Herbicide and conservative tracer movement through the soil profile and to subsurface drains under no-till and chisel plow systems

Syed Imran Ahmed
Iowa State University

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Herbicide and conservative tracer movement through the soil profile and to subsurface drains under no-till and chisel plow systems

by

Syed Imran Ahmed

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

Major: Agricultural Engineering
Major Professor: Dr. Rameshwar S. Kanwar

Iowa State University
Ames, Iowa
1999

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Graduate College
Iowa State University

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Syed Imran Ahmed

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Major Professor

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For the Major Program

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For the Graduate College
DEDICATION

I dedicate this dissertation to my great grandfather, Syed Ghulam Husnain (Late), who taught me some of the best things of the world.
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ABSTRACT

Adoption of conservation tillage has increased the role of macropore flow on the transport of agricultural chemicals to groundwater. Therefore, it is important to understand the role of macropore flow in the transport of water through the vadose zone and to the shallow groundwater. Two field studies were conducted at Iowa State University’s Agricultural Research Center near Boone, Iowa, to determine the effect of two tillage practices (chisel plow and no-till) on the transport of herbicides and tracers. with applied water, through the soil profile and to the shallow groundwater. Two herbicides, atrazine [(6-chloro-N-ethyl-N-(1-methylethyl-1,3,5 triazine)-2-4-diamine] and alachlor [2-chloro-N-(2, 6-diethylphenyl-N-(methoxymethyl) acetamide], and a variety of conservative tracers such as chloride (Cl\textsuperscript{-}), bromide (Br\textsuperscript{-}), pentafluorobenzoate (PFBA), o-trifluoromethylbenzoate (o-TFMB), and 2,6-difluorobenzoate (2,6-DFBA) were applied on the cropland before and during irrigation events to investigate the effect of no-till and chisel plow systems on the movement of chemicals and water to shallow groundwater. Water samples were collected using suction lysimeters and continuous monitoring of subsurface drain flow during and after various irrigation events. Soil samples were collected before and after the irrigation events and were analyzed for various chemical concentrations. The results of the study showed that significant amount of herbicides and tracers were not found to be lost with subsurface drain flow under either tillage system. Also, it was found that macropore flow did not contribute significantly in the transport of solutes through the soil under chisel plow system, however, it contributed significantly under no-till system. Atrazine leaching losses were found to be higher than alachlor under chisel plow and no-till systems. First irrigation or simulated
rainfall event immediately after chemical application resulted in higher peak concentrations of tracers and herbicides in the subsurface drain water under both tillage systems compared to subsequent irrigation events. The LEACHP model was also evaluated in predicting the chemical movement through the soil profile. The LEAC HP, on the average, predicted the transport of water and solutes through the soil profile reasonably well. The LEACHP model could not accurately predict the effect of rainfall events on the subsurface drain flows, although predicted flow for the no-till system was closer to the observed values. Predicted chemical losses with subsurface drain flow were correlated to the amount of water drained as subsurface drain flow.
GENERAL INTRODUCTION

The extensive use of agricultural chemicals for crop production in the last few decades and subsequent contamination of groundwater from leaching of chemicals has raised a major environmental concern. A National Research Council report (1989) stated that agricultural chemicals are the major source of water pollution. In the United States, the average corn yield has increased by 300 percent in the past 40 years. This increase is associated with the extensive use of fertilizers (Aldrich, 1980). Chances of environmental pollution of surface and groundwaters by nitrates are very high (Bauder et al., 1993). National use of pesticides on cropland and pasture has increased from 86 million kg (190 million pounds) of active ingredient in 1964 to 300 million kg (660 million pounds) in 1993 (Aspelin, 1994). The extensive use of pesticides in agricultural areas has resulted in contamination of groundwater as well. A study by Hallberg (1985) in Iowa reported that wells less than 15 m (50 feet) deep are especially vulnerable to agricultural contamination.

Determining the transport of agricultural chemicals in and below the root zone is a complex process. The variability in soil types, rainfall conditions, and tillage practices are some of the factors, which effect the movement of chemicals in soils. The presence of different pesticide residues in streams and rivers has raised serious environmental concerns in the public. Kenimer et al. (1997) found that the losses in surface runoff of surface applied alachlor were higher from up-and-down tillage directions than the losses of alachlor from contour tillage, under simulated rainfall conditions. Recent monitoring studies have detected more than 70 pesticides in groundwaters of 38 states (Parsons and Witt, 1988; Ritter, 1990). Clark (1990) also found several pesticides in the shallow groundwater under normal agricultural management practices.
Tillage practices and chemical application methods are important factors in controlling agro-chemical leaching losses through the soil profile. One of the popular practices among farmers to reduce the production costs is conservation tillage or reduced tillage system. Although conservation tillage minimizes the runoff losses, the effect of reduced or no-till on groundwater is not clear. A major issue with conservation tillage practices is the preferential transport of chemicals to groundwater through macropores. Macropores are formed due to shrinking and swelling of soils, plant roots, and wormholes. Generally, macropores are evident where soils are well-structured (Beven and Germann, 1981); however, formation of macropores has been also reported in weakly structured soils (Coles and Trudgill, 1985; Kung, 1993). Li and Ghodrati (1997) reported more macropore flow in fine-textured soils than in the coarser soils.

Since many studies have reported that preferential flow can cause rapid transport of water through the soil profile, there is a good chance of surface applied chemicals to move quickly through macropores to shallow groundwater (Beven and Germann, 1981, Everts et al., 1989). Some studies found solute velocities up to two times greater than the conventional piston flow due to preferential flow in the soil profile (Richard and Steenhuis, 1988; Rice et al., 1991). Similar results of preferential transport of water and chemicals in different studies have been documented by many researchers (Singh and Kanwar, 1991; Porro et al., 1993).

Factors such as rainfall intensity, tillage practices, chemical properties, and timing of chemical application influence the movement of chemicals. Baker and Johnson (1983) reported that chemical application before an irrigation or rainfall event can enhance the chemicals leaching from the root zone. Several researchers have documented the agricultural
chemical losses during and after the first rainfall event (Schwab et al., 1973; Spencer et al., 1985; Shipitalo et al., 1990).

Agro-chemical losses in subsurface water can represent a substantial loss of nitrogen fertilizers and pesticides. These losses are directly related to the application rate of chemicals. Milburn and Richard (1991) found that fields fertilized with 80 to 105 kg ha\(^{-1}\) of inorganic N fertilizer and animal manure had nitrogen losses of 10 to 30 kg N ha\(^{-1}\).

Madramootoo et al. (1992) found that 26% of the 270 kg N ha\(^{-1}\) was lost with subsurface drain water between April and September. Some experimental studies also showed that higher concentrations of NO\(_3\)-N tend to persist in shallow groundwater and subsurface tile effluents for a few years after N applications are reduced or stopped (Patni, 1995).

Tracers are often used to evaluate the preferential flow and movement of agricultural chemicals in the soil profile. The ideal groundwater tracer is non-toxic, inexpensive, chemically stable, and not naturally present in the soil. The use of rainfall simulation experiments with and chemical tracers can illustrate water and chemical transport in the soil profile and help to evaluate best management practices. Variety of inorganic and organic tracers have been used in hydrological studies (Davis et al., 1980; Bensen and Bowman, 1994). Many researchers have used fluorobenzoates tracers to predict water and solute movement in soils (Bowman and Rice, 1986, Boggs and Adams, 1992). However, chloride and bromide are mostly used to represent water and chemicals movement in the soil profile. Bromide is used as a nonreactive tracer that moves similarly to nitrate (Smith and Davis, 1974, Jaynes et al., 1992, Kranz et al., 1998. Everts and Kanwar (1990) and Jaynes et al. (1992) used conservative tracers to represent the effect of chemigation on solute transport through the soil profile in different field conditions.
The use of rainfall simulations and chemical tracers can be helpful in understanding and evaluating the water and chemical transport processes in the soil profile for controlling surface and ground water contamination. Studies have shown that conservative tracers are a better alternative to understand the water and solutes movement in the soil profile (Smith and Davis, 1974). Reeves et al. (1996) found in a column study that fluorobenzoates demonstrated very similar behavior to bromide in loam soil.

The results of toxicity of fluorobenzoates to crops have been in disagreement among investigators. Pearson et al. (1992) reported some adverse effects on crops whereas Ghauri et al. (1992) reported no adverse effects on crops at low concentrations of fluorobenzoates. In addition, Seufere et al. (1979) found fluorobenzoates toxic to microorganism at high concentrations. Fluorobenzoates were found to be suitable tracers as they are not naturally present in soil and groundwater and are not toxic to plant at low concentrations (Jaynes, 1994).

Since inorganic and organic tracers have been used and recommended in several soil water studies to determine complex flow pathways, it is important to find simple and better techniques to understand soil water movement in soils. The previous work shows that transport of agricultural chemicals in the environment depends upon many factors such as soil type, rainfall intensity, tillage practices, and time of chemical applications. It is also difficult to address all the major factors that affect the movement of chemicals in soil, however, studies on individual factors can be useful to predict the impact of different tillage and chemical practices.

Although evaluation of transport of agricultural chemicals in the soil profile is complex due to variable climatic conditions, solute transport models are becoming important
tools for predicting the movement of chemicals applied to soils. Use of field data for computer modeling is an effective way to plan and test new agricultural management systems (Hanson et al., 1998). Computer simulation models are also effective tools in predicting the physical, biological, and chemical processes to evaluate best management practices (BMP). Even though the use of computer models is becoming more popular, there have been relatively few field studies designed to verify the performance of these models.

In recent years, many mathematical computer models have been developed to simulate transport of water and chemicals in the surface and subsurface environment. ANSWERS (Beasley et al., 1977) and CREAMS (Knisel, 1980) are used to predict the impact of BMP's on surface water quality. Skaggs (1978) developed DRAINMOD that predicts the movement of soil water as affected by various subsurface water management practices. LEACHM is a one-dimensional model (Hutson and Wagenet, 1989) and simulates the solute transport, degradation, and adsorption in the unsaturated zone of the soil profile. The RZWQM (USDA, 1994) has also the capability of predicting tillage effects on water and pesticide transport through the soil profile.

Use of computer models by comparing observed field data and predicted solute transport have shown some convincing results (Pennell, 1990; Singh et al., 1996; Azevedo et al., 1997; Elliotte et al., 1998). However, some researchers have reported some discrepancies between observed and predicted solute movement in soil (Soulsby and Reynolds, 1992). Therefore, calibration and validation of computer simulation models are very important according to the soil and climatic conditions. However, it requires a large amount of field data to make the model reliable for specific conditions.
The phenomenon of preferential flow and its effect on groundwater quality is still not clear. The literature suggests that recharge of groundwater can begin before soil reaches field capacity and agricultural chemicals can move to deeper depths with water. Therefore, it is important to determine the effect of macropore flow on groundwater quality. Additionally, it is also necessary to understand the role of macropores in conservation tillage systems where more preferential flow is possible due to undisturbed soil surface.

Two rainfall simulation studies were conducted at the Agricultural Engineering and Agronomy Research Center near Ames, Iowa in the growing season of 1997 and 1998. The main objective of these studies was to determine factors that control the movement of surface applied herbicides and conservative tracers through the unsaturated zone to the shallow groundwater under chisel plow and no-till systems. The specific objectives of these studies were:

1. to develop a better understanding on the movement of water, and adsorbed and non-adsorbed tracers through the soil profile under two tillage systems.
2. to determine the losses of herbicides and tracers to subsurface drain water under chisel plow and no-till systems.
3. to calibrate and evaluate LEACHP (pesticide version of LEACHM 3.0) model by using the observed data on subsurface drain flows and chemical concentrations in drain water collected from field experiments conducted in 1997 and 1998.

**Dissertation Organization**

This dissertation consists of three papers, each presented as a separate chapter. Each chapter was written in a format suitable for submission for publications in technical journals.
The first chapter reports the transport of surface applied herbicides and conservative tracers through the soil profile and to subsurface drain water for a chisel plow system under simulated rainfall conditions for the growing season of 1997. This paper has been submitted to "Journal of Environmental Quality" for possible publication.

The second chapter describes the transport of herbicides and tracers to subsurface drain water for no-till system. The paper also compares the chemical leaching losses between no-till and chisel plow systems. This paper will be submitted for possible publication to the "Transactions of the ASAE". The third chapter illustrates the use of LEACHP in predicting chemical concentrations in the soil profile and in subsurface drain water. All three chapters are preceded by a general introduction and are followed by a general summary and conclusions. The references for the general introduction are given at the end of the dissertation.
HERBICIDE AND TRACER MOVEMENT TO SUBSURFACE DRAIN WATER UNDER SIMULATED RAINFALL CONDITIONS

A paper submitted to Journal of Environmental Quality


Abstract

A field experiment was conducted to evaluate the movement of two herbicides, atrazine [(6-chloro-N-ethyl-N-(1-methylethyl-1,3,5 triazine)-2-4-diamine] and alachlor [2-chloro-N-(2, 6-diethylphenyl-N-(methoxymethyl) acetamide], and a variety of conservative tracers such as chloride (Cl\textsuperscript{-}), bromide (Br\textsuperscript{-}), pentafluorobenzoate (PFBA), o-trifluoromethylbenzoate (o-TFMBA), and 2,6-difluorobenzoate (2,6-DFBA) through the soil profile and to the subsurface drain water under simulated rainfall conditions. An area of 61 m x 38 m was selected for this study which has been under chisel plow conditions for the past 5 years. Chemicals and tracers were applied on a strip of 56.7 m x 0.76 m with in the experimental area which was next to a subsurface drain. A portable sprinkler system was used to apply rain water at four different times after chemical applications. 32 suction lysimeters were installed at depths of 30, 61, 91, and 122 cm at eight different locations within the field strip. Water samples were collected from these suction lysimeters and

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\[2\] The authors are: **S.I. Ahmed**, Graduate Research Assistant; **R.S. Kanwar**, Professor, Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, Iowa, 50011. **D.B. Jaynes**, Soil Scientist, USDA, National Soil Tilth Laboratory, Ames, Iowa, 50011. **S. J. Kung**, Professor, Department of Agronomy, University of Wisconsin, Madison, Wisc.
subsurface drain and were analyzed for chemical concentrations. The results of this study showed that a major portion of the solutes moved through the soil profile with matrix flow, however, preferential flow also contributed to the movement of solutes to subsurface drain water. In addition, the rate of movement of solutes was greater immediately after the beginning of rainfall and then decreased with the passage of time. Early detection of atrazine and alachlor (within two hours after the beginning of rainfall) at 91 cm and 122 cm depths indicated the presence of preferential flow. The total herbicide loss with subsurface drain water was found to be less than 1% of the applied amount. It was also observed that atrazine moved deeper into the soil profile in comparison with alachlor, and the total losses to subsurface drainage water were higher for atrazine. Also, 44% and 42% of the applied atrazine and alachlor were found to be retained in the 122 cm soil profile, respectively, at the end of third irrigation. The movement of Cl\(^-\), Br\(^-\), and fluorobenzoates through the soil profile indicated a transport pattern directly associated with water fluxes through the soil. Overall, the results of this study showed that adsorbed and non-adsorbed chemicals are susceptible to leaching to shallow groundwater with preferential and matrix flow systems.

**Introduction**

The use of fertilizers and pesticides, to maintain high crop yields has rapidly increased during the last few decades. Although modern herbicides have the capacity to control weeds without cultivation, increasing evidence is available that agricultural chemicals move below the root zone and eventually contaminate the groundwater. The impact of nutrients and pesticide losses through the soil profile to groundwater has raised concern
regarding pollution of water supplies (Kolpin et al., 1996). More than 90% of the rural and 75% of the urban population in the United States depend on the groundwater as a water source for consumption (CAST, 1992). The USEPA’s national survey of drinking water wells indicated that nitrate (NO$_3$-N) was the most commonly found contaminant with 2.4% of the rural and 1.2% of community water supplies exceeding the drinking water standard of 10 mg L$^{-1}$ (USEPA, 1989).

