Processes affecting solute transport through soils: preferential flow and microbial degradation
by Heiko Walter Langner

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Crop and Soil Science
Montana State University
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Abstract:
Preferential flow of water through soil macropores has been of concern because it may be a source of accelerated contaminant transport into underlying groundwater. We designed an experimental system to study effects of soil matric potential (h) on the occurrence of nonequilibrium (preferential) flow conditions in four intact cores (15 cm diameter, 30 cm length) of a permanent grassland soil.
Nonequilibrium transport of a nonsorbing tracer (3H2O) was consistently observed at h > -5 cm, while equilibrium conditions were consistent at h < -10 cm. This suggests that soil pores with equivalent radii larger than 150 to 300 μm may contribute to preferential flow. However, no relationship between the soil volume occupied by macropores and preferential flow was identified. Although the onset of nonequilibrium transport was associated with increases in pore water velocity (v) within each individual soil column, no consistent dependency of the occurrence of nonequilibrium on v was observed among replicate soil columns. Since the pore water velocities associated with preferential flow observed in the current study are often exceeded under local climatic conditions, preferential flow events may be important under local field conditions.

For many organic solutes, microbial degradation is one of the most important processes controlling contaminant fate and transport. We used 2,4-dichlorophenoxyacetic acid (2,4-D) as a model compound to (i) test the applicability of first-order and logistic growth models for describing microbial degradation under batch and transport conditions, (ii) determine the applicability of batch-derived degradation parameters under a wide range of transport conditions, and (iii) separate effects of column residence time (RT) and v on degradation rate parameters. Degradation of 2,4-D under batch conditions was best described by a logistic growth model. Under transport conditions (repacked soil columns), a continuous pulse of 1 mg L⁻¹ 2,4-D in the eluent solution resulted in a wide range of steady state 2,4-D effluent concentrations (0.063-0.92 mg L⁻¹). Although degradation of 2,4-D under transport conditions was best described by first-order degradation kinetics, estimated first-order degradation rate constants (μ1s) ranged from 0.007 to 0.071 h⁻¹ as a function of v. Estimated values of μ1s were not correlated with RT, but could be explained by invoking a relationship between v and a local opportunity time (time per unit length).
PROCESSES AFFECTING SOLUTE TRANSPORT THROUGH SOILS:
PREFERENTIAL FLOW AND MICROBIAL DEGRADATION

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of the requirements for the degree
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in
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APPROVAL

of a thesis submitted by

Heiko Walter Langner

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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# TABLE OF CONTENTS

APPROVAL .................................................................................................................. ii

STATEMENT OF PERMISSION TO USE .............................................................. iii

VITA ................................................................................................................................. iv

ACKNOWLEDGEMENTS .............................................................................................. v

TABLE OF CONTENTS ................................................................................................. vi

LIST OF TABLES ........................................................................................................... viii

LIST OF FIGURES .......................................................................................................... ix

ABSTRACT .................................................................................................................. xii

1. INTRODUCTION .......................................................................................................... 1

2. APPARATUS FOR CONSTANT-POTENTIAL SOLUTE TRANSPORT AND SOIL WATER CHARACTERISTIC DETERMINATION ................................................. 6
   INTRODUCTION ........................................................................................................ 6
   MATERIALS AND METHODS ............................................................................... 8
   Measurement of Soil Water Characteristic .......................................................... 12
   Setting Unit Potential Gradient ............................................................................ 13
   Monitoring Column Hydraulic Conditions ......................................................... 14

3. PREFERENTIAL FLOW THROUGH INTACT SOIL CORES: EFFECTS OF MATRIC POTENTIAL ........................................................................................................ 17
   INTRODUCTION ...................................................................................................... 17
   MATERIALS AND METHODS ............................................................................... 20
   Soil .......................................................................................................................... 20
   Experimental Setup ................................................................................................ 20
   Transport Experiments ......................................................................................... 21
   Modeling .................................................................................................................. 22
   Local Equilibrium Assumption ......................................................................... 23
LIST OF TABLES

Table

1. Experimental conditions of the transport experiments using four undisturbed soil cores, and optimized model parameters from fitting $^3$H$_2$O BTCs to solute transport models based on local equilibrium (LEA) and physical nonequilibrium (PNE) models ........................................................ 32

2. Optimized parameters from fitting van Genuchten's (1980) model to $\theta(h)$ data collected during wetting and drying cycles of selected soil columns ...................... 38

3. Experimental conditions for the column experiments ................................................ 52

4. Estimated parameters obtained by fitting the logistic growth model to CO$_2$ evolution data of 2,4-D degradation experiments conducted under various batch conditions .................................................................................................................... 64

5. Resulting parameters from fitting the physical NE model to the $^3$H$_2$O BTCs ........ 65

6. The fate of 2,4-D in soil column experiments ............................................................ 71

7. Estimated first-order degradation rate constants and nonequilibrium parameters for nonsterile column experiments obtained using different modeling approaches (values of $R_f$ and $D$ obtained independently) ........................................................... 76
LIST OF FIGURES

1. Schematic diagram of soil column control and monitoring system with valves in collecting mode (a) and sampling mode (b). .............................................................. 9

2. Experimental wetting and drying curves for one TDR waveguide-tensiometer pair. The wetting and drying limbs were individually fit to the van Genuchten (1980) model ........................................................................................................................12

3. Measured soil water content (θ) during a ³H₂O miscible displacement experiment at h = -24 cm. Upper and lower θ refer to two TDR probe positions in the intact soil column. Increasing θ indicates gradually degrading pore system in the upper layer of the core after two previous leaching experiments (approximately 10 pore volumes) with insignificant changes ........................................................-..............15

4. Measured soil water content (a) and soil matric potential (b) during a ³H₂O miscible displacement experiment at h = -5 cm. Upper and lower θ or h refer to two TDR probe or tensiometer positions in the intact soil column. The irregularity in h at about 0.7 pore volumes indicates slight flow disruption during switching of eluent from pulse to background solution .......................................................................... 16

5. Example series of observed and fitted (LEA and PNE models) BTCs collected with soil column PN11 at various values of h. Each plot contains two series of soil matric potentials measured at the two tensiometer locations. Note the positive pressures at both tensiometer positions in D, which were caused by low hydraulic conductivity of the bottom porous plate .................................................................31

6. Water characteristic relationships [θ(h)] for soil column PN14 generated at two depths (8 and 20 cm). Symbols represent measured θ(h) values, lines are least square fits to the van Genuchten (1980) model (optimized parameter values are shown in Table 2) ...................................................................................................... 35

7. Fitted wetting (A) and drying curves (B) for both upper (closed symbols) and lower (open symbols) instrumented positions (indicated in legend by U or L, respectively). Optimized parameters (Table 2) were obtained by fitting van Genuchten's (1980, Eq. [16]) model to θ(h) pairs between h = 0 and -70 cm ......................... 37
8. Estimated drained porosities \( \theta_s - \theta(h) \) derived from the \( \theta(h) \) curves shown in Fig. 7. Minimum drained pore radii \( (r) \) were calculated as a function of \( h \) using Eq. [17]............................................................................................................................ 39

9. Example series of observed and fitted (LEA and PNE models) BTCs at various values of \( h \) collected for experiments having similar \( v \) ............................................44

10. Diagram of the experimental apparatus for solute transport and degradation studies in soil columns .............................................................................................................................. 53

11. Degradation of \( ^{14}C \)-2,4-D (measured as fraction of total added \( ^{14}C \) recovered as \( ^{14}CO_2 \), \( P/S_b \)) in batch experiments performed under various conditions. Error bars for moist, previously dry soil were generated using data from all soil water contents tested. Filled symbols represent initial aqueous phase 2,4-D concentrations of 1.0 mg L\(^{-1}\); open symbols represent 0.1 mg L\(^{-1}\) initial aqueous phase 2,4-D concentration ......................................  62

12. \( ^3H_2O \) breakthrough curves of all column experiments. Identical symbol fills represent identical column lengths; identical symbol shapes designate identical target residence times ........................................................................................................ 66

13. Observed and predicted [LEA model using independent estimates of \( R_f \) (3.89) and \( D \) (0.22 cm\(^2\) h\(^{-1}\))] 2,4-D breakthrough curves (BTCs) for sterile column experiment. Fitted BTCs were generated using (i) the LEA model where \( R_f \) was optimized (3.49) and (ii) the chemical nonequilibrium model where nonequilibrium parameters were optimized (\( \beta = 0.76, \omega = 0.42 \)) using fixed \( R_f \) (3.89) and \( D \) (0.22 cm\(^2\) h\(^{-1}\)) ........................................................................................................................68

14. Comparison of observed and predicted 2,4-D BTCs for nonsterile column experiments. Predicted BTCs were generated using (i) the LEA model with logistic degradation kinetics and independent estimates of \( R_f \) (from \( K_d = 0.66 \) L kg\(^{-1}\)), \( D \) (Table 5), \( X_0 \) (0.02 mg L\(^{-1}\)), \( Y \) (0.31) and \( \mu_L \) (0.13 L mg\(^{-1}\) h\(^{-1}\)), (ii) the LEA model with first-order degradation kinetics and independent estimates of \( R_p \), \( D \) and \( \mu_{is} \) (0.066 h\(^{-1}\)), and (iii) the LEA model with first-order degradation kinetics and independent estimates of \( R_p \), \( D \) and \( \mu_{is} \) (calculated from \( C_s \) using Eq. [26], Table 6) ................................................................. 70
15. Comparison of observed 2,4-D BTC at column RT = 16 h, L = 28.5 cm, and v = 1.5 cm h⁻¹ (experiment RT16_L28) with predicted BTCs using logistic degradation kinetics with four cases of logistic model parameters determined from batch experiments (Table 4): Case a - prewetted soil, water content = 0.25 L (kg soil)⁻¹, initial 2,4-D concentration (S₀) = 1.0 mg L⁻¹; Case b - previously dry soil, water content 0.23 L (kg soil)⁻¹, S₀ = 1.0 mg L⁻¹; Case c - stirred slurry, S₀ = 1.0 mg L⁻¹; Case d - stirred slurry, S₀ = 0.1 mg L⁻¹. The symbols in the simulation curves correspond to those of the corresponding batch experiments in Fig. 11 ................. 73

16. First-order degradation rate constants derived from ¹⁴C-2,4-D steady-state effluent concentrations as a function of column residence time (A), pore water velocity (B), and column averaged local opportunity time, v⁻¹ (C). The curves in B and C represent best-fit empirical functions as described in the text ....................... 79
ABSTRACT

Preferential flow of water through soil macropores has been of concern because it may be a source of accelerated contaminant transport into underlying groundwater. We designed an experimental system to study effects of soil matric potential ($h$) on the occurrence of nonequilibrium (preferential) flow conditions in four intact cores (15 cm diameter, 30 cm length) of a permanent grassland soil. Nonequilibrium transport of a nonsorbing tracer ($^3$H$_2$O) was consistently observed at $h > -5$ cm, while equilibrium conditions were consistent at $h \leq -10$ cm. This suggests that soil pores with equivalent radii larger than 150 to 300 µm may contribute to preferential flow. However, no relationship between the soil volume occupied by macropores and preferential flow was identified. Although the onset of nonequilibrium transport was associated with increases in pore water velocity ($v$) within each individual soil column, no consistent dependency of the occurrence of nonequilibrium on $v$ was observed among replicate soil columns. Since the pore water velocities associated with preferential flow observed in the current study are often exceeded under local climatic conditions, preferential flow events may be important under local field conditions.

For many organic solutes, microbial degradation is one of the most important processes controlling contaminant fate and transport. We used 2,4-dichlorophenoxyacetic acid (2,4-D) as a model compound to (i) test the applicability of first-order and logistic growth models for describing microbial degradation under batch and transport conditions, (ii) determine the applicability of batch-derived degradation parameters under a wide range of transport conditions, and (iii) separate effects of column residence time (RT) and $v$ on degradation rate parameters. Degradation of 2,4-D under batch conditions was best described by a logistic growth model. Under transport conditions (repacked soil columns), a continuous pulse of 1 mg L$^{-1}$ 2,4-D in the eluent solution resulted in a wide range of steady state 2,4-D effluent concentrations (0.063-0.92 mg L$^{-1}$). Although degradation of 2,4-D under transport conditions was best described by first-order degradation kinetics, estimated first-order degradation rate constants ($\mu_{1s}$) ranged from 0.007 to 0.071 h$^{-1}$ as a function of $v$. Estimated values of $\mu_{1s}$ were not correlated with RT, but could be explained by invoking a relationship between $v$ and a local opportunity time (time per unit length).
CHAPTER 1

INTRODUCTION

The introduction and misuse of anthropogenic chemicals around the globe has created serious environmental health problems. For example, in 1975, the U.S. Environmental Protection Agency (EPA) identified 154 organic compounds in drinking water supplies of towns and cities along the Ohio, Potomac, and Mississippi rivers. The source of these chemicals included industrial and municipal discharges, accidental spills, runoff from agricultural and urban areas, and chlorination processes at water treatment plants (Sparks, 1993). In 1990, the U.S. EPA published a survey of pesticides and nitrates in community and well water supplies. About 10% of the community water supplies and 4% of the rural water wells had detectable concentrations of pesticides. More than 50% of the wells had detectable nitrate concentrations (Carey, 1991). Unfortunately, we are often not able to predict if a chemical released into the environment will cause pollution or not. Detrimental effects of chemicals on biological species can be complex, long-term and spatially variable. Environmental scientists are challenged to elucidate this complexity and to suggest management practices or alternatives which minimize and ideally eliminate pollution. In fact, the U.S. National Research Council identified the reduction of adverse impacts of chemicals in the environment to be one of six research areas that are most vital
to society within the coming 20-25 years (National Research Council, 1996; Glaze, 1997).

Inevitably, soil and water are major sinks for many pollutants. Agricultural fertilizers resulting in increased levels of phosphates and nitrates in soils may cause eutrophication of surface waters and contribute to the degradation of groundwater resources. Many pesticides used to control weed species, invertebrate pests, and plant pathogens in both agricultural and residential systems have been found in groundwater. Acid rain deposition has caused deforestation of significant areas in Central Europe. Trace metals, introduced from sewage sludge, industrial wastes, or mining tailings often have toxic effects on organisms living in or on soil. As of 1992, more than 28,000 hazardous waste sites were present in the United States and 1177 contaminants were on the National Priority Superfund List (Yong et al., 1992).

With increasing concern over soil and water contamination, interest in predicting the fate and transport of chemicals in soils has grown rapidly over the last two decades. However, there is considerable uncertainty regarding the long-term fate of chemicals in soils. This uncertainty is due, in part, to our limited ability to describe the complexity and heterogeneity of soils, and to the difficulty of integrating chemical, biological, hydrological and atmospheric processes. Under these constraints, simplified models, which have been derived under idealized and isolated conditions, are usually combined to predict more complex processes of transformation and transport of chemicals in soils (Carsel et al., 1984; Nofziger and Hornsby, 1987; Steenhuis et al., 1987; Knisel et al., 1989; Wagenet and Hutson, 1987).
The movement of chemicals through soil is often modeled as transport through a homogeneous porous medium using mean advective transport superimposed with random dispersion (advection-dispersion model; Jury and Flühler, 1992). It is, however, well known that homogeneity is a valid assumption only under certain soil conditions, such as exist in structureless soils with little pore size heterogeneity. Consequently, it is not uncommon for these models to fail under nonideal soil and hydraulic conditions present in many field situations. Water flow through soils may occur preferentially through large pores caused by biological activity or along structural boundaries, essentially bypassing a significant volume of the soil matrix. Under preferential flow conditions, spatially variable pore water velocities can result in rapid movement and early arrival of solutes, which is not consistent with model descriptions based on equilibrium advective-dispersive transport. For example, in one field study on the transport of napropamide through sprinkler-irrigated Etiwanda sandy loam soil, the mean predicted depth of napropamide was about 13 cm, whereas traces of the compound were found as deep as 190 cm (Clendening and Jury, 1990). On the same site, triallate reached 100 cm with the application of 5 cm of water, whereas the mean predicted depth of leaching was only 3 mm for this strongly sorbing compound. The accelerated breakthrough of chemicals caused by preferential flow has serious implications for the contamination of groundwater, because transformation rates are often lower below the biologically active soil zone and chemicals persist longer. It is well known that preferential flow through structured soils occurs primarily when the soil is saturated, and is often unimportant under unsaturated conditions. There is, however, a lack of information on the transition...
from preferential flow to matrix flow with changing soil hydraulic conditions. One of the goals of the current study was to identify soil hydraulic conditions associated with preferential flow. Specific objectives under this goal included the investigation of effects of soil matric potential \((h)\) and pore water velocity \((v)\) on the occurrence of preferential flow through intact soil cores from native and tilled sites. Results from this study (Chapters 2 and 3) may be used to assist in the identification of field conditions under which preferential flow events are likely to occur.

