Quantifying Preferential Flow by Breakthrough of Sequentially Applied Tracers: Silt Loam Soil

K.-J. S. Kung,* E. J. Kladivko, T. J. Gish, T. S. Steenhuis, G. Bubenzer, and C. S. Helling

ABSTRACT

Field experiments were conducted on tile-drained plots at the South East Purdue Agricultural Center in Butteville, Indiana, to quantify contaminant transport via preferential flow paths in a silt loam soil. Breakthrough patterns of three fluorobenzoeic acids (pentfluorobenzoic acid [PFBA], o-trifluoromethylbenzoic acid [o-TFMB], and 2,6-difluorobenzoic acid [2,6-DFBA]) in a preliminary study indicated that they were transported as conservatively as is bromide (Br\(^{-}\)). These four tracers were then sequentially applied, in an adjacent plot, during simulated precipitation (3 mm h\(^{-1}\) intensity, 10-h duration). Bromide was sprayed shortly before irrigation started, while PFBA, o-TFMB, and 2,6-DFBA were applied at 2, 4, and 6 h thereafter, respectively. The flow began increasing at around 3 h, and Br\(^{-}\) appeared in tile drain flow = 4 h after irrigation started, yet benzoic acids, PFBA, o-TFMB, and 2,6-DFBA, were detected in the tile drainage at 102 min, 42 min, and 18 min after their applications, respectively. Tracer mass recovery from tile drainage was Br\(^{-}\) (7.0%), PFBA (13.9%), o-TFMB (18.7%), and 2,6-DFBA (19.7%) of applied mass. The faster arrival time and greater recovery of sequentially applied tracers confirmed that water movement and contaminant transport shifts toward increasingly larger pores of the preferential flow paths as soil becomes wet during a precipitation event. The breakthrough patterns of these tracers can be used to quantify the water flux distributions of preferential paths. Because \(\approx90\)% of the chemical leached from this precipitation event occurred during the first day, it was critical to intensively monitor contaminant transport during the first 24 h after a rainfall. A soil sampling protocol based on collecting soil cores at random locations once every several days is unsuitable for determining the deep leaching under field conditions.

FERTILIZERS AND PESTICIDES have played essential roles in helping to provide high agricultural output per unit area of arable land. After extensive use, however, some chemicals have resulted in non-point water contamination. Water contamination by pesticides and nitrate is now perceived as one of our nation’s most significant, long-term environmental problems. During the last three decades, researchers have sought to understand the fundamental transport processes leading to water contamination, hoping thereby to eventually diminish its impact. Soil physicists have focused tremendous effort on measuring soil hydraulic properties and devising statistical methods to comprehend their spatial variability; this is based on the premise that one must first quantify water flux distribution before solute transport can be resolved. On the other hand, soil chemists and microbiologists have characterized adsorption and degradation of agrichemicals, in part assuming that the leaching of agrichemicals can be minimized if optimum combinations of adsorption and degradation can be achieved.

Currently, efforts to directly measure soil hydraulic properties have been gradually decreasing because field results show that, with limited budget and instruments, the soil hydraulic properties and their spatial and temporal variability are too complex to be grasped, and field-scale water flux distribution cannot be directly and adequately characterized. Furthermore, results from field experiments demonstrated that strongly adsorbing chemicals can move as fast and deep into a soil profile as more mobile chemicals. For example, using a tile drain as an alternative sampling protocol, Everts et al.

**Abbreviations:** BTC, breakthrough curve; HPLC, high performance liquid chromatography; IC, ion chromatography; o-TFMB, o-trifluoromethylbenzoic acid; PFBA, pentfluorobenzoic acid; WT. water tracer; 2,6-DFBA, 2,6-difluorobenzoic acid.


