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Herbicide and tracer movement in soil

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Iowa State University, 1990

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Herbicide and tracer movement in soil

by

George Frank Czapar

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

**Department: Agronomy
Major: Crop Production and Physiology**

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**Iowa State University
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1990**

TABLE OF CONTENTS

	Page
LITERATURE REVIEW	1
Introduction	1
Field movement	2
Soil columns	23
Tracer studies	27
SECTION I. A FIELD HYDROLOGY LABORATORY FOR MEASURING PESTICIDE AND FERTILIZER MOVEMENT THROUGH THE ROOT ZONE	34
INTRODUCTION	35
MATERIALS AND METHODS	37
RESULTS AND DISCUSSION	43
CONCLUSIONS	48
REFERENCES	49
SECTION II. HERBICIDE AND TRACER MOVEMENT TO FIELD DRAINAGE TILES UNDER SIMULATED RAINFALL CONDITIONS	52
INTRODUCTION	53
MATERIALS AND METHODS	56
RESULTS AND DISCUSSION	65
CONCLUSIONS	80
REFERENCES	82

SECTION III. HERBICIDE AND TRACER MOVEMENT IN SOIL	86
COLUMNS CONTAINING AN ARTIFICIAL MACROPORE	
INTRODUCTION	87
MATERIALS AND METHODS	90
RESULTS AND DISCUSSION	97
CONCLUSIONS	103
REFERENCES	106
GENERAL SUMMARY	108
REFERENCES CITED	112
ACKNOWLEDGEMENTS	129

LITERATURE REVIEW

Introduction

The effect of agricultural chemicals on groundwater quality continues to be a major issue. A National Research Council report (1989) recently suggested that water pollution is the most damaging and widespread environmental effect of agricultural production. Similarly, agricultural practices are often cited as the most pervasive source of nonpoint water pollution (Myers et al., 1985).

Since herbicides are used on approximately 98% of the corn and soybeans acres in Iowa (Wintersteen and Hartzler, 1987), protecting groundwater from herbicide contamination is an important concern. Although water contamination can occur in many ways, the extent and importance of herbicide leaching from normal field use is not clear.

Point source contamination near mixing/loading areas is becoming more widely recognized as a significant factor affecting water quality (Long, 1987; Habecker, 1989). In addition, sinkholes and agricultural drainage wells can allow agricultural chemicals to reach groundwater (Fawcett, 1989).

It also appears that herbicide loss to surface water is a significant source of contamination (Baker, 1980; Baker and Laflen, 1983; Leonard, 1988; Wauchope, 1978). Frank et al. (1982), found that 60% of the pesticides lost to water from conventionally tilled watersheds were the result of storm

runoff. In contrast, only 18% was attributed to leaching. Since an estimated 675 million to one billion tons of eroded agricultural soils are deposited in waterways each year (National Research Council, 1986; USDA, 1986), pesticides adsorbed to soil may also be a source of contamination.

Interest in the effects of agricultural chemicals on water quality has resulted in considerable research and numerous publications on groundwater contamination. Canter (1988) reviewed some the information available through a computer-based literature search for case studies of pesticides in groundwater, transport and fate, and mathematical models. Other bibliographic searches concerning pesticides and water quality are also available (NTIS, 1984; USDA, 1988).

Field Movement

Herbicide characteristics It was recognized early that leaching can be an important factor affecting herbicide loss from soil (Ogle and Warren, 1954; Holstun and Loomis, 1956). Burnside et al. (1963) noted that atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) and simazine (2-chloro-4,6-bis(ethylamino)-s-triazine) moved through the soil profile below the two foot soil depth and suggested that leaching is an important avenue for dissipation of these herbicides.

The potential for any pesticide to contaminate

groundwater is dependent on several factors. Since herbicides have distinct chemical and physical properties, their leaching potentials are quite different. Bailey and White (1970) reviewed seven factors known to influence the fate and behavior of pesticides in soil systems. They included: 1) chemical decomposition, 2) photochemical decomposition, 3) microbial decomposition, 4) volatilization, 5) movement, 6) plant or organism uptake, and 7) adsorption.

Weber et al. (1986) suggest that the mobility of a herbicide in soil is dependent upon the ionizability, water solubility, vapor pressure, and lipophilic nature of each compound.

For a specific herbicide, other routes of dissipation can be far more important than surface runoff or leaching. In one study, 90% of the applied trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine) volatilized from moist, bare soil in 2-3 days after application (Taylor, 1978). Similarly, 74% of the applied EPTC (S-ethyl dipropylthiocarbamate) volatilized over a 52 hour period following flood irrigation of an alfalfa field (Cliath et al., 1980).

Microbial degradation is another important mechanism for thiocarbamate breakdown and greatly reduces the amount of herbicide that could potentially leach. In some soils having a history of thiocarbamate use, enhanced microbial degradation

results in rapid chemical breakdown (Moorman, 1988; Wilson, 1984).

Water solubility, herbicide persistence, and the extent of soil adsorption are frequently identified as primary factors affecting field movement. In general, chemicals with a high water solubility and a low degree of soil adsorption will be more mobile in soil.

The extent of pesticide adsorption to clay and organic matter has been the subject of several critical reviews (Bailey and White, 1970; Hamaker and Thompson, 1972; Green, 1974; Weed and Weber, 1974; Calvet, 1980; Weber, 1986; Hance, 1988). Many investigators have used the Freundlich equation to describe the extent of pesticide adsorption (Freundlich, 1926):

$$C_s = K C_e^{1/n} \quad (1)$$

where:

C_s - $\frac{\text{Mass of chemical adsorbed (ug)}}{\text{Mass of soil (g)}}$

C_e - $\frac{\text{Mass of chemical in solution (ug)}}{\text{Volume of water (ml)}}$

K - Partitioning Coefficient (ml/g)

$1/n$ - constant (values are between 0.7 and 1 for most herbicides)

Giles et al. (1960) developed a classification of adsorption isotherms which has been used to describe the

adsorption of various organic herbicides by clay minerals and organic colloids. They identified four basic types of adsorption isotherms (normal or L-type, S-type, C-type, and H-type) based on the affinity between solid and solute and the effects of solute concentration.

Organic carbon is often cited as the most important factor affecting adsorption (Bohn et al., 1985; Grover, 1977; Lambert et al., 1965). As a result, the concentration of adsorbed material is often expressed per unit of organic carbon (OC):

$$K_{OC} = \frac{\% \text{ } 100 \text{ } K}{\% \text{ } OC} \quad (2)$$

where K preferably should be the Freundlich K (Equation 1), but is often the distribution ratio (K_d) obtained from an observation at only one concentration, using the assumption that the value of $1/n$ in the Freundlich relationship is close to one (Hance, 1988). Since soil adsorption is positively correlated to organic carbon content, K_{OC} is more nearly constant among soils than is K_d (Hamaker and Thompson, 1972).

There has been some interest in the role of water soluble soil organic matter (WSSOM) in assessing pesticide mobility and transformation. Ballard (1971) and Madhun et al. (1986) indicated that WSSOM may enhance the solubility of certain pesticides and act as a vehicle for pesticide transport.

Since adsorption is known to be related to the

lipophilicity of a molecule, some have tried to correlate adsorption with octanol/water partitioning and water solubility (Briggs, 1981; Hance, 1967; Kenaga and Goring, 1978; Lambert, 1967). Cohen et al. (1984), however, caution that adsorption predictions based on solubility alone can be misleading. The authors use simazine as an example of a pesticide having a predicted K_{oc} of 2,700, based on its low water solubility, yet the measured K_{oc} is 138.

It seems apparent the mobility alone is not a good indicator of groundwater pollution potential. Rather, the combination of mobility and persistence determine whether a compound will be degraded to an innocuous form during its residence time above groundwater (Jury et al., 1984; Jury et al., 1987a). Individual chemical properties help explain why some pesticides are more frequently identified in groundwater while other are rarely found.

In many statewide water quality surveys, atrazine has been detected more often than any other pesticide (Klaseus et al., 1988; LeMasters and Doyle, 1989; Spalding et al., 1989). Barrett and Williams (1989) noted that the prevalence of atrazine in groundwater is a function of its persistence, moderate mobility, and widespread use.

When Pionke et al. (1988) monitored 20 wells in a Pennsylvania agricultural watershed for the most intensively applied pesticides, atrazine was detected in 70% of the wells.

In contrast, metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide) and alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) were not detected, while cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile) was found in only one well.

Cohen et al. (1984) listed several pesticide characteristics and field conditions that suggest high potential for groundwater contamination, if they occur in combination. Specific pesticide characteristics included: water solubility greater than 30 ppm; adsorptivity, K_{oc} less than 300 to 500; Henry's law constant less than $0.01 \text{ atm-m}^3 \text{ mol}^{-1}$; negatively charged at soil pH; soil half-life greater than 2 to 3 weeks; hydrolysis half-life greater than 25 weeks; and photolysis half-life greater than 1 week. Field conditions listed were: total groundwater recharge greater than 250 mm year⁻¹; presence of high nitrate levels as an indicator of agricultural recharge source; unconfined aquifer with porous soil above it; and soil pH providing high stability to the pesticide residues.

