTED BY APPLICATION RATE AND ADDED WHEAT STRAW

Literature Review

Imazethapyr [(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazole-2-yl]-5-ethyl-3-pyridine-carboxylic acid] is an imidazolinone herbicide developed for the control of broadleaf weeds in soybean (*Glycine max* L.) It is applied to the soil preplant incorporated, preemergence, or postemergence. Due to the very recent introduction of imazethapyr, little research has been performed to show the influence of soil chemical and physical properties on the degradation, adsorption, and mobility of this compound. However, considerable research has been done with the closely related imazaquin [2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl)-3-quinoline-carboxylic acid], which is similar in structure but has considerably different properties (Table II.1). Comparison of environmental fate of the two compounds from the same herbicide family may provide insight to structure and activity relations governing their environmental fate.

In a field study of persistence, Loux and Slife (1987) applied imazethapyr to the soil and sampled at monthly intervals for 12 months to determine residual concentration. No herbicide was detected in a Cisne silt loam (Mollic

Table II.1. Chemical and physical properties of imazethapyr and imazaquin.

	Imazethapyr*	Imazaquin+
Structure		
Empirical Formula	$C_{15}H_{19}N_3O_3$	$C_{17}H_{17}N_3O_3$
Molecular Weight	289.3	311.3
Solubility in Distilled Water (mg L^{-1} @ 25 °C)	1400	60-120

* American Cyanamid, 1985

+ American Cyanamid, 1986

Albaqualf) four months after application. Two months after application to Drummer silty clay loam (Typic Haplaquoll), 70% of the applied imazethapyr had been lost, but the remaining herbicide persisted throughout the sampling period. Due to the experimental conditions it is difficult to determine whether the disappearance was the result of degradation or movement.

Ketchersid and Merkle (1986) studied the persistence and mobility of imazaquin in Vamont clay (Aquentic Chromudert) and Lakeland fine sand (Typic Quartzipsamment). The pH of each soil was adjusted to 4.5, 6.0, and 7.5 by the addition of 1 M H_3PO_4 or commercial lime. At least 45% of the applied imazaquin remained in the soil four months after application. Persistence tended to increase with decreasing pH and was greater in clay than sand. Mobility was examined by packing soil into columns 20 cm long and 6.5 cm in diameter. Imazaquin was applied to the surface at a rate of 1.1 kg ha^{-1} and allowed to equilibrate for 24 h, after which 9 cm of simulated rainfall was added to the column. Leaching was greater in sand than clay and increased with increasing pH, but amounts recovered in the leachate were not specified.

Adsorption, persistence, and mobility of imazaquin were studied by Basham et al. (1987) in Taloka silt loam (Mollic Albaqualf), Sharkey silty clay (Vertic Haplaquept), and Crowley silt loam (Typic Albaqualf). Imazaquin adsorption was described by the Freundlich equation, and K values ranged from

0.14 to 0.30 L kg^{-1} for solution concentrations of 0.5 to 128 μmols L^{-1}. No difference in distribution coefficients was observed between Taloka and Crowley soils. A higher K value was observed for the Sharkey soil, which was attributed to its higher clay and organic matter content. In the field leaching study, 3 cm of irrigation water leached only 16% of applied imazaquin out of the top 5 cm of soil, while 98% of applied Cl^- was leached from this layer. Eight cm of irrigation water leached 22% of the applied imazaquin out of the top 5 cm, but 97% remained in the top 10 cm. Following 8 cm of rainfall, nearly 75% of the applied imazaquin was leached from the top 5 cm, but 90% remained in the top 26 cm. The different leaching patterns were attributed to the greater intensity of rainfall as compared to irrigation, as well as the covering of plots between rainfall events to prevent drying and photodegradation.

Goetz et al. (1986) measured imazaquin sorption by both soil solution and batch equilibration methods for Lucedale fine sandy loam (Rhodic Paleudult), Dothan sandy loam (Plinthic Paleudult), Decatur silt loam (Rhodic Paleudult), Eutaw clay (Entic Pelludert), and Sumter clay (Rendollic Eutochrept). Using the batch equilibration method, imazaquin sorption was measurable only with the Lucedale fine sandy loam (K_d=0.21). The other soils displayed negligible adsorption, giving K_d values of 0.001. The soil solution technique was more sensitive in measuring imazaquin sorption, with Lucedale

fine sandy loam still exhibiting the greatest adsorption. Adsorption was found to be pH dependent, and increased with decreasing pH. For the Lucedale soil, 100% of applied imazaquin was in solution at pH 6.6, whereas at pH 5.8 only 47% was in solution. Using a Hiwassee sandy clay loam (Rhodic Kanhapludult) which has a high hematite content, batch equilibration yielded a K_d of 0.27, indicating the role of hematite as an adsorbent of the anionic herbicide.

Wolt et al. (1989) found that application rate, straw amendment, and incubation time interacted to influence the concentration of imazaquin in the soil solution from Etowah silt loam (Typic Paleudult). Imazaquin concentration in solution was higher in the presence of added wheat straw, which was attributed to competition for anion adsorption sites by decomposition products of the straw. All treatments exhibited a gradual linear decline in solution concentration over the 4-day sampling period, with the amount of applied imazaquin in solution ranging from 105 to 57%.

The potential mobility of a chemical may be a function of several soil-chemical interactions. These include reversible adsorption, chemical reaction, irreversible adsorption, pore geometry, entrance into solution, amount and average flow velocities, and the soil moisture content at the time of application (Bailey and White, 1970). Due to the number of factors influencing chemical mobility, it may be

difficult to predict the potential for mobility by adsorption isotherms alone.

Leaching through small columns of sieved hand-packed soil has been used extensively to evaluate the mobility of herbicides. Anderson et al. (1968) demonstrated leaching patterns of benefin (N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine), trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine), and nitralin (4-(methylsulfonyl)-2,6-dinitro-N,N-dipropylaniline) in small columns of packed soil. Although each herbicide has a water solubility of 0.5 mg L^{-1} at 25 °C, the chemicals showed markedly different leaching patterns. Nitralin was leached more than trifluralin, which leached slightly more than benefin. This indicates the effect of the type and arrangement of functional groups on the potential mobility of a chemical.

The effect of soil properties on the movement and distribution of buthidazole (3-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-4-hydroxy-1-methyl-2-imidazolidinone) was studied by Weber and Peeper (1982) in small columns of disturbed soil. Soils used for the study were Alamance silt loam (Typic Hapludult), Davidson clay (Rhodic Paleudult), Lakeland sand (Typic Quartzipsamment), and Norfolk loamy sand (Typic Paleudult). Soils were incubated for 30 days after application of the chemical, followed by 45 days of leaching at a rate of 1.27 cm d^{-1}. The amount of applied buthidazole

recovered in the leachate ranged from 13.8% (Alamance silt loam) to 19.1% (Norfolk loamy sand), with relatively even distribution found in the sandy soils.

The objective of this research was to determine the persistence of imazethapyr in soil solution over a 16-day period as affected by application rate and the addition of organic matter to the soil.

Materials and Methods

Field-moist loam (clayey, kaolinitic, thermic Typic Hapludult) which had been mapped as Etowah (Typic Paleudult) was collected from the Ap horizon and passed through a 2-mm screen and amended with finely ground wheat (*Triticum aestivum* L.) straw at rates of 0 and 2 g kg^{-1}. Three days after the addition of straw, imazethapyr was added as an aqueous solution at rates of 0, 31, 62, and 124 μg kg^{-1}. Quadruplicate samples of the treated soil were packed into 50-mL syringes and brought to a moisture content of 0.35 g g^{-1}. Soils were incubated at 25 °C for 0, 1, 2, 4, 8, and 16 days after treatment. Soil solution was obtained by vacuum displacement (Wolt and Graveel, 1986) using a procedure similar to that employed in previous investigations with imazaquin (Wolt et al., 1989). The solution was immediately analyzed to determine pH and electrical conductivity (EC), and the remaining solution was stored in polypropylene vials at -11 °C until analyzed for imazethapyr concentration.

Imazethapyr concentration in the solutions was determined by high performance liquid chromatography. The system consisted of Waters model 481 LC spectrophotometer, model 501 pumps, and model 740 data module. The mobile phase consisted of 65:35 (v:v) 4% aqueous acetic acid:acetonitrile at a flow rate of 1 mL min^{-1}. The stationary phase consisted of a 25 cm x 4.6 mm i.d. C-8-DB column and a 5 cm x 4.6 mm i.d. C-8 guard column. Imazethapyr was detected by UV absorbance at 254 nm, and a 200 μL injection yielded a sensitivity of 5 μg L^{-1}.

Distribution coefficients were calculated by plotting the concentration of imazethapyr in the soil solution (μg L^{-1}) against the concentration in the solid phase (μg kg^{-1}) for each time of incubation. The solid phase concentration was assumed to be the difference between the total applied imazethapyr and the measured concentration in solution. The K_d was the determined from the slope of the best fit line through the points of solid versus solution phase concentrations.

Results and Discussion

Application rate, incubation time, and the addition of wheat straw interacted to influence the soil solution composition (Table II.2). Soil solution from the straw-amended samples tended to have a higher pH and lower EC, indicating a buffering effect of the straw. The addition of straw also tended to increase the concentration of imazethapyr in the soil solution, which may be the result of anionic decomposition products from the straw competing for limited

Table II.2 Main effects and sources of variation for soil solution components.

Effect	pH	EC	Imazethapyr
		dS m^{-1}	$\mu g\ L^{-1}$
Straw (g kg^{-1})			
0	5.88	375	77.9
2	6.10	337	86.5
Rate ($\mu g\ kg^{-1}$)			
0	5.90	359	0
31	5.97	350	44.2
62	5.98	350	90.6
124	6.09	365	194.1
Time (days)			
0	5.92	395	128.0
1	6.11	398	103.9
2	6.19	367	90.7
4	6.11	340	81.4
8	5.71	308	58.0
16	5.88	334	31.3
Source		Significance[+]	
Straw	**	**	*
Rate	***	NS	***
Time	***	***	***
Straw*Rate	*	NS	**
Rate*Time	***	NS	***
Straw*Rate*Time	*	***	***

[+]Significant at the 5(*), 1(**), or 0.1(***)% level of probability or not significant (NS).

anion adsorption sites on the soil surfaces (Wolt et al., 1989). Soil solution sampled immediately after application showed this effect only at the highest rate of imazethapyr, while the lower rates tended to have lower solution imazethapyr concentrations in the presence of added straw. The influence of straw on solution imazethapyr was more pronounced at the 4- and 8-day sampling times. This delay in the straw effect may be related to the decomposition rate of the straw, with little competition for adsorption sites at the initial time of application. In a study of imazaquin in soil solution, Wolt et al. (1989), using the same soil and experimental protocol, observed elevated imazaquin levels in solution for straw-amended soil from the initial time of sampling, especially at rates of 62 and 124 $\mu g\ kg^{-1}$.

The percentage of applied imazethapyr in solution ranged from 96 to 16% over the 16-day sampling period (Table II.3), with the solution concentration declining exponentially as a function of time (Figure II.1). Wolt et al. (1989) noted a linear decline of imazaquin in solution, ranging from 80-105% at the time of application to 57-76% after 4 days. The apparently greater adsorption of imazethapyr as compared to imazaquin is interesting in that imazethapyr has a much greater water solubility. This indicates that the type and arrangement of functional groups plays a larger role in the solid-liquid phase partitioning than does water solubility. This is consistent with the findings of Anderson et al. (1968)

Table II.3. Mean percent of imazethapyr in soil solution relative to total amount applied to soil.

