Transport of Atrazine and Dicamba through Silt and Loam Soils

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Abstract: The objectives of this research were to determine the role of preferential flow paths in the transport of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) and dicamba (3-6-dichloro-2-methoxybenzoic acid) through silt and loam soils overlying the High Plains aquifer in Nebraska. In a previous study, 3 of 6 study areas demonstrated high percentages of macropores; those three areas were used in this study for analysis of chemical transport. As a subsequent part of the study, 12 intact soil cores (30-cm diameter by 40-cm height), were excavated sequentially, two from each of the following depths: 0-40cm and 40-80cm. These cores were used to study preferential flow characteristics using dye staining and to determine hydraulic properties. Two undisturbed experimental field plots, each with a 3-m^2 surface area, were installed in three study areas in Nebraska. Each was instrumented with suction lysimeters and tensiometers at depths of 10cm to 80cm in 10-cm increments. Additionally, each plot was planted with corn (*Zea mays*). A neutron probe access tube was installed in each plot to determine soil water content at 15-cm intervals. All plots were enclosed with a raised frame (of 8-cm height) to prevent surface runoff. All suction lysimeters were purged monthly for three months and were sampled immediately prior to pre-plant herbicide application to obtain background chemical concentrations. Atrazine and dicamba moved rapidly through the soil, but only after a heavy rainfall event, probably owing to the presence of preferential flow paths and lack of microbial degradation in these soil areas. Staining of laboratory cores showed a positive correlation between the percent area stained by depth and the subsequent breakthrough of Br- in the laboratory and leaching of field-applied herbicides owing to large rainfall events. Suction lysimeter samples in the field showed increases in concentrations of herbicides at depths where laboratory data indicated greater percentages of what appeared to be preferential flow paths. Concentrations of atrazine and dicamba exceeding 0.30 and 0.05μg m1^{-1} were observed at depths of 10-30cm and 50-70cm after two months following heavy rainfall events. It appears from the laboratory experiment that preferential flow paths were a significant factor in transport of atrazine and dicamba.

Keywords: Chemical transport, macropores, preferential flow, aquifer, contamination, bypass flow.

1. INTRODUCTION

Atrazine (2-chloro-4-(ethylamino)-6-isopropylamino)-s-triazine) and dicamba (3-6-dichloro-2-methoxybenzoic acid) are commonly used in agriculture to control weeds. Greater crop production globally has resulted from using agricultural chemicals, but concentrations of residual chemicals also have been increasing in some groundwater and surface waters (Nebraska Department Environmental Quality [1, 2, 3, 4]. Atrazine and other common post-emergent herbicides used on corn, soybeans, and various field crops have been detected in numerous U.S. states [5]. Residues of these herbicides are commonly found in the Midwest and also in California. Atrazine, at concentrations as high as 10μg L^{-1}, have been reported in groundwater in Iowa [6].

The mechanisms by which these compounds are transported to surface water and groundwater are somewhat better understood now than in the past, especially in terms of soil matrix and preferential pathway(s) transport. Additionally, the processes of sorption, volatilization, degradation, mobility, and plant uptake interact over time to determine the fate and transport of herbicides [7, 8, 9, 10]. Environmental factors, such as evapotranspiration, precipitation, and temperature, also affect herbicide transport [7, 10]. The presence of preferential pathways, defined here as areas of lower density in the soil than that of the surrounding soil matrix, may or may not contain macropores (i.e. cracks, root channels, worm burrows, etc.). However, they can promote rapid, deep movement of chemicals within soils. Also, preferential flow may reduce chemical movement, owing to entering water (considered clean) bypassing the soil-matrix water that has the chemicals diffused within it [11, 12, 13]. Other researchers have discovered that true macropore flow (defined in this paper as flow through cracks and pores of more than 1mm effective

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diameter) occurs only under saturated or near-saturated conditions (0 to -20kPa) and that preferential flow takes place when the soil-moisture pressure potential is between about 0 and -30kPa [10, 14], while matrix flow takes place at soil pressures (matric suction) less than about -30kPa. This is similar to reports by others [15, 16, 17]. Changes in hydraulic conductivity seem to occur at each of these relatively distinct pressure ranges as a result of soil physical characteristics, which is confirmed by results of standard soil moisture measurements. Therefore, instead of attempting to characterize or measure macropore continuity, measuring the area of preferential flow paths may be used to correlate transport of chemicals with water flow, on both a quantitative and qualitative basis. Although a significant volume of fluid (owing to macropore flow) may be transported at sub-atmospheric conditions, the soil pressures used in that study were -1.4kPa or more (very near saturation), which fall into the category given above.

It is commonly known that, unlike macropores, preferential flow paths may accept stains from various dyes because they are of lower resistance or bulk density than the surrounding soil matrix. This is because macropores may contain organic linings that retard cations to a greater extent than macropores with mineral coatings. Hence, macropores have less chemical retention than the general soil matrix. Consequently, the stained area of a preferential pathway may be used to compare flow characteristics. Also, the stained area, which represents preferential flow, is easier to measure than macropore size and continuity. It is therefore likely that a preferential flow path will exhibit greater continuity than do macropores. Nevertheless, preferential flow paths are frequently associated with macropores in porous media, which may cause some measurement problems, such as distinguishing the differences between a preferential flow path and macropore on a qualitative basis.

The study areas for this research (Figure **1**) were selected within Nebraska, which had been selected as one of the 14 initial study areas by the U.S. Geological Survey (NAWQA Program) because much of the State is underlain by the High Plains aquifer [3, 7].

This aquifer is a primary groundwater source for eight States in the High Plains, which include Wyoming, South Dakota, Nebraska, Colorado, Kansas, Oklahoma, New Mexico, and Texas. It is also an important area because large quantities of agricultural fertilizers and pesticides are applied annually for food production. Nebraska is typical of many High Plains States in which agriculture is dependent on fertilizers and pesticides to sustain adequate production for a constantly increasing global population. Agricultural-chemical use in Nebraska has been increasing substantially since the early 1970's. During 1985 an estimated 200 million pounds of fertilizer and 30 million pounds of pesticides (active ingredients) were applied in Nebraska [18]. From 1985 to 1997 use slowly increased to about 28 percent more, but by 2004 had declined to 1985 levels [1, 2].