Since herbicides are widely used on 98% of the corn and soybean hectares in Iowa, it is important to protect groundwater from herbicide contamination (Wintersteen and Hartzler, 1987). Several studies have been conducted to study the movement of NO$_3$-N into groundwater (Rice and Smith 1982; Kladivko et al., 1991; Kanwar and Baker, 1993). Several researchers have documented pesticide movement through the unsaturated zone of the soil profile to the water table (Yoo et al., 1981; Czapar and Kanwar, 1991). In Iowa, concentration of atrazine in tile effluent from corn plots was found to be 1.3 to 5.1 μg L$^{-1}$ and exceeded the 3 μg L$^{-1}$ USEPA advisory in more than 40% of the water samples (Jayachandran et al., 1994).

The fate of agricultural chemicals in the environment depends on many factors such as soil type, rainfall conditions, and tillage and chemical management practices. In the last few years, the use of conservation tillage and no-tillage has increased to reduce soil erosion and energy input costs. Conservation tillage practices can reduce soil erosion by reducing runoff. However, the increased amount of infiltration of water can pose a threat to groundwater quality. Tillage practices and chemical application methods are important factors in controlling agro-chemical leaching losses throughout the soil profile. Nitrate
leaching is affected by tillage practices and chemical application methods (Russelle et al., 1983; Boddy and Baker, 1990; Hamlett et al., 1990). Kamau et al. (1996) found that solute transport properties vary according to method of application, position relative to the crop row, tillage, stage of growth, and crop species.

Masse et al. (1998) investigated the movement of herbicides into groundwater under conventional tillage (CT) and no-till (NT). They reported that concentration of atrazine, diethylatrazine, and metolachlor in groundwater were usually below the USEPA drinking water standard in comparison with CT treatment. However, atrazine and deethylatrazine concentrations in groundwater were significantly higher under NT in comparison to CT at 1.8 and 3.0 m depths. Serem et al. (1997) found deeper leaching of nitrate in NT treatment than in the CT treatment. Moreover, they reported that method of fertilizer application also affected the leaching process. Sadeghi and Isensee (1997) found herbicide persistence two times higher for the CT treatment than for the NT treatment. Masse et al. (1996) studied the effect of NT and CT on the concentrations and losses of atrazine and metolachlor in tile effluent and found that losses of these two herbicides were higher under NT in comparison with CT treatment.

Conservation tillage systems result in the formation of preferential flow paths (channels formed by plant roots, soil cracks, and soil animals) in the soil profile. Preferential transport of water and chemicals through macropores have been observed by many researchers (Singh and Kanwar, 1991; Porro et al., 1993). Many researchers found that macropores can have a significant influence on infiltration in structured soils (Beven and
Germann, 1981; Rice et al., 1986) or through finger or funnel flow in sandy, unstructured soil (Kung, 1993).

Li and Ghodrati (1997) observed greater preferential transport of solutes under unsaturated flow conditions in fine-textured soils than in coarser soils. They also reported that preferential flow increases with increasing water fluxes and pore density. NO$_3$-N concentration in subsurface drain effluent has been reported to be higher under conventional tillage than no-till (Angle et al., 1993). Some studies found similar tile flows and losses of NO$_3$-N under both tillage practices (Randall, 1990; Logan et al., 1994). Heatwole et al. (1997) reported that herbicide leaching due to early rainfall was higher in NT plots than in CT plots, however, preferential movements of herbicides occurred under both tillage practices.

Review of literature has shown that although preferential movement of pesticides, nitrate, and tracers is known, the contribution and importance of macropores in the transport of solutes in the field under different climatic and chemical management conditions are less well known. Studies have also shown that more field research is needed to understand the movement of water and transport of solutes in the soil matrix and through larger pathways (macropores) to shallow groundwater under different tillage systems.

Therefore, a simulated rainfall study was conducted to investigate the movement of applied water, herbicides and conservative tracers in neutral and high organic fraction soils, common in the Midwest, under chisel plow system during the growing season of 1997. The main objective of the study was to evaluate the transport of pesticides and conservative tracers with water after sequential applications of herbicides (adsorbed tracers), anionic
tracers (non-adsorbed), through the unsaturated zone of the soil profile and to the shallow groundwater. The specific objectives of this study were:

- to investigate the relationships between movement of water and adsorbed and non-adsorbed tracers in the soil profile.
- to assess the losses of herbicides and tracers to subsurface drain water under simulated and natural rainfall conditions.

**Materials and Methods**

Field experiment was conducted at Iowa State University’s Agronomy and Agricultural Engineering Research Center near Boone, Iowa, during the growing season of 1997 on a 61 m x 38 m plot under a chisel plow system. A field strip of 56.7 m in length and 0.76 m in width, near the subsurface drain, was selected within the plot for chemical and tracer applications (Figure 1). The soils at this site are predominantly Nicollet, fine loamy, mixed, mesic Aquic Hapludolls in the Clarion-Nicollet-Webster Soil Association (USDA-SCS, 1981). The Nicollet soils are characterized as being moderately permeable and somewhat poorly drained. These soils are derived from glacial till and have a slope of 1 to 3% (Kanwar et al., 1990). The Nicollet series, a glacial till soil, is a productive soil and covers 4.9 x 10^3 ha in Iowa (Fenton et al., 1971). Selected physical properties of the soil are provided in Table 1 (Azevedo et al., 1996).

Conservative tracers have been widely used to demonstrate the nature of soil-water flow in soils in both laboratory and field situations (Davis et al., 1980; Bowman, 1984;
Kluitenberg and Horton, 1990; Jaynes et al., 1992; Beven et al., 1993). The ideal groundwater tracer is non-toxic, inexpensive, chemically stable, and isn't present in the soil. Kranz et al. (1998) reported that Br is an inexpensive means of simulating different nitrogen application methods to predict \( \text{NO}_3 \)-N leaching losses. Tracers have also been dissolved in the irrigation water to represent the effect of chemigation on nutrient transport (Everts and Kanwar, 1990; Jaynes et al., 1992).

Two herbicides, atrazine [(6-chloro-N-ethyl-N-(1-methylethyl)-1,3,5 triazine)-2-4-diamine)] and alachlor [2-chloro-N-(2, 6-diethylphenyl-N-(methoxymethyl) acetamide], were uniformly applied as a spray on the strip before irrigations. Also, five different tracers, chloride, bromide, pentafluorobenzoate (PFBA), \( o \)-trifluoromethylbenzoate (\( o \)-TFMBA), and \( 2,6 \)-difluorobenzoate (\( 2,6 \)-DFBA) were applied to the strip before and during irrigations. All herbicides and tracers were sprayed in the strip before and during irrigation events. Irrigation schedule, and rates and dates of application of chemicals of the experiment are described in Tables 2 and 3.

A portable sprinkler irrigation system was used for rainfall simulations to provide several irrigations. The experimental plot was pre-irrigated before chemical application and every irrigation. The purpose was to raise the water table depth to make sure that subsurface drains were flowing to collect water samples during irrigations (Figure 2). Soil and water samples were collected along the strip at various depths. 32 suction lysimeters were installed at depths of 30, 61, 91, and 122 cm along the strip and were used to collect water samples before, during, and after every irrigation during the experiment (Figure 1). Subsurface drain water samples were collected during and after irrigations. These samples were collected at
15, 30, 60, and 120 minutes intervals during and after every irrigation depending on subsurface drain flow rate. Soil samples were randomly taken from 8 locations along the strip. The depth increments were 7.6 cm between 0 to 61 cm, and 15.2 cm between 61 to 122 cm to determine the amount of herbicides and tracers in the soil profile.

The soil and water samples from the experimental site were analyzed at USDA-ARS National Soil Tilth Laboratory, Ames, Iowa, for herbicides and conservative tracers. The extraction procedure for herbicides from soil samples was performed on a Zymark robotic system (Zymark Corporation, Hopkinton, Massachusetts). The analysis was based on the method described by Koskinen et al. (1991) and EPA method 507. Analysis was performed by a Hewlett-Packard 5890 GC with a HP-5 (cross-linked 5% phenyl, 95% methylsilicone) column, 25 m by 0.32 mm. i.d. with a 0.52 μm film thickness with a flow rate of 1 ml min⁻¹. Quantitation limit in the soil was 5 ppb for atrazine and alachlor. The detection limit for soil and water samples for herbicides was 0.1 ppb. The extraction procedure of herbicides from water samples was also performed on a Zymark robotic system by using the procedure described by Thurman et al. (1990) by activating 500 mg C-18 (SPE) cartridge with 2 ml of methanol followed by a 2ml of water. Analysis was performed on a Hewlett-Packard GC/MS 5970 operating in SIM mode with a HP ultra-1 (cross-linked 100% methylsilicone) column with a 12 m by 0.2 mm i.d. and 0.33 μm film thickness.

The analysis of Cl⁻ and Br⁻ was conducted with a Dionex 4500i Ion Chromatograph. The columns used were Ion Pac AG9-SC and Ion Pac AS9-SC (Dionex Corporation, Sunnyvale, CA). Flow rate was 1 ml min⁻¹ under a pressure of 1700 psi depending on the cleanliness of the column. The buffer solution was 25 mM Na₂CO₃ and 0.75mM of Na₂CO₃...
and suppressed with anion micro-membrane suppressor. The detection limit for all non-adsorbed tracers was 0.1 ppm.

Analysis of fluorobenzoate tracers (o-TFMB, PFBA, and 2,6-DFBA) was performed on a Dionex Ion Chromatographic System using the method described by Bowman and Gibbens (1992). The Regis-SAX column (Regis Chemical Co., Morton Grove, IL) was used with 30 mM KH₂PO₄, adjusted to a pH of 2.65 and 20% acetonitrile (v/v) as eluting solution. Flow rate was 1 ml min⁻¹ and detection UV wavelength was 205 nm. All laboratory results for soil samples were converted from mg L⁻¹ or mg kg⁻¹ to gram using appropriate unit conversions for each segment of depth.

Results and Discussion

Figure 2 gives the amounts of irrigation water applied and natural rainfall during the study period of the experiment. The experimental plot was pre-irrigated before every irrigation to cause the subsurface drain flow for water samples during irrigation. However, the plot was not irrigated before the third irrigation because it received 43.4 mm of rainfall (11.4 mm/hr) on 6/21/97. In addition, due to intended low intensity of simulated rainfalls, negligible amounts of runoff and ponding were observed in the experimental plot during irrigations.

Movement of herbicides and conservative tracers through the soil profile

A background soil sampling was done to estimate the amount of residual herbicides and tracers present in the soil. The cumulative residual amounts of atrazine and alachlor in
the soil profile (0-122 cm) of the strip were found to be 0.03 and 0.36 g, respectively. Figure 3 shows the relative amounts (g/g, which is the ratio of the amount retained in the soil profile to the amount initially applied) of herbicides at various incremental depths after three irrigations (23 days after application of atrazine, and four days after application of alachlor). The relative amount of atrazine and alachlor varied from 0 to 0.29 and 0 to 0.38 in the soil profile, respectively, at various increments of soil depths on June 27, 1997. The total amount of atrazine and alachlor retained in the soil profile (0-122 cm) was found to be 42 and 41 g after three irrigations on June 27, 1997, respectively. Although the amount of application was equal (96 g) for both herbicides, more atrazine was leached out of the top 7.6 cm soil layer in comparison with alachlor. Moreover, atrazine was also applied before the first irrigation and alachlor was applied before the third irrigation, which resulted in more leaching of atrazine due to two extra irrigations.

A pattern of decrease in the amount of herbicides with increase in soil depth can also be observed in Figure 3. Alachlor has a higher value of soil partitioning coefficient (K_d) than that of atrazine resulting in more adsorption of alachlor on soil particles than atrazine, which might have affected the transport patterns of these two herbicides in the soil profile (K_d for alachlor is 3.4 L kg^{-1}, and K_d for atrazine is 2 L kg^{-1}, Cooperative Extension Services, 1992). The loss of herbicides in the soil profile could be due to degradation caused by microbial activity (the half-life of atrazine is 60-73 days, and the half-life of alachlor 10-25 days, Gish et al., 1991a). Using the first order reaction for atrazine and alachlor, the mass recovered after degradation was found to be approximately 73.6 g (78%) and 79.8 g (83%), respectively. It showed that model under predicted the degradation rate for herbicides in the
soil profile. Almost 88% and 96% of the recovered atrazine and alachlor on June 27, 1997, respectively, was found to be in the top 15 cm of the soil profile. Similar results were reported by Weed et al. (1995) when almost 70% and 84% of the applied atrazine and alachlor, respectively, were retained in the top 10 cm up to 48 days after application.

Figure 4 illustrates the percent of mass recovery (cumulative amount retained in soil) of herbicides in the soil profile (0-122 cm) on June 27, 1997 (23 days and four days after application of atrazine and alachlor, respectively). The amounts of atrazine and alachlor retained in the soil profile were found to be 44% and 42% of the applied amount, respectively, on June 27, 1997. However, approximately 95% and 97% of available atrazine and alachlor were found to be in the top 0-30 cm of the soil profile. The amount of atrazine was found to be higher than that of alachlor at all increments of depths. However, at 95% probability level there were no statistically significant differences in the amounts of atrazine and alachlor retained in the soil profile.

Figure 5 shows the relative amounts of conservative tracers Br⁻, PFBA, o-TFMBA, 2,6-DFBA, and Cl⁻ retained in the soil profile after 210, 203, 196, 189, and 175 mm of water application, respectively, on June 27, 1997. The background level of tracers in the soil profile of the field strip was found to be 20.9, 0.0, 0.92, 0.0, and 170.4 g for Br⁻, PFBA, o-TFMBA, 2,6-DFBA, and Cl⁻, respectively. The higher residual amount of Cl⁻ is due to KCl fertilizer application in the field for the past 30 years at this site. The background concentration of Cl⁻ in agricultural soils commonly ranges from 1 to 100 ppm (Davis et al., 1980). The relative amount of Br⁻ varied from 0.005 to 0.13 in the soil profile. Moreover, Br⁻ was mostly found in the bottom part of the soil profile, which indicates the leaching of Br⁻
with water and movement of non-adsorbed chemicals (such as NO$_3$-N) to the lower part of the soil profile.

The relative amount of Cl$^-$ in the soil profile varied from 0.02 to 0.09. Although a higher residual amount of Cl$^-$ was present in these soils, the relative concentration curve shown in Figure 5 for applied Cl$^-$ effectively represents the movement of Cl$^-$ with water to lower soil depths. Figure 5 also shows that the Cl$^-$ curve lagged behind when compared with the Br$^-$ curve, which simply shows the deeper leaching of Br$^-$ with water than that of Cl$^-$ because of one extra irrigation to Br$^-$ (i.e., Br$^-$ was applied before the first irrigation and Cl$^-$ was applied before the second irrigation). Approximately 41% of the retained Br$^-$ was found in the lower portion (61-122 cm) of the soil profile after 23 days of tracer application. Almost 75% and 36% of available Cl$^-$ and Br$^-$, respectively, were present in the top 45 cm of the soil profile.

Relative distribution curves for fluoro-organics in the soil profile showed similar trends to that of bromide (Figure 5). The sequence of application of fluorobenzoate tracers (Table 3) also affected the amount of tracers at various depths in the soil profile. The relative amounts of PFBA, o-TFMB, and 2,6-DFBA varied from 0 to 0.25, 0 to 0.16, and 0 to 0.14, respectively, in the soil profile. However, trends of fluorobenzoates movement in soil were similar to Br$^-$ (Figure 5). In addition, most of the retained fluorobenzoates and Br$^-$ were found to be in the lower half of the root zone. Figure 5 also shows a pattern of decrease in concentrations of tracers at the 45-61 cm depth increment (Bimodal distribution). The reason of this distribution is not known, however, it could be due to presence of a sandier layer (Table 1) which helped leach the tracers to deeper depths. Consistent higher relative
concentrations of fluorobenzoates compared to Br$^-$ and Cl$^-$ in the soil profile are in disagreement with the results reported by Bowman (1984), Reeves et al. (1996), and Abdulkabir et al. (1996).

Figure 6 shows the percent of mass recovery for all non-adsorbed tracers in the soil profile on June 27, 1997. The mass recoveries for Cl$^-$ and Br$^-$ were almost 54% and 61%, respectively. Fluorobenzoates recoveries were found to be 125% for PFBA, 98% for o-TFMB, and 84% for 2,6-DFBA. It is obvious from the percentage of mass recoveries of all inorganic and organic tracers that organic tracers recoveries were higher than that of Br$^-$ and Cl$^-$ recoveries. The reason for higher percent mass recoveries of fluorobenzoates is not known, however, it might be due to the non-uniform chemical application which might have affected the amounts of tracers in the soil profile.