Pesticide mobility studies Several laboratory techniques have been utilized to estimate pesticide leaching under field conditions. Helling (1970), Wu and Santelmann (1975), and Weber et al. (1986) reviewed the methods commonly employed to study pesticide movement in soils.

Soil columns have been frequently used to measure pesticide mobility in soils (Grover, 1977; Harris, 1967; Weber and Whitacre, 1982). Weber et al. (1986) reviewed column leaching techniques for hand-packed and intact cores.

Soil thin-layer chromatography (TLC) uses a ground soil thinly applied to a glass plate (Helling and Turner, 1968; Helling, 1971). Radioactive pesticide solutions are spotted at the bottom of the plate which is then developed with water using techniques analogous to conventional TLC. Immobile herbicides are strongly adsorbed and do not ascend the plate, while highly mobile herbicides are not adsorbed and move freely (Weber et al., 1986).

Soil thick-layer chromatography uses soil trays placed in a horizontal position (Gerber et al., 1970; Wu and Santelmann, 1975). A cotton cloth attached to the base of the tray is used as a wick to draw up water for the development of the chromatogram. After the leaching process, the tray is divided into 2-cm sections and a bioassay is conducted for the presence of herbicides.

Pesticide mobility studies, required by the EPA to support product registration (Environmental Protection Agency, 1982), are based mainly on chemical characteristics, with less emphasis placed on field behavior. Although the EPA guidelines require leaching studies on a minimum of four soils, each of the three approved laboratory techniques (soil

thin-layer chromatography, soil column studies, or batch equilibrium (adsorption/desorption) studies) minimize the importance of natural soil structure on pesticide mobility. Further, soil column leaching studies are often conducted by applying 50.8 cm of water to the column. This may not accurately reflect field movement of pesticides under extreme rainfall conditions.

Modeling chemical movement Numerous mathematical models have also been developed for describing the transport and fate of surface-applied chemicals in the subsurface environment (Addiscott and Wagenet, 1985; Javandel et al., 1984; Jury et al., 1987a,b; Dean et al., 1984; Rao and Jessup, 1982). Wagenet and Rao (1985) reviewed several approaches to modeling pesticide fate in the root zone.

Many models, however, are often limited by considering solute movement under uniform flow conditions, and that water initially in the soil profile is completely displaced ahead of infiltrating water (Nofziger and Hornsby, 1988). Furthermore, field studies of solute movement often reveal large discrepancies between measured and computed values (Rao et al., 1979; Biggar and Nielsen, 1976; Van De Pol et al., 1977; Jury et al., 1982).

Wehtje et al. (1984) measured atrazine leaching below an irrigated cornfield and suggested that atrazine moved through the profile in a "wave-like" or "pulse" manner. When a model

(Rao et al., 1976) predicted that 1.32 m of water would be needed to displace atrazine through 1.5 m of soil, they concluded that the atrazine detected was the result of application the previous year.

Several models have been developed which consider solute transport in non-uniform, structured soils (White, 1985a; van Genuchten, 1985; van Genuchten and Dalton, 1986; Wierenga and Van Genuchten, 1989). White (1985b) stressed that the recognition of two domains of different flow characteristics is an essential feature of any solute transport model for structured soils.

Macropores and preferential flow Although the rapid movement of water through open channels in the soil was identified early (Schumacher, 1864; cited in Beven and Germann, 1982; Lawes et al., 1882), the significance of preferential flow has only recently been widely recognized. Soil macropores or large cracks, root channels and wormholes, can be important for the movement of water and solutes under certain conditions. Since preferential flow bypasses the soil matrix, surface applied agricultural chemicals may also be able to move rapidly through the root zone (Everts et al., 1989; Priebe and Blackmer, 1989; Thomas and Phillips, 1979; Smetten et al., 1983; White et al., 1986).

Beven and Germann (1982) reviewed the importance of macropores and their implications for rapid movement of

pollutants through soils. They suggest that large voids can be separated between those which are hydrologically effective in terms of channeling flow through the soil (macropores), and those which are not. Further, the effect of the macropores is dependent on the spacing between large pores, the pattern of rainfall intensities, and the hydraulic characteristics of the matrix.

Anderson and Bouma (1977b) outlined four factors which govern the depth of water penetration and the amount of movement into and through soil peds. Loading rate, soil capillary conductivity within the peds, hydraulic gradients present within the peds, and the patterns and number of large vertical voids and macropores all influence water and solute movement within a structured soil.

Germann et al. (1984) measured bromide and water distribution in soil as the result of macropore structure and irrigation rate. Applying the concept of two domains of flow, the contribution of macropore and matrix flow varied according to both hydraulic conditions existing prior to infiltration, and the rate and amount of infiltrating water.

Several researchers have demonstrated that macropores do not have to be continuous to the soil surface to facilitate rapid solute movement (Shuford et al., 1977; Thomas and Phillips, 1979). Phillips et al. (1989) showed that water under negative pressure can enter simulated macropores.

Luxmoore (1981) and Boumma (1981) suggested that "micro, meso, and macroporosity" were more useful terms for describing preferential flow paths in soil. The proposed definitions were based on pore diameters or capillary pore pressure. In contrast, Beven (1981) and Skopp (1981) argued that the processes occurring within soil pores are more important than indirect measures of pore-size class ranges. Skopp defines macroporosity as interaggregate pore space, shrink-swell cracks, root channels, or faunal tunnels that provide preferential flow so that mixing and transfer between such pores and remaining pores (matrix porosity) is limited. Although macropores may only comprise 0.5% to 5% of the total pore space in many agricultural soils (German and Beven, 1981; Kneale, 1985), they can account for the bulk of water movement under certain conditions. Watson and Luxmoore (1986) found that under ponded flow into a forest floor, 90% of the volume flux was through 0.32% of the soil volume.

Shaffer et al. (1979) found that 72% of the total water flow through a Hublersburg silt loam occurred in the large pores drained by water potentials of 0 to -10 cm, and that smaller pores need not be saturated for channelization to occur. They further suggest that porous cup samplers were unsuitable for monitoring solute movement through the soil profile since channeling caused the bulk of added water to bypass the sample instrument.

Edwards et al. (1988) installed sampling equipment beneath 50 large earthworm (Lumbricus terrestris L.) burrows to monitor water and nitrate movement during a 5 month growing season. Although wormhole >5mm in diameter accounted for only 0.3% of the horizontal area at the 30 cm depth, flow in these holes accounted for an average of 3.9% of the rainfall during the growing season.

The importance of preferential flow through macropores is also recognized in the design of on-site waste disposal systems. Hagedorn et al. (1981) proposed that a primary research need is the development of soil suitability indices for various disposal systems. Further, the formation, distribution, and proportion of pore space represented by macropores must be quantified.

Although macropore flow is most evident in well structured soils, water movement by preferential flow paths has been shown to exist even in weakly structured soils (Coles and Trudgill, 1985). In addition to preferential flow through worm holes, cracks, and root channels, small volumes of water may penetrate deeply due to wetting front instability or "fingering" (Hillel, 1987; Raats, 1973; White et al., 1976; Glass et al., 1988).

Wetting front instability occurs in layered soils whose upper layer is finer and less conductive than the coarser layer beneath. The wetting front becomes unstable and breaks

into fingers consisting of a saturated inner core percolating downward surrounded by an unsaturated outer core (Hill and Parlange, 1972).

Tamai et al. (1987) demonstrated that unstable flow can occur under homogeneous conditions in porous media using uniform glass beads of three different diameters. Following infiltration of a ponded liquid, instability appeared on the front and gradually transformed into fingers.

Rainfall timing and duration The amount, intensity, and frequency of rainfall has a significant effect on water and herbicide movement in soil (Upchurch and Pierce, 1957). Stockinger et al. (1965) suggested that the amount of water entering the soil as a function of time was the most important aspect of water and chemical movement in soil. Burnside et al. (1971) observed that atrazine leaching was dependent on the frequency and intensity of rainfall as well as soil type and organic matter content.

The first rainfall event following chemical application has been shown to greatly impact the extent of chemical loss in surface runoff and leaching (Wauchope, 1978; Baker, 1980; Baker and Laflen, 1983). Wauchope (1987a, 1987b) measured surface runoff of atrazine following a rainfall simulation. Total atrazine loss ranged from 4 to 12% of the amount applied. However one-fifth of the total loss occurred in the first liter of runoff, with concentrations as high as 23 parts

per million.

Schwab et al. (1973) showed that irrigation water applied shortly after atrazine and dicamba (3,6-dichloro-2-methoxybenzoic acid) application greatly increased loss in surface runoff and herbicide movement to field drainage tiles.

Spencer et al. (1985) measured pesticide transport from irrigated fields in surface runoff and tile drain waters. The loss was greatest in the first irrigation following pesticide application. Further, the time elapsed between application and the first irrigation was inversely related to pesticide concentrations in the runoff water.

