In situ measurements and LEACHM predictions of the transport and fate of nonreactive tracers and dicamba in a silt loam Montana soil

by Robert John Pearson

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Soils
Montana State University

Abstract:
Groundwater contamination by pesticides has been documented in thirty-eight states. Regionally, seven pesticides have been detected in Montana groundwater. Solute transport models such as LEACHM, PRZM and CMLS have become increasingly important tools for predicting the fate of chemicals applied to soils. Computer simulation models based on analytical solutions of the convective dispersion equation (CDE) have been developed to screen pesticides for their leaching potential, to screen soil mapping units for pesticide leaching potential, and to predict the fate of chemicals at specific locations. Despite growing interest in the application of solute transport models such as LEACHM for predicting chemical movement in soils, there have been relatively few studies conducted to test model performance under field conditions. Groundwater tracers used in validation studies differ in their suitability for studies of solute transport in soils. Bromide has long been accepted as a good soil water tracer, however Br has recently been shown to be absorbed by plants. Under these conditions Br mass would not remain constant in the soil profile. In situ transport studies involving fluorobenzoate tracers, bromide and 14C ring-labelled dicamba (3,6-dichloro-2-methoxybenzoic acid) were performed to evaluate tracer suitability, pesticide behavior and to validate the Leaching Estimation and Chemistry Model (LEACHM) under field conditions in a silt loam Montana soil. Prior to field work, a laboratory study was conducted to develop methodology for the analysis of fluorobenzoate tracers using an ion chromatograph (IC) equipped with an electrical conductivity detector. Two successive field studies were then conducted at a field site near Manhattan, MT during the summers of 1991 and 1992. Two treatments, fallow and crop (Hordeum vu/gare L.), over three different water regimes were established perpendicular to a single line source irrigation system. The IC methodology developed allowed for expedient analysis of fluorobenzoate tracers and Br Results of tracer evaluation indicated that significant plant uptake of Br occurred. Leaching of tracers and dicamba occurred to depths greater than 1.0 m. Dicamba's primary metabolite- 3,6-dichlorosalicylic acid (DCSA) was less mobile and persisted longer than dicamba LEACHM performed best under 1991 field conditions relative to 1992 field conditions. Evidence of preferential flow was greatest in the 1992 field data where decaying plant roots from the previous study possibly contributed to the discrepancies between predicted and observed data.

IN SITU MEASUREMENTS AND LEACHM PREDICTIONS OF THE TRANSPORT AND FATE OF NONREACTIVE TRACERS AND DICAMBA IN A SILT LOAM MONTANA SOIL

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APPROVAL

of a thesis submitted by

Robert John Pearson

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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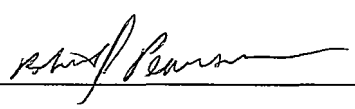
Signature 

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ABSTRACT

Groundwater contamination by pesticides has been documented in thirty-eight states. Regionally, seven pesticides have been detected in Montana groundwater. Solute transport models such as LEACHM, PRZM and CMLS have become increasingly important tools for predicting the fate of chemicals applied to soils. Computer simulation models based on analytical solutions of the convective dispersion equation (CDE) have been developed to screen pesticides for their leaching potential, to screen soil mapping units for pesticide leaching potential, and to predict the fate of chemicals at specific locations. Despite growing interest in the application of solute transport models such as LEACHM for predicting chemical movement in soils, there have been relatively few studies conducted to test model performance under field conditions. Groundwater tracers used in validation studies differ in their suitability for studies of solute transport in soils. Bromide has long been accepted as a good soil water tracer, however Br^- has recently been shown to be absorbed by plants. Under these conditions Br^- mass would not remain constant in the soil profile. *In situ* transport studies involving fluorobenzoate tracers, bromide and ^{14}C ring-labelled dicamba (3,6-dichloro-2-methoxybenzoic acid) were performed to evaluate tracer suitability, pesticide behavior and to validate the Leaching Estimation and Chemistry Model (LEACHM) under field conditions in a silt loam Montana soil. Prior to field work, a laboratory study was conducted to develop methodology for the analysis of fluorobenzoate tracers using an ion chromatograph (IC) equipped with an electrical conductivity detector. Two successive field studies were then conducted at a field site near Manhattan, MT during the summers of 1991 and 1992. Two treatments, fallow and crop (*Hordeum vulgare* L.), over three different water regimes were established perpendicular to a single line source irrigation system. The IC methodology developed allowed for expedient analysis of fluorobenzoate tracers and Br^-. Results of tracer evaluation indicated that significant plant uptake of Br^- occurred. Leaching of tracers and dicamba occurred to depths greater than 1.0 m. Dicamba's primary metabolite 3,6-dichlorosalicylic acid (DCSA) was less mobile and persisted longer than dicamba. LEACHM performed best under 1991 field conditions relative to 1992 field conditions. Evidence of preferential flow was greatest in the 1992 field data where decaying plant roots from the previous study possibly contributed to the discrepancies between predicted and observed data.

CHAPTER ONE

INTRODUCTION

Well water monitoring surveys conducted in Montana have detected several pesticides including aldicarb, atrazine, 2,4-D, dicamba, MCPA, picloram and simazine (Deluca et al., 1989; Clark, 1990). Migration of these pesticides into groundwaters has occurred presumably through normal agricultural management practices. Nationally, over 70 pesticides have been found in groundwater in 38 states with 17 pesticides detected at concentrations above health advisory limits (Ritter, 1990; Parsons and Witt, 1988). The presence of pesticides in groundwaters has increased concern about the role of agricultural practices in the degradation of water quality, and has resulted in the development of numerous predictive computer models for evaluating the movement of pesticides through soils.

Computer models such as CMLS (Nofziger and Hornsby, 1987), PRZM (Carsel et al., 1984), GLEAMS (Leonard et al., 1987) and LEACHM (Wagenet and Hutson, 1989) have been used in a variety of applications including educational tools, screening pesticides for their leaching potential, screening mapping units for leaching potential and for predicting absolute concentrations of pesticides as a function of soil depth and time. Of the currently used deterministic transport models, LEACHM contains numerous subroutines

necessary to couple water flow, heat flow, solute sorption, solute degradation and plant water uptake. As such, LEACHM requires an exhaustive set of input data on soil properties, solute properties, climate parameters and plant (crop) parameters. Generally, the required set of input parameters limits the use of LEACHM for research scale experimental plots; detailed site measurements cannot be obtained realistically for landscape or mapping unit scale applications. Recent access to digital soils and climate data bases (SCS, MAPS, Nielsen et al., 1990) coupled with pedotransfer functions (Rawls and Brackensick, 1989; Vereecken, et al., 1992) may be useful for screening soil mapping units for pesticide leaching potential. However, these efforts will require validation of transport model predictions within and between mapping units to determine the adequacy of transport predictions given different methods of obtaining input data. An important step in testing solute transport models under field conditions is a comparison of observed and predicted solute movement in controlled *in situ* experimental plots (e.g. research scale), where detailed measurements can be obtained for solute transport as a function of soil depth and time, and where input data can be obtained using independent estimates of soil, climate, chemical and plant input parameters.

Solute transport studies were conducted at a field site near Manhattan, MT (Gallatin Co. Sec. 20, T1N, R3E) in a Brocko silt loam during the summers of 1991 and 1992. Studies were conducted to evaluate the fate and transport of several tracers and dicamba and to test the predictive capabilities of

LEACHM under field conditions. Two fluorobenzoates, pentafluorobenzoic acid (PFBA) and 2,6-difluorobenzoic acid (2,6-DFBA) (Bowman, 1984a; 1984b; Bowman and Gibbens, 1992), were used as nonreactive tracers, and in one study, PFBA was compared to Br^- to evaluate differences in tracer performance under crop conditions where previous studies have shown that Br^- is susceptible to plant uptake.

Prior to our field work, a methodology study was conducted to develop analytical procedures for measuring fluorobenzoates simultaneously with Br^- using ion chromatography. The analytical procedure described in Chapter 2 is capable of analyzing aqueous solutions containing common soil anions (e.g. Cl^-, NO_3^-, SO_4^{2-}), orthotrifluoromethylbenzoic acid (*o*-TFMBA), 2,6-DFBA, PFBA, and Br^- using an ion chromatograph equipped with an electrical conductivity (EC) detector (Pearson et al., 1992).

The objectives of these studies were to i) monitor *in situ* transport and fate of several conservative tracers (Br^-, PFBA, 2,6-DFBA) and a commonly used herbicide (dicamba) in a silt loam Montana soil over varying soil water regimes, under both cropped (barley - *Hordeum vulgare* L.) and fallow (bare soil) management conditions and ii) evaluate the predictive capabilities of LEACHM (Wagenet and Hutson, 1989) given specific soil and climate input parameters for predicting the fate of these compounds under field conditions over varying soil water regimes.

CHAPTER TWO

ANALYSIS OF FLUOROBENZOATE TRACERS BY ION CHROMATOGRAPHY

Introduction

Pentafluorobenzoic acid (PFBA), 2,6 difluorobenzoic acid (2,6 DFBA), and orthotrifluoromethylbenzoic acid (O-TFMBA) are three fluorobenzoates that have recently been used as tracers to monitor soil water and solute movement in soil systems. These fluorobenzoates are typically analyzed by high-performance liquid chromatography (HPLC) - UV detection and have reported retention times ranging between 9 and 12.5 mins. Ion chromatography (IC) analysis of these fluorobenzoates using conductivity detection is possible and faster than the currently used HPLC methodology. This study demonstrates the reliability of IC for fluorobenzoate tracer analysis. Mixed and single standard solutions (0.10 to 25 mg L^{-1}) of PFBA, 2,6 DFBA, O-TFMBA and LiBr were prepared and analyzed using IC-conductivity detection. High resolution among all four tracers was achieved by the methodology presented. However, Cl interfered with O-TFMBA analysis even at low concentrations (1.0 mg Cl L^{-1}). Retention times of O-TFMBA, 2,6 DFBA, and PFBA by IC analysis ranged between 1.79 and 2.62 min with a linear detection response achieved over a 0.25 to 25 mg L^{-1} concentration range. These results indicate that IC analysis is an accurate and

expedient means of determining both single and multiple fluorobenzoate and Br concentrations in soil solutions and natural waters.

Chemical tracers are commonly used to monitor soil water and solute movement in the vadose zone. By definition, (Davis et al., 1980) an ideal soil water tracer should be nontoxic, inexpensive, move with the water front, and be easy to detect in trace amounts. In addition, a conservative tracer should not alter the natural direction of water flow; it should be chemically stable and should not be sorbed or filtered by the solid medium through which the water moves (Davis et al., 1980). For most laboratory and field experiments, halides have been traditionally used as soil water tracers. As an alternative to halides, Bowman (1984a) introduced the use of fluorobenzoates as tracers for solute transport studies. Young and Boggs (1990) found that the fluorobenzoates, pentafluorobenzoic acid (PFBA), 2,6 difluorobenzoic acid (2,6 DFBA), and orthotrifluoromethylbenzoic acid (O-TFMBA) had mobility characteristics similar to Br. Of the three fluorobenzoates, PFBA and 2,6 DFBA have shown the most promise by demonstrating long-term resistance to chemical and biological degradation in the environment (Bowman and Gibbens, 1991). The current methodology used for fluorobenzoate analysis employs high-performance liquid chromatography (HPLC) coupled with variable wavelength ultraviolet (UV) photometric detection (Bowman, 1984b). Analysis times of PFBA, 2,6 DFBA, and O-TFMBA by this methodology are between 9 and 12.5 mins (Bowman, 1984b).

The pKa's of PFBA, 2,6 DFBA and O-TFMBA range between 2.7 and 3.0 (Bowman and Gibbens, 1991). Consequently, these compounds are anionic at most soil pH's. The anionic nature of these fluorobenzoates allows for analysis by ion chromatography-conductivity detection using anion separator columns with low retention times.

The need for expedient analysis of soil solutions containing these fluorobenzoates prompted the development of a method employing ion chromatography where retention and sample analysis times were less than current HPLC methodologies.

Materials and Methods

Standard solutions of PFBA, 2,6 DFBA, 0-TFMBA (Aldrich Chemical Co., Milwaukee, WI) and LiBr (Morton Thiokol Inc., Danvers, MA) were prepared from high purity compounds (>98%). Individual and mixed solutions of these fluorobenzoates and Br were prepared gravimetrically by carefully weighing the salts on an analytical balance and dissolving them in double deionized H_2O. Solution concentrations included 0.10, 0.25, 0.50, 0.75, 1.0, 3.0, 5.0, 10, and 25 mg L^{-1}. Analyses were performed on a Dionex 4000i ion chromatograph (Dionex Corp., Sunnyvale, CA) using a Dionex AS4A column with an eluting solution of 0.85 mM $NaHCO_3$ and 0.90 mM Na_2CO_3. Electrical conductance detection levels used include: 3 μS (0.10, 0.25, 0.50, 0.75 mg L^{-1} standard solutions); 10 μS (1.0 mg L^{-1}); and 30 μS (3.0, 5.0, 10 and 25 mg

L^{-1}). Chromatochart-PC (Interactive Microware, Inc. State College, PA) was used to integrate peak areas. All analyses were performed in triplicate. Retention times of the tracers were first determined using individual standards. Once this was accomplished, mixed standards of all four tracers were analyzed and linear plots of relative peak areas verses concentrations were developed. A 50 μl sample loop was used for solution analyses. Resolution comparisons were also made using a 100 μl sample loop.

Results and Discussion

Retention times of the mixed organic tracers and Br standard by IC analysis were found to range between 1.79 and 3.20 mins and are significantly less than the HPLC retention times presented by Bowman (1984b) (Table 1). Retention times of each tracer by IC analysis were slightly less when analyses were performed on individual standards (10 mg L^{-1}) rather than mixed standards (10 mg L^{-1}). This difference in retention times varied by no more than 0.59 mins ($n = 3$).

Table 1. Retention times of mixed organic tracers and bromide standard (25 mg L^{-1}) using IC analysis and corresponding retention times using HPLC analysis.

Tracer	IC analysis retention time*	HPLC analysis retention time Bowman (1984b)
	min	min
O-TFMBA	1.79 (0.00)	10.4
2,6 DFBA	2.05 (0.00)	12.5
PFBA	2.62 (0.01)	9.0
Bromide	3.20 (0.01)	16.1

*Values in parentheses indicate sample standard deviation of mean (n = 3).

A mixed standard of Cl (1.0 mg L^{-1}) and 25 mg L^{-1} of Br, NO_3, and the three fluorobenzoates were analyzed by IC. Nitrate and Cl are commonly found in soil extracts and were added to the mixed tracer standard to demonstrate possible interferences. Ion chromatography analysis of the mixed standard indicated that high resolution among the four tracers was achieved by this methodology (Figure 1). Common soil anions that could be expected to interfere with tracer analysis included: Cl with O-TFMBA and NO_3 with Br. Other anions commonly found in soil solutions such as PO_4 and SO_4 are eluted after the NO_3 peak and will not interfere with tracer analysis. Nitrate interference with Br analysis is a common problem with HPLC analysis. The chromatograph illustrated in Figure 1 was generated using a Dionex AS4A column and demonstrates that NO_3 did not interfere with Br analysis at the concentrations injected (25 mg L^{-1}). Greater resolution between Br and NO_3

can be achieved using a Dionex AS9 column and may be useful for analyzing Br solutions that contain high NO_3 concentrations (data not presented). Although the AS9 column is useful for avoiding NO_3 interferences, it has longer retention times for the inorganic anions than the AS4A column. Chloride interference with O-TFMBA is a problem even at Cl concentrations of 1.0 mg L^{-1}. Resolution between Cl and O-TFMBA was not improved using the AS9 column (data not presented).

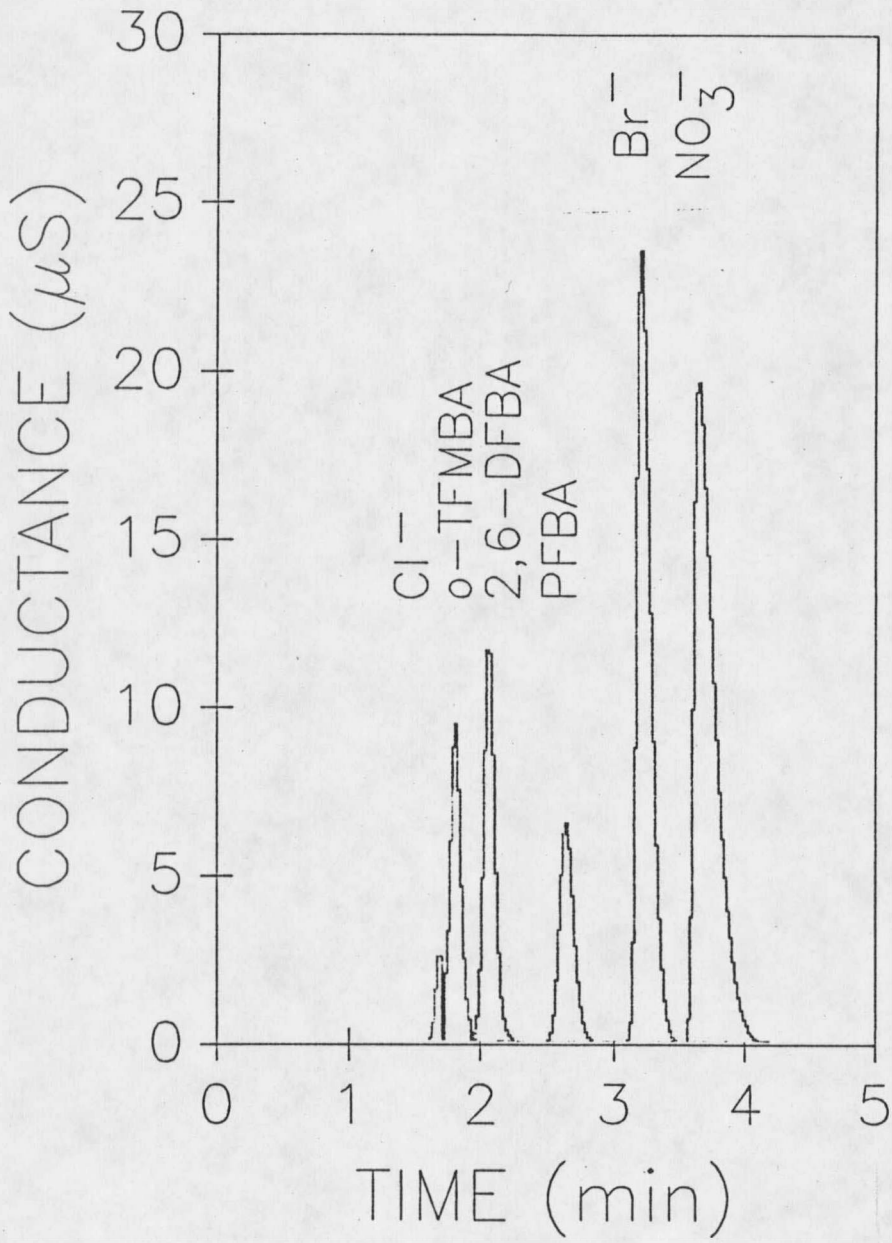

Figure 1. Mixed ion chromatograph of 3 fluorobenzoates, Br^- and NO_3, at 25.0 mg L^{-1} and Cl^- at 1.0 mg L^{-1} using an output range detection of 30 μS and an AS4A column.