Mass recovery in soils was relatively low for all adsorbed and inorganic tracers as compared to the results reported by other investigators. There were some other factors such as degradation and volatilization of chemicals, which might have reduced the amount of applied chemicals in the soil profile. For organic tracers, the percentage of mass recoveries for fluorobenzoates were relatively higher than those of inorganic tracers, this contradicts the results of other studies. With the exception of high percentage of mass recovery in these soils, transport patterns of fluorobenzoates with water found in this study were similar to the results reported by Bowman and Gibbens (1992), Jaynes (1994), and Reeves et al. (1996). The disagreements of results from this field study to the column studies reported by other researchers may indicate the effect of variable field conditions compared to a controlled laboratory environment.
Figure 7 illustrates the relationship between applied water and center of mass for all of the non-adsorbed tracers in the soil profile. It shows that applied water during irrigations directly affects movement of conservative tracers in the unsaturated zone. The tracer that was applied earlier than the other tracers moved deeper in the soil profile (Table 3 and Figure 7). Chloride, which was applied before second irrigation, did not move to deeper depths in comparison with other conservative tracers, which were applied before and during the first irrigation. The stable trend of movement of tracers in the soil profile with applied water supports the role of water in the transport of solutes in soil. These results clearly indicate that adsorbed and non adsorbed chemicals have the potential of leaching to groundwater provided adequate water flux exist from either irrigation or rain water.

**Lysimeter study results**

Figure 8 shows average concentrations of alachlor and atrazine in water samples collected from suction lysimeters at two depths (91 cm and 122 cm) in the soil profile. Unfortunately, lysimeters yielded no water samples at 30.4 cm and 61 cm depths. This could have been due to poor soil-lysimeter contact, lysimeter installation problem, or low suction or leakage in the lysimeters. The water samples were collected before, during, and after each irrigation events.

During the first irrigation (Figures 8a and 8b), the water samples were collected after every 2-hr period. Alachlor concentration varied from 0 to 23.8 µg L⁻¹ whereas atrazine concentration varied from 0.6 to 22.3 µg L⁻¹ in the soil profile which exceeded the USEPA’s MCL (Maximum Contamination Limit) drinking water standard. Generally, alachlor
concentrations were found to be higher than atrazine concentrations in water samples, which could be due to the earlier application of alachlor on entire field [approximately 510 g (2.2 kg ha\(^{-1}\)] over the entire plot] on May 19, 1997. The peaks of alachlor concentration in some samples might be due to the contamination of lysimeters during the installation process from the earlier applied alachlor present on the soil surface. Application of atrazine (96 g) before the first irrigation increased the atrazine concentration in the water samples collected in the lower portion of the soil profile. The presence of alachlor and atrazine, in samples collected at 2-hr increments during irrigation, indicates the role of preferential flow in moving these two herbicides to lower soil profile (Figures 8a and 8b).

During the second irrigation, alachlor concentrations tended to be lower in suction lysimeter water samples at the 91 cm depth (Figures 8c and 8d). The samples were collected before irrigation (0 hr), at 5-hr intervals during irrigation, and after irrigation. The leaching and peaks of atrazine and alachlor at 0 hr (Figures 8c and 8d) may be attributed to the rainfall event on 6/16/97 before the second irrigation. However, atrazine and alachlor concentrations found in water samples from the second irrigation did not increase to more than 9.7 and 7.0 \(\mu g\) L\(^{-1}\), respectively.

Figures 8e and 8f show the concentrations of herbicides after the third irrigation. The concentrations of atrazine and alachlor further decreased compared to the concentrations from previous irrigations, however, alachlor concentration was found to be higher than the atrazine concentration in water samples collected at 122 cm depth. It can also be seen that application of alachlor (96 g) before the third irrigation contributed to increased alachlor concentration in the lower half of the soil profile during third irrigation which could be due to
the movement of alachlor through macropores in the soil profile. Similar pattern of herbicide concentrations was found during and after the fourth irrigation (Figures 8g and 8h).

The overall conclusion from the lysimeter water samples was the rapid transport and early detection of herbicides in soil water possibly due to macropore flow during the first irrigation. Gish et al. (1991b) also found that atrazine appeared to be susceptible to preferential flow with the first water input subsequent to application. Moreover, concentration of alachlor was found to be higher than atrazine during the first and second irrigations, which could be due to the earlier application of alachlor (510 g over the entire field) on May 19, 1997. In the third and fourth irrigations, concentrations of atrazine were found to be higher than the concentrations of alachlor, which indicated leaching of atrazine through soil matrix after two irrigations. The amount of irrigation water or rainfall events played a significant role in the leaching of chemicals through the soil profile and to shallow groundwater.

**Herbicide concentrations in subsurface drain water**

Data on herbicide losses to subsurface drain effluent versus time are shown in Figure 9a. The detection limit for herbicides in subsurface drain effluent samples was 0.1 µg L⁻¹. The concentrations of atrazine in subsurface drain flow followed the pattern of subsurface drain flow rate. Atrazine concentration was detected in subsurface drain flow 22 minutes after the start of the first irrigation. Presence of atrazine in tile effluent in such a short time during first irrigation could possibly be due to the presence of macropore flow. Kanwar (1991) also reported that herbicides quickly reached to subsurface drain flow after application by flowing
with infiltrating water through macropores. Although 510 g alachlor was applied 17 days before the first irrigation on the entire field, it was detected in tile effluent after 8 hours from the start of the first irrigation event. However, concentrations of both herbicides in tile effluent did not exceed MCL drinking water standards. Early arrival of herbicides, as reported in this study, was consistent with the findings from other studies and has been attributed to macropore flow. Similar results were found by Bottcher et al. (1981) when they detected small amounts of applied chemicals in subsurface drain effluent within four days of application. Everts et al. (1989) also reported the detection of two adsorbed and two non-adsorbed tracers in tile effluent within one hour of the start of irrigation. They also concluded that adsorbed chemicals tend to move in relatively short time intervals during rainfall events because of preferential flow.

During the second irrigation (Figure 9b), herbicides were found in tile effluent as soon as irrigation started. Figure 9b shows two peaks in subsurface drain flow that were due to the two rainfall events on June 19, 1997, and June 21, 1997. During the heavy rainfall event on June 21, 1997 (Figure 2), higher atrazine concentrations in water samples might have been due to the presence of macropores.

Figure 9c illustrates the subsurface drain flow and herbicide concentrations with time during the third irrigation. Atrazine and alachlor concentrations in tile effluent were detected after 4.5 and 8.5 h after the start of irrigation, respectively (no samples were collected from 0-1.25 hours from the start of third irrigation). Subsurface drain flow rates directly affected the concentrations of herbicides in subsurface drain effluent, especially alachlor concentrations, which decreased rapidly after tile flow rate decreased. However, atrazine leaching was
correlated with subsurface drain flow rate that indicates the transport of atrazine with matrix flow as well. A similar pattern of herbicide concentration was observed during the fourth irrigation (Figure 9d). Out of all the analyzed water samples from subsurface drain flow, only three samples exceeded the MCL drinking water standard. The overall conclusion that can be drawn from the subsurface drain flow data is that the concentrations of herbicides in subsurface drain water depends on the amount of macropore flow created by either irrigation or natural rainfall.

Movement of conservative tracers in subsurface drain water

The results of the conservative tracers study indicated that Br⁻ and fluorobenzoates were not detected in subsurface drain water during and after the first irrigation event (Figure 10a). The detection limit for all conservative tracers in water samples was 0.1 mg L⁻¹. None of the applied conservative tracers were detected in subsurface drain water during the first irrigation. Although no Cl⁻ was applied before the first irrigation, it was detected in the subsurface drain water during the first irrigation because of the availability of residual Cl⁻ in the soil profile. In addition, Cl⁻ concentration was not affected by subsurface drain flow rate. However, Cl⁻ was applied to the furrow strip before the start of the second irrigation. Br⁻ was found in the subsurface drain water after second irrigation (Figure 10b). Br⁻ was first detected in subsurface drain water 17 days after application, following a heavy rainfall event on June 21, 1997. However, as subsurface drain flow decreased, Br⁻ was not detected in subsurface drain water until the start of the third irrigation.
For fluorobenzoates, the tracer which was applied first was also detected in subsurface drain water earlier than the other two fluorobenzoate tracers. The PFBA was the first tracer detected in subsurface drain water 18 days after application, following a rainfall event on June 21, 1997. After the third irrigation, o-TFMB was also detected in subsurface drain water. The trend of increasing tracer concentrations in the subsurface drain water with time was observed for Br⁻ and fluorobenzoates during and after the fourth irrigation (Figure 10d). The consistency in tracer concentration curves in the third and fourth irrigations depicts the contribution of soil matrix flow in increasing the concentration of tracers in tile effluent.

Overall, it can be concluded from the subsurface drain water data that early detection of herbicides in the subsurface drain flow during the first two irrigations could be due to the presence of macropore flow. It is important to mention that the detection limit in water samples for herbicides was 1000 times higher than that of conservative tracers (0.1 ppb for herbicides and 0.1 ppm for conservative tracers). Therefore, conservative tracers with concentrations of less than 0.1 ppm might have not been detected during earlier irrigations. Consistent amounts of chloride in subsurface drain water throughout the study period indicate the contribution of matrix flow. In addition, detection of herbicides and zero detection of conservative tracers, except for chloride, during the first two irrigation events shows the contribution of preferential flow in leaching of herbicides through macropores.

Table 4 shows the amount of irrigation water applied, rainfall, and amount of water drained during the study period of 1997. A total of 27.1% of applied water was drained through subsurface drains during the study period. It can be seen that the ratio of drained
water to applied water decreased from the first irrigation to the fourth irrigation. The higher percentage of drained water during the first and second irrigations could be due to the shorter crop canopy height, lower temperatures, and lower consumptive crop use. As the crop matured, it obstructed the amount of water reaching the soil surface. In addition, evapotranspiration rate also increased due to the maturity of the crop and thus the water requirements. Moreover, the usual increase in temperature in late June and early July increased the evapotranspiration rate during the study period. All of these factors significantly reduced the amount of subsurface drain flows during the third and fourth irrigation events.

Table 5 shows the loss of atrazine, alachlor, Cl⁻, Br⁻, o-TFMB, PFBA, and 2,6-DFBA with subsurface drain water for all four irrigations and rainfall events during the study period. The amounts of loss of adsorbed and non-adsorbed tracers were calculated by interpolation between the measured data points for various time intervals during all four irrigations. However, the amounts of loss of adsorbed and non-adsorbed tracers in subsurface drain water were negligible. A total of about 0.17% and 0.02% of applied atrazine and alachlor were lost with subsurface drain water during four irrigations and six natural rainfall events. Similar losses of herbicide were reported by Kaladivko et al. (1991). Mass et al. (1996) also found that approximately 0.2% of applied atrazine was lost with subsurface drain water during a four-year study. Although the amount of parent compound loss was negligible for the herbicides, there may have been a significant loss of metabolites of atrazine and alachlor as reported by Kolpin et al. (1996).
The highest loss of chloride was found during the first and second irrigations (Table 5). It could be concluded that this was due to the residual soil Cl⁻ present in the soil profile and the higher percentage of applied water drained. Therefore, measured Cl⁻ load in subsurface drain water might not be a good representative of applied Cl⁻. In addition, Cl⁻ may not be a good tracer in a macropore flow study for these soils. Almost 21%, 1.9%, 1.47%, 0.81%, and 0.19% of applied Cl⁻, Br⁻, PFBA, o-TFMB, and 2,6-DFBA, respectively, were lost with subsurface drain water during 33 days of this study.

Conclusions

A field study was conducted to investigate the movement of herbicides and conservative tracers through the unsaturated zone of the soil profile and into the shallow groundwater. Following are some of the key conclusions:

1. The solute concentration in the soil water and subsurface drain water showed that major portion of solutes has moved through the soil profile with matrix flow, however, preferential flow was observed immediately following the rainfall events.

2. Solute concentration data from suction lysimeters showed that faster leaching of herbicides to shallow groundwater is evident with rainfall events occurring immediately after the application of herbicides.

3. The amounts of atrazine and alachlor in the soil profile were found to be 44% and 42% of the applied amounts, respectively, after the third irrigation. However, 39% and 41% of the applied atrazine and alachlor, respectively, were found in the top 15 cm of the soil profile.
4. Transport trends for all non-adsorbed tracers through the soil profile were found to be similar to each other throughout the study period. Because of earlier application of bromide and fluorobenzoates, these tracers moved deeper into the soil profile in comparison to chloride. The total amounts of tracers recovered in soil for Cl\(^-\), Br\(^-\), PFBA, o-TFMB, and 2,6-DFBA were 54%, 61%, 125%, 98%, and 84%, respectively, at the end of third irrigation.

5. Although significant amount of residual chloride was present in soil, the applied chloride effectively represented its distribution and movement directly controlled by water fluxes in the soil profile. However, chloride is of limited use for monitoring macropore flow for these soils. Bromide was detected in subsurface drain water after two irrigations and approximately 1.9% of the applied bromide was found in the subsurface drain water during 33 days of this study. The losses of PFBA, o-TFMB, and 2,6-DFBA in subsurface drain water were found to be 1.47%, 0.81%, and 0.19% of the applied amounts, respectively.

6. This study is of great significance in understanding the transport behavior of adsorbed and non adsorbed chemicals through the soil profile. Chemicals were applied on a very small strip but still were transported to subsurface drain water within a short time indicating the contributions of both, matrix and macropore flow. Therefore, the threat to groundwater contamination from agricultural chemicals is a real one.

References


Table 1. Selected physical properties of Nicollet soil at the experimental site (from Azevedo et al., 1996).

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Soil depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-7.5</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity, cm sec⁻¹</td>
<td>4.45x10⁻⁴</td>
</tr>
<tr>
<td>Texture</td>
<td></td>
</tr>
<tr>
<td>% sand</td>
<td>51.6</td>
</tr>
<tr>
<td>% coarse silt</td>
<td>17.2</td>
</tr>
<tr>
<td>% fine silt</td>
<td>12.4</td>
</tr>
<tr>
<td>% clay</td>
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<td>Bulk density, gm cm⁻³</td>
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Table 2. Irrigation schedule during the 1997 growing season.

<table>
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<tr>
<th>Date</th>
<th>Day of the Year</th>
<th>Irrigation #</th>
<th>Duration (minute)</th>
<th>Amount applied (mm)</th>
</tr>
</thead>
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<td>155</td>
<td>1</td>
<td>515</td>
<td>35.4</td>
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<tr>
<td>6/18/97</td>
<td>169</td>
<td>2</td>
<td>595</td>
<td>33.1</td>
</tr>
<tr>
<td>6/23/97</td>
<td>174</td>
<td>3</td>
<td>600</td>
<td>50.0</td>
</tr>
<tr>
<td>7/2/97</td>
<td>183</td>
<td>4</td>
<td>600</td>
<td>39.2</td>
</tr>
</tbody>
</table>

Table 3. Herbicides and tracers applications during the 1997 growing season.

<table>
<thead>
<tr>
<th>Herbicides and tracers</th>
<th>mass applied, g</th>
<th>date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>510 (over entire plot)</td>
<td>5/19/97</td>
</tr>
<tr>
<td>Atrazine</td>
<td>96, before first irrigation</td>
<td>6/4/97</td>
</tr>
<tr>
<td>Bromide</td>
<td>4002, before first irrigation</td>
<td>6/4/97</td>
</tr>
<tr>
<td>PFBA</td>
<td>1500, after irrigating 2hr during first irrigation</td>
<td>6/4/97</td>
</tr>
<tr>
<td>o-TFMBA</td>
<td>1500, after irrigating 4hr during first irrigation</td>
<td>6/4/97</td>
</tr>
<tr>
<td>2, 6-DFBA</td>
<td>1500, after irrigating 6hr during first irrigation</td>
<td>6/4/97</td>
</tr>
<tr>
<td>Chloride</td>
<td>3656, before second irrigation</td>
<td>6/18/97</td>
</tr>
<tr>
<td>Alachlor</td>
<td>96, before third irrigation</td>
<td>6/23/97</td>
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</tbody>
</table>
Table 4. Amount of irrigation, rainfall, and subsurface drainage under chisel plow system, 1997.