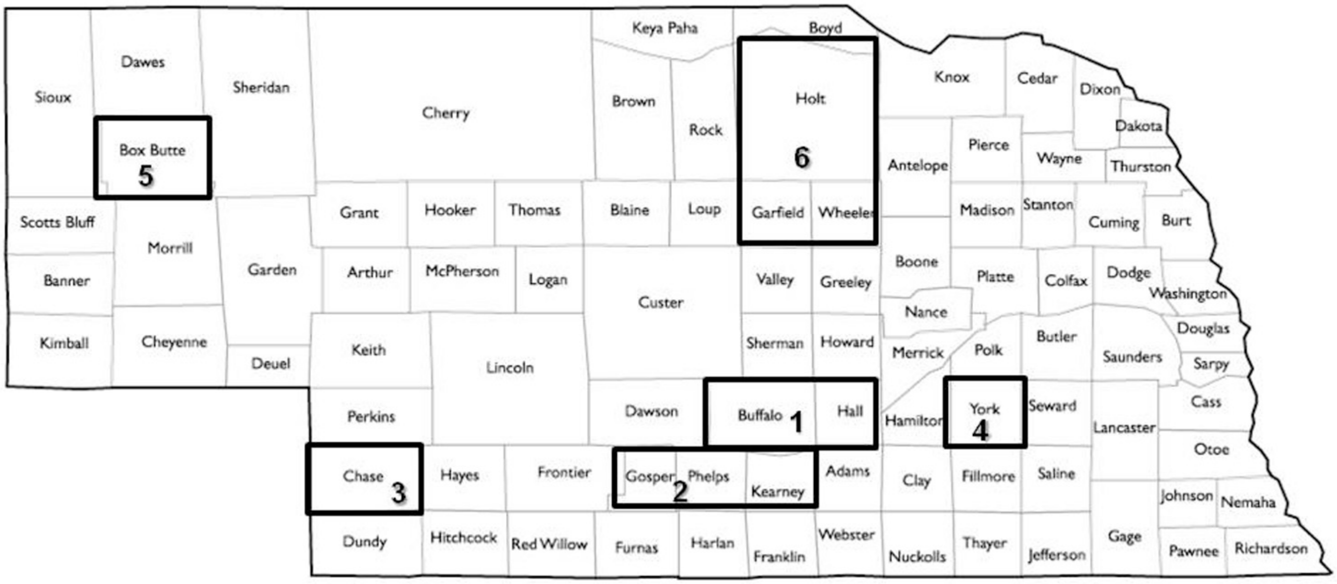

Figure 1: Location of study areas. Source: Tindall and Chen, 2014.

Agricultural chemicals have been frequently detected in groundwater in some locations in Nebraska. Nitrate contamination of groundwater, which results primarily from fertilizer application [1], has been detected in intensively farmed areas of Nebraska for many years and has been a problem since the late 1970s [19]. Many scientists since the early 1980s believe this could potentially be in response to presence of [20, 21]. Similarly, pesticide contamination of groundwater has been detected in various areas throughout the State [1, 5]. It has been difficult to determine the magnitude and extent of groundwater contamination that results from the nonpoint application of pesticides. However, several variables (hydraulic gradient and conductivity, depth to water, soil permeability, etc.) and their relative importance are known to control the access of these chemicals to the aquifer [7, 10, 22, 23, 24].

The objectives of this study were to: (1) determine the transport of atrazine and dicamba applied to the selected study areas that are underlain by the High Plains aquifer; and (2) determine the potential role of macropores in that transport.

2. BACKGROUND MATERIALS AND METHODS

2.1. Description of the Study Area(s)

Six areas in Nebraska (Figure **1**) that are underlain by the High Plains aquifer were used in this study [7]. These were selected due to diversity and availability of hydrogeologic, climatic, soils, and land-use data. They also are representative of major groundwater provinces and principal land use in Nebraska. The six areas also are characterized by either existing or potential groundwater contamination by nitrate resulting from application of agricultural [2, 7].

3. LAND USE IN THE SIX STUDY AREAS

The six study areas consist of 12 counties constituting 13% of the State. An average of 94% of the six study areas is used for agriculture for which corn is the dominant crop. The study areas in the western part of the State tend to be drier and support fewer acres of row crops. Irrigated cropland accounts for about 50% of the total farmland in the southeastern study areas (areas 1, 2, and 4) and accounts for about 20% in the western and northeastern study areas (areas 3, 5, and 6). Agricultural land-use and irrigation data for the six study areas are tabulated in Table **1**. A summary of crops grown in the six study areas is presented in Table **2**.

Crop-production techniques require large quantities of nitrogen fertilizers and pesticides, despite split application and time release fertilizers and newer technologies used for production. The Cooperative Extension Service of the University of Nebraska recommends total-nitrogen content in the soil of 113kg (250 pounds) per acre to produce 210 bushels of corn

Table 1: Agricultural Land Use and Irrigation Data for Study Areas (Source: Nebraska Department of Agriculture 1960-2004)

Study Area	Land Area (ha)	Farmland (%)	Irrigated Farmland (%)	Irrigation Wells (number)	Estimated Water Use for Irrigation during Study, (cubic meters per year)	Major Crops	Estimated Area Groundwater Nitrate Concentration Exceeded $10 mgL^{-1}$ (km^2)
1	383,882	96	49	6,407	750820405	Alfalfa corn soybeans wheat	404
2	393,486	94	50	3,872	585657185	Corn sorghum soybeans wheat	215
3	416,167	98	21	1,648	222396778	Corn sorghum wheat	<3
4	149,121	95	63	2,583	331066530	Corn sorghum soybeans	<3
5	278,942	97	19	886	133709433	Alfalfa corn edible beans wheat	153
6	919,748	89	15	2,866	504000686	Alfalfa corn	585

Table 2: Total Crop Acreage (Upper Number); Percentage of Total Crop Planted Area of all Crops (Lower Number). Source: Tindall and Chen, 2014

Area	Row Crops			Small-grain Crops			Other Crops	
	Corn	Sorghum	Soybeans	Wheat	Oats	Barley	Alfalfa	Hay
1	150543 39	8053 2	18211 5	19830 5	2307 1	324 *	22055 6	27923 7
2	162278 41	22662 6	21448 5	36017 9	1902 *	121 *	11331 3	16592 4
3	67582 16	16187 4	4775 1	57870 14	1902 *	648 *	5625 1	11736 3
4	72843 49	28733 19	19020 13	6475 4	283 *	--- *	2711 2	3642 2
5	14164 5	364 *	12950 5	46539 17	4654 2	44112	5018 2	10522 4
6	123024 15	3399 *	4775 1	2752 *	4452 *	81 *	23350 3	151352 16

*Less than 40 ha planted.

---Less than 1 percent of total crop planted area.

per acre [25]. Farmers commonly apply from 36-113kg (80 to 250 pounds) of total nitrogen per acre, depending on soil permeability and structure, mostly as anhydrous ammonia to supplement residual nitrogen in the soil. Most of the applied nitrogen not used by crops is oxidized to nitrate in the soil, which is water soluble and very mobile [26]. Thus, under oxidizing conditions in shallow and moderately permeable aquifers, nitrate can contaminate the groundwater and migrate downgradient from application areas and discharge into surface-water bodies.