(1989) observed that both non-adsorbing Br⁻ and adsorbing rhodamine water tracer (WT) dye had fast breakthrough patterns within the first 4 h after the initiation of the irrigation. Klavivko et al. (1991, 1999) demonstrated that pesticides were most susceptible to leaching during rainfall events that occur shortly after chemical application in spring, and more adsorbing pesticides atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] and alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide] can be transported to shallow groundwater (between 0.8-1.0 m) as rapidly as more mobile chemicals such as carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuran methylcarbamate) during this period. Kung et al. (2000) applied a pulse of chloride and rhodamine WT dye solution in a field experiment on a clay loam soil. They found that both tracers arrived at the tile after 13 min after application. Saturated soil hydraulic conductivity of the field, based on soil cores collected at different depths, ranged from 0.5 to 5.0 × 10⁻⁴ m s⁻¹. According to the conventional conceptualization, neither the conservative nor the reactive tracers should have reached the tile drain within 2 d.

The term preferential flow paths was coined to describe the fast contaminant transport that bypassed the vast soil matrix (Kung, 1990). It is critical to comprehend preferential flow in order to develop conceptual and numerical models to predict contaminant transport in unsaturated soils. Ju and Kung (1997) conducted numerical experiments in sandy soils with layering structures to characterize the water dynamics of the funnel-type preferential flow pathways and their impact on contaminant transport in an unsaturated sandy soil profile. They justified their numerical approach by the following two reasons: (i) the impact of a funnel mechanism that is caused by layered structure on contaminant transport was well understood (Kung, 1993; Ju and Kung, 1993); and (ii) the multiple-layered soil structures in an unsaturated sandy profile that trigger funnel flow are permanent and can be characterized by the ground-penetrating radar technique (Kung and Lu, 1993; Casper and Kung, 1996). In contrast, in unsaturated soils with finer textures, field-scale preferential flow mechanisms are not expressly understood. The preferential flow paths have a dynamic formation-destruction cycle, and there are no instruments to accurately map or reveal these paths. The preferential flow paths are three-dimensional, occupy only a very small volumetric fraction of the soil matrix, and cannot be quantified by the conventional techniques designed to measure the hydraulic properties of the bulk soil matrix. Therefore, the impacts of preferential flow paths on contaminant transport in fine-textured soils still cannot be numerically examined.

Jury (1982) introduced the transfer function concept to bypass the necessity of accurately and directly measuring the soil hydraulic properties of unsaturated soils in order to predict contaminant transport. In his approach, the breakthrough curve (BTC) of a conservative tracer was used to reflect the convoluted impact of the water dynamics on solute transport under field conditions. Jury’s concept was adopted in this study; i.e., BTCs of conservative tracers were used to quantify the impact of the water dynamics of preferential flow on solute transport. In Jury’s approach, the breakthrough of a single pulse of a conservative tracer was used and it was implicitly assumed that the water flux distribution was a stationary property of a soil profile. The rainfall intensity-duration from individual precipitation events were not considered as parameters. Instead, only the total net infiltration from all precipitation events during a period was used to drive the contaminant transport.

Experimental results from Kung et al. (2000) showed that as a soil profile became wetter during a precipitation event, the arrival time of both conservative and reactive tracers to a tile drain shortened. This indicated that the water flux distribution of preferential flow paths change during a precipitation event; i.e., some preferential flow paths were not hydraulically active when a soil profile was initially dry. This implied that the water flux distribution of preferential flow paths was not a stationary property of a soil profile but depended primarily on soil water content of the soil profile. As a result, each rainfall event can have a different impact on the contaminant transport through preferential paths. In this study, different conservative tracers were sequentially applied during a single precipitation event. As the soil surface became wetter, the breakthrough patterns of tracers applied at different times reflected the impact of the change of the pore spectrum of hydraulically active preferential flow paths on contaminant transport.

The success of using a chemical BTC to quantify the water dynamics of preferential flow paths hinged on whether a representative breakthrough pattern could be measured to accurately reflect the convoluted impact of water fluxes along preferential flow paths on contaminant transport. As demonstrated by Ghodrati and Jury (1990), Ju et al. (1997), and Kung et al. (2000), conventional sampling protocols (e.g., soil coring and soil lysimeter methods) are unsuitable to monitor the field-scale chemical sampling patterns through preferential flow paths. Richards and Steenhuis (1988), Klavivko et al. (1991, 1999), and Czapat et al. (1994) showed that tile drain facilities can be used as an alternative.