Hall et al. (1989) collected pan lysimeter percolates below conventional and no tillage corn fields. Although total rainfall was similar for the two year study, the extent of leaching losses were strongly related to rainfall distribution and number of leaching events proximal to herbicide application. In one plot, rainfall 11 and 21 days after herbicide application accounted for 57% of the total atrazine leached from a no-till plot over the entire year.

Tillage effects It is widely held that tillage can affect the extent of rainfall infiltration and runoff. Any tillage operation that changes soil bulk density, in turn modifies pore size distribution, water holding capacity, infiltration rate, soil aeration, and may also influence chemical movement (Schepers, 1987).

Blevins et al. (1977) noted that the additional soil surface residues and reduced soil mixing of conservation tillage may greatly modify the soil environment. They found greater water transmission in no-tilled soil due to better pore continuity and increased earthworm activity.

Further, tillage effects on earthworm numbers and activity has received some attention. Mackay and Kladivko (1985) surveyed earthworm populations in a long-term trial comparing conventional and no-till corn and soybeans. Although the earthworm population doubled under no-till soybeans as compared to conventionally tilled plots, tillage had little effect on earthworm populations in corn.

Edwards et al. (1988) measured surface water runoff from no-till and conventionally tilled cornfields. Runoff from the long-term no-till watershed was one eightieth of that from the conventionally tilled corn watershed. Following one heavy storm event, runoff was 40% from the conventionally tilled watershed and less than 3% from the no-till watershed, respectively.

The effects of tillage on pesticide and fertilizer movement is unclear. Considerable variation exists in the literature comparing chemical leaching between conventional and reduced tillage. Variable boundary conditions such as rainfall intensity, duration, and timing probably contributed to differences in experimental results. In addition, similar

tillage operations may not always produce similar macropores due to differences in tillage timing, sequence, soil moisture, wheel traffic, rainfall energy, and soil freeze/thaw cycles (Onstad and Voorhees, 1987).

Fermanich and Daniel (1987) found differences in the movement of the insecticide carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranylmethylcarbamate) between conventional and no-till systems. The average time to reach peak concentration of ^{14}C carbofuran in the leachate from intact columns (0.2m by 0.9m) was 44 days for conventional till and 79 days for no-till. Further, the average peak concentration for conventional till was twice that of no-till.

Recently, Hall et al. (1989) found that herbicide leaching to pan lysimeters was greater in no tillage corn than in conventional tillage fields. The highest loss of applied herbicide, 8.4 and 9.6% for simazine and atrazine respectively, were recorded from no-tillage plots.

Kanwar et al. (1985) examined the movement of $\text{NO}_3\text{-N}$ through no-till and moldboard plowed fields. No-till plots retained significantly greater amounts of $\text{NO}_3\text{-N}$ near the soil surface and showed reduced leaching losses relative to moldboard plowed plots. In the moldboard plowed plots, 26% of the total $\text{NO}_3\text{-N}$ (residual plus applied) had moved below the 150 cm depth after 12.7 cm of rain compared to only 6% in the no-till plots. The authors suggest that tillage destroyed

large pores near the soil surface and exposed more surface area to water movement. In contrast, the undisturbed plots contained intact macropores and water may have bypassed NO_3^- -N within soil aggregates.

Quisenberry and Phillips (1976) observed that macropore flow can be initiated below the soil surface. They later added that water entering a macropore originating below the soil surface could have higher concentrations of soluble compounds than water flowing down macropores open to the soil surface (Phillips et al., 1989).

Wild (1972) also attributed the slow leaching of mineralized nitrogen to the presence of cracks and channels in the soil which allowed water to pass by quickly, without leaching the newly mineralized nitrate. The author, however, speculates that leaching of surface applied fertilizer nitrogen might be more rapid than the nitrate slowly mineralized within the soil aggregates.

Baker (1987) noted that increased water infiltration and preferential flow resulting from reduced tillage could potentially have positive or negative effects on water quality depending on solute application and the timing of leaching events.

Similarly, Wagenet (1987) reviewed advantages and disadvantages of intact macropores under reduced tillage systems. A high intensity rainfall shortly after pesticide

application may allow dissolved chemical to bypass the soil matrix and travel rapidly through preferential flow paths. In contrast, a soluble pesticide applied to the soil surface, but not immediately leached, will be distributed in the smaller pores. Subsequent rainfall may bypass the chemical by traveling through intact macropores, and produce less pesticide leaching.

Spatial variability Field studies of pesticide behavior are often complicated by the spatial variability of the experimental site. Soil physical, chemical, and biological characteristics as well as pesticide residue concentrations can vary both spatially and temporally. Rao and Wagenet (1985) described spatial variability as the combined result of intrinsic and extrinsic factors. Soil texture, organic matter, hydraulic conductivity, and pesticide sorption coefficients are considered intrinsic factors. In contrast, extrinsic variation arises from management practices such as tillage, irrigation, and chemical application.

Biggar and Nielsen (1976) outlined the difficulty in measuring solute concentration and pore water velocity in field soils due to natural spatial variability. After intensively sampling 20 field plots, they concluded that 100 observations would allow the mean pore water velocity to be estimated within plus or minus 50% of its true value. They cite the large range of particle diameters and pore sizes in

field soils as significant factors affecting variability.

Amoozegar-Fard et al. (1982) also recognized that the variability of pore water velocity (v) has a significant impact on solute movement properties, and the accuracy of predictive models. They noted sharp differences between the solute profile when a deterministic value of v is used as compared to the average salt profile for 2,000 random values of v .

Tile drainage studies Since approximately 53 million hectares of cropland in the United States are artificially-drained, monitoring tile effluent is a natural index for assessing the contaminating effects of farming practices (Jury, 1975a).

There are several advantages to using tile lines to measure water quality. Tile effluent has been shown to reflect groundwater quality (Hallberg et al., 1986). Since tiles drain large areas and do not disrupt the natural soil structure, they are useful for larger-scale, more realistic, studies of agricultural management impacts on water quality.

Richard and Steenhuis (1988) used tile drainage sampling as an alternative to geostatistical approaches which aggregate many small scale sample results. Drainage tile studies were effective for measuring solute movement and integrating the high spatial variability normally found with field studies.

Jury (1975a) proposed a model for estimating solute

travel times for tile-drained fields based on drain spacing, depth of tile, depth to impermeable zone, soil porosity, and mean discharge rate over the time of study. In a companion paper, Jury (1975b) applied this model to data from published studies of tile drain effluent concentrations and solute flux. He cautions against assuming a correlation between surface practices and effluent concentrations without taking travel times into consideration.

Field drainage tiles have been used extensively to measure nutrient loss from row-cropped land (Johnson et al., 1965; Schwab et al., 1973; Baker et al., 1975; Burwell et al., 1976; Logan and Schwab, 1976; Gast et al., 1978; Baker and Johnson, 1981; Smettem et al., 1983; Randall and Kelly, 1986; Kanwar et al., 1988). Tile lines have also been used to study pesticide movement, although less frequently.

Schwab et al. (1973) measured atrazine and dicamba loss in tile drainage effluent and in surface runoff. Average losses to the three-foot tile lines were 4.2 and 4.6% of applied atrazine and dicamba, respectively.

Muir and Baker (1976) analyzed tile drain waters over a nine month period for herbicides and degradation products. They measured approximately 0.15% of the applied atrazine, cyprazine (2-chloro-4-cyclopropylamino-6-isopropylamino-1,3,5-triazine), cyanazine, and metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one)

appearing in tile effluent as either parent herbicide or as degradation products.

In a later study, Muir and Baker (1978) found that over a three year period an average of 0.19% of the applied atrazine was recovered from tile lines in the form of parent herbicide and degradation products. Highest percentage losses occurred during the spring months when tile flow rates increased.

Von Stryk and Bolton (1977) investigated the effects of crop rotation and soil fertility on atrazine movement to field drainage tiles. Although atrazine concentrations remained fairly constant under different cropping practices and fertility levels, there were differences in tile flow which affected total loss. Losses for the fertilized continuous corn averaged 0.8% of the applied atrazine, while 0.25% of applied atrazine was recovered from tiles draining unfertilized corn in a rotation.

Kladivko et al. (1989) monitored tile effluent for atrazine, cyanazine, alachlor, carbofuran, terbufos (S-[[(1,1-dimethylethyl)thio]methyl]O,O-diethyl phosphorodithioate) and chlorpyrifos (O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate) on a low organic matter, poorly structured silt loam soil. Although carbofuran losses ranged from 0.05 to 0.94% of the applied chemical, losses of all other pesticides were less than 0.06% of the amount applied.

Randall et al. (1990) monitored atrazine and alachlor

content in tile drainage effluent from a Webster silty clay loam soil. They reported that atrazine, averaging 1 ppb, was consistently detected in tile samples, while alachlor was not found in any sample.

In contrast, Gaynor et al. (1990) observed considerable losses of alachlor through surface and subsurface transport. Alachlor losses averaged 0.3, 0.2, and 0.5% of the amount applied to ridge, minimum, and conventional tillage treatments, respectively. They did, however, note that surface transport accounted for more herbicide loss than tile discharge.