During 2008 and 2012, an estimated 11.1 million kg (24.5 million pounds) and 13.4 million kg (29.6 million pounds) of pesticides (active ingredients) were applied on agricultural lands in Nebraska [27, 28]. Herbicides accounted for 8.5 million kg (18.8 million pounds) in 2008 (77%) and 11 million kg (24.3 million pounds) in 2012 (80%), and insecticides accounted for 2.59 million kg (5.7 million pounds) in 2008 and 2.4 million kg (5.3 million pounds) in 2012. Most of these chemicals were applied to corn. The application rates of many of the more commonly used herbicides range from 2.5 to 5kg/ha (1 to 2 pounds per acre); insecticide rates range

Table 3: Chemical Characteristics of Pesticides Commonly Used in Nebraska. Source: Weed Science Society of America (MacKay *et al*., 2010)

Pesticide	Recommended Application Rate (lbs/acre)	Solubility in Water (mg/L)	Half Life in Soil (weeks)	Half Life in Water (weeks)	Mobility mg/ml*
Herbicide					
Alachlor	1-4	242	1-10	---	0.6-8.1
Atrazine	2-4	33	4-57	10-106	0.4-8.0
Butylate	3-4	45	1.5-3	---	1.4-8.9
Cyanazine	1.2-5	171	1-5	---	3.4-4.6
Dicamba	1	500	1-6	3-4	4.5 -
Propachlor	2-4	700	1-4	---	0.3-5.4
Insecticide					
Carbofuran	1	700	1-37	2.5	0.25-8.7
Chlorprifos	1	2	1-17	4-5	49.5-99.7
Fonofos	1	<1	3-24	---	---
Terbifos	1	15	---	---	---

*Measured as Koc (the sorption coefficient adjusted for organic carbon content. This is the ratio of adsorbed to solution-phase pesticide normalized with respect to organic matter content). A value of <50 implies weak chemical adsorption to soil and thus, higher chemical mobility.

from 10 to 20kg/ha (4 to 8 pounds per acre). The solubility, half-life in soil and water, and mobility of some of these pesticides are such that significant groundwater contamination may occur in moderately permeable sediments (Table **3**) [20, 21].

4. SOIL PERMEABILITY

Contaminants can be stored within, degraded, or transported through the soil; therefore, the hydrological, physical, and chemical characteristics of the soil often greatly affect groundwater quality. Seprate research has quantified soil permeability, available water capacity, slope, and other hydrological soil characteristics for Nebraska [29]. The less permeable a soil is, the longer a solute will remain near the surface of the soil profile, and the more likely the solute will be removed in runoff, adsorbed onto the soil, degraded, or consumed by plants. However, macropores, preferential flow paths, etc. can short-circuit this process and transport chemicals faster and deeper within profiles and to groundwater than generally anticipated [10, 16]. Sandy soils generally are more permeable, contain less available water, and have less ion-adsorption capability than silty and clayey soils; therefore, the mobility of contaminants is greater in sandy soils than in other soil types. This was supported by data collected in the Midwest [30].

The permeability, measured by determining intake rate using single-ring infiltrometer onsite after Bouwer (1986), of a 1.5-m (60-inch) soil profile for 82 sample sites in the six study areas ranged from 1.93cm (0.76 inch) per hour for clayey soils to 22.9cm (9.0 inches) per hour for sandy soils (Table **4**). Both of these extremes occurred in Area 3. Area 4 had the minimum overall soil permeability of the six study areas with a median of 2cm (0.8 inch) per hour; area 6 had the maximum overall soil permeability with a median of 6.1cm (2.4 inches) per hour.

5. LABORATORY EXPERIMENT

Twelve intact cores (30cm diameter by 40cm height; 2 from each study the six areas), were extracted from 0-40cm and 40-80cm, and analyzed for unsaturated hydraulic conductivity using methods of other researchers [14, 31]. In undisturbed, naturally structured soils with existing macropores and flow channels, only partial displacement of resident soil water and solutes by incoming solutions occur. This behavior is commonly referred to as preferential flow [16, 24, 32].

Intact soil cores are a common tool to address questions involving the characterization of water movement in structured soils. This is especially true of core size since it will have a significant effect on

Table 4: Descriptive Statistics and Frequency Data for Independent Variables for the Six Study Areas (Source: Tindall and Chen, 2014)

Independent Variable	Measurement Unit	Descriptive Statistics				Percent of Sites where Values were Equal to or Less than those Shown				
		Max	Min	Mean	Standard Deviation	90	75	50	25	10
HYDROGEOLOGIC										
Hydraulic Gradient	---	0.0053	0.0006	0.0023	0.0011	0.0038	0.0029	0.0020	0.0014	0.0011
K	Ft/day	149	5	52	36	106	78	40	23	11
Specific Discharge	Ft/day	0.2998	0.0128	0.0759	0.0576	0.1425	0.0931	0.0565	0.0418	0.0253
Depth to Water	Ft	239	3	73	60	165	88	47	30	16
Well depth	Ft	550	40	199	109	341	275	180	100	75
CLIMATIC										
Annual Precipitation	In	39.3	12	25.2	6.5	32	29.2	26.2	20.5	15.7
SOIL										
Soil Permeability	Inches/hr	9	0.76	2.46	2.12	6.63	2.54	1.3	1.17	0.74
LAND USE										
Irrigation Well Density	Well/mile squared	8	0	3.1	2.2	5.4	4.1	2.6	0.68	0
Nitrogen Fertilizer Use	Lb/acre	260	0	124.8	81.6	210	188.6	147.3	30	--

results. Researchers in Europe discovered that field variability is strongly reduced by using cores with a volume of at least 10L [33, 34]; the cores in this study measured 28.3L. The authors have found that the intact core method used herein, due to core size (28L), does in fact generally mimic field behavior [13, 14, 33, 34, 35, 36]. Three cores from each depth (one from each study area) were used to study preferential flow characteristics using dye staining experiments and also for Br^- tracer studies, as well as determination of saturated (Ks) and unsaturated (K(θ)) hydraulic conductivity. Staining of each core was not performed until all Br^- and K studies were complete. Each core was numbered during the extraction process. All experiments were performed to ensure that each subsequent two cores (1 and 2; 3 and 4; 5 and 6 and 7 and 8; 9 and 10, 11 and 12) were from 0-40cm and 40-80cm depths (from areas 1, 2, and 6: denoted as A1, A2, and A6), respectively. At the same longitudinal location (i.e. the 0-40cm core was extracted from directly above the same location where the 40-80cm cores were next extracted). Soil from each of the study areas (1, 2, and 6) were collected from the 0-40cm depth and the loose soils were repacked to the same bulk density as measured in the field and also using cores of the same 28.3L size mentioned previously. This was done to ensure elimination of potential preferential flow paths or macropores. The utmost care was used to ensure that each layer was compacted to the same degree by determining distance from top of the core to the top of each successive layer, thus enabling the average bulk density to be calculated. The repacking was accomplished in 2-cm layers by thoroughly mixing [37], and then pouring equal quantities of soil into the core. This sand layer was then packed by hand using a weighted steel plate. This method appeared to ensure sample uniformity.

Laboratory set up and procedures used for core analysis followed a previously described research method [14]. However, a vacuum pump in lieu of a hanging water column was used to maintain pressure at the soil core/ceramic-plate interface. All cores were purged with CO_2 from the bottom and then saturated with water from the bottom as well. The upper boundary was the core surface. Boundary conditions for the core experiment were: $\theta = f(z)$ for $z \leq 0$ and $t = 0$; top boundary: $|Jw| < Ks$ for $z = 0$ and $t > 0$; bottom boundary: semi-infinite media, where θ is volumetric water content; z is depth (in cm); and Jw is flux density at the soil surface. The volume of effluent collected over time varied; however, one pore volume for each core was about 10-11 L (soil porosity averaged about 0.38).