<table>
<thead>
<tr>
<th>Irrigation #</th>
<th>water applied (mm)</th>
<th>rainfall (mm)</th>
<th>subsurface drain flow (mm)</th>
<th>% of applied water drained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.4</td>
<td>0</td>
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<td>2</td>
<td>33.1</td>
<td>46.0</td>
<td>28.0</td>
<td>35.4</td>
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<td>3</td>
<td>50.1</td>
<td>6.6</td>
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<td>4</td>
<td>39.2</td>
<td>0</td>
<td>4.8</td>
<td>12.2</td>
</tr>
<tr>
<td>Total</td>
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<td>52.6</td>
<td>57.0</td>
<td>27.1</td>
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</table>

Table 5. Losses of herbicide and tracers in subsurface drainage for four irrigation and rainfall events, 1997.

<table>
<thead>
<tr>
<th>Herbicides and tracers</th>
<th>first irrigation</th>
<th>second irrigation</th>
<th>third irrigation</th>
<th>fourth irrigation</th>
<th>Total</th>
<th>% of applied</th>
</tr>
</thead>
<tbody>
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<td>0.11</td>
<td>0.035</td>
<td>0.01</td>
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</tr>
<tr>
<td>Alachlor</td>
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<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
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<td>382.00</td>
<td>140.00</td>
<td>97.80</td>
<td>767.80</td>
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</tr>
<tr>
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<td>25.30</td>
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</tr>
<tr>
<td>PFBA</td>
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<td>14.30</td>
<td>6.60</td>
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</tr>
<tr>
<td>o-TFMBA</td>
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<td>0.00</td>
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<td>7.40</td>
<td>12.20</td>
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</tr>
<tr>
<td>2, 6-DFBA</td>
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<td>0.00</td>
<td>0.90</td>
<td>1.90</td>
<td>2.80</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Figure 1. Diagram of field layout for the rainfall simulation study under chisel plow system for the growing season of 1997.
Figure 2. Amount of water applied during irrigations and rainfall events during the study period of 1997.
Figure 3. Relative amount of herbicides as a function of soil depth.

Figure 4. Percent recovery of herbicides at all increments of depths in the soil profile under chisel plow system, 1997. The bars show the standard error.
Figure 5. Relative amount of conservative tracers at all increments of depths in the soil profile under chisel plow system for 1997

Figure 6. Percent recovery of conservative tracers at all increments of depths in the soil profile under chisel plow system for 1997

Figure 7. Center of mass for all conservative tracers after three irrigations under chisel plow system for 1997
Figure 8. Average herbicide concentrations in water samples collected by suction lysimeters at various depths for four irrigations under chisel plow system for 1997.
Figure 9. Atrazine and alachlor concentrations in subsurface drains versus time for all four irrigations under chisel plow system for 1997.
Figure 10. Concentrations of conservative tracers in subsurface drains versus time for all four irrigations under chisel plow system for 1997.
TRANSPORT OF HERBICIDES AND TRACERS TO SUBSURFACE DRAIN WATER IN NO-TILL SOIL UNDER SIMULATED RAINFALL CONDITIONS

A paper to be submitted to the Transactions of the ASAE


Abstract

A field experiment was conducted to investigate the transport of two herbicides, atrazine [(6-chloro-N-ethyl-N-(1-methylethyl-1,3,5 triazine)-2-4-diamine] and alachlor [2-chloro-N-(2, 6-diethylphenyl-N-(methoxymethyl) acetamide], and a variety of conservative tracers such as bromide (Br), pentafluorobenzoate (PFBA), o-trifluoromethylbenzoate (o-TFMB), and 2,6-difluorobenzoate (2,6-DFBA), through the soil profile and to the subsurface drain water under the no-till and simulated rainfall conditions. A field plot of 22.8 m x 34.3 m under no-till system was selected for this study. Herbicides and conservative tracers were applied on a field strip of 22.8 m x 1 m within the study area. A sprinkler system was used to irrigate the plot area. Soil and water samples were collected along the strip at various depths. 16 suction lysimeters were used at four locations to

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2 The authors are: S.I. Ahmed, Graduate Research Assistant; R.S. Kanwar, Professor, Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, Iowa, 50011. D.B. Jaynes, Soil Scientist, USDA, National Soil Tilth Laboratory, Ames, Iowa, 50011. S. J. Kung, Professor, Department of Agronomy, University of Wisconsin, Madison, Wisc.
collect water samples at 30, 61, 91, and 122 cm depths along the strip. Subsurface drain flow rate was monitored during the entire study period. Water samples were also collected from subsurface drains during the study period. Soil and water samples were analyzed for chemical concentrations. The results of the field study suggest that macropore flow plays an important role in the transport of herbicides and conservative tracers through the soil profile to subsurface drain flow under the no-till system. In addition, leaching of herbicides and tracers is possible if irrigation or rainfall occurs shortly after application of chemicals. The observed concentrations of atrazine and alachlor in water samples intercepted by suction lysimeters at various depths could be due to the influence of preferential flow through macropores in the soil profile. Atrazine and alachlor detection in tile effluent 2 hr after beginning of simulated rainfall supported the contribution of macropores to water and solute movement through the soil profile. However, less than 1% of applied herbicides and 3 to 4% of applied conservative tracers, respectively, were found to be lost to subsurface drain water during the study period. Although equal amounts of atrazine and alachlor were applied, atrazine moved deeper into the soil profile in comparison with alachlor. The total losses with subsurface drain flow were also higher for atrazine (0.8%) than that of alachlor (0.3%). However, 35% and 20% of the applied atrazine and alachlor were retained in the 122 cm soil profile, respectively. Applied Br⁻ and fluorobenzoates showed consistent trends in predicting the transport of solute with water in the soil profile. In conclusion, the results of this study showed that both adsorbed and non-adsorbed chemicals could move through the soil profile to subsurface drain flow with applied water under the no-till system.
Introduction

The primary media in which pesticides and fertilizers are transported from agricultural fields to other parts of environment is water. The use of fertilizers and pesticides in crop production has increased significantly since the early 1960's. Modern pesticides have capacity to control weeds without mechanical cultivation. The detection of pesticides in groundwater has raised a major national issue, because groundwater is used for drinking water by about 50 percent of the nation's population (Moody et al., 1988). Pesticide applications have increased the potential of their movement into and through the soil and Earth's hydrosphere as detected in surface waters, groundwaters, and precipitation (USEPA. 1992). The detection of pesticides in drinking water increases concern involving human health risks associated with pesticides exposure (Wauchope, 1978; Majewski and Capel. 1995). However, understanding of the extent of environmental pollution by pesticides, and their transport and transformation processes, is still limited (Wauchope, 1987). Since Iowa is known for extensive row-crop agriculture and 94% of the state's area is under farmland, it is important to protect groundwater from herbicide contamination. Wintersteen and Hartzler (1987) reported that herbicides are widely used on 98% of the corn and soybean hectares in Iowa. Some researchers found that Iowa applies a greater mass of pesticide active ingredients than any other state in the USA (Gianessi et al., 1986; Hallberg, 1989).

Environmentalists and agricultural scientists are concerned about the fate and transport of pesticides in ecosystems. Many researchers have documented the importance of field and laboratory scale methods to study the fate and transport of agricultural chemicals through the soil profile to groundwater. Several field scale studies have been conducted to
investigate the movement of pesticides in the soil profile and to the shallow groundwater (Kanwar et al., 1985; Kladivko et al., 1991; Troiano et al., 1993). To simulate NO$_3$-N and pesticides under field conditions, many studies have been conducted in the laboratory using soil columns (Singh and Kanwar, 1991; Gish et al., 1991a; Azevedo et al., 1996). Several researchers have documented the pesticide movement through the unsaturated zone of the soil profile to the water table (Yoo et al., 1981; Czapor and Kanwar, 1991).

The transport of pesticides in the environment depends on many factors such as soil type, temperature, soil-water content, rainfall conditions, tillage, and chemical management practices. The use of conservation tillage and no-till, which leaves some or all of the previous year’s crop residue on the soil surface, has been very effective in controlling soil erosion. No-till system can reduce soil erosion to 36% or less of that for conventional tillage systems (Laflen and Colvin, 1981). However, no-till increases the extent of water infiltration through the soil profile (Edwards et al., 1988). The increased amount of water and chemicals in no-till soils depends on timing of chemical application and rainfall events (Wagenet, 1987).

Kanwar et al. (1997a) found higher losses of nitrate and pesticides to the subsurface drainage water under the no-till plots than under the moldboard plow and chisel plow plots under continuous corn cropping. No significant difference was found by Xue et al. (1997) in retention of alachlor between the no-till (NT) and the conventional tillage (CT) treatments, however, alachlor retention was greater in the NT treatment. Levanon et al. (1993) also reported higher concentrations of herbicides in the leachates of CT soils compared with NT soils because of higher organic matter in no-till soils.
The formation of macropores by plant roots, soil cracks, and soil animals in the soil profile is common in undisturbed or minimally tilled soils. Many researchers have reported that solutes entering the subsurface can move through the soil profile at rates that are relatively faster than those calculated on the basis of uniform transport (Rao et al., 1974; Singh and Kanwar, 1991; Komor and Emerson, 1994). Preferential flow has also been observed in irrigated agricultural soils where cracks and other macropores were not visible (Steenhuis et al., 1990; Bouwer, 1990; Czapar et al., 1994). The concept of formation of macropores is favored in clay or fine-grained soils (Rice et al., 1986), however, some researchers have also observed the preferential solute transport through sandy soils (Cohen et al., 1990; Kung, 1990). Li and Ghodrati (1997) found that preferential flow pathways played a major role in the chemical transport under unsaturated flow conditions in fine-textured soils than in the coarser soils. Kanwar et al. (1997b) found that atrazine showed a greater degree of preferential movement through no-till soil columns.

Chemical application methods play an important role in leaching of pesticides through the soil profile. Baker (1992) reported that application of a pesticide without incorporation increased the amount of pesticide leaching shortly after application. Jaynes et al. (1988) applied chemicals with irrigation water and observed quick leaching due to macropores in the soil profile. Hallberg (1995) found that pesticide incorporation increased their concentrations in subsurface waters under conventional tillage than under reduced tillage, while the opposite results were found after surface application of pesticides.

Many researchers have documented contradictory data and conclusions regarding the transport of agrochemicals in soils under different tillage systems. Edwards et al. (1992)
observed, in a no-till soil columns study, that a high intensity storm following chemical application resulted in higher concentration of chemicals in the percolate than that of a lower intensity storm. In addition, they reported that chemical transport was strongly affected by percolate volume. Gish et al. (1991b) found enhanced pesticide movement in the soil profile in the no-till system compared with a conventional tillage system. Logan et al. (1994) found no difference between the losses of herbicides with subsurface drain flows under both tillage practices on a poorly drained soil. Ritter et al. (1994) detected higher concentrations of pesticides in subsurface drain waters under no-till areas than conventionally tilled fields. Heatwole et al. (1997) reported higher herbicide leaching in NT plots than in CT plots due to early rainfall after herbicide application. Therefore, it is important to understand the transport behavior of solutes with water in the soil matrix and through macropores to shallow groundwater under different field conditions.

Many researchers have found that significant amounts of chemical loss in runoff and leaching occurs during the first rainfall event after chemical application (Spencer et al., 1985; Baker, 1992; Heatwole et al., 1997). This indicates that monitoring of subsurface drains and surface runoff after the first rainfall event can be helpful in understanding solute movement in soils to subsurface drainage. Rainfall simulations and conservative tracers have been used to investigate the water and chemical transport processes in the soil profile (Edwards et al., 1992; Czarap et al., 1994).

Several studies have been conducted by using conservative tracers to demonstrate the agrochemical movement with water in soils (Bowman, 1984; Jaynes et al., 1992; Beven et al., 1993). The ideal groundwater tracer can be defined as non-toxic, inexpensive, chemically
stable, and not naturally present in the soil. Everts and Kanwar (1990) observed effect of chemigation on water quality by dissolving tracers in the irrigation water. Shipitalo and Edwards (1996) used RbCl as a tracer in a simulated rainfall study to distinguish between resident water and applied water in the soil profile. Kranz et al. (1998) also used Br\textsuperscript{-} to simulate different nitrogen application methods to predict NO\textsubscript{3}-N leaching losses.

The literature review regarding transport of herbicides and conservative tracers through soil profile have provided much data, but have also emphasized the complex nature of preferential flow transport of chemicals in different tillage systems. Although results from different studies can provide useful information, it is important to understand the preferential movement of agricultural chemicals in different tillage conditions. In addition, careful designed experiments can provide informative data to predict water and solute movement in various conditions. A study by Ahmed et al. (1999) was conducted in Iowa to evaluate the movement of two herbicides and a variety of conservative tracers through the soil profile to the subsurface drains under simulated rainfall and chisel plow conditions. The results of the study showed the minor contribution of macropores to the transport of solutes to subsurface drains. Although there were some early detection of chemicals after the first irrigation, overall results showed very little preferential flow contribution to the transport of water and chemicals to the subsurface drains.

Therefore, another simulated rainfall study was conducted to investigate the movement of water, herbicides and conservative tracers for similar soils under the no-till system in 1998. The main objective of this study was to evaluate the contribution of macropores in the transport of solutes by continuous monitoring of subsurface drain flows during and after the
first rainfall event following sequential application of herbicides, and conservative tracers. The specific objectives of this study were:

• to investigate the movement of water, adsorbed and non-adsorbed chemicals with time of application as they move through the soil profile, and
• to quantify the losses of herbicides and tracers with subsurface drain water under simulated and natural rainfall conditions, and
• to make a comparison of herbicide and conservative tracer losses with subsurface drain flow between chisel plow and no-till systems using data from field experiments of 1997 and 1998.

**Materials and Methods**

This experiment was conducted at Iowa State University’s Agronomy and Agricultural Engineering Research Center near Boone, IA. The soil at this site is classified predominantly as Nicollet loam (fine loamy, mixed, mesic Aquic Hapludolls) in the Clarion-Nicollet-Webster soil association (USDA-SCS, 1981). Nicollet soils are characterized as being moderately permeable and somewhat poorly drained. Some physical properties of the soil are provided in Table 1 (Kanwar et al., 1987). These soils are derived from glacial till and have a slope of about 1 to 3% (Kanwar et al., 1991).

The experiment was conducted during the growing season of 1998 on a 22.8 x 34.3 m plot under the no-till system. A field strip of 22.8 m in length and 1 m in width, approximately 1 m near the subsurface drains, was selected for tracer application. Two
herbicides, atrazine [(6-chloro-N-ethyl-N-(1-methylethyl)-1,3,5 triazine)-2-4-diamine] and alachlor [2-chloro-N-(2, 6-diethylphenyl-N-(methoxymethyl) acetamide], were uniformly applied as a spray on this strip before irrigation. Also, four additional tracers: bromide, pentafluorobenzoate (PFBA), o-trifluoromethylbenzoate (o-TFMBA), and 2,6-difluorobenzoate (2,6-DFBA) were applied to the strip before and during irrigation events. All herbicides and tracers were sprayed in the strip before and during irrigation. Rates and dates of applications for herbicides and tracers are given in Table 2.

A portable sprinkler irrigation system was used for rainfall simulation. Soil and water samples were collected along the strip at various depths. Sixteen suction lysimeters were installed, four at each of the depths of 30, 61, 91, and 122 cm along the strip as shown in Figure 1. Water samples from suction lysimeters were collected before, during, and after irrigation. Subsurface drain water samples were collected at 15, 30, 60, and 120 minute intervals during and after the irrigation event, depending on the subsurface drainage rate. Water table depths were monitored by two sets of 8 observation wells installed along the strip (Figure 1). The water table depths were recorded once an hour during irrigation. Two weeks after application, soil samples were randomly taken from eight locations along the strip. At each location, soil samples were collected in increments of 15.2 cm, with a depth between 0 and 122 cm, to determine the amount of herbicides and tracers in the soil profile. Soil samples were also collected for background and off-site analysis.