Although tile lines may reduce the sampling variability of pesticide movement, they are subject to some of the same limitations of other field studies. Gast et al. (1978) noted considerable variation in total tile line flow between plots for a given treatment. They attributed the differences to natural soil variation and/or variations in the hydraulic properties among the plots.

Soil columns

Soil column experiments have been used extensively to predict herbicide movement in soils. Clearly, the boundary conditions associated with a column leaching experiment can have a significant impact on the movement of water and solutes. Weber and Whitacre (1982) showed that terbuthion (N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-

dimethylurea) leaching, in a Lakeland loamy sand, was 30 times greater under saturated-flow conditions as under unsaturated-flow conditions.

Many researchers have removed intact or undisturbed soil columns from the field for solute leaching studies (Priebe and Blackmer, 1989; Hanson and Binning, 1990; Isensee, 1990). Since intact cores retain much of the natural soil structure present in the field, they give a more realistic estimate of water and solute movement.

Smith et al. (1985) compared the movement of antibiotic resistant Escherichia coli suspensions through intact soil cores and mixed, repacked soil columns. After applying bacterial suspensions at rates of 5 to 40 mm h⁻¹ they found rapid movement of suspended bacteria through the well-structured intact cores. In contrast, columns prepared from sieved, repacked soil were much more effective bacterial filters, and retained 93% of the applied cells.

Similarly, Anderson and Bouma (1977a) measured chloride movement through intact soil columns under different moisture regimes. Dispersion was very pronounced when the tracer solution was applied to initially drained columns of a medium subangular blocky structured soil. Chloride was detected after only 1.3 hours in the initially drained columns as compared to 18.2 hours for the same columns under saturated conditions. The applied solution moved almost instantly

through large soil voids.

White et al. (1986) studied the transport of bromacil (5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,3H)pyrimidinedione) and napropamide (N,N-diethyl-2-(1-naphthalenyloxy)propanamide) through large undisturbed cores of a well structured clay soil at different initial water contents. While 85% of the napropamide leached through the initially dry soil, only 28% was leached through the prewet soil. Similar patterns were seen for bromacil.

Kluitenberg and Horton (1989) reported that, for soil with a significant degree of macroporosity, the method of solute application, or solute boundary condition, has a large impact on the subsequent transport of the solute through the soil. Also the initial water content of soil macropores was important in determining the degree of dispersion that took place in intact cores.

Although intact soil cores maintain much of the natural soil structure, large variation between cores has been noted. Priebe and Blackmer (1989) used six undisturbed columns (20-cm diameter, 50-cm height) to measure preferential movement of isotopically labeled water and nitrogen. Total amounts of labeled nitrogen in the leachate varied among columns from 0.2 to 70 mg, while total amounts of labeled water ranged from 0.2 to 191 g.

Artificial macropores

As an alternative to working

with intact soil cores, artificial or simulated macropores have been used to study preferential flow. This approach reduces much of the variability associated with undisturbed field samples and provides insight to solute movement.

Kluitenberg and Horton (1989) modified soil columns to demonstrate the importance of a small continuous crack on preferential solute movement through clay liners used in hazardous waste sites. The "worst case" scenario for a region of high conductivity penetrating the entire clay liner was developed by removing a 6.35 mm diameter vertical core and packing sand into the opening to preserve the hole. Although the hole represented less than 1/250 of the total flow area, convective transport of the chloride tracer was greatly increased. The time of first chloride breakthrough was 3 minutes for the modified column compared to 18.8 hours for the soil column without a crack.

Bouma and Anderson (1977) drilled small vertically continuous holes through the center of soil columns to simulate macropores in two different soil types. The artificial macropores were largely responsible for chloride breakthrough in a clay loam column, but appeared less important in a sandy loam column. The amount of initial soil water displaced by the chloride solution was 7% for the clay loam column and 68% for the sandy loam column. They concluded that identical macropores can have different hydraulic

functions in different soil materials.

Phillips et al. (1989) simulated macropores by placing hollow, straight-walled glass tubes against a porous glass plate. They demonstrated that water under negative pressure can enter simulated macropores after first establishing a film of water on the macropore walls.

Zins et al. (1988) examined preferential flow of atrazine and alachlor through root mediated macropores. Alfalfa was grown in soil columns for 6 months, and then killed with glyphosate (N-(phosphonomethyl)glycine) to establish root channels. Although these root channels did increase herbicide movement, they were not found to be major pathways for preferential flow.

Tracer studies

Chemical tracers have been widely used to study water and solute movement in soil. Davis et al. (1980) reviewed some of the tracers commonly used to determine water direction, velocity, and the transport of potential contaminants. Aley (1984) provided an overview of groundwater tracing in water pollution studies.

Many researchers have used anions such as bromide (Rice et al., 1986; Gish and Coffman, 1987; Everts et al., 1989) or chloride (Quisenberry and Phillips, 1976; Tyler and Thomas, 1977; Tyler and Thomas, 1981) as tracers. Bromide and chloride are favored because they are not usually adsorbed,

and behave similar to the nitrate ion in soil and water, but without biological transformation (Shuford et al., 1977).

Fluorescent dyes have also been commonly used for tracing the movement of surface water, groundwater, and water movement through soils (Atkinson et al., 1973; Reynolds, 1966; Smettem and Trudgill, 1983). In an extensive review, Smart and Laidlaw (1977) compared the usefulness of eight fluorescent dyes (amino G, photine CU, fluorescein, lissamine FF, pyranine, rhodamine B, rhodamine WT, and sulpho rhodamine B) for quantitative tracing experiments. More recently, Trudgill (1987) summarized the utility of rhodamine WT, lissamine FF, and amino G acid for soil water tracing.

Although the acute and chronic toxicity is low for most fluorescent dyes used in water tracing, some compounds have other undesirable characteristics. Smart (1984) reviewed the toxicity of twelve fluorescent dyes used for water tracing. Of the tracers evaluated, only rhodamine WT, fluorescein, and tinopal CBS-X could be shown not to provide a carcinogenic or mutagenic hazard.

Bouma and Dekker (1978) used methylene blue as a tracer to study water infiltration patterns into four clay soils with different macrostructures. After applying the dye solution, entire plots were excavated and the dye stained pore walls were observed and counted.

Saffigna et al. (1976) used a 1:1 mixture of water and

rhodamine WT to trace water infiltration patterns in an irrigated potato field. Deep penetration of dye was noted directly beneath plants, without uniform wetting of the root zone.

Omoti and Wild (1979a) used the fluorescent dyes pyranine and fluorescein to mark pathways of solute movement in soil columns under saturated flow conditions. They also used the same dyes to identify the pathways of solute movement in field plots (Omoti and Wild, 1979b).

Everts et al. (1989) compared the mobility of several tracers applied in irrigation water above a tile line. Total amounts of tracers reaching the tile line were 3.0, 2.5, 0.46, and 0.15%, respectively, of the nitrate, bromide, lithium, and rhodamine WT applied with irrigation water.

Glass et al. (1988) measured wetting front instability with rhodamine WT and a non-adsorbing dye, USDA green #2 food coloring. Since rhodamine WT is strongly adsorbed, it delineated areas where most of the flow was occurring. In contrast, the green dye moved with the wetting front and was a good indicator of water infiltration.

Kung (1988) examined water flow patterns in an irrigated potato field with rhodamine WT and pyranine 10G. Rhodamine WT was surface-applied to furrow bottoms, while pyranine was injected into the centers of potato hills. Although both dye patterns indicated preferential flow paths, the pyranine 10G

front penetrated only 0.7 to 0.9 m deep. In contrast, one dye column of rhodamine WT was found below 5 m. The author suggested that since irrigation was applied only to meet evapotranspiration needs, potato roots absorbed most of the water entering into the potato hills.

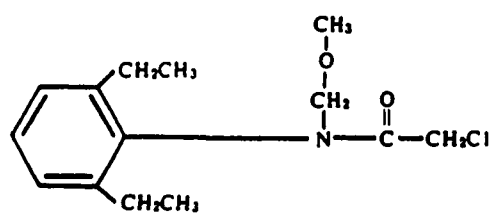
Conclusions The following research had three primary objectives: 1.) To measure the extent of herbicide and tracer movement to field drainage tiles under natural and simulated rainfall. Since two Iowa Outlying Research Centers had drainage tiles in place for over ten years, they could be readily adapted for monitoring of tile discharge and controlled leaching experiments. Detailed records on cropping history, tillage, pesticide and fertilizer use, and weather data were available. The first rainfall event following chemical application has been shown to be important for chemical loss. Herbicide and tracer movement was examined during a rainfall simulation study 24 hours after chemical application,

2.) To determine the effect of tillage on herbicide and tracer movement. Although conservation tillage practices can greatly reduce soil erosion, their impact on groundwater quality is still unclear. Herbicide and tracers were either surface applied or mechanically incorporated prior to rainfall simulation

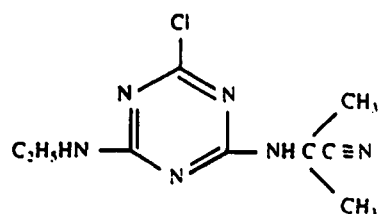
3.) To examine herbicide and tracer movement in soil columns containing artificial macropores. Intact soil

columns, taken directly from field sites, have been frequently used for chemical leaching experiments. Although they provide insight into solute movement through structured soils, large differences due to field spatial variability have been noted. In contrast, packed soil columns, containing an artificial macropore, would be more uniform and reproducible. This type of modified column may be useful for initial screening of prospective herbicides to assess potential field movement. The standardized columns would represent a worst case scenario for chemical leaching, and could be used to supplement current EPA requirements for pesticide mobility studies.