Another important process controlling the fate and transport of contaminants through soils is microbial degradation. Numerous kinetic models have been proposed for describing microbial degradation rates of chemicals in soils under well-controlled batch conditions. Only a few studies exist, however, where the performance of these models has been critically examined under transport conditions, which are typical of field soils. Because of its simplicity, the first-order kinetic expression has been used in the majority of fate and transport models for describing microbial degradation during transport (Pennell et al., 1990). However, there are many instances documented in the literature where first-order kinetics are unsuitable for describing contaminant degradation in soils (Alexander and Scow, 1989). Furthermore, independent of the model used to describe microbial degradation during transport, there is uncertainty regarding the appropriate choice of rate parameters necessary for predicting degradation. Some studies suggest that rate parameters obtained under batch conditions may not be appropriate under transport conditions (Estrella et al., 1993), and further that rate parameters may depend on the solute flow regime (Kelsey and Alexander, 1995). If this is generally true, then our ability
to predict the degradation of organic chemicals under a wide range of transport conditions using a single set of rate parameters is reduced significantly. Increasing residence times of chemicals in soil will generally result in increasing amounts of the chemical degraded. This is consistent with first-order degradation kinetics. However, there is little published information concerning potential effects of pore water velocity (v) on apparent degradation rate parameters observed during transport. Since most experiments employ constant column lengths, changes in residence time are generally associated with changes in v and vice-versa. Therefore, a second goal of this thesis was to investigate the influence of varying transport conditions on the degradation behavior of an organic chemical. Specific objectives included (i) to test the applicability of first-order and logistic growth models for the description of 2,4-D (2,4-dichlorophenoxyacetic acid) degradation across a wide range of transport conditions, (ii) to determine the applicability of degradation rate parameters derived under batch conditions for describing 2,4-D degradation across a wide range in column conditions, and (iii) to separate effects of column residence time and pore water velocity on degradation rate parameters determined from transport experiments.
CHAPTER 2

APPARATUS FOR CONSTANT-POTENTIAL SOLUTE TRANSPORT AND SOIL WATER CHARACTERISTIC DETERMINATION

INTRODUCTION

Many investigations concerning unsaturated soil water or chemical movement require imposition of steady (or near-steady) state hydraulic conditions. This is generally addressed by controlling the rate of solution inflow (e.g., van Genuchten and Wierenga, 1986; Gaber et al., 1995) or by applying a constant negative supply pressure to the inlet end of the soil column during infiltration (e.g. Nielsen and Biggar, 1961; Seyfried and Rao, 1987; Munyankusi et al., 1994; Magesan et al., 1995, Vogeler et al., 1996). While an advantage of the first approach is ease in switching between eluent sources, the latter facilitates setting a desired matric potential \( h \) at the column inlet. Negative pressure at the base is often achieved by placing the soil column on a porous plate (e.g., stainless steel or ceramic) through which a known vacuum may be applied. If equal negative pressure is applied to the top and bottom of the column, the overall hydraulic potential energy gradient along the vertical column is unity. In a homogeneous porous medium, this will result in a uniform, steady state matric potential with water flow driven by the unit gradient gravitational potential only. However, soil columns will often deviate from
unit gradient because of heterogeneities in the pore system with depth; this is particularly true for intact or "undisturbed" soils. Pore discontinuities at the interface of the porous plate and soil which result in low interfacial hydraulic conductivity may also interfere with establishment of unit gradient within soil cores. In this situation, effects of a drop in $h$ above the porous bottom plate can potentially be avoided by measuring $h$ within the core and adjusting the bottom plate suction. Failure to achieve or to maintain constant potential steady flow conditions in soil columns will result in inaccurate or inappropriate results and conclusions.

Another common problem during soil column leaching experiments involves changes in soil properties during the course of an investigation (e.g., Vandevivere and Baveye, 1992). Continuous monitoring of $\theta$ and $h$ can alert an investigator to changes in the $\theta(h)$ relationship that may affect experimental results.

We designed and tested a system to impose, maintain, and monitor uniform soil matric potential during miscible displacement experiments in large intact soil cores. In addition, during column conditioning (sequential wetting and drying) a detailed soil water characteristic relationship may be determined in situ by simultaneous measurements of $\theta$ and $h$ using time domain reflectometry (TDR) and pressure transducer tensiometry (Wraith and Baker, 1991; Hudson et al., 1996). Novel aspects of our approach include an effective means to ensure that unit gradient flow conditions are established and maintained, simultaneous collection of large effluent volumes without interruption of the outlet pressure, and continual monitoring of column $\theta(h)$ during the course of single or multiple experiments. This paper describes the system for constant-potential solute
transport and θ(θ) determination, discusses some of its advantages and disadvantages compared with conventional approaches, and briefly illustrates its application to monitoring and evaluating miscible displacement of tritiated water in large intact soil cores.

While not specifically addressed in this paper, the system described here may also be used to quantify the column hydraulic conductivity [K(θ)] relations (e.g., Hussen et al., 1994), and/or to monitor the movement of ionic solutes using TDR (Wraith et al., 1993; Vogeler et al., 1996; Risler et al., 1996), under controlled and well-characterized column transport conditions.

MATERIALS AND METHODS

We obtained intact soil cores (15.2 cm diameter, 30 cm length) from the A. H. Post Experimental Farm near Bozeman, MT by forcing beveled and lubricated PVC pipe into the soil using a hydraulic core sampler. Soils at this location are classified as Amsterdam silt loam (fine-silty, mixed Typic Haploboroll). Transducer tensiometers (0.6 cm width, 6.5 cm length high-flow ceramic cups, Soil Moisture Equipment Co., Santa Barbara, CA; model 141PCG sensors, Micro Switch, Freeport, IL), fabricated in our laboratory, were horizontally inserted in the column at depths of 9 and 21 cm (Fig. 1) and connected to a data logger (model 21X, Campbell Scientific, Logan, UT). Pressure transducers were individually calibrated using a water manometer. A 10-cm long 3-rod TDR waveguide (Midwest Industries, St. Paul, MN) was installed normal to each tensiometer and was offset by about one centimeter vertical distance.

A modified disk permeameter (Perroux and White, 1988) base allowed eluent to be
applied at the top of columns under controlled ponded or negative supply pressure (Fig. 1). Air entry pressure of the permeameter membrane was about 30 cm. One 3-way and

Figure 1. Schematic diagram of soil column control and monitoring system with valves in collecting mode (a) and sampling mode (b).
one 2-way valve (Elliptic Valves ½" NPT, Cole Parmer Instrument Co., Niles, IL) connected in series allowed switching between different eluent solutions. Switching eluents by replacing the permeameter (Magesan et al., 1995) was not feasible with our test soil because of mechanical damage of the soil surface layer and subsequent changes in the soil column hydraulic characteristics. All solution inlet lines that simultaneously transmitted liquid and air required a flow diameter of at least 1.0 cm to allow free opposite movement of the phases, or air and solution lines needed to be separated, e.g. by inserting a smaller air tube into a larger liquid-filled tube. The permeameter was equipped with a flushing port similar to that of Seyfried and Rao (1987) which facilitated rapid exchange of eluent sources without measurable supply pressure fluctuation. To switch between eluent solutions, the valve connecting to the eluent reservoir was closed. Then, a pressure slightly lower than the pressure set with the Mariotte Device was applied to the flushing port and the appropriate valve to the new reservoir was slowly opened. To minimize mixing of eluent solutions within the permeameter foot, the valve controlling the new eluent reservoir was opened and closed several times while solution was continuously removed through the flushing port. The radius of the infiltrometer base was about 0.5 centimeter less than that of the soil surface, allowing air exchange as the column was wetted or drained. Additional air entry ports at several depths in the column wall did not appear to affect wetting and draining and were omitted after preliminary studies. To ensure good contact between the soil and infiltrometer membrane, we severed any above-ground vegetative residue, slightly leveled the soil surface if necessary, and added a 1-cm layer of graded fine silica sand (Grade 70 sieved through 149 μm screen).
The column base was designed to allow simultaneous application of negative pressure and collection of large effluent volumes without interruption of pressure at the column base. The lower surface of the soil rested on a porous stainless steel plate (Mott Metallurgical Corp., Farmingdale, CT) with an air entry pressure of 300 cm and was sealed with rubber O-rings in an acrylic endcap. Outlet pressure was controlled by a vacuum regulator (model 44-20, Moore Products Co., Spring House, PA) and measured with a water manometer. Column effluent was stored in a glass reservoir between two 3-way solenoid valves (model B14DK1030, Skinner Valve Div., New Britain, CT) during collection mode (position "a" in Fig. 1). After tubes advanced in the fraction collector (Retriever II, ISCO, Lincoln, NE) under the column, a timed controller switched the valves to sampling mode (position "b") and allowed the collected effluent to rapidly drain into a sample tube. The solenoid valves were set back to the collection position about 10 s later. Pressure fluctuations during a collection/sampling cycle were dependent on the amount of liquid in the glass reservoir. Since the net bottom plate pressure was offset from the pressure at the vacuum regulator by the height of the water column in the collection reservoir, we noted fluctuations in \( h \) of 1 to 2 cm at the lower tensiometer. These fluctuations could be reduced by shortening the collection cycle and thus reducing the depth of water in the reservoir. However, this would increase the number of sampling tubes collected. A reservoir with wider diameter thus seems a likely solution to this issue.
Measurement of Soil Water Characteristic

The soil water characteristic relationship (Fig. 2) was measured for the instrumented soil columns by simultaneously monitoring soil matric potential and volumetric water content during preliminary column wetting and drying cycles (Wraith and Baker, 1991). During wetting to saturation, a 3 mM CaCl₂ solution was incrementally added from the column base over a period of at least 72 h. The water retention curve was measured by first draining the soil column at $h = 0$ for 24 h. The effluent collected during this cycle was used to calculate drained porosity (Kluitenberg and Horton, 1990; data not shown). Additional soil water was then removed by stepwise application of tension (to -200 cm) at

![Image showing wetting and drying curves](image)

Figure 2. Experimental wetting and drying curves for one TDR waveguide-tensiometer pair. The wetting and drying limbs were individually fit to the van Genuchten (1980) model.
the bottom plate. Paired $h$ and $\theta$ readings, taken at least one hour after each water
addition or removal step (i.e., after establishing quasi-static conditions; Vachaud et al.,
1972), were used to fit a model describing $\theta(h)$ (van Genuchten, 1980) using nonlinear
least squares optimization. Tensiometer readings were compensated for the difference in
elevation between tensiometer cups and TDR probes.

Setting Unit Potential Gradient

Following wetting from the base, the disk permeameter supply pressure was adjusted
to the desired column matric potential ($h$). Increasingly negative pressure was then
applied at the base until the top and bottom tensiometer readings were equal, i.e., unit
gradient conditions had been reached. Achieving equivalent top and bottom tensiometer
readings usually required the bottom plate pressure to be 5 to 25 cm lower than the target
column $h$ value. We were able to maintain measured deviations from the target $h$ value to
less than 1 cm for complete transport experiments lasting one or two weeks. Due to
alteration in soil pore arrangement during transport experiments, tensiometer and TDR
readings sometimes changed over time. Periodic adjustment of the bottom plate pressure
on the order of fractions of a centimeter to several centimeters were necessary to maintain
constant matric potential throughout an experiment. These adjustments were required at
intervals of several days at $h < -10$ cm, and every few hours at $h$ between -2 and -5 cm.
We were not able to establish $h = 0$ throughout a soil column for sufficient periods of
time to complete transport experiments because of soil column heterogeneities. Saturated
solute transport experiments were therefore performed at a permeameter pressure of zero
and bottom plate pressures of -50 cm, which resulted in positive pressure at the tensiometers. Our system design was restricted to the range between ponding and $h = -25$ cm, with the limiting factor being the air entry pressure of the disk permeameter membrane. Use of finer mesh or alternative materials would extend this range.

**Monitoring Column Hydraulic Conditions**

It is often desirable to conduct multiple transport experiments using the same soil core because of variability in physical attributes among individual cores. However, alteration of the pore system caused by physical/chemical effects of hydration, particle movement, or microbial growth can create substantial problems during repeated wetting and drying or prolonged exposure to high wetness. Figure 3 illustrates that combined continuous measurement of water content and matric potential during our transport experiments facilitated identification of a gradual change in the $\theta(h)$ relationship. Increasing water content at a constant $h = -24$ cm indicated the filling of previously drained soil volumes. Figures 4a and 4b show measured soil matric potential and water content at two heights during a solute transport experiment at $h = -5$ cm. The tensiometer readings were periodically checked and the bottom plate suction adjusted as needed during the course of the experiment. We have also successfully used the experimental control and monitoring system to study the effects of matric potential ($h$) on the occurrence of nonequilibrium transport in intact soil cores during steady unit gradient saturated and unsaturated water flow (Langner et al., 1994). Two to four transport experiments with transport of six pore volumes each were generally possible with a single soil column before significant
Figure 3. Measured soil water content ($\theta$) during a $^3$H$_2$O miscible displacement experiment at $h = -24$ cm. Upper and lower $\theta$ refer to two TDR probe positions in the intact soil column. Increasing $\theta$ indicates gradually degrading pore system in the upper layer of the core after two previous leaching experiments (approximately 10 pore volumes) with insignificant changes.

changes of the pore systems were observed. Similarly, continuous monitoring of the soil matric potential explained observed anomalies in some BTCs.

The preliminary quantification of the soil water characteristic shortened the usable life of soil cores for subsequent transport studies. After generating a complete water characteristic in the range $h = 0$ to $-70$ cm, we were able to run only two to three transport experiments (6 pore volumes per experiment) on the same soil core. In cores where we did not characterize $\theta(h)$ we did not observe significant alteration of the apparent soil pore size distribution until after the fourth transport experiment.
Figure 4. Measured soil water content (a) and soil matric potential (b) during a $^{3}$H$_{2}$O miscible displacement experiment at $h = -5$ cm. Upper and lower $\theta$ or $h$ refer to two TDR probe or tensiometer positions in the intact soil column. The irregularity in $h$ at about 0.7 pore volumes indicates slight flow disruption during switching of eluent from pulse to background solution.
CHAPTER 3

PREFERENTIAL FLOW THROUGH INTACT SOIL CORES:
EFFECTS OF MATRIC POTENTIAL

INTRODUCTION

Numerous studies have shown that water and solutes can move through soil along preferred pathways, bypassing much of the soil matrix (Ehlers, 1975; Quisenberry and Philips, 1976; Kanwar et al., 1985; Rice et al., 1986; Wagenet, 1987; Seyfried and Rao, 1987). Such transport behavior is known as channel, bypass, or preferential flow (Singh and Kanwar, 1991), and has been identified as a major cause of groundwater contamination by agrichemicals (Jaynes et al., 1995). Preferential flow can result in rapid solute movement into the vadose zone or to groundwater where it is common to observe lower microbial degradation rates that result in increased persistence.

Due to its potential importance in impacting the fate of agrichemicals, preferential flow has been studied intensively during the past two decades. Numerous studies have evaluated the dependence of preferential flow on soil macroporosity (Germann and Beven, 1981; Luxmoore et al., 1990; Li and Ghodrati, 1994) or on management practices (e.g., tillage or application of manure) which influence soil macroporosity (Singh and
Kanwar, 1991; Wu et al., 1995; Munyankusi et al., 1994). Results indicate that preferen­
tial flow is generally correlated with the number or volume of soil macropores. Although
it is well recognized that the potential for preferential water and solute flow will increase
with increases in macroporosity, it has been difficult to determine relationships among
specific properties of soil pores (especially pore sizes) and the susceptibility to preferen­
tial flow.