The soil and water samples from the experimental site were analyzed at the USDA-ARS National Soil Tilth Laboratory, Ames, Iowa, for herbicides and conservative tracers.
The extraction procedure for herbicides from soil samples was performed on a Zymark robotic system (Zymark Corporation, Hopkinton, Massachusetts). The analysis was based on the method described by Koskinen et al. (1991) and EPA method 507. Analysis was performed by a Hewlett-Packard 5890 GC with a HP-5 (cross-linked 5% phenyl, 95% methylsilicone) column, 25 m by 0.32 mm i.d. with a 0.52 μm film thickness with a flow rate of 1 ml min⁻¹. Quantitation limit in the soil was 5 ppb for atrazine and alachlor. The detection limit for soil and water samples for herbicides was 0.1 ppb.

The extraction procedure of herbicides from water samples was also performed on a Zymark robotic system by using the procedure described by Thurman et al. (1990) by activating a 500 mg C-18 (SPE) cartridge with 2 ml of methanol followed by 2 ml of water. Analysis was performed on a Hewlett-Packard GC/MS 5970 operating in SIM mode with a HP ultra-1 (cross-linked 100% methylsilicone) column with a 12 m by 0.2 mm i.d. and 0.33 μm film thickness.

The analysis of Br⁻ was conducted with a Dionex 4500i Ion Chromatograph. The columns used were Ion Pac AG9-SC and Ion Pac AS9-SC (Dionex Corporation, Sunnyvale, CA). Flow rate was 1 ml min⁻¹ under a pressure of 1700 psi depending on the age of the column. The buffer solution was 25 mM Na₂CO₃ and 0.75 mM of Na₂CO₃ and suppressed with an anion micro-membrane suppressor. The detection limit for non adsorbed tracers was 0.1 ppm.

Analysis of fluorobenzoate tracers (o-TFMB, PFBA, and 2,6-DFBA) was performed on a Dionex Ion Chromatographic System using the method described by Bowman and Gibbens (1992). The Regis-SAX column (Regis Chemical Co., Morton Grove,
IL) was used with 30 mM KH$_2$PO$_4$, adjusted to a pH of 2.65 and 20% acetonitrile (v/v) as eluting solution. Flow rate was 1 ml min$^{-1}$ and detection UV wavelength was 205 nm. All laboratory results for each segment of depth of soil samples were converted from mg L$^{-1}$ or mg kg$^{-1}$ to gram using appropriate unit conversions for further analysis.

**Results and Discussion**

The total amount of water applied with the irrigation was 63.4 mm on July 1, 1998, and the amount of natural rainfall was 59.8 mm during the study period from July 1 to July 21, 1998. Although negligible amounts of runoff and ponding were observed in the field strip, soil samples were collected from the top 15 cm of the soil profile at 0.5 m, 1 m, and 2 m, perpendicular from the edge of the strip to determine the magnitude of runoff.

**Transport of herbicides and conservative tracers in the soil profile**

Analysis of background soil sampling showed that the cumulative residual amounts of atrazine and alachlor in the soil profile (0-122 cm) of the strip were found to be 0.0 and 0.06 g, respectively. Figure 2 depicts the relative amounts (g/g, the ratio of amount retained in the soil profile to the amount initially applied) of atrazine and alachlor at various incremental depths within the tracer strip after one simulated rainfall on July 1, 1998, and seven natural rainfall events within 21 days after herbicide application. The relative amount of atrazine and alachlor varied from 0 to 0.39 and 0 to 0.20, respectively, at various soil depths on July 21, 1998. The total amount of atrazine and alachlor retained in the soil profile (0-122 cm) was found to be 28.79 and 17.02 g on July 21, 1998, respectively. Although the amount of
application was almost equal for both herbicides (Table 2), the amount of alachlor residue was lower than the amount of atrazine residue at all depth increments. This was probably due to the higher degradation rate of alachlor (the half-life of alachlor is 10-25 days, and the half-life of atrazine is 60-73 days, Gish et al., 1991a). The recovered mass of atrazine and alachlor after degradation on the basis of half lives (60 days for atrazine and 15 days for alachlor, and using the first order reaction for this soil) would be approximately 78.5% (38.8 g) and 38% (19.7 g), respectively, of the applied amount. However, it also showed that the first order model underestimated the degradation rate for herbicides. Helling et al. (1988) also found persistence of atrazine higher than alachlor in no-till maize plots 42 days after application. A pattern of decrease in the amount of herbicides with increase in soil depth can also be observed in Figure 2. Almost 65% and 60% of the recovered atrazine and alachlor on July 21, 1998, respectively, was found to be in the top 15 cm of the soil profile.

Figure 3 shows the percent of mass recovery (cumulative amount retained in soil) of herbicides in the soil profile (0-122 cm) on July 21, 1998 (21 days after application of herbicides). The amounts of atrazine and alachlor recovered in the soil profile were found to be 59% and 34% of the applied amount, respectively. Approximately 81% and 74% of the retained atrazine and alachlor in the soil profile, respectively, were found to be in the top 0-30 cm soil layer. The amount of atrazine was found to be higher than that of alachlor at all increments of soil depths.

Off-site sampling showed that as the distance from the strip increased, the amount of herbicides decreased in the top 0-15 cm of the soil profile. The amount of herbicides found at a distance of 0.5 m from the strip were 0.18 g of atrazine and 0.08 g of alachlor. The
amounts of herbicides decreased even more at distance of 1 m and 2 m from the strip. Thus, although some runoff was observed, negligible amounts of herbicides were transported off the strip due to irrigation and rainfall events.

The background level of applied tracers in the soil profile was found to be 6.48, 0.0, 0.0, and 0.0 g for Br⁻, PFBA, o-TFMB, and 2,6-DFBA, respectively. Figure 4 shows the relative amounts of non-adsorbed tracers Br⁻, PFBA, o-TFMB, and 2,6-DFBA recovered in the soil profile after 123.2, 110.6, 98.0, and 83.8 mm of water application, respectively. on July 21, 1998. The relative amount of Br⁻ varied from 0.0 to 0.16 in the soil profile. Moreover, Br⁻ was mostly found in the upper part (0-61 cm) of the soil profile. Almost 41% of retained Br⁻ was present in the top 0-30 cm of the soil profile.

Figure 4 also depicts the amounts of fluorobenzoates recovered in the soil profile on July, 21, 1998. The organic tracers’ curves were found to be similar to that of bromide. However, the sequence of application of fluorobenzoate tracers (Table 2) affected the amount of tracers at various depths in the soil profile. The relative amounts of PFBA, o-TFMB, and 2,6-DFBA varied from 0 to 0.09, 0 to 0.06, and 0 to 0.06, respectively, in the soil profile. Most of the retained fluorobenzoates and Br⁻ were found to be in the upper half of the soil profile. The relative concentrations of Br⁻ and fluorobenzoates recovered in the soil profile concurred with results found by Bowman (1984) and Reeves et al. (1996).

Figure 5 shows the percent of mass recovery for all non-adsorbed tracers in the soil profile on July 21, 1998. The mass recoveries for Br⁻, PFBA, o-TFMB, and 2,6-DFBA were found to be 70%, 94%, 67%, and 60%, respectively, in the soil profile. It can also be observed that, except bromide, the percent mass recovery was higher for the tracer which was
applied earlier than other tracers. In general, the curves in Figures 3a-3b show that the amount of water applied after application of tracers played major contribution to the transport of chemicals in the soil profile.

Mass recovery in soils was similar for all adsorbed and inorganic tracers as compared to the results reported by other investigators. There were some other factors, such as degradation and volatilization of herbicides, which might have reduced the amount of applied chemicals in the soil profile. The transport patterns of conservative tracers with applied water was similar to the results observed by other researchers (Jaynes, 1994; Reeves et al., 1996).

Figure 6 illustrates the relationship between applied water and center of mass for all of the non-adsorbed tracers in the soil profile. It shows that applied water during irrigation played an important role in the transport of conservative tracers in the soil profile. Although the earliest applied tracer did not move deeper than the others in the soil profile, the trend of transport of tracers in the soil profile with applied water illustrates how water and chemicals move according to time of application in the soil profile.

Lysimeter and well data results

Figure 7 illustrates average concentrations of atrazine and alachlor in water samples collected from suction lysimeters to indicate the transport of herbicides to four depths 30 cm, 61 cm, 91 cm, and 122 cm, in the soil profile. The water samples were collected before irrigation (at 0 hr), at 2-hr intervals during irrigation, and after irrigation (14 h after irrigation stopped).
The concentration of atrazine and alachlor in water samples collected by lysimeters at 30 cm depth before the start of the irrigation were found to be 0.3 and 0.6 μg L⁻¹, respectively. During the irrigation, the average concentration of atrazine and alachlor varied from 197.1 to 1019 μg L⁻¹ and 91.4 to 683.5 μg L⁻¹, respectively, at 30 cm depth (Figure 7a). However, atrazine concentrations were found to be higher than alachlor in all the water samples collected at 30 cm depth. It is likely due to the higher soil partitioning coefficient (Kₐ) of alachlor in comparison with atrazine which resulted in more adsorption of alachlor to soil particles and in less leaching. Suction lysimeters could not extract water samples at 30 cm depth in the soil profile at the 2nd hr and 6th hr after irrigation started. However, the early detection of alachlor and atrazine concentrations in water samples collected during the irrigation indicated the role of preferential flow in the soil profile.

At 61 cm depth, average atrazine and alachlor concentrations in water samples were found to be lower than those of 30 cm depth (Figure 7b). Suction lysimeters could not collect water samples at the 8th hr, at 61 cm depth, after irrigation started. The leaching and concentration of herbicides in water samples increased with time and the amount of water applied during irrigation. However, atrazine and alachlor concentrations found in water samples, at 61 cm depth, did not exceed more than 259.7 and 204.5 μg L⁻¹, respectively.

Figure 7c shows average concentrations of herbicides at 91 cm depth, which ranged from 0.5 to 66.3 μg L⁻¹ for atrazine and from 1.7 to 25.8 μg L⁻¹ for alachlor. The concentrations of atrazine and alachlor in water samples collected at 91 cm depth further decreased compared to the concentrations at 30 cm and 61 cm depths. Figure 7d shows a similar pattern of herbicide concentrations at 122 cm depth except a peak in concentrations occurred after 6
hours of irrigation. Overall, the herbicide concentration data from suction lysimeters suggest that lysimeters were able to intercept the movement of herbicides through the soil profile. In addition, the detection of herbicides in water samples at 122 cm depth, off the 4th and 6th hr after irrigation started, shows the contribution of preferential flow to the transport of chemicals in the soil profile.

It is also important to mention that concentrations of herbicides in water samples collected by lysimeters under the no-till system from the 1998 rainfall simulation study were found to be higher in comparison to the concentrations of herbicides under the chisel plow system as observed in the 1997 study (Ahmed et al., 1999). After the first irrigation under the chisel plow system in 1997, the maximum concentrations of atrazine, at 91 cm and 122 cm depths, were found to be 7.0 and 22.3 μg L⁻¹, respectively, as compared with 66.3 and 226.6 μg L⁻¹, respectively, in 1998 under the no-till system. Similarly, maximum alachlor concentrations were also higher at 91 cm and 122 cm depths under the no-till system, and were found to be 25.8 and 289.2 μg L⁻¹, respectively, when compared with 23.8 and 18.7 μg L⁻¹ under the chisel plow system, respectively. These higher concentrations under the no-till system could be attributed to preferential flow through macropores in the soil profile.

Jayachandran et al. (1994) also found water samples exceeding MCL of the drinking water standard at various depths in the no-till plots because of preferential flow in macropores. In addition, role of macropore flow in no-till plots has been well documented by other investigators (Isensee et al., 1990; Kanwar, 1991; Heatwole et al., 1997).

The water samples collected by suction lysimeters were also analyzed for different tracers at various depths (Figure 8). The background concentration of Br⁻, PFBA, o-TFMB,
and 2,6-DFBA (at 0 hr) were found to be 1.7, 6.04, 0.0, 0.0, and 0.0 mg L$^{-1}$, respectively. Br$^-$ and PFBA were detected at 4 h and 2 h after their applications, respectively, in the water samples collected at 30 cm depth. Two tracers o-TF MBA and PFBA were detected 4 h after of their application. The maximum concentrations of Br$^-$, PFBA, o-TF MBA, and 2,6-DFBA in water samples collected at 30 cm depth, were found to be 1560.7, 56.5, 41.4, and 21.3 mg L$^{-1}$, respectively (Figure 8a).

The Br$^-$ concentration in water samples collected at 61 cm depth were found to be lower than that of at 30 cm depth (Figure 8b). However, PFBA and o-TF MBA concentrations were found to be higher at 61 cm depth than those of at 30 cm depth indicating the presence of macropore flow. No 2,6-DFBA was detected in the water samples collected at 61 cm depth. Figure 8c shows that at 91 cm depth, concentrations of all tracers decreased as compared to the concentrations at 30 cm and 61 cm depths. Moreover, 2,6-DFBA was detected in water samples at 91 cm of the soil profile. A similar pattern of tracer concentrations was observed in water samples collected at 122 cm depth.

Overall, Figure 8 shows that concentration of tracers in water samples at all depths sharply decreased 14 h after irrigation was stopped. Therefore, it can be concluded that the amount and time of application of irrigation water played an important role in leaching of herbicides and non-adsorbed tracers through the soil profile. The conclusion from the lysimeter study data was the rapid transport and early detection of herbicides and conservative tracers in water samples possibly due to preferential flow through macropores during the irrigation. Starr and Glotfelty (1990) also reported that in the event of rainfall soon after herbicide application, herbicides at high concentrations could travel from the soil
surface to deeper depths by preferential flow through macropores, bypassing the soil matrix. In addition, other studies have also reported the higher losses of herbicides due to macropore flow under a no-till system (Schwab et al., 1985; Kaladivko et al., 1991; Buhler et al., 1993).

Thirty-two water samples were also collected from observation wells before (0 h) and 14 h after irrigation to observe the change in tracer concentrations in the shallow groundwater. The average water table depth during and after irrigation was found to be approximately 91 cm. The well data showed almost no difference between the concentrations of tracers in water samples before and after the irrigation event. However, the lysimeter data showed that tracers moved to 91 and 122 cm depths during irrigation event, therefore, it can be concluded that addition of shallow groundwater through the perforated end of the observation wells, might have helped in diluting the chemical concentrations in water samples from wells.

**Herbicides transport with subsurface drain flow**

Herbicide losses to subsurface drains versus time are shown in Figure 9. The concentration of atrazine in subsurface drain flow was found to be higher than alachlor throughout the study period in 1998. Herbicide concentrations were well correlated to the subsurface drain flow rate. Subsurface drain flow peaks resulted in peak concentrations of atrazine and alachlor in subsurface drain water. Herbicide concentrations were detected in subsurface drain water 2 h after the start of irrigation. Presence of atrazine and alachlor in subsurface drain flow in such a short time during irrigation could be due to preferential flow through macropores. As a result of preferential flow, Isensee et al. (1990) reported that a
rainfall 12 h after application of herbicides resulted in a peak atrazine concentration of about 200 µg L⁻¹ in shallow groundwater. They also found alachlor in shallow ground water shortly after its application under the no-till system. Everts et al. (1989) also reported early arrival of chemicals in subsurface drain water due to preferential flow. Xue et al. (1997) also indicated that preferential flow in no-till soil limited alachlor adsorption during transport.

Figure 9 also shows the peaks of subsurface drain flow were affected by natural rainfall events during the first week of July, 1998. This shows that the amount of water applied after application of chemicals plays an important role in the transport of chemicals through the soil profile. The concentrations of atrazine and alachlor varied from 0.5 to 19 µg L⁻¹ and 0.3 to 10.3 µg L⁻¹, respectively, in subsurface drain water during the study period. The total loss of atrazine and alachlor to subsurface drain flow was found to be 0.38 g (0.8%) and 0.15 g (0.3%), respectively, after one irrigation and five natural rainfall events during the study period.