As indicated by the chromatograph peak areas (Figure 1), and the slopes of the peak areas versus concentrations (Figure 2), the sensitivity of the IC conductivity detector (with respect to peak area) was roughly 30 to 40 % greater for Br than for the organic tracers (by mass). Comparisons of all peak resolutions between the 50 μL and 100 μL sample loops indicated no difference when the total mass injected into the column was constant (data not presented).

When the attenuation (conductance output range) was set to 3μS, peak areas of all fluorobenzoates and Br were reproducible by IC analysis at concentrations of 0.25 mg L^{-1}, but not 0.10 mg L^{-1}. However, by lowering the attenuation to 0.3 μS, peak areas of all tracers were reproducible at concentrations 0.025 mg L^{-1} (data not presented). Although a detection limit of 0.25 mg L^{-1} should suffice for tracer experiments, detection limits of 0.025 mg L^{-1} are attainable with careful analytical work and stable eluant baselines.

Plots of concentrations versus peak areas for the three organic tracers and Br were developed to portray the linearity of the IC analysis (Figure 2). The coefficient of determination (R^2) for relative peak area versus concentration (0.25 to 25 mg L^{-1}) of the fluorobenzoates and Br were all greater than 0.99. The results presented (Figure 2) illustrate the linearity of the IC detector over three attenuations (3, 10, and 30 μS). For greater accuracy, most analysts will want their standards to bracket their sample concentrations within one attenuation.

The influence of fluorobenzoates on seed germination and vegetative growth have not been previously reported. As a cautionary note to future users of fluorobenzoates on cropped experiments, we found that when PFBA (112 kg ha^{-1}) was applied in conjunction with KBr (37 kg Br ha^{-1}) in a field experiment, barley (Hordeum vulgare L.) growth was reduced by approximately 35% (observed at boot stage). We also observed in a laboratory experiment that barley seed germination was reduced in the presence of PFBA (112 kg ha^{-1}) and bromide (56 kg ha^{-1}) (unpublished data) but not in the sole presence of either PFBA (112 Kg ha^{-1}) or Br (56 kg ha^{-1}).

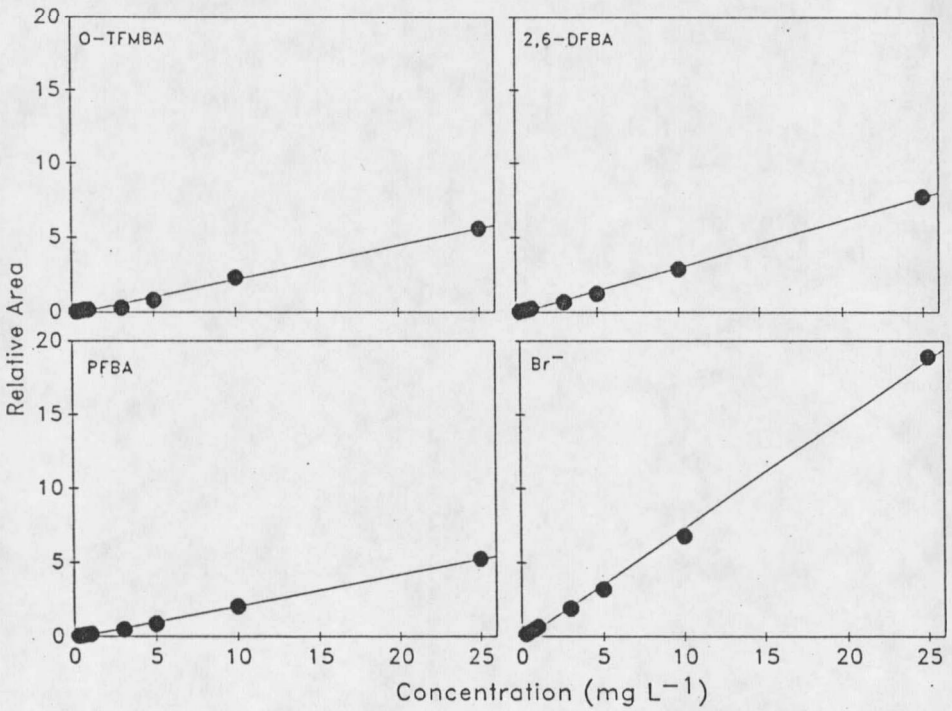

Figure 2. Relative peak areas of O-TFMBA, 2,6-DFBA, PFBA and Br^- versus concentrations using ion chromatography. Data points represent means of three replicates; all standard error bars fall within symbols.

In summary, the fluorobenzoates PFBA, 2,6 DFBA and O-TFMBA plus Br were successfully analyzed by ion chromatography using conductivity detection. The IC methodology presented, provides an expedient and accurate means of determining fluorobenzoate concentrations. Retention and sample analysis times were found to be less than currently used HPLC methodologies. These results support the use of the IC method presented for both single and multiple fluorobenzoate analysis of soil solutions and natural waters.

CHAPTER THREE

IN SITU MEASUREMENTS AND LEACHM PREDICTIONS OF THE TRANSPORT OF PENTAFLUOROBENZOIC ACID AND BROMIDE IN A MONTANA SILT LOAM SOIL

Introduction

Solute transport models such as LEACHM (Wagenet and Hutson; 1989) are becoming increasingly important tools for predicting the fate of chemicals applied to soils. Deterministic transport models based on analytical or numerical solutions of the convective dispersion equation (CDE) yield unique predictions for a given set of site specific soil, chemical, vegetation and climatic properties. Such models are being used for a variety of purposes including education, screening pesticides for leaching potential, screening soil mapping units for leaching potential, and predicting the fate of chemicals at specific locations. These models are also becoming popular with government agencies and environmental consulting firms for evaluating the fate of contaminants, and to support decisions regarding management practices which minimize the potential for leaching chemicals into shallow groundwater aquifers.

Despite growing interest in the application of solute transport models such as LEACHM for predicting chemical movement in soils, there have been relatively few studies designed to verify model performance under field

conditions. Results of previous field studies (Pennel et al., 1990; Soulsby and Reynolds, 1992; Comfort et al., 1993; Jabro et al., 1993) have shown mixed results. Pennel et al. (1990) found that simulation results of Br^- and aldicarb leaching for five models, including LEACHM, were similar. Based on a normalized objective function (NOF) data, these authors reported discrepancies of 30 to 45% between observed and predicted distribution of aldicarb and Br, and further stated that none of the models tested accurately predicted the distribution of Br and aldicarb in the soil profile. Jabro et al. (1993) compared movement of NO_3-N to LEACHM predictions (N subroutine) and noted that, despite calibration of model parameters to site specific soil conditions, the model did not accurately predict NO_3-N leaching at 1.2 m depth. Soulsby and Reynolds (1992) modeled soil water flux for an Al leaching study using LEACHM. They calibrated the model (i.e. optimized parameters such as K_s) using *in situ* tensiometer data, then compared model predictions against measured tensiometer data for the remainder of the year. Despite good convergence of simulated and measured matric potentials throughout their calibration period, LEACHM predicted greater summer drying than actually occurred and required further optimization of K_s. In all of these studies, poor model performance was thought to result in part from the inability of LEACHM to simulate preferential flow.

The criteria for evaluating the performance of solute transport models has been the subject of some debate. Pennel et al. (1990) suggested that the most

rigorous test of a model is a direct comparison of observed and predicted distribution of solute concentrations in the soil profile, and that pesticide simulation models should perform well enough to predict the center of solute mass and mass recoveries to within 50% of observed values. Smith et al. (1991) outlined Environmental Protection Agency (EPA) criteria for model acceptance. They noted that for screening applications with limited site-specific data and where model inputs have not been calibrated to the site, the model should be able to predict measured field data to within an order of magnitude. For site-specific applications where model calibration has been performed and on-site input parameters measured, the model should be able to match field data to within a factor of two. Smith et al. (1991) reported that the site specific criteria may be "too difficult to meet by even the best models using carefully measured site-specific parameters". Certainly, the predictive capability of deterministic models which do not accomodate preferential flow mechanisms may be limited to screening applications where such processes are important to water and chemical movement.

Ad hoc stochastic methods using deterministic models may be achieved by using confidence intervals of site-specific input parameters as representative of the inherent variability of soil properties within a given soil type. This approach was used by Comfort et al. (1993) in a field study of Br^- transport under varying water regimes. Values representing upper and lower confidence intervals for independently measured soil retention coefficients (Campbell's

(1974) equation) were used as inputs to LEACHM, and reasonable agreement between observed and predicted soil water contents and Br^- breakthrough curves (BTCs) was obtained. The study of Comfort et al. (1993) was conducted under fallow conditions on a spatially uniform loessal soil. The studies reported here (see also Chapter 4) for the 1991 and 1992 field seasons were conducted at the same site as those of Comfort et al. (1993), but were expanded to include transport of additional nonreactive tracers (fluorobenzoates) and dicamba under both fallow and cropped conditions, under several water regimes.

Although Br^- is widely considered as one of the best anionic nonreactive tracers (Davis et al., 1980), fluorobenzoates may be advantageous because their molecular weight and size is more similar to many organic solutes (Brusseau, 1993). Studies using fluorobenzoates (Bowman, 1984a; Bowman and Gibbens, 1992) have shown that pentafluorobenzoic acid (PFBA) and 2,6-difluorobenzoic acid (2,6-DFBA) are acceptable tracers for field studies. As these fluorobenzoates have pK_a values less than 3.0, they are anionic at most soil pH's. Results from a multiyear aquifer tracer test (Young and Boggs, 1990) indicate that PFBA and 2,6-DFBA behave essentially identically to Br^-. Results from a laboratory study (Bowman, 1984a) indicate that PFBA, 2,6-DFBA and Br^- behave similarly in repacked soil columns in the absence of plants. Although anion exclusion of nonreactive anionic tracers (Biggar and Nielsen, 1962; Thomas and Swoboda, 1970; Smith and Davis, 1974) may introduce

some discrepancy between water and solute movement (depending on soil type), a more important problem may be uptake of nonreactive tracers by plants. The uptake of Br^- has been reported for potatoes (*Solanum tuberosum* L.), orchardgrass (*Dactylis glomerata* L.) and Kentucky bluegrass (*Poa pratensis* L.) during Br^- transport experiments (Kung, 1990; Owen et al., 1985). If significant plant uptake of a tracer occurs, the mass of tracer in the soil volume is not constant, and if not accounted for, resulting changes in the shape of solute breakthrough curves (BTCs) may translate to erroneous interpretations of transport parameters. In addition, significant redistribution of tracer within the soil profile as a result of plant cycling can be especially problematic for long term tracer studies. Data from our laboratory has shown significant uptake of Br^- by barley with subsequent release to the soil surface near plant senescence (unpublished data, in preparation). Hydraulic lift of soil water by roots from deep soil layers to surface soils having lower water potential has been documented in several studies (Corak et al., 1987; Richards and Caldwell, 1987; Baker and van Bavel, 1986) and may represent an additional mechanism for the redistribution of tracers which are susceptible to plant uptake. To our knowledge, there is no information currently available on whether fluorobenzoate tracers are taken up by plants to the same extent as Br^-. Nonreactive tracers not susceptible to plant uptake would be particularly advantageous for solute transport studies under cropped or natural ecosystems.

Specific objectives of this study were to (i) compare *in situ* transport of Br^- and PFBA under cropped and fallow conditions over a range in soil water content and actual evapotranspiration, and (ii) evaluate the suitability of LEACHM using independent estimates of required input parameters for predicting solute movement over a wide range of environmental conditions. This study is the first of a two part series which is followed by an evaluation of observed and predicted transport of 2,6-difluorobenzoic acid (2,6-DFBA) and the herbicide, dicamba.

Materials and Methods

A field experiment was conducted during the summer of 1991 to study *in situ* transport of nonreactive tracers under cropped (*Hordeum vulgare* L.) and fallow conditions at three different water regimes. Twenty-four PVC columns (0.20 m diameter, 1.22 m depth) were installed in a Brocko silt loam (Borollic Calciorthid) at a field site near Manhattan, MT (Gallatin Co. Section 20, Township 1°N Range 3°E) (Table 2) using a hydraulic post pounder. The PVC columns were fitted with steel or Al cutting heads to facilitate column insertion and to prevent soil compaction. Each column was equipped with three ceramic suction cup lysimeters (6 mm diam. X 80 mm length, air entry value -100 kP, Soil Moisture Equipment Corp., Santa Barbara, CA) at 0.36, 0.66 and 0.96 m soil depths. Each lysimeter was installed horizontally through the column wall by drilling a hole and removing a soil core of equal dimension to the sample cup. A slurry of silica flour was injected into the hole prior to inserting the

ceramic lysimeters to ensure maximum soil-ceramic contact. The suction cup lysimeters were attached to polypropylene tubing equipped with quick release couplers at the soil surface for solution sampling using dual port vacuum collection vials (20 ml).

The columns were arranged in three rows of eight columns per row parallel to a line source irrigation system (Hanks et al., 1976), at distances of 1.5, 5.1 and 8.5 m, to establish decreasing soil water regimes (high, medium and low). Cropped and fallow treatments were imposed perpendicular to the line source irrigation system, resulting in four replications per water regime per cropped/fallow treatment. Adjacent fallow and crop treatments were separated by a 2 m fallow border and 2 m crop border.

The crop treatments were seeded to barley (*Hordeum vulgare* L., cv. Klages) on May 24, 1991. On June 10, seventeen days after seeding, tracer solutions (100 ml) were applied uniformly to the surface of each column using an eyedropper. PFBA was applied at a rate of 112 kg ha^{-1} to all columns and KBr at a rate of 37 kg $Br^{-}ha^{-1}$ to only the crop columns. Bromide was not applied to the fallow columns because they had previously been used to study Br^{-} transport during the summer of 1990 (Comfort et al., 1993) and may have contained some residual Br^{-}.

Table 2. Profile characterization data of Brocko silt loam.

Soil depth	Bulk density	AEV†	BCAM†	K_s	pH (1:1H_2O)	Organic matter	Sand	Silt	Clay
--m--	--Mg m^{-3}--	--kPa--	mm d^{-1}			g Kg^{-1}	------%------		
0.00-0.06	1.23	-1.65 (.311)‡	4.64 (.227)	124(7.91)	8.1	15.0	24	56	20
0.06-0.14	1.29	-4.63 (.655)	3.87 (.192)						
0.14-0.30	1.22	-2.70 (.270)	4.37 (.130)	377(94.0)	ND§	11.7	18	62	20
0.30-0.60	1.25	-9.72 (1.98)	1.65 (.157)	825(96.6)	ND	4.0	22	67	11
0.60-0.80	1.31	-9.60 (1.69)	1.63 (.134)	585(229)	ND	1.3	27	65	8
0.80-1.12	1.32	-6.55 (.688)	1.83 (.077)						

† AEV and BCAM determined by fitting the Campbell equation $h = AEV(\theta v/\theta sat)^{-BCAM}$ to soil water release data using nonlinear regression (θv determined at h values of 2.0, 5.0, 10.0, 20.0, 30.0, 50.0, 75.0 and 100 kPa).
‡ Standard errors in parenthesis.
§ ND = Not determined.

Water was applied nine times over a 59-day period following chemical application (Table 3). Seven irrigations were applied with the line source system, followed by two manual applications resulting in a total of 51.6, 42.0 and 31.1 cm of applied water (precipitation plus irrigation) for the high, medium and low water regimes, respectively.

Soil water contents (θv, m^3m^{-3}) were measured throughout the experiment using a neutron moisture meter (CPN Corp., Martinez, CA), calibrated at this field site for converting neutron probe readings to volumetric water content ($r^2=0.95$). Probe readings were taken adjacent to the *in situ* soil columns at 0.2, 0.4, 0.6, 0.8 and 1.0 m soil depths, with 2 replications for fallow and 3 replications for crop treatments for each water regime. Bare soil evaporation was measured in July over two independent wetting-drying cycles (5 replications per cycle) using 0.1 m diam by 0.2 m length minilysimeters (Lascano and Van Bavel, 1986).

Sample Analysis

Soil solution samples were collected 20 times during the 59-day period following chemical application, by vacuum extraction using a Cenco vacuum pump (Central Scientific Co., Chicago, IL) attached to the dual port collection vials (described previously). Minimal soil solution (approximately 3 ml) was collected from each lysimeter during sampling, while providing adequate volume for ion chromatography analysis. To prevent contamination between sample dates, the first 1 ml collected was discarded and new vials were used to collect

the fresh samples. Soil solution samples were analyzed for PFBA and Br^- using a Dionex 4000i ion chromatograph equipped with an AS4A column (Dionex Corp., Sunnyvale, CA) (Pearson et al., 1992).

Whole plant samples from the cropped columns were collected following the final soil solution sampling event, at Feekes growth stage 11.4 (Large, 1954). These were dried, weighed, ground and extracted using 25 mL 0.1M $NaNO_3$ per gram dry matter (Abdalla and Lear, 1975). The extracts were analyzed for Br^- using an ion-specific electrode (model 9435BN, Orion Research Inc., Boston, MA), calibrated with Br^- standards in a background matrix of extracting solution.

Concentrations of PFBA and/or Br^- were plotted as functions of time for each lysimeter depth (0.36, 0.66 and 0.96 m) to establish breakthrough curves (BTCs) for each chemical. Moment analysis (Skopp, 1984) of complete BTCs (primarily the 0.36 and 0.66 m depths) was used to estimate centers of mass (d), dispersion coefficients ($cm^2\ d^{-1}$) and mean pore water velocities ($mm\ d^{-1}$). Average θv values from each lysimeter depth were used to estimate mean soil water fluxes ($mm\ d^{-1}$) and total water fluxes (mm) over the 59 d experiment. The mass of PFBA and Br^- moving through the 0.36 and 0.66 m depths was then calculated based on the total water flux and individually measured PFBA and Br^- concentrations. Percent recoveries for each chemical were calculated based on the fraction of applied chemical mass measured in the BTC at each lysimeter depth.

Table 3. 1991 Precipitation-irrigation and evaporation data used in LEACHM simulations.