Germann and Beven (1981) have suggested that the minimum radius of macropores
(i.e., pores potentially forming preferential flow paths) is 1.5 mm, while Luxmoore
(1981) defined macropores as pores > 0.5 mm. In one transport study using undisturbed
cores of an aggregated tropical soil, Seyfried and Rao (1987) observed significant
preferential flow at matric potentials ($h$) of 0 and -1 cm; when $h$ was lowered to -10 and
-20 cm, no preferential flow was observed. This suggests that pores with equivalent radii
smaller than 0.150 mm (water-filled at $h = -10$ cm) did not contribute to preferential flow
in their test soil. Other suggestions of macropore sizes range from >0.005 to >1.5 mm
[see tables in Beven and Germann (1982) and Luxmoore et al. (1990)]. Although factors
other than pore size (such as pore structure and pore continuity) undoubtedly influence
the potential for preferential flow (Bouma, 1990; Logsdon et al., 1993), the wide range in
estimated macropore radii is due partly to our inability to identify water-conducting pore
sizes responsible for preferential flow events. To narrow this range, experiments would
be necessary where (i) the water content (drained or filled) of various pore size fractions
in the soil can be effectively controlled, and (ii) simultaneously, the transport behavior of
solutes can be tested for the presence of preferential flow conditions.
Preferential flow can often be interpreted as a nonequilibrium transport process, where the soil profile may contain discrete water domains or regions. While one-region models assume a homogeneous pore water velocity throughout the porous medium, two-region models divide the porous medium into a mobile domain, where solute transport occurs by advection and dispersion, and an immobile domain, in which there is minimal advective flow (van Genuchten and Wierenga, 1976). Rapid transport in the mobile domain is accompanied by diffusive mass transfer of solutes between mobile and immobile regions. Because diffusive mass transfer rates may constrain equilibrium between the immobile and the advective domains, solutes in the system may be considered to be in a state of nonequilibrium. This phenomenon has been termed transport or physical nonequilibrium (PNE; Brusseau and Rao, 1990; van Genuchten and Wierenga, 1976). When preferential flow conditions are present, a two-region (or PNE) model will generally fit the observed solute breakthrough data better than a one region (or local equilibrium) model. In the absence of preferential flow, the PNE model reduces to a local equilibrium model.

The primary objective of the present study was to examine soil matric potentials and corresponding pore sizes associated with nonequilibrium transport in naturally structured soils. Tracer transport experiments through large intact soil cores were performed at several matric potentials, and the observed BTCs were analyzed for physical nonequilibrium using a comparison between fitted local equilibrium and physical nonequilibrium models.
MATERIALS AND METHODS

Soil

Intact soil cores (15.2 cm diameter, 30 cm length) were obtained at the A. H. Post Experimental Farm near Bozeman, MT from a permanent grassland site. Soils at this location are classified as Amsterdam silt loam (fine-silty, mixed Typic Haploboroll). A hydraulic core sampler was used to force beveled and lubricated PVC pipe into the moist (approximate field capacity) soil. Cores were carefully excavated and stored upright in sealed plastic bags at 4°C prior to their use in leaching experiments. Large numbers of vertical wormholes and root channels were visible at both ends of the soil cores (e.g., >20 tubular pores with radii > 1 mm).

Experimental Setup

The preparation of soil cores and the experimental column apparatus were described in detail in Chapter 2 of this thesis. The soil columns were used for both the generation of soil water characteristics [$\theta(h)$ relationship] and for performing unit gradient solute transport experiments. Soil cores were equipped with transducer tensiometers and TDR waveguides at two depths (about 8 and 20 cm) within the column. A modified disk permeameter was used to deliver eluent solutions to the top of the column. The column bottom rested on a porous stainless steel plate allowing uninterrupted application of constant negative pressure as well as collection of large volumes of effluent.
Transport Experiments

A series of 2 to 4 transport experiments under steady-state hydraulic conditions was performed with each of 4 undisturbed soil cores. The matric potential \( h \) was varied between experiments with identical soil columns. The primary goal was to obtain breakthrough curves (BTCs) of \(^3\text{H}_2\text{O}\) and pentafluorobenzoic acid (PFBA) at a minimum of three matric potentials per column. Across all columns, matric potentials ranged from \( h = 0 \) (ponding, column experiments PN12_2 and PN11_1) to \( h = -24 \) cm (PN14_4).

Soil columns were gradually saturated from the bottom over a period of 2 d using 3 mM CaCl\(_2\). Following saturation, the disk permeameter supply pressure was adjusted to deliver 3 mM CaCl\(_2\) at the desired column matric potential. Increasingly negative pressure was then applied to the porous plate at the column base until the top and bottom tensiometer readings were equal. To ensure approximate unit gradient conditions within the soil column (i.e., equal tensiometer readings at both positions within the column) the bottom plate pressure had to be adjusted to between 5 and 25 cm lower than the target column \( h \) value. Pressure transducer tensiometer readings were periodically checked throughout the experiments and the base pressure was adjusted if necessary to account for temporal drift in \( h \) resulting from changes in pore arrangement within the soil core (Chapter 2, p. 13).

Unit gradient hydraulic conditions could not be established at \( h = 0 \) because of insufficient flow rate through the bottom porous plate. In an attempt to overcome flow limitations through the porous plate under saturated conditions, we conducted a preliminary experiment where the plate pressure was decreased until the tensiometer readings
were zero. However, we were not able to establish steady-state flow conditions within the column and a very irregular BTC (not shown) was obtained. Saturated solute transport experiments were therefore performed at disk permeameter pressures of zero and bottom plate pressures of -50 cm, which resulted in positive pressures at the tensiometer locations.

After steady state hydraulic conditions had been established, the eluent was switched to a pulse solution containing 3 mM CaCl₂, $^{3}$H₂O (specific activity, $1.67 \times 10^{5}$ Bq L⁻¹, Sigma Chemical Co., St. Louis, MO), and 0.1 g L⁻¹ PFBA (Sigma Chemical Co.). Eluent was switched back to 3 mM CaCl₂ when approximately 0.7 pore volumes of pulse solution had been applied. Experiments were continued for 4 pore volumes, after which the column was resaturated and reconditioned for subsequent transport experiments at different levels of $h$. Two to four transport experiments were generally possible with a single soil column before significant changes in hydraulic conductivity and $\theta(h)$ indicated changes of the pore systems of the soil cores (Chapter 2, p. 14).

Effluent fractions were analyzed for $^{3}$H₂O using a Packard 2200CA liquid scintillation analyzer (Packard Instrument Co., Downers Grove, IL) and for PFBA using a Dionex 4000i ion chromatograph (Dionex Corp., Sunnyvale, CA; Dionex AS4A column).

**Modeling**

Solute BTCs were evaluated using two forms of the advection-dispersion equation (ADE) as a mechanism for identifying the presence or absence of physical nonequilibrium: (i) the local equilibrium assumption (LEA), and (ii) a two-region physical
nonequilibrium (PNE) model (Toride et al., 1995).

**Local Equilibrium Assumption**

The advection dispersion equation (ADE) used to describe one-dimensional transport of a sorbing solute under steady-state fluid flow conditions through homogeneous porous media is given by (Lapidus and Amundson, 1952)

\[
\frac{\partial c}{\partial t} + \frac{\rho}{\theta} \frac{\partial s}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \nu \frac{\partial c}{\partial x}
\]  

[1]

where \( c \) is the solution-phase solute concentration (e.g., mg L\(^{-1}\)), \( t \) is time (h), \( \rho \) is soil bulk density (kg L\(^{-3}\)), \( \theta \) is volumetric water content (m\(^3\) m\(^{-3}\)), \( s \) is sorbed-phase solute concentration [mg kg\(^{-1}\)], \( D \) is the hydrodynamic dispersion coefficient (cm\(^2\) h\(^{-1}\)), \( x \) is the distance from solute application (cm), and \( v \) is the average pore water velocity (cm h\(^{-1}\)).

Assuming conditions of sorption-desorption equilibrium throughout the soil profile, isotherm singularity and linearity \([s = K_d c, \text{ where } K_d \text{ is the linear equilibrium sorption coefficient (L kg}^{-1})]\), the \( \partial s/\partial t \) term becomes \( K_d \partial c/\partial t \), and Eq. [1] may be simplified:

\[
R_f \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \nu \frac{\partial c}{\partial x}
\]  

[2]

where \( R_f = 1 + (\rho/\theta)K_d \) is the retardation factor. The LEA model (Eq. [2]) may be written in nondimensional form (Brusseau and Rao, 1989)
with the dimensionless parameters defined as follows

\[ C = \frac{c}{c_0} \]  \hspace{1cm} [4]

\[ P = \frac{vL}{D} \]  \hspace{1cm} [5]

\[ T = \frac{vt}{L} \]  \hspace{1cm} [6]

\[ X = \frac{x}{L} \]  \hspace{1cm} [7]

where \( C \) is the relative solute concentration, \( c_0 \) is the eluent solute concentration (mg L\(^{-1}\)), \( P \) is the Peclet number describing the shape of the solute BTC (i.e., relative magnitude of dispersion), \( L \) is column length (cm), \( T \) is dimensionless time (i.e., pore volumes) and \( X \) is dimensionless distance.

**Physical Nonequilibrium**

The LEA model (Eq. [2]) does not appropriately describe solute transport under conditions where macropores form preferential flow paths, which result in significant heterogeneities in pore water velocity (\( v \)). Substantial spatial variation in \( v \) can affect the
transport of sorbing and nonsorbing solutes, and its results have generally been described as physical nonequilibrium (PNE) or transport-related nonequilibrium (van Genuchten and Wierenga, 1976; Brusseau et al., 1989). Van Genuchten and Wierenga (1976) modified the ADE to explicitly differentiate two soil water regions where all advective-dispersive transport is assumed to occur in the mobile region, and transport in the immobile region is restricted to diffusion. Again, sorption-desorption is assumed to be an equilibrium process following a linear, singular isotherm. The governing differential equations for this model (referred to here as the PNE model) are given as

\[
(\theta_m + f\rho K_d) \frac{\partial c_m}{\partial t} + \left[ \theta_{im} + (1 - f)\rho K_d \right] \frac{\partial c_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial x^2} - v_m \theta_m \frac{\partial c_m}{\partial x} \quad [8]
\]

\[
[\theta_{im} + (1 - f)\rho K_d] \frac{\partial c_{im}}{\partial t} = \alpha (c_m - c_{im}) \quad [9]
\]

where \( \theta_m \) and \( \theta_{im} \) are mobile and immobile volumetric water contents, respectively (m\(^3\) m\(^{-3}\)), \( \theta_m + \theta_{im} = \theta \), \( c_m \) and \( c_{im} \) are solution-phase solute concentrations in the mobile and immobile regions, respectively (mg L\(^{-1}\)), \( f \) is the fraction of sorption sites that equilibrate with the mobile region, \( v_m \) is the average pore water velocity in the mobile region (cm h\(^{-1}\)), and \( \alpha \) is the first-order mass transfer coefficient between the two regions (h\(^{-1}\)). In analogy to the LEA model (Eq. [2]), the PNE model (Eq. [8] and [9]) may be written in nondimensional form.
where in addition to Eq. [5] - [7] the following dimensionless parameters are defined

\[ C_m = \frac{c_m}{c_0} \]  

\[ C_{im} = \frac{c_{im}}{c_0} \]  

\[ \beta = \frac{\theta_m + \rho f K_d}{\theta + \rho K_d} \]  

\[ \omega = \frac{\alpha L}{\theta_m v_m} \]

where \( C_m \) and \( C_{im} \) represent relative solute concentrations in the mobile and immobile regions, respectively. The variable \( \beta \) is a partition coefficient describing the fraction of sorption in the mobile region (Brusseau and Rao, 1989). For nonsorbing solutes \( (K_d = 0) \), \( \beta \) reduces to the fraction of mobile water \( (\theta_m/\theta) \). The parameter \( \omega \) is a dimensionless rate
coefficient describing the mass transfer between the mobile and immobile regions. For nonsorbing solutes such as $^3$H$_2$O, values of $\beta$ and $\omega$ can be used to evaluate potential contributions from physical nonequilibrium. For reactive (sorbing) solutes, effects of both sorption nonequilibrium and PNE may be confounded in the fitted values of $\beta$ and $\omega$ (van Genuchten, 1981; Parker and van Genuchten, 1984; Brusseau et al., 1989). Physical equilibrium conditions are approached when $\theta_m$ and $f$ approach $\theta$ and 1, respectively, and $\beta$ approaches 1. When $\beta = 1$, the PNE model (Eq. [10] and [11]) reduces to the LEA model (Eq. [3]). Similarly, if the mass transfer parameter $\omega$ in Eq. [11] increases, the rate of convergence of $C_m$ and $C_{im}$ increases. In the limit $\omega \rightarrow \infty$, $C_m = C_{im}$ because solutes in each domain mix instantaneously, and the PNE model again reduces to the LEA model. Several researchers have shown that optimized values of $\omega \geq 100$ indicate the absence of nonequilibrium conditions (Valocchi, 1985; Bahr and Rubin, 1987).

**Estimating Transport Parameters from Breakthrough Curves**

To distinguish between local equilibrium vs PNE conditions, results from miscible displacement experiments were analyzed using both LEA and PNE models. Model parameters $L$ and $v (q\theta^{-1})$ were obtained from direct measurement where the solute flux, $q$ (cm h$^{-1}$), was calculated for each experiment from the steady-state effluent flow rate, and the volumetric soil water content, $\theta$, was determined by averaging the measured volumetric water content (TDR) at both instrumented positions. Observed $^3$H$_2$O BTCs were fit to the LEA model under flux type boundary conditions using CXTFIT2, a least squares parameter optimization method (Toride et al., 1995). Values of $P$ and $R$, were optimized
for the low-\(h\) experiments (-10 to -24 cm) of each column. Batch experiments performed to assess sorption of \(^{3}\text{H}_{2}\text{O}\) to the Amsterdam soil suggested that \(^{3}\text{H}_{2}\text{O}\) was not sorbed (data not shown), providing justification for fixing \(R_f = 1\) in the transport model optimizations. However, model fits using \(R_f = 1\) did not yield reasonable agreement between observed and fitted data, which is consistent with observations of previous studies (e.g., Gaber et al., 1995; Seyfried and Rao, 1987; Wierenga et al., 1975). Therefore, \(R_f\) was optimized for the low-\(h\) experiment of each column, resulting in \(R_f\) values between approximately 1.2 and 1.4. This is justified by the fact that PNE was not observed in any of these experiments (shown below). The estimated values of \(R_f\) for low-\(h\) experiments were then used as fixed parameters for fitting \(^{3}\text{H}_{2}\text{O}\) effluent data from experiments at higher \(h\), where \(P\) was the only parameter optimized. Tritiated water BTCs were also fit using the PNE model where fitted parameters included \(P\), \(\beta\), \(\omega\) and \(R_f\) (again, \(R_f\) only fitted for the low-\(h\) experiments).

The same method was applied to test for the presence of PNE using the PFBA breakthrough curves. Optimized \(R_f\) values for PFBA ranged from 0.84 to 1.00 indicating slight anion exclusion. Results concerning the presence or absence of PNE conditions were identical based on fitting BTCs of both tracers. We will therefore limit our discussion to \(^{3}\text{H}_{2}\text{O}\) BTCs in the Results and Discussion section of this chapter.

**Criteria for Distinguishing Equilibrium vs Nonequilibrium Transport**

Equilibrium transport conditions were assumed when (i) the goodness of fit (\(r^2\)) using the PNE model did not result in improved \(r^2\) values compared to the LEA model and (ii)
the optimized nonequilibrium parameters $\beta$ and $\omega$ were 1 or $\geq 100$, respectively. When these criteria were met, optimized values of $P$ and $R_f$ were identical for both the PNE and LEA models. Conversely, PNE conditions were assumed, when higher $r^2$ values were obtained with the PNE model, and when $\beta < 1$ and $\omega < 100$.