Straw Rate	Imazethapyr Rate	Incubation Time, days					
		0	1	2	4	8	16
g kg^{-1}	μg kg^{-1}	% imazethapyr in soil solution					
0	31	96	46	36	25	19	11
	62	73	55	46	37	24	11
	124	59	55	53	45	31	20
2	31	76	54	43	44	37	16
	62	67	61	47	46	31	18
	124	71	60	53	51	37	18

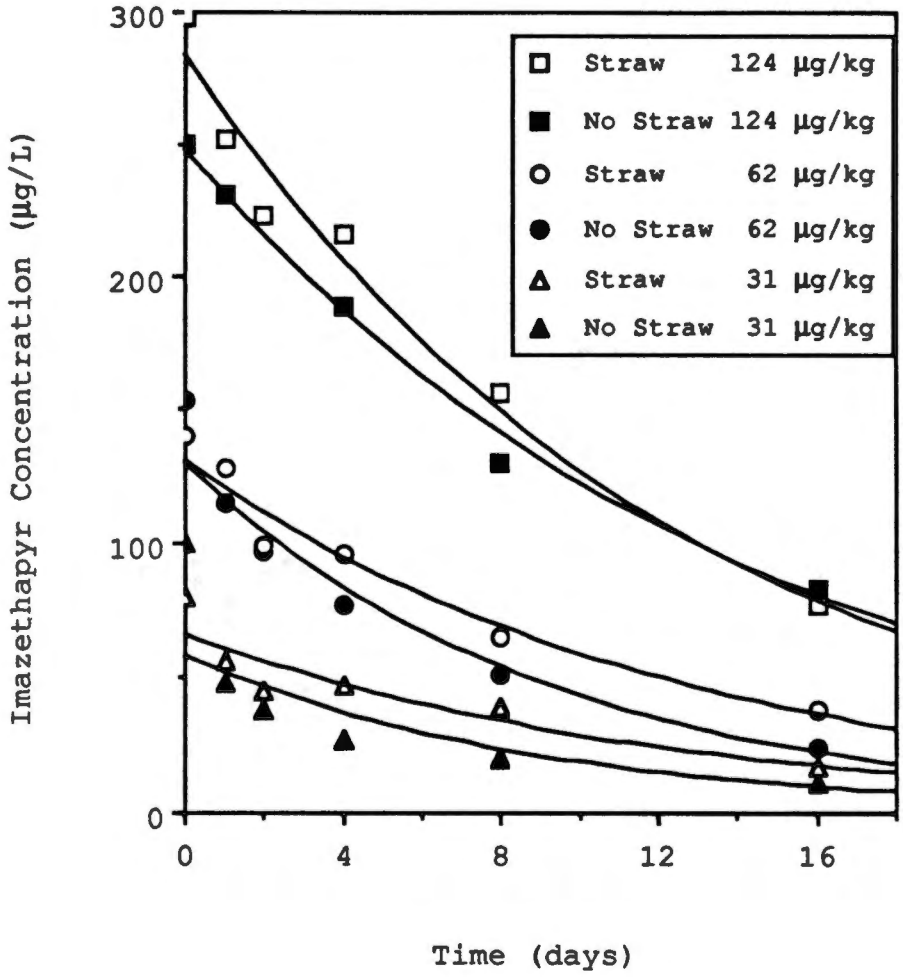
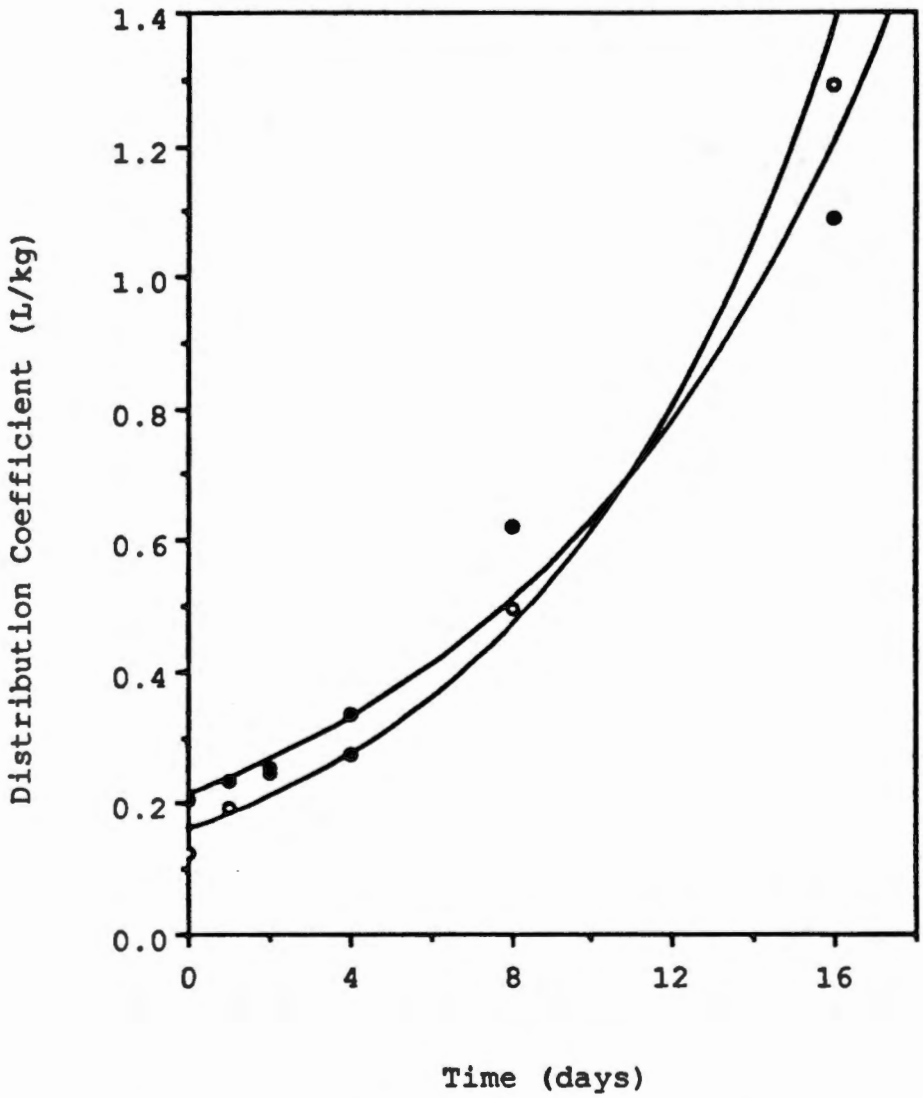


Figure II.1. Concentration of imazethapyr in the soil solution as a function of time.

for herbicide leaching in packed soil columns where varying mobility was observed among herbicides, even though theherbicides used had the same water solubility and only slight structural differences.

The more rapid disappearance of imazethapyr from solution during the first four days of the sampling period may be due to adsorption onto sites surrounding the larger pores in the soil, with the following gradual decline in solution concentration due to diffusion of the herbicide into water held in smaller pores where it encounters additional adsorptive sites. This diffusion is enhanced at higher application rates, as is indicated by the more rapid decline in solution imazethapyr concentration with the 62 and 124 μg kg^{-1} rates. It is difficult to ascertain that adsorption has taken place after diffusion occurs, however. It is possible that the herbicide is still in solution which is held at energy levels too great to be recovered by the displacement procedure. Although imazethapyr which is in the solution close to the soil surface may be available for uptake by plant roots, it is unlikely that it would be susceptible to leaching unless diffusion back into the mobile portion of the soil water occurs.

Distribution coefficients (K_d) increased exponentially as a function of time during the 16-day sampling period, and in general were lower in the straw-amended soils (Figure II.2). In soils not amended with straw, the K_d ranged from 0.18 to



o Straw y = 0.16*10^(5.83e-2x) R^2 = 0.97

● No Straw y = 0.21*10^(4.69e-2x) R^2 = 0.97

Figure II.2. Imazethapyr distribution coefficients as a function of time for soil with and without straw amendment.

1.08 L kg^{-1} (Figure II.3), while the range was 0.12 to 1.25 L kg^{-1} for straw-amended soil over the 16-day sampling period (Figure II.4). Using a batch equilibration method, Goetz et al. (1986) obtained K_d's ranging from 0.001 to 0.21 for imazaquin with five Alabama soils ranging from sandy loam to clay. Using a soil-slurry technique Basham et al. (1987) found that equilibrium was reached in 3 hours, and imazaquin adsorption was described by the Freundlich equation. Using three Arkansas soils, distribution coefficients for imazaquin ranged from 0.14 to 0.30.

The time-dependent distribution coefficients observed in this study contribute to the difficulty of modeling the transport of imazethapyr through the soil. Since the distribution coefficient increases with time after application, the amount of time between herbicide application and rainfall events must also be considered when attempting to predict transport.

The adsorption of imazethapyr is likely due to attraction of the negatively charged carboxylate ion on the molecule to positively charged sites on the surface of iron and aluminum oxyhydroxides. This was observed by Goetz et al. (1986) for imazaquin when adsorption was greater at lower pH and was much greater in a soil containing a high amount of hematite. These positively charged sites are dependent upon pH, and occur when the pH of the soil is below the zero point of charge. Iron oxides have also been shown to adsorb the sulfate ion under

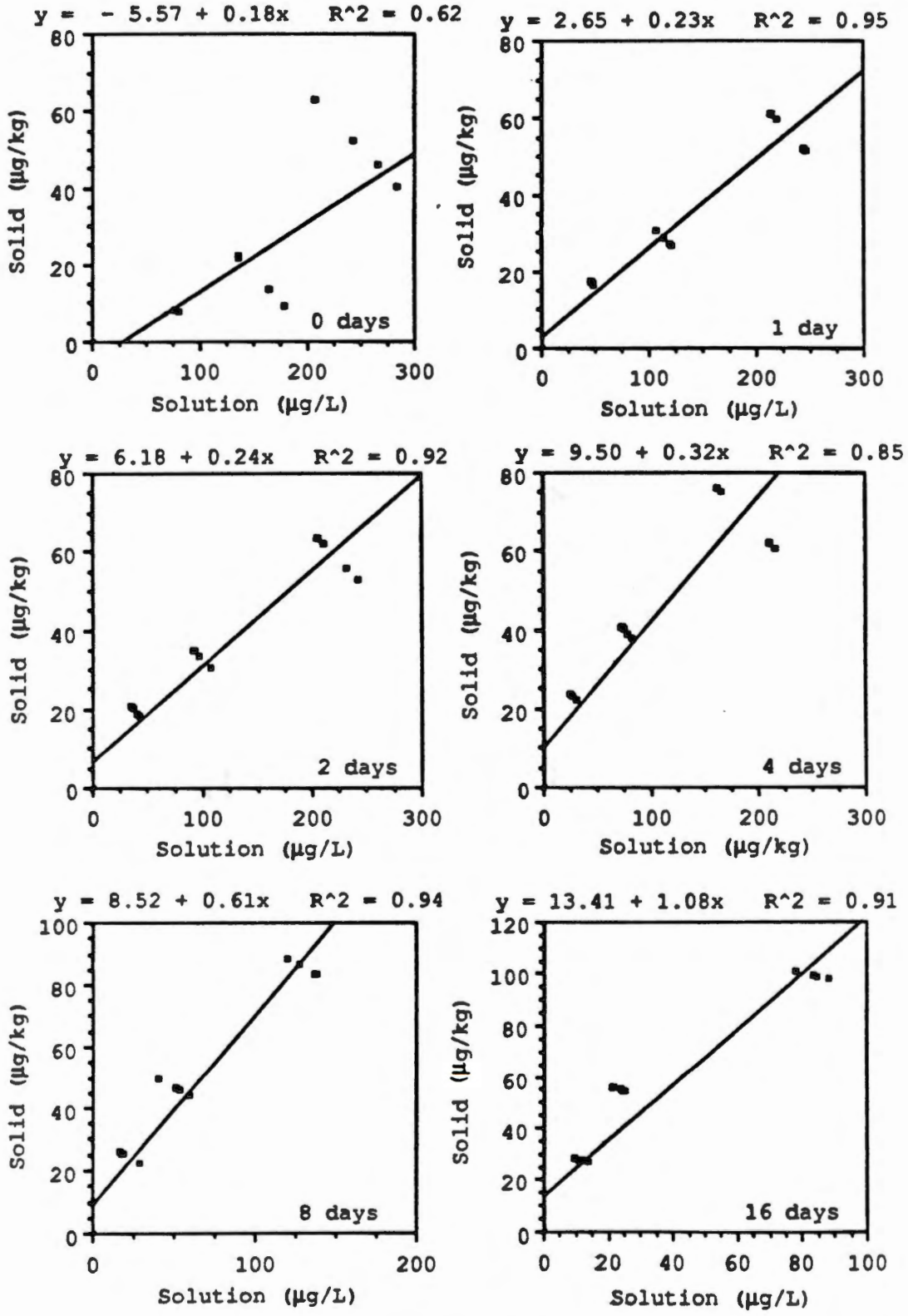


Figure II.3. Adsorption isotherms for imazethapyr in soil not amended with wheat straw.