A comparison of herbicide losses to subsurface drainage water under the no-till system in 1998 and the chisel plow system in 1997 showed that atrazine and alachlor losses were higher under no-till system. The losses of atrazine and alachlor under the chisel plow system (CP) were found to be 0.13% and 0.02%, respectively, when compared with 0.8% and 0.3% under the no-till (NT) system, of the applied amounts. Early arrival of herbicides in subsurface drain flow, as reported in this study, is consistent with the findings from other studies (Isensee et al., 1990; Hall et al., 1991; Weed et al., 1995) and has been attributed to macropore flow. Masse et al. (1998) also reported that atrazine leaching appeared to be higher under the no-till system than the conventional tillage system. Similar results were
found by Weed et al. (1995) when they detected higher losses to subsurface drains for atrazine than that of alachlor under a NT system.

A comparison of the amount of water drained for CP and NT years showed that approximately 27% (57 mm), and 45% (55.4 mm), respectively, of the irrigation water and natural rainfall drained to the subsurface drainage system. It shows that almost 18% more water drained under the NT system than under the CP system. This indicates that higher chemical losses are directly associated with higher leaching of water under the NT system. Radcliffe et al. (1988) also found faster rate of infiltration under NT than conventional tillage because of a combination of surface cover and macropores. Overall, it can be concluded that macropore flow and the pattern and amount of subsurface drain flow during irrigation and natural rainfall events affected the concentrations of herbicides in subsurface drain water.

**Movement of conservative tracers to subsurface drain flow**

The data for conservative tracers showed that Br\textsuperscript{−} and all fluorobenzoates were detected in subsurface drain flow during and after the irrigation (Figure 10). Br\textsuperscript{−}, which was applied before irrigation, was found in subsurface drain flow 1.75 h after the start of irrigation. For fluorobenzoates, the PFBA, which was applied first, was detected in subsurface drain water 40 minutes after its application. Similarly, o-TF MBA and 2,6-DFBA were detected in subsurface drain flow 57 and 27 minutes, respectively, after their application. In addition, the concentrations of Br\textsuperscript{−} and fluorobenzoates in subsurface drain water were consistent and correlated with subsurface drain flow rate. The trend of increasing concentrations in subsurface drain water was observed for Br\textsuperscript{−} and fluorobenzoates during and
after the irrigation. However, concentrations of conservative tracers decreased as subsurface drain flow rate decreased after the end of irrigation. The three rainfall events on the 186th, 187th, and 188th days of 1998, also contributed in increasing the subsurface drain flow rate as shown in Figure 10. The concentration of tracers in subsurface drain water also increased due to increased subsurface drain flow rate due to various rainfall events. It is also shown in Figure 10 that Br\(^-\) concentration was not affected by subsurface drain flow rate in drained water after day 191.

Almost 53% (55 mm) of applied water and natural rainfall was drained through subsurface drainage system during the study period. The total losses of Br\(^-\), PFBA, o-TFMB, and 2,6-DFBA with subsurface drain water were found to be 71, 48, 47, and 51 g, respectively. Overall, it can be concluded that early detection of herbicides in subsurface drain water during rainfall simulation could be due to the presence of macropore flow. Approximately 2.7%, 3.2%, 3.1%, and 3.4% of applied Br\(^-\), PFBA, o-TFMB, and 2,6-DFBA, respectively, were lost with subsurface drain water during the study period.

**Summary and Conclusions**

A field experiment was conducted under a no-till system and simulated rainfall conditions to investigate the transport of herbicides and conservative tracers through the unsaturated zone of the soil profile into shallow groundwater. The following are some specific conclusions from the results of this study:

1. The simulated and natural rainfalls showed that a major portion of solutes in the soil profile has moved through the soil matrix; however, preferential flow had a significant
role in solute transport into shallow groundwater for these soils under a no-till system. Rapid transport of herbicides and tracers through preferential pathways were observed in subsurface drain water during irrigation and natural rainfall. Interception of herbicides and tracer concentrations by suction lysimeters at various depths in the soil profile showed that leaching of herbicides into shallow groundwater is possible through macropores if irrigation or rainfall occurs shortly after chemical application.

2. The amounts of atrazine and alachlor in the soil profile were found to be 35% and 20% of the applied amounts, respectively, after the simulation study. Approximately 81% and 74% of the recovered atrazine and alachlor, respectively, were retained in the top 0-30 cm of the soil profile. Movement of all conservative tracers in the soil profile was consistent throughout the study period and directly affected by the amount of water received after the chemicals’ application.

3. Almost 0.8% and 0.3% of the applied atrazine and alachlor, respectively, were lost with subsurface drain flows. Bromide was detected in subsurface drain water 1.75 h after the start of irrigation and approximately 2.7% of applied bromide was lost with subsurface drain water 15 days after application (during one irrigation and five natural rainfall events). The losses of PFBA, o-TFMB, and 2,6-DFBA with subsurface drain flows were found to be 3.2%, 3.1%, and 3.4% of the applied amounts during the study period.

4. Overall conclusions from the studies (chisel plow system for 1997 and no-till system for 1998) showed that more leaching of herbicides and tracers is possible under NT than CP due to more macropore flow under NT. Chemical transport in these soils was directly affected by the amount of water applied after chemicals' application. In addition, atrazine
is more susceptible to leaching to shallow groundwater than alachlor. However, conservative tracers behaved identically in these soils.

References


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Logan, T.J., D.J. Eckert, and D.G. Beak. 1994. Tillage crop and climatic effects on runoff and tile drainage losses of nitrate and four herbicides. Soil Tillage Res. 30:75-103


Table 1. Selected physical Properties of Nicollet soil at the experimental site (from Kanwar et al., 1987).

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Soil depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-30</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydraulic conductivity\textsuperscript{a}, cm sec\textsuperscript{-1}</td>
<td>(2.7 \times 10^{-3})</td>
</tr>
<tr>
<td>Texture</td>
<td></td>
</tr>
<tr>
<td>% sand</td>
<td>38.9</td>
</tr>
<tr>
<td>% coarse silt</td>
<td>36.7</td>
</tr>
<tr>
<td>% clay</td>
<td>24.5</td>
</tr>
<tr>
<td>Bulk density, gm cm\textsuperscript{3}</td>
<td>1.43</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.47</td>
</tr>
<tr>
<td>Organic matter(%)</td>
<td>4.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Olson (1995).

Table 2. Herbicides and tracers applied (spray) over the strip on 7/1/98.

<table>
<thead>
<tr>
<th>Herbicides and tracers</th>
<th>Mass applied, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>49.45, before irrigation</td>
</tr>
<tr>
<td>Alachlor</td>
<td>51.86, before irrigation</td>
</tr>
<tr>
<td>Bromide</td>
<td>2619.5, before irrigation</td>
</tr>
<tr>
<td>PFBA</td>
<td>1500, after irrigating 2hr during irrigation</td>
</tr>
<tr>
<td>o-TFMBBA</td>
<td>1500, after irrigating 4hr during irrigation</td>
</tr>
<tr>
<td>2, 6-DFBA</td>
<td>1500, after irrigating 6hr during irrigation</td>
</tr>
</tbody>
</table>
Figure 1. Diagram of field layout for the rainfall simulation study under no-till system for the growing season of 1998.
Figure 2. Relative amount of herbicides as a function of soil depth on July 21, 1998 (21 days after application).

Figure 3. Percent mass recovery of herbicides at all increments of depths on July 21, 1998 (21 days after application).
Figure 4. Relative amount of conservative tracers at all increments of depths in the soil profile under no-till system on July 21, 1998 (21 days after application).

Figure 5. Percent mass recovery of conservative tracers at all increments of depths in the soil profile under no-till system on July 21, 1998 (21 days after application).

Figure 6. Center of mass for conservative tracers in the soil profile after irrigation in the soil profile under no-till system on July 21, 1998 (21 days after application).
Figure 7. Average herbicide concentrations in water samples collected by suction lysimeters at various depths for irrigation under no-till system for 1998. (Y-axis for Figure 4a is different)
Figure 8. Average tracer concentrations in water samples collected by suction lysimeters at various depths for irrigation under no-till system for 1998. (Y-axis is different in Figure 8a)
Figure 9. Atrazine and alachlor concentrations in subsurface drains versus time for irrigation under no-till system for 1998.
Figure 10. Average concentrations of conservative tracers in subsurface drains versus time for irrigation under no-till system for 1998.
COMPUTER SIMULATION OF HERBICIDE AND TRACER MOVEMENT THROUGH THE SOIL PROFILE USING LEACHP

A paper prepared for submission to Journal of Environmental Quality


Abstract

Use of mathematical computer models to predict water and chemical movement in the soil-water environment is increasing. The objective of this study was to evaluate the predictive capability of a computer model (LEACHP 3.0, pesticide version of LEACHM) in simulating the movement of herbicides and tracers through the soil profile. The data for water and chemical transport from two field studies under both chisel plow and no-till systems in 1997 and 1998, respectively, were used in the calibration and validation of the model. The LEACHP model was used to study the movement of a herbicide (atrazine) and a conservative tracer (bromide) through the soil profile and to subsurface drains under irrigation and natural rainfall events. Comparison between observed and predicted concentrations of atrazine showed a good agreement for the upper part (0-30cm) of the soil profile. However, the model did not show movement of atrazine to the deeper depths. Also, the model over predicted the amount of bromide in the soil. Although the model did not

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2 The authors are: S.I. Ahmed, Graduate Research Assistant; R.S. Kanwar, Professor, Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, Iowa, 50011. D.B. Jaynes, Soil Scientist, USDA, National Soil Tilth Laboratory, Ames, Iowa, 50011. S. J. Kung, Professor, Department of Agronomy, University of Wisconsin, Madison, Wisc.
predict atrazine concentration in subsurface drain flow, it predicted bromide losses to the subsurface drains. LEACHP overestimated (68%) the subsurface drain flows in 1997 and underestimated (9%) in 1998. The predicted chemical losses with subsurface drain flows were correlated to the amount of water drained. In addition, the model could not accurately predict the subsurface drain flow rates after high intensity rainfall events during the study period in both years. Lack of a macropore flow component and a runoff component could have caused discrepancies between the observed and predicted subsurface drain flows. However, the results of this study showed that LEACHP has the capability of simulating solute transport through the soil profile for these soils.

Introduction

Transport of agricultural chemicals from the vadose zone to groundwater has been an important environmental issue for the last few decades. The impact of the use of fertilizer and pesticides in agriculture on contamination of ground and surface water supplies is of great concern. The presence of agricultural chemicals in groundwater has enhanced the necessity of understanding the transport of these pollutants through and beyond the root zone. Transport of agricultural chemicals though the unsaturated zone to shallow groundwater seldom occurs uniformly though the soil matrix (Jury, 1986; Hornsby et al., 1990).

The transport of agricultural chemicals in the soil vary widely depending on soil type, soil condition, tillage practices, amount and timing of water application, chemical properties and environmental conditions (Kanwar et al., 1988; Logsdon et al., 1990). Preferential transport of water and chemicals through macropores (pores greater than 1 mm diameter) in
the soil profile, bypassing much of the soil matrix, has been reported by many researchers (Thomas and Phillips, 1979; Jaynes et al., 1988; Jabro et al., 1991). Many researchers have reported herbicide concentrations in subsurface drain flow. However, the losses of herbicides varied greatly in subsurface drain water in different soil and climatic conditions (Jayachandran et al., 1994; Gaynor et al., 1995). The amount and timing of water applied can also increase the losses of chemicals to subsurface drainage (Logan et al., 1994). In a watershed study in Iowa, Moorman et al. (1999) found that atrazine leaching to subsurface drain water was due to persistence of atrazine in soil and seasonal rainfall events.

Tillage practices can also affect the transport of water and pesticides in the soil. However, there are limited and contradictory results concerning the transport of chemicals in soils under different tillage conditions (Singh and Kanwar, 1991; Levanon et al., 1993). Tillage practices disturb the continuity of soil macropores and may prevent the rapid transport of water and chemical to shallow groundwater. Many researchers have reported higher losses of chemicals under the no-till than the conventional tillage conditions and have attributed the difference to the preferential movement of water and agricultural chemicals through macropores in the soil profile (Tan et al., 1993; Weed et al., 1995; Azooz and Arshad, 1996). Some researchers detected higher concentrations of herbicides in the leachates of conventional soils rather than in no-till soils (Starr and Glotfelty, 1990; Xue et al., 1997).

A variety of physical, chemical and biological factors affect the movement of pesticides in soil and water. Although the efforts to understand the complex nature of chemical movement through the soil profile have helped researchers to predict the transport of chemicals, interpretation of chemical movement in soil is still limited. Therefore, due to
the complexity of the soil-water processes in the soil, it is important to understand the leaching of solutes through the soil profile under different tillage and soil conditions.

Field studies and computer simulation modeling are two important methods to understand the processes governing the transport of chemicals through the soil profile and to the shallow groundwater. Use of computers with mathematical models has been a recognized scientific practice. In the last few years, computer models based on field data have been developed to predict the environmental problems resulting from agricultural chemical transport through soil into groundwater. These models vary widely in their complexity and their results are influenced by environmental conditions (Hutson and Wagenent, 1989; Pennell et al., 1990; Jarvis et al., 1991; Mullins et al., 1993). Although use of models reduces laborious field work, time, and capital, currently there is little agreement concerning model validity and applicability in varied soils (Hutson, 1988; Soulsby and Reynolds, 1992; Jabro et al., 1993). However, use of models to predict solute transport is becoming popular among environmentalists and researchers (Pearson et al., 1996). The discrepancies in the results from model simulations could be due to the soil physical and chemical properties, and environmental conditions (Cheng, 1990). Therefore, it is important to understand which type of computer simulation model should be used to describe specific processes for model validity (Saleh et al., 1990).

The computer models, currently in use, are of two different types, empirical and deterministic. Empirical models have been developed for environmental screening of pesticides through the soil profile (Enfield et al., 1982; Wagenet and Hutson, 1986). Deterministic models are used to describe the effect of best management practices (BMP) on water quality. For example, CREAMS (Chemicals, Runoff, and Erosion from Agricultural
Management System) (Knisel, 1980) model evaluates the impact of BMP on surface water quality. PRZM (Pesticide Root zone Model) (Carsel et al., 1985) and GLEAMS (Groundwater Loading Effect of Agricultural Management System) (Leonard et al., 1987) are two well known deterministic models. GLEAMS is a continuous simulation model which gives the prediction of water and pesticide movement within and through the root zone.

In recent years, many computer models have been developed to evaluate the impact of agricultural practices on shallow groundwater quality. Kanwar et al. (1988) developed a computer simulation model to predict nitrate losses with subsurface drainage water. Alexander (1988) developed ADAPT (Agricultural Drainage and Pesticide Transport) to simulate the quality and quantity of flows with water table management systems. Wagenet and Hutson (1989) developed LEACHM (Leaching and Estimation and Chemistry Model) to estimate the water flow and chemical transport through the soil profile. Workman and Skaggs (1990) developed a water-management model capable of simulating preferential flow. The new version of RZWQM (USDA-ARS, 1992) also simulates the subsurface drain flow and evaluates the effect of various tillage practices on shallow groundwater.

Although considerable work has been done in the development of various computer models for estimating movement of water and agricultural chemicals (Wagenet and Rao, 1990), little work has been done to validate these models. The limitations for this could be the capital and environmental regulations. In addition, models which have been validated have rarely been tested with independent data sets from various soil types and environmental conditions (Addiscott and Wagenet, 1985; De Willingen et al., 1990). Comparison of observed and predicted solute movement under different tillage conditions is necessary for
verifying the predictive capabilities of solute transport models. Most models were validated by using the laboratory data or data from soil columns studies. However, use of the same model for similar field conditions may not predict similar results because of variability in field and laboratory conditions.

LEACHM was developed by Wagenet and Hutson (1989) to model water flow, chemical transport, plant uptake, and solute distribution in the soil profile. Although models developed to simulate macropore flow have advantages compared with LEACHM (Whitmore and Addiscot, 1988), many researchers have used LEACHM successfully (Pennell et al., 1990; Lotse et al., 1992; Jabro et al., 1994) to simulate solute transport under laboratory and field conditions. Previous field and laboratory studies to compare observed and predicted chemical movement have reported mixed results (Pennell et al., 1990; Soulsby and Reynolds, 1992; Comfort et al., 1993). Although researchers found a general agreement in their results, they reported 30% to 45% discrepancies between observed and predicted distribution of solutes in the soil profile. Comfort et al. (1993) found close agreement between LEACHM predictions and observed Br\(^-\) values to depth of 96 cm. Pearson et al. (1996) also reported the predicted distribution of tracers similar to the observed movement of tracers in the soil profile.