Multiple conservative tracers with similar properties must first be chosen in order to reflect the impact of preferential flow paths on contaminant transport as a soil profile becomes wetter. Currently, Br⁻ and Cl⁻ are regarded as the most suitable conservative tracers and are commonly used to indicate water movement and solute transport. Bowman and Gibbens (1992) and Jaynes (1994) explored the transport properties of several fluorobenzoic acids, comparing them with Br⁻. Among the tested fluorobenzoic acid isomers, three were recommended (because they had the least adsorption and degradation) as alternative conservative tracers: PFBA, 2,6-DFBA, and α-TFMB. The breakthrough patterns of these alternative tracers were rigorously tested in laboratory soil column studies (Jaynes, 1994). Under field conditions, only their recoveries in soil matrix from soil cores were compared, and the deep leaching through preferential paths could not be assessed by the soil coring method.

In this study, the primary objective was to use a tile
drain monitoring facility to quantify the water dynamics of the preferential flow pathways and their impact on contaminant transport in a fine-textured, unsaturated soil profile. A preliminary experiment was first conducted to determine whether the three fluorobenzoic acids mentioned above would have the same breakthrough patterns as those of Br\textsuperscript{−} and Cl\textsuperscript{−} under field conditions in a soil profile with preferential flow paths. Although not a conservative tracer, nitrate has recently been blamed as a major cause of oxygen-depleted water (hypoxic zone) in the Gulf of Mexico and the USA. U.S. Geological Survey data indicated that >70% of the total N delivered to the Gulf by the Mississippi River originates above the confluence of the Ohio and Mississippi Rivers (Alexander et al., 1995; USDA-NRCS, 1996). A secondary objective of the preliminary study was to determine whether Br\textsuperscript{−}, Cl\textsuperscript{−}, and these fluorobenzoic acids have the same breakthrough patterns as freshly applied nitrate in a soil profile with preferential flow paths. After examining the suitability of three alternative tracers, the objective of our main experiment was then to quantify the water dynamics of preferential flow paths and their impact on contaminant transport in an unsaturated silt loam soil.

**MATERIALS AND METHODS**

**Preliminary Study**

Experiments were conducted in a field at the South East Purdue Agricultural Center of Purdue University in Butlerville, Indiana, in November 1996. This site was chosen because tile monitoring stations had been installed in the early 1980s and preferential flow had been observed (Kladivko et al., 1991, 1999). The cropping system was a corn–soybean rotation and the soil had been under no-till management for three years. The slope at the site is approximately 1%. The experimental plot is 225 m long and 20 m wide, with a center tile drain that is monitored for flow and chemical flux. Border tiles (not monitored) at 10 m on either side of the center tile were installed to accurately partition the water input area to the center tile. The soil is Clermont silt loam soil (fine-silty, mixed, superactive, mesic Typic Glossaqualfs) with approximately 20% sand, 70% silt, and 10% clay. This loess soil has 1% soil organic matter in the top 45-cm depth and is typical of the southern portion of very extensive Midwest Corn Belt soils, extending from southwestern Ohio, across southern Indiana and southern Illinois, through Missouri, into southern Iowa and eastern Kansas (Kladivko et al., 1991). The perched groundwater at this site is maintained at approximately 0.75- to 0.9-m depth by tile drainage.

The five conservative tracers Br\textsuperscript{−}, Cl\textsuperscript{−}, PFBA, 2,6-DFBA, o-TFMBA, as well as nitrate, were co-applied to determine whether they had similar breakthrough patterns. The total masses of tracers applied were Br\textsuperscript{−} (2.0 kg), Cl\textsuperscript{−} and nitrate (2.4 kg each), and the benzoic acids (0.45 kg each). Each chemical was first dissolved separately (pH of each benzoic acid solution was adjusted to 7 by slowly adding KOH solution), and then all were combined into a 115-L tank mix to be applied uniformly through a sprayer. In most published results from field experiments, chemicals were applied to an entire field. However, in this preliminary study, the six tracers were applied only to a 1.5-m by 24-m strip. The long side of the strip was parallel to the long side of the plot and offset 0.3 m from the center tile line. The down-slope end of the chemical strip was located 33 m from the lower end of the field. The main reason for applying chemicals only to a strip was to reduce cost, because the benzoic acids were too expensive to be used throughout the entire field. This preliminary study was only to determine whether the benzoic acids had similar BTCs to those of Br\textsuperscript{−}, Cl\textsuperscript{−}, and nitrate. Also, because the watertable near the tile line has the steepest gradient, applying chemicals to a narrow strip close to the tile line could minimize the time required for the lateral transport of chemicals within a saturated zone to the tile line, so that the travel time of contaminants through preferential flow paths within the unsaturated soil profile can be accurately estimated.