**Soil Water Characteristic and Pore Size Distribution**

The procedure for obtaining $\theta(h)$ data (soil water characteristics) during soil column wetting and drying cycles was described in Chapter 2 (p. 12). Volumetric water contents obtained at $h$ values between 0 and -70 cm were used to fit a parametric $\theta(h)$ model (van Genuchten, 1980):

$$\frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \left[1 + (\alpha|h|)^n\right]^{-m}$$  \[16\]

where $\theta_s$ represents the soil-water content measured at saturation ($m^3 m^{-3}$), $\theta_r$ is residual water content ($m^3 m^{-3}$, fitted), and $\alpha$, $n$ and $m$ are fitting parameters describing the shape of the $\theta(h)$ relationship. The pore size distribution was estimated by relating the drained porosity [$\theta_s - \theta(h)$] to the minimum drained pore radius $r$ as a function of $h$. Values of $r(h)$ may be obtained from the capillary equation (Jury et al., 1991):

$$r = \frac{2\sigma \cos \gamma}{\rho_w g h}$$  \[17\]

where $\sigma$ is the surface tension of water (0.073 N m$^{-1}$ at 23°C), $\gamma$ is the contact angle.
between soil water and solids (assumed $\gamma = 0^\circ$), $\rho_w$ is the density of water ($10^3$ kg m$^{-3}$), and $g$ is the gravitational constant (9.8 m s$^{-2}$). The drained porosity at any $h$ should consist of soil pores having radii larger than $r$.

RESULTS AND DISCUSSION

Effects of Matric Potential

An example series of $^3$H$_2$O breakthrough curves (BTCs) as a function of $h$ acquired with a single soil column is shown in Figure 5A-D. Each plot contains fitted BTCs obtained with the equilibrium (LEA) and nonequilibrium (PNE) models, and soil matric potentials measured at two column locations. At $h = -11$ cm (Fig. 5A), the $^3$H$_2$O BTC is reasonably symmetrical and typical of equilibrium conditions. This observation was confirmed by the fact that (i) optimized Peclet numbers ($P$) and retardation factors ($R_d$) from the PNE and LEA models were identical, and (ii) $\beta$ and $\omega$ of the PNE model were 1 and 100, respectively (Table 1). The optimized value $R_d = 1.22$ was used in model fits to the BTCs obtained at higher $h$.

Physical nonequilibrium conditions were evident in the $^3$H$_2$O BTCs collected at $h = -5$ (PN11_4) and -3 cm (PN11_3). These BTCs occur earlier than at $h = -11$ cm, and exhibit a more rapid increase in $C/C_0$. Further, the PNE model fit the observed BTCs better than the LEA model ($r^2$ increased from 0.94 to 0.99 for PN11_4 and from 0.95 to 0.98 for PN11_3, Table 1), resulting in optimized values for the fraction of mobile water ($\beta$) of 0.44 (PN11_4) and 0.43 (PN11_3). The $^3$H$_2$O BTC obtained under ponded conditions
Figure 5. Example series of observed and fitted (LEA and PNE models) BTCs collected with soil column PN11 at various values of \( h \). Each plot contains two series of soil matric potentials measured at the two tensiometer locations. Note the positive pressures at both tensiometer positions in D, which were caused by low hydraulic conductivity of the bottom porous plate.
Table 1. Experimental conditions of the transport experiments using four undisturbed soil cores, and optimized model parameters from fitting $^3$H$_2$O BTCs to solute transport models based on local equilibrium (LEA) and physical nonequilibrium (PNE) models.

<table>
<thead>
<tr>
<th>Experiment ID†‡</th>
<th>Matric potential (h)</th>
<th>Soil water content (θ)</th>
<th>Relative saturation (θ/θ_s)</th>
<th>Pore water velocity (v)</th>
<th>Column length (L)</th>
<th>Pulse width</th>
<th>Fitting parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>m$^3$ m$^{-3}$</td>
<td>cm h$^{-1}$</td>
<td>cm</td>
<td>LEA model</td>
<td>PNE model</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$R_f$</td>
<td>$P$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>Column PN14</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>PN14_3</td>
<td>-10</td>
<td>0.374</td>
<td>0.96</td>
<td>0.91</td>
<td>26.3</td>
<td>0.57</td>
<td>1.18</td>
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<tr>
<td>PN14_4</td>
<td>-24</td>
<td>0.367</td>
<td>0.94</td>
<td>0.20</td>
<td>26.3</td>
<td>0.65</td>
<td>1.18</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PN13_5</td>
<td>-3</td>
<td>0.360</td>
<td>0.98</td>
<td>0.96</td>
<td>25.9</td>
<td>0.79</td>
<td>*1.40</td>
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<tr>
<td>PN13_4</td>
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<td>0.350</td>
<td>0.96</td>
<td>1.24</td>
<td>25.9</td>
<td>0.72</td>
<td>1.40</td>
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<td></td>
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<tr>
<td>PN12_2</td>
<td>ponded</td>
<td>0.394</td>
<td>1.00</td>
<td>2.64</td>
<td>25.8</td>
<td>0.68</td>
<td>*1.21</td>
</tr>
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<td>0.98</td>
<td>1.14</td>
<td>25.8</td>
<td>0.77</td>
<td>*1.21</td>
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<td>1.00</td>
<td>1.00</td>
<td>27.0</td>
<td>0.72</td>
<td>*1.24</td>
</tr>
<tr>
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<td>27.0</td>
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<td>0.99</td>
<td>0.35</td>
<td>27.0</td>
<td>0.75</td>
<td>1.24</td>
</tr>
</tbody>
</table>

† Asterisks indicate fixed values in fitting procedure.
‡ Notation: P (Location: A. H. Post Experimental Farm), N (native grassland site), 11-14 (core number), 1-5 (experiment number).
exhibited significant asymmetry, an extreme shift to the left and tailing, all characteristic of PNE (Fig. 5D). As expected, the PNE model fit the observed BTC better than the LEA model, resulting in optimized values of $\beta$ and $\omega$ of 0.20 and 0.52, respectively.

The set of $^3$H$_2$O BTCs obtained with column PN11 suggested that the transition from equilibrium to nonequilibrium transport conditions occurred between $h$ of -5 and -11 cm. Experiments with additional undisturbed columns confirmed and narrowed the range of $h$ values corresponding to the onset of PNE. All experiments performed at $h$ of -5 cm (PN11_4 and PN13_4) or higher exhibited PNE, while experiments at $h$ of -10 cm (PN14_3 and PN12_5) and lower exhibited equilibrium transport conditions (Table 1). Similar to the results of Seyfried and Rao (1987), there was no evidence from our data of increases in PNE when $h$ was further decreased to -24 cm. These findings differ from results reported by Biggar and Nielsen (1960) and several other researchers (cf. references in Brusseau and Rao, 1990) who observed an increase in transport nonideality with decreasing values of $h$ in homogeneous porous media. Apparently, the pore network in the soils used by Seyfried and Rao (1987) and in the current study were sufficiently interconnected that drainage of large pores did not result in the isolation of immobile water regions. The pore systems of homogeneously packed sand or soil columns may be more susceptible to forming immobile regions with decreasing water content (Brusseau and Rao, 1990).
Effects of Soil Properties

It must be stressed that physical nonequilibrium (PNE) does not depend directly on $h$, but $h$ controls whether soil pores contain water, and hence potentially contribute to preferential flow. The presence of macropores in the soil is therefore essential for PNE to occur. Several studies have qualitatively found that with decreasing macroporosity (e.g., due to traffic, cropping system or tillage practice) the potential for PNE decreases (Li and Ghodrati, 1995; Singh and Kanwar, 1991; Wu et al., 1995; Munyankusi et al., 1994). Hypothetically, if the fraction of soil volume occupied by macropores was known, quantitative inferences about the potential extent of preferential flow events would be possible. The capillary equation (Eq. [17]) can be used to relate values of $h$ corresponding to preferential flow to specific pore radii.

For undisturbed cores used in the current study, a transition from equilibrium to nonequilibrium transport conditions was observed at values of $h$ between -5 and -10 cm. These matric potentials correspond to minimum drained pore radii of 300 and 150 μm, respectively. Because only one soil was tested, the current study was not suited for determining if these radii are representative for a wide variety of soils. In the following section, we show how our experimental design was used to determine pore size distributions in test columns. However, similar studies using a variety of soils would be necessary to verify the results and to correlate pore size distributions with the probability of PNE.
Paired measurements of $\theta$ and $h$ were obtained during both wetting and drying cycles of columns PN14, PN13 and PN12, in hopes of determining the pore size fraction.

![Minimum Drained Pore Radius (10^{-6} m)](image)

**Figure 6.** Water characteristic relationships [$\theta(h)$] for soil column PN14 generated at two depths (8 and 20 cm). Symbols represent measured $\theta(h)$ values, lines are least square fits to the van Genuchten (1980) model (optimized parameter values are shown in Table 2).
responsible for nonequilibrium solute transport. Figure 6 shows a typical example of the combined \( \theta(h) \) relationships for wetting and drying (water characteristic) obtained at the two instrumented positions within column PN14. Establishing meaningful pore size distributions is complicated by the presence of considerable hysteresis between wetting and drying curves for both column positions, and by the variability in hysteresis observed between the two measurement locations within a column. For example, in column PN14, hysteresis was more pronounced at the upper than at the lower TDR waveguide–tensiometer position (6\% vs 3\% difference in \( \theta \), respectively, at \( h = -20 \) cm; Fig. 6A and B). Furthermore, some of the \( \theta(h) \) curves exhibit no change in \( \theta \) between \( h = 0 \) cm and -10 cm. For example, the water retention (or drying) curve at the lower position of column PN14 (Fig. 6B) shows a constant value of \( \theta \) between \( h = 0 \) and -7 cm. This phenomenon is typically explained for retention curves by invoking an air entry pressure necessary for any initial displacement of pore water with air. However, another column (PN13, upper instrumented position) exhibited no significant change in \( \theta \) between \( h = 0 \) and -10 cm for both wetting and drying curves (Fig. 7A and B).

The water characteristic data were fit to van Genuchten's model (van Genuchten, 1980; Eq. [16]) using nonlinear least squares optimization (Fig. 7, Table 2). Optimized parameters were obtained based on measured \( \theta(h) \) pairs in the range \( h = 0 \) to -70 cm, which represents only the very wet portion of commonly studied \( \theta(h) \) relationships [commonly, \( \theta(h) \) values at dryer conditions include field capacity (\( h = -3 \) m) and permanent wilting point (-150 m)]. Inferences about the \( \theta(h) \) relationship for the Amsterdam soil in the dryer range based on the optimized parameters using only the wet
Minimum Drained Pore Radius (10^-6 m)

Figure 7. Fitted wetting (A) and drying curves (B) for both upper (closed symbols) and lower (open symbols) instrumented positions (indicated in legend by U or L, respectively). Optimized parameters (Table 2) were obtained by fitting van Genuchten's (1980, Eq. [16]) model to measured \(\theta(h)\) data between \(h = 0\) and -70 cm.
Table 2. Optimized parameters from fitting van Genuchten's (1980) model to $\theta(h)$ data collected during wetting and drying cycles of selected soil columns.

<table>
<thead>
<tr>
<th>Instrumented Position</th>
<th>Cycle</th>
<th>$\theta_s$ (measured)</th>
<th>$\theta_r$</th>
<th>$\alpha$</th>
<th>$n$</th>
<th>$m$</th>
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</table>

range are therefore not reliable. General features of the combined drying and wetting curves are as expected with more gradual slopes near saturation ($h = 0$ to approximately -5 cm), and a steeper portion at lower values of $h$ (approximately -5 to -30 cm). At matric potentials below approximately -30 cm, the slopes become more gradual again and asymptotically approach the residual water content ($\theta_r$). Figure 7 illustrates the wide range in $\theta(h)$ at values of $h > -20$ cm obtained from three undisturbed soil cores.

The optimized model parameters from the van Genuchten Equation (van Genuchten,
Drained Porosity ($m_{39}$) were used to estimate drained porosities [$\theta_s - \theta(h)$] as a function of $h$ and the corresponding minimum drained pore radius $r$ (Fig. 8). Using this approach, pore size distributions at each instrumented position can be determined from individual wetting or drying cycles.

![Figure 8](image_url)

Figure 8. Estimated drained porosities [$\theta_s - \theta(h)$] derived from the $\theta(h)$ curves shown in Fig. 7. Minimum drained pore radii ($r$) were calculated as a function of $h$ using Eq. [17].
drying curves. The fractional soil volume corresponding to a range in pore radii can be obtained by the difference between drained porosities across the range of pore radii. Results of fractional soil volumes corresponding to a constant range in pore radii vary widely between and within columns, and do not allow for more than general conclusions. For example, the soil volume fractions represented by pores draining at $h = -10$ cm (radii of 150 µm and larger) range between 0.2% (PN13U) and over 6% (PN12L) of the soil volume as determined from the various wetting curves. For drying curves, soil volumes between 0.3% (PN12U) and 3% (PN12L) correspond to the same pore size fraction (i.e., $r > 150$ µm). Since all undisturbed soil cores were collected within 10 m from a consistent landscape position, the observed variation is most likely due to small-scale heterogeneities in $\theta$ within the soil columns. The TDR waveguides sample a limited soil volume weighted toward the paired rods (Knight, 1992). Small changes in $h$ which cause a few large macropores to drain or fill may or may not correspond to changes in measured $\theta$, depending on the position of the TDR waveguide relative to the affected pores. Gravimetric measurements may have yielded more representative results of average column $\theta$.

In summary, preferential flow in several intact soil cores was consistently observed at values of $h$ between 0 and approximately -10 cm. Based on the capillary equation, values of $h > -10$ cm correspond to pore sizes >150 µm. However, wide variations in pore size distributions and fractional drained porosities determined over this range in $h$ do not support definitive conclusions concerning the fractional soil volume which contributes to preferential flow. Specifically, the drained porosities between $h = 0$ and -10 cm ranged from 0 and 6% of the total soil volume depending on which $\theta(h)$ curve is used to obtain
pore size distribution (Fig. 8). Our results represent an additional example of the
difficulties in accurately defining the $\theta(h)$ relationship at the wet range, which would be
necessary to assign specific fractions of soil volume responsible for the occurrence of
nonequilibrium transport (Beven and Germann, 1982; Luxmoore et al., 1990). The
authors believe, however, that the experimental apparatus employed in the current study
could potentially generate pore size distribution data that are much more reproducible. In
particular, the method of determining $\theta$ would have to be modified such that the measure­
ments were representative of a large soil volume (ideally, the representative elementary
volume; Hubbert, 1956; Bear, 1972). This could be accomplished by modifying the
dimensions or number of TDR waveguides or by using gravimetric measurements.

Pore Water Velocity and Matric Potential

Pore water velocities ($v$) observed during the transport experiments decreased with
decreasing matric potential ($h$). This was expected because of the reduction in the largest
water-transmitting pores with decreasing $h$. However, observed decreases in $v$ associated
with the transition from saturated to unsaturated conditions were lower than those
reported by other authors. Data presented in Germann and Beven (1981) show a differ­
ence of about two orders of magnitude between the hydraulic conductivity at saturation
and at $h = -10$ cm. Seyfried and Rao (1987) observed an approximately twenty-fold
decrease in $v$ when $h$ was reduced from 0 to -10 cm and more than a 100 fold decrease in
$v$ when $h$ was reduced from 0 to -20 cm. In the current study, changes in $v$ (corresponding
to changes in $h$) did not exceed one order of magnitude (Table 1), which was due in part
to flow restrictions through the porous plate under saturated (ponded) conditions. Positive pressures observed within our columns during saturated transport experiments indicated that pore water velocities at saturation were constrained by the hydraulic conductivity of the porous plate rather than the saturated hydraulic conductivity of the soil. Although this was also true for the saturated experiments performed by Seyfried and Rao (1987), their bottom column boundary (fritted glass plate) supported a higher flow rate than the stainless steel plates used in this study. There were no indications in the current study that the bottom porous plates caused restrictions in water flow at values of $h < 0$.

Another reason for the relatively minor decrease in $v$ with decreasing $h$ observed in the current study may be due to the relatively small number of soil macropores which drained within $h = 0$ and $h = -10$ cm. Specifically, Seyfried and Rao (1987) reported a decrease in $\theta$ of $0.04 \text{ m}^3 \text{ m}^{-3}$ (0.57 to 0.53) when $h$ was reduced from 0 to -10, compared to reductions in $\theta$ of $<0.02 \text{ m}^3 \text{ m}^{-3}$ in the current study over the same range in $h$. This suggests the presence of a considerably higher number of soil pores with radii $>150 \mu$m (drained at $h = -10$ cm) in Seyfried and Rao's (1987) soil than in the soil used in this study.