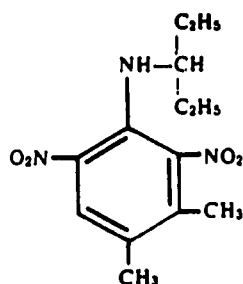
The structures of herbicides and dye used in this research are shown in Figure 1. A partial list of physical and chemical characteristics is shown in Table 1.



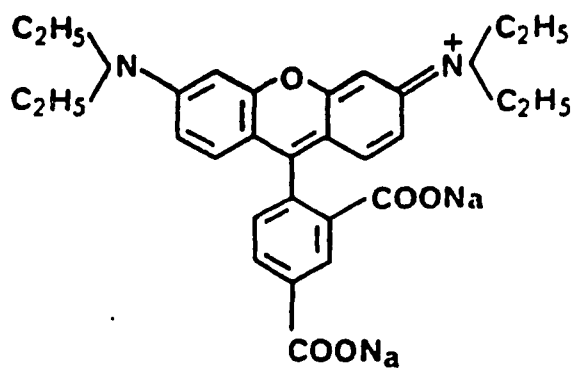
alachlor



cyanazine



pendimethalin



rhodamine WT

Figure 1. Structures of herbicides and dye

Table 1. Characteristics of herbicides and dye

	alachlor	cyanazine	pendimethalin	rhodamine WT
Molecular weight (g)	269.8	240.7	281.3	567
Water solubility (ppm)	240	170	0.3	20,000
Soil half life (days)	15	14	90	---
Soil sorption (K _{oc})	170	190	24,300	1400 to 3700

**SECTION I. A FIELD HYDROLOGY LABORATORY FOR MEASURING
PESTICIDE AND FERTILIZER MOVEMENT THROUGH THE ROOT ZONE**

INTRODUCTION

Groundwater contamination by agricultural chemicals continues to be a major environmental concern. A recent National Research Council (1989) report suggested that water pollution is the most damaging and widespread environmental effect of agricultural production. Although herbicides are used on approximately 98% of the corn and soybean hectares in Iowa (Wintersteen and Hartzler, 1987), the extent of leaching from normal field use is not clear.

The effects of conservation tillage practices on chemical movement to surface and groundwater have received considerable attention (Baker and Laflen, 1983; Kanwar et al., 1985; Tyler and Thomas, 1977; Hall et al., 1989). Reduced tillage has been shown to modify the soil environment and affect water transmission (Blevins et al., 1977). Reduced tillage may have both positive and negative effects on chemical movement depending on factors such as rainfall timing and intensity (Baker, 1987; Wagenet, 1987).

Field studies of pesticide behavior are often complicated by the spatial variability of the experimental site. Soil physical, chemical, and biological characteristics as well as pesticide residue concentrations can vary both spatially and temporally (Rao and Wagenet, 1985).

As an alternative to geostatistical approaches which aggregate many small scale sample results, tile drainage lines

have been useful as a sampling technique. Richard and Steenhuis (1988) found that tile lines were effective for measuring solute movement through the unsaturated zone, and integrating spatial variability found with field studies.

Field drainage tile lines have several advantages as a sampling device and have been used extensively to measure chemical loss from row-cropped land (Hallberg et al., 1986; Schwab et al., 1973; Baker and Johnson, 1981; Kladivko et al., 1989; Von Stryk and Bolton, 1977). Since approximately 53 million hectares of cropland in the United States are artificially-drained, monitoring tile effluent is a natural index for assessing the contaminating effects of farming practices (Jury, 1975).

The objectives of this project are to study the effects of four tillage systems and two crop rotation practices on pesticide and fertilizer movement into subsurface drainage water. The extent of leaching to the 1.2 m tile depth may help predict chemical leaching to deeper groundwater. An established field site was modified to allow extensive sampling of tile effluent.

MATERIALS AND METHODS

A large-scale tillage and crop rotation study has been in place since 1976 at the Northeast Research Center at Nashua, Iowa. Four tillage systems (plow, chisel plow, ridge-till, and no-till) in combination with three crop rotations (continuous corn, corn following soybeans, and soybeans following corn) are replicated three times. Soils are Floyd and Readlyn (Aquic Hapludolls) and Kenyon (Typic Hapludolls), somewhat poorly drained and moderately well drained, respectively. A field map identifying plot location is shown in Figure I-1 (Honeyman et al., 1990).

Chemical use for each 0.4 ha plot is shown in Table I-1. Since 1976, the only pesticides used were alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide), atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine), cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile), metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one), and terbufos (S-[[[(1,1-dimethylethyl)thio]methyl]O,O-diethyl phosphorodithioate).

In 1979, drainage tiles were installed through the center of each plot using a trenchless tile plow. Tile lines are 10.2 cm diameter and installed 1.2 m deep. A second tile line was trenched in along the border between plots. Since border tiles minimize subsurface drainage flow among plots, center

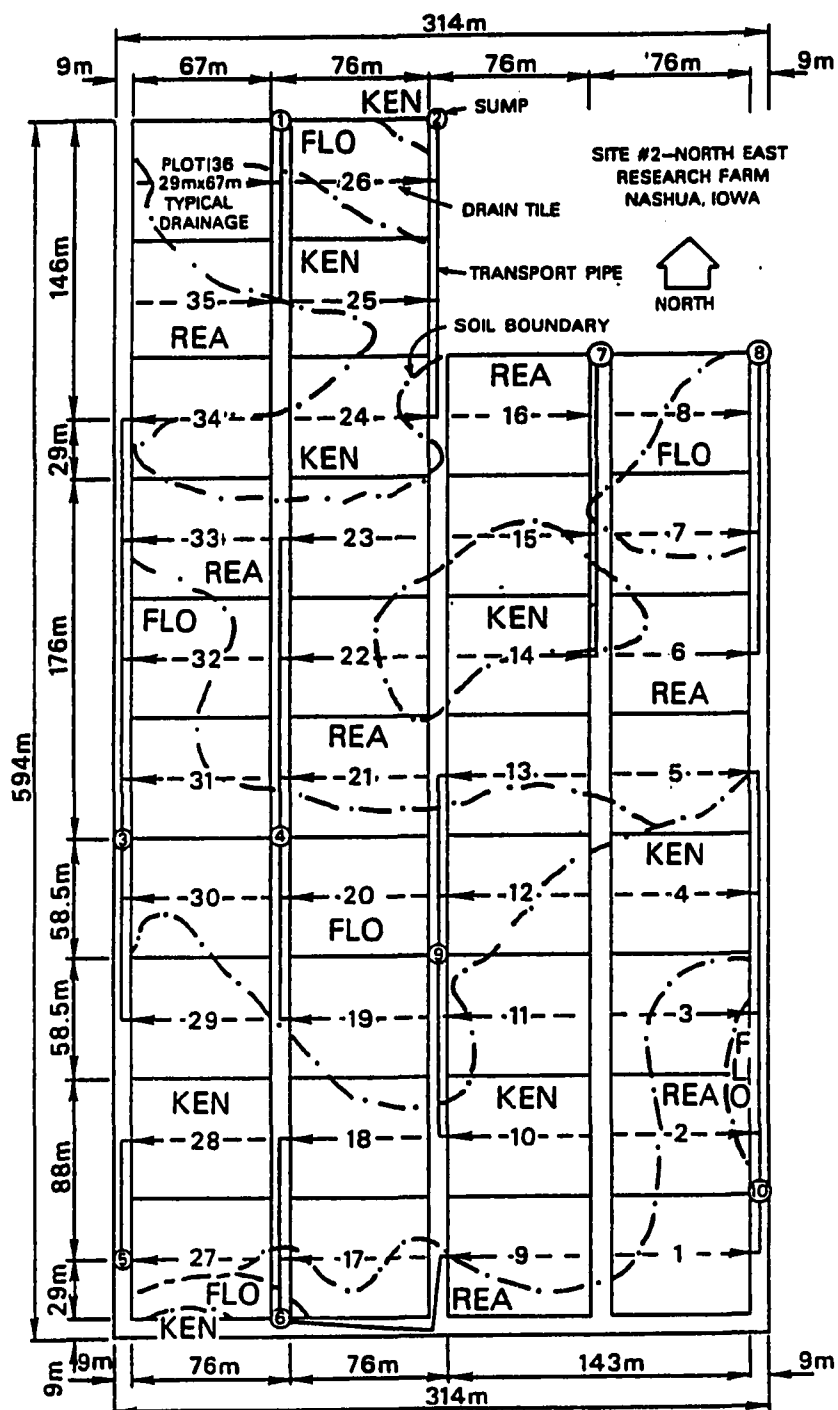


Figure I-1. Plot map of tillage-rotation study

Table I-1. Chemical use in the tillage-rotation experiment

Treatment	Continuous Corn	<u>Corn</u> -Soybeans	<u>Soybeans</u> -Corn
	-----kg/ha-----		
Nitrogen	202	168	0
Alachlor	2.2	2.2	2.2
Atrazine	2.8	0	0
Cyanazine	0	2.8	0
Metribuzin	0	0	0.5
Terbufos	8.4	0	0

tile lines allow sampling of discrete plots.