In order to bring the watertable up to the tile line, the site had been pre-irrigated with 15 mm water (6.2 mm h\textsuperscript{−1} intensity) one day before the experiment with a solid-set sprinkler system. Then on the morning of the experiment, a 1-h pre-irrigation added another 6.2 mm water. After waiting for an hour, tracers were applied. Shortly after the tracer application, irrigation with the same intensity was applied for 35 min to leach these chemicals into the soil profile. The chemical application strip was located in the center of the irrigated area (24 m × 60 m). Again, the long sides of the irrigated area and the plot were parallel. Because of the plot's configuration (border tiles 10 m offset from the center tile), a 24-m-wide irrigation width extended beyond the adjacent border tiles and ensured that leachate originated from the treated chemical strip would only enter the center tile being monitored. The irrigation water was from the local municipal water supply and had none of the applied chemicals, except for 2.5 mg L\textsuperscript{−1} Cl\textsuperscript{−}.

After the chemical application and initial irrigation, there was a 15-mm rainfall (Day 1), a 6.2-mm irrigation (Day 3), 11.7-mm of precipitation (Day 5), and 5.8-mm of precipitation (Day 8). The tile flow was continuously measured by the tipping-bucket method. Water samples were collected from the tile flow to determine the mass flux of these chemicals. The frequency of water sample collection was determined by the flow rate of the tile drainage. For example, shortly after each irrigation or precipitation event, when tile flow was relatively high, a 100-mL sample was collected every 10 min and three such samples were composited into a final water sample. As tile flow started to decrease, 100-mL samples were collected at 20-min intervals and three samples were composited into a final water sample. About two days after each irrigation or precipitation event, a 50-mL sample was collected at 30-min intervals and six samples were composited.

**Main Experiments of Sequentially Applied Conservative Tracers**

Field experiments were conducted at another 20-m by 225-m no-till plot at the South East Purdue Agricultural Center in Butlerville, Indiana, in May of 1997, when corn was starting to emerge. The tile flow rate was 1 mL s\textsuperscript{−1} (caused by a 1.2-cm pre-irrigation event 2 d earlier) and there was no precipitation in the five-day weather forecast. Irrigation (3 mm h\textsuperscript{−1} intensity) was continuously applied for 10 h to simulate a prolonged mild spring shower by a solid-set sprinkler system. The sprinkler system was made of two lines that were 12 m apart. Within each line, the distance between two adjacent nozzles was 12 m. Nozzles between the two lines were staggered by 6 m. The low intensity was chosen to avoid any surface runoff so that mass recovery could be accurately calculated. The irrigated area (24 m × 60 m) was about 73 m from the lower end of the field, where the tile monitoring facility was installed.

The conservative tracers tested in the preliminary study
were sequentially applied. Shortly before the irrigation started, Br\textsuperscript{+} (1.93 kg in 20 L water) was uniformly sprayed on a 1.5-m by 24-m strip. The strip was positioned at the center of the irrigated area and the long side of the strip was parallel to the tile line with 0.3 m offset. At 2 h after irrigation commenced, PFBA (1.37 kg in 16 L water) was sprayed on the same strip. Then, at 4 and 6 h after the irrigation started, o-TFMB (1.5 kg in 16 L water) and 2,6-DFBA (1.5 kg in 20 L water) were sprayed on the same strip, respectively. For each acid tracer solution, pH was adjusted to 7 by slowly adding KOH solution during mixing. Each tracer was applied through a sprayer within 5 min; irrigation was continuous when tracers were applied. This sequential tracer application scheme was intended to explore how water and tracers would move through the larger end of the pore spectrum of preferential flow paths as a soil profile became wetter.