**Pore Water Velocity and Physical Nonequilibrium**

Within each individual column tested, the onset of PNE conditions associated with greater $h$ was also associated with increases in pore water velocity ($v$, Table 1). Consequently, effects of $h$ on PNE were confounded with possible effects of changing $v$. A series of experiments with relatively uniform $v$ ($= 1 \text{ cm h}^{-1}$) was selected from replicate
columns where increases in $h$ exhibited the same effects on PNE as discussed for each individual column (Fig. 9). Optimized values for $\beta$ and $\omega$ are 1 and 100, respectively, for the experiment at $h = -10$ cm (PN12_5, Fig. 9A) indicating equilibrium transport conditions. For other experiments at $h \geq -5$ cm, optimized values for $\beta$ and $\omega$ are $<1$ and $<100$, respectively, suggesting that PNE was important. The changes in relative saturation ($\theta/\theta_s$, Fig. 9) indicate that with increasing $h$, pores with increasing radii contribute to the water transport. The relative uniformity of $v$ in the unsaturated columns ($h < 0$) can therefore only be explained in terms of differences in (water conducting) pore size distribution, although results from $\theta(h)$ curves under wetting and drying conditions were not sensitive enough to reveal these (cf. p. 34-41).

Inferences concerning the likelihood of nonequilibrium transport under field conditions can be made using information on (i) pore water velocities necessary for occurrence of PNE, and (ii) expected pore water velocities as a result of rainfall or irrigation events. PNE was observed in our soil columns at pore water velocities ranging from 0.73 to 2.64 cm h$^{-1}$. The lowest $v$ used in our experiments which resulted in preferential flow was 0.73 cm h$^{-1}$ (PN11_4). This $v$ corresponds to a water flux density (Darcy velocity) of 0.27 cm h$^{-1}$, which is often exceeded for this soil during moderate rain events, irrigation, and during snowmelt. Of course, this can only be a rough estimation; calculating actual probabilities of preferential flow events from our experimental data is difficult, since tracer transport experiments were performed under steady state conditions and did not consider effects of the initial soil water content (Shipitalo and Edwards, 1996). Also, lateral surface water flow, even in moderate amounts, may influence locally observed
Figure 9. Example series of observed (circles) and fitted (LEA and PNE models; dashed and solid lines, respectively) BTCs at various values of $h$ collected for experiments having similar $v$. 
pore water velocities (Bouma, 1990) and would tend to contribute to preferential flow in localized regions. Even with these uncertainties, the results of our study suggest that preferential flow events resulting in rapid movement of soluble chemicals under field conditions is indeed possible in soils of the Amsterdam series.
CHAPTER 4

PORE WATER VELOCITY AND RESIDENCE TIME EFFECTS ON THE DEGRADATION OF 2,4-D DURING TRANSPORT

INTRODUCTION

Models intended to predict the fate and transport of organic solutes in soils require integration of chemical (e.g. sorption-desorption), biological (e.g. microbial degradation) and physical (e.g. advective transport, diffusion) processes. For many organic solutes, microbial degradation is one of the most important processes controlling the amount of chemical transported in soils and aquifers. Consequently, accurate model predictions require appropriate rate equations describing microbial degradation, in addition to independent estimates of degradation rate parameters (e.g. rate constants). Uncertainties in appropriate rate expressions and/or rate parameters can result in significant variation in model predictions of solute fate and transport. For example, Boesten and van der Linden (1991) showed that for weakly sorbing pesticides, an increase in the half-life from 10 to 20 d resulted in an increase in the fraction of solute leached by approximately two orders of magnitude. Similarly, model simulations performed by Villeneuve et al. (1988) showed that a 15-22 % variation in the first-order degradation rate constant led to a 100% uncertainty in the amount of aldicarb leached below the root zone.
The majority of fate and transport models use a first-order kinetic expression to describe microbial degradation during transport (Carsel et al., 1984; Nofziger and Hornsby, 1987; Wagenet and Hutson, 1989; Toride, 1995), due primarily to the simplicity and convenience of assuming that the rate constant (and half-life) is independent of substrate concentration. Certainly, there are examples in the literature which demonstrate both situations where first-order kinetic expressions have been suitable and unsuitable for describing solute fate and transport. For example, Angley et al. (1992) successfully described breakthrough curves (BTCs) of various alkylbenzenes using first-order kinetics. Estrella et al. (1993) also used first-order kinetics to describe 2,4-D BTCs (initial 2,4-D concentration of 100 mg L\(^{-1}\)) under saturated conditions; however, under unsaturated conditions, a microbial growth based model (Monod expression) was required to adequately describe 2,4-D transport. Under unsaturated conditions with continuous input of 2,4-D, effluent concentrations of 2,4-D increased to a maximum value, then decreased to zero. Similar shapes of solute BTCs were reported by Kelsey and Alexander (1995) using p-nitrophenol (10 mg L\(^{-1}\)) and by Pivetz and Steenhuis (1995) using 2,4-D. In all of these examples, the slow development of a microbial population (or the induction of enzyme systems necessary for solute degradation) resulted in a period of increasing effluent concentrations followed by a period of rapid mineralization with effluent concentrations near zero. Under these circumstances, rate expressions based on microbial growth (e.g. Monod or logistic growth models) are necessary for adequate descriptions of solute transport.

Independent of the model used to describe microbial degradation during transport,
there is uncertainty regarding the appropriate choice of rate parameters necessary for predicting degradation. Estrella et al. (1993) showed that degradation rate parameters determined under batch conditions were not suitable for predicting 2,4-D BTCs. In addition, results obtained by Kelsey and Alexander (1995) suggest a strong dependence of p-nitrophenol degradation rate parameters on the solute flow regime (path length and flow rate). If these findings are generally true for organic solutes subject to microbial degradation, then our ability to predict degradation across a wide range of transport conditions using a single set of batch determined parameters is reduced significantly. For first-order kinetics, it is expected that changes in residence time will influence the total amount of substrate degraded during transport (i.e., assuming that the first-order rate constant is indeed constant over a range in pore water velocities). However, there is little published information concerning potential effects of pore water velocity (v) on apparent degradation rate parameters observed during transport. Since most experiments employ constant column lengths, changes in residence time are generally associated with changes in v and vice-versa. Consequently, the objectives of this study were to (i) test the applicability of first-order and logistic growth models for describing 2,4-D degradation, at concentrations representative of typical field application rates, across a wide range in column conditions, (ii) determine the applicability of degradation rate parameters derived under batch conditions for describing 2,4-D degradation across a wide range in column conditions, and (iii) separate effects of column residence time and pore water velocity on degradation rate parameters determined from transport experiments. 2,4-D was chosen as a test compound because of its importance as a broadleaf herbicide in numerous agricul-
tural, aquatic and residential systems, and its similarity to other chlorinated contaminants. Further, 2,4-D generally does not sorb appreciably to soils so that the amount of 2,4-D transported through soils is largely determined by microbial degradation rates. Consequently, model predictions of 2,4-D transport are especially sensitive to assumptions concerning rate parameters describing microbial degradation.

MATERIALS AND METHODS

Soil

All experiments were performed using Flathead fine sandy loam (coarse-loamy, mixed Pachic Udic Haploboroll) surface soil (0 - 0.20 m) collected at the Northwest Agricultural Experiment Station (Creston, MT). After collection, the soil was air dried, sieved (< 2 mm), and stored at room temperature prior to the experiments. This sample contained 2.0 % organic C, 3 % clay, 12 % silt, 85 % sand and had a soil pH of 7.0 (1 : 1 soil : water mass ratio).

Batch Sorption Isotherms

A preliminary study of the rate of 2,4-D sorption by the Flathead soil was used to establish necessary equilibration times for batch sorption isotherms. At a solid : solution ratio of 1 : 1 and an initial 2,4-D concentration of 1.0 mg L\(^{-1}\) (containing 3.2 x 10\(^5\) Bq L\(^{-1}\) carboxyl-\(^{14}\)C-2,4-D), the ratio of solid phase to aqueous phase 2,4-D concentration remained constant after 10 h of equilibration, consistent with results obtained by
Baskaran et al. (1996). For batch adsorption isotherms, 10 g of soil and 10 mL of 3 mM CaCl₂ containing various concentrations of 2,4-D (two separate experiments, each in triplicate) were shaken in centrifuge tubes for 24 h (23±2°C) on a horizontal shaker at approximately 80 rpm using initial aqueous phase 2,4-D concentrations of 0, 0.15, 0.3, 0.6, and 1.0 mg L⁻¹. The range of initial aqueous phase 2,4-D concentrations was chosen to bracket the range of concentrations present during column experiments. The applied 2,4-D solution contained approximately 3.2 x 10⁵ Bq L⁻¹ (0.15 mg 2,4-D L⁻¹) of carboxyl-¹⁴C-labeled 2,4-D (specific activity of 4.70 x 10¹¹ Bq mol⁻¹, Sigma Chemical Co. St. Louis, MO), in addition to unlabeled 2,4-D (analytical grade 2,4-D with a stated purity of 99 %, Aldrich Chemical Co., Milwaukee, WI). Sterile control sorption experiments containing 0.08 M NaN₃ as a biocide under otherwise identical conditions showed that 2,4-D degradation was insignificant during the 24 h equilibration period. After shaking, the tubes were centrifuged for 20 min at 10,000 x g and the supernatant solution decanted and filtered (0.45 μm). The amount of radioactivity in the aqueous phase was determined using a Packard 2200CA liquid scintillation analyzer (Packard Instrument Co., Downers Grove, IL). The sorption of 2,4-D was described by the Freundlich equation $Q = K C^{1/n}$, where $Q$ is the mass of 2,4-D adsorbed per mass of adsorbent at equilibrium (mg kg⁻¹), $K$ is the Freundlich distribution coefficient, $C$ is the aqueous phase 2,4-D concentration at equilibrium (mg L⁻¹), and $n$ is a constant. A linear batch sorption coefficient ($K_d$) was obtained by optimizing $K$ in the Freundlich equation with $n = 1$. 
Batch Degradation Experiments

Batch degradation studies were conducted using 10-g samples of soil in gas-tight Erlenmeyer flasks containing two ports for continuous gas exchange. Preliminary studies showed that initial degradation rates were sensitive to the duration of prewetting the soil prior to 2,4-D application. Therefore, soils were wetted and kept at a water content of 0.15 L (kg soil)\(^{-1}\) three d prior to initiation of degradation experiments, in attempt to simulate the conditions of the transport experiments discussed below. All liquids added to the batch reactors contained a background solution of 3 mM CaCl\(_2\). The head space was continuously purged with humidified, CO\(_2\)-free air at a flow rate of approximately 100 mL h\(^{-1}\), and passed through 10 mL of 0.5 M NaOH. The NaOH solution was then analyzed for \(^{14}\)CO\(_2\) using liquid scintillation.

A series of degradation experiments was conducted to evaluate the effect of variable soil water content on 2,4-D degradation. Soil water contents of 0.18, 0.23, and 0.27 L (kg soil)\(^{-1}\) were evaluated (in triplicate) using an initial aqueous phase 2,4-D concentration of 1.0 mg L\(^{-1}\). For each water content, one control experiment was conducted under sterile conditions with autoclaved soil (two consecutive treatments of 40 min at 100 kPa and 120°C). Additional degradation experiments were conducted with slurries (shaken on a rotary shaker at 130 rpm) to reduce potential effects of rate limited transport of 2,4-D to sites of microbial degradation. These experiments were conducted using a soil : water ratio of 1 : 3 (g : g) and two initial 2,4-D concentrations (1.0 and 0.1 mg L\(^{-1}\)): 1.0 mg L\(^{-1}\) was chosen to expose the microorganisms to the same initial 2,4-D concentration as in the
nonstirred experiments, and 0.1 mg L\(^{-1}\) represented a similar absolute mass of 2,4-D per g of soil as in the nonstirred experiments.

### Column Transport Experiments

A series of soil column experiments with varying column lengths and solute flow rates was performed to separate effects of pore water velocity (\(v\)) and residence time (\(RT\)) on the rate of 2,4-D degradation during transport (Table 3). Soil columns were prepared by uniformly packing air dry soil into PVC tubes with an inner diameter of 5.1 cm (Fig. 10). Bulk densities were 1.4 Mg m\(^{-3}\) (±0.1 Mg m\(^{-3}\)) and column lengths were 9.5, 28.5, or

<table>
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<th>Table 3. Experimental conditions for the column experiments.</th>
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\(^\dagger\) \(RT = L/v\).
\(^\ddagger\) \(v = J_w/\theta\), where \(J_w\) is volumetric water flux density.
\(^\S\) RT05, RT16, or RT48 for residence times 5.3, 16, or 48h; L09, L28, L85 for column lengths of 9.5, 28.5, or 85.5 cm.
85.5 cm leaving a headspace of 1 cm. The ends of the columns were secured with polycarbonate caps containing rubber O-rings. The bottom end cap supported a porous plastic plate with an air entry pressure of 100 kPa (Soil Measurement Systems, Tucson,

![Diagram of the experimental apparatus for solute transport and degradation studies in soil columns.](image-url)
Columns were equipped with an air entry port near the bottom and an air outlet in
the top end cap. Valved quick disconnect couplings (Cole Parmer Instrument Co., Niles,
IL) and Luer Lock-valve combinations enabled frequent detaching and weighing of the
columns for monitoring soil water contents. Eluent was supplied with a precision syringe
pump (Soil Measurement Systems) at variable rates depending on the desired v. A
fraction collector (Retriever II, ISCO Inc., Lincoln, NE) housed in a vacuum chamber
(Soil Measurement Systems) was used to collect effluent (up to 13 mL per sample) while
maintaining a constant negative pressure at the bottom plate of the soil column (van
Genuchten and Wierenga, 1986). A peristaltic pump was used to provide a continuous air
stream of approximately 15 to 40 mL h\(^{-1}\) to the air inlet port (the higher flow rates were
used in the longer soil columns). The slow upward stream of air through the column was
intended to minimize the potential occurrence of anaerobic conditions within the column.

Soil columns were wetted from the bottom over 8 to 48 h depending on the column
length, after which the bottom plate pressure was set to -30 kPa and 3 mM CaCl\(_2\) was
supplied to the top of the column. Soil water content was monitored daily by detaching
and weighing the columns throughout individual experiments. The desired column
residence times \([\text{column } RT = L/v, \text{ where } L = \text{ column length (cm)}; v = \text{ pore water
velocity (cm h}^{-1})]\) were achieved by varying the eluent delivery rate. Target residence
times were 5.3 h (columns RT05_L09 and RT05_L28), 16 h (RT16_L09, RT16_L28,
RT16_L85, and SX16_L09), and 48 h (RT48_L09, RT48_L28, and RT48_L85); however, deviations in eluent pump rates and soil water contents resulted in actual
residence times within 27 % of the targeted values (Table 3). Although all calculations
and conclusions were based on actual values of RT and v, the target residence times are
used in the text for simplicity.

After steady state flow conditions were established (constant water content and v), the
eluent solution was switched from 3 mM CaCl₂ to a continuous pulse of 1.0 mg L⁻¹ 2,4-D
containing ^1⁴C-labeled 2,4-D (specific activity of 1.2 x 10⁵ to 5.7 x 10⁵ Bq L⁻¹ depending
on the anticipated amount of degradation), ^3H₂O as a tracer (specific activity between 3.3
x 10⁴ and 1.7 x 10⁵ Bq L⁻¹), and 3 mM CaCl₂. Column effluent fractions were analyzed for
^1⁴C and ^3H using liquid scintillation. The evolution of ^1⁴CO₂(g) was periodically deter­
mined by sampling CO₂ traps located at the air outlet port and within the vacuum
chamber. Selected effluent samples were analyzed before and after acidification and
purging with N₂(g) to determine the contribution of dissolved ^1⁴CO₂ to total ^1⁴C in the
effluent. Effluent samples from representative experiments were also analyzed using
HPLC-radioisotope detection to determine the fraction of total ^1⁴C present as 2,4-D.

Experiments were continued until approximate steady-state concentrations of 2,4-D
were obtained in the effluent (9 to 14 pore volumes), at which time the eluent was
switched back to 3 mM CaCl₂. Column experiments were terminated when the effluent
^1⁴C concentrations approached zero. Soil columns were frozen until they were sectioned
into 3.5 cm (upper 9.5 cm) or 9.5 cm (below 9.5 cm) segments. The individual segments
were analyzed for soil residual ^1⁴C using biological oxidation (R. J. Harvey Instr. Corp.,
Hillsdale, NJ) and liquid scintillation.