Date†		Precipitation-irrigation‡						Evaporation	
		Fallow			Crop				
		High	Medium	Low	High	Medium	Low	Week	Weekly pan
			---mm---			---mm---			---mm---
10 June	(0)	22.5	21.4	13.0	22.5	21.4	13.0	1	45.5
14 June	(4)	1.0	1.0	1.0	1.0	1.0	1.0	2	48.3
19 June	(9)	62.9	50.5	33.5	58.9	49.7	34.0	3	32.0
22 June	(12)	1.0	1.0	1.0	1.0	1.0	1.0	4	46.0
23 June	(13)	1.0	1.0	1.0	1.0	1.0	1.0	5	64.5
25 June	(15)	81.9	61.5	41.6	71.8	58.8	40.0	6	53.1
27 June	(17)	2.0	2.0	2.0	2.0	2.0	2.0	7	64.8
28 June	(18)	2.0	2.0	2.0	2.0	2.0	2.0	8	53.3
30 June	(20)	4.0	4.0	4.0	4.0	4.0	4.0	9	47.5
2 July	(22)	62.7	45.7	39.7	51.8	42.1	35.1	10	53.3
4 July	(24)	1.0	1.0	1.0	1.0	1.0	1.0		
10 July	(30)	2.0	2.0	2.0	2.0	2.0	2.0		
11 July	(31)	1.0	1.0	1.0	1.0	1.0	1.0		
15 July	(35)	65.9	50.8	42.3	56.9	45.7	43.6		
19 July	(39)	33.0	25.2	17.6	28.8	19.0	16.8		
20 July	(40)	60.2	53.8	43.2	58.3	49.3	42.3		
25 July	(45)	3.0	3.0	3.0	3.0	3.0	3.0		
29 July	(49)	64.5	52.1	32.5	64.5	52.1	32.5		
1 August	(52)	1.0	1.0	1.0	1.0	1.0	1.0		
5 August	(56)	63.5	51.1	31.5	63.5	51.1	31.5		
Total		536.1	431.1	313.9	496.0	408.2	307.8		508.3

† Values in parentheses indicate days after chemical application; dates are all 1991.

‡ Rates of irrigation used for simulations were calculated based on actual application time. An average precipitation rate of 60 mm d^{-1} was used for all precipitation events.

LEACHM simulations

Predicted BTCs for PFBA and Br^- were generated using the LEACHP subroutine in LEACHM (version 2, Wagenet and Hutson, 1989) using independent measurements or estimates of chemical, soil, climate and plant parameters (Tables 2, 3, 4). The source code array dimensions were modified to accommodate a greater number of depth nodes (56 nodes were used in our simulations). Soil physical parameters including bulk density, saturated hydraulic conductivity (K_s), and $\psi(\theta)\psi$-θv relationships were determined as functions of soil depth using 4 replicate intact cores. Volumetric water contents (θv) were determined at pressures of 2, 5, 10, 20, 30, 50, 75 and 100 kPa by placing intact soil cores in Tempe cells (SoilMoisture Equip. Corp., Santa Barbara, CA). The resultant soil water release data were fit to Campbell's (1974) equation using nonlinear regression to obtain the air entry value (AEV) and exponent coefficient (BCAM) for model input (Table 2). The crop cover factor was estimated at 0.95 for the site, and the physiological maturity as defined by LEACHM was assumed to correspond to the booting stage, which occurred 58 d after seeding (41 d after chemical application). The uptake of nonreactive tracer (PFBA or Br^-) by plants was prohibited in the LEACHM simulations.

Table 4. Physical, chemical and crop input parameters used in LEACHM simulations.

Input parameter	Unit	Value
Profile depth	mm	1120
Segment thickness	mm	20
Boundary condition†		
Molecular diffusion coefficients‡§		
Do	$mm^2\ d^{-1}$	0.01
DIFFA		0.001
DIFFB		10.0
Dispersivity	mm	3.2
PFBA and Br^- properties¶		
Solubility	$mg\ L^{-1}$	9.8×10^5
Vapor density	$mg\ L^{-1}$	0.0
$K_{oc.}$	$L\ kg^{-1}$	0.0
Degradation constant	d^{-1}	0.0
Application rate	$mg\ m^{-2}$	
PFBA		11200
Br		3700
Crop inputs		
Crop cover		0.95
Date of physiological maturity#	d	58

† Boundary condition 2 = unit gradient drainage.
‡ From Bresler (1973).
§ Do: molecular diffusion coefficient in aqueous solution; DIFFA, DIFFB: constants a and b, respectively, in $D_p = D_o\ a \exp(b\theta)$, where D_p is the effective diffusion coefficient.
¶ K_{oc}: organic C distribution coefficient.
# Expressed as days after seeding. Equivalent to 41 days after chemical application.

Results and Discussion

Observed PFBA Transport

Travel times required to detect initial solute fronts for PFBA (i) increased with soil depth under a given water regime, and (ii) increased with decreasing water application at a given soil depth (Figures 3, 4). Under fallow conditions, the leading edges of PFBA BTCs were detected within 8, 11 and 18 d at 0.36 m, within 17, 25 and 40 d at 0.66 m, and within 25, 40 and 51 d at 0.96 m, for the high, medium and low water regimes, respectively (Figure 3). The travel times required to detect PFBA solute fronts at 0.36 m under high and medium water regimes were essentially identical under the cropped treatment (Figure 4). However, for the majority of BTCs at other depths and for the low water regime, slower and more disperse PFBA breakthrough occurred under cropped compared to fallow conditions. For example, under the low water regime, PFBA solute fronts were detected at 0.36 m within 23 d for the crop treatment compared to 18 d for the fallow treatment. In addition, PFBA remained at 0.36 m for considerably greater duration under cropped vs fallow conditions (Figures 3, 4). Travel times required to detect PFBA solute fronts were generally higher for the cropped treatments at 0.66 and 0.96 m. For example, under the high water regime, PFBA solute fronts were detected at 0.96 m within 46 d for the crop treatment compared to 25 d for the fallow treatment. These observations suggest first that greater water use by the crop (ET) relative to fallow conditions (E) generally resulted in delayed PFBA transport and broader PFBA

BTCs. Secondly, effects of transpiration on solute transport were not significant at 0.36 m under high and medium water regimes because water application for these treatments far exceeded root water uptake early in the growing season during the time when PFBA was moving into the 0.36 m depth. Generally, the effects of root water uptake on solute transport were most significant at the lower depths (0.66 and 0.96 m) and under the low water regime. Although no PFBA was detected at 0.66 m under cropped conditions under the low water regime, several samples (between 29 and 43 d after chemical application) could not be obtained due to the unavailability of soil water. Also, soil solution samples could not be obtained at 0.96 m where soil water contents dropped below 0.15 (Figure 6).

Moment analysis (Skopp, 1984) was performed on those BTCs where solute mass returned to near baseline levels by 60 d after chemical application. Centers of mass (d) increased with increasing soil depth or with decreasing water application (Table 5). Under the high water regime, centers of mass (d) were significantly lower for fallow versus crop conditions at both the 0.36 and 0.66 m depths. Although this is consistent with the effects of crop water use on solute movement, the same trend was not observed under the medium water regime, where centers of mass were essentially identical for crop versus fallow conditions at both the 0.36 and 0.66 m depths.

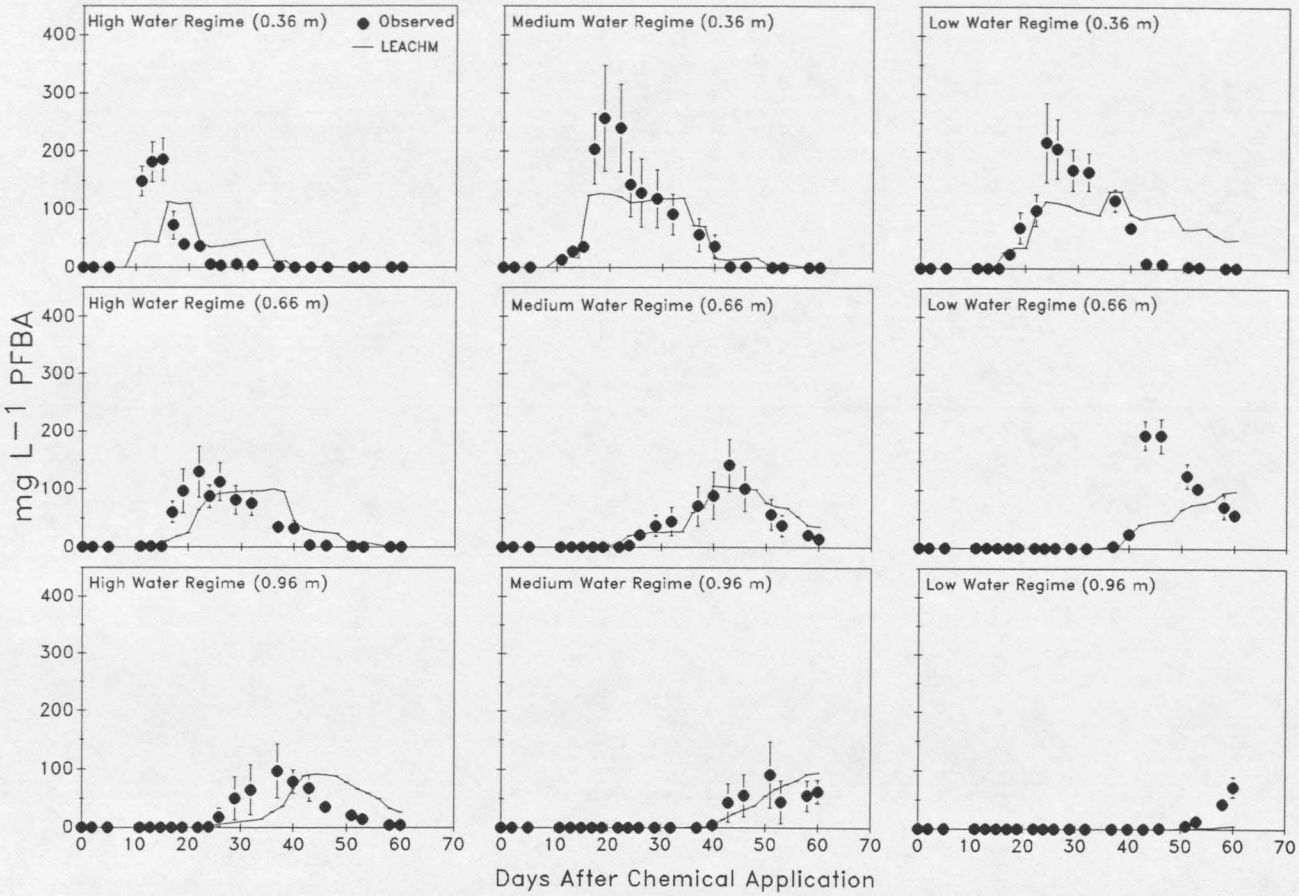

Fig. 3. Observed and simulated PFBA concentrations at 0.36, 0.66 and 0.96 m depths under high, medium and low water regimes for fallow treatments. Vertical bars on symbols (observed data) indicate standard errors (n = 4), where absent, bars fall within symbols.

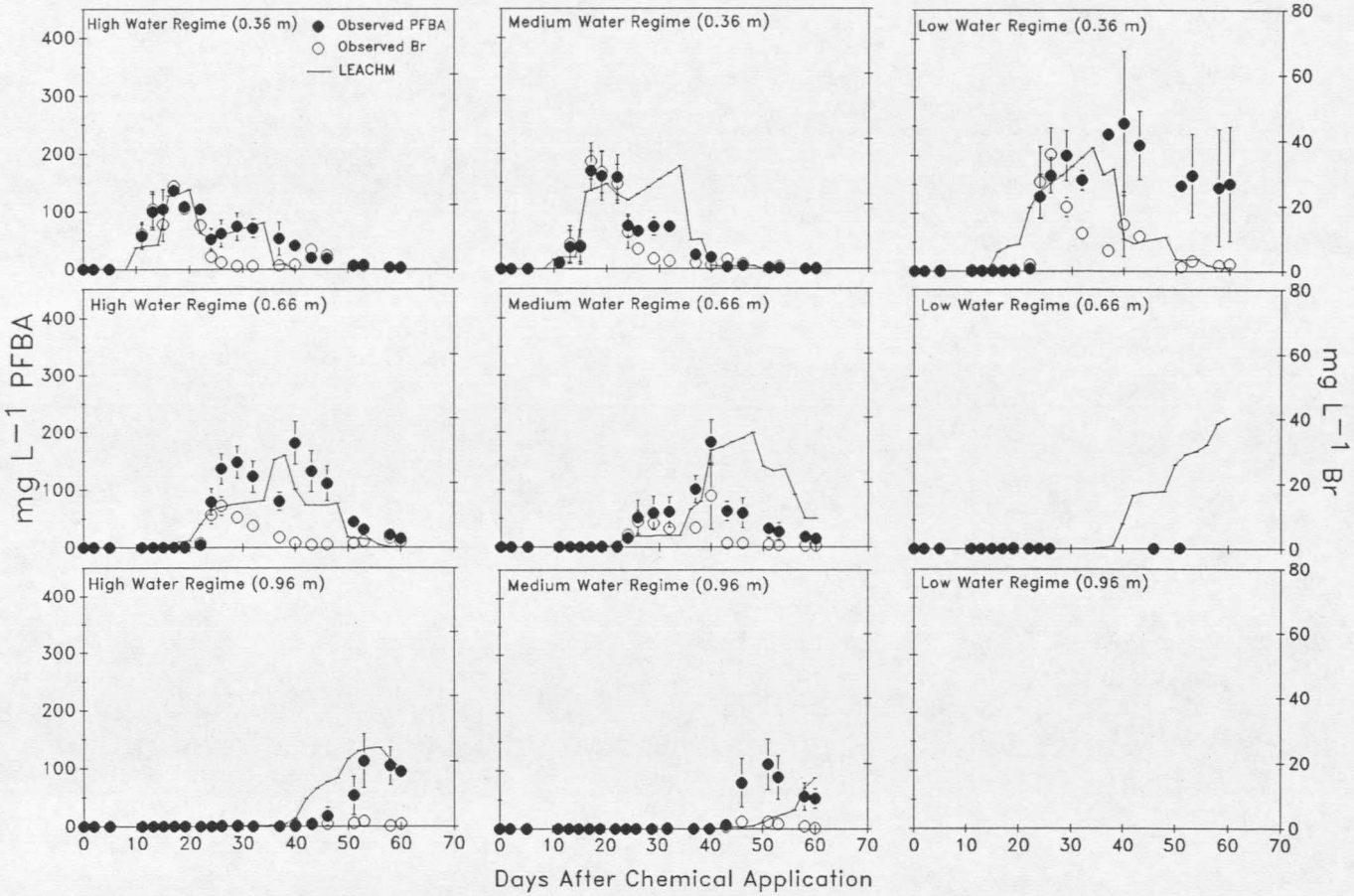

Fig. 4. Observed and simulated PFBA and Br^- concentrations at 0.36, 0.66 and 0.96 m depths under high, medium and low water regimes for crop treatments. Vertical bars on symbols (observed data) indicate standard errors (n = 4), where absent, bars fall within symbols.

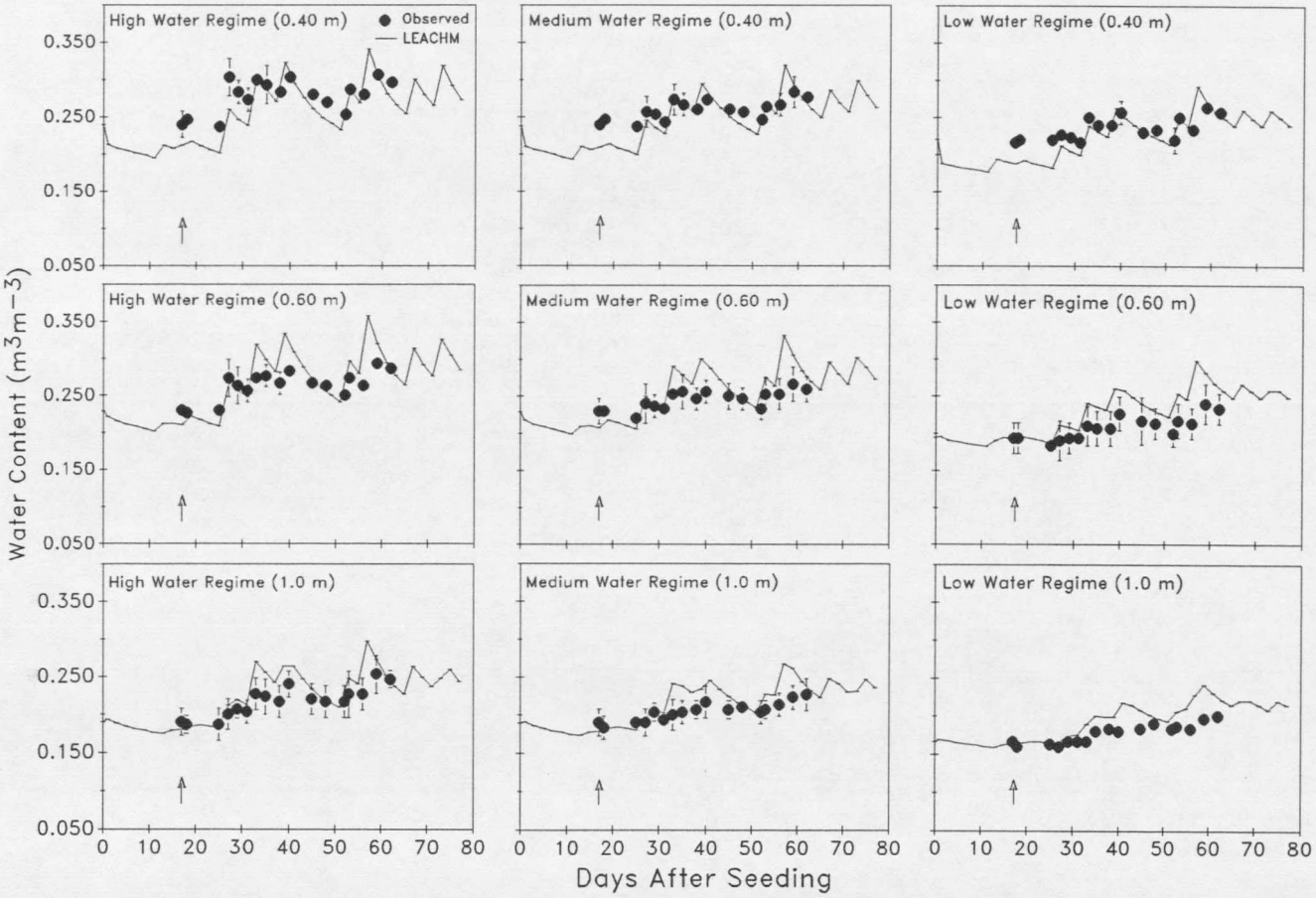

Figure 5. Observed and simulated soil volumetric water contents at 0.40, 0.60 and 1.0 m depths under high, medium and low water regimes for fallow treatments. ↑ indicates day of chemical application. Vertical bars on symbols (observed data) indicate standard errors (n = 2), where absent, bars fall within symbols.