During the first 12 h after the irrigation started, water samples were collected from the tile onset every 6 min. From 12 h to 24 h, water samples were collected at 10-min intervals and sequentially composited into 30-min samples. From the second to the fourth days, samples were collected every 40 min, with three samples composited to give 2-h samples. This intense sampling frequency was designed to register the fast contaminant breakthrough observed by Kung et al. (2000). The samples were stored at 5\textdegree C until analyzed, except during a short period of shipping. Flow rate of the tile drain was continuously measured by using the tipping-bucket method.

**Chemical Analyses**

A 3-mL aliquot from each sample was filtered (0.2 \(\mu\)m) and then analyzed by high performance liquid chromatography (HPLC) for the benzoic acids and by ion chromatography (IC) for Br\textsuperscript{+}, Cl\textsuperscript{−}, and nitrate. The HPLC conditions were as follows: mobile-phase, acetonitrile 15 mM KH\textsubscript{2}PO\textsubscript{4} (titrated to pH 2.6 with phosphoric acid) (35:65, v/v); flow rate, 1.7 mL min\textsuperscript{−1}; guard column, Spherisorb SAX (10 mm \(\times\) 4.6 mm \(\times\) 5-\(\mu\)m i.d.; Waters, Milford, MA); analytical column, Supelcosil SAX1 (25 cm \(\times\) 4.6 mm \(\times\) 5-\(\mu\)m i.d.; Sigma-Aldrich, St. Louis); injection volume, 50 \(\mu\)L; and UV detection, 205 nm. The detection limit for each benzoic acid was 50 \(\mu\)g L\textsuperscript{−1}. The IC conditions were: mobile-phase, 1 mM CH\textsubscript{3}CO\textsubscript{2}H; guard column, Waters IC-Pak anion; analytical column, IC-Pak anion (6 cm \(\times\) 4.6 mm \(\times\) 5-\(\mu\)m i.d.); injection volume, 50 \(\mu\)L. The detection limit for Br\textsuperscript{+}, Cl\textsuperscript{−}, and nitrate were 0.25, 0.5, 0.5 mg L\textsuperscript{−1}, respectively.

**RESULTS AND DISCUSSION**

**Preliminary Study**

The mass flux normalized by the mass applied of each tracer sampled from the tile drain during the first 10 days after chemical application is shown in Fig. 1. The results indicated that all tracers had very similar breakthrough patterns. The similarity of these leaching patterns confirmed that the three benzoic acids were as conservative as Br\textsuperscript{+}, Cl\textsuperscript{−}, and nitrate. This suggested that it was valid to use these three benzoic acids to quantify water movement in a soil profile with preferential flow paths. The similarity between the mass flux pattern of nitrate and those of the other five tracers indicated that it was also valid to use the breakthrough of conservative tracers to indicate the transport of recently surface-applied nitrate through preferential flow paths. However, it must be stressed that this similarity was partly because this field experiment was conducted in November 1996, when the temperature of the soil profile measured in a nearby weather station fluctuated between 3 to 15\textdegree C. There was little microbial activity for N transformation and no nitrate uptake by plant roots during this period.

The BTCs of Cl\textsuperscript{−} and nitrate in Fig. 1 are higher than the rest because some Cl\textsuperscript{−} and nitrate were already stored in the soil profile before the tracer application from this experiment. The concentrations of Cl\textsuperscript{−} and nitrate in the background flow from the tile drain before the chemical application of this experiment were 8.4 and 4.5 mg L\textsuperscript{−1}, respectively, while the concentrations of the other tracers were below their detection limits. That Cl\textsuperscript{−} had higher mass recovery was partly because there was 2.5 mg L\textsuperscript{−1} Cl\textsuperscript{−} in the irrigation water. The total mass recoveries during the first 10 days were Br\textsuperscript{−} (2.59\%), 2,6-DFBA (2.41\%), o-TFMB (2.56\%), and PFBA (2.50\%). The mass recoveries of Cl\textsuperscript{−} and nitrate were unknown because it was impossible to partition the percentages of these two chemicals contributed from the soil matrix.