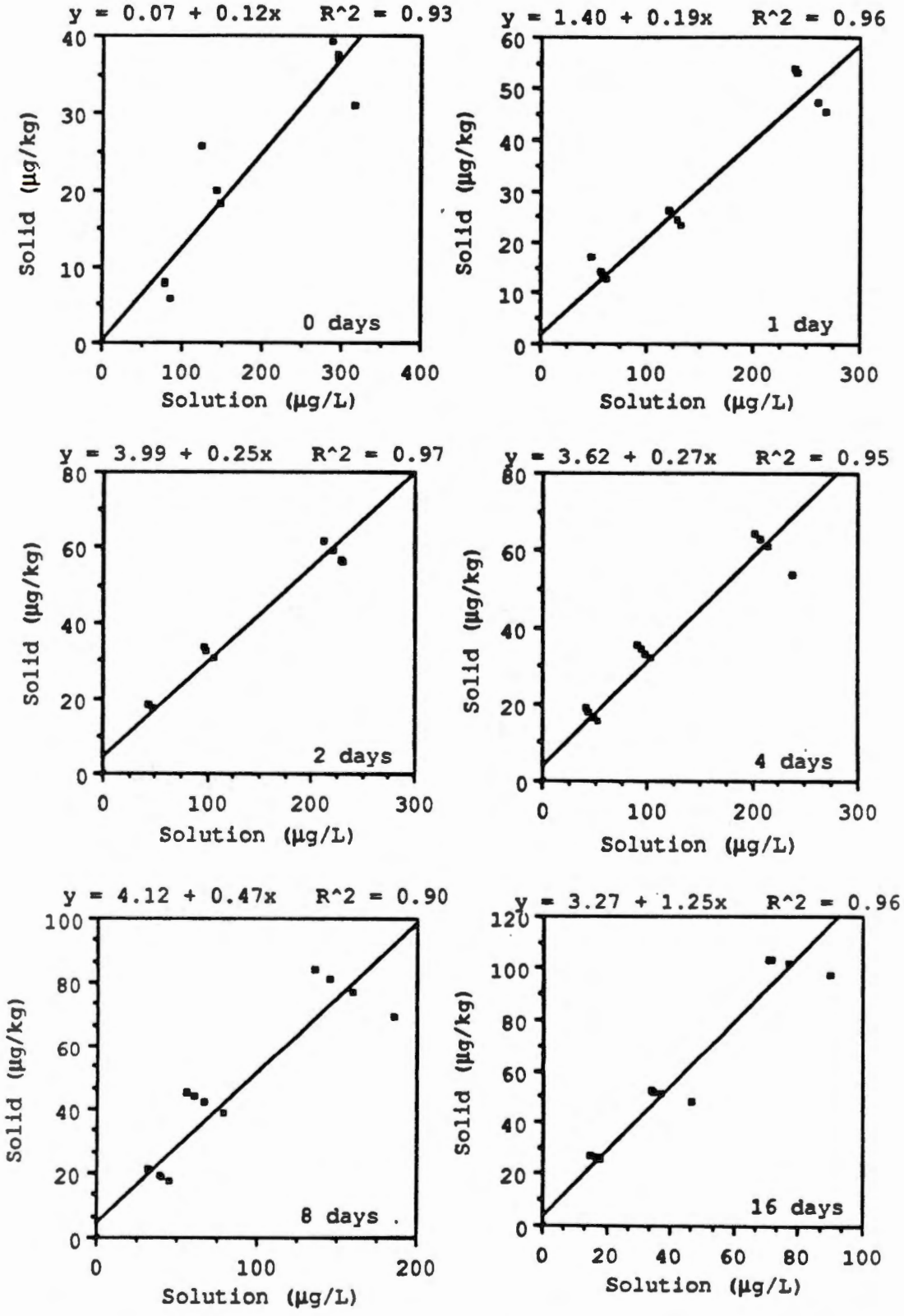


Figure II.4. Adsorption isotherms for imazethapyr in soil amended with wheat straw.

acidic conditions (Parfitt and Smart, 1978). The sulfate was observed to replace two hydroxyl groups on the surfaces of iron-containing minerals.

CHAPTER III

A TRACTOR MOUNTED SAMPLER FOR OBTAINING LARGE UNDISTURBED SOIL CORES

Literature Review

Studies of chemical movement in undisturbed soil cores have been limited in part by the difficulty of obtaining undisturbed cores large enough to accurately represent the soil as a whole. One of the more primitive methods involves driving steel or PVC pipe into the soil with a hammer, then excavating from around the pipe to remove it from the surrounding soil. Bitton and Boylan (1985) used this method to obtain soil cores 7.6 cm in diameter and 36 cm in length from Eustis fine sand (Psammentic Paleudult), Okeechobee (Hemic Medisaprist), Candler (Typic Quartzipsamment), Pomona (Ultic Haplaquod), and Apopka (Grossarenic Paleudult). In heavier soils and when larger cores are desired, however, this method may not be practical.

Tackett et al. (1965) pushed steel pipe of varying diameter to depths up to 2.7 m in a Houston Black clay (Udic Pellustert). This was done by using a fork lift to place steel plates on the pipe until the force was sufficient to push the pipe into the soil. When the pipe had been pushed to the desired depth, the fork lift was used to pull the pipe and enclosed soil from the ground. The mass required to push a 72-cm diameter pipe 2.7 m into the soil was approximately

24 000 kg. Little compaction was observed and the soil separated evenly at the bottom of the column.

Brown et al. (1985) describe a procedure for obtaining large undisturbed soil monoliths in which soil is excavated from around a cylindrical area so that a length of steel casing can be pushed over the monolith with a backhoe bucket. This method is time consuming, however, because the soil must be carefully removed from around the monolith in order to obtain a column which fits well into the pipe.

A self-contained soil coring apparatus described by Swallow et al. (1987) has been used to obtain soil cores having a diameter of 25 cm to a depth of 90 cm. The machine operates by pushing a metal tube of sufficient size to contain a 25-cm diameter PVC pipe into the soil by means of 2 hydraulic cylinders. The sampling cylinder, PVC pipe, and enclosed soil are then pulled from the ground with the hydraulic cylinders, and the PVC pipe and soil removed from the sampling cylinder. This method allows for a rapid and relatively easy means of obtaining large undisturbed cores, but the cost of materials (>$5 000) and the time required for construction (160 h) may be prohibitive.

The sampler used for this study was designed to be constructed with a minimum investment of time and labor, and to be capable of securing undisturbed soil cores 30 cm in diameter and at least 60 cm deep with a minimal amount of disturbance.

Materials and Methods

The sampler is designed to be mounted on the 3-point hitch of a tractor, and utilizes the tractor's existing hydraulic system. The frame of the core sampler is constructed of 7.5-cm angle iron and is 2.4 m high x 0.6 m wide x 0.6 m deep (Figure III.1). (Braces are omitted from the drawing for clarity of presentation.) A 10-cm diameter 89 000 N hydraulic cylinder with a 60-cm stroke is mounted between two plates which move vertically within the frame. The plates are constructed of 1.25-cm plate steel welded to a 20-cm length of 60-cm x 60-cm channel iron. Holes are drilled through two sides of the channel to align with holes in the frame of the sampler which are 1.5 cm in diameter and 30 cm apart. This allows each plate to be made stationary by inserting steel rods through the holes. Vertical plates are welded to the underside of the lower plate with holes enabling the sampling cylinder to be attached to the lower plate by pinning with a steel rod.

The sampling cylinder (Figure III.2) is constructed of a 110-cm length of 34-cm i.d. steel pipe. A 20-cm length of 30.5-cm i.d. tapered steel pipe is welded to the end of the larger pipe to cut a column of equivalent diameter to the PVC pipe. The inside of the cylinder is blocked so that a length of 30.5 cm i.d. schedule 40 PVC pipe fits securely. After insertion of the PVC pipe into the sampling cylinder, holes are drilled through the pipe to align with the holes in the

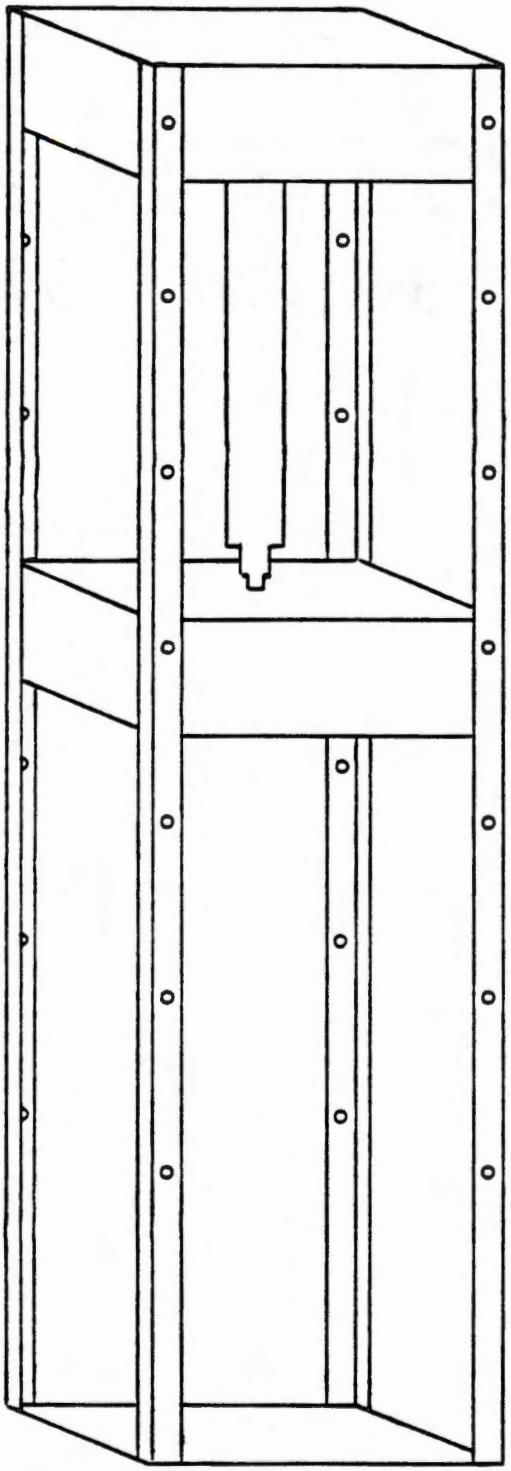


Figure III.1. Diagram of core sampler.

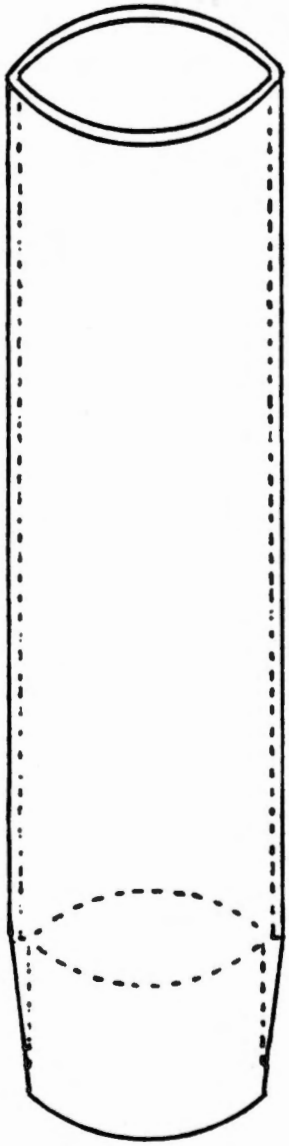


Figure III.2. Diagram of sampling cylinder.

cylinder so that it can be pinned to the lower plate on the sampler. The core sampler described can be constructed in approximately 50 h using readily available materials (Table III.1). Machining of the tapered pipe at the end of the sampling cylinder was done by a private machine shop.

In order to hold the sampler down while the pipe is being pushed into the soil, the sampler is secured to four anchors with chains and binders. The anchors are 150 cm in length and have four 10-cm diameter screws attached to the shaft, and were made by welding together two 75-cm mobile home anchors. A high-torque electric motor powered by a small generator was used to insert the anchors into the soil.

After the sampler is secured to the anchors, the hydraulic cylinder is extended to push the sampling cylinder into the soil. When the hydraulic cylinder has been extended to the full 60-cm stroke, the steel rods are removed from the upper plate and the cylinder retracted to align the upper plate with another set of holes in the frame of the sampler. The upper plate is then pinned to the frame again, and the cylinder extended to push the pipe to the desired depth in the soil. The hydraulic cylinder is then retracted to pull the sampling cylinder from the surrounding soil, and a tractor mounted boom pole used to pull the PVC pipe and enclosed soil from the sampling cylinder.

Table III.1. List of materials needed for construction of core sampler.

Angle iron	
Frame--7.5 cm x 6.3 cm x 0.6 cm	16 m
Braces-5 cm x 5 cm x 0.3 cm	10 m
Channel iron	
60 cm x 60 cm x 20 cm	2
Plates	
60 cm x 60 cm x 1.35 cm	2
Chain	
1 cm	15 m
Rods	
75 cm x 1.3 cm, stainless	6
Hydraulic cylinder	
89 000 N, 60 cm stroke	
Hydraulic hose	
3 m x 1.9 cm, with couplers	2
Pressure gauge	
0-20.7 MPa	
Sampling cylinder	
PVC pipe	
Schedule 40, 30.5 cm i.d.	