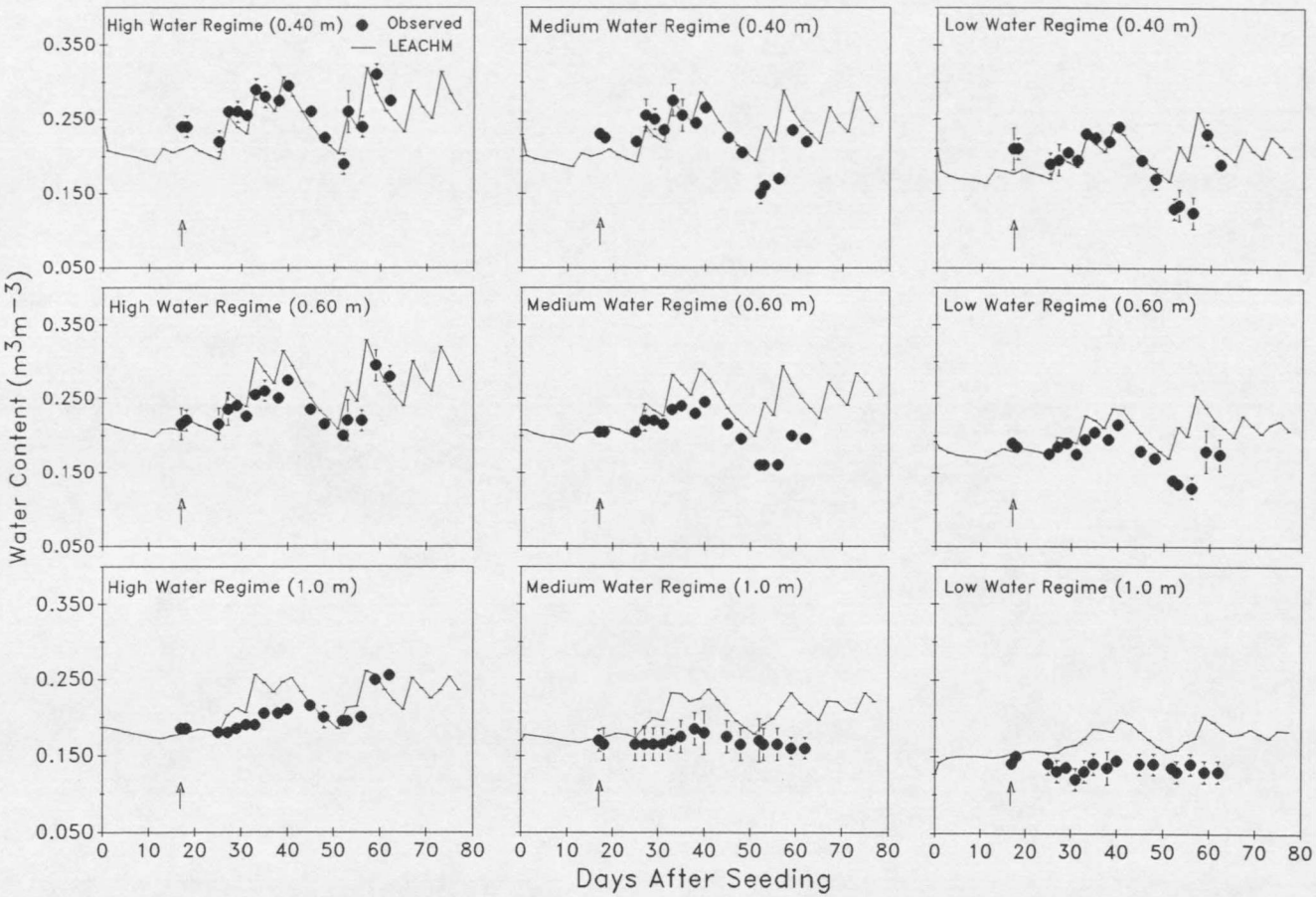

Figure 6. Observed and simulated soil volumetric water contents at 0.40, 0.60 and 1.0 m depths under high, medium and low water regimes for crop treatments. ↑ indicates day of chemical application. Vertical bars on symbols (observed data) indicate standard errors (n = 3), where absent, bars fall within symbols.

Table 5. Moment analysis results based on selected† observed and predicted PFBA and Br breakthrough curves.

Soil Depth(m)	Water Regime	Treatment	Center of mass(d) Observed PFBA	Observed Br	LEACHM PFBA	D(cm^2d^{-1})§ PFBA	D Br	Recovery(%) PFBA	Br
0.36	High	Fallow	14.1	ND‡	21.5	4.74	ND	116.2	ND
		Crop	24.8	16.6	22.5	4.93	2.92	86.8	27.4
	Medium	Fallow	24.4	ND	27.0	2.17	ND	101.5	ND
		Crop	24.0	20.6	26.0	2.70	2.30	65.0	22.6
	Low	Fallow	29.6	ND	37.2	1.06	ND	67.0	ND
0.66	High	Fallow	26.8	ND	32.3	5.27	ND	91.9	ND
		Crop	37.6	29.0	36.2	3.12	2.08	120.5	14.3
	Medium	Fallow	42.3	ND	43.8	1.67	ND	63.1	ND
		Crop	39.3	34.3	45.5	2.26	2.08	63.5	11.9
0.96	High	Fallow	38.7	ND	46.2	1.06	ND	61.3	ND

† Values from truncated breakthrough curves do not represent true moments and are not presented.

‡ ND = Not determined - Br was not applied to fallow treatments.

§ D = dispersion coefficient.

Observed Br^- Transport and Plant Uptake

Bromide was applied only to the cropped treatments (Figure 4) during the present study, because fallow columns had received a Br^- application during the previous field season (Comfort et al., 1993). Travel times required to detect initial solute fronts for Br^- were essentially identical to PFBA for all water regimes and for all depths where solute was detected. However, Br^- BTCs at 0.36 and 0.66 m consistently showed a loss of Br^- relative to PFBA (Figure 4), beginning 25 to 30 d after chemical application (42 to 47 d after seeding). By this time, barley was at Feekes growth stage 10 (Large, 1954) and would likely have developed a functional root system to depths > 0.66 m (Borg and Grimes, 1986; Reid, 1985). Observed θv's for the crop and fallow treatments were similar at 0.4 and 0.6 m for any given water regime up to approximately 40 to 45 d after seeding (23 to 28 d after chemical application). After this time, observed θv's at 0.4 and 0.6 m for the crop treatments declined significantly relative to the fallow treatment (Figures 5, 6), indicating root water uptake. The onset of significant crop water use at these depths corresponded to the time (± 2 d) when soil solution Br^- began to decline relative to PFBA. By the time PFBA reached 0.96 m under the high and medium water regimes (45 d after chemical application and 62 d after seeding), Br^- concentrations had declined significantly to near background levels, and Br^- BTCs were essentially nonexistent. Interestingly, soil solution Br^- reappeared several days after the original Br^- BTCs reached baseline levels for several treatments (e.g. high water,

0.36 and 0.66 m and medium water, 0.36 m). The reason for this observation is not completely understood, but may relate to Br^- cycling via plant roots. The differential response of PFBA and Br^- BTCs under cropped conditions observed in this study suggests that PFBA may not be taken up by plants to the same degree as Br^-, and may thus be a more suitable tracer in the presence of plants.

Further evidence of differential Br^- uptake by barley relative to PFBA was obtained using moment analysis (Skopp, 1984) of the solute BTCs in the crop treatments (Table 5). As mentioned previously, PFBA and Br^- BTCs were similar up to approximately 25 d after chemical application, after which Br concentrations declined significantly relative to PFBA (Figure 4). These changes in the shape of the BTC are reflected in the estimated centers of mass, dispersion coefficients, and the calculated percent recoveries of applied chemical detected under the solute BTCs obtained with moment analysis. Centers of mass (d) for Br^- BTCs were consistently lower than PFBA BTCs due to the more rapid decline of Br^- BTCs. In addition, dispersion coefficients at a given depth and water regime were lower for Br^- compared to PFBA, again due to the earlier decline of Br^- BTCs. Moreover, the percent recoveries of Br^- calculated based on moment analysis ranged from 23 to 27 % at 0.36 m, and from 12 to 14 percent at 0.66 m. The decline in Br^- recovery with increasing soil depth (and time) is consistent with the expected effects of increased cumulative plant uptake of Br^- with respect to time. More importantly, the Br^- recoveries were significantly lower than calculated recoveries of 63 to 120 %

for PFBA BTCs under crop conditions. There appeared to be no significant difference in PFBA recoveries under crop versus fallow conditions. Although percent recoveries calculated from moment analysis are subject to some uncertainty due to the sensitivity of the calculation to variable solute concentrations (e.g. see error bars in Figure 4), it is clear that Br^- recoveries were significantly lower than PFBA. This is consistent with the hypothesis that Br^- is taken up by plants to a much greater degree than PFBA.

Concentrations of Br^- in plant tissue were measured at harvest (Feekes growth stage 11.4, Large, 1954) and ranged from 1.52 to 1.22 g Br^-kg^{-1} for the high to low water regimes (Table 6). Concentrations of plant tissue Br^- were converted to total Br^- uptake per column using the measured dry matter produced per column. The total amount of applied Br^- recovered in plant tissue at harvest ranged from 24% for the high to 18 % for the low water regime, indicating that significant Br^- uptake occurred relative to the total mass of Br^- applied to the soil surface. Other studies at this same field site have demonstrated significant plant uptake of Br under cropped (*Hordeum vulgare* L.) conditions. We have found that as much as 85 to 95 % of applied Br^- (100 lbs $acre^{-1}$) was taken up by barley by physiological maturity. However, between physiological maturity and harvest, Br^- was lost from the above ground plant tissue and reappeared in the soil surface (0-6 cm). The measurements of Br^- uptake obtained in this study were only obtained at harvest because we could not afford a sequential loss of plant tissue (the *in situ* columns have an area of

298.65 cm^2). As a result, the percent recoveries of Br^- based on plant tissue analysis at harvest (Table 6) probably underestimated the amount of uptake which occurred earlier in the growing season when Br^- was moving through the soil profile. In fact, recoveries of soil solution Br^- estimated using moment analysis suggest that approximately 80 to 90 % of the applied Br^- may have been taken up by barley between 42 and 62 d after seeding (Feekes growth stage 10, Large, 1954), whereas only 18 to 23 % of applied Br^- was accounted for in the plant tissue at harvest. These observations are essentially identical to our previous measurements of Br^- uptake by barley with respect to plant growth stage obtained at the same site (unpublished data, in preparation). Finally, although the uptake of PFBA by barley was not measured directly, the peak concentrations of PFBA BTCs (Figures 3, 4) and total PFBA recoveries (Table 5) were similar under cropped vs fallow conditions. Consequently, our data suggests that PFBA was not subject to plant uptake to the same extent as Br^- and may therefore be a more suitable nonreactive tracer for transport studies under cropped conditions.

Table 6. Average Br^- concentrations in whole plant (*Hordeum vulgare* L.) tissue samples and percent of applied Br^- measured as plant uptake at harvest (Feekes growth stage = 11.4)‡

Water regime	g Br^-(kg plant)$^{-1}$ †	% Br^- Recovery in plant mass†
high	1.52 (0.41)	23.35 (3.06)
medium	1.36 (0.26)	20.89 (2.26)
low	1.22 (0.25)	17.99 (2.04)

† Standard errors in parenthesis (n=4).
‡ Large (1954).

LEACHM Predicted Soil Water Contents

A comparison of observed and LEACHM predicted and soil volumetric water contents as a function of soil depth and time is critical to understanding differences between observed and LEACHM predicted water and solute fluxes. Under fallow conditions, predicted and observed θv values were in reasonable agreement for all depths (0.4 to 1.0 m) throughout the majority of the growing season (Figure 5). However, under cropped conditions, LEACHM predicted θv's were higher than observed in several cases (Figure 6). At 0.4 and 0.6 m, LEACHM predicted θv's were significantly higher than actual θv's from approximately 45 to 55 d after seeding (Feekes growth stage 10, Large, 1954). At 1.0 m, LEACHM predicted θv's were higher than observed during much of the growing season (Figure 6). Under cropped conditions, the root distribution function used in LEACHM plays an important role in determining predicted plant water uptake and subsequent water contents as a function of soil depth. The lack of agreement between predicted and observed θv's suggests that this root growth and distribution function may not have adequately predicted root water uptake by the barley crop. As expected, LEACHM predicted cumulative evaporation plus transpiration was higher for crop versus fallow conditions (Table 7). However, predicted plant water uptake was heavily weighted within profile depths < 0.8 m. Roughly 57% of plant water uptake was predicted to occur from depths < 0.4 m and 98% from profile depths < 0.8 m. Insufficient simulated water uptake may explain the higher LEACHM predicted θv values relative to observed, especially at the 1.0 m depth.

Table 7. Observed and predicted water budget components from time of chemical application (t=0) to final sampling event (t=59).

	Treatment					
	Fallow			Crop		
	Water regime					
	High	Medium	Low	High	Medium	Low
Observed			-----mm-----			
Soil profile (t=0)	248	245	222	242	235	205
Cumulative precip./ irrigation	536	431	314	496	408	308
Cumulative drainage†	322	230	173	252	208	102
LEACHM						
Soil profile (t=0)‡	237	235	222	232	227	209
Final profile (t=59)	318	306	279	311	292	247
Cumulative Evap.	184	178	93	54	54	50
Cumulative Trans.	0	0	0	183	184	185
Cumulative drainage	271	182	164	180	106	34

† Observed drainage calculations based on moment analysis from observed PFBA breakthrough curves.

‡ LEACHM soil profiles at time of chemical application (t=0) differ from observed profiles at this same date due to the fact that LEACHM runs were initiated at time of planting (17 days prior to chemical application).

LEACHM uses a root growth function based on corn in the midwest (Davidson et al., 1978), where a maximum rooting depth of 1 m was obtained by 86 d after seeding. Cereal crops grown in our region generally have a much shorter growing season and maximum rooting depths to > 1 m. Thus the mid and lower soil profile would likely experience plant water uptake sooner than predicted from the Davidson et al. (1978) model, and to a greater depth. Although this would potentially explain the lower observed soil water contents deep in the profile, one might also expect predicted water flow to be greater than observed due to higher conductivity with increased soil wetness. However, the LEACHM predicted drainage component was far less than

calculated using moment analysis of the solute BTCs. Several additional factors other than the root distribution function may be important in explaining deviations between observed and predicted soil water contents and drainage components. First, soil retention coefficients (Campbell's equation) used to predict $K(\theta)$ play a critical role in determining water flux and the availability of soil water for plant uptake within any given soil layer. Higher predicted θv's suggest that the soil water retention function or our measured input coefficients overpredicted the water holding capacity of a portion of the soil profile. This would help explain why the drainage component predicted using LEACHM was less than that calculated using moment analysis. Second, it is important to note that the drainage component calculated using moment analysis is based on solute BTCs. Any preferential water or solute flow which may have occurred in the field is implicit in this estimate, whereas LEACHM does not currently incorporate preferential flow mechanisms.

Deviation in predicted and observed θv values at lower profile depths (0.4 to 1.0 m) do not appear to be related to problems with predicted surface evaporation. Evaporation from the soil surface plays an important role in determining θv values in the 0 to 0.2 m zone, and on subsequent water availability for transport deeper into the soil profile. Evaporation from bare soil was measured using minilysimeters (Lascano and van Bavel, 1986) over two independent wetting-drying cycles, and showed excellent agreement with LEACHM predicted evaporation (Figure 7). Consequently, predicted evaporation

does not appear to be a source of error between observed and predicted soil water contents. Sensitivity analyses of LEACHM inputs indicated that changes in coefficients of Campbell's equation (BCAM and AEV), K_s, pan factor, and crop maturity date all influenced predicted θv values. It would have been possible to obtain predicted θv values which more closely matched observed values at lower profile depths by adjusting or fitting these parameters to the observed data. However, our objectives were to test predictions for transient water and solute flow under field conditions using a carefully measured set of input parameters determined *in situ* or using undisturbed soil cores. Moreover, any adjustments to the input parameters as required to improve agreement between observed and predicted θv at lower soil depths resulted in poorer agreement at other depths (0.4 and 0.6 m).

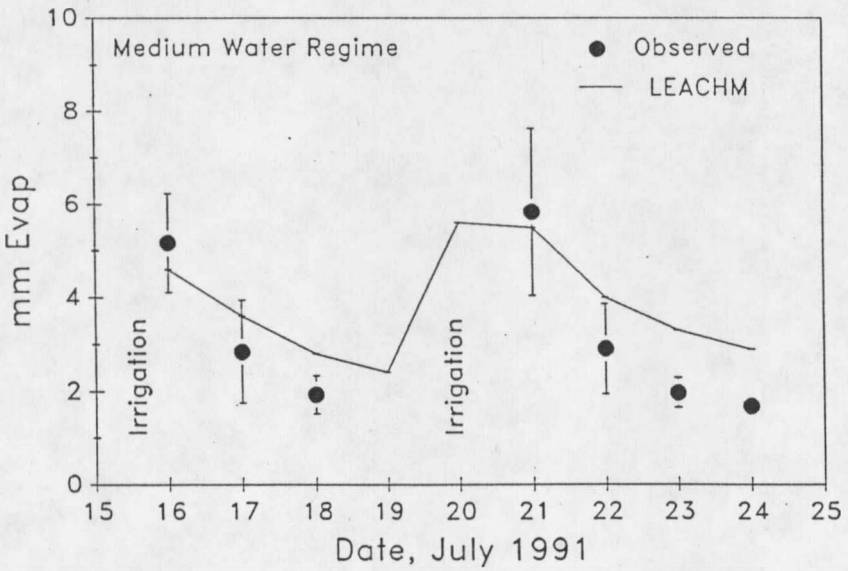

Figure 7. Observed and simulated daily surface evaporation from bare soil.

LEACHM Predicted BTCs

Predicted PFBA BTCs (equivalent to predicted Br^- BTCs) were close to observed BTCs in many cases (Figures 3 and 4). Under fallow conditions, predicted BTCs exhibited some shift to the right of observed BTCs for the high and low water regime. Centers of mass for observed and predicted PFBA BTCs (Table 5) were 14 and 22 d at 0.36 m, 27 and 32 d at 0.66 m, and 39 and 46 d at 0.96 m. Although greater preferential flow might be expected at higher θv values and under higher pore water velocity (Beven and Germann, 1982) no consistent trends were noted in our data for early solute breakthrough (relative to predicted) versus water application levels. Even the low water regime received approximately 30 cm of total water during the growing season, consequently, preferential flow may have been feasible in all of the water regimes studied. Under cropped conditions, predicted PFBA BTCs (Figure 4) and centers of mass (Table 5) were generally very close to observed values. No significant evidence of preferential flow was observed under crop conditions, perhaps with the exception of the 0.96 m depth under the medium water regime (Figure 4). In fact, LEACHM predicted BTCs were shifted to the left of observed BTCs in several cases. For example, in the low water regime, the observed PFBA BTC at 0.36 m shows signs of delay due to crop water use, whereas the LEACHM curve does not. At 0.66 m the LEACHM predicted BTC appears to be far ahead of any measurable PFBA. Finally, it should be noted that predicted PFBA BTCs were generated assuming no solute uptake by plants.