The dye used for this research was methylene blue ($C_{16}H_{18}ClN_3S \cdot x\ H_2O$; 82% dye by weight) from Sigma-Adrich, hereafter referred to as blue dye. This dye was chosen because most soils interact strongly with dye molecules, thus the best results for tracing water movement is generally obtained through use of non-fluorescent (to prevent fading), anionic dyes. Prior to blue dye application, potassium bromide (KBr) was applied at a concentration of 300mg L^{-1} (pulse application) [14], to each core. A pressure of -20kPa was maintained at the soil core/ceramic-plate interface throughout the application procedure. After KBr transport and hydraulic conductivity (K) studies were completed, the blue dye solution was ponded atop each core to a depth of 5cm. This head was maintained by a Marriott apparatus under which a magnetic stirrer was placed to maintain equilibrium conditions in the blue dye/tap-water mixture. By volume, the dye was mixed at 2 parts solid per 20 parts water. The total amount of blue dye solution applied to each core was equivalent to one pore volume. Each core was sectioned immediately at 5cm horizontal intervals to reduce diffusion. The total stained area vs. soil core surface area was then measured. The dyed areas were easily distinguishable from the surrounding soil, i.e., the dyed areas were blue while surrounding area remained unstained (Figure **2**).

Figure 2: Dyed soil core showing substantial differences between stained versus unstained areas.

A lighter-colored peripheral area (0.25-0.6cm) surrounded the darkest stained areas. As a result of the dye's properties, it was difficult to distinguish diffusive from convective flow. However, the author's previous experience illustrates that the lighter area was due to diffusive flow, which was not measured as part of the percent stained area. The darker stained areas were traced and the percent stained area versus total area was determined using a densitometer. Because ponding of the dye was artificial, the results must be viewed in that light, as the process may cause macropores to operate that would not normally do so under field conditions [38]. The percent stained areas of the cores (Table **5**) were of the same size proportion and almost exactly matched the percent stained area in the field [7].

Table 5: Percent of Macropore Presence by Laboratory Cores; Numbers Represent Stained Area by Percent. NU Refers to not used, which was Due to Significant Staining

Depth (cm)	Cores (average of 2 per depth)		
	A1	A2	A6
Surface	NU	NU	NU
10	23	12	15
20	16	17	15
30	10	11	13
40	10	8	6
50	5	5	6
60	4	4	5
70	6	2	1
80	4	1	1

As a note, for all laboratory experiments, tap-water was used instead of deionized or distilled water. The latter water type generally extends the thickness of the electrical double layer, which increases dispersive effects related to a decreased electrolyte concentration. Thus, in the event amounts of clay(s) were present; increased swelling would be prevented, which could reduce matrix permeability and bias results. Soils extracted in this study were less than about 8% clay content measured by the hydrometer method after [39].

6. FIELD EXPERIMENT

Six undisturbed experimental plots with a 3-m^2 surface area (two plots each) were instrumented in three study areas (1, 2, and 6 - Figure **1**) in Nebraska. The soil types for each of the study areas utilized in this research included the following:

- Study area 1 and 2: Holdrege-Uly-Coly Association, ***Uly***: Very deep, gently sloping to steep, well-drained, silty soils on uplands; Typic Haplustolls, fine-silty.
- Study area 6: ***Jansen:*** Moderately deep over sand and gravel, nearly level to moderately steep, well-drained, loamy soils formed in loamy sediments over sand and gravel on uplands; Typic Argiustolls, fine-loamy over sandy or sandy-skeletal.

Additionally, each plot was planted with corn (*Zea mays*), and instrumented with suction lysimeters (these were submersed in 0.1 N HC1 prior to installation to saturate all possible exchange sites in the ceramic cups) and tensiometers—a set of each at 15-cm depth increments. The tensiometers were automated with transducers attached to a data logger. Neutron probe access tubes were installed in each plot and were read at 15-cm increments to determine moisture content. Due to measurement requirements of the neutron probe, 15-cm rather than 10-cm measurement increments were selected for the field. During this period, all suction lysimeters were purged monthly and were sampled and purged immediately prior to herbicide application. Background atrazine and dicamba concentrations were less than equipment detection limits for both constituents (0.05 μg mL^{-1}). After the plots had been saturated for 1 week the instantaneous profile method was used to determine K(θ) for each of the six field plots [31].

7. HERBICIDE APPLICATION AND SAMPLING

After determining K(θ), the plots were re-saturated and allowed to drain for 72 h, at which time the herbicides atrazine and dicamba were sprayed uniformly at rates of 1.4kg ha^{-1} and 0.84kg ha^{-1} (active ingredient), respectively, typical application rates on crops. About 6 h after application (to simulate normal thunderstorm activity), an infiltrometer was used to apply 5cm of water to each plot (1.5cm h^{-1}). Samples for herbicide analysis were collected from suction lysimeters (about 5-30mL) about monthly and analyzed. A suction equivalent to soil pressure (-10 to -60kPa, dependent on antecedent moisture content as obtained by tensiometers) was applied for 24-48 h prior to each lysimeter sampling. Each of the six sampling dates was approximately 30 days apart and corresponded to Julian Days 164, 192, 220, 248, 276, and 304 (June-October).

The average sample volume collected from the suction lysimeters ranged from about 5 to 25mL; occasionally, some samples were less, especially near the surface 15-cm depth, owing to low soil moisture content (volumetric). Prior to applying suction, all suction lysimeters were purged to ensure that no residual herbicide remained inside the ceramic cup. Additionally, no research evidence suggests that these herbicides adsorb to the ceramic material from which the lysimeters are constructed. Mass balance was not performed because no radio-labeled herbicides were used and because amounts of the herbicides lost owing to the processes of volatilization, plant uptake, and irreversible adsorption of some of the herbicides to soil particles were not measured.

8. ATRAZINE

Chemical analysis for both atrazine and dicamba was modified after other research [40, 41] respectively, in which leachate samples for analysis of atrazine were stored in glass scintillation vials (20mL) and then frozen at -10°C pending analysis. Immediately prior to analysis, samples were passed through a 0.45-μm Nalgene filter using a syringe, which sometimes causes about 10% loss in atrazine mass. This potential loss was not measured for this experiment. The leachate was analyzed by high-precision liquid chromatography (HPLC), using a 25-mm by 4.6-mm column and an 80:20 v/v methanol-to-water ratio (adjusted to pH 7.4 with 0.05 M ammonium acetate). Wavelength was set at 222nm with a retention time of 9.5 min and a flow rate of 0.8mL min^{-1}. Atrazine concentrations were determined from standards that defined a linear regression curve (r^2 = 0.992). Standards and blank samples were inserted during analysis, at blind intervals, to ensure quality control. Additionally, soil samples were extracted from adjacent plots (to avoid disturbance of the intact plots) at each 10-cm interval down to 80cm. Further, a 20 g sample of soil was cored from each depth and atrazine was extracted by adding 42mL of 90% methanol and 10% HPLC-grade water, shaking for 2 h, and centrifuging. The supernatant was collected, filtered, and analyzed by an HPLC.