Results and Discussion

The core sampler was used to sample intact columns of loam (clayey, kaolinitic, thermic Typic Hapludult) which had been mapped as Etowah (Typic Paleudult) for use in a column leaching study (Chapter IV). The soil was moistened to near field capacity in the upper solum by the addition of approximately 400 L of water per day to each sampling site for six days. The sampling cylinder was pushed to a depth of 90 cm with a hydraulic cylinder pressure of approximately 10 MPa. A layer of compacted alluvium was encountered at this depth which the sampling cylinder could not penetrate. After subtracting the loss of the soil held in the tapered pipe at the bottom of the cylinder, columns were 68 cm in length. Compaction was observed to be approximately 2 cm, and examination of the soil at the termination of the leaching study revealed little disturbance of the soil in the columns.

The sampler has also been used to push 30-cm i.d. PVC pipe 1 m into the soil without using the sampling cylinder. The hydraulic pressure required is then greatly reduced, and no soil is lost to the volume at the end of the sampling cylinder. However, some distortion of the PVC pipe is observed, making the columns somewhat elliptical rather than round.

CHAPTER IV

MOBILITY OF IMAZETHAPYR IN UNDISTURBED SOIL COLUMNS

Literature Review

The transport of solutes through soil columns is of particular interest in predicting chemical movement through the soil profile. Since field-scale solute transport studies are difficult to evaluate and interpret, laboratory soil columns are commonly used to determine water and chemical movement under more controlled conditions. Many studies of herbicide transport have been performed on small columns of sieved, hand-packed soil (Anderson et al., 1968; Selim et al., 1977; Weber and Peeper, 1982). However, these disturbed soil columns lack the structure and pore size distribution of undisturbed soils, thus altering the nature of the solute transport observed.

The differences between breakthrough curves (BTC) for disturbed and undisturbed soil columns have been well documented. Elrick and French (1966) performed Cl^- leaching on 15-cm cores of disturbed and undisturbed Honeywood silt loam. Chloride BTC were symmetrical from both cores, but Cl^- appeared much earlier in the effluent from the undisturbed core, suggesting flow through channels in the soil. The dispersion coefficient was approximately one order of magnitude lower in the packed column, indicating more uniform movement of the Cl^- through the relatively homogeneous soil.

The difference between dispersion coefficients from disturbed and undisturbed swelling clay soil was also observed by Cassel et al. (1974), although less than a twofold difference occurred. One possible reason for the less pronounced difference is that the disturbed columns were packed by horizon, thus reducing the homogeneity of the column. Larger soil columns were also used, having a diameter of 30 cm and a length of at least 80 cm. The disturbed cores required a greater volume of water to displace the applied solutes, and also had a higher volumetric water content than the undisturbed cores.

McMahon and Thomas (1974) investigated Cl^- and ^3H_2O movement through disturbed and undisturbed cores of Maury silt loam (Typic Paleudalf), Pembroke silt loam (Mollic Paleudalf), and Eden silty clay loam (Typic Hapludalf). Breakthrough curves were relatively symmetrical, with the solutes appearing earlier in the leachate from undisturbed cores. Chloride appeared ahead of tritiated water in the Maury and Eden soils, which tend to exclude anions. In the Pembroke soil, which displays anion adsorption, Cl^- was retarded in relation to ^3H_2O. Although dispersion coefficients were not calculated, breakthrough curves from the disturbed and undisturbed cores indicated that greater dispersion occurred in the undisturbed cores.

In a study of solute transport in Houston Black clay (Udic Pellustert) in the field, Kissel et al. (1973) used Cl^-

and fluorescein dye to determine pathways of water movement. Examination of a cross-section of the soil profile after ponding of the tracers for 1.5 d showed distinct areas containing fluorescein-tagged water. Chloride concentrations in soil samples taken from the areas containing fluorescein were much greater than those taken from the surrounding soil. When the soil was ponded for 18 d the difference was less pronounced, indicating that the smaller pores do conduct Cl^- but at a slower rate than the larger pores. The smaller difference observed may also have been the result of diffusion of the Cl^- from the larger pores into the smaller via hydraulic and concentration gradients.

In another study of water movement in Houston Black clay, Ritchie et al. (1972) applied fluorescein-tagged water to undisturbed soil columns. Examination of the cross-section of the columns at the termination of leaching revealed dye throughout most of the area at a depth of 5 cm. At 20 cm the fluorescein was visible over 60% of the area, and at 35 cm approximately 10% of the area showed signs of the tagged water. By the time the fluorescein reached the 50-cm depth, only about 2% of the area appeared to be active in the transport of the dye. In a disturbed column of the same soil, the distribution of fluorescein was uniform throughout the depth of the core.

The effects of soil structure were shown by Tyler and Thomas (1981) in a study of Cl^- movement in three soils.

Structured soils were represented by Huntington silt loam (Fluventic Hapludoll) and Karnak silty clay loam (Vertic Haplaquept), while unstructured was represented by Bruno sandy loam (Typic Udifluvent). Undisturbed soil columns were 15 cm in diameter and 24 cm in length, and were subjected to a tension of 1.5 cm Hg (-2 kPa). Chloride breakthrough curves were similar for the Huntington and Karnak soils, and were characterized by rapid initial appearance of Cl^- in the leachate with maximum concentrations occurring well in advance of one pore volume of the column. Fluorescein dye patterns indicated that water was moving through distinct pathways at depths greater than 15 cm. The Bruno soil yielded a more ideal breakthrough curve, with the maximum concentration in the leachate observed at approximately one pore volume.

Bouma and Wösten (1979) examined the effect of macrostructure on the breakthrough of Cl^- from undisturbed columns of two swelling clay soils. One soil was characterized by rough peds and vertical worm channels, while the other soil had smooth peds and no channels. Initial Cl^- breakthrough occurred earlier in the effluent from the more structured soil, with the volume of immobile water estimated at 60% as compared to 22% in the less structured soil. This indicates the importance of flow through worm channels and pores around structural units as pathways for solute transport.

Seyfried and Rao (1987) conducted experiments with tritiated water flow through undisturbed columns of Instituto clay loam (Typic Dystropept). Leaching was performed under saturated and unsaturated conditions by varying the tension on the columns from 0 to -2 kPa. Breakthrough curves from saturated columns were asymmetrical and showed a high degree of tailing, with the curves becoming more symmetrical as the tension was increased to -2 kPa. The symmetry of the unsaturated breakthrough curves was accompanied by later appearance of ^3H_2O in the effluent and a lower degree of tailing. The Darcy flux decreased by about two orders of magnitude as the tension was increased from 0 to -2 kPa. This was attributed to disruption of the water-conducting pore geometry in the presence of tension, and the increased flow through large pores under saturated conditions.

Movement of the herbicides napropamide [N,N-diethyl-2-(naphthalenyloxy)propanamide] and bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,3H)pyrimidinedione] was investigated by White et al. (1986) using undisturbed cores of Evesham clay (Aquic Eutrochrept). Leaching was studied under continuous and discontinuous watering and at different initial water contents, with Cl^- used as a tracer for water flow. After continuous leaching of one pore volume from an initially dry core, 85% of the applied napropamide and nearly 100% of the applied bromacil had been recovered from the column. Herbicide retention was greater in initially wet cores, which

was probably due to enhanced diffusion of the chemicals to adsorption sites at the higher moisture content. Leaching of the herbicides was reduced under discontinuous watering, which allowed the solutes to diffuse into regions of less mobile water during the time that water was not flowing through the column. Only 28% of the applied napropamide (K_d=17.7 L kg^{-1}) was leached from the prewet column by one pore volume of discontinuous watering. This difference was less pronounced with the weakly adsorbed bromacil (K_d=1.73 L kg^{-1}).

The objective of this research was to determine the degree of mobility of imazethapyr in undisturbed soil columns, and to relate the mobility to the persistence of imazethapyr in soil solution.

Materials and Methods

Two undisturbed soil columns, 30 cm in diameter and 68 cm in length, were obtained from a loam (clayey, kaolinitic, thermic Typic Hapludult) mapped as Etowah (Typic Paleudult) from the Knoxville Plant Sciences Field Laboratory. Columns were obtained as described in Chapter III, and the ends of the column covered with plastic film to prevent drying prior to initiation of the leaching study.

The columns were mounted vertically on a rack in the laboratory at ambient temperature (Figure IV.1). The bottom of each column was fitted with a 33-cm x 33-cm PVC plate welded to the column with PVC rod. A 1-cm hole was drilled in the center of the plate and a 10-cm length of 1-cm i.d. PVC

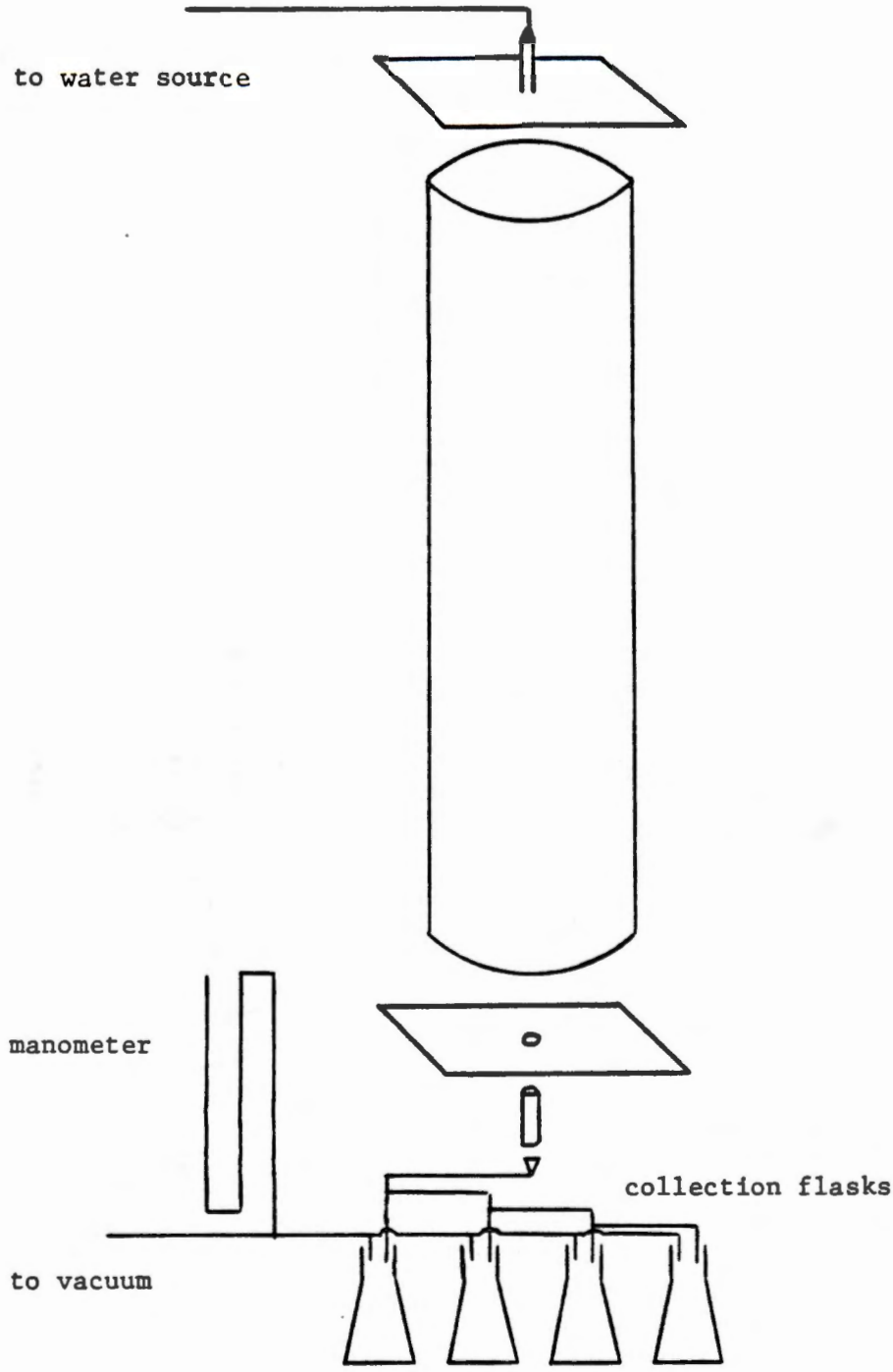


Figure IV.1. Schematic diagram of column leaching apparatus.

tubing attached to the outside of the plate. The inside of the plate was slightly concave to facilitate drainage of the leachate. Leachate was collected in four 500-mL Erlenmeyer flasks connected in series, with each flask connected to a vacuum source. Vacuum was regulated by a Fairchild model 16 two-stage regulator and monitored by a water-filled manometer.