**Main Experiment: Sequentially Applied Tracers**

Based on 55 rain gauges, the measured total water applied during the 10-h irrigation was 28.8 mm with the Christianson uniformity of 0.85. The measured breakthrough patterns of the four applied tracers and the tile hydrograph are shown in Fig. 2. The tile hydrograph showed that tile flow started to increase at 2 h and 50 min after irrigation started. Bromide was applied shortly before the irrigation started, while the PFBA was applied 2 h after the irrigation started. According to the conventional conceptualization of Darcian flow and convection–dispersion transport, Br\textsuperscript{−} should reach the shallow groundwater first (i.e., first in, first out); however, PFBA was detected in the tile drainage at 3 h and 42 min after the irrigation started (i.e., 102 min after its application), while Br\textsuperscript{−} was not detected until 4 h after its application. On the other hand, the o-TFMB was applied at 4 h after the irrigation and arrived at the tile 4 h 42 min after the irrigation started (i.e., only 42 min after its application). The fourth tracer, 2,6-DFBA, was applied 6 h after the irrigation began and arrived at the tile at only 18 min after its application. Figure 2 shows that the mass flux of the 2,6-DFBA at the first detection is much higher than those of the other three tracers. The water samples were collected once every 6 min in the first 12 h. It was very possible that the 2,6-DFBA actually first appeared in the tile drain shortly after the water sample taken at 12 min after application.

Water movement and contaminant transport occurs through a spectrum of pores in an unsaturated soil under field conditions. The preliminary study had already shown that the four tracers were equally mobile through the preferential flow paths, while the main study showed that the later a tracer was applied during a simulated precipitation event, the faster the tracer arrived at the tile line. The dramatically shorter time for a
tracer applied at later time indicated that different preferential flow paths were utilized for different tracers; i.e., the fourth tracer was transported through preferential flow paths with the largest pores, hence, arriving fastest at the groundwater surface. The slower break-through for the tracers applied earlier was because water and water-borne chemicals were sucked into the matrix pores along wall of the pathways when the profile was dry.

A preferential flow path is defined as hydraulically active when water and water-borne contaminants can directly reach the shallow groundwater surface through the preferential flow pathway. Let us assume there is a preferential flow path labeled “A”. The tracers applied earlier entered into the Pathway A and were later sucked into small matrix pores along wall of the Pathway A. On the other hand, let us assume that the tracers applied later entered into the identical preferential flow Pathway A and reached groundwater through the Pathway A. Although both tracers passed through certain identical portions of flow Pathway A, the tracers should be considered to have traveled through two different flow paths. Because Br\(^{-}\) from the first tracer pulse could not directly reach the shallow groundwater surface through the Pathway A, the preferential flow Pathway A was not hydraulically active to transport Br\(^{-}\). Alternatively, it can be said that Br\(^{-}\) had traveled through a preferential flow Pathway B, which was made of two parts. The first part was made of the upper part of preferential flow Pathway A, while the lower part was made of some matrix pores. Therefore, the Pathway B had a smaller overall equivalent pore size than that of Pathway A. Later, when the soil profile became wet enough, the preferential flow Pathway A became completely hydraulically active to the fourth tracer. In other words, it can be described that preferential flow paths with larger equivalent pore sizes became hydraulically active later, when a soil profile became wetter.

The mechanism in which applied water and tracers would enter pores of a wide size-spectrum was not considered as a parameter in the conventional conceptualization of Darcian flow and convective-dispersive transport. As a result, a tracer applied early was expected to arrive at the tile first. The fact that Br\(^{-}\) had the slowest arrival time indicated that the larger end of the pore spectrum of the preferential flow paths were not hydraulically active when the soil surface was relatively dry. Therefore, it is critical to consider how and when contaminants enter preferential flow paths with different pore sizes. The overall results from four tracers indicated that, as a soil profile becomes wetter during precipitation, water movement and contaminant transport would continuously shift toward the larger end of the pore spectrum of the preferential flow paths.