In April of 1987, 18 plots were identified which drained through a separate center tile. In some cases, continuous tile drains two plots, making it possible to monitor only the top (uphill) plot. The remaining 18 tile lines were connected in a manner which prohibited sampling of individual plots.

Tile lines were accessed, and a copper tube was inserted through the top of each tile. A 15 cm³ hand vacuum pump (Nalgene model 6131-0010) was used to draw tile effluent samples into a 3.8 L collection jar. After collection, water samples were refrigerated until they could be analyzed. Pesticide analysis was done at the Iowa Hygienic Laboratory, Iowa City, Iowa. Nitrate analysis was done in the Agricultural Engineering chemistry lab at Iowa State University.

Rainfall was well below normal in 1987 and 1988 and tile lines did not flow on a regular basis. Although tile sampling was done 12 to 18 hours following significant rainfall events, only limited data were collected. Dates of chemical application, pertinent rainfall events, and sampling are shown in Table I-2.

In 1989, modifications were made to allow sample collection from all 36 plots. Tile lines were intercepted and rerouted to individual metering sumps. Tile flow volumes are

Table I-2. Summary of field and rainfall data for 1987

DATE	
<hr/>	
April 17	Sample tiles
April 27	Nitrogen fertilizer applied
May 4	Corn planted
May 5-6	Corn herbicides applied
May 10-20	33.5 mm rain
May 21	Soybeans planted
May 23-25	Soybean herbicides applied
May 25-26	30.7 mm rain
May 27	Sample tiles
June 2	13.9 mm rain
June 3	Sample tiles

recorded through multichannel data loggers and then routed to one of ten collection sumps, where water samples are taken. Monitoring wells at 1.8 m and 2.4 m were also installed in each plot.

RESULTS AND DISCUSSION

Pesticide concentration data for 1987 are presented in Table I-3. Prior to spring chemical application, atrazine was the only pesticide detected, and concentrations were less than $1 \mu\text{g L}^{-1}$. Following pesticide application and subsequent rainfall events, atrazine, alachlor, cyanazine, and metribuzin were detected in tile effluent, while the insecticide terbufos was not found in any samples.

The first rainfall or irrigation event following chemical application has been shown to greatly affect the extent of chemical loss in surface runoff and leaching (Baker, 1980; Baker and Laflen, 1983; Schwab et al., 1973; Spencer et al., 1985;). Relatively high concentrations of alachlor and metribuzin were recovered from plots 1 and 10 on May 27. Figure I-2 shows herbicide concentration averaged across tillage for these two plots.

Since rainfall occurred shortly after herbicide application (Table I-2), chemical movement was more likely. The rapid appearance of alachlor and metribuzin immediately following rainfall, appears to be related to preferential water flow through macropores.

On the May 27 sampling date, alachlor concentrations were lower in plots 3 and 4 than for plots 1 and 10 (Figure I-3). Since planting and herbicide application for corn was 20 days earlier than for soybeans, field degradation probably

Table I-3. Pesticides detected in tile effluent in 1987

Tile	Rotation ^a	Tillage	Treatment	Sampling Date		
				4/17	5/27	6/03
-----µg/L-----						
1	<u>S</u> -C	Chisel	Metribuzin	ND ^b	1.2	0.3
			Alachlor	ND	3.2	0.4
2	<u>S</u> -C	Plow	Metribuzin	ND	--- ^c	---
			Alachlor	ND	---	---
3	<u>C</u> -S	No-till	Alachlor	ND	1.5	0.4
			Cyanazine	ND	0.8	1.5
4	<u>C</u> -S	Chisel	Alachlor	ND	2.1	0.4
			Cyanazine	ND	1.4	0.2
5	<u>C</u> -C	Chisel	Atrazine	0.7	1.1	0.5
			Alachlor	ND	0.2	ND
			Terbufos	ND	ND	ND
10	<u>S</u> -C	No-till	Metribuzin	ND	1.7	1.4
			Alachlor	ND	4.5	2.3
13	<u>C</u> -C	Plow	Atrazine	ND	---	---
			Alachlor	ND	---	---
14	<u>C</u> -C	No-till	Atrazine	0.7	---	---
			Alachlor	ND	---	---

^a Crop in 1987 is underlined (S = soybeans and C = corn).

^b ND-None detected at the 0.1 µg L⁻¹ detection limit.

^c Insufficient tile flow to sample.

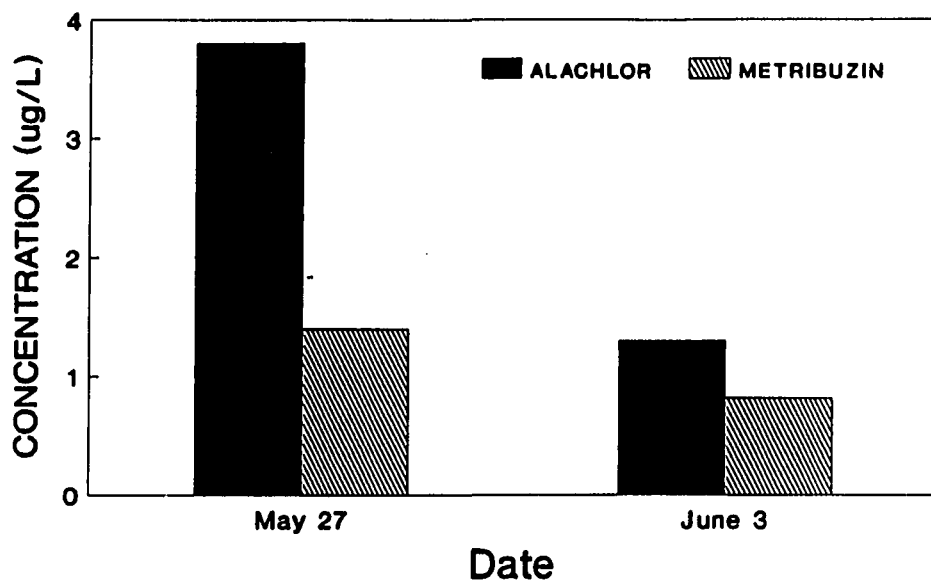


Figure I-2. Average concentrations for tiles 1 and 10

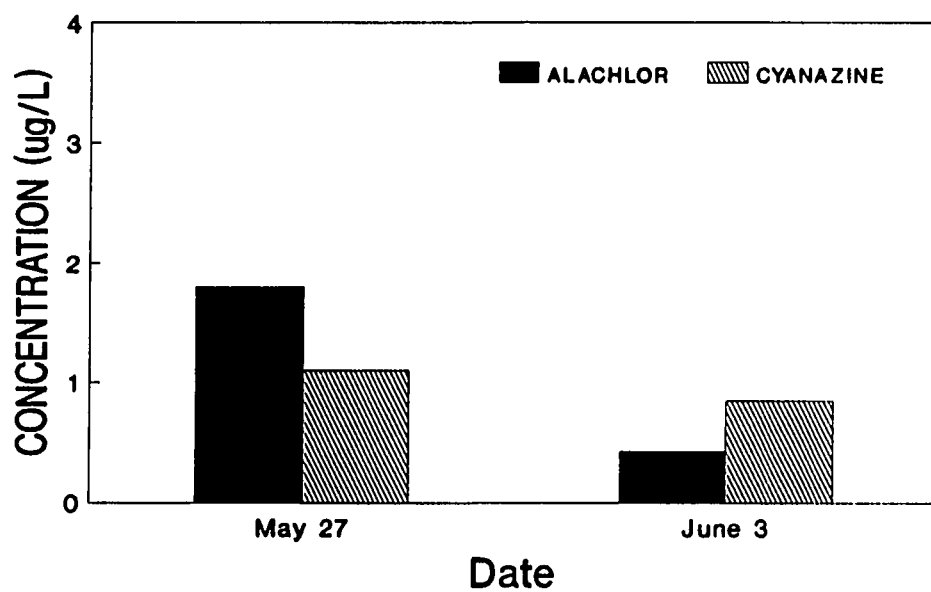


Figure I-3. Average concentrations for tiles 3 and 4

accounted for much of this difference. In addition, a total of 33.5 mm of rain was recorded over a 10 day period from May 10 to May 20, but never occurring in the form of a significant rainfall resulting in tile flow. This may have moved herbicides into the soil matrix and made them less vulnerable to preferential movement.