The top 6 cm of soil was removed from each column and passed through a 2-mm screen, and the plant material discarded. The soil was replaced onto the surface of the column, and a 30-cm diameter filter paper placed on the soil surface. A 10-cm diameter watch glass was placed convex side up on the center of the paper to aid in lessening the force of the applied water.

A 33-cm x 33-cm acrylic sheet with a 1-cm diameter hole in the center and a 10-cm length of acrylic tubing glued around the hole was attached to the top of each column. Deionized water was supplied at a rate of approximately 90 mL h^{-1} by a Technicon peristaltic pump. This rate was equivalent to 3 cm of rainfall in a 24-h period. The average flow rate was determined by the volume of leachate recovered at the termination of leaching.

Deionized water was applied continuously to the freely draining columns for 10 d, after which the vacuum was applied. One column was maintained at a potential of -0.5 kPa (5 cm H_2O), and another column maintained at -2.0 kPa (20 cm H_2O).

After a 5-d equilibration period, a 25-mL pulse of 100 mmol L^{-1} bromide (as KBr) and 0.518 mmol L^{-1} imazethapyr (technical material, 99.4% purity) in deionized water was applied to each column by a pipette. This concentration was equivalent to an application rate of 0.5 g imazethapyr ha^{-1}, which was four times the recommended high rate at the time the experiment was performed. Leachate was collected in 100-mL increments until 1 L was recovered, then was collected in approximately 600-mL increments as the Erlenmeyer flasks were filled. The flasks were connected to the column in a manner to allow the flasks to fill one at a time and in a specific order. Leaching was continued for a period of 23 d, after which the water flow was stopped and the column allowed to drain for 24 h. Leachate samples were stored in capped polypropylene vials at -11 °C prior to analysis.

At the termination of leaching, the PVC pipes were cut lengthwise and removed from around the soil cores. Each core was then segmented into five sections and each section divided into equally sized quadrants. Subsamples were taken from each quadrant for moisture determination by drying to constant mass at 105 °C. The volumetric water content was determined by multiplying the gravimetric moisture content by the mean bulk density (1.44 g cm^{-3}, data not presented).

Leachate samples were analyzed for bromide concentration using a Dionex Model 2120i high performance ion chromatograph. The mobile phase consisted of 2 mM Na_2CO_3 and 0.75 mM $NaHCO_3$,

and the stationary phase consisted of a 25-cm IonPac AS-4A column with a 5-cm guard column. Bromide was detected by chemically suppressed conductivity using 12 mM H_2SO_4 as the regenerant. Imazethapyr concentration was determined by high performance liquid chromatography as described in Chapter II.

Bromide and imazethapyr BTC were analyzed using the Fortran program CXTFIT (Parker and van Genuchten, 1984). The data from the Br^- BTC was used to fit the dispersion coefficient and the pulse duration, with the pore-water velocity, pulse concentration, and retardation factor specified in the model. Since bromide was assumed to be non-reactive in the column, the retardation factor was set to 1. The first-order decay of imazethapyr from soil solution (Chapter II) was then calculated and specified with the parameters fit from the Br^- data (except the retardation factor) to fit the retardation factor and predict the elution of imazethapyr from the column.

Results and Discussion

Breakthrough curves of Br^- and imazethapyr from both columns were asymmetrical and displaced to the left of one pore volume. Both Br^- and imazethapyr were detected in the first 100 mL of leachate collected from the -0.5 kPa system, while 300 mL of leachate had been collected from the -2 kPa system before detection of the solutes. Concentrations in the leachate reached a maximum of 334 μmol L^{-1} Br^- (Figure IV.2) and 1.03 μmol L^{-1} imazethapyr (Figure IV.3) in the -0.5 kPa

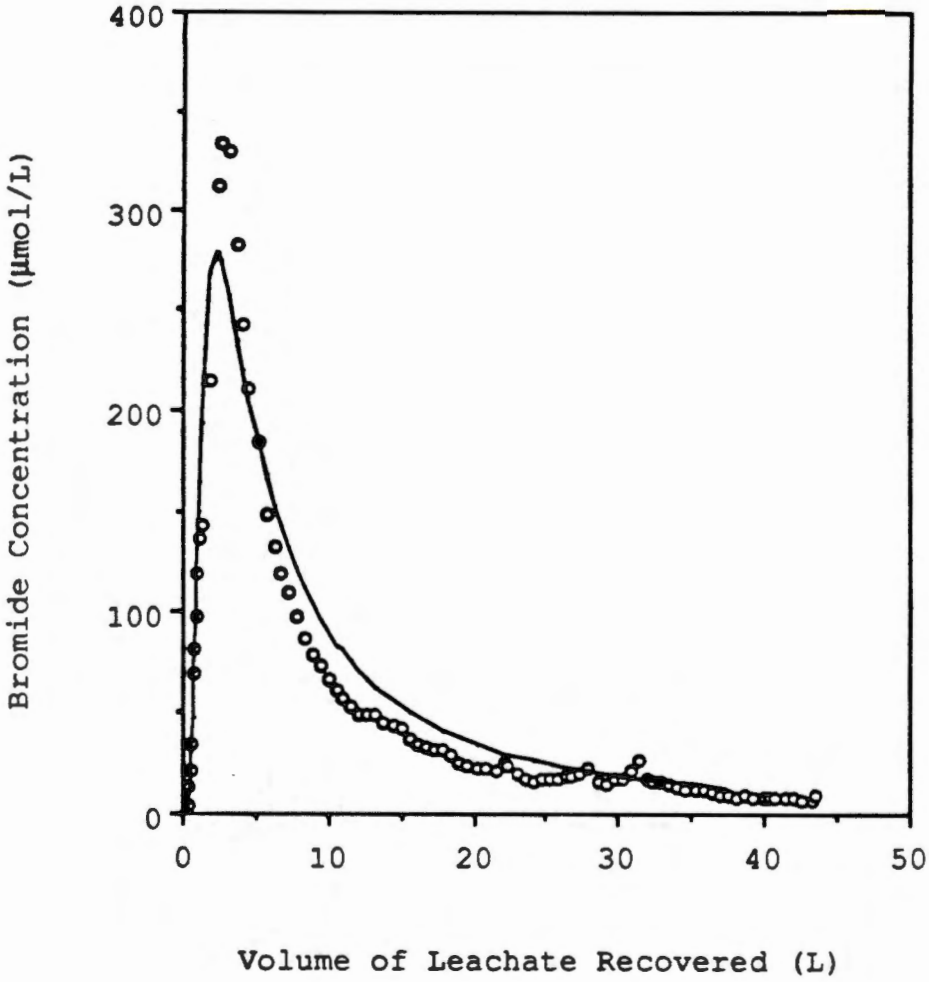


Figure IV.2. Breakthrough of bromide in a soil column at -0.5 kPa moisture potential. The solid line represents the best fit of the convective-dispersive model.

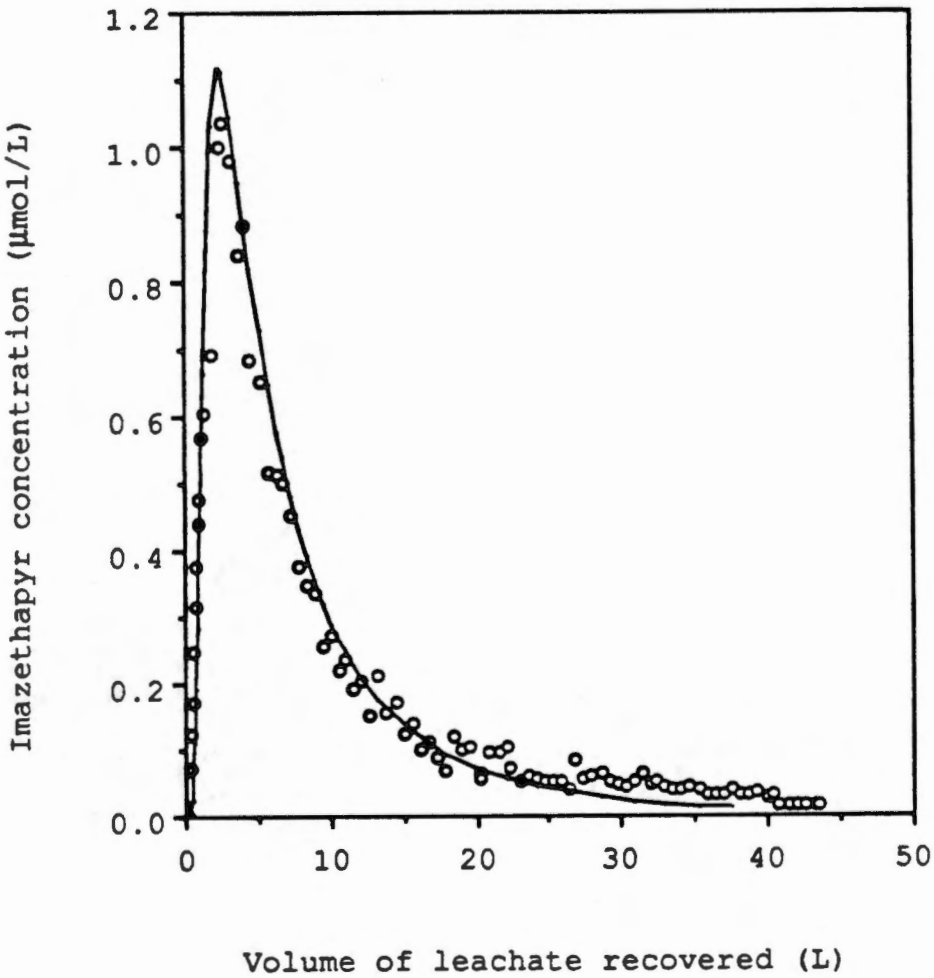


Figure IV.3. Breakthrough of imazethapyr in a soil column at -0.5 kPa moisture potential. The solid line represents the best fit of the convective-dispersive model.

system, with the -2 kPa system having maximum concentrations of 262 μmol L^{-1} Br^- (Figure IV.4) and 0.87 μmol L^{-1} imazethapyr (Figure IV.5).

If water were moving through the columns by ideal diffuse flow, the breakthrough curve of a non-reactive tracer would be symmetrical with the maximum concentration occurring at one pore volume of leachate recovered (approximately 20 L), at which time 50% of the applied tracer would have been eluted from the column. Assuming that Br^- is non-reactive in the soil column, the displacement of the curve to the left of one pore volume indicates that much of the soil water is inactive in the transport process. Rather than displacement of the soil water by the applied water, flow occurs through pores such as worm channels and voids around the structural units. This is consistent with the results of a leaching study by Bouma and Wösten (1979) in which Cl^- breakthrough occurred earlier in a soil having well developed structure and vertical worm channels than in a soil with weaker structure and no worm channels.

The displacement of the breakthrough curves to the left of one pore volume could also be the result of solute exclusion by the soil, which would cause the solute to move through the column faster than the water. The extent of the displacement of the breakthrough curves, however, supports preferential flow rather than anion exclusion as the reason for rapid breakthrough. The physical properties of the soil,

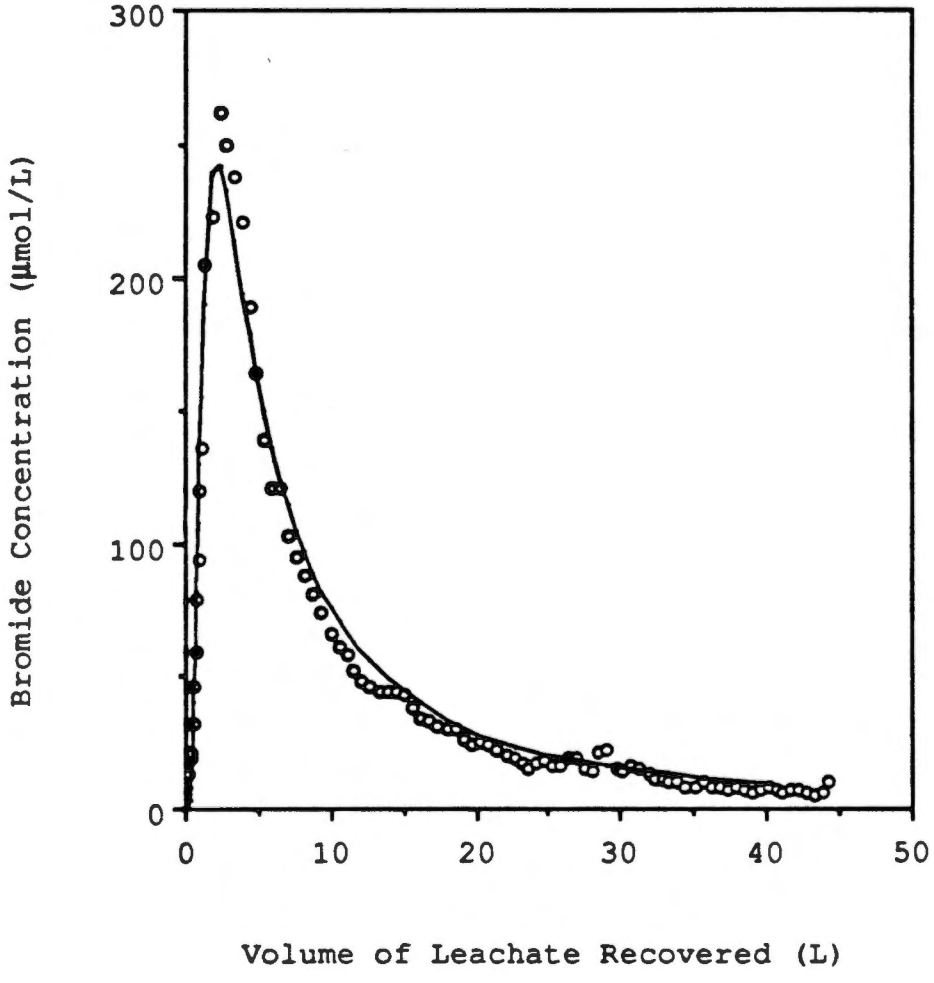


Figure IV.4. Breakthrough of bromide in a soil column at -2 kPa moisture potential. The solid line represents the best fit of the convective-dispersive model.