A sterile column experiment (L = 8.2 cm, column RT = 13.4 h) was performed to
separate biotic and abiotic factors influencing transport of 2,4-D. We premixed 250 g of
soil (preincubated for 2 d at a water content of 0.2 L [kg soil]$^{-1}$) with crystalline HgCl$_2$ at a rate of 1.0 g (kg soil)$^{-1}$ (Wolf et al., 1989). All column parts, tubing and background solutions were either autoclaved twice or stored in 70% ethanol for several days before assembling the column. The soil was packed uniformly into the column and treated as the other columns.

**Modeling Approaches**

**Batch Degradation Models**

**Logistic Growth Model.** A solution to a logistic growth model was used to describe the degradation kinetics of 2,4-D in the batch degradation experiments. The logistic model is based on the Monod equation relating bacterial growth rate and concentration of a single substrate (Monod, 1949; Simkins and Alexander, 1984; Characklis and Marshall, 1990). Monod kinetics can be expressed as

$$ \mu = \frac{\mu_{\text{max}} C}{K_s + C} \quad [18] $$

where $\mu = \frac{dX}{dt}(1/X)$ is the specific growth rate (h$^{-1}$), $\mu_{\text{max}}$ is the maximum growth rate (h$^{-1}$), $C$ is the aqueous-phase 2,4-D concentration (mg L$^{-1}$), $K_s$ is the half-saturation constant for growth (mg L$^{-1}$), and $X$ is the 2,4-D degrader population density present at time $t$ (mg L$^{-1}$). This expression is based on the assumption that only aqueous-phase 2,4-D can be degraded by both attached and suspended bacteria, which has been shown to be
appropriate for 2,4-D degradation in soils (Ogram et al., 1985). When $K_s \gg C$, the Monod equation reduces to the logistic rate expression

$$\frac{dX}{dt} = \mu_L CX$$  \hspace{1cm} [19]$$

where $\mu_L = \mu_{\text{max}}/K_s$ is the logistic rate constant (L mg$^{-1}$ h$^{-1}$). It is commonly assumed that a constant fraction of $C$ from degrading 2,4-D is incorporated into biomass, and the remaining evolves as CO$_2$ (Simkins and Alexander, 1984). While this is strictly true for total carbon only if 2,4-D is completely mineralized, it may be more accurately applied to the $^{14}$C label on the carboxyl group. Based on this assumption, the following mass-balance relationship applies:

$$S - S_0 = \frac{X - X_0}{Y} = \frac{P - P_0}{1 - Y}$$  \hspace{1cm} [20]$$

where $S$ represents the total (sorbed plus solution phase) 2,4-D concentration (mg L$^{-1}$), $Y$ is the yield or fraction of 2,4-D converted into biomass during 2,4-D degradation, $P$ is the cumulative amount of 2,4-D converted into CO$_2$ (mg L$^{-1}$), and the subscript 0 designates the initial parameter values. Assuming a linear sorption isotherm ($Q = K_dC$), the total substrate concentration may be expressed as $S = C + (\rho/\theta)K_dC$, where $\rho$ is bulk density (Mg m$^{-3}$) and $\theta$ is volumetric soil water content (m$^3$ m$^{-3}$). This expression can be substituted into Eq. [20], and rearranged to yield

$$C = \frac{S_0 - (X - X_0)/Y}{1 + (\rho/\theta)K_d}$$  \hspace{1cm} [21]$$
After substitution of Eq. [21], Eq. [19] may be integrated, and the result can be written in terms of \( P \) using Eq. [20]:

\[
P = \frac{(z - 1)(1 - Y)X_0}{zX_0/S_0 + Y}
\]  \[22\]

where

\[
z = \exp\left(\frac{S_0X_0/Y}{1 + (\rho/\theta)K_d\mu t}\right)
\]  \[23\]

The parameters of the logistic model, \( X_0, Y, \) and \( \mu_L \), were estimated by fitting \(^{14}\text{CO}_2\) evolution data from the batch degradation experiments to Eq. [22] using a nonlinear least-squares optimization method (TableCurve 2D, Jandel Scientific, San Rafael, CA).

**First-Order Degradation Model.** In order to assess the performance of the transport model including first-order degradation, a batch-derived first-order degradation rate constant (\( \mu_{lb} \)) was obtained by fitting a first-order degradation expression to the \(^{14}\text{CO}_2\) evolution data of the batch experiment (prewetted moist soil). If only liquid-phase 2,4-D can be degraded (Ogram et al., 1985), the first-order degradation equation for substrate disappearance may be written as \( \frac{dS}{dt} = -\mu_{lb} C \). Assuming the transformation of a constant fraction of degrading 2,4-D into \( \text{CO}_2 \), the mass-balance relationship in Eq. [20] applies. As shown with the logistic model, \( C \) in the first-order degradation equation can be substituted using Eq. [21] and the resulting equation can be integrated to yield after
substitution of the mass-balance relationship and assuming relative concentrations:

\[
P = (1 - Y) \left[ 1 - \exp \left( -\frac{\mu_{ib} t}{1 + (\rho/\theta) K_d} \right) \right]
\]  

[24]

Least-squares optimization was used to estimate \( \mu_{ib} \) and \( Y \) for the CO\(_2\) evolution data of the batch experiment with prewetted, moist soil.

**Transport Experiments**

Tritiated water and 2,4-D breakthrough curves were analyzed using the advection dispersion equation (ADE) including equilibrium (local equilibrium assumption, LEA) and nonequilibrium (physical and chemical NE) options as well as two different model descriptions for 2,4-D degradation (i.e., logistic vs first order) during transport (Brusseau and Rao, 1989).

**Dispersion Coefficients and Retardation Factors.** Tritiated water (\(^3\)H\(_2\)O) breakthrough curves (BTCs) were used to obtain soil dispersion coefficients (\(D\)) for each column and to test for the presence of physical nonequilibrium (Brusseau et al., 1989; Gaber et al., 1995). Breakthrough curves for \(^3\)H\(_2\)O were fit to both the LEA and two-region physical nonequilibrium (physical NE) versions of the ADE using a nonlinear least-squares parameter optimization method (CXTFIT2, Toride et al., 1995). Retardation factors (\(R_f\)) were derived from the linear 2,4-D batch sorption coefficient (\(K_d\)), column water contents (\(\theta\)) and bulk densities (\(\rho\)) as \(R_f = 1 + (\rho/\theta)K_d\). Values of \(D\) and \(R_f\) were used to predict BTCs for 2,4-D in the sterile column experiments, for comparison to observed data. A
solution to the ADE with a two-site chemical nonequilibrium (chemical NE) option (Toride et al., 1995) was also fit to the 2,4-D BTC of the sterile column and the nonequilibrium parameters \( \omega \) and \( \beta \) (defined in Table 5; van Genuchten and Wagenet, 1989) were obtained in order to evaluate potential contributions of chemical nonequilibrium.

Transport Model Predictions. 2,4-D BTCs of all nonsterile columns were predicted independently using dispersion coefficients \( (D) \) from \( ^3\text{H}_2\text{O} \) BTCs, \( R_f \) values from 2,4-D sorption isotherms, and two different approaches for describing microbial degradation (logistic growth and first-order models). The logistic degradation model (Eq. [19]) was combined with the ADE based on the LEA to yield

\[
R_f \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\mu_c CX}{Y}
\]

where \( C \) is the volume averaged 2,4-D concentration in the aqueous phase (mg L\(^{-1}\)), \( x \) is soil depth (cm) and the other symbols are as defined earlier. Eq. [25] and Eq. [19] were numerically solved for the initial conditions \( C(x, 0) = 0 \) and \( X(x, 0) = X_0 \), and the boundary conditions \( C(0, t) = C_0 \) and \( \partial C/\partial x = 0 \) at \( x = \infty \) (van Genuchten and Parker, 1984) using a fully-implicit finite difference scheme. All logistic model parameters were obtained independently from batch degradation experiments.

Likewise, a first-order rate constant \( (\mu_{ib}) \) from batch experiments (prewetted soil) was used to independently predict \( (CXTFIT2) \) 2,4-D BTCs for all nonsterile columns. In
addition, an analytical solution to the ADE containing a first-order decay term (case C1 of van Genuchten and Alves, 1982) was used to approximate steady-state first-order degradation rate constants $\mu_{1s}$ (h$^{-1}$) from the steady-state sections of the 2,4-D BTCs. A similar approach was used by Angley et al. (1992) and Estrella et al. (1993). The solution in van Genuchten and Alves (1982) was solved for $\mu_{1s}$ to obtain (assuming relative concentrations)

$$\mu_{1s} = \frac{\ln C_s (D \ln C_s - xv)}{x^2}$$

where $C_s$ is the relative steady-state effluent concentration of 2,4-D (i.e. $C/C_0$ at steady state) and the other symbols are as defined earlier. Values of $\mu_{1s}$ were calculated for each column based on known values of $D$ (Table 5), $v$ and $x$ (Table 3). Values of $C_s$ were estimated from the 2,4-D BTCs as weighted averages of the relative 2,4-D concentrations during steady state.

RESULTS AND DISCUSSION

Batch Sorption Isotherms

Sorption of 2,4-D under batch conditions was described using the Freundlich isotherm yielding values of $K = 0.62 (\pm 0.04)$ L kg$^{-1}$ and $n = 1.08 (\pm 0.09)$; nonlinear regression, $r^2 = 0.93$). Isotherm data was also adequately described using the linear adsorption model ($n = 1$), where $K = 0.66 (\pm 0.02)$ L kg$^{-1}$ ($r^2 = 0.92$). A linear equilibrium
sorption isotherm was therefore assumed for calculating 2,4-D retardation factors \( (R_p) \).

### 2,4-D Degradation under Batch Conditions

Degradation curves of 2,4-D under batch conditions show the effects of soil wetness, pretreatment, mixing environment, and initial substrate concentration (Fig. 11). The absence of \(^{14}\text{CO}_2\) evolution in autoclaved soils supported the assumption that abiotic sources of 2,4-D degradation were insignificant under batch conditions. The sigmoidal

![Degradation of \(^{14}\text{C}-2,4\text{-D}\) (measured as fraction of total added \(^{14}\text{C}\) recovered as \(^{14}\text{CO}_2, P/S_0\)) in batch experiments performed under various conditions. Error bars for moist, previously dry soil were generated using data from all soil water contents tested. Filled symbols represent initial aqueous phase 2,4-D concentrations of 1.0 mg L\(^{-1}\); open symbols represent 0.1 mg L\(^{-1}\) initial aqueous phase 2,4-D concentration.](image-url)
shape of the degradation curves as well as the low initial aqueous-phase 2,4-D concentrations justify the use of a logistic degradation model to describe the batch degradation data (Alexander and Scow, 1989; Table 4). Variations in water content did not significantly affect rates of $^{14}$CO$_2$ evolution within the moisture range tested; for example, the error bars in Figure 11 for previously dry, moist soil were generated including data from all batch reactors at water contents of 0.18, 0.23, and 0.27 L (kg soil)$^{-1}$. Water contents of all column transport experiments [0.17 to 0.27 L (kg soil)$^{-1}$] were bracketed by this range, consequently, variations in soil water content within column experiments are not expected to cause significant variations in 2,4-D degradation rate. However, soils prewetted for 3 d prior to 2,4-D application exhibited more rapid onset of 2,4-D degradation compared to soil not prewetted (resulting in a 10 fold increase in model estimates of $X_0$, Table 4). The estimated parameters obtained with prewetted, moist soil were used in the logistic transport model to predict 2,4-D BTCs under column conditions, because of the similarity in batch and column soil pretreatment and water content conditions.

Changing from a stationary, moist soil environment to a well-stirred soil slurry generally resulted in lower estimates of $X_0$ (e.g., $X_0 = 0.02$ mg L$^{-1}$ for the prewetted, moist soil versus $X_0 = 6 \times 10^{-8}$ mg L$^{-1}$ for the prewetted soil in 1 mg L$^{-1}$ slurry). A tenfold increase in initial 2,4-D concentration in the slurry experiments increased the duration of the lag phase (lag phase used here to simply describe the period of lower degradation rate preceding a rapid linear rate) and resulted in a 10 fold reduction of $\mu_c$ and a 100 fold reduction of $X_0$ as estimated by the curve fitting procedure (Table 4). A similar dependence of 2,4-D degradation kinetics on initial 2,4-D concentration was reported by Parker
<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Fitting parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_0$, $X_0$, $Y$</td>
<td>$\mu_L$, $r^2$</td>
</tr>
<tr>
<td>Soil pretreatment</td>
<td>L (kg soil)$^{-1}$</td>
<td>mg L$^{-1}$</td>
</tr>
<tr>
<td>prev. dry</td>
<td>0.18</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>1.0</td>
</tr>
<tr>
<td>prewetted</td>
<td>0.25</td>
<td>1.0</td>
</tr>
<tr>
<td>3.0 (slurry)</td>
<td>1.0</td>
<td>$6 \times 10^8$ ($7 \times 10^8$)</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>$6 \times 10^6$ ($4 \times 10^6$)</td>
</tr>
</tbody>
</table>

$^\dagger$ Values in parentheses designate standard errors.
and Doxtaeder (1982).

Transport Experiments

Behavior of $^3$H$_2$O

Tritiated water ($^3$H$_2$O) BTCs (Fig. 12) were analyzed for the presence of physical nonequilibrium (NE) conditions (Brusseau et al., 1989, Gaber et al., 1995) and to obtain column dispersion coefficients ($D$). Although the $^3$H$_2$O BTCs exhibited differences among several treatments (especially the 9.5-cm columns and the 85.5-cm columns), CXTFIT2 (Toride et al., 1995) analysis of the BTCs did not suggest physical NE conditions in any of the columns. Curve fitting to the physical NE model did not result in an improvement of $r^2$ compared to fits using the LEA model (Table 5). Furthermore, the

<table>
<thead>
<tr>
<th>Experimental ID</th>
<th>$D$  (cm$^3$ h$^{-1}$)</th>
<th>$\beta$†</th>
<th>$\omega$‡</th>
<th>$R_f$</th>
<th>$r^2$§</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT05_L09</td>
<td>1.53</td>
<td>1.0</td>
<td>100</td>
<td>0.99</td>
<td>0.992</td>
</tr>
<tr>
<td>RT16_L09</td>
<td>1.35</td>
<td>1.0</td>
<td>100</td>
<td>1.06</td>
<td>0.997</td>
</tr>
<tr>
<td>RT48_L09</td>
<td>0.22</td>
<td>0.99</td>
<td>100</td>
<td>1.09</td>
<td>0.996</td>
</tr>
<tr>
<td>RT05_L28</td>
<td>4.97</td>
<td>1.0</td>
<td>100</td>
<td>1.06</td>
<td>0.998</td>
</tr>
<tr>
<td>RT16_L28</td>
<td>1.07</td>
<td>1.0</td>
<td>100</td>
<td>1.01</td>
<td>0.999</td>
</tr>
<tr>
<td>RT48_L28</td>
<td>0.48</td>
<td>1.0</td>
<td>30.7</td>
<td>1.06</td>
<td>0.999</td>
</tr>
<tr>
<td>RT16_L85</td>
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<td>1.0</td>
<td>100</td>
<td>1.11</td>
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<td>RT48_L85</td>
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<td>1.0</td>
<td>100</td>
<td>1.02</td>
<td>0.994</td>
</tr>
<tr>
<td>SX16_L09</td>
<td>0.22</td>
<td>1.0</td>
<td>100</td>
<td>1.03</td>
<td>0.996</td>
</tr>
</tbody>
</table>

† $\beta = [1 + (\rho/\theta)FK_d]/R_o$, where $F$ is the fraction of sorbent for which sorption is instantaneous.
‡ $\omega = [k_d(1 - \beta)R_dL]/v$, where $k_d$ is the desorption rate constant.
§ $r^2$ values from fitting data to the LEA and physical NE models were identical.
estimated nonequilibrium parameters $\beta$ and $\omega$ of the physical NE version were close or identical to 1 and 100, respectively (Table 5). This supports the assumption that physical nonequilibrium processes were not significant (Valocchi, 1985; Bahr and Rubin, 1987), and nonequilibrium processes observed with the 2,4-D BTCs must be sorption or degradation-related (Brusseau and Rao, 1989).
Sterile Control Column Experiment

The lack of detectable $^{14}$CO$_2$ evolution in the gas phase of the sterile column suggested that abiotic pathways of 2,4-D degradation were insignificant under these conditions. Conversely, 98% of the applied $^{14}$C-2,4-D was recovered in the column effluent indicating that only a small fraction of the applied 2,4-D was sorbed irreversibly to the soil. This provides important evidence that $^{14}$C measured as soil residue in nonsterile column systems was present as biomass $^{14}$C or as degradation products which may have different sorption characteristics than 2,4-D, rather than as irreversibly bound 2,4-D.