9. DICAMBA

Glass bottles were also used to store leachate samples for dicamba. During sample collection 10mL of HC1 per liter was added to each sample to acidify the extract. Afterward, samples were stored at 4°C to reduce the rate of pesticide degradation and to prevent pesticide adhesion to the sample container. Immediately prior to extract analysis, an esterification process [42] was performed. A 61Ni electron-capture detector (ECD) was used on a gas chromatograph with a 180-mm by 4-mm glass column packed with 1.5% SP-2250 and 1.95% SP-2401 on a 100/120 mesh support (Supelco, Inc., Bellefonte, PA). Column, injection port, and detector temperatures were set to 175°C, 250°C, and 300°C, respectively. Concentrations of dicamba were determined from standards and linear regression curves (r^2 = 0.99) for dicamba.

10. RESULTS AND DISCUSSION

10.1. Soil Hydraulic Properties

The intact soil cores had a higher conductivity (averaged for two cores; each depth; each area) than the single repacked core (Figure **3**). Hydraulic conductivities were measured through the entire soil profile (0-40 and 40-80cm). At about -60kPa, K(θ) was nearly the same for the intact versus repacked cores (Figure **3**), as well as for unsaturated conductivity (Figure **4**). This soil pressure (-60 to -80kPa) represents the soil pressure at which flow through the soil matrix is due primarily to gravitational and capillary forces [10, 14].

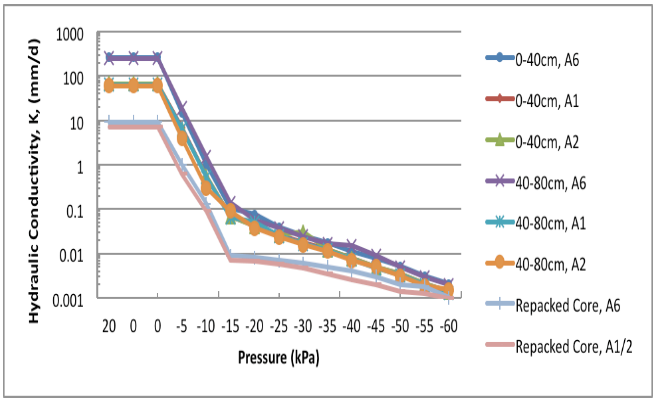

Figure 3: Hydraulic conductivity, K, for both intact and repacked soil cores versus soil pore pressure (kPa). All cores except repacked cores are an average of two cores per depth, i.e., 0-40 and 40-80cm. A1, A2, and A6 refers to areas 1, 2 and 6 respectively as shown on Figure **1**.

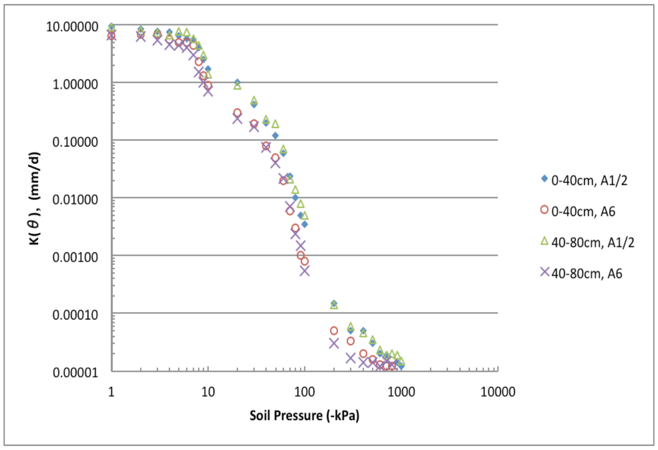

Figure 4: Unsaturated hydraulic conductivity, K(θ), versus matric suction (soil pore pressure). A1 and 2 are well-drained loamy soils and A6 are well-drained silty soils.

11. STAINING

The top few cm of each core were not used for preferential flow path measurement to avoid bias by heavy staining at the surface, where the dye solution generally had a longer residence time. Being mostly silty and loamy type soils, there were only a few cracks, beginning at the surface by plant residues, most of which appeared to be old root tunnels, i.e., macropores. Water and subsequently the dye flowed around these areas, which confirmed the hypothesis that most of the water was moving more as preferential flow in areas of lower density than as true macropore flow – through cracks, worm holes, or decayed root channels. The lack of dye observed in the cracks also may have resulted from entrapped air causing a bypass of water flow. However, this is unlikely because the cores had been purged with CO_2 prior to saturation and KBr application. Also, flow into such cracks would need to overcome atmospheric potential for fluid to move into them [10].

The amount of area stained (Table **5**), using Kendall's rank correlation coefficient (τ), matches well with the time, pore volume, and center of mass of breakthrough of Br- (Figure **5**). It also closely estimates the percent stained area observed in the field [7]. One could reasonably argue that it is the rate of travel through the preferential flow paths, not their areal extent, which affects breakthrough; however, the stained area does not provide a measure of flow rate. Also, it was found that the greater the amount of stained area present, the faster the breakthrough of Br^-; this is in agreement with other research [43]. Cores from areas 1, 2, and 6 (10-40cm (Table **5**), had the most stained area by depth, a maximum of 23% at 10cm to a minimum of about 5% at 50cm (first section of second core depth: 40-80cm). They also required the longest period of time to peak reduction in concentration of Br^- (Figure **5**). Cores from the three areas at the 40-80cm depths showed a rapid decrease with depth in stained area; from a maximum of 6% at 50cm to 4% at 80cm (Table **5**). Cores from these depths corresponded to a slower breakthrough of Br- (Figure **5**). Irrespective of the variability with depth, the overall percent stained area correlates well with the time and pore volume of Br-breakthrough for all soil cores (Table **5** and Figure **5**). Additionally, the stained areas decreased steadily with depth from about 10 to 50cm between the sets of cores, which corresponded closely to the percent macropores measured with depth in the field in a previous study [7].

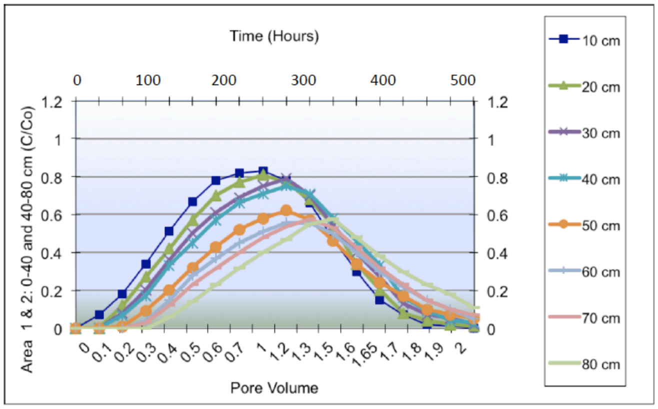

Figure 5: Bromide breakthrough curves for depths 0-40 and 40-80cm cores from areas 1 and 2. [C, measured concentration; C_o, original concentration].

Also, from field observation, a large portion of what appeared to be decayed root channels from the corn crop had been filled with finer material, i.e., sands, silt, and organic matter, due to normal soil processes. From the measurement of stained areas and correlation of Br^- breakthrough for those areas, it is clear that most of the blue dye moved through preferential flow paths, the majority of which were found within the upper 10 to 30cm of soil (Table **5**).