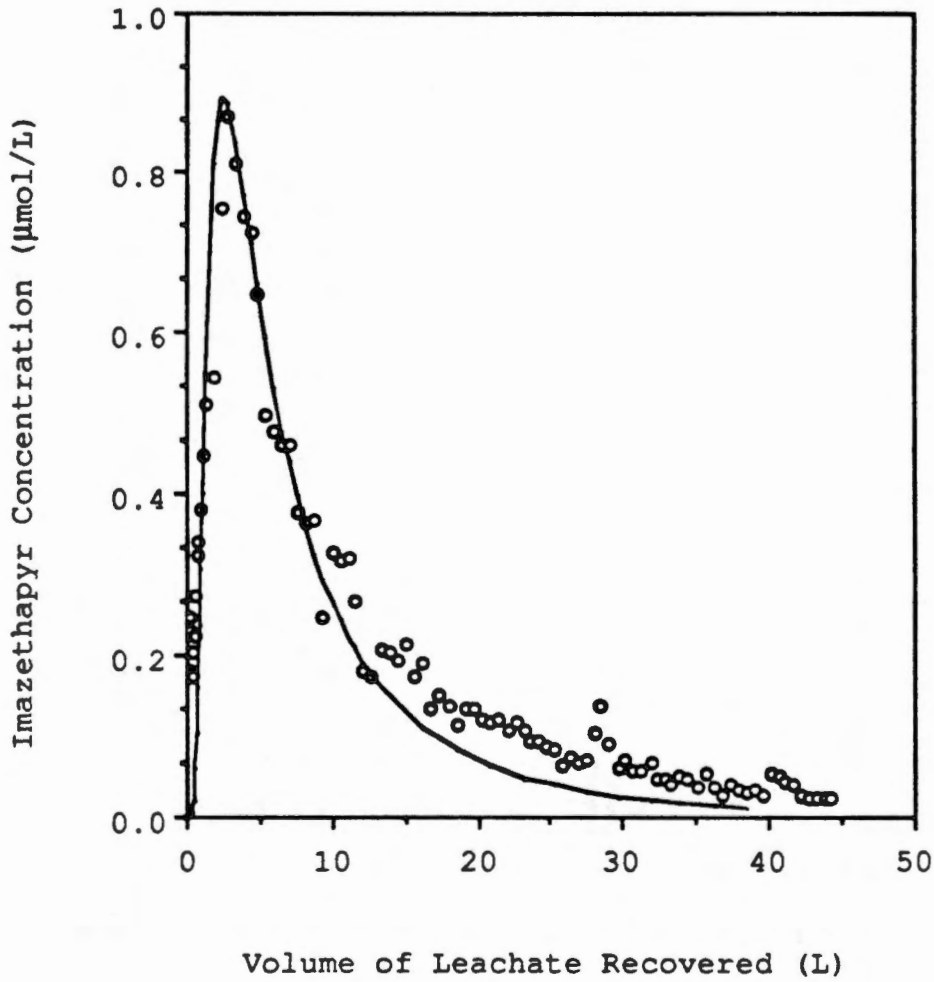


Figure IV.5. Breakthrough of imazethapyr in a soil column at -2 kPa moisture potential. The solid line represents the best fit of the convective-dispersive model.

such as medium-sized moderate subangular blocky structure and the presence of vertical worm channels (table IV.1), also suggest the potential for substantial preferential flow.

Boundary flow (flow of the water along the sides of the column) could also result in rapid breakthrough of the solutes. However, boundary flow would allow little potential for interaction of the solute with the soil solid phase, so the difference in the magnitude of Br^- and imazethapyr breakthrough which was observed would not be expected. The hydrophobic properties of the PVC pipe would also tend to discourage flow down the sides of the column. Post-leaching dissection of the columns showed no evidence of edge flow. The large column diameter used effectively eliminated edge effects in biasing the results obtained.

The width of the breakthrough curves is a result of hydrodynamic dispersion, which includes both dispersion of the solute due to varying velocity within the porous media and molecular diffusion radially and longitudinally within the soil (Biggar and Nielsen, 1980). Since the radii of soil pores may vary by a range of at least three orders of magnitude, the velocity of the soil water is highly variable within the column. This results in rapid elution of the solute contained in larger pores, with longer residence time of the solute held in smaller pores.

The extended tailing of the breakthrough curves may be an indication of diffusion of the solutes into water held in

Table IV.1. Morphology of soil used in column leaching study.

Horizon	Lower depth	Texture	Structure	Consis-tence	Roots	Pores
	cm					
A	6	l	2msbk	vfr	c-1,2	--
Ap	20	l	1fsbk	fr	c-1,2	f-1
Bt1	45	c	2msbk	fr	f-1,2	c-1,2
Bt2	60	c	2msbk	fr	f-1	c-1,2
Bt3	95	c	2msbk	fr	--	c-1,2

the soil micropores. In the presence of larger pores, flow of water through these micropores may be negligible. Since only 83-93% of the applied Br^- had been recovered with the elution of 2 pore volumes of leachate (Table IV.2), it appears that relatively little transport of the solutes is due to diffuse flow. Therefore once the solute has diffused into the smaller pores of the soil, there is a much lower potential for further leaching until the solute has diffused into water held in the larger pores.

Bromide and imazethapyr BTC were of the same magnitude for a short time, followed by increasing suppression of the imazethapyr peak as the herbicide was removed from the soil solution. This is consistent with the results of the soil solution study (Chapter II), in which the concentration of imazethapyr in the soil solution decreased exponentially as a function of time. This decline can be used to determine a first-order decay constant by the equation

$$\ln(C_o/C_t) = kt$$

where C_o is the initial concentration of imazethapyr in the soil solution, C_t is the concentration at time t, and k is the first-order decay constant. Calculated decay constants are shown in table IV.3. Although imazethapyr is probably not being degraded during the duration of the study, its disappearance from the soil solution may be considered analogous to decay from the standpoint of potential mobility.

Table IV.2. Percent of applied bromide and imazethapyr recovered in column effluent.

Moisture Potential	Pore Volume	Bromide	Imazethapyr
(-kPa)		----- % recovered -----	
0.5	0.5	64	43
	1.0	80	54
	2.0	93	62
2.0	0.5	56	38
	1.0	72	53
	2.0	83	64

Table IV.3. Calculation of first-order decay constants for imazethapyr disappearance from soil solution.

Straw Rate	Imazethapyr Rate	C_0	C_{16}	k
g kg^{-1}	$\mu g\ kg^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	d^{-1}
0	31	100.7	11.4	0.136
	62	153.9	23.6	0.117
	124	250.0	83.6	0.068
2	31	80.4	16.7	0.098
	62	140.9	37.9	0.082
	124	298.3	77.2	0.084

The one-dimensional convective-dispersive model of solute transport has been commonly used to describe chemical movement in soil columns (Elrick and French, 1966; Jardine et al., 1988; Seyfried and Rao, 1987). In the case of flux-averaged concentrations and first-order decay of the solute, the governing transport equation is given by (Parker and van Genuchten, 1984)

$$R\ \partial C/\partial t = D\ \partial^2 C/\partial x^2 - v\ \partial C/\partial x - \mu C$$

where C is the solute concentration in the leachate (M cm^{-3}), x is distance (cm), t is time (h), D is the dispersion coefficient ($cm^2\ h^{-1}$), v is the average pore water velocity (cm h^{-1}) which is the Darcy flux divided by the volumetric water content, μ is the first-order decay constant of the solute (h^{-1}), and R is the dimensionless retardation factor. The retardation factor is a measure of the interaction of the solute with the soil and is defined as

$$R = 1 + \rho K_d/\theta$$

where ρ is the bulk density (g cm^{-3}), K_d is the distribution coefficient (L kg^{-1}), and θ is the volumetric water content ($cm^3\ cm^{-3}$). The dispersion coefficient is a measure of the diffusion of the solute and its dispersion in the column as a result of the unequal velocity distribution. Biggar and Nielsen (1980) present methods used by various researchers to calculate the dispersion coefficient.

In order to compare columns of different length and at different flow velocities, the dimensionless Peclet number is calculated as

$$P = vL/D$$

where L is the column length (cm). Transport parameters for the columns are presented in table IV.4.

The upper boundary condition of the column is such that

$$C - D/v \; \partial C/\partial x \; |_{x=0}$$

$$= C_0 \text{ when } 0 < t < t_0 \text{ and } = 0 \text{ when } t > t_0$$

where C_0 is the concentration of solute in the influent solution. In order to obey this boundary condition, the tracer solution is introduced to the column at time t, and is applied to the column until time t_0, when deionized water is introduced to the column. This boundary condition was not strictly adhered to in the experiment. Rather than pumping the pulse onto the column at the same rate as the deionized water, the pulse was applied from a pipette. As a result, the pore water velocity was greatly increased at the instant the solution from the pipette was applied to the column. Therefore the pulse duration (t_0 - t) had to be calculated by the model using the pore water velocity and the time at which the bromide concentration was greatest.

After fitting of the retardation factor by the model, the distribution coefficient can be calculated by

$$K_d = \theta/\rho \; (R-1)$$

Calculation of K_d based on the fitted retardation factor

Table IV.4. Transport parameters for soil columns used in leaching study.

Moisture potential	ρ	θ	v	D	P	R
(-kPa)	(g cm^{-3})	(cm^3 cm^{-3})	(cm h^{-1})	(cm^2 h^{-1})		
0.5	1.44	0.42	0.2747	27.87	0.67	1.26
2.0	1.44	0.41	0.2638	26.62	0.67	1.15

tended to underestimate the distribution coefficient as compared to those observed in the soil solution study (Chapter II). This was probably due to the relatively small percentage of soil surfaces that come into contact with the solute when undisturbed soil is used. Distribution coefficients calculated from the model retardation factors were 0.076 L kg^{-1} for the -0.5 kPa column and 0.043 L kg^{-1} for the -2.0 kPa column.

The difference in the tension applied to the bottom of the columns had little effect on the volumetric water content of the columns. In the -0.5 kPa column, the volumetric water content was 0.42 cm^3 cm^{-3}, while a potential of -2 kPa resulted in a volumetric water content of 0.41 cm^3 cm^{-3}. Similarly, little difference in solute breakthrough curves was observed between the columns at different potentials. Seyfried and Rao (1987) found ^3H_2O breakthrough curves to be relatively symmetrical when leaching was conducted at a potential of -2 kPa, but rather asymmetrical in columns at a potential of -0.5 kPa. The lack of difference observed in this study suggests that the pore size distribution is such that a very small percentage of the soil water is held at potentials between -0.5 and -2 kPa.

CHAPTER V

SUMMARY

Imazethapyr was observed to reside primarily in the solution phase shortly after application to the soil, with the concentration of imazethapyr in solution decreasing exponentially as a function of time. The disappearance of imazethapyr from soil solution may have been the result of adsorption by positively-charged sites on iron-containing minerals, as well as diffusion of the chemical into water which is not recovered by the soil solution displacement procedure. In the latter case, the herbicide may be available for uptake by plant roots but is probably not susceptible to leaching unless diffusion into mobile water occurs.