Visual inspection of observed and predicted BTCs under cropped conditions (Figure 4) shows that this appears to be a much better assumption for PFBA than for Br.

Conclusions

As expected, *in situ* measurements of the transport of PFBA (and Br^- under cropped conditions) demonstrated increasing solute travel times with increasing soil depth and decreasing water application. The presence of barley in the cropped treatments caused measurable delays in the transport of PFBA, especially under the low water regime where the total amount of applied water (31 cm) did not greatly exceed plant consumptive demand.

Independent estimates or measured values of soil, climate, and plant parameters were used as input data to the transport simulation model, LEACHM. Comparisons between measured and LEACHM predicted θv's at 0.4m and bare soil surface evaporation were generally in good agreement. Predicted θv's at lower profile depths (0.6 to 1.0m), particularly under cropped conditions, were often higher than measured values. This appears to be a result of inadequate assumptions in LEACHM concerning the root growth function, which influences the amount of predicted plant water uptake from a given soil layer. Predicted breakthrough curves (BTCs) and centers of mass (d) of the nonreactive tracer, PFBA, were generally in good agreement with measured values. Under cropped conditions, the transport of Br^- and PFBA was similar up to about 40d after seeding. After this time, Br^- BTCs showed a marked

decension relative to PFBA BTCs, as a result of plant uptake of Br^-. Consequently, our data suggest that PFBA is a more suitable *nonreactive*, conservative tracer than Br^-.

Validation of transport models under field conditions is necessary for verifying model predictive capabilities under a wide range of environmental conditions. LEACHM is a research oriented simulation model requiring extensive inputs. Our evaluation of LEACHM supports the use of this model based on the criteria presented by Pennel and others (1990), i.e., predicted centers of solute mass are within 50% of observed values. Furthermore, simulation results nearly met the EPA criteria for site specific, calibrated models where predicted profile concentrations are required to be within a factor of two, despite the fact that we did not attempt to calibrate LEACHM to our specific soil hydraulic conditions.

CHAPTER FOUR

IN SITU MEASUREMENTS AND LEACHM PREDICTIONS OF THE TRANSPORT AND FATE OF 2,6-DIFLUOROBENZOIC ACID AND DICAMBA IN A SILT LOAM MONTANA SOIL

Introduction

Pesticide leaching and subsequent contamination of groundwaters from land under agricultural production is becoming a significant national concern. Recent monitoring programs have detected over 70 pesticides in groundwaters of 38 states (Ritter, 1990; Parsons and Witt, 1988). In one of these surveys, 17 pesticides were detected at concentrations above health advisory limits. DeLuca et al. (1989) and Clark (1990) conducted well water monitoring surveys in agricultural areas in Montana and documented that several pesticides (including aldicarb, atrazine, 2,4-D, dicamba, MCPA, picloram and simazine) have migrated into shallow groundwaters, presumably through normal agricultural management practices.

Dicamba (3,6-dichloro-2-methoxybenzoic acid) is commonly used in Montana to control broadleaf weeds in small grain production systems and has been found in groundwater samples regionally (DeLuca et al., 1989). Dicamba has a pk_a of 1.95, is anionic at ambient soil pH's (Weber, 1977) and is highly soluble in water (6.5×10^3 mg L^{-1}) (Pesticide Manual - 9th ed., 1991).

Consequently, dicamba has a low affinity for soil colloids (Burnside and Lavy, 1966; Grover and Smith, 1974; Jury et al., 1987) and is considered highly mobile in most soils (Friesen, 1965; Grover, 1977; Scifres and Allen, 1973). Soil environmental conditions play a significant role in the fate and mobility of dicamba applied to soils. Degradation rates of dicamba in surface soils are generally fairly rapid with half-lives ranging from 13.5 to 45 days (Comfort et al., 1992; Krueger et al., 1991; Smith, 1974). The primary metabolite of dicamba degradation is 3,6-dichlorosalicylic acid (DCSA), which is more persistent and not nearly as mobile as the parent compound (Smith, 1973a; Smith, 1974). Consequently, the potential for dicamba to leach out of the rooting zone increases dramatically if soil conditions limit its degradation rate. Conditions which limit the degradation rate of dicamba in soils include low soil organic C content (Smith, 1973b), low soil temperature (Smith and Cullimore, 1974; Comfort et al., 1992), soil pH > 7.5 (Corbin and Upchurch, 1966) and high water application rate (Comfort et al., 1992). These conditions may result in the transport of dicamba out of the root zone and into shallow groundwaters. In a laboratory column and incubation study, Comfort et al. (1992) showed that transport and subsequent loss of dicamba out of soil columns could be substantially reduced by delaying water application, thus providing sufficient time for the formation of DCSA. The current study was designed in part to broaden our understanding of the fate of dicamba in field soils under a range of soil water and evapotranspiration conditions (i.e., crop vs. fallow).

In response to regional concerns about the potential mobility of broadleaf herbicides under irrigated conditions we have been studying the fate and mobility of 2,4-D and dicamba under different soil water regimes, under both laboratory (Comfort et al., 1992) and field conditions. In addition, we are interested in potential applications and limitations of solute transport modeling for indexing soil mapping units according to their susceptibility for pesticide leaching (Wilson et al., 1993). As part of an overall process to evaluate the suitability of transport models for predicting solute transport under field conditions at landscape scales, models should be tested against observed data using input data sets generated from different scales of observation. This study was conducted at a research plot scale using a fairly intensive set of independently measured model input parameters. The specific objectives of this study were to (i) monitor the transport and fate of dicamba and a nonsorbing, nondegrading tracer, 2,6-difluorobenzoic acid (2,6-DFBA) under fallow (bare soil) and cropped (barley - *Hordeum vulgare* L.) conditions and varying soil water regimes, and (ii) evaluate the suitability of LEACHM (Wagenet and Hutson, 1989) for predicting the fate of these compounds under field conditions, given specific soil and climate input parameters. This is the second of two manuscripts (see Chapter 3) which evaluate the transport of nonreactive tracers and dicamba over a range of applied water and evapotranspiration conditions.

Materials and Methods

Field study

A field experiment was conducted to study *in situ* transport of ^{14}C ring-labeled dicamba (Sigma Chemical Company, St. Louis, MO) and 2,6-difluorobenzoic acid (2,6-DFBA) (Aldrich Chemical Co., Milwaukee, WI) during the summer of 1992. Eighteen of the 24 PVC columns (0.20 m diameter, 1.22 m depth) described in the companion paper (Chapter 3) were used in the current study on a Brocko silt loam (Borillic Calciorthid) near Manhattan, MT (Gallatin Co. Sec 20, T1N, R3E). Three rows of six columns per row were positioned parallel to a line source irrigation system (Hanks et al., 1976) at distances of 1.5 and 5.1 and 8.5 m to establish decreasing soil water regimes (high, medium and low). Two treatments, crop (barley, *Hordeum vulgare* L.) and fallow, were imposed at each soil water regime, with three replications per treatment. The fallow treatment columns were installed in 1990 and had been previously used in Br^- and pentafluorobenzoic acid (PFBA) transport experiments. The crop treatment columns were originally installed in 1991 and had been previously used in PFBA and Br^- transport experiments under cropped conditions.

The crop treatments were seeded to barley (*Hordeum vulgare* L. - cv. Klages) on May 1, 1992. Solutions (100 ml) containing dicamba (^{14}C-ring labelled) and 2,6-DFBA (nonreactive tracer) were uniformly applied dropwise to the surface of each soil column on June 18, 1992 (48 d after crop treatments

were seeded). Dicamba was applied at a normal field application rate of 0.26 kg ha^{-1} (2.04 X 10^4 mCi ^{14}C kg^{-1}) and 2,6-DFBA at 112 kg ha^{-1}(Table 8). Dicamba was applied only to the high and medium water regime columns. Water was applied eight times to the experimental site over a period of 67 days following chemical application (Table 9). Six irrigations were made using the line source irrigation system plus two final applications by hand, resulting in a total water application (irrigation plus precipitation) of 40.6, 34.4, and 27.8 cm to the high, medium, and low water regimes, respectively. Soil solution samples were vacuum extracted 27 times during the experiment to monitor the transport of 2,6-DFBA and ^{14}C-dicamba. Minimum soil water was collected during each sampling event (approximately 3 to 5 ml per lysimeter) to minimize soil solution disturbance in the vicinity of the lysimeters.

Volumetric soil water contents (θ_v, m^3m^{-3}) were monitored at each sampling date by neutron attenuation using a Campbell hydroprobe (CPN Corp., Martinez, CA). A field calibration was used to convert neutron meter readings to volumetric water content ($r^2 = 0.94$). Probe readings were taken adjacent to the *in situ* soil columns at 0.2, 0.4, 0.6, 0.8 and 1.0 m depth increments with two replications for the fallow treatment and three replications for the cropped treatment at each water regime. Bare soil evaporation was measured using 10 cm dia. by 20 cm length minilysimeters (Lascano and van Bavel, 1986) in late July, 1992 over two independent wetting-drying cycles.

Table 8. Physical, chemical and crop input parameters used in LEACHM simulations.

Input parameter	Unit	Value
Profile depth	mm	1120
Segment thickness	mm	20
Boundary condition†		
Molecular diffusion coefficients‡§		
Do	$mm^2\ d^{-1}$	0.01
DIFFA		0.001
DIFFB		10.0
Dispersivity	mm	3.2
Chemical properties		
Solubility	$mg\ L^{-1}$	
Dicamba		6.5×10^3
DCSA		6.5×10^3
2,6-DFBA		9.8×10^5
Vapor density	$mg\ L^{-1}$	
Dicamba		4.1×10^{-4}
DCSA		4.1×10^{-4}
2,6-DFBA		0.0
K_{oc}¶	$L\ kg^{-1}$	
Dicamba		0.0
DCSA		5.0×10^2
2,6-DFBA		0.0
Degradation rate constant	d^{-1}	
Dicamba		5.1×10^{-2}
DCSA		1.7×10^{-2}
2,6-DFBA		0.0
Application rate	$mg\ m^{-2}$	
Dicamba		23.15
2,6-DFBA		11200
Crop inputs		
Crop cover		0.90
Date of physiological maturity#	d	70

† Boundary condition = 2 unit gradient drainage.

‡ From Bresler (1973).

§ Do: molecular diffusion coefficient in aqueous solution; DIFFA, DIFFB: constants a and b, respectively, in $D_p = D_o\, a \exp(b\theta)$, where D_p is the effective diffusion coefficient.

¶ K_{oc}: organic C partition coefficient.

Expressed as days after seeding. Equivalent to 22 days after chemical application.

Table 9. Precipitation-irrigation and evaporation data used in LEACHM simulations.

Date†		Precipitation-irrigation‡						Evaporation	
		Fallow			Crop				
		High	Medium	Low	High	Medium	Low	Week	Weekly pan§
		---mm---			---mm---				---mm---
18 June	(0)	20.5	17.7	9.7	20.7	17.0	9.9	1	48.2
23 June	(5)	44.3	33.4	22.1	41.9	33.5	23.3	2	35.2
24 June	(6)	1.0	1.0	1.0	1.0	1.0	1.0	3	38.2
25 June	(7)	2.0	2.0	2.0	2.0	2.0	2.0	4	35.8
1 July	(13)	1.0	1.0	1.0	1.0	1.0	1.0	5	38.6
2 July	(14)	14.0	14.0	14.0	14.0	14.0	14.0	6	53.2
3 July	(15)	1.0	1.0	1.0	1.0	1.0	1.0	7	55.4
4 July	(16)	2.0	2.0	2.0	2.0	2.0	2.0	8	52.8
5 July	(17)	1.0	1.0	1.0	1.0	1.0	1.0	9	53.6
6 July	(18)	12.0	12.0	12.0	12.0	12.0	12.0	10	38.3
7 July	(19)	33.9	26.5	17.9	32.6	24.4	17.1		
13 July	(25)	3.0	3.0	3.0	3.0	3.0	3.0		
14 July	(26)	42.0	35.8	25.0	35.7	33.6	24.0		
21 July	(33)	45.5	37.8	26.9	41.3	35.3	28.6		
23 July	(35)	4.0	4.0	4.0	4.0	4.0	4.0		
28 July	(40)	38.8	35.2	27.3	38.0	32.9	23.0		
11 Aug.	(54)	63.5	50.7	38.1	63.5	50.7	38.1		
19 Aug.	(60)	50.7	38.1	38.1	50.7	38.1	38.1		
21 Aug.	(62)	23.0	23.0	23.0	23.0	23.0	23.0		
22 Aug.	(65)	1.0	1.0	1.0	1.0	1.0	1.0		
23 Aug.	(66)	6.0	6.0	6.0	6.0	6.0	6.0		
24 Aug.	(67)	3.0	3.0	3.0	3.0	3.0	3.0		
Total		413.2	349.4	279.1	398.5	339.5	276.2		449.3

† Values in parentheses indicate days after chemical application; dates are all 1992.

‡ Rates of irrigation used for simulations were calculated based on actual application time. An average precipitation rate of 60 mm d^{-1} was used for all precipitation events.

§ Daily pan evaporation was collected on site from a Class A National Weather Service evaporation pan.

Sample Analysis

All soil solution samples were analyzed for total ^{14}C using a Packard 2200 CA liquid scintillation analyzer. Selected samples were analyzed for dicamba and metabolites using an HPLC equipped with a Lichrosorb RP-18 column (EM Science, Gibbstown, NJ) and Beckman model 171 radioisotope detector (Beckman Instruments Inc., Fullerton, CA). In all cases, soluble ^{14}C was identified as dicamba with no detectable levels of the principle metabolite, DCSA. All lysimeter samples were analyzed for 2,6-DFBA using ion chromatography - electrical conductivity detection (Dionex 4000i) with a Dionex AS4a column (Dionex Corp., Sunnyvale, CA) following the procedures outlined in Pearson et al. (1992).

On August 27, 1992 all soil columns were removed and later sectioned in 0.1 m depth increments. The soil was dried at 37°C, then ground to pass through a 2 mm sieve. A 1.0 g subsample from each 0.10 m depth increment was oxidized with a model OX300 Biological Oxidizer (Model OX300, R.J. Harvey Instrument Corp., Hillsdale, NJ) and analyzed for total ^{14}C using liquid scintillation analysis. In addition, selected samples based on the distribution of total ^{14}C with respect to soil depth were solvent extracted (Smith and Muir, 1980) to determine the amount of ^{14}C present as dicamba or secondary metabolites. The extracting solution contained 70% acetonitrile, 27% H_2O, and 3% glacial acetic acid. Fifty grams of soil were combined with 100 mls of extracting solution and were shaken for 12 hrs. After agitation, the suspension

was filtered and 50 mls of the filtrate were combined with 100 mls of 1*M* HCl and successive additions of 26 and 13 mls of methylene chloride (CH_2Cl_2). A separatory funnel was used to collect the CH_2Cl_2 fraction which was then evaporated to 1 ml. These solutions were analyzed using HPLC-radioisotope detection (described previously). Percent recoveries of spiked soil samples for dicamba and DCSA using this methodology were 86% and 47%, respectively.

Concentrations of ^{14}C-dicamba and 2,6-DFBA were plotted as functions of time for each lysimeter depth (0.36, 0.66 and 0.96 m) to establish breakthrough curves (BTCs) for each chemical. Moment analysis (Skopp, 1984) of complete BTCs (primarily the 0.36 and 0.66 m depths) was used to estimate centers of mass (d), dispersion coefficients (cm^2d^{-1}) and average pore water velocities (mm d^{-1}). Average θv values at each lysimeter depth were used to calculate average water fluxes (mm d^{-1}) and total water fluxes (mm) over the 67 day experiment. The mass of dicamba and 2,6-DFBA moving through the 0.36 and 0.66 m depths was then calculated based on the average total water flux and individually measured dicamba or 2,6-DFBA concentrations. Percent recoveries for each chemical were calculated based on the fraction of applied chemical mass measured in the BTC at each lysimeter depth.

LEACHM Simulations

Predicted BTCs for 2,6-DFBA and dicamba were generated using the LEACHP subroutine in LEACHM (version 2, Wagenet and Hutson, 1989) with independent measurements or estimates of chemical, soil, climate and plant

parameters (Tables 8, 9). Soil physical and hydraulic input parameters were described in detail in a companion paper (e.g. see Table 2, Chapter 3).

Batch adsorption studies were used to obtain independent estimates of K_{oc} for dicamba and its principle metabolite, DCSA. Duplicate soil suspensions (10 grams soil from 0 to 15 cm:10 mls H_2O) were spiked with ^{14}C ring labeled dicamba or DCSA at concentrations ranging from 0.24 to 2.25 mg L^{-1} (4.56 X 10^{-7} to 4.56 X 10^{-5}mCi ^{14}C ml^{-1}) and 0.01 to 0.70 mg L^{-1} (4.81 X 10^{-7} to 4.81 X 10^{-5}mCi ^{14}C ml^{-1}) for dicamba and DCSA, respectively. These concentration ranges bracketed the levels of dicamba and DCSA measured in lysimeter soil solutions during the field experiment. The soil suspensions were shaken for 48 hrs, then centrifuged at 2000 *g* for 15 min. A 1 ml aliquot of the supernatant solution was used to determine ^{14}C activity by liquid scintillation analysis (defined previously), and the amount of DCSA or dicamba sorbed was determined by difference between total added and that remaining in the supernatant. The amount of dicamba sorbed was not statistically different than 0 (i.e., K_{oc} = 0) over the range of dicamba levels investigated, while the sorption coefficient (K_{oc}) for DCSA was 504 L kg^{-1}.

First-order degradation rate constants for dicamba and DCSA for the soil surface horizons were estimated from previous batch studies in our laboratory (Comfort et al., 1992) and from published values (Smith, 1974; Krueger et al., 1991). Values of 0.051 d^{-1} ($t_{1/2}$ = 13.5 d) for dicamba and 0.017 ($t_{1/2}$ = 40 d) for DCSA were used for the soil surface horizon (0 to 30 cm). Degradation

rates of herbicides often decrease with soil depth as a result of reduced microbial numbers or microbial activity (Moorman and Harper, 1989; Pothuluri et al., 1990; Veeh and Inskeep, 1990). Rate constants for soil depths greater than 30 cm were calculated using an exponential decay function as outlined in Jury et al. (1987):

$$t_{1/2}(\text{depth}) = t_{1/2}(\text{surface})e^{\gamma(Z-L)}$$

where γ is a depth constant (1.5 m^{-1}), Z is depth to the ith layer and L is the depth of the surface layer. Although these are estimated values we have found that this function provides a reasonable estimate of the variation in 2,4-D degradation as a function of soil depth (Veeh and Inskeep, 1990) and the behavior of organic matter (which often relates to microbial activity) as a function of soil depth (Wilson et al., 1993).