**Objectives**

There is a need for validating computer simulation models under different environmental and field conditions. Therefore, two field experiments were conducted to investigate the transport of water, herbicides, and a variety of conservative tracers through the soil profile and to the subsurface drain flow under chisel plow (CP) and no-till (NT).
systems during the growing seasons of 1997 and 1998. One of the purposes of the study was
to calibrate and evaluate a computer model (LEACHP, the pesticide version of LEACHM
3.0) by using the observed soil and subsurface drain flow data from the field studies. The
specific objectives of this study were:

1. to calibrate and validate LEACHP by using observed subsurface drain flow data
   from chisel plow (CP) and no-till (NT) systems for 1997 and 1998 under
   irrigation and natural rainfall conditions.

2. to evaluate the predictive capability of LEACHP for describing solute transport in
   the soil profile under varying tillage practices for the growing season of 1997 and
   1998.

3. to evaluate the capability of LEACHP to model herbicide and tracer leaching to
   the subsurface drains under CP and NT systems.

**Materials and Methods**

Data used to evaluate LEACHP were collected from two field experiments conducted
at the Iowa State University Experiment Station near Boone, IA. The data were collected
during the growing seasons of 1997 and 1998 under chisel plow (CP) and no-till (NT)
systems, respectively. The study period was 34 days in 1997 and 21 days in 1998. The soil
at the site is classified as predominantly Nicollet loam in the Clarion-Nicollet-Webster soil
association (USDA-SCS, 1981). The selected properties of the soil at the site are presented
in Tables 1-2. The fields were irrigated by a portable sprinkler system for various irrigation
depths. Subsurface drain flow rates and applied chemical concentrations in subsurface drain
flow were continuously monitored during the entire study period for each year. Collection of
water samples from the subsurface drain water integrates the spatial variability of the sampling volume and gives an average of matrix flow and preferential movement of water through the soil profile (Richard and Steenhuis, 1988). Soil samples were collected after three irrigation events in the year 1997, and after one irrigation event in 1998. Tables 3-5 present the rates and dates of chemical and water application for the study periods of 1997 and 1998.

Inputs and calibration of LEACHP

LEACHP 3.0, the pesticide version of LEACHM, is a deterministic model capable of predicting water flow, solute transport, plant uptake of chemicals, and solute distribution in the soil profile. The model numerically solves the Richard’s equation for water flow and the convection-dispersion equation (CDE) for solute transport in a one-dimensional layered soil profile. LEACHP is user friendly and requires a manageable amount of input field data. A complete description of all equations used in the model can be found in the LEACHM manual (Wagenet and Hutson, 1989).

The current literature review has shown that very little work has been done to validate LEACHP under field conditions of the Midwest. The purpose of this study was to evaluate LEACHP to simulate water and chemical leaching under field conditions for Iowa soils. One of the reasons for using LEACHP was its simulated hourly output for drainage losses of water and chemicals which could be compared with the hourly observed data. In addition, LEACHP also gives the simulated residual amount of water and chemicals in the soil profile at specified time intervals.
Model inputs were selected from the observed data during the experiments. However, some physical properties of soil were taken from the literature. The hydrological portion of the input file in the LEACHP model requires rainfall, pan evaporation rate, air temperature, bulk density, saturated hydraulic conductivity, air entry value, and the ‘b’ exponent for Campbell’s equation (Campbell, 1974). LEACHP uses bulk density and particle size distribution data to predict soil water retention parameters using one of five empirical equations (Hutson and Wagenet, 1992). Soil physical properties from Table 1 and Table 2 were used to estimate the soil-water retention function parameters by using the retention model 5 (Rawls and Brakensiek, 1985) for CP and NT systems, respectively. Rainfall, pan evaporation, and air temperature data were taken from a weather station near the experimental site (Agricultural and Biosystems Engineering and Agronomy Experiment Station, Boone, IA). An estimate of saturated hydraulic conductivity ($K_s$) was obtained from previous research done on the same field by other researchers (Kanwar et al., 1987; Olson, 1995; Azevedo et al., 1996).

LEACHP was applied to a soil profile consisting of 12 layers, each 100-mm thick. The inputs of the model for chemical properties were obtained from the literature (Table 5). Constant linear sorption coefficients and first-order degradation rates options were used for the simulation. The half life for degradation rate for atrazine was used as 60 d (Gish et al., 1991). The model requires a single value for $K_{oc}$ (the organic carbon partitioning coefficient) for pesticides for the soil profile; therefore, an average value of 120 L kg$^{-1}$ was used as an input for value for $K_{oc}$ for atrazine (Jayachandran et al., 1994). The model also requires initial concentration of chemicals in each layer of the soil profile, the observed values from field data were used as inputs in the model. The lower boundary condition was modeled as
free-drainage, having a unit hydraulic gradient at the lowest node. The upper boundary conditions were non-ponded infiltration and evaporation on the soil surface. Initial soil water contents were read as volumetric moisture content. The LEACHP model does not have a specific subsurface drain flow component, therefore, the amount of water drained through the soil profile (below 120 cm) was considered as the predicted subsurface drain flow for the specific time interval.

Amounts of water applied, water application rates, and applied chemical rates were used from the observed data for the years 1997 and 1998. Water application rates for irrigation and rainfall events were calculated by dividing the amount of water applied by the duration of event. The crop factor, the fraction of ground surface blanketed by leaves, was estimated as 0.8. Plant uptake for herbicide and tracer was simulated in 1997, however, the model was run without plant uptake in 1998 (chemical were applied on a bare field strip in 1998). Richards's equation with the CDE (Convection-Dispersion Equation) option was used to predict water and chemical flow through the soil profile. LEACHP uses the partitioning equations with the CDE to obtain the relationship between sorption, desorption, and chemical movement.

LEACHP was calibrated using the measured hourly subsurface drain flow data for the year 1997. The model was run for five days before the start of the first actual irrigation or rainfall event. The model was calibrated for the first irrigation for the growing season of 1997 under the chisel plow system. The criterion used for model calibration was to minimize the difference of cumulative subsurface drain flow for the first irrigation. Water retentivity models, initial soil moisture and various values of hydraulic conductivities were used in different combinations to minimize the difference between cumulative observed and
cumulative predicted subsurface drain flow amounts. The calibration was continued until the shape of the predicted hydrograph was found to be similar to the observed hydrograph. After calibration, the model was used to simulate the water and chemical movement for the entire study periods of 1997 and 1998.

Results and Discussion

Comparison between the observed and LEACHP predicted chemical concentrations in the soil profile

Tables 3-4 present the irrigation and rainfall events for the growing season of 1997 and 1998, respectively. Table 5 gives the chemical application rates for both study years. Figure 1 shows the relative amounts (g/g, the ratio of the amount of chemical retained in the soil profile to the amount of chemical applied to the soil surface) of predicted and observed atrazine at various increments of depths, 23 days after application for 1997 under the chisel plow system. The relative amount of observed and predicted atrazine in the soil profile varied from 0 to 0.30 and 0 to 0.36, respectively. The surface (0-7.5 cm) layer had the maximum amount of atrazine in both observed and predicted cases. However, the model over predicted approximately 20% of the observed amount of atrazine in the surface layer. The model did not predict any amount of atrazine below 30 cm of the soil profile for the study period of 1997. In addition, total observed and predicted relative amounts of atrazine were found to be 44% and 78%, respectively, of the applied amount in the soil profile. The over prediction of atrazine could be because the model could not accurately predict the degradation rate for atrazine in the upper part of the soil profile. However, the model
simulated a trend: a decrease in the amount of atrazine with an increase in depth similar to the observed field data.

Figure 2 shows the relative amounts of atrazine in no-till soil for the study period of 1998. LEACHP predicted a peak in the amount of atrazine similar to the observed peak in the surface layer (0-7.5 cm) of the soil profile. However, the model over predicted by 42% the peak of atrazine compared to the observed atrazine peak in soil. The pattern of decrease in the amount of atrazine with increase in depth was also similar for observed and predicted values. In 1998, the model prediction of atrazine was not different from the year 1997 (Figure 1-2). In addition, the model over predicted total relative mass of atrazine by 24% when compared with the observed mass in the soil profile.

Bromide was applied as a conservative tracer before the first irrigation in 1997. Figure 3 shows the observed and predicted relative amount of Br\(^-\), 23 days after application in the soil profile. The model could not accurately predict the transport of Br\(^-\) through the soil profile for the year 1997. The amount of predicted Br\(^-\) was found to be higher than the observed amount of Br\(^-\) in the upper part (0-60 cm) of the soil profile for 1997. Also, the model could not accurately predict the observed bimodal distribution of Br\(^-\) in soil. However, the pattern of decrease in the amount of Br\(^-\) in the lower part (60-120 cm) of the soil profile was similar in observed and predicted values. The model over predicted the Br\(^-\) mass recovery in the soil profile by 96% compared to the observed mass recovery of 62% in 1997. Figure 4 shows the observed and predicted amounts of Br\(^-\) in the soil profile for the growing season of 1998 under the NT system. The model over predicted the relative amount of Br\(^-\) in the top 45 cm of the soil profile by 58%, however, the predicted values of Br\(^-\) were similar to the observed values in the lower part of the soil profile for NT system.
Overall, comparison of observed and predicted soil data showed that LEACHP overestimated the amount of atrazine in the upper 30 cm of the soil profile in 1997 (Figures 1 and 2). Although observed amounts of atrazine below 30 cm of the soil profile were negligible, the model did not predict accurately the movement of atrazine to the bottom part of the soil profile. Similar results were found by Lesikar et al. (1997) when they found in a column study that LEACHP underestimated the transport of herbicide through the soil at higher application rates. Chammas et al. (1997) reported that LEACHP simulations showed an overestimation of atrazine movement in the upper 15 cm but a fairly accurate estimation in the lower 15 cm, 29 days after application in the soil profile. A comparison between observed and LEACHP predicted values of atrazine for three different soils in Minnesota showed that predicted depths of peak atrazine concentration and residual amounts of atrazine found in the soil profile were close to the observed values. However, the model did not predict significant amounts of atrazine at depths greater than 45 cm in soil (Khukharlal et al., 1995), which is similar to the results of this study.

Predicted Br⁻ distribution in soil for 1997 was different from the observed field results. The model could not predict the observed bimodal distribution of Br⁻ in the soil profile (Figure 3). Therefore, it can be concluded that localized distribution of solutes can be missed in simulation modeling. In 1998, the model predicted Br⁻ distribution fairly close to the observed amount of Br⁻ below 30 cm of the soil profile (Figure 4). Similar results were reported by Pennell et al. (1990) and Jabro et al. (1994). Pearson et al. (1996) also found favorable agreement between the observed and LEACHM predicted breakthrough curves for bromide under cropped and fallow conditions.
Subsurface drain flow simulations by the LEACHP

Figure 5 presents the observed and predicted hourly subsurface drain flow rates for all irrigation and rainfall events for the study period of 1997 under the CP system. Figure 5 also shows that the model under predicted the peak subsurface drain flows for the first irrigation. However, the model over predicted by 23% the cumulative subsurface drain flow compared to the cumulative observed flow for the first irrigation. It is important to mention that since there is no exact subsurface drain flow component in the model, the amount of water drained through the soil profile at a depth of 120 cm was considered as the predicted subsurface drain flow for the specific time intervals. Although the model predicted the peak flows with a late response during the second irrigation, as compared to the observed peak, the shape of predicted and observed subsurface drain flow hydrographs were similar in shape. Cumulative predicted amounts of water drained during second irrigation and the rainfall events (170th and 172nd day of the year) was 27% higher than the observed amount of subsurface drain flow.

During the third irrigation, the model substantially over predicted the water drained through the soil profile. The reason for this over prediction could be the effect of a rainfall event on the 172nd day of the year. It also shows the delayed response of subsurface drain flow predicted by the model for rainfall events. Total predicted cumulative drainage by the model for the third irrigation was 239% higher than the observed cumulative amount of subsurface drain flow. The model also over predicted the amount of water drained in the fourth irrigation; however, the pattern of subsurface drain flow was similar to observed drain flow at the start of fourth irrigation.
Figure 6 gives the hourly observed and predicted subsurface drain flow rates for the growing season of 1998 under no-till conditions. For 1998, predicted and observed values for subsurface drain flows were in general agreement with each other. In addition, LEACHP predicted the peaks of subsurface drain flows at the same time as they were observed in the field, however, peak drain flows after the rainfall events were substantially under predicted by the model.

The evaluation of observed and simulated subsurface drain flow data also showed that LEACHP did not predict loss of atrazine with subsurface drain water for the year 1997 and 1998. Atrazine, on the other hand, was found in the subsurface drain flow immediately after its application during the field experiment, which could be due to the preferential transport of atrazine with water to deeper depths in a matter of few hours. The underestimation of predicted atrazine in subsurface drain flow could be due to the lack of a macropore flow component in the model. The model does not account for preferential flow of water and chemicals through the soil profile (Wagenet and Hutson, 1989). The comparison of observed and predicted atrazine losses with subsurface drain flows also supports the role of macropores in movement of water and chemicals through the soil profile in field conditions. However, the model predicted Br⁻ losses to subsurface drains in both study years. The predicted losses of Br⁻ to subsurface drains were 4.7% and 0.15% in 1997 and 1998, respectively, and the observed losses of Br⁻ were found to be 2% and 2.7% in 1997 and 1998, respectively. It shows that model over predicted in 1997, and under predicted in 1998. It can be concluded that predicted Br⁻ losses to subsurface drainage were correlated to the predicted subsurface drain flows.
The literature review showed that not many studies have used this model to predict subsurface drain water under different environmental conditions. However, the results of this study have shown that regarding predicted subsurface drainage flows have some similarities and some discrepancies when compared to observed data and the results reported by other researchers. Jemison et al. (1994) found that underestimation of drainage by LEACHM also resulted in underestimation of Br leaching. In another study, Elliott et al. (1998), in a 50-day irrigation study in Saskatchewan, Canada, found good agreement between measured and simulated water flows and chemical losses with subsurface drains; however, no rainfall event occurred in the study period. It shows that a high intensity rainfall event could be one of the factors in overestimation of predicted subsurface drain flow rate.

Overall, LEACHP simulated the subsurface drain flows with good agreement only for the irrigation events in 1997. The model could not accurately predict the effect of rainfall events on subsurface drain flows. Table 6 presents the percent difference between the total observed and predicted subsurface drain flows for 1997 and 1998. The cumulative predicted flows in 1997 were substantially different from the cumulative observed flow in 1997. One of the reasons for this difference in observed and simulated subsurface drain flows could be the occurrence of runoff due to high intensity rainfall events. The intended water application rates during irrigations in 1997 were as low as 3 to 5 mm hr\(^{-1}\) to prevent any runoff from the field plot. Also, no significant amount of runoff was observed during irrigations in the field. The rainfall events on 170\(^{th}\) day (of 8 mm hr\(^{-1}\)) and 172\(^{nd}\) day (of 10.5 mm hr\(^{-1}\)) in 1997 caused runoff which was not accounted for by the model. LEACHP is not intended to predict runoff quality and quantity (Hutson and Wagenet, 1992). Therefore, it can be concluded that the model predicted subsurface drain flows better for irrigation events (almost
without any observed runoff during irrigation) as compared to the high intensity rainfall events. It is important to mention that if the water application rate is higher than the infiltration rate of the soil, the model assigns the extra water to an excess water term that is included in the mass balance calculation. Therefore, the total amount of water for rainfall events used in the mass balance by the model after each time interval caused overestimation of subsurface drain flows. In addition, drifting of irrigation water due to high winds during the experiment was also observed in 1997. The model did not account for the drift losses and assumed applied water as the water application depth. It is also important to mention that subsurface drainage system in the field may not collect all the water that passes through the soil profile under field conditions. It could also affect the observed subsurface drain flow rate. On the other hand, the assumption of the model is that the amount of water that passes through the profile is drainage water and uses it in mass balance as drainage losses.