Elevated imazethapyr concentration in soil solution was observed when finely ground wheat straw was incorporated into the soil three days before application of the herbicide. A similar trend was observed by Wolt et al. (1989) for imazaquin, and was attributed to competition for limited anion adsorption sites by decomposition products of the straw. Straw amendment, however, had little influence on K_d with time as determined by soil solution displacement.

A tractor-mounted core sampler was constructed and used to obtain undisturbed soil columns 30 cm in diameter to a depth of 68 cm. A hydraulic cylinder pressure of approximately 10 MPa was required to push the sampling

cylinder into the soil, with the sampler held down by four 1.5-m anchors. Soil separated evenly at the bottom of the column when removed from the ground, and compaction was observed to be less than three percent. Examination of the columns at the termination of the leaching study revealed little disturbance to the enclosed soil.

After application of both bromide and imazethapyr to the surface of the columns, applied water rapidly leached both chemicals through the column. Breakthrough curves were asymmetrical and characterized by early appearance of both bromide and imazethapyr in the leachate. Breakthrough curves were of the same magnitude for a short time, followed by suppression of the imazethapyr peak as the herbicide was removed from the soil solution. Maximum concentrations of both solutes occurred well ahead of one pore volume of the column, indicating that a small percentage of the soil pores were involved in conducting the chemicals through the column.

A first-order decay constant for imazethapyr in the Ap horizon was calculated from the disappearance of imazethapyr in soil solution from samples not amended with wheat straw. After determining transport parameters using bromide breakthrough curves, the decay constant was useful in predicting the elution of imazethapyr from the column. Distribution coefficients calculated from soil solution displacements tended to overestimate adsorption taking place in the undisturbed soil columns. The time-dependent

distribution coefficients further complicated the modeling of imazethapyr transport in the undisturbed columns. The effect of time on the distribution coefficient was probably a result of physical rather than chemical processes, with the imazethapyr diffusing into regions of solution which could not be recovered by the soil solution displacement procedure.

The conditions used for the column leaching experiment were somewhat different than those existing in a cultivated field. The Ap horizon of the columns was more structured than one would expect in a soil under conventional tillage, thus increasing the probability of preferential flow in the upper horizon. The soil was also at field capacity immediately before and after application of bromide and imazethapyr, which probably favors the movement of both chemicals.

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LITERATURE CITED

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APPENDICES

APPENDIX A

CHEMICAL AND PHYSICAL PROPERTIES OF TYPIC HAPLUDULT USED FOR SOIL SOLUTION AND COLUMN LEACHING STUDIES

Table A.1. Soil solution composition of Ap horizon from Typic Hapludult used for imazethapyr persistence study.

Straw	EC	Ca	Mg	Na	K	Cl	NO_3	SO_4
g kg^{-1}	dS M^{-1}	----------	----------	----------	mmol L^{-1}	----------	----------	----------
0	375	0.93	0.56	0.17	0.17	0.60	2.75	0.047
2	337	1.06	0.60	0.20	0.24	1.90	1.62	0.062

Table A.2. Physical, chemical, and morphological properties of Typic Hapludult used for imazethapyr experiments.

Horizon	Lower depth	Color	Mottles	Texture	Structure	Consis-tence	C	Fe*	Mn+	pH
	cm						g kg^{-1}		mg kg^{-1}	
A	6	10YR 3/4	--	l	2msbk	vfr	28.8	17.0	462	5.8
Ap	20	10YR 4/4	--	l	1fsbk	fr	10.4	19.9	406	6.0
Bt1	45	7.5YR 4/6	--	c	2msbk	fr	4.00	33.1	83	6.4
Bt2	60	7.5YR 5/6	5YR 4/6	c	2msbk	fr	2.09	37.4	15	5.4
Bt3	100	7.5YR 5/6	5YR 4/6	c	2msbk	fr	1.74	38.4	6	5.3
BC1	128	10YR 6/8	5YR 4/6	cl	1msbk	fr	1.43	36.0	7	5.2
BC2	236	10YR 6/8	5YR 4/6	l	1fsbk	fr	0.70	29.3	53	5.0
C	311	10YR 5/6	10YR 7/8	l	0ma		0.51	27.3	236	5.1
Bwb	361	10YR 5/6	10YR 6/4	l	1fsbk		0.56	26.9	272	5.2
BCb	435	10YR 5/6	10YR 6/3	fsl	1fsbk		0.53	25.3	310	5.2
C1b	510	10YR 5/6	10YR 6/3	fsl	0sg		0.44	24.4	270	5.3
C2b	525	10YR 5/6		sl	0sg		0.51	21.4	265	5.2

* Free iron oxides, citrate dithionite extractable (Olson and Ellis, 1982)
+ Manganese oxides, hydroxylamine hydrochloride extractable (Chao, 1982)

Table A.3. Particle size analysis of Typic Hapludult used for imazethapyr experiments.

Horizon	Clay	Silt	Sand	VCOS	COS	MS	FS	VFS
	----------	----------	----------	----------	g kg^{-1}	----------	----------	----------
A	257	447	296	6.8	18.3	22.1	107	136
Ap	262	464	274	5.1	13.0	20.8	101	129
Bt1	458	360	182	3.8	7.5	10.9	65	94
Bt2	500	300	200	1.7	4.3	9.5	42	105
Bt3	448	329	223	2.7	5.3	12.0	92	113
BC1	389	340	271	14.0	17.3	18.3	111	106
BC2	266	319	415	2.7	9.3	29.8	214	159
C	212	403	385	1.8	3.6	17.1	153	209
Bwb	217	382	401	0.9	7.6	36.7	177	180
BCb	161	276	563	2.7	14.6	77.6	285	179
C1b	155	280	565	2.7	21.2	58.8	270	214
C2b	102	191	707	7.3	150.6	163.2	250	138

APPENDIX B

COMPUTER OUTPUT FROM CXTFIT

SOLUTE TRANSPORT MODEL

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*************************************************************
*                                                           *
*   ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION      *
*          NON-LINEAR LEAST-SQUARES ANALYSIS                *
*                                                           *
*  DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR PULSE    *
*INJECTION WITH FIRST- AND ZERO-ORDER PRODUCTION AND DECAY *
*            SOLUTION FOR FLUX CONCENTRATIONS               *
*                                                           *
*             BROMIDE BREAKTHROUGH -0.5 kPa                 *
*                  UNITS CM μM HOURS                        *
*                                                           *
*************************************************************
```

INITIAL VALUES OF COEFFICIENTS
==========

NAME	INITIAL VALUE
V.....	.2638
D.....	30.0000
R.....	1.0000
PULSE.....	.2800
RX1.....	.0000
RX0.....	.0000
CI.....	.0000
C0.....	100000.0000

ITERATION	SSQ	D.....	PULSE.
0	71091.421790	30.00000	.28000
1	28620.479170	25.51582	.37915
2	26948.455157	26.68135	.38137
3	26945.204217	26.61593	.38195
4	26945.178709	26.61793	.38194

CORRELATION MATRIX
==========

	1	2
1	1.0000	
2	-.4445	1.0000

RSQUARE FOR REGRESSION = .93

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
==========

VARIABLE	VALUE	S.E.COEFF.	T-VALUE	95% CONF. LIMITS LOWER	UPPER
D.....	26.62	.80600	33.02	24.99	28.24
PULSE...	.3819	.01208	31.61	.35760	.40628

BROMIDE -0.5 kPa, CONT.

NO	DISTANCE	TIME	CONCENTRATION OBS	CONCENTRATION FITTED	RESI-DUAL
1	68.0000	1.1490	.0000	.0000	.0000
2	68.0000	2.1710	.0000	.0000	.0000
3	68.0000	3.2950	.0000	.0330	-.0330
4	68.0000	4.7380	3.5000	1.4756	2.0244
5	68.0000	5.5170	13.4000	4.6676	8.7324
6	68.0000	6.4500	21.7000	12.3002	9.3998
7	68.0000	7.7780	35.2000	30.9603	4.2397
8	68.0000	8.6970	69.1000	48.3535	20.7465
9	68.0000	9.7320	80.9000	70.7548	10.1452
10	68.0000	10.8810	97.3000	97.2249	.0751
11	68.0000	11.8900	118.3000	120.4717	-2.1717
12	68.0000	13.2180	135.7000	149.5571	-13.8571
13	68.0000	15.5170	142.3000	192.9597	-50.6597
14	68.0000	22.9880	214.2000	267.9186	-53.7186
15	68.0000	30.4210	311.4000	278.9269	32.4731
16	68.0000	33.3590	333.8000	275.1076	58.6924
17	68.0000	40.7410	329.4000	257.0532	72.3468
18	68.0000	48.2380	283.3000	234.4008	48.8992
19	68.0000	53.0910	242.4000	219.7406	22.6594
20	68.0000	58.0720	210.0000	205.3802	4.6198
21	68.0000	65.6960	183.9000	185.2308	-1.3308
22	68.0000	73.1670	148.0000	167.7691	-19.7691
23	68.0000	80.6130	132.5000	152.4880	-19.9880
24	68.0000	84.9550	118.4000	144.4648	-26.0648
25	68.0000	92.4900	109.9000	131.9199	-22.0199
26	68.0000	100.0890	97.9000	120.8253	-22.9253
27	68.0000	106.6670	86.5000	112.3084	-25.8084
28	68.0000	113.8190	78.6000	104.0354	-25.4354
29	68.0000	121.3540	72.8000	96.2805	-23.4805
30	68.0000	128.8890	66.0000	89.3739	-23.3739
31	68.0000	136.4240	61.7000	83.1977	-21.4977
32	68.0000	139.6810	57.7000	80.7288	-23.0288
33	68.0000	146.8960	53.9000	75.6445	-21.7445
34	68.0000	154.3040	49.3000	70.9190	-21.6190
35	68.0000	161.8390	48.9000	66.5629	-17.6629
36	68.0000	169.0550	49.0000	62.7653	-13.7653
37	68.0000	198.6840	36.8000	50.1960	-13.3960
38	68.0000	228.8250	31.5000	40.9777	-9.4777
39	68.0000	257.8800	23.1000	34.3388	-11.2388
40	68.0000	281.8900	24.8000	29.9956	-5.1956
41	68.0000	308.1990	16.2000	26.1302	-9.9302
42	68.0000	336.8070	18.2000	22.7178	-4.5178
43	68.0000	364.4570	16.2000	20.0146	-3.8146
44	68.0000	394.0870	21.8000	17.6151	4.1849
45	68.0000	420.0770	16.0000	15.8434	.1566
46	68.0000	450.0260	11.4000	14.1077	-2.7077
47	68.0000	479.9110	9.6000	12.6381	-3.0381

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*************************************************************
*                                                           *
*   ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION      *
*          NON-LINEAR LEAST-SQUARES ANALYSIS                *
*                                                           *
*  DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR PULSE    *
*INJECTION WITH FIRST- AND ZERO-ORDER PRODUCTION AND DECAY *
*          SOLUTION FOR FLUX CONCENTRATIONS                 *
*                                                           *
*           IMAZETHAPYR BREAKTHROUGH -0.5 kPa               *
*                 UNITS CM µG/L HOURS                       *
*                                                           *
*************************************************************
```

INITIAL VALUES OF COEFFICIENTS
==========

NAME	INITIAL VALUE
V.....	.2638
D.....	26.6179
R.....	1.0000
PULSE.....	.3819
RX1.....	.0045
RX0.....	.0000
CI.....	.0000
C0.....	150000.0000

ITERATION	SSQ	R.....
0	59235.012116	1.00000
1	36073.432100	1.10160
2	34286.903742	1.13717
3	34206.172762	1.14609
4	34205.414494	1.14707
5	34205.436513	1.14721

RSQUARE FOR REGRESSION = .90

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
==========

			95% CONFIDENCE LIMITS	
VARIABLE	VALUE	S.E.COEFF.	LOWER	UPPER
R.....	1.15	.02711	1.09	1.20

IMAZETHAPYR -0.5 kPa, CONT.