Table I-4 gives nitrate nitrogen ($\text{NO}_3\text{-N}$) concentrations measured in tile effluent samples. For the three sampling dates shown, $\text{NO}_3\text{-N}$ concentrations remained fairly constant.

Table I-4. Concentrations of NO₃-N measured in tile effluent in 1987

Tile	Rotation ^a	Tillage	Sampling Date		
			4/17	5/27	6/03
-----mg/L-----					
1	<u>S</u> -C	Chisel	14.4	11.9	15.7
2	<u>S</u> -C	Plow	12.4	--- ^b	---
3	<u>C</u> -S	No-till	13.3	15.2	14.6
4	<u>C</u> -S	Chisel	16.1	---	16.8
5	<u>C</u> -C	Chisel	32.0	26.2	34.5
9	<u>S</u> -C	Ridge-till	10.7	---	---
10	<u>S</u> -C	No-till	13.6	14.7	14.4
11	<u>C</u> -S	Ridge-till	12.9	---	---
12	<u>C</u> -S	Plow	13.8	---	---
13	<u>C</u> -C	Plow	25.1	---	---
14	<u>C</u> -C	No-till	23.6	---	---
15	<u>S</u> -C	No-till	9.6	---	---

^a Crop in 1987 is underlined (S = soybeans and C = corn).

^b Insufficient tile flow to sample.

CONCLUSIONS

The rapid appearance of herbicides in tile effluent following a rainstorm suggests that preferential flow is an important mechanism affecting chemical movement. Highest concentrations were detected when rainfall occurred 1 to 2 days after herbicide application.

Prior to spring chemical application, atrazine was the only pesticide found. In contrast, the less persistent pesticides were not detected, indicating that chemical movement is dependent on both site characteristics and pesticide properties.

The main limitations to these field data from 1987 include lack of sufficient rainfall to allow repeated sampling and tile flow rate measurements to assess the extent and percent loss of surface-applied herbicides, insecticides, and fertilizer. Significant modifications made in 1989 will allow tile sampling of all 36 plots, flow rate measurements, and sampling of deeper chemical movement using monitoring wells. The establishment of a field hydrology laboratory represents a large scale effort to document the effects of tillage and crop rotation on groundwater contamination.

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**SECTION II. HERBICIDE AND TRACER MOVEMENT TO FIELD DRAINAGE
TILES UNDER SIMULATED RAINFALL CONDITIONS**

INTRODUCTION

The effects of agricultural chemicals on groundwater quality continues to be a major issue. A National Research Council report (1989) recently suggested that water pollution is the most damaging and widespread environmental effect of agricultural production. Although point source contamination has been well documented (Long, 1987; Habecker, 1989; Fawcett, 1989), the extent of herbicide leaching from normal field use is still unclear.

There has been considerable interest in preferential water and solute movement through large cracks, root channels, and worm holes in structured soils. Since preferential flow bypasses the soil matrix, surface-applied agricultural chemicals may also be able to move rapidly through the root zone (Beven and Germann, 1982; Everts et al., 1989; Priebe and Blackmer, 1989; Thomas and Phillips, 1979; Smettem et al., 1983; White et al., 1986).

At the present time, the impact of tillage practices on groundwater quality is not clear. Conservation tillage reduces surface water runoff and increases the extent of water infiltration (Baker and Laflen, 1983; Blevins et al., 1977; Edwards et al., 1988). The effects of increased water infiltration and preferential flow on groundwater quality depends partly on chemical application and timing of leaching events (Baker, 1987; Wagenet, 1987).

The spatial variability of field soils is a major factor affecting water and solute movement through the root zone (Biggar and Nielsen, 1976; Jury et al., 1987). Rao and Wagenet (1985) described spatial variability due to both intrinsic and extrinsic factors which complicate field studies of pesticide behavior.

As an alternative to geostatistical approaches, field drainage tiles have been used to measure solute movement in the field, and integrate some of the spatial variability (Richard and Steenhuis, 1988). Established tile lines allow for repeated sampling without disturbing natural soil structure and are useful for large-scale studies of the impact of agricultural chemicals on water quality (Hallberg et al., 1986). Field drainage tiles have been used to measure nutrient loss from row-cropped land (Logan and Schwab, 1976; Gast et al., 1978; Baker and Johnson, 1981; Kanwar et al., 1988) and to study pesticide movement (Schwab et al., 1973; Von Stryk and Bolton, 1977; Muir and Baker, 1976; Kladivko et al., 1989).

Several researchers have shown that the extent of chemical loss in surface runoff and leaching is often highest during the first rainfall event following chemical application (Baker, 1980; Baker and Laflen, 1983; Spencer et al., 1985; and Schwab et al., 1973). Since pesticide loss may be greatest at this time, continuous monitoring of tile lines

following the first rainfall event should identify peak chemical concentrations reaching tile depth.

The objectives of this study were to 1) intensively monitor herbicide and tracer concentrations in field drainage tiles immediately after a simulated, heavy rainfall event and 2) to investigate the effect of tillage on chemical movement under these conditions.

MATERIALS AND METHODS

Field studies were conducted in 1988 and 1989 at the Northern Iowa Research Center at Kanawha, Iowa. The experimental area was located above eight drainage tiles (1.2 m deep and 3.4 m long) arranged in a wagon wheel configuration (Figure II-1). The tiles were originally installed in 1953 to compare the effectiveness of two backfill materials for draining a ponded area or "pot-hole". Four tiles were installed with a sand filter used as a "blind" or "French" drain. The remaining four tiles had normal soil backfill. (Kirkham et al., 1953).

The soil is an Okoboji silty clay loam (Fine, montmorillonitic, mesic Cumulic Haplaquoll). A partial list of soil properties at this site is presented in Table II-1. In 1987, four rows of soybeans were planted over each of the tile lines to establish crop residue for the leaching experiments the following year. In 1988, corn was planted in the same way.

In both years, glyphosate (2 percent solution) was spot sprayed 10 days prior to the experiment to kill all emerged vegetation. The entire plot area (0.02 ha) was irrigated 3 to 4 days before the experiment with the equivalent of 100 mm of water. Background soil samples were taken from areas adjacent to the plots, and gravimetric water content and chloride concentrations were determined prior to rainfall simulation.

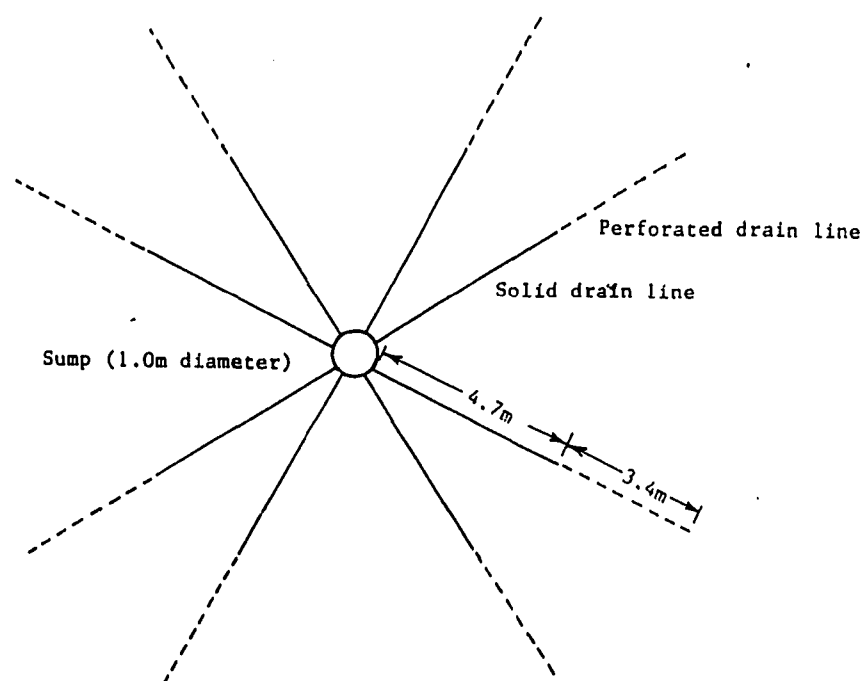


Figure II-1. Wagon wheel configuration of eight tile lines

Table II-1. Soil properties of Okoboji silty clay loam at Kanawha, Iowa

Depth	Sand (2-0.05mm)	Silt (50-2 μ m)	Clay (<2 μ m)	Bulk Density ^a	pH	Organic Carbon
(cm)	-----%-----			(g cm ⁻³)		(%)
0-15	19.8	45.4	34.8	1.24 (.06)	6.6	4.39
15-30	20.5	46.0	33.5	1.17 (.08)	6.9	4.34
30-61	33.2	40.7	26.1	1.29 (.06)	6.8	3.09
61-91	28.3	48.2	23.5	1.33 (.04)	6.7	1.84
91-122	42.8	35.1	22.1	1.40 (.09)	7.0	1.27
122-152	37.5	41.8	20.7	1.39 (.08)	7.1	1.40

^a Standard deviations are in parentheses.