Results and Discussion

Observed Dicamba and 2,6-DFBA Breakthrough Curves

As expected, travel times required to detect solute fronts for dicamba and 2,6-DFBA increased with increasing soil depth at all water regimes, under crop and fallow conditions (Figures 8 to 11). At a given sample depth, the travel time required to detect solute fronts generally increased with decreasing water application; this observation was most consistent for solute BTCs on the fallow treatments (Figures 8, 10). For example, dicamba fronts (Figure 8) were detected within 5 and 15 d at 0.36 m and within 26 and 39 d at 0.66 m for the high and medium water regimes, respectively (^{14}C-labeled dicamba was not

applied to the low water regime treatment). The leading edges of 2,6-DFBA BTCs were detected within 5, 13 and 22 d at 0.36 m and within 26, 36 and 57 d at 0.66 m for the high, medium and low water regimes, respectively (Figure 10). Under cropped conditions, very little difference in travel times was observed for solute BTCs under high and medium water regimes (Figures 9, 11), and travel times were significantly shorter at a given depth than under fallow conditions. For example, 2,6-DFBA and dicamba fronts were observed within 5 d at 0.36 m and at 22 d at 0.66 m for both the high and medium water regimes (Figures 9, 11). Even the 2,6-DFBA front for the low water regime at 0.36 m had a shorter travel time under crop (16 d) vs fallow (22 d) conditions.

Results from moment analysis (Skopp, 1984) are presented (Table 10) only for those solute BTCs where solute concentrations returned to near baseline levels by 67 d after chemical application (last day of lysimeter sampling). Estimated centers of mass (d) for dicamba and 2,6-DFBA BTCs ranged from 21 to 29 d at 0.36 m and 41 to 47 d at 0.66 m. Average centers of mass appear to be slightly greater for 2,6-DFBA than dicamba for all depths, water regimes and crop vs. fallow treatments. Measured K_{oc} values for dicamba for the surface (0 to 15 cm) layer were essentially 0 for this soil. Although it is assumed that K_{oc} values for 2,6-DFBA are also 0 based on other studies (Bowman, 1984a, 1984b; Bowman and Gibbens, 1992; Young and Boggs, 1990), it is possible that given such low sorption for dicamba, 2,6-DFBA may

be sorbed slightly more than dicamba. Dicamba and 2,6-DFBA BTCs consistently showed increasing centers of mass with decreasing water regimes for the fallow treatment (Table 10). However, for the cropped treatment, centers of mass are essentially identical at high and medium water regimes (i.e. 21 and 20.5 d for dicamba at 0.36 m, and 41.4 and 43 d for dicamba at 0.66 m under high and medium water regimes, respectively). Finally, 2,6-DFBA BTCs consistently showed lower centers of mass at a given depth and a given water regime under crop vs fallow conditions (Table 10).

Originally, we expected that the transport of dicamba and 2,6-DFBA would be delayed considerably under cropped conditions, similar to PFBA transport observed in our previous study (Pearson et al., this issue). However, despite higher evapotranspiration (ET) in crop treatments, dicamba and 2,6-DFBA transport was as fast, if not faster under crop conditions. Two factors may have been responsible for this observation. First, evaporation from the soil surface (0 to 15 cm) would likely be greater under fallow than crop conditions, allowing a greater fraction of applied water to move more deeply into the soil profile under crop conditions (discussed further in section on LEACHM predictions). Secondly, there may have been differences in temporally variable soil hydraulic properties related to differences in macroporosity between the crop and fallow columns. The Brocko silt loam was formed from loessal parent material and the spatial variability of soil properties at this field site is rather low. Soil water retention relationships for four replicate intact soil cores taken

near the *in situ* columns show fairly low variability; standard errors of the exponent in the Campbell equation were typically less than 10 percent (Table 2, Chapter 3). Consequently, it is highly unlikely that spatial variability would have coincidentally biased the *in situ* columns used for either the crop or fallow treatments. More importantly, the columns used for the fallow and crop treatments during this field season had slightly different management histories. The fallow columns were installed in 1990 and had been in fallow consecutively since then. The crop columns were installed in 1991 and had one year of barley prior to this study. Results from the previous study with PFBA transport (Chapter 3) showed no consistent evidence of any preferential water flow. However, decaying or active root channels might increase the potential for preferential solute movement in columns under crop conditions. Results from studies conducted by Meek et al. (1992) and Zins et al., (1991) have shown that the presence of alfalfa roots increase infiltration rates through soils. Beven and German (1982) suggested that preferential flow pathways are associated with live and decayed roots. Gish and Jury (1983) reported dispersivities of Cl transport through a sandy loam soil as influenced by dead wheat root systems. The dispersivities they observed were characteristic of dispersivities obtained in a "porous medium with significant flow occurring in large pores". In fact, moment analysis of our data showed that dispersion coefficients at 0.36 m for both 2,6-DFBA and dicamba were roughly 3 times higher in cropped than fallow columns (Table 10) for both the high and medium

water regimes. Given that the cropped and fallow columns were subjected to nearly identical water applications, one explanation for the observed increases in solute dispersion in the crop treatments is a greater heterogeneity of pore water velocities resulting from root channels.

Moment analysis was also used to estimate the percent of applied solute measured in individual solute BTCs (Table 10). Percent recoveries ranged from 91 to 150 % for 2,6-DFBA and from 42 to 117 % for dicamba over all treatments where analysis of complete BTCs was possible. Values greater than 100% are obviously not possible; given the variability of solute concentrations in replicate columns as functions of time (see error bars in Figures 8 to 11), estimated recoveries should not be considered absolute. However, the percent recoveries for 2,6-DFBA BTCs do suggest that the lysimeters adequately sampled the solute breakthrough at 0.36 and 0.66 m, and that significant bypass flow around the lysimeters did not occur. In addition, the fact that recoveries for dicamba were roughly 20 to 40% lower (average of 33%) than recoveries for 2,6-DFBA indicates that degradation of dicamba was occurring during transport.

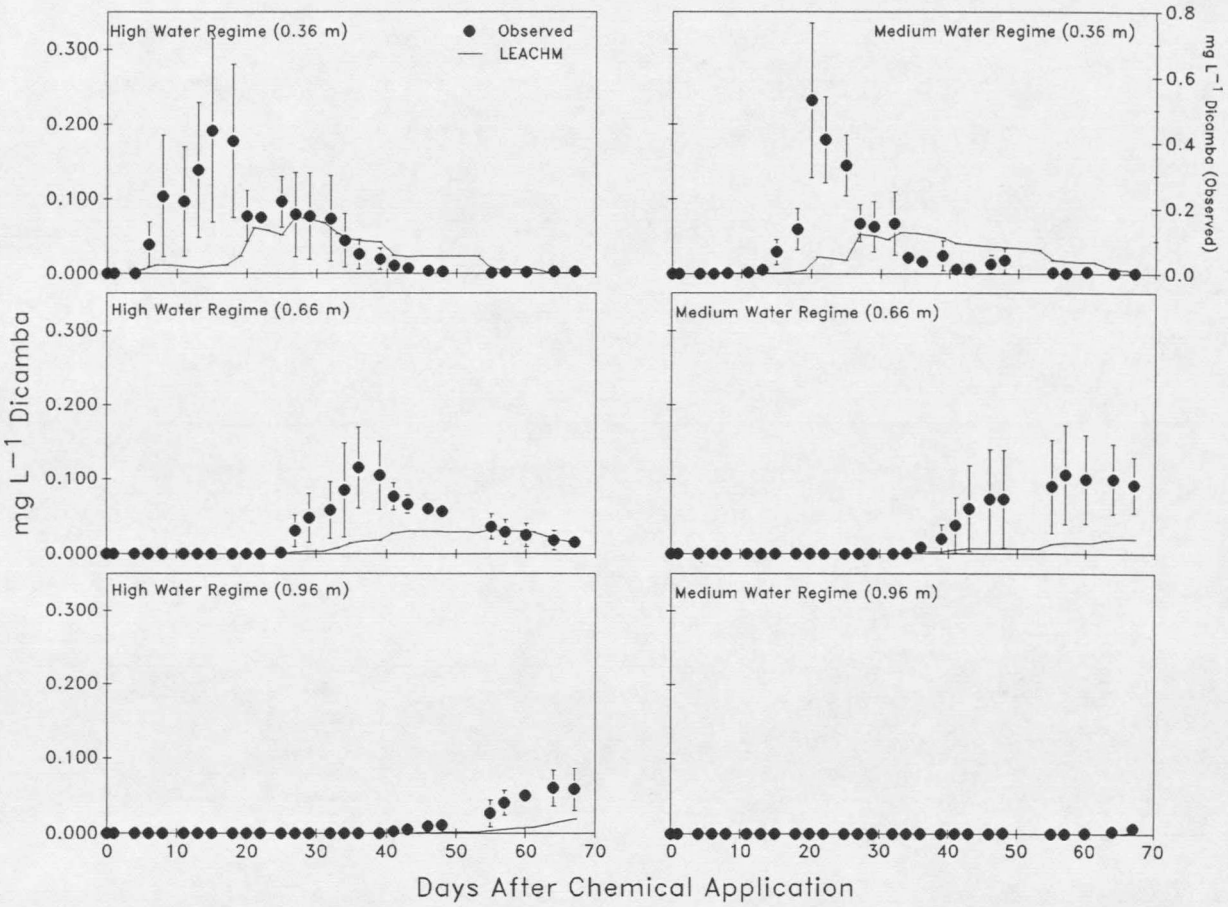

Fig. 8. Observed and simulated dicamba concentrations at 0.36, 0.66 and 0.96 m depths under high and medium water regimes for fallow treatments. Vertical bars on symbols (observed data) indicate standard errors (n = 3), where absent, bars fall within symbols.

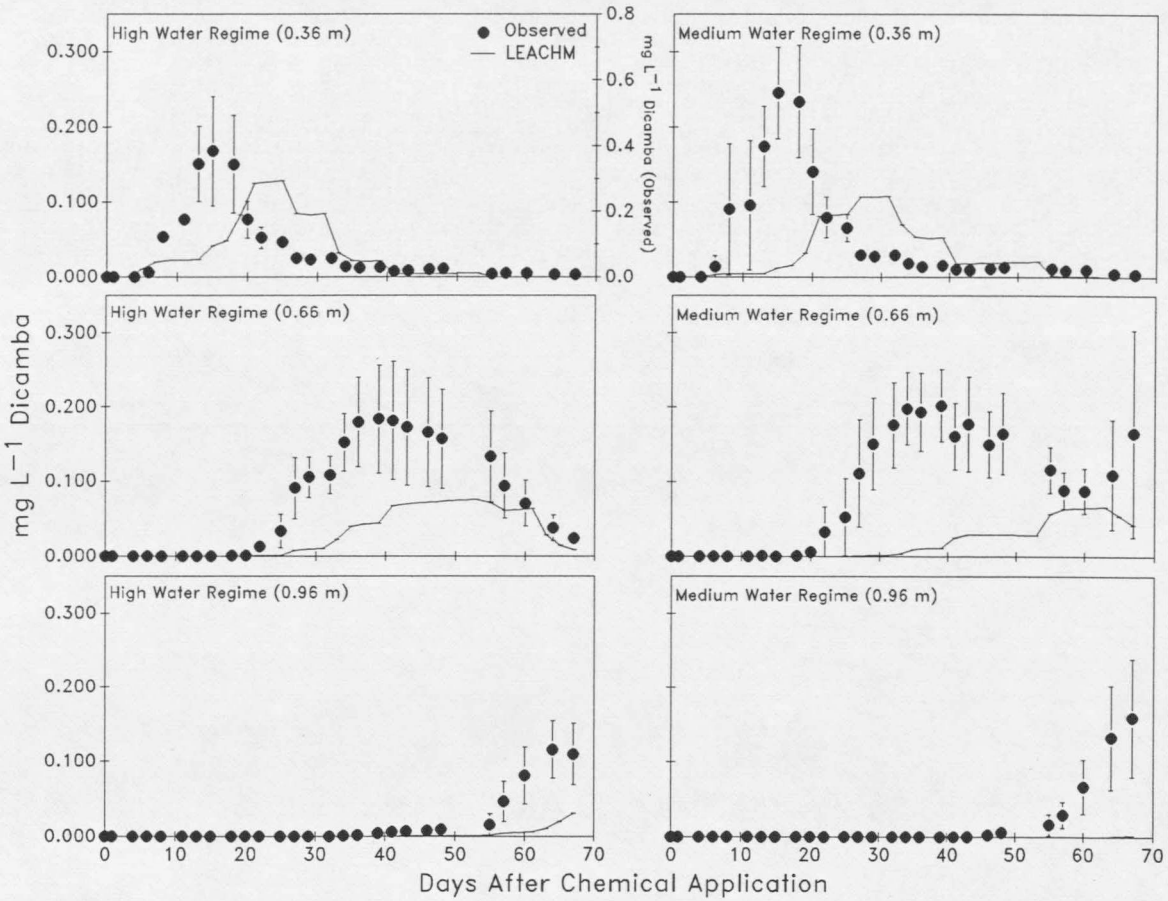

Fig. 9. Observed and simulated dicamba concentrations at 0.36, 0.66 and 0.96 m depths under high and medium water regimes for crop treatments. Vertical bars on symbols (observed data) indicate standard errors (n = 3), where absent, bars fall within symbols.

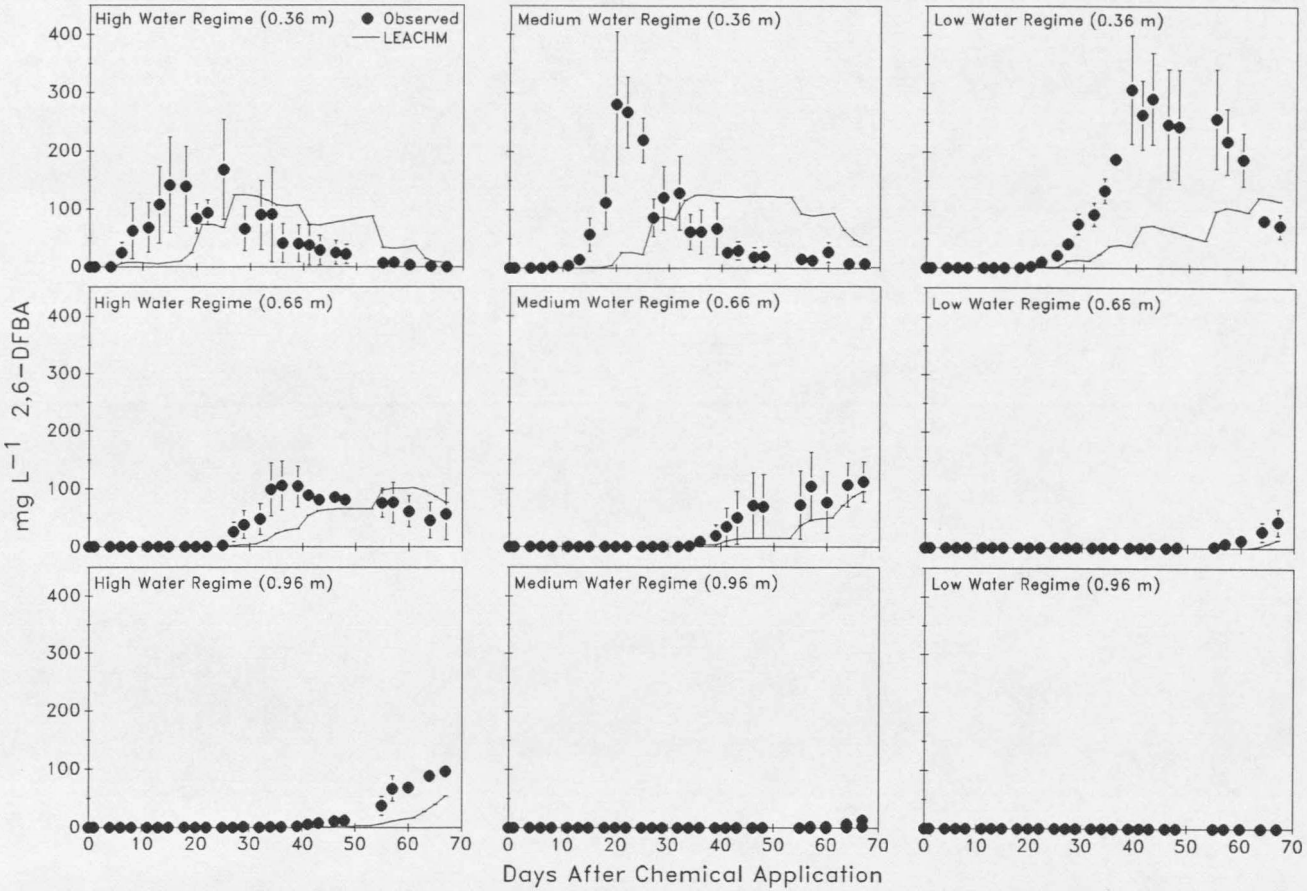

Fig. 10. Observed and simulated 2,6-DFBA concentrations at 0.36, 0.66 and 0.96 m depths under high, medium and low water regimes for fallow treatments. Vertical bars on symbols (observed data) indicate standard errors (n = 3), where absent, bars fall within symbols.