12. FIELD

The results of the instantaneous profile tests indicate that the soils had fairly high saturated hydraulic conductivity (Ks) values; about 260mm day^{-1}. Field determinations of hydraulic conductivity were similar to those obtained from the laboratory experiments at soil suction/pressure less than zero. For the 40-80cm interval, the range of pressures for which K(θ) was determined was 0 to -49kPa. For pressures less than -29 and -49kPa, field data were not available for direct measurement, consequently K(θ) was computed using the soil moisture characteristics (as described above in the laboratory experiment).

The high K values are likely a result from soil type, as well as macro-porosity derived from crop growth. Unsaturated hydraulic conductivities (Figure **4**) of the laboratory cores were in the same range as those measured in the field plots ($1\text{-}10^{-2}$mm day^{-1}) at the same relative water content (θ = 0.23).

13. HERBICIDE TRANSPORT

13.1. Atrazine

Concentrations of atrazine at 10 to 40cm and 50 to 70cm depths (Figure **6**) two months after application are greater than would be expected if flow and chemical transport were through the soil matrix alone. Based on calculations from K(θ) data and published retardation values; atrazine would normally be diffused within the soil matrix, allowing for little or no transport below 10-30cm depths and would likely have been degraded by microbial processes. Further, based upon measured K(θ), both the concentration and arrival of KBr breakthrough are much higher than suggested by other researchers [44, 45], using published retardation coefficients and half-life values. This indicates that, in this soil, the half-life was greater than suggested, potentially due to entrapment in occluded pores, i.e., a dual-porosity soil.

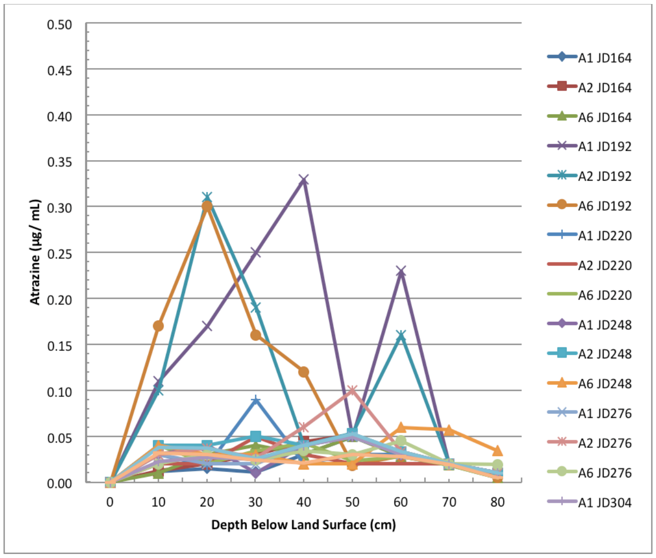

Figure 6: Atrazine concentrations from suction lysimeters for A1, A2, and A6. Herbicide was applied Julian Day (JD) 134. Equipment detection limits 0.05µg/mL.

Generally, atrazine concentrations decreased with depth for all areas sampled (Figure **6**) although larger than expected concentration peaks were observed at various depths and times. Based on sampling date, these peaks seem to confirm that atrazine was transported to a depth below 15cm relatively quickly. Despite that concentrations were lower than those at the time of application; much atrazine was transported within the soil profile, as evidenced by the high peaks in Julian Day 192 samples (Figure **6**). Negligible amounts (below detection limits of equipment; 0.05 µg/mL) of the metabolites de-ethylatrazine and de-isopropylatrazine were detected in the samples.

On Julian Day 183, about 85mm of rainfall was recorded, which may explain the peak concentration on JD192 sampling of atrazine. Precipitation was measured using a Texas Electronics TE525MM tipping-bucket rain gage equipped with a 24.5-cm funnel and calibrated to measure rainfall in 0.1-mm increments. The gauge was attached to the CR-10 Campbell Scientific data logger. High atrazine concentrations observed as late as Julian Day 276 likely reflect entrapment and partial desorption of atrazine from soil within the macropore system, where it likely remained in immobile pockets until it was later flushed into larger pores and perhaps macropores by recharging water.

13.2. Dicamba

Dicamba samples were generally less than detectable limits throughout the study (Figure **7**). However, the overall trend for dicamba movement was similar to that for atrazine. Concentrations remained relatively stable with depth, but during the second month, dicamba moved rapidly through the soil, as is evidenced by the peak for Julian Day 192 at the 10 to 40cm depth and also the 60 to 70cm depths (Figure **6**). This suggests that dicamba as well as atrazine were moving relatively quickly through the soil profile and presumably through preferential flow paths within the porous media matrix, as both K data from the laboratory for both intact and repacked cores (Figure **3**), as well as K(θ) data from the field (Figure **4**), indicate much slower arrival times. Indeed, K for the repacked core (Figure **3**) was much less than that for the intact cores or field plots. Also, sampling and dye staining indicated the strong presence of macropores beginning at the 10-cm depth (Table **5**).

Because the cores were repacked, they represent a collapsed structure with a lack of preferential flow paths or macropores, and will thus be more representative of chemical transport arrival times. Data (Figure **7**) illustrated little difference in concentration at greater depths, except for Julian Day 192. Julian Day 192 samples denote increasing concentrations below the 10-cm depth generally for areas 1 and 6 (Figure **7**) for dicamba, although excepting Julian Day 192, most deeper-depth samples were generally less than detection limits. As discussed above, the peak concentrations generally peaked after a heavy rainfall event (Julian Day 192; Figure **7**).

Compared with concentrations in the extracted water samples, the concentrations of both herbicides in soil samples (data not shown) are generally stable with depth, as would be expected for bulk soil. Soil samples collected on Julian Day 192 indicate that large rainfall events caused fluctuations in atrazine concentrations in the soil matrix similar to fluctuations in the suction lysimeter extracts. The same trends were noticeable in both soil and solution extract samples.

The difference in both herbicide concentrations in soil and lysimeter samples with depth, results from the fact that the suction lysimeters (when at matching soil pore pressures) collect water that is moderately mobile within the soil matrix excluding macropores [35]. Others have recommended that the suction applied to lysimeters be equivalent to the matric potential of the soil, and determined that when the applied suction creates percolation rates near the cup equal to those in the soil at the same depth, the amount of sample is directly related to the soil percolation rate [46]. Others have repeated similar findings [35]. As a result, the lysimeters in this study would more probably sample preferentially flowing fluid, but not macropore flow.

14. GENERAL MODELING AND TRANSPORT

The one-dimensional convection-dispersion equation;

$$\frac{\partial C}{\partial t} = \nabla.\left(D\nabla C\right) - \nabla.\left(\nabla C\right) + R$$

(where c is concentration, t is time, D is diffusion coefficient, ∇ is average velocity, R is source/sink for quantity c) was initially determined adequate to model transport through these soils [47]. The basic procedure involved estimating model parameters (e.g. average velocity, dispersion coefficient, and pulse duration) that minimized the sum-squared differences between observed and predicted concentrations (less than 10^{-5}) as a function of time. Given the changing saturation with depth, modeling of concentration profiles was conducted at the following depths: 10, 20, 30, 40, 50, 60, 70, and 80cm. The general trend in parameters included increasing velocities and dispersion coefficients, and decreasing pulse duration.