The tracer recovery (percentage of total applied mass) from tile drainage during the 100-h period were Br\(^{-}\) (7.04%), PFBA (13.9%), o-TFMB (18.7%), and 2,6-DFBA (19.7%). The mass leached increased among the sequentially applied tracers; i.e., the later a tracer was applied, the more mass was leached. The fact that Br\(^{-}\) had the least mass leached and the 2,6-DFBA had the most was consistent with their arrival times; i.e., Br\(^{-}\) arrived the latest and the 2,6-DFBA arrived the earliest after application. Because Br\(^{-}\) was applied to a rela-
Fig. 2. The breakthrough curves of the four conservative tracers and tile flow hydrograph.

Of the adsorbing tracer BTC trailed much faster than those of the non-adsorbing tracers. In other words, an adsorbing chemical had more of its leaching occur during the first day than a non-adsorbing chemical.

Among the deterministic models which simulate fast solute leaching through soil structural pores, the two-region (or two-domain) mobile-immobile conceptualization (Skopp and Warrick, 1974) was first proposed to explain the fast leaching observed in aggregated soils under laboratory conditions. Gerke and van Genuchten (1993) proposed the dual porosity model, in which water and solutes moved through two distinct and interacting domains simultaneously. Similarly, Gwo et al. (1995) proposed a multiple-porosity model, where soil is partitioned into many interacting domains. The arrival times and mass recovery patterns from our sequentially applied tracers and those from Kung et al. (2000) showed that the spectrum of hydraulically active preferential flow paths expanded continuously during a precipitation event; i.e., preferential flow paths with larger pore sizes became hydraulically active and contributed to contaminant transport as a soil profile became wetter. Because 90% or more of the contaminants that leached from the root zone in the 100-h sampling period were leached during the first 24 h through preferential flow paths, the contribution of the so-called immobile, or matrix, or micropore domain to contaminant transport was almost irrelevant during this time frame. Whether those contaminants that entered into soil matrix pores could move back into preferential flow paths and reach the watertable during subsequent precipitation events was beyond the scope of the current study.

One can use the BTCs of the sequentially applied tracers to make inferences about the behavior of fresh applied nitrate fertilizers, since the short time scale of
Fig. 3. The breakthrough curves of the four conservative tracers plotted against the times since their applications.

The vast leaching (i.e., 1 d) would not likely provide time for significant N transformations and uptake to occur. Our data suggested that, after the application of nitrate fertilizer in spring to a relatively dry soil surface, as much as 7% of nitrate could be leached out of a root zone by a single 10-h precipitation event as mild as 3 mm h⁻¹. On the other hand, if the nitrate were applied to relatively wet soil surface, as much as 20% could be rapidly leached out from a root zone after a mild precipitation event. This strongly suggested that highly soluble agrichemicals such as nitrate should never be applied to a wet soil surface. The question then becomes how wet is “wet”? In most cases it is impractical for N fertilizer to be applied in the middle of a rainstorm or immediately following 1.8 cm rain, as was 2,6-DFBA, but how long a delay would be required before the chemical behavior matches that of the Br⁻ in this experiment is unknown. The current experiment cannot answer that question. The data do clearly indicate that fertigation of nitrate on wet soils could lead to substantial losses of compounds through preferential flow.

The fast arrival time and the vast transport during the first day after precipitation strongly suggested that, in order to collect representative samples to assess total deep leaching, it was extremely critical to intensively monitor contaminant transport during the first day after a rainfall event. Soil sampling protocols based on the coring method of collecting soil samples at random locations once every several days is inadequate to determine contaminant leaching under field conditions. On the other hand, a field where the tiles are installed with even spacing and depth and border tiles are installed to partition the water input area would behave like a huge, enclosed and undisturbed lysimeter. Water and contaminants leached from such fields can be accurately and holistically assessed, regardless of how rapidly and preferentially the contaminants are being transported downward.

The mass flux of each tracer plotted against time since application is shown in Fig. 3 (for Br⁻, time coincides with the onset of irrigation). The results show that the BTCs shifted toward the left when a tracer was applied to wetter soil during a precipitation event. Jury (1982) proposed to derive the travel-time probability density function from the tracer breakthrough patterns. The physical factors that determine the travel time under field conditions encompass the size spectrum of hydraulically active pores, chemical retardation and transformation, uptake, and degradation. Results from this study showed that much of the mass that would be leached out from a root zone was leached through preferential flow paths within the first 24 h of a precipitation.