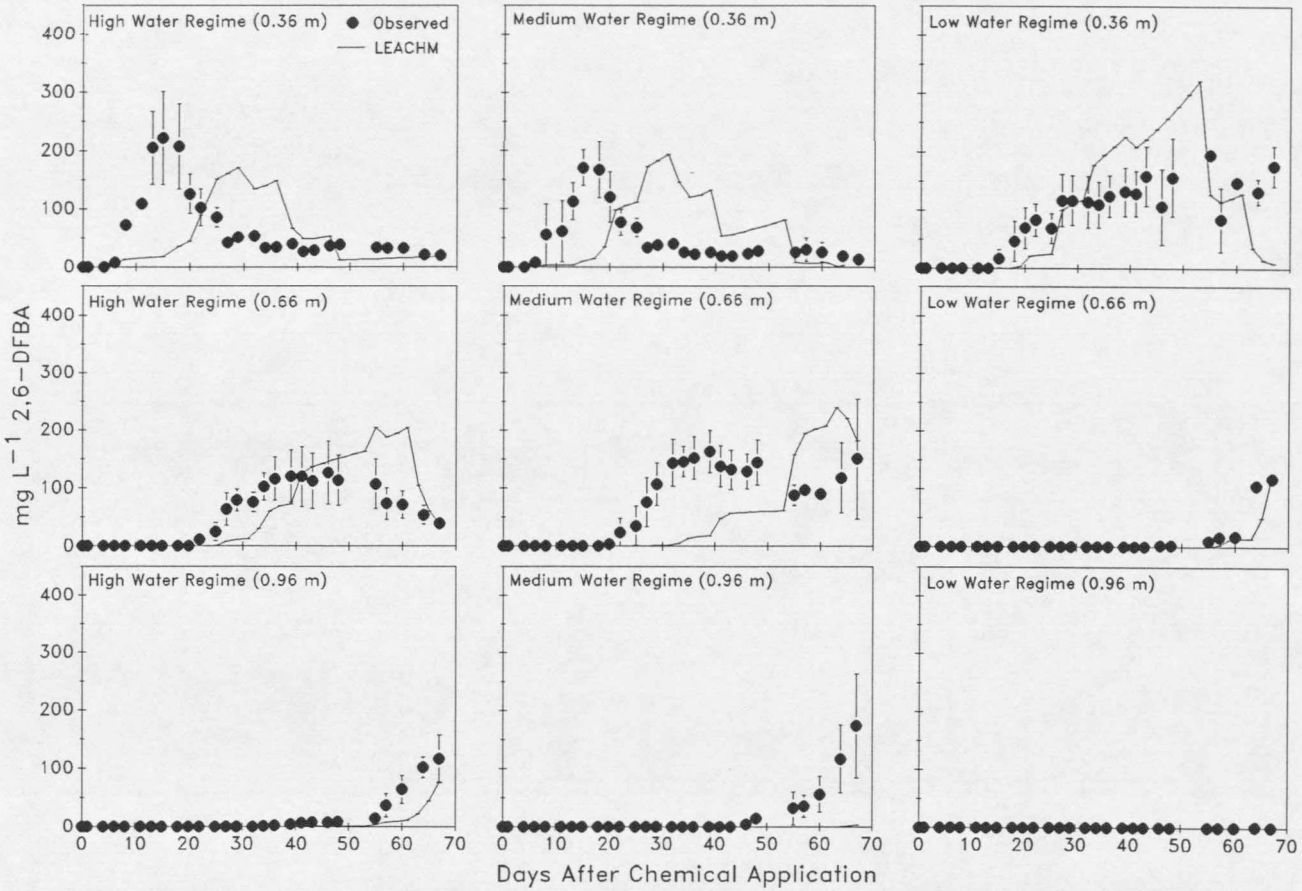

Fig. 11. Observed and simulated 2,6-DFBA concentrations at 0.36, 0.66 and 0.96 m depths under high, medium and low water regimes for crop treatments. Vertical bars on symbols (observed data) indicate standard errors (n = 3), where absent, bars fall within symbols.

Table 10. Moment analysis results based on selected† observed dicamba and 2,6-DFBA breakthrough curves.

Soil	Water		Center of mass(d)		D(cm^2d^{-1})§		Recovery(%)	
Depth(m)	Regime	Treatment	dicamba	2,6-DFBA	dicamba	2,6-DFBA	dicamba	2,6-DFBA
0.36	High	Fallow	21.4	23.0	3.4	3.6	78.1	131.7
		Crop	21.0	26.9	10.1	8.1	116.7	139.3
	Medium	Fallow	25.9	29.4	2.1	2.7	90.6	130.6
		Crop	20.5	26.2	8.9	7.6	67.7	94.6
	Low	Fallow	ND‡	46.6	ND	0.6	ND	120.1
		Crop	ND	46.1	ND	1.2	ND	91.4
0.66	High	Fallow	43.6	46.2	1.7	1.8	42.4	100.1
		Crop	41.4	43.4	2.8	3.2	97.6	138.0
	Medium	Crop	43.0	44.7	3.0	3.1	103.5	153.9

† Values from truncated breakthrough curves do not represent true moments and are not presented.
‡ Not determined - dicamba was not applied to low water regime treatments.
§ D = Dispersion Coefficient.

LEACHM Predicted BTCs

Predicted BTCs for dicamba (Figures 8, 9) and 2,6-DFBA (Figures 10, 11) were obtained using the chemical fate and transport model, LEACHM (Wagenet and Hutson, 1989). The majority of data required as model input was obtained from *in situ* field measurements or from laboratory characterization of intact soil cores taken within 3 m of the *in situ* columns (Tables 8-9; Table 2, Chapter 3). Predicted dicamba and 2,6-DFBA BTCs were significantly slower than observed BTCs for the majority of treatment conditions (Figures 8 to 11). Predicted BTCs for the nonreactive tracer, 2,6-DFBA, are based predominantly on input parameters which influence water movement. Consequently, lack of agreement between observed and predicted 2,6-DFBA BTCs was due to physical processes not described by the model or by inappropriate input data for soil physical properties. Predicted BTCs for dicamba are essentially identical to those for 2,6-DFBA (K_{oc} for both solutes was set to 0), with the exception that dicamba is degraded to its principle metabolite, DCSA, during transport. Predicted solution concentrations of DCSA are not reported here since the majority of DCSA is sorbed.

Input parameters having significant influence on predicted water flux include amount of applied water, water application rate, pan evaporation, pan factor, coefficients of Campbell's (1974) equation, K_s, and soil bulk density. Under cropped conditions, additional input parameters of importance in the soil water balance include a crop cover factor and the date of physiological

maturity. Carefully measured independent estimates were obtained for the majority of these parameters, consequently, we feel that the input data set represents an accurate characterization of average site-specific soil and climatic properties. In fact, adequate agreement between model predictions and observed data was obtained for evaporation under fallow conditions (Figure 12) and for volumetric water contents at 0.4, 0.6 and 1.0 m soil depths (Figures 13-14). The only major disagreement between observed and predicted θv was at 1.0 m for the low water regime under cropped conditions, where LEACHM overestimates the measured θv. This may be due to an inadequate description of the Ψ-K(θv) relationship at low θv's using the Campbell's equation.

Interestingly, Comfort et al. (1993) reported on a similar study in 1990 using Br^- under fallow conditions in the same soil columns and found reasonable agreement between observed and predicted Br BTCs. In addition, the same *in situ* columns were used during 1991 (Chapter 3) to study Br^- and PFBA transport under fallow and crop conditions and closer agreement was found between observed and predicted BTCs than in the current study. Finally, a sensitivity analysis of model predictions using 95% confidence intervals of independently measured soil hydraulic property inputs (K_s, BCAM, AEV) did not account for the discrepancy between observed and predicted BTCs obtained in this study. The study of Comfort et al. (1993) was conducted shortly after spring tillage to depths of 0.15 to 0.2 m. In contrast, the present study was conducted on soils which had not been disturbed for one (cropped) and two

(fallow) years. Consequently, temporal changes in soil physical properties (e.g., soil aggregation, biopore formation) of particular importance in surface horizons (Hamblin, 1982; Hamblin and Tennant, 1981; Beven and Germann, 1982) may have contributed to the lack of agreement between observed and predicted BTCs in the current study. Such changes would be most important in surface horizons (0 to 0.2 m) and would not have been accurately represented using input data based on adjacent intact soil cores. However, the fact that model predictions using input parameters (K_s, BCAM, AEV) which varied by a factor of two from the measured values did not significantly improve agreement with observed data suggests that physical nonequilibrium processes not described by LEACHM were occurring in the field. Input parameters controlling water flux (BCAM, K_s) could likely be adjusted to improve agreement between predicted and observed BTCs; this approach results in fitting the model to the observed data rather than testing the model with a set of independently measured soil physical parameters. We speculate that the presence of root channels and the development of greater macroporosity in the absence of tillage may have provided a potential for preferential solute transport not described by LEACHM. If this were true, agreement between observed and predicted BTCs should improve under the low water regime where preferential solute flow would be expected to be less important. This is in fact what we observed for 2,6-DFBA transport at the low water regime (Figures 10 - 11).

As stated previously, we originally expected that the transport of dicamba and 2,6-DFBA would be considerably slower under crop compared to fallow conditions, due to higher ET under crop conditions. However, predicted solute BTCs also showed more rapid transport under cropped conditions (Figures 8 to 11), especially at 0.36 and 0.66 m. Evaluation of LEACHM output indicated that, despite greater cumulative ET under cropped conditions, lower evaporation from the soil surface allowed more applied water to move into the profile where root uptake occurs. For example, from the time of chemical application (t=0) to the center of mass for the 2,6-DFBA BTCs at 0.36 m, LEACHM predicted that approximately 72, 71 and 66 mm of additional water moved into the profile for the high, medium and low water regimes under cropped as compared to fallow conditions. From the time of chemical application to the center of mass for 2,6-DFBA BTCs at 0.66 m, predicted cumulative evaporation was 116, 113 and 105 mm greater for fallow than cropped conditions for the three water regimes. Since predicted root water uptake occurred primarily in the 0.05 to 0.8 m zone, a greater fraction of applied water moved past the 0.36 and 0.66 m lysimeters under cropped than fallow conditions. Also, predicted θv's in the upper profile were higher under crop compared to fallow treatments. Although a greater fraction of applied water was predicted to evaporate under fallow conditions, the predicted drainage component for fallow treatments is greater because water is not removed from the mid and deep soil layers (Table 11). The net effect of these

processes is that predicted solute BTCs under cropped conditions are significantly faster at 0.36 and 0.66 m, but slightly slower at 0.96 m. Estimated cumulative drainage based on moment analysis of the observed 2,6-DFBA BTCs also showed greater cumulative drainage under fallow conditions which agreed reasonably well with predicted drainage from LEACHM (Table 11). Conversely, estimated cumulative drainage (moment analysis) for the crop treatments is significantly higher than LEACHM predicted drainage (100 mm higher for the medium water regime). The drainage component calculated based on moment analysis of the 2,6-DFBA BTCs at 0.36 and 0.66 m depths under crop conditions does not reflect any transpiration occurring after those BTCs move deeper into the soil profile, and as a result, overestimates drainage as compared to LEACHM.

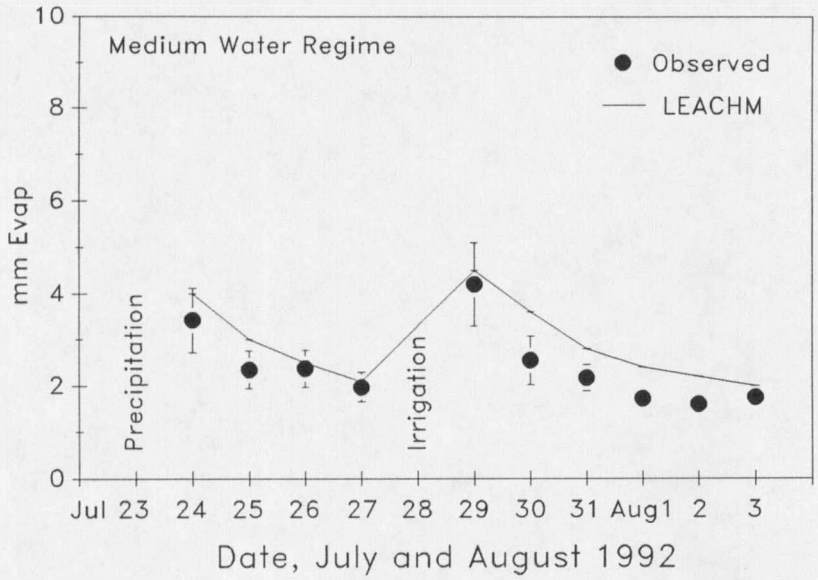

Figure 12. Observed and simulated daily surface evaporation from bare soil.

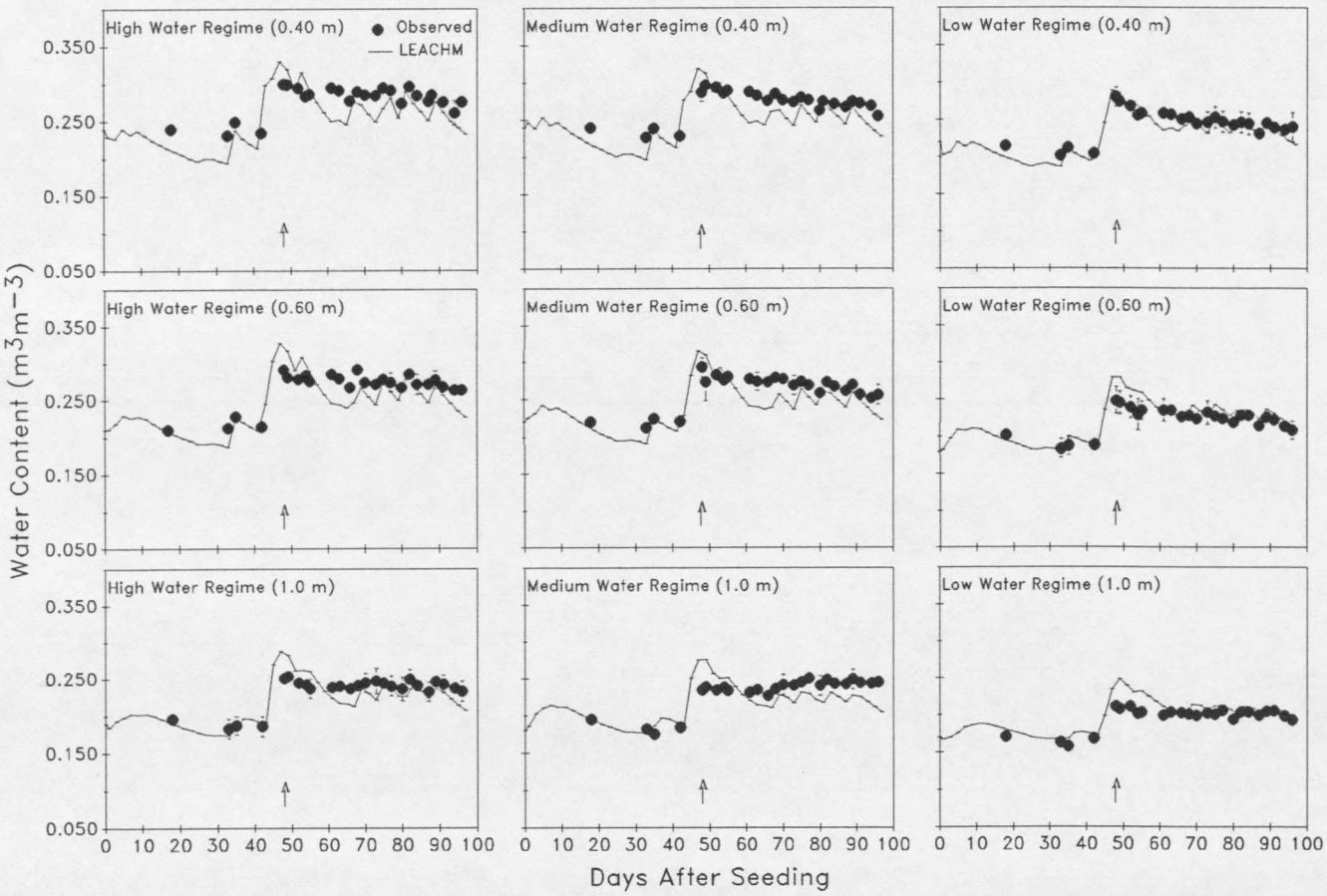

Figure 13. Observed and simulated soil volumetric water contents at 0.40, 0.60 and 1.0 m depths under high, medium and low water regimes for fallow treatments. ↑ indicates day of chemical application. Vertical bars on symbols (observed data) indicate standard errors (n = 2), where absent, bars fall within symbols.

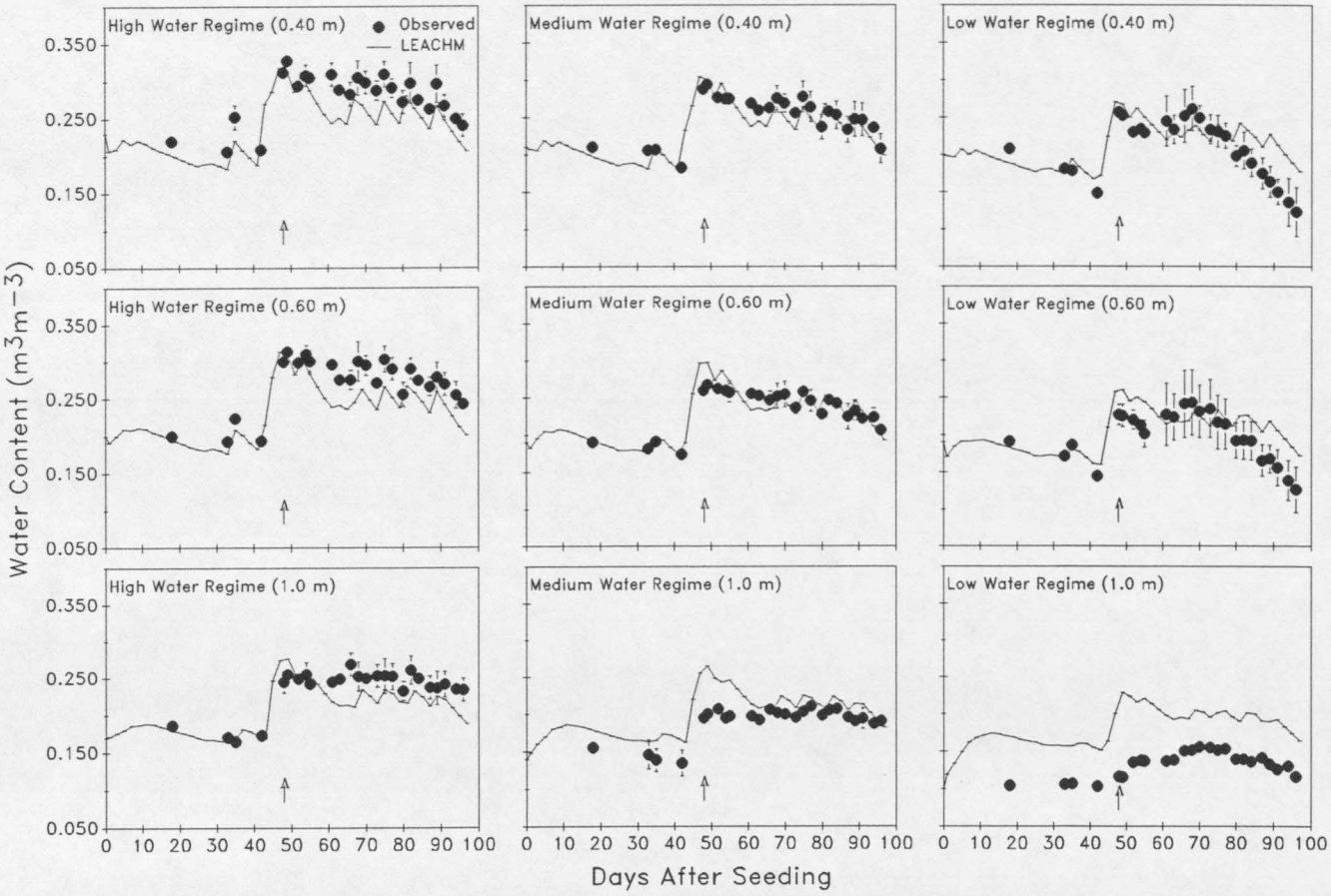

Figure 14. Observed and simulated soil volumetric water contents at 0.40, 0.60 and 1.0 m depths under high, medium and low water regimes for crop treatments. ↑ indicates day of chemical application. Vertical bars on symbols (observed data) indicate standard errors (n = 3), where absent, bars fall within symbols.