Modeling by depth [47] is illustrated in figures **8-11** (note that these illustrations were chosen as representative – other depths are not shown). Figure **8** illustrates a poor fit of observed versus predicted concentrations of atrazine for those times when heavy rainfall events caused significant flushing of the chemical through the soil (compare Figure **8** to the 60-cm depths in Figure **6**) and demonstrates that the model used was insufficient in predictability for such

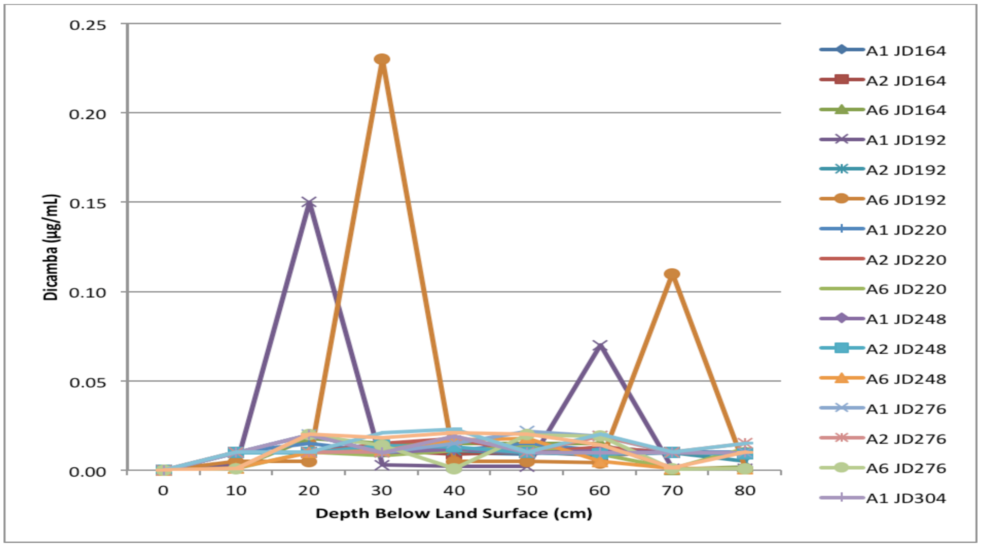

Figure 7: Dicamba concentrations from suction lysimeters for A1, A2, and A6. Herbicide was applied Julian Day (JD) 134. Equipment detection limits 0.05 µg/mL.

events, i.e., a very poor fit. The observed versus predicted concentrations shown in Figure **9** indicate a better fit of the data, but still not as predictable as preferred. However, Figure **9** observations are representative of times and depths where significant rainfall did not appear to cause flushing of atrazine (see Figure **6**).

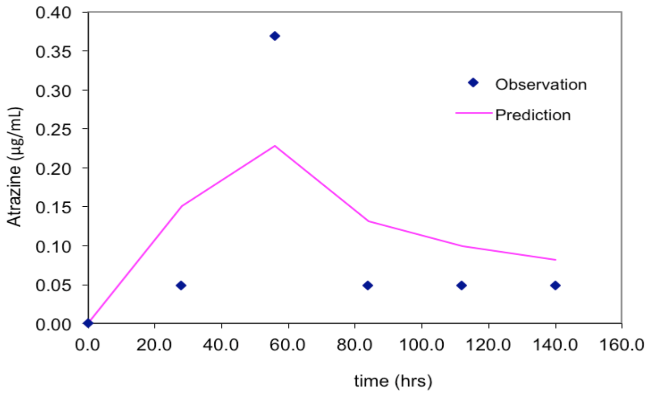

Figure 8: Modeled atrazine concentrations (predicted vs observed) for area 1 (A1) from 60-cm depth.

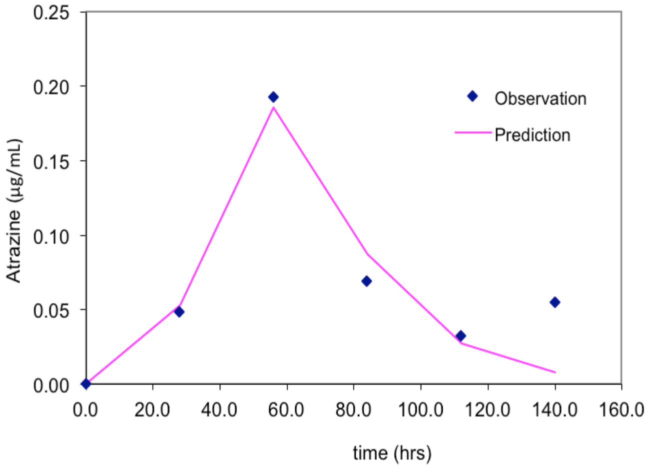

Figure 9: Modeled atrazine concentrations (predicted vs observed) for area 6 (A6) from 40-cm depth.

The results for dicamba (Figures **10** and **11**) were similar to those for atrazine. During significant rainfall events, the observed versus predicted concentrations show a poor fit (Figure **10**) while for other times and depths without such events occurring, the fit was better (Figure **11**).

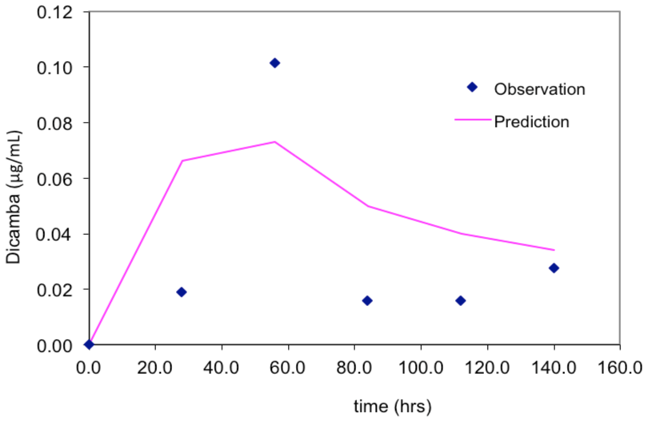

Figure 10: Modeled dicamba concentrations (predicted vs observed) for area 1 (A1) from 60-cm depth.

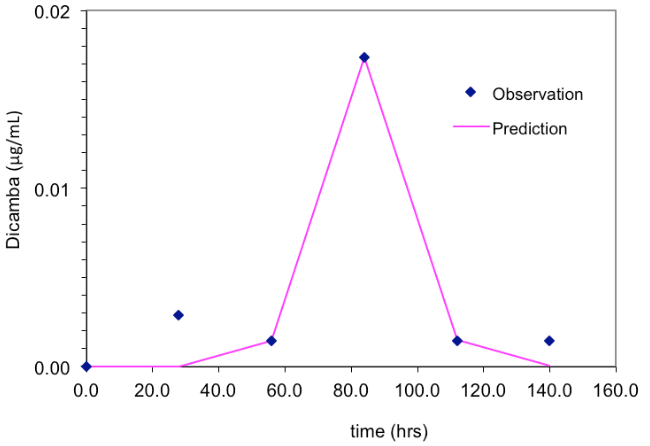

Figure 11: Modeled dicamba concentrations (predicted vs observed) for area 6 (A6) from 80-cm depth.