To investigate the contribution of nonequilibrium sorption processes under abiotic conditions, the observed 2,4-D BTC from the sterile column was compared to predicted and fitted BTCs using transport models based on the local equilibrium (LEA model) and two-site chemical nonequilibrium assumptions (chemical NE model, Toride et al., 1995; Fig. 13). The BTC was reasonably well described by a prediction based on the LEA model, using $D$ (0.22 cm$^2$ h$^{-1}$, Table 5) from the $^3$H$_2$O BTC and a batch-derived retardation factor $R_f = 3.89$ (Fig. 13); however, some deviations from the observed BTC are evident in both the breakthrough and elution fronts. These deviations may be explained partially by inadequacy of batch $K_d$ (or $R_f$) values or as true chemical nonequilibrium. For example, fitting the LEA model by optimizing $R_f$ improved the description of the BTC by shifting the positions of the breakthrough and elution fronts (Fig. 13). Alternatively, the chemical NE model with fixed $R_f$ and estimated nonequilibrium parameters ($\beta = 0.76$, $\omega = 0.42$) provided an excellent fit to the observed BTC ($r^2 = 0.995$) with a good description
of early breakthrough and tailing. The improved description using the chemical NE model, and given that the $^3$H$_2$O BTC showed no physical NE, suggests contributions of chemical nonequilibrium to 2,4-D transport under conditions specific to the sterile column control (i.e., $v = 0.6$ cm h$^{-1}$, column RT = 13.4 h).

It should be emphasized that although chemical nonequilibrium causes shifts in the breakthrough and elution fronts of the BTCs, it does not affect the final position of the steady-state effluent concentration, provided that the 2,4-D pulse is long enough to achieve true steady-state 2,4-D concentrations. In fact, it can be shown that at steady state, Eq. [26] is valid for chemical or physical NE models as well (Angley et al., 1992). As

![Graph](image)

**Figure 13.** Observed and predicted [LEA model using independent estimates of $R_f$ (3.89) and $D$ (0.22 cm$^2$ h$^{-1}$)] 2,4-D breakthrough curves (BTCs) for sterile column experiment. Fitted BTCs were generated using (i) the LEA model where $R_f$ was optimized (3.49) and (ii) the chemical nonequilibrium model where nonequilibrium parameters were optimized ($\beta = 0.76$, $\omega = 0.42$) using fixed $R_f$ (3.89) and $D$ (0.22 cm$^2$ h$^{-1}$).
will be discussed further, potential contributions of chemical nonequilibrium in nonsterile columns may have varied with column conditions (e.g., v), but did not have a significant impact on the identification of steady-state 2,4-D effluent concentrations.

2.4-D Transport under Nonsterile Conditions

Acidification of effluent samples with HCl and subsequent purging with N₂ did not reduce the concentrations of ¹⁴C indicating that ¹⁴CO₂ concentrations in the column effluents were insignificant. Analysis of selected effluent samples using HPLC radioisotope detection showed that the majority of ¹⁴C was in fact ¹⁴C-2,4-D. This observation coupled with the nearly complete 2,4-D recovery in the effluent of the sterile control column lead us to the simplifying assumptions that (i) ¹⁴C found in the column effluent was representative of ¹⁴C-2,4-D, and (ii) ¹⁴CO₂ in the gas phase as well as residual ¹⁴C in the soil represented microbiologically altered or degraded compound.

Under nonsterile column conditions, the amount of 2,4-D degraded varied considerably as a function of column residence time (RT) and pore water velocity (v, Fig. 14). Most 2,4-D BTCs exhibited steady-state 2,4-D effluent concentrations (Cₛ) after approximately 6 pore volumes (Fig. 14) with values ranging from 0.063 to 0.92 across all conditions (Table 6). At the shortest column RT (5.3 h), steady-state Cₛ was not observed until approximately 10 pore volumes. Amounts of 2,4-D recovered in column effluent always decreased with increasing column RT among experiments at constant column length. For example, at L = 9.5 cm, the fraction of applied 2,4-D recovered in column effluent dropped from 0.89 (RT = 5.3 h) to 0.58 (16 h) and 0.07 (48 h). This is consistent
Figure 14. Comparison of observed and predicted 2,4-D BTCs for nonsterile column experiments. Predicted BTCs were generated using (i) the LEA model with logistic degradation kinetics and independent estimates of $R_f$ (from $K_i = 0.66 \text{ L kg}^{-1}$), $D$ (Table 5), $X_0$ (0.02 mg L$^{-1}$), $Y$ (0.31) and $\mu_L$ (0.13 L mg$^{-1}$ h$^{-1}$), (ii) the LEA model with first-order degradation kinetics and independent estimates of $R_f$, $D$ and $\mu_{ib}$ (0.066 h$^{-1}$), and (iii) the LEA model with first-order degradation kinetics and independent estimates of $R_f$, $D$ and $\mu_{ls}$ (calculated from $C_s$ using Eq. [26], Table 6).
Table 6. The fate of 2,4-D in soil column experiments.

<table>
<thead>
<tr>
<th>Experimental ID</th>
<th>C_s</th>
<th>µ_1,</th>
<th>Half-life</th>
<th>¹⁴C recovery in</th>
<th>Total ¹⁴C recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>h⁻¹</td>
<td>d</td>
<td>Effluent</td>
<td>CO₂ trap</td>
<td>Soil</td>
</tr>
<tr>
<td>RT05_L09</td>
<td>0.862</td>
<td>0.031</td>
<td>0.95</td>
<td>0.89</td>
<td>0.02</td>
</tr>
<tr>
<td>RT16_L09</td>
<td>0.548</td>
<td>0.035</td>
<td>0.83</td>
<td>0.58</td>
<td>0.15</td>
</tr>
<tr>
<td>RT48_L09</td>
<td>0.063</td>
<td>0.071</td>
<td>0.39</td>
<td>0.07</td>
<td>0.37</td>
</tr>
<tr>
<td>RT05_L28</td>
<td>0.923</td>
<td>0.015</td>
<td>1.97</td>
<td>0.91</td>
<td>0.01</td>
</tr>
<tr>
<td>RT16_L28</td>
<td>0.683</td>
<td>0.021</td>
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<td>0.05</td>
</tr>
<tr>
<td>RT48_L28</td>
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<td>0.038</td>
<td>0.69</td>
<td>0.18</td>
<td>0.21</td>
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<td>RT16_L85</td>
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<td>0.015</td>
<td>1.98</td>
<td>0.85</td>
<td>0.01</td>
</tr>
<tr>
<td>RT48_L85</td>
<td>0.697</td>
<td>0.007</td>
<td>4.26</td>
<td>0.67</td>
<td>0.03</td>
</tr>
</tbody>
</table>

† Steady-state relative 2,4-D concentration in column effluents.
‡ First-order degradation rate constants and corresponding half lives derived from C_s using Eq. [26].
§ as fractions of applied ¹⁴C as ¹⁴C-2,4-D.

with the expected relationship between 2,4-D degradation and column RT (i.e., increases in time available for 2,4-D degradation result in greater amounts of 2,4-D degraded).

The effect of pore water velocity (v) on degradation can be understood qualitatively by comparing effluent 2,4-D recoveries across columns with similar column residence times (RTs) but varying column length (L). At constant column RT, amounts of 2,4-D recovered in column effluent always decreased with decreasing v (or decreasing L, Table 6). For example, at RT = 48 h, the fractions of applied 2,4-D recovered in column effluent decreased from 0.67 (L = 85.5 cm, v = 1.8 cm h⁻¹) to 0.18 (L = 28.5 cm, v = 0.6 cm h⁻¹) and 0.07 (L = 9.5 cm, v = 0.2 cm h⁻¹). This indicates an increase in 2,4-D degradation rate with decreasing v, because the time available for degradation was approximately constant for each column. Similar results for the dependence of p-nitrophenol degradation on both the residence time and pore water velocity were obtained by Kelsey and Alexan-
der (1995), although effluent concentrations of \( p \)-nitrophenol always dropped to zero after 4 d.

In our study, lower effluent 2,4-D recoveries always corresponded to higher amounts of \( ^{14} \)C recovered as \( ^{14} \)CO\(_2\) (g) and soil residual \( ^{14} \)C (Table 6). However, as values of \( ^{14} \)C recovered in effluent decreased (i.e. experiments exhibiting greater 2,4-D degradation), total recoveries of applied \( ^{14} \)C decreased from 96\% to 48\%. The accuracy of \( ^{14} \)C analyses in column effluent (scintillation), soil (biological oxidation and scintillation), and CO\(_2\) traps (scintillation) were found to be high. Consequently, we believe that the lower total \( ^{14} \)C recoveries in experiments which exhibited the greatest 2,4-D degradation were due to loss of \( ^{14} \)CO\(_2\) (g) through gas leaks\(^1\).

Transport Simulations with Logistic Growth Model. Independent estimates of model input parameters, obtained from \( ^{3} \)H\(_2\)O BTCs (\( D \), Table 5), batch sorption isotherms (\( R_f \)) and the batch degradation experiment with prewetted, moist soil (\( X_0 = 0.02 \) mg L\(^{-1} \), \( Y = 0.31 \), \( \mu_L = 0.13 \) L mg\(^{-1} \) h\(^{-1} \), Table 4), were used to predict 2,4-D BTCs using a numerical solution to the ADE (Eq. [25]). Given this set of input data, the logistic model did not accurately predict the observed 2,4-D BTCs (Fig. 14). Specifically, the observed 2,4-D BTCs occurred earlier than predicted, which may be partially explained by chemical nonequilibrium, especially at the faster pore water velocities. More importantly, the logistic transport model did not predict a non-zero steady-state 2,4-D effluent concentra-

\(^1\)To minimize the effects of gas leaks in similar batch or column systems, air flow through the system could be attained by using a vacuum at the air outlet port instead of applying pressure at the air inlet port.
tion, characteristic of observed BTCs. Rather, all of the predicted curves show a period of slow growth (low degradation rate) followed by a period of rapid growth (high degradation rate) where the predicted effluent substrate concentration diminishes dramatically until $C_s$ approaches zero.

Figure 15 illustrates that the inappropriateness of the logistic model is not a result of choosing a specific set of model parameters. Four 2,4-D BTCs were predicted using the

<table>
<thead>
<tr>
<th>Case</th>
<th>$\mu_L$ (mg h$^{-1}$)</th>
<th>$Y$ (mg L$^{-1}$)</th>
<th>$X_0$ (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.13</td>
<td>0.31</td>
<td>2E-2</td>
</tr>
<tr>
<td>b</td>
<td>0.17</td>
<td>0.26</td>
<td>2E-3</td>
</tr>
<tr>
<td>c</td>
<td>1.3</td>
<td>0.21</td>
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</tr>
<tr>
<td>d</td>
<td>0.14</td>
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<td>6E-8</td>
</tr>
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</table>

Observed BTC

Figure 15. Comparison of observed 2,4-D BTC at column RT = 16 h, $L = 28.5$ cm, and $v = 1.5$ cm h$^{-1}$ (experiment RT16/L28) with predicted BTCs using logistic degradation kinetics with four cases of logistic model parameters determined from batch experiments (Table 4): Case a - prewetted soil, water content = 0.25 L (kg soil)$^{-1}$, initial 2,4-D concentration ($S_0$) = 1.0 mg L$^{-1}$; Case b - previously dry soil, water content 0.23 L (kg soil)$^{-1}$, $S_0$ = 1.0 mg L$^{-1}$; Case c - stirred slurry, $S_0$ = 1.0 mg L$^{-1}$; Case d - stirred slurry, $S_0$ = 0.1 mg L$^{-1}$. The symbols in the simulation curves correspond to those of the corresponding batch experiments in Fig. 11.
wide range of logistic model parameters obtained from fitting our batch degradation results (Fig. 15, Table 4). Effects of \( X_0 \) (initial 2,4-D degrader population density) on predicted BTCs are illustrated best by comparing Cases \( a \) and \( d \) in Fig. 15, where values of \( \mu_L \) and \( Y \) were relatively constant. The low value of \( X_0 \) (6 x 10^8 mg L\(^{-1}\)) obtained from the stirred slurry batch experiment resulted from a longer lag phase prior to maximum degradation rate, and caused a correspondingly longer delay in 2,4-D degradation (i.e. higher \( C/C_0 \) values) during transport (Fig. 15). Similarly, the lower \( X_0 \) value (2 x 10^3 mg L\(^{-1}\)) obtained from the moist but previously dry soil (Case \( b \)) caused a slight delay in 2,4-D degradation relative to the moist, prewetted soil (Case \( a \)). Effects of \( \mu_L \) on predicted BTCs are best illustrated by comparing Cases \( c \) and \( d \), corresponding to the slurry experiments at initial 2,4-D concentrations of 0.1 and 1.0 mg L\(^{-1}\), respectively. At an initial 2,4-D concentration of 0.1 mg L\(^{-1}\), \( \mu_L \) is roughly 10 fold higher and results in predicted BTCs reflecting greater 2,4-D degradation. Since the rate constant (\( \mu_L \)) in the logistic model is concentration dependent, it is not appropriate to use \( \mu_L \) values determined at 0.1 mg 2,4-D L\(^{-1}\) for predicting 2,4-D BTCs at 1.0 mg 2,4-D L\(^{-1}\). Additional sensitivity analyses of the effects of logistic model parameters on 2,4-D BTCs show that uncertainty of independent parameter estimates is not responsible for lack of agreement between predicted and observed 2,4-D BTCs. The prediction of a steady-state effluent concentration other than \( C/C_0 = 0 \) or 1 is impossible with any set of logistic model parameters.

Estrella et al. (1993) also studied 2,4-D (100 mg L\(^{-1}\)) degradation during transport and found that at these higher substrate concentrations, a Monod-based growth model was
necessary to describe 2,4-D degradation during transport. Likewise, although no modeling
efforts were reported in Kelsey and Alexander (1995), their data on p-nitrophenol (10 mg
L⁻¹) degradation during transport appear consistent with a Monod or logistic growth
model. At lower pesticide concentrations, such as those used in the current study (1 mg L⁻¹),
the implicit assumption of a growth based model may not be valid, especially if the
substrate concentration is low relative to native soil C, and results only in increased
metabolic activity of a steady-state microbial population.

Transport Modeling with First-Order Degradation. Although first-order kinetics did
not adequately describe 2,4-D degradation under some batch conditions (primarily due to
observed lag phases lasting 2 - 5 d), experiments performed at initial concentrations of
0.1 and 1 mg 2,4-D L⁻¹ (stirred slurry, prewetted soil) showed that maximum degradation
rates exhibited first-order dependence on initial 2,4-D concentration. A first-order rate
constant, \( \mu_{lb} \), of 0.023 ± 0.004 h⁻¹ was obtained by fitting the complete set of batch
degradation data for prewetted moist soil to the first-order kinetic model (Eq. [24], \( Y =
0.05 \pm 0.10, r^2 = 0.93 \)). Because of the continuous exposure of the soil microbial commu­
nity to 2,4-D during transport experiments, any effects of a degradation lag phase would
likely be insignificant after 2 to 3 d. We therefore used the same batch degradation data to
obtain another set of optimized first-order model parameters by omitting the phase of low
degradation kinetics (0 to 36 h). Optimized parameters resulting from this fit were \( \mu_{lb} =
0.066 \pm 0.003 \text{ h}^{-1} \) and \( Y = 0.28 \pm 0.01 \) (\( r^2 = 0.98 \)). Predicted 2,4-D BTCs using a first-
order kinetic model (using \( \mu_{lb} = 0.066 \text{ h}^{-1} \)) coupled with the ADE (LEA, Fig. 14)
accurately reflected (i) the development of steady-state effluent 2,4-D concentrations ($C_s$) and (ii) the general effects of column RT on values of $C_s$ where increasing column RT resulted in decreasing values of $C_s$. However, independent of which $\mu_{ib}$ was selected for the predictions, a single batch-determined $\mu_{ib}$ value did not accurately describe 2,4-D degradation for all column conditions.