NO	DISTANCE	TIME	CONCENTRATION OBS	CONCENTRATION FITTED	RESI-DUAL
1	68.0000	1.1490	.0000	.0000	.0000
2	68.0000	2.1710	.0000	.0000	.0000
3	68.0000	3.2950	.0000	.0069	-.0069
4	68.0000	4.7380	21.4000	.5743	20.8257
5	68.0000	5.5170	36.4000	2.2188	34.1812
6	68.0000	6.4500	49.7000	6.9621	42.7379
7	68.0000	7.7780	72.0000	20.8182	51.1818
8	68.0000	8.6970	91.5000	35.4780	56.0220
9	68.0000	9.7320	108.8000	56.0928	52.7072
10	68.0000	10.8810	126.9000	82.4632	44.4368
11	68.0000	11.8900	137.9000	107.1709	30.7291
12	68.0000	13.2180	164.8000	139.9516	24.8484
13	68.0000	15.5170	174.9000	192.6597	-17.7597
14	68.0000	22.9880	200.7000	298.0727	-97.3727
15	68.0000	30.4210	288.9000	323.1844	-34.2844
16	68.0000	33.3590	299.4000	321.1694	-21.7694
17	68.0000	40.7410	283.5000	302.1849	-18.6849
18	68.0000	48.2380	243.0000	274.4614	-31.4614
19	68.0000	53.0910	256.2000	255.6816	.5184
20	68.0000	58.0720	197.4000	236.9288	-39.5288
21	68.0000	65.6960	188.7000	210.2483	-21.5483
22	68.0000	73.1670	149.4000	186.9392	-37.5392
23	68.0000	80.6130	148.5000	166.5013	-18.0013
24	68.0000	84.9550	144.6000	155.7840	-11.1840
25	68.0000	92.4900	131.3000	139.0813	-7.7813
26	68.0000	100.0890	108.8000	124.4009	-15.6009
27	68.0000	106.6670	100.1000	113.2155	-13.1155
28	68.0000	113.8190	97.7000	102.4405	-4.7405
29	68.0000	121.3540	73.9000	92.4424	-18.5424
30	68.0000	128.8890	78.8000	83.6391	-4.8391
31	68.0000	136.4240	64.2000	75.8627	-11.6627
32	68.0000	139.6810	68.2000	72.7827	-4.5827
33	68.0000	146.8960	55.4000	66.4983	-11.0983
34	68.0000	154.3040	58.9000	60.7352	-1.8352
35	68.0000	161.8390	44.3000	55.4976	-11.1976
36	68.0000	169.0550	61.3000	50.9974	10.3026
37	68.0000	198.6840	40.4000	36.6348	3.7652
38	68.0000	228.8250	20.2000	26.7737	-6.5737
39	68.0000	257.8800	18.4000	20.1415	-1.7415
40	68.0000	281.8900	30.1000	16.0933	14.0067
41	68.0000	308.1990	16.4000	12.7061	3.6939
42	68.0000	336.8070	11.0000	9.9228	1.0772
43	68.0000	364.4570	18.5000	7.8788	10.6212
44	68.0000	394.0870	15.4000	6.2018	9.1982
45	68.0000	420.0770	13.0000	5.0569	7.9431
46	68.0000	450.0260	11.6000	4.0211	7.5789
47	68.0000	479.9110	11.2000	3.2172	7.9828

```
*************************************************************
*                                                           *
*   ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION      *
*          NON-LINEAR LEAST-SQUARES ANALYSIS                *
*                                                           *
*  DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR PULSE    *
*INJECTION WITH FIRST- AND ZERO-ORDER PRODUCTION AND DECAY *
*            SOLUTION FOR FLUX CONCENTRATIONS               *
*                                                           *
*              BROMIDE BREAKTHROUGH -2 kPa                  *
*                UNITS CM μM HOURS                          *
*                                                           *
*************************************************************
```

INITIAL VALUES OF COEFFICIENTS
==========

NAME	INITIAL VALUE
V.....	.2747
D.....	10.0000
R.....	1.0000
PULSE.....	.2800
RX1.....	.0000
RX0.....	.0000
CI.....	.0000
C0.....	100000.0000

ITERATION	SSQ	D.....	PULSE.
0	261389.640830	10.00000	.28000
1	60487.223183	23.13648	.25234
2	8350.425730	29.49383	.31386
3	6433.918457	27.86430	.31854
4	6433.220411	27.87474	.31880
5	6433.220959	27.87461	.31881

CORRELATION MATRIX
==========

	1	2
1	1.0000	
2	-.4770	1.0000

RSQUARE FOR REGRESSION = .97

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
==========

VARIABLE	VALUE	S.E.COEFF.	T-VALUE	95% CONF. LIMITS LOWER	UPPER
D.....	27.87	.45717	60.97	26.95	28.80
PULSE...	.3188	.00583	54.66	.30706	.33056

BROMIDE -2 kPa, CONT.

NO	DISTANCE	TIME	CONCENTRATION OBS	CONCENTRATION FITTED	RESI-DUAL
1	68.0000	1.2310	13.1000	.0000	13.1000
2	68.0000	2.2610	20.1000	.0002	20.0998
3	68.0000	3.4300	18.2000	.0884	18.1116
4	68.0000	5.0630	19.3000	3.1770	16.1230
5	68.0000	5.8040	21.3000	7.7755	13.5245
6	68.0000	6.7840	31.7000	18.0887	13.6113
7	68.0000	8.1660	46.4000	40.0375	6.3625
8	68.0000	9.1580	59.3000	59.4249	-.1249
9	68.0000	10.2510	79.1000	82.3574	-3.2574
10	68.0000	11.4820	94.2000	108.2379	-14.0379
11	68.0000	12.5750	120.0000	130.0340	-10.0340
12	68.0000	13.9700	136.5000	155.1709	-18.6709
13	68.0000	16.4070	204.7000	190.4774	14.2226
14	68.0000	23.3160	223.4000	238.6363	-15.2363
15	68.0000	30.7160	262.4000	241.7017	20.6983
16	68.0000	35.2390	250.2000	233.3590	16.8410
17	68.0000	42.6510	237.9000	214.0589	23.8411
18	68.0000	49.7490	220.8000	194.3060	26.4940
19	68.0000	55.4650	188.8000	179.1744	9.6256
20	68.0000	60.6160	164.3000	166.5317	-2.2317
21	68.0000	67.9020	139.1000	150.4077	-11.3077
22	68.0000	75.2510	121.0000	136.1557	-15.1557
23	68.0000	82.6260	121.2000	123.6768	-2.4768
24	68.0000	88.2160	102.8000	115.2880	-12.4880
25	68.0000	95.6030	94.8000	105.4304	-10.6304
26	68.0000	102.9520	87.7000	96.8221	-9.1221
27	68.0000	110.3020	80.8000	89.2311	-8.4311
28	68.0000	117.7140	74.4000	82.4559	-8.0559
29	68.0000	125.1260	66.5000	76.4361	-9.9361
30	68.0000	132.4750	60.8000	71.1079	-10.3079
31	68.0000	139.8870	57.6000	66.2908	-8.6908
32	68.0000	144.9120	52.5000	63.3045	-10.8045
33	68.0000	152.3240	48.4000	59.2633	-10.8633
34	68.0000	159.7360	46.2000	55.6059	-9.4059
35	68.0000	167.0850	44.0000	52.3118	-8.3118
36	68.0000	174.4970	44.3000	49.2840	-4.9840
37	68.0000	203.6430	34.4000	39.6487	-5.2487
38	68.0000	232.5380	29.8000	32.6771	-2.8771
39	68.0000	262.0600	24.1000	27.3145	-3.2145
40	68.0000	291.3320	17.0000	23.2103	-6.2103
41	68.0000	317.4620	15.6000	20.2819	-4.6819
42	68.0000	346.1050	15.3000	17.6640	-2.3640
43	68.0000	372.7390	14.7000	15.6554	-.9554
44	68.0000	400.7540	13.1000	13.8862	-.7862
45	68.0000	425.2510	10.0000	12.5692	-2.5692
46	68.0000	454.8990	7.9000	11.2056	-3.3056
47	68.0000	484.1080	7.1000	10.0621	-2.9621

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*    ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION     *
*            NON-LINEAR LEAST-SQUARES ANALYSIS              *
*                                                           *
*  DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR PULSE    *
*INJECTION WITH FIRST- AND ZERO-ORDER PRODUCTION AND DECAY *
*           SOLUTION FOR FLUX CONCENTRATIONS                *
*                                                           *
*              IMAZETHAPYR BREAKTHROUGH -2 kPa              *
*                  UNITS CM µG/L HOURS                      *
*                                                           *
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INITIAL VALUES OF COEFFICIENTS
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NAME	INITIAL VALUE
V.....	.2747
D.....	27.8746
R.....	1.0000
PULSE.....	.3188
RX1.....	.0045
RX0.....	.0000
CI.....	.0000
C0.....	150000.0000

ITERATION	SSQ	R.....
0	99320.938000	1.00000
1	53164.755550	1.15621
2	48028.854832	1.22869
3	47676.854601	1.25117
4	47663.254162	1.25677
5	47663.292472	1.25693

RSQUARE FOR REGRESSION = .74

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
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VARIABLE	VALUE	S.E.COEFF.	95% CONFIDENCE LIMITS LOWER	UPPER
R.....	1.25693	.04301	1.17035	1.34351

IMAZETHAPYR -2 kPa, CONT.

NO	DISTANCE	TIME	CONCENTRATION OBS	CONCENTRATION FITTED	RESI-DUAL
1	68.0000	1.2310	66.6000	.0000	66.6000
2	68.0000	2.2610	71.0000	.0000	71.0000
3	68.0000	3.4300	52.3000	.0058	52.2942
4	68.0000	5.0630	49.9000	.6008	49.2992
5	68.0000	5.8040	59.0000	1.9476	57.0524
6	68.0000	6.7840	64.8000	5.9670	58.8330
7	68.0000	8.1660	78.8000	17.3242	61.4758
8	68.0000	9.1580	93.2000	29.6669	63.5331
9	68.0000	10.2510	98.8000	46.5594	52.2406
10	68.0000	11.4820	110.0000	68.3386	41.6614
11	68.0000	12.5750	110.2000	88.8543	21.3457
12	68.0000	13.9700	128.8000	115.0784	13.7216
13	68.0000	16.4070	147.3000	157.2731	-9.9731
14	68.0000	23.3160	157.5000	234.0247	-76.5247
15	68.0000	30.7160	218.4000	258.3539	-39.9539
16	68.0000	35.2390	251.7000	256.9049	-5.2049
17	68.0000	42.6510	234.3000	242.2647	-7.9647
18	68.0000	49.7490	214.8000	222.4823	-7.6823
19	68.0000	55.4650	209.1000	205.7053	3.3947
20	68.0000	60.6160	186.9000	190.9632	-4.0632
21	68.0000	67.9020	143.4000	171.4511	-28.0511
22	68.0000	75.2510	138.0000	153.7030	-15.7030
23	68.0000	82.6260	133.2000	137.8789	-4.6789
24	68.0000	88.2160	132.6000	127.1327	5.4673
25	68.0000	95.6030	108.6000	114.4303	-5.8303
26	68.0000	102.9520	105.2000	103.3017	1.8983
27	68.0000	110.3020	106.3000	93.4856	12.8144
28	68.0000	117.7140	71.0000	84.7415	-13.7415
29	68.0000	125.1260	94.2000	77.0024	17.1976
30	68.0000	132.4750	91.7000	70.1893	21.5107
31	68.0000	139.8870	92.4000	64.0707	28.3293
32	68.0000	144.9120	76.7000	60.3020	16.3980
33	68.0000	152.3240	51.7000	55.2380	-3.5380
34	68.0000	159.7360	50.6000	50.6973	-.0973
35	68.0000	167.0850	59.5000	46.6478	12.8522
36	68.0000	174.4970	59.3000	42.9649	16.3351
37	68.0000	203.6430	54.9000	31.5628	23.3372
38	68.0000	232.5380	33.0000	23.7205	9.2795
39	68.0000	262.0600	33.8000	18.0175	15.7825
40	68.0000	291.3320	30.7000	13.9094	16.7906
41	68.0000	317.4620	24.3000	11.1496	13.1504
42	68.0000	346.1050	20.1000	8.8294	11.2706
43	68.0000	372.7390	17.1000	7.1603	9.9397
44	68.0000	400.7540	19.0000	5.7827	13.2173
45	68.0000	425.2510	14.3000	4.8213	9.4787
46	68.0000	454.8990	10.8000	3.8904	6.9096
47	68.0000	484.1080	8.5000	3.1659	5.3341

VITA

James David O'Dell was born August 21, 1965 and is the son of Mr. and Mrs. James R. O'Dell of Spencer, West Virginia. He graduated from Spencer High School in May 1983.

In September 1983 he entered Berea College where he received a Bachelor of Arts degree in agriculture in May 1987. The following summer was spent working for the USDA Forest Service Northeast Forest Experiment Station in Berea, Kentucky, where he performed soil and water analysis.

In September 1987 he entered the Graduate School of the University of Tennessee at Knoxville. He received the Master of Science degree in Plant and Soil Science with an emphasis in environmental soil chemistry in August 1989.

The author is a member of the American Society of Agronomy and the Soil Science Society of America.