LEACHP predicted subsurface drain flow rates were in close agreement with the observed subsurface drain flow rates for the growing season of 1998 (Figure 6). No significant amount of runoff was observed due to crop residue on the soil surface and low water application rate during irrigation for the no-till study in 1998. Many researchers have reported the reduced runoff under no-till conditions than under conventional tillage (Baker et al., 1978; Johnson et al., 1979; Malinda et al., 1998; Schreiber and Cullum, 1998). Therefore, 53% of applied water in irrigation and rainfall drained through subsurface drainage in the field. The model also accurately predicted the time of peak of subsurface drain flow during and after irrigation, and the cumulative amount of water drained through the soil profile for 1998. Table 6 also shows that cumulative predicted flow was within 9% of cumulative observed flow. However, the model under predicted the peak of subsurface
drain flow during irrigation and rainfall events for no-till soil. The peak of observed subsurface drain flow in the field is attributed to the quick movement of water through macropores in the soil profile (White, 1985, Everts and Kanwar 1990; Kanwar et al., 1997). LEACHP has no component to simulate macropore flow in soil. Therefore, the model did not accurately predict the observed peaks of subsurface drain flow rates due to macropore flow during the field experiment under the no-till system.

Summary and Conclusions

In this study, observed field data on soils and subsurface drain flows for the growing season of 1997 and 1998, were used to calibrate and evaluate the usefulness of LEACHP model. The LEACHP model (version 3.0) was calibrated by minimizing the differences between the cumulative amount of predicted and observed subsurface drain flows and shape of subsurface drain flow hydrographs for two tillage practices, chisel plow (CP) and no-till (NT).

The results of this study showed that there was generally a good agreement in the pattern of predicted subsurface drain flow hydrographs after irrigation events under CP system. However, the model could not accurately predict the subsurface drain flow hydrographs after rainfall events for both study years. In addition, model predicted subsurface drain flow volumes were in better agreement for the NT system than the CP system. Predicted time of peak subsurface drain flows after irrigation, cumulative volume of predicted subsurface drain flows, and shape of subsurface drain flow hydrographs were in close agreements with the observed values for the NT system. Distribution of chemicals in
the soil profile was in good agreement with the observed data for the years 1997 and 1998. This model simulation study resulted in the following specific conclusions.

1. Comparison between the observed and predicted atrazine amounts in the soil data showed that LEACHP over predicted the atrazine amount in the top 0-15 cm of the soil profile. In addition, the model underestimated the amount of atrazine leached to the deeper depths (>30 cm).

2. The simulation model did not predict any loss of atrazine with subsurface drain flow for the years 1997 and 1998. Br\(^-\) losses with subsurface drains were over predicted in 1997 and under predicted in 1998. The predicted losses of bromide were directly related to the amount of water leached through the soil profile.

3. LEACHP overestimated the amount of subsurface drain water for the study period of 1997 under the CP system. Model could not accurately predict subsurface drain flows after rainfall events. However, predicted hydrographs after irrigation events were in good agreement with the observed hydrographs. For no-till conditions in 1998, model predictions were very close to the observed subsurface drain flows except underestimation of peaks subsurface drain flows after two rainfall events.

The overall conclusion of the study indicates that LEACHP predicted chemical movement in the soil profile to subsurface drains is correlated to the amount of water percolated beyond the soil profile. In addition, lack of macropore flow and runoff components may be the two major factors which might have affected the simulation results of LEACHP. Considering the range in soil properties and climatic conditions used in validating LEACHP for the soils in Iowa, the model performance was good for different soil and tillage conditions. However, LEACHP users should be careful about the model
limitations and errors with the input field data, especially where conditions are favorable for runoff and formation of preferential flow paths (macropores) in the soil profile. However, the results showed that a simple model has the capability of simulating water and chemical movement through the soil profile to shallow groundwater.

References


Agricultural and Biosystems Engineering and Agronomy Experiment Station. Boone, IA. Alexander, C., 1988. ADAPT: a model to simulate pesticide movement into drain tiles. MS Thesis, Ohio State Univ., Columbus, OH.


Table 1. Selected physical properties of Nicollet soil at the experimental site under chisel plow system (from Azevedo et al., 1996).

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Soil depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-7.5</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity, cm sec⁻¹</td>
<td>4.45x10⁻²</td>
</tr>
<tr>
<td>Texture</td>
<td></td>
</tr>
<tr>
<td>% sand</td>
<td>51.6</td>
</tr>
<tr>
<td>% coarse silt</td>
<td>17.2</td>
</tr>
<tr>
<td>% fine silt</td>
<td>12.4</td>
</tr>
<tr>
<td>% clay</td>
<td>18.8</td>
</tr>
<tr>
<td>Bulk density, gm cm⁻³</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Table 2. Selected physical properties of Nicollet soil at the experimental site under no-till system (from Kanwar et al., 1987).

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Soil depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-30</td>
</tr>
<tr>
<td>Hydraulic conductivity, cm sec⁻¹</td>
<td>2.7x10⁻²</td>
</tr>
<tr>
<td>Texture</td>
<td></td>
</tr>
<tr>
<td>% sand</td>
<td>38.9</td>
</tr>
<tr>
<td>% coarse silt</td>
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</tr>
<tr>
<td>% clay</td>
<td>24.5</td>
</tr>
<tr>
<td>Bulk density, gm cm⁻³</td>
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</tr>
<tr>
<td>Porosity</td>
<td>0.47</td>
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<tr>
<td>Organic matter(%)</td>
<td>4.2</td>
</tr>
</tbody>
</table>

### Table 3. Irrigation and rainfall schedule during the growing season of 1997.

<table>
<thead>
<tr>
<th>Date</th>
<th>Day of the year</th>
<th>Irrigation (mm)</th>
<th>Rainfall (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/3/97</td>
<td>154</td>
<td>40*</td>
<td></td>
</tr>
<tr>
<td>6/4/97</td>
<td>155</td>
<td>35.4</td>
<td></td>
</tr>
<tr>
<td>6/12/97</td>
<td>163</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>6/16/97</td>
<td>167</td>
<td>19.3*</td>
<td></td>
</tr>
<tr>
<td>6/17/97</td>
<td>168</td>
<td>44.4*</td>
<td></td>
</tr>
<tr>
<td>6/17/97</td>
<td>168</td>
<td>14.4*</td>
<td></td>
</tr>
<tr>
<td>6/18/97</td>
<td>169</td>
<td>33.1</td>
<td></td>
</tr>
<tr>
<td>6/19/97</td>
<td>170</td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>6/21/97</td>
<td>172</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>6/23/97</td>
<td>174</td>
<td>50*</td>
<td></td>
</tr>
<tr>
<td>6/25/97</td>
<td>176</td>
<td></td>
<td>6.6</td>
</tr>
<tr>
<td>6/29/97</td>
<td>180</td>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td>7/2/97</td>
<td>183</td>
<td>25.6*</td>
<td></td>
</tr>
<tr>
<td>7/3/97</td>
<td>184</td>
<td>39.2</td>
<td></td>
</tr>
</tbody>
</table>

* Pre-irrigation to start subsurface drain flow before actual irrigation event

### Table 4. Irrigation and rainfall schedule during the growing season of 1998.

<table>
<thead>
<tr>
<th>Date</th>
<th>Day of the year</th>
<th>Irrigation (mm)</th>
<th>Rainfall (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/28/98</td>
<td>180</td>
<td></td>
<td>24.5</td>
</tr>
<tr>
<td>6/29/98</td>
<td>181</td>
<td></td>
<td>20.3</td>
</tr>
<tr>
<td>7/1/98</td>
<td>183</td>
<td>63.4</td>
<td></td>
</tr>
<tr>
<td>7/3/98</td>
<td>185</td>
<td></td>
<td>4.8</td>
</tr>
<tr>
<td>7/4/98</td>
<td>186</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>7/5/98</td>
<td>187</td>
<td></td>
<td>7.8</td>
</tr>
<tr>
<td>7/6/98</td>
<td>188</td>
<td></td>
<td>16.5</td>
</tr>
<tr>
<td>7/7/98</td>
<td>189</td>
<td></td>
<td>12.0</td>
</tr>
<tr>
<td>7/15/98</td>
<td>197</td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td>7/17/98</td>
<td>198</td>
<td></td>
<td>9.4</td>
</tr>
</tbody>
</table>
Table 5. Herbicide and tracer applied (spray) over the strip during the growing season of 1997 and 1998.

<table>
<thead>
<tr>
<th>Herbicide and tracer</th>
<th>1997 mass applied, g</th>
<th>1998 mass applied, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>96, before first irrigation on 6/4/97</td>
<td>49.4, before irrigation on 7/1/98</td>
</tr>
<tr>
<td>Bromide</td>
<td>4002, before first irrigation on 6/4/97</td>
<td>2619, before irrigation on 7/1/98</td>
</tr>
</tbody>
</table>

Table 6. A summary of total observed and predicted subsurface drain flows for 1997 and 1998.

<table>
<thead>
<tr>
<th>Year</th>
<th>total predicted (mm)</th>
<th>total observed (mm)</th>
<th>percent difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>98.3</td>
<td>60</td>
<td>+68.6</td>
</tr>
<tr>
<td>1998</td>
<td>60.2</td>
<td>55.4</td>
<td>+8.6</td>
</tr>
</tbody>
</table>
Figure 1. Relative amount of observed and predicted atrazine as a function of soil depth on June 27, 1997 (23 days after application)

Figure 2. Relative amount of observed and predicted atrazine as a function of soil depth on July 21, 1998 (21 days after application)
Figure 3. Relative amount of observed and predicted bromide as a function of soil depth on June 27, 1997 (23 days after application)

Figure 4. Relative amount of observed and predicted bromide as a function of soil depth on July 21, 1998 (21 days after application)
Figure 5. Observed and predicted subsurface drain flows under chisel plow system for 1997.
Figure 6. Observed and predicted subsurface drains flows under no-till system for 1998.
GENERAL CONCLUSIONS AND SUMMARY

The main objective of the study was to have a better understanding of the movement of applied water, herbicides, and conservative tracers and role of preferential flow for an agricultural soil of Iowa under different field conditions. As conservation tillage practices hold a potentially greater threat for more leaching of agricultural chemicals to the shallow groundwater, this study focused on the significance of preferential flow under both conventional and conservation tillage systems.

Two field studies were conducted to investigate the movement of herbicides and conservative tracers through the unsaturated zone of the soil profile into the shallow groundwater under simulated rainfall conditions in the growing seasons of 1997 and 1998. However, the effect of natural rainfall events during the study on solute transport was also incorporated into the analysis and conclusion of the experiments. The data for chisel plow and no-till systems were collected in the growing seasons of 1997 and 1998, respectively. The field data from these two studies were also used to calibrate and evaluate LEACHP 3.0 for different tillage conditions. The observed chemical concentrations in subsurface drains and soil were compared with the model predicted values on solute transport in the soil profile.

Herbicides (atrazine and alachlor) and conservative tracers (chloride, bromide, and fluorobenzoates) were sprayed on a strip before and during rainfall simulations. Since transport of water and solutes is a complex process in soil, data were collected on soils and subsurface drain water using subsurface drains. Suction lysimeters and soil samples were also used to understand both water and chemical movement in the soil profile to shallow groundwater. The soil cores were collected for background sampling, and at the end of the
study period. The suction lysimeters were installed at the strip at various depths to extract
the soil-water samples before, during, and after every irrigation event. Subsurface drain data
were collected for solute concentrations by continuous monitoring of subsurface drain flow
throughout the study period.

Although the data presented in this study for two different tillage systems are based on
two short-term studies, the conclusions from the study can be helpful in understanding the
role of macropore flow in transporting water and chemicals to groundwater under chisel plow
and no-till systems. Some of the specific conclusions of this study were:

1. The use of rainfall simulation and chemical tracers has provided useful data to
   understand the role of macropore flow under different field conditions. It can be
   concluded from the study that the first rainfall after chemical application was a major
   factor affecting the leaching losses of various solutes to shallow groundwater. The
   study also showed that a major portion of solutes in the soil profile moved through
   the soil matrix, and that preferential flow has little contribution to solute transport into
   shallow groundwater for these soils under the chisel plow system. Moreover,
   preferential flow had a greater role in solute transport to shallow groundwater under a
   no-till system.

2. The data collected by suction lysimeters to extract water samples at various depths
   showed that leaching of herbicides and conservative tracers is possible through
   macropores if irrigation or rainfall occurs shortly after chemical application. Also,
   early detection (2 h after irrigation started) and higher concentrations of chemicals in
   the water samples from suction lysimeters in no-till soil as compared with suction
Lysimeter data under chisel plow soil support the significant role of macropores in no-till soils.

3. The amount of atrazine was always found to be higher than the amount of alachlor in the soil profile in both tillage systems, which was due to the higher degradation rate of alachlor than that of atrazine. In addition, movement of all non-adsorbed tracers in the soil profile was consistent throughout the study period in both tillage systems, and directly affected by the amount of water applied after chemicals' application. The earlier application of a conservative tracer during irrigation event resulted in deeper leaching of that tracer under the chisel plow system. However, this phenomenon was not true under the no-till system.

4. No significant amount of herbicide (less than 1%) was detected in subsurface drain flow under both tillage systems. However, herbicide losses with subsurface drain flow were higher under the no-till plot compared to the chisel plow plot. Due to a significant amount of residual soil chloride present in soil, applied chloride could not effectively represent its movement with water to subsurface drains under the chisel plow system in 1997. Therefore, chloride is of limited use for monitoring macropore flow for these soils and was not used as a tracer in 1998. Conservative tracers were detected in subsurface drain water 17 days after solute application under the chisel plow system (after two irrigations) as compared within 2 h during the first irrigation under no-till soil. This primarily appears to be due to the role of macropore flow in the soil profile. In 1998 (no-till), conservative tracer concentrations in subsurface drain water were also higher than those in 1997 (chisel plow).
5. The calibration and evaluation of LEACHP for two tillage systems (chisel plow and no-till) demonstrated that the predicted depth of atrazine was in good agreement with the observed concentration in the upper part (0-30 cm) of the soil profile. However, the model did not predict any atrazine movement below 30 cm of the soil profile. Predicted bromide distribution in the soil profile was in close agreement in the bottom part (60-120 cm) of the soil profile. However, the model did not predict the bimodal distribution of bromide in 1997.

6. Generally, there was a good agreement in the pattern of observed and predicted subsurface drain flows by the LEACHP after irrigation events for the years 1997 and 1998. However, the model could not accurately predict the effect of rainfall events on subsurface drain flow rates.

7. The overall conclusion from the study was that total losses of applied herbicides and conservative tracers with subsurface drainage were negligible. A natural rainfall or irrigation event after chemical application enhances the leaching of chemicals to the shallow groundwater. However, more leaching of herbicides and tracers is possible under the no-till system than the chisel plow system due to preferential flow. Solute movements in these soils were governed by the amount of water applied after chemical application. LEACHP simulations also showed a correlation of chemical transport with the amount of water percolated to the subsurface drains. The discrepancies of observed and predicted solute transport could be due to the lack of macropore flow, and runoff components. Model predictions could be improved by accounting for runoff, tillage and macropore flow effects on water and pesticide transport.
SUGGESTIONS FOR FUTURE WORK

The short-term rainfall simulation study resulted in some specific conclusions regarding movement of water and chemicals at various times after application and solute movement through the soil profile to the shallow groundwater. However, the results of the study may not be able to answer all the questions about the transport of water and chemicals through macropores or the soil matrix.

The results showed some similarities to the findings of some other research work in different environmental conditions. However, there were some differences in the results when compared with other studies; for example, a higher percent of mass recoveries for fluorobenzoates under the chisel plow system. Use of suction lysimeters in the field study was found to be an interesting and effective tool in predicting the solute movement through various depths in the soil profile. However, extreme care is needed in installing the lysimeters in the field because soil water samples were not attainable unless the lysimeters were properly installed or the soil was saturated. Computer modeling showed similar results when compared with observed solute transport. However, LEACHP needs to incorporate the effect of runoff, macropore flow and tillage to improve the predictive abilities of the model.

Future studies are needed to have a better explanation of water and solute movement to prevent groundwater contamination. In addition, more detailed data is needed by replicating a similar study for long term experiments under different crops and soil types and weather conditions. Additionally, calibration and validation of computer models using the field data can help in evaluating the effect of different management scenarios to predict the water and chemical movement through the soil profile in different conditions. Finally, similar studies may be helpful in determining the best management practices for the area.
REFERENCES


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