Table 11. Observed and LEACHM predicted water budget components from time of chemical application (t=0) to final sampling event (t=67).

	Treatment					
	Fallow			Crop		
	Water regime					
	High	Medium	Low	High	Medium	Low
Observed	-----mm-----					
Soil profile (t=0)	334	330	297	342	295	233
Cumulative precip./ irrigation	413	349	279	399	340	276
Cumulative drainage†	314	231	127	256	240	109
LEACHM						
Soil profile (t=0)‡	362	351	320	350	335	299
Final profile (t=67)	312	300	290	301	280	256
Cumulative Evap.	192	188	176	27	27	27
Cumulative Tran.	0	0	0	215	216	216
Cumulative drainage	271	213	132	206	153	76

† Observed drainage calculations based on moment analysis from observed 2,6-DFBA breakthrough curves.

‡ LEACHM soil profiles at time of chemical application (t=0) differ from observed profiles at this same date due to the fact that LEACHM runs were initiated at time of planting (48 days prior to chemical application).

Dicamba and DCSA Concentrations in the Soil Profile

At 67 d after chemical application, the total amount of ^{14}C remaining in the soil columns was determined as a function of soil depth (0.1 m increments) using total oxidation. The majority of soil columns showed a bimodal distribution of total ^{14}C with respect to soil depth, with a peak in the 0 to 0.3 m zone and a broad peak in the 0.8 to 1.2 m zone (Figure 15). Total recoveries calculated as a fraction of applied ^{14}C ranged from 47 to 67 % (Table 12), indicating that some of the applied ^{14}C-dicamba was completely mineralized to CO_2. Selected soil samples having the highest total ^{14}C contents were solvent extracted and analyzed for dicamba and the principle metabolite, DCSA. The percent of ^{14}C extracted with acetonitrile ranged from 2 to 5% for surface samples and 50 to 130% for deep samples (Table 13). Dicamba was consistently identified as the predominant ^{14}C constituent at lower depths, consistent with the position of lysimeter measured dicamba concentrations at the time the columns were taken from the field and sectioned. Roughly 90% of the extracted ^{14}C from deep samples was identified as dicamba while the remaining 10% was identified as DCSA (Table 13). Solvent extraction recoveries of total ^{14}C were extremely poor in surface samples (2 to 5 %) and the only ^{14}C-labeled constituent identified in these extracts was DCSA. This observation is consistent with the fact that dicamba will degrade to DCSA fairly rapidly in surface horizons ($t_{1/2}$ = 13 d), leaving a greater fraction of the less mobile DCSA (measured K_{oc} value for DCSA = 504 L kg^{-1} compared to 0 for

dicamba). Moreover, once DCSA is formed, its degradation rate ($t_{1/2}$ > 40 d) is considerably slower than dicamba. The nonextractable portion of the total ^{14}C in surface samples was probably due to the formation of irreversibly bound DCSA residues, although we cannot rule out the possibility of other nonextractable metabolites or the incorporation of ^{14}C into nonextractable biomass. The difference in extraction recoveries of ^{14}C in surface (DCSA) compared to deep samples (dicamba) is also consistent with the extraction recoveries measured on samples which were spiked with known amounts (but not aged) of ^{14}C-labeled DCSA (47% recovery) and dicamba (86% recovery).

Predicted (LEACHM) soil concentrations of dicamba plus DCSA (i.e. total residual ^{14}C expressed as $\mu g\ kg^{-1}$; molecular weights of dicamba and DCSA differ by less than 7.5%) follow trends similar to the observed total residual ^{14}C (Figure 15). Comparison of observed and predicted dicamba BTCs (previous section) and distribution of residual dicamba plus DCSA (Figure 15), suggest that field degradation rates were slower than predicted. This is also demonstrated by comparing the observed recovery of total ^{14}C to predicted recovery (i.e. amount of chemical left in the profile vs amount applied), where LEACHM overestimated the amount of applied chemical completely mineralized to $CO_2(g)$ (Table 13). LEACHM predictions show that essentially 100% of the parent dicamba is absent from the 0 to 0.4 m zone, where predicted DCSA concentrations are very close to observed total residual concentrations. However, at depths greater than 0.4 m, LEACHM predictions show (i) slower

travel times for dicamba compared to the observed residual ^{14}C distribution, and (ii) less total residual dicamba plus DCSA than observed. Slower predicted travel times were discussed in the previous section. The predicted rate of dicamba and DCSA degradation is a function of the first-order rate constants (i.e. half-lives) used as input data to LEACHM. For surface horizons, we used $t_{1/2}$ values of 13 and 40 d for dicamba and DCSA, respectively, based on batch studies in our laboratory. These values are consistent with ranges reported in the literature for dicamba (13 to 40 d) and DCSA (11 to 170 d) (Comfort et al., 1992; Krueger et al., 1991; Smith, 1974). For soil depths > 0.30 m, $t_{1/2}$ values were assumed to increase based on an exponential function presented in Eq. (1) (Jury et al., 1987). It is quite probable that actual degradation rates in the field were different than those estimated from laboratory experiments due to temporal variation in soil temperature (Comfort et al., 1991) and soil moisture (Smith, 1973b) *in situ*. Furthermore, it appears that actual degradation rates at lower soil depths were slower than those estimated using Eq. (1).

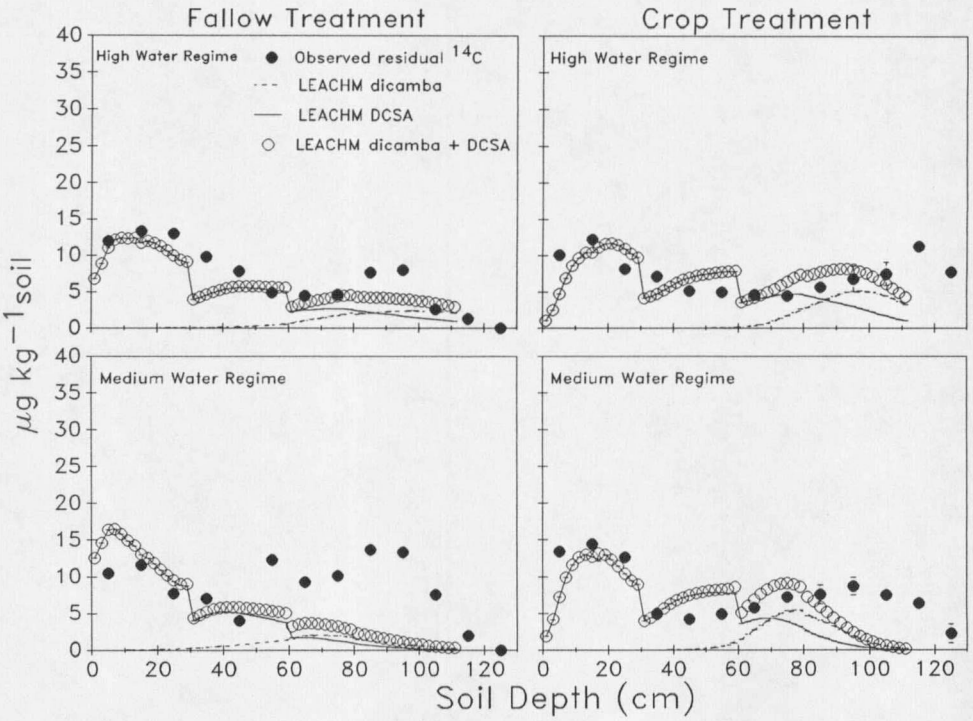

Figure 15. Final observed and simulated dicamba and DCSA concentrations as a function of soil depth.

Table 12. Observed and predicted ^{14}C recoveries in *in situ* soil columns as a percent of total ^{14}C applied as dicamba.

Water Treatment Regime		Observed		Predicted
		% ^{14}C in 1.3 m	% ^{14}C in 1.1 m	% ^{14}C in 1.1 m
fallow	high	50.97 (0.65)†	45.22 (5.66)	38.56
	medium	60.53 (3.25)	60.05 (3.15)	36.65
crop	high	55.31 (4.69)	44.31 (3.95)	44.73
	medium	64.27 (6.71)	60.97 (8.34)	42.98

† Standard errors in parenthesis.

Table 13. Characterization of 14C fractions in selected soil samples at termination using solvent extraction, HPLC-radioisotope detection and total oxidation.

Water regime	Soil depth	----------^{14}C----------				% Extracted ^{14}C as‡		Total§
		Soil start†	Extracted	Residual†	% Extracted	Dicamba	DCSA	Recovery
Fallow								
high	0.1-0.2	596.93	20.05	524.54	3.36	0.00	100.00	91.23
	0.9-1.0	356.02	479.71	449.90	134.74	88.47	11.53	261.11
medium	0.1-0.2	517.95	16.06	460.32	3.10	0.00	100.00	91.97
	0.8-0.9	611.03	432.17	246.86	70.73	87.76	12.24	111.13
Crop								
high	0.1-0.2	571.32	27.52	709.85	4.82	0.00	100.00	129.06
	0.9-1.0	409.17	221.52	27.91	54.14	90.22	9.78	60.96
medium	0.1-0.2	614.81	14.40	504.50	2.34	0.00	100.00	84.40
	0.9-1.0	443.78	373.30	95.97	84.12	90.24	9.76	105.74

† Soil samples were oxidized before and after solvent extraction.

‡ Percent of total ^{14}C extracted as dicamba or 3,6-dichlorosalicyclic acid (DSCA). No other ^{14}C metabolites identified.

§ Total ^{14}C Recovered = ((^{14}C extracted + ^{14}C residual)/^{14}C soil) X 100.

Conclusions

Observed dicamba BTCs show that it is mobile and will move significantly under irrigated conditions. Dicamba behaves much like a nonsorbing tracer with the exception of any degradation which might occur. Consequently, the amount of dicamba which moves out of the root zone and potentially into shallow groundwaters is very sensitive to the rate of movement out of the biologically active surface zone. Once dicamba degrades to DCSA, mobility is very low even under irrigated conditions. Management practices such as a delay in irrigation after dicamba application will significantly reduce the potential for transport of dicamba out of the root zone. These observations are consistent with those made by Comfort et al. (1992).

Model predictions in this study were based on independently measured or estimated input parameters. Our intent was to compare a noncalibrated simulation of solute BTCs with observed data to assess LEACHM performance under field conditions. LEACHM predicted travel times were significantly slower than observed for both dicamba and the nonreactive tracer 2,6-DFBA. Probable causes may include inappropriate input parameters for hydraulic properties, and perhaps more importantly, the inability of LEACHM to describe macropore induced preferential flow. The agreement between observed and predicted BTCs may vary dramatically as a function of tillage history, and the subsequent temporal changes in soil hydraulic properties. The columns used in this study had not been disturbed

for two to three years, and may have developed significantly more macroporosity (root channels within cropped columns, etc.) compared to the previous field season where PFBA and Br^- were used as tracers (Chapter 3).

Despite the potential for discrepancies between predicted and observed data obtained at the field plot level, simulation models will continue to play an important role in screening pesticides for their leaching potential, or in screening soil mapping units for pesticide leaching potential. Furthermore, the use of deterministic transport models in an *ad hoc* stochastic manner, where repeated execution using model inputs covering a range in observed soil properties, may result in model predictions which can be expressed in terms of probabilities of solute transport (Wagenet and Hutson, 1989).

CHAPTER FIVE

SUMMARY

Groundwater contamination by pesticides is often assumed to have occurred through normal agricultural practices (Clark, 1990; Deluca et al., 1989). These concerns have increased the use of computer models for predicting pesticide fate and transport in soil systems. Modeling chemical behavior in soils can be used as a tool to assess the leaching potential of a specific pesticide or conservative tracer, given site specific soil and environmental conditions, and chemical properties as model inputs.

Solute transport models are increasingly being used by government agencies and private consulting firms to support environmental management and policy decisions. One of the more exhaustive deterministic solute transport models available is LEACHM (Leaching Estimation and Chemistry Model, Wagenet and Hutson, 1989). Despite continued application of solute transport models such as LEACHM for predicting the fate of chemicals in soils, studies to assess LEACHM performance under field conditions have been limited. Furthermore, proper selection of nonreactive tracers for use under certain field conditions is essential for model validation experiments. Model validation

results may be erroneous if nonreactive tracers, which are assumed to behave conservatively, are absorbed by plants during transport experiments.

The objectives of these studies were to i) develop an expedient and accurate method to simultaneously analyze fluorobenzoate tracers and Br^- in soil water samples containing common soil anions, ii) monitor the transport and fate of Br^-, PFBA, 2,6-DFBA and dicamba in a silt loam Montana soil over varying soil water regimes under cropped and fallow management conditions, and iii) evaluate the capabilities of LEACHM given specific soil and climate input parameters for predicting the fate of these compounds under field conditions.

Laboratory and Field Studies

Bromide has long been accepted as an ideal tracer for water movement in soil and aquifer systems (Davis et al., 1980). Alternative nonreactive tracers such as fluorobenzoates (Bowman, 1984a; Bowman and Gibbens, 1992), may be useful in transport experiments, and previous studies have shown that fluorobenzoates behave similarly to Br^- in the absence of plants (Bowman, 1984a; Young and Boggs, 1990). Recent studies showing that Br^- is taken up by plants in significant amounts (Kung, 1990; Hengel et al., in preparation), has resulted in increased interest in fluorobenzoate tracers. Results from our 1991 field study using PFBA and Br^- under crop treatment conditions suggest that Br^- is significantly more susceptible to plant uptake (at least in barley) than PFBA. Mass recoveries of PFBA and 2,6-DFBA in solute breakthrough curves

were similar (ranging from 80 - 120 %) under fallow and crop conditions for both 1991 and 1992 field studies. Conversely, mass recoveries of Br^- dropped to approximately 20 % under cropped conditions, indicating that significant quantities of Br^- were lost to plant uptake. Consequently, PFBA and 2,6-DFBA may be more suitable tracers in ecosystems where plant uptake is likely to be important. Although the cost of fluorobenzoates relative to Br^- salts (e.g. KBr) may make them unsuitable for larger field studies, the analysis of fluorobenzoates in soil solutions can be performed as easily as Br^- using ion chromatography - electrical conductivity detection (Pearson et al., 1992).

Results of our field studies for two different growing seasons (1991-1992) demonstrated the potential for non-sorbing solutes to leach below the rooting zone in the Brocko silt loam under irrigated small grain production. For both the 1991 and 1992 field studies, solute leaching increased with increasing water application under both crop and fallow treatments. In 1991, PFBA transport was delayed under crop conditions relative to fallow due to greater ET demands under crop treatment conditions. However, in 1992, the observed transport of 2,6-DFBA and ^{14}C ring-labeled dicamba was faster under cropped treatment conditions relative to fallow. Centers of solute mass (days), dispersion coefficients (cm^2d^{-1}) and BTC characteristics at three depths (0.36, 0.66 and 0.96 m) indicated the occurrence of significant preferential flow under crop vs. fallow treatment conditions. Increased preferential flow in 1992 vs. 1991 may have been due to (i) increased macroporosity from decayed

barley root systems remaining after the 1991 field season, and (ii) higher soil profile water contents at the time of chemical application in 1992.

A significant amount of applied dicamba was transported through the soil profile, to depths of 1 m within 55 days after chemical application. Mass recoveries of dicamba in the soil solution ranged from 42 to 117 %. Dicamba is anionic over a pH range of 4.1 to 9.4 (Burnside and Lavy, 1966) and essentially behaves like an anionic tracer, with the exception that its degradation rate in surface soils can be fairly rapid (e.g. half-life approximately 14 days). Once dicamba is degraded to its primary metabolite, the transport and degradation decreases dramatically. Batch sorption studies confirmed that DCSA is sorbed significantly greater than dicamba (K_{oc} values of near 0 and 504 L kg^{-1} for dicamba and DCSA, respectively), and has a much longer half-life than dicamba (14 and greater than 40 days for dicamba and DCSA, respectively). The movement of DCSA was limited to the upper 0.30 m soil depths. Total recoveries of ^{14}C - labeled compound indicated that roughly 36 to 50 % of applied dicamba was lost as $^{14}CO_2$ during the 67 day experiment. These findings are consistent with those of Smith (1974) showing $^{14}CO_2$ production from applications of ^{14}C - labeled dicamba, with concomitant declines in DCSA concentrations. The fact that DCSA is significantly less mobile than dicamba suggests that management practices which allow for maximum conversion of dicamba to DCSA prior to significant irrigation, will minimize the leaching of dicamba. This has been shown to significantly reduce

the leaching of applied dicamba in laboratory columns (Comfort et al., 1992).

LEACHM performance

Predicted (LEACHM) PFBA BTCs from the 1991 field season were close to observed BTCs in many cases; however, predicted BTCs generally were shifted to the right of measured BTCs. Results from moment analysis supported this trend, where predicted center of mass values (days) were greater than observed center of mass values. Discrepancies between predicted and observed 2,6-DFBA and dicamba BTCs (1992 field season) were greater than during the 1991 field season, despite the fact that the solute transport experiments were conducted on the same columns. Predicted soil volumetric water contents (m^3m^{-3}) at 0.4 - 1.0 m and bare soil evaporation (mm) generally agreed well with observed data for each field season. Consequently, inputs relating to soil hydraulic properties were not grossly in error. In fact, a sensitivity analysis of parameters used as input to LEACHM demonstrated that substantial changes in the input hydraulic retentivity values (BCAM and AEV) and hydraulic conductivity values (K_{sat}), did not significantly improve the agreement between observed and predicted solute BTCs, and generally resulted in poorer agreement between observed and predicted soil water contents. The lack of agreement between observed and predicted solute BTCs obtained in our studies was likely the result of physical nonequilibrium conditions caused by the preferential flow of water through macropores. The degree of preferential flow observed in the *in situ* soil columns increased over the course of three

field seasons presumably due to the development of macroporosity in the absence of tillage disturbance. A significant increase in preferential flow within the crop columns from the 1991 to 1992 field seasons suggests that previous root channels contribute to macropore induced physical nonequilibrium.

Despite discrepancies between measured and LEACHM predicted solute concentrations observed in this and other studies (Jabro et al., 1993; Pennel et al., 1990; Soulsby and Reynolds, 1992), LEACHM remains a potentially valuable management tool. However, accurate predictions may be limited by spatial and temporal variations in soil hydraulic properties which control water and solute flow. Modeling efforts designed to screen pesticide leaching potential at specific sites or within soil mapping units should include a sensitivity analysis of model output as a function of a range of input parameters which bracket actual field conditions. It is logistically impossible for field studies on pesticide fate and transport to be performed at all sites and with all pesticides. Consequently, solute transport models will likely continue to be used as a cost effective method to estimate the behavior of chemicals in soils as a function of various management alternatives.

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