The observed BTCs were then used to optimize first-order degradation rate constants ($\mu_{is}$) as a function of different column conditions to separate effects of column RT and v. Observed values of $C_s$ were used to calculate (Eq. [26]) column-specific $\mu_{is}$ values (Table 6), which were then used to predict 2,4-D BTCs (Fig. 14). This approach is similar to fitting the observed BTCs to the ADE including first-order degradation where the degradation rate constant ($\mu_{LEA}$ for LEA model and $\mu_{NE}$ for chemical NE model fits) is optimized. In fact, with the exception of one experiment (RT05_L09), values of $\mu_{is}$

<table>
<thead>
<tr>
<th>Experimental ID</th>
<th>$\mu_{is}$ from $C_s$</th>
<th>$\mu_{LEA}$ from LEA model fit</th>
<th>Chemical NE model fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>h$^{-1}$</td>
<td>h$^{-1}$</td>
<td>h$^{-1}$</td>
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<td>RT05_L09</td>
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<tr>
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</tr>
<tr>
<td>RT48_L85</td>
<td>0.007</td>
<td>0.008</td>
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</tr>
</tbody>
</table>

† using Eq. [26]
(using Eq. [26]) were not significantly different from optimized $\mu_{1,\text{LEA}}$ values using the LEA model (Table 7). Also, since it was shown that chemical NE may have been important in the sterile control column, observed BTCs were fitted using the chemical NE model where $\beta$, $\omega$, and $\mu_{1,\text{NE}}$ were optimized (Table 7). Values of $\mu_{1,\text{NE}}$ are, again, essentially identical to $\mu_{1s}$ values obtained from Eq. [26] (or LEA fitted $\mu_{1,\text{LEA}}$ values) for all conditions except those at a column RT of 5.3 h.

The variation of model estimates for degradation rate constants at the shortest column RT (5.3 h) can be partially explained by the fact that very little degradation occurred during transport in these columns ($C_s$ values of 0.86 and 0.92), which results in extreme sensitivity of the optimized rate constants to fluctuations in observed data about the steady-state position. Furthermore, the assumption that 2,4-D degradation rates follow first-order kinetics is more appropriate after steady-state 2,4-D concentrations are established (Angley et al., 1992), and will not describe periods of slower degradation kinetics at the early stages of a column experiment. Naturally, the relative effect of this slow-degradation period is most important for short-duration experiments, and may result in inaccurate parameter estimates using both the LEA and the chemical NE models. Consequently, for short-RT experiments (5.3 h), calculated $\mu_{1s}$ values (Eq. [26]) were based on $C_s$ values observed after 10 pore volumes (after 2 d).

**Effects of Pore Water Velocity on 2,4-D Degradation Rate Constants.** Although the general effects of column RT on the amount of 2,4-D degraded during transport (i.e., increased amounts of 2,4-D degraded with increasing RT) were explained using a first-
order model, a single batch-derived rate constant did not accurately predict the amount of 2,4-D degraded over a wide range in column conditions. Column-derived $\mu_{1s}$ values varied by approximately one order of magnitude (0.007-0.071 h$^{-1}$, Table 6) for the eight different column RT and $v$ treatments. This range bracketed values of rate constants derived from batch experiments ($\mu_{1b} = 0.023 - 0.066$ h$^{-1}$) and values reported in Estrella et al. (1993) for their saturated, untreated (i.e., not preexposed to 2,4-D) soil column ($\mu_{1s} = 0.04$ h$^{-1}$, RT = 1.1 h, $v = 4.7$ cm h$^{-1}$). The variation in column-derived rate constants obtained in this study cannot be explained by variations in column RTs (Fig. 16A).

However, the relationship between optimized $\mu_{1s}$ values and $v$ showed that $\mu_{1s}$ values remained relatively low at $v$ above 1 cm h$^{-1}$, but increased sharply at $v$ below 1 cm h$^{-1}$ (Fig. 16B). To illustrate the observed relationship, a best-fit curve was included in Fig. 16B of the form

$$\mu_{1s} = a + b v^{-1}$$

where $a$ and $b$ are fitted constants ($a = 0.0137$ h$^{-1}$, $b = 0.0105$ cm h$^{-2}$, $r^2 = 0.88$).

The effects of $v$ on column-derived rate constants observed in this study are in general agreement with results observed in Estrella et al. (1993) and Kelsey and Alexander (1995). First-order 2,4-D degradation rate constants obtained by Estrella et al. (1993) increased from 0.04 h$^{-1}$ at $v$ of 4.7 h$^{-1}$ (albeit from a saturated column experiment) to 0.14 h$^{-1}$ at $v$ of approximately 0.6 cm h$^{-1}$ (unsaturated column). Higher $v$ resulted in lower amounts of $p$-nitrophenol degradation during the early stages of column transport, causing Kelsey and Alexander (1995) to suggest that more microorganisms may be flushed out of
the column at high vs low \( v \), thus requiring more time to establish a population large enough to metabolize the incoming substrate. However, in the current study, degradation of 2,4-D was characterized by the development of steady-state 2,4-D concentrations, suggesting that microbial populations were not exhibiting significant growth in response

Figure 16. First-order degradation rate constants derived from \(^{14}\)C-2,4-D steady-state effluent concentrations as a function of column residence time (A), pore water velocity (B), and column averaged local opportunity time, \( \nu^{-1} \) (C). The curves in B and C represent best-fit empirical functions as described in the text.
to 2,4-D inputs.

Our results suggest that variations in pore water velocity, rather than column RT, describe variations in 2,4-D degradation rate constants across a range of transport conditions. At higher flow velocities, column derived rate constants reach a minimum, but increase sharply when velocities drop below 1 cm h\(^{-1}\) (Fig 16B).

One hypothesis explaining this behavior is that apparent rate constants determined under transport conditions are dependent on the solute residence time per unit length (or per unit area or volume), which can be thought of as a local opportunity time. At sufficiently high pore water velocities, apparent degradation rate constants decline because local opportunity times are too small relative to times required for the sequence of elementary reactions describing microbial degradation. A plot of the column-derived first-order rate constants obtained in the current study vs the column averaged local opportunity time \(v^{-1}, \text{h cm}^{-1}\) demonstrates that apparent rate constants do indeed increase with increases in the residence time per unit length (Fig. 16C). Note that the same best-fit function illustrating the relationship between \(\mu\text{,s}\) and \(v\) in Fig 16B (Eq. [27]) becomes a line in the representation of Figure 16C. One might hypothesize that a maximum rate constant would be obtained at sufficiently large local opportunity times, where reactions describing the rate of 2,4-D uptake, (i.e. rate of 2,4-D transport into microbial cells) or the enzymatic breakdown of 2,4-D truly became the rate limiting steps. Although no such maximum was observed in this study, additional experiments would be necessary at higher local opportunity times to determine if such a maximum in the column-derived rate constant is attainable. It should be pointed out that as local opportunity times
approach infinity (e.g., batch conditions with no flow), apparent rate constants may again decline as diffusional constraints limit the mass transfer of 2,4-D to sites of microbial degradation (Scow and Alexander, 1992; Chung et al., 1993).

Although we have discussed the possibility that local opportunity times may affect the apparent rate constants describing 2,4-D degradation during transport, it should be noted that pore water velocity (v) may also influence mass transfer rates. Several studies have shown that increases in v result in greater estimates of column-derived mass transfer rate parameters affecting sorbing solutes (e.g., values of ω in the chemical NE model; Gamerdinger, 1991; Brusseau, 1992; Gaber et al., 1995; Darland and Inskeep, 1997). These results might lead to the hypothesis that increases in v with resultant increases in diffusion controlled desorption rates may actually increase degradation rates during transport, especially in light of the fact that degradation rates of organic contaminants are often considered desorption limited (Pignatello and Xing, 1996). However, pore water velocities necessary for observing higher apparent mass transfer rates may result in decreases in local opportunity times, which would result in lower degradation rates. In summary, the effects of v on degradation rates during transport are complicated by the confounding effects of velocity on (i) mass transfer rates and (ii) local opportunity times required for microbial degradation. Our results suggest that the latter is more important for describing effects of pore water velocity on degradation rates of 2,4-D in transport environments.
CHAPTER 5

SUMMARY

In the first part of this thesis, an experimental setup is described which can be used to impose, maintain and monitor constant target matric potential \((h)\) in large soil cores, for use in miscible displacement experiments. Establishing and maintaining steady state hydraulic conditions with unit potential energy gradient (constant \(h\)) is often required for interpreting solute transport phenomena. However, it is unlikely that this condition is routinely achieved using conventional soil column configurations. In the described system, a disk permeameter applied water and chemicals to the top of the column under constant negative supply pressures. An automated solenoid apparatus at the column base facilitated simultaneous application of negative pressure and collection of large volumes of effluent. Time domain reflectometry (TDR) probes and transducer tensiometers continuously monitored volumetric soil water content \((\theta)\) and \(h\) at two soil depths. In addition to facilitating establishment of desired column transport conditions, and confirming they were sustained during the course of individual experiments, we obtained detailed \textit{in situ} soil water characteristics during sequential wetting and drying cycles.

In Chapter 3, we investigated the effects of matric potential \((h)\) on the presence or
absence of preferential flow conditions in a permanent grassland soil (Amsterdam silt loam). The experimental system described above was used to establish conditions of unit potential energy gradient (constant \( h \)) during individual column leaching experiments. Two to four tracer transport experiments at \( h \) between 0 and -24 cm were performed with each of four intact soil cores (26 cm length, 15 cm diameter). \(^3\)H\(_2\)O breakthrough curves (BTCs) were analyzed using the local equilibrium (LEA model) and two-region physical nonequilibrium (PNE model) forms of the advection dispersion equation. The magnitude of the fitted nonequilibrium parameters \( \beta \) and \( \omega \) in the PNE model and a comparison of the \( r^2 \) obtained with the PNE and LEA model fits were used as criteria for the presence or absence of PNE (i.e., preferential flow). The transition between physical equilibrium and nonequilibrium transport conditions occurred consistently between \( h = -10 \) cm and \( h = -5 \) cm. This suggests that soil pores with equivalent radii larger than 150 to 300 \( \mu \)m may contribute to preferential flow through soils if they are water-filled. Knowledge of the pore size distribution within this pore size range may potentially allow predictions of the potential for preferential flow events through a soil. In an attempt to verify this thesis, we experimentally estimated macropore size distributions in our test columns using combined tensiometer and TDR measurements. Although our soil cores had been collected from a fairly homogeneous area, the estimated pore size distributions obtained between \( h = 0 \) and -20 cm exhibited significant variation within and among columns, and did not facilitate assignment of specific fractional soil volumes associated with preferential flow. Furthermore, estimated volumes of water-filled macropores (\( h \) dependent) were not related to variations in pore water velocity. The resolution of measuring techniques
employed to estimate pore size distribution at the wet end was not sufficient to identify consistent changes in \( \theta \). Specifically, the TDR method used to determine soil water contents (\( \theta \)) near saturation may have produced values for \( \theta \) representative of a small soil volume, but not of the whole soil column. To investigate the effects of pore size distribution on the potential for preferential flow we suggest that a more representative method of measuring \( \theta \) and a series of soils with varying macropore size distribution be used in the experiments.

For individual soil columns, an increase in matric potential (\( h \)) always caused an increase in pore water velocity. This was expected due to the increasing number of large water-filled soil pores. Consequently, effects of \( h \) on PNE were confounded with possible effects of changing \( v \). A series of column experiments was selected with nearly constant values of \( v \) (approximately 1 cm h\(^{-1}\)) where increasing \( h \) had the same effect as observed in any single soil column. The lowest pore water velocity at which preferential flow conditions was observed in any of the soil columns was 0.73 cm h\(^{-1}\). This value of \( v \) corresponds to a water flux density of 0.27 cm h\(^{-1}\), which is often exceeded under the local climatic conditions. Occurrences of preferential flow may therefore be common on field soils of the Amsterdam series.

For many organic solutes, microbial degradation is one of the most important processes controlling the amount of solute transported in soils and aquifers. Consequently, accurate model predictions of the transport of these solutes require knowledge of both appropriate rate equations describing microbial degradation and appropriate
estimates of degradation rate parameters. Objectives of Chapter 4 of this thesis were to (i) test the applicability of first-order and logistic growth models for describing 2,4-dichlorophenoxyacetic acid (2,4-D) degradation at concentrations representative of typical field application rates across a wide range in column transport conditions, (ii) determine the applicability of degradation rate parameters derived under batch conditions for describing 2,4-D degradation across a wide range in column conditions, and (iii) separate effects of column residence time (RT) and pore water velocity (v) on degradation rate parameters determined from transport experiments.

Degradation of 2,4-D (partially carboxyl-\(^{14}\)C-labeled) under batch conditions was described best by a logistic growth model. A first-order degradation model described the observed data after omitting initial phases of slow degradation lasting 2 to 5 days, depending on soil prewetting, soil water content, mixing (moist soil vs stirred slurry), and initial 2,4-D concentration.

To study 2,4-D degradation during transport, continuous pulses of 1.0 mg 2,4-D L\(^{-1}\) (partially carboxyl-\(^{14}\)C-labeled) and \(^{3}\)H\(_{2}\)O (tracer) were applied to each of nine repacked, unsaturated soil columns. Experiments with three different column RTs (approximately 5.3, 16, and 48 h) were performed in soil columns of variable length (9.5, 28.5, and 85.5 cm). This was achieved by varying v in the range from 0.2 to 5.7 cm h\(^{-1}\).

No physical nonequilibrium conditions were detected in any of the soil columns as tested by fitting a two-region physical nonequilibrium version of the advection-dispersion equation (ADE) to the \(^{3}\)H\(_{2}\)O BTCs. A column experiment performed under sterile conditions indicated (i) absence of any significant source of abiotic 2,4-D degradation,
and (ii) no significant irreversible sorption of 2,4-D to the test soil. Under nonsterile conditions, relative $^{14}$C-2,4-D effluent concentrations ($C_s$) reached steady state at values lower than one ($0.063 - 0.92$), indicating microbial 2,4-D degradation. The observed BTCs could not be described by a transport model (ADE) including logistic growth kinetics, since logistic growth generally precludes the establishment of steady state degradation conditions. We then predicted the 2,4-D breakthrough in the soil columns using the ADE including first-order degradation kinetics with batch-derived degradation rate constants ($\mu_{ib}$). Predicted 2,4-D BTCs accurately reflected (i) the development of steady-state $C_s$ values and (ii) the general effects of column RT on the position of $C_s$, where increasing column RT resulted in decreasing $C_s$. However, a single batch-determined $\mu_{ib}$ did not accurately describe 2,4-D degradation for all column conditions. Column-specific first-order degradation rate constants ($\mu_{is}$) were calculated from observed $C_s$ values using an analytical solution to the ADE. Calculated values of $\mu_{is}$ varied by about one order of magnitude ($0.007 - 0.071 \text{ h}^{-1}$) across the eight different nonsterile column conditions. The variation in $\mu_{is}$ could not be explained by variations in column RTs. However, the relationship between values of $\mu_{is}$ and pore water velocities ($v$) showed that $\mu_{is}$ values remained relatively low at $v$ above $1 \text{ cm h}^{-1}$, but increased sharply at $v$ below $1 \text{ cm h}^{-1}$. Our results suggest that variations in $v$, rather than column RT, describe variations in 2,4-D degradation rate constants across a range of transport conditions. We hypothesize that apparent rate constants determined under transport conditions may be dependent on the solute residence time per unit length, which can be thought of as a local opportunity time. At sufficiently high pore water velocities, apparent
degradation rate constants decline because *local opportunity times* are too small relative to times required for the sequence of elementary reactions describing microbial degradation. It should be noted that increasing $\nu$ may also cause an increase in mass transfer rates, e.g., an increase in 2,4-D desorption rates. This may lead to the hypothesis that increases in $\nu$ with resultant increases in diffusion controlled desorption rates may actually increase degradation rates during transport. Our results of the effects of pore water velocity on 2,4-D degradation rates are better described by the *local opportunity times* hypothesis.
REFERENCES CITED