Generally, the observed versus predicted results are poor. Because of the proven presence of macropores in the research area (from dye staining; see Table **5**), the transport of both chemicals was likely *via* dual-porosity pathways, which is why concentrations of each of the chemicals was witnessed at higher levels than expected after application (Figures **6** and **7**). The dual-porosity concept [48, 49] is an approach which is useful in cases where the flow domain is structured, and in those cases where exchange processes between the soil matrix and macropores are very likely to play a role in the water flow and solute transport behavior. It is often stated that the macropore domain is mainly gravity driven [50]. Despite this, there is the question of how to interpret transport relative to matrix vs preferential flow vs matrix plus preferential flow. Given that both velocity (v) and time (t) were similar for each herbicide, this suggests that the dispersion coefficient, in addition to the presence of macropores, had the greatest influence on transport and indicates that a large dispersivity also can be associated with an isolated spike in herbicide concentration. Similar results were found in which studies with large cores [51], utilizing the analysis method of Others, demonstrated that with the presences of more mobile transport areas, i.e., macropores and preferential flow paths, that dispersivity increased and chemical spikes were shown in the data. Therefore, the spikes illustrated for transport of atrazine and dicamba in this study (Figures **6** and **7**) likely indicate the presence of macropores. This is potentially due to increased dispersivity that has the greatest influence on transport. In this case, soil-physical parameter values should be close such that the response characteristic of the macropore domain is according to what one might expect, such as a near-zero water retention and fast transport capability due to a large hydraulic conductivity.

To derive the general equations of water flow, the volumetric flux density equation is according to Darcy's law, combined with the continuity or mass balance equation (conservation of mass). Transport of water by soil vapor movement in the gas phase is taken into account. The continuum approach neglects boundaries between phases and assumes that physical properties in any phase can be described at a point within the representative elemental volume. Further more, the porous medium is rigid and has a stable geometry. Air in the porous medium is present at atmospheric pressure. Input data for the model [47] for atrazine and dicamba are listed in Tables **6**; output data are listed in Table **7**.

15. SUMMARY AND CONCLUSIONS

As water and chemicals flow into the soil matrix, flow is retarded by the small size of the pores, which restricts the flow of water to large conducting pores; because of these zones of restricted flow, some of the herbicides may become entrapped in the soil water in dead-end pores whereas additional amounts are adsorbed onto soil particles. Consequently, herbicide concentration in the matrix may be higher than can be sampled by the lysimeters, and recharge events probably flushed each of the herbicides from isolated or immobile areas within the soil matrix into preferential flow paths where they became much more mobile and

Table 6: Input data for Figures 8-11 for use in Tang, *et al*. (2010) model: http://www.ornl.gov/~t6g/cxtfit/

Figure 8 - Atrazine		**Figure 9 - Atrazine**		**Figure 10 – Dicamba**		**Figure 11 – Dicamba**	
Time (hrs)*	**Observed (μg/mL)**	**Time (hrs)**	**Observed (μg/mL)**	**Time (hrs)**	**Observed (μg/mL)**	**Time (hrs)**	**Observed (μg/mL)**
0	0.00	0	0.00	0	0.0000	0	0.0000
28	0.05	28	0.05	28	0.0188	28	0.0029
56	0.37	56	0.19	56	0.1013	56	0.0014
84	0.05	84	0.07	84	0.0159	84	0.0174
112	0.05	112	0.03	112	0.0159	112	0.0014
140	0.05	140	0.05	140	0.0275	140	0.0014

Table 7: Output data for Figures 8-11 for use in Tang, *et al*. (2010) model: http://www.ornl.gov/~t6g/cxtfit/

Figure 8 - Atrazine		**Figure 9 - Atrazine**		**Figure 10 – Dicamba**		**Figure 11 – Dicamba**	
Time (hrs)*	**Predicted (μg/mL)**	**Time (hrs)**	**Predicted (μg/mL)**	**Time (hrs)**	**Predicted (μg/mL)**	**Time (hrs)**	**Predicted (μg/mL)**
0	0.00000	0	0.00000	0	0.000000	0	0.00000
28	0.15112	28	0.05274	28	0.066147	28	0.00000
56	0.22786	56	0.18537	56	0.072809	56	0.00145
84	0.13156	84	0.08698	84	0.049662	84	0.01736
112	0.09951	112	0.02743	112	0.039867	112	0.00149
140	0.08143	140	0.00762	140	0.034000	140	0.00002

were sampled later by suction lysimeters. With continual recharge and subsequent flushing during the growing season, herbicide concentrations in water from the suction lysimeters will gradually decrease to less than detectable limits, whereas concentrations will remain high within the soil matrix; accordingly, soil samples would represent the amount of herbicide stored in the soil. The results indicate that a portion of this soil-stored herbicide may become available for transport and potentially may be flushed during large rainfall events. Also, these soils with macropores present had an increased dispersivity, which was also a factor in chemical transport.

Thus, it is probable that preferential flow paths resulting from soil variability were a factor in transport of atrazine and dicamba at the field site. These herbicides were not adsorbed irreversibly to the soils, and during early stages of the growing season (within two months of application) they were subsequently leached after periods of heavy rainfall. Because large cracks and pores within the soil profile are at atmospheric potential, saturated or near-saturated (sub-atmospheric: -1 to -2kPa, but near-zero) conditions would be required for water to infiltrate the land surface in these areas. Consequently, a management system, excepting no-till, that reduces surface cracking and interrupts access to preferential flow paths and or macropores, thereby preventing chemical inputs from reaching them, could play a significant role in lessening groundwater contamination in the Midwest. However, herbicides may continue to be transported in preferential flow paths that are lower in density than the surrounding matrix, but are not cracks. Within these, flow will likely occur at soil pressures of 0 to -30kPa [10, 14, 35, 51]. These preferential flow paths could also be blocked by conventional tillage operations that homogenize the tilled layer of soil, ensuring an even density that may prevent rapid flow during heavy rainfall events. However, during and immediately after heavy rainfall event(s) in which this layer approaches saturation, significant flow would likely occur within preferential flow paths at the bottom of the plow-layer interface. Results also indicate that a dual porosity/modeling process would be more accurate in predicting chemical transport than a conventional advection-dispersion model as used herein. The continuation of this research will therefore focus on the development of a dual-porosity model.

As staining of laboratory cores indicated high percentages of what appeared to be preferential flow paths, a qualitative study of percent area of preferential flow paths by depth could be beneficial. Because these preferential flow paths seem more continuous than macropores, it is likely that the measurement process as well as modeling incorporation for preferential flow paths will be less complicated than size and continuity measurements of macropores. Subsequent research will be concerned with modeling these processes using a dual-permeability approach and potentially on a much broader scale, perhaps at state to regional. Subsequent research also will seek to quantify and effectively use advanced modeling techniques, being developed, on the results of this study and additional data.

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