Furthermore, Kung et al. (2000) showed that the initial transport of an adsorbing tracer was almost identical to that of a non-adsorbing tracer. These results together suggested that chemical retardation, transformation, uptake, and degradation had only secondary effects in determining the initial deep leaching of agrichemicals through preferential flow paths. Under this condition, the travel-time probability density function is dictated by the field-scale size spectrum of hydraulically active pores of the preferential flow paths.

Kladivko et al. (1991) observed that a pesticide was most susceptible to deep leaching shortly after its application.
cation. Most pesticides are applied in spring when soil water content near the soil surface varies greatly. If a pesticide were applied to a relatively dry soil surface, the Br⁻ breakthrough pattern would reflect the most relevant water flux distribution of preferential paths that contribute to the pesticide leaching. However, if a pesticide were applied to a wet soil surface, the water flux distribution of preferential paths reflected by the breakthrough patterns of the three benzoic acids would become more relevant in predicting the total deep leaching.

CONCLUSIONS

A preliminary study was conducted using a tile drain facility to monitor breakthrough patterns of Br⁻, Cl⁻, PFBA, o-TFMBF, and 2,6-DFBA, and nitrate applied to a silt loam soil. The similarity of all BTCs suggested that the three fluorobenzoic acids were as conservative tracers as are Br⁻ and Cl⁻ under field conditions. A tile drain facility in an adjacent plot was used to monitor breakthrough of Br⁻ and the three fluorobenzoic acids sequentially applied during a 10-h precipitation event with 3 mm h⁻¹ intensity. The overall results showed that the impact of the water dynamics of preferential flow paths on contaminant transport can be quantified by the breakthrough patterns of sequentially applied conservative tracers. The water flux distribution of preferential flow paths was not a stationary property of a soil profile but depended primarily on soil water content of the soil profile. Each rainfall event may have a different impact on the contaminant transport through preferential paths. Specific results indicated the following:

1. The tile flow increased at around 3 h after irrigation started; Br⁻ breakthrough patterns started around 4 h after irrigation started. The three benzoic acids, PFBA, o-TFMBF, and 2,6-DFBA, were detected in the tile drainage at 102 min, 42 min, and 18 min after their applications, respectively. These patterns of fast arrival times of sequentially applied tracers proved that preferential flow dictates the deep leaching of agrichemicals.

2. The percentages of total applied mass of the tracer recovered from tile drainage were as follows: Br⁻ (7.04%), PFBA (13.9%), o-TFMBF, (18.7%), and 2,6-DFBA (19.7%). The fact that Br⁻ had the least mass leached and the 2,6-DFBA had the most was consistent with their arrival times; i.e., Br⁻ arrived the latest and the 2,6-DFBA arrived the earliest after their applications. This demonstrated that a contaminant moves through the preferential flow paths with larger pores when a soil profile becomes wetter during a precipitation event.

3. The fact that 90% of the deep leaching after a prolonged precipitation event occurred during the first day suggested that tracer behavior could be used to model leaching of recently applied nitrate, since there would be little time for N transformation and uptake to occur. This implied that, after the application of nitrate fertilizer in spring to a relatively dry soil surface, as much as 7% of the nitrate could be quickly leached from a root zone by a single 10-h precipitation event as mild as 3 mm h⁻¹. On the other hand, if the nitrate was applied to a relatively wet soil surface through fertigation, as much as 20% could be rapidly leached out of a root zone.

4. Because contaminant transport is dictated by fast flow through preferential paths, it was extremely critical to intensively monitor contaminant transport during the first day of a rainfall event in order to collect representative samples to assess total deep leaching. Soil sampling protocol based on the coring method of collecting soil samples at random locations once every several days is completely unsuitable to determine deep leaching of agrichemicals under field conditions. On the other hand, a tiled field behaves like a huge, enclosed, independent and undisturbed lysimeter. Contaminants leached from such a field can be accurately and holistically assessed, regardless of how rapidly and preferentially contaminants are being transported downward.

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