Chemical and tillage treatments Chemicals applied in 1988 and 1989 are listed in Table II-2. In 1988, alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) and cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile) were applied in combination with rhodamine WT, while in 1989 alachlor, cyanazine, and pendimethalin (N-(1-ethylpropyl)-3,4 dimethyl-2,6 dinitrobenzenamine) were included. Rhodamine WT is an orange fluorescent dye that has been widely used for tracing water movement (Smart and Laidlaw, 1977; Trudgill, 1987). Since rhodamine WT is strongly adsorbed to soil, there has been interest in using it in place of pesticides for leaching studies (Everts et al., 1989; Sabatini, 1989).

Herbicides and dye were applied with a bicycle sprayer calibrated to deliver 280 L ha⁻¹. Bromide or chloride tracers were dissolved in water and sprayed in a separate application. Since spray volume was small, solubility became limiting, and three or four spray passes were necessary to apply the intended rate of bromide or chloride.

After chemical application, metal borders (5 cm in the ground and 15 cm above ground) were installed around each 1.5 m X 3.0 m plot to prevent surface runoff. Chemicals were applied a minimum of 24 hours before rainfall simulation. Number of days between chemical application and simulated rainfall, and treatments assigned to each tile are listed in

Table II-2. Chemicals applied in tile drain experiment

Chemical	<u>Application rate^a</u>	
	1988	1989
	----kg ha ⁻¹ ----	
alachlor	2.8	2.2
cyanazine	2.8	2.2
pendimethalin	---	1.1
rhodamine WT	2.8	2.2
KBr	175	---
CaCl ₂	---	134
CaNO ₃	175	175

^a Rates are listed as the amount of active ingredient for herbicides and dye and actual Br, Cl, and NO₃.

Table II-3.

In 1988, chemicals were either applied to untilled plots (PRE), or applied and incorporated immediately with a rototiller (PPI) to a depth of 5 to 7.5 cm. Bromide was applied to control plots but not incorporated. The three treatments were randomly assigned to tiles. In order to achieve three replications, one tile was used twice. Tile 5 was initially used as a control on day 2. Following data collection, chemical treatments were applied to this plot, including a second application of bromide. This experimental unit was then used as a PRE treatment, and is referred to as tile 9.

In 1989, the experiment was modified to account for differences in tile flow characteristics. The treatments (PRE or PPI) were randomly assigned within four blocks based on tile backfill. Since no herbicides were detected in control plots in 1988, lateral movement between tiles was not considered to be a problem. As a result, an untreated control was not included in 1989. In 1988, crop residue cover prior to the experiment was approximately 30 percent. Crop residue cover in 1989 was not uniform among plots, so all residue was removed by hand prior to chemical application.

Rainfall simulation A rainfall simulator, as described by Kay and Baker (1989), was operated at 40 kPa producing a rainfall intensity of 52 mm hr⁻¹. A series of ten

Table II-3. Treatments and days between chemical application and simulated rainfall

Tile	1988		1989	
	Day	Treatment	Day	Treatment
1	1	Control	1	Surface
2	2	Surface	2	Incorporated
3	3	Incorporated	1	Incorporated
4	1	Surface	2	Surface
5	2	Control	1	Incorporated
6	3	Control	2	Surface
7	1	Incorporated	1	Surface
8	2	Incorporated	2	Incorporated
9 (5)	3	Surface	-	-----

rain gauges were placed within each plot area to record actual rainfall amounts (Table II-4). In 1988, an average of 52.7 mm of water were applied in one hour, while the rainfall simulation lasted 1.5 hours in 1989 resulting in 80.8 mm of water being applied.

Tile effluent samples were collected with 946 ml glass jars. Time required to fill each jar was recorded and used to calculate tile flow rates. In 1988, tiles lines were flowing prior to rainfall simulation and background samples were taken. Tile lines were not flowing in 1989 prior to rainfall simulation and the first samples were collected a minimum of 45 minutes after the start of the simulated rainfall. Background samples had been taken of earlier flow from the tile lines in 1989.

Samples were taken for 8 to 10 hours following the start of rainfall (time zero) or until tile flow ceased. Sampling frequency varied with tile flow rate. As flow rate initially increased, samples were taken every 5 to 10 minutes. After flow rate had peaked, sampling intervals were extended to 15, 30, 60, 120, 240, and 480 minutes. Since the time of peak flow varied among tiles, some were sampled for over 10 hours.

Immediately after sample collection, jars were placed in a cooler and were then transferred to a refrigerator. Pesticide analysis was done at the Iowa Hygienic Laboratory, Iowa City, Iowa. Pesticide detection limits were $0.1 \mu\text{g L}^{-1}$,

Table II-4. Simulated rainfall totals for 1988 and 1989

Tile Number	Rainfall applied	
	1988	1989
	----- mm -----	
1	53.3	82.0
2	60.9	83.8
3	58.4	80.0
4	45.7	83.3
5	49.0	80.0
6	55.1	80.3
7	50.5	78.5
8	50.3	78.7
9	51.3	----
MEAN	52.7	80.8

using a modified EPA technique (EPA-600/8-80-038/June, 1980).

In 1988, bromide and rhodamine WT analysis was done by E. C. Alexander, Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN. Bromides were analyzed with an ion chromatograph, while rhodamine WT analysis was done using a filter fluorometer.

In 1989, chloride and rhodamine WT analysis was done in the Agricultural Engineering chemistry laboratory at Iowa State University. For rhodamine WT analysis, detects below $0.2 \mu\text{g L}^{-1}$ were considered background fluorescence.

One day after rainfall simulation, three soil cores were taken from each plot for bromide or chloride analysis. Soil sampling was done in six increments to a depth of 152 cm. Soil samples were kept refrigerated until analysis.

RESULTS AND DISCUSSION

The type of backfill originally used during tile installation had a pronounced effect on flow characteristics, and subsequent solute breakthrough curves. Flow rates for tiles with a sand backfill (1, 2, 5, and 6) were substantially lower than those installed with a soil backfill (3, 4, 7, and 8) as shown in Figure II-2. Silt accumulation in the sand backfill tiles apparently created a region of low hydraulic conductivity (Personal communication, Dr. Donald Kirkham, Professor Emeritus, Iowa State University). Consequently, herbicides and dye were not detected in any samples from the sand backfill tiles in 1988. In 1989, only trace levels of herbicide were found, while rhodamine WT was not detected in any effluent sample from the sand backfill tiles.

Tile flow rates and halide breakthrough curves for sand backfill tiles (Figures II-3 and II-4) demonstrate that conductivity over the tile line has been substantially reduced compared to soil backfill tiles. Total sampling times, drainage and percent bromide and chloride recoveries are shown in Table II-5. The hydraulic response of soil backfill tiles was considerably different and is discussed in detail by year.

1988 Experiment Tile flow and bromide concentration curves (Figure II-5) suggest that the soil backfill tiles were functional for subsurface drainage. Time zero is the start of the rainfall simulation. In 1988, tile flow rates peaked

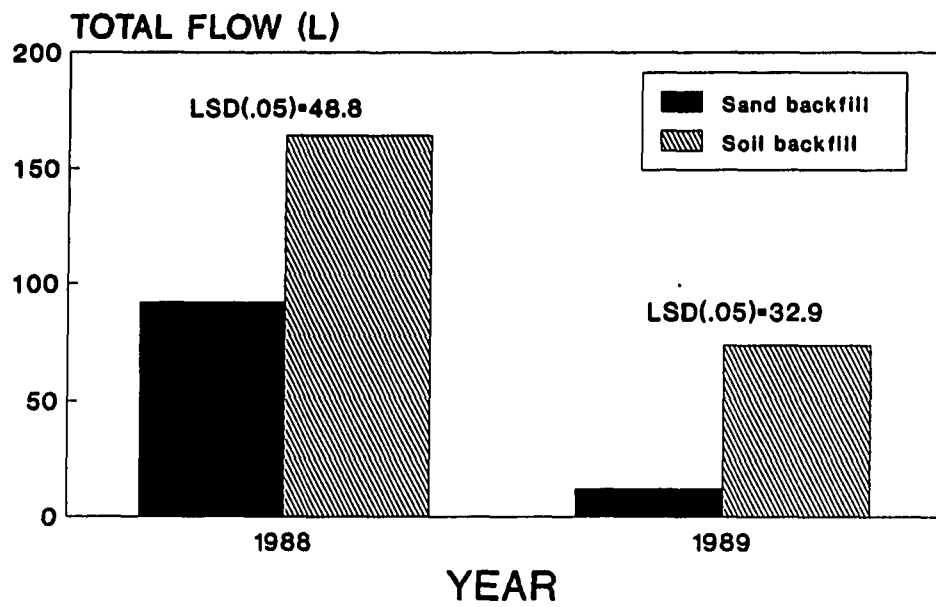


Figure II-2. Total drainage from sand and soil backfill tiles in 1988 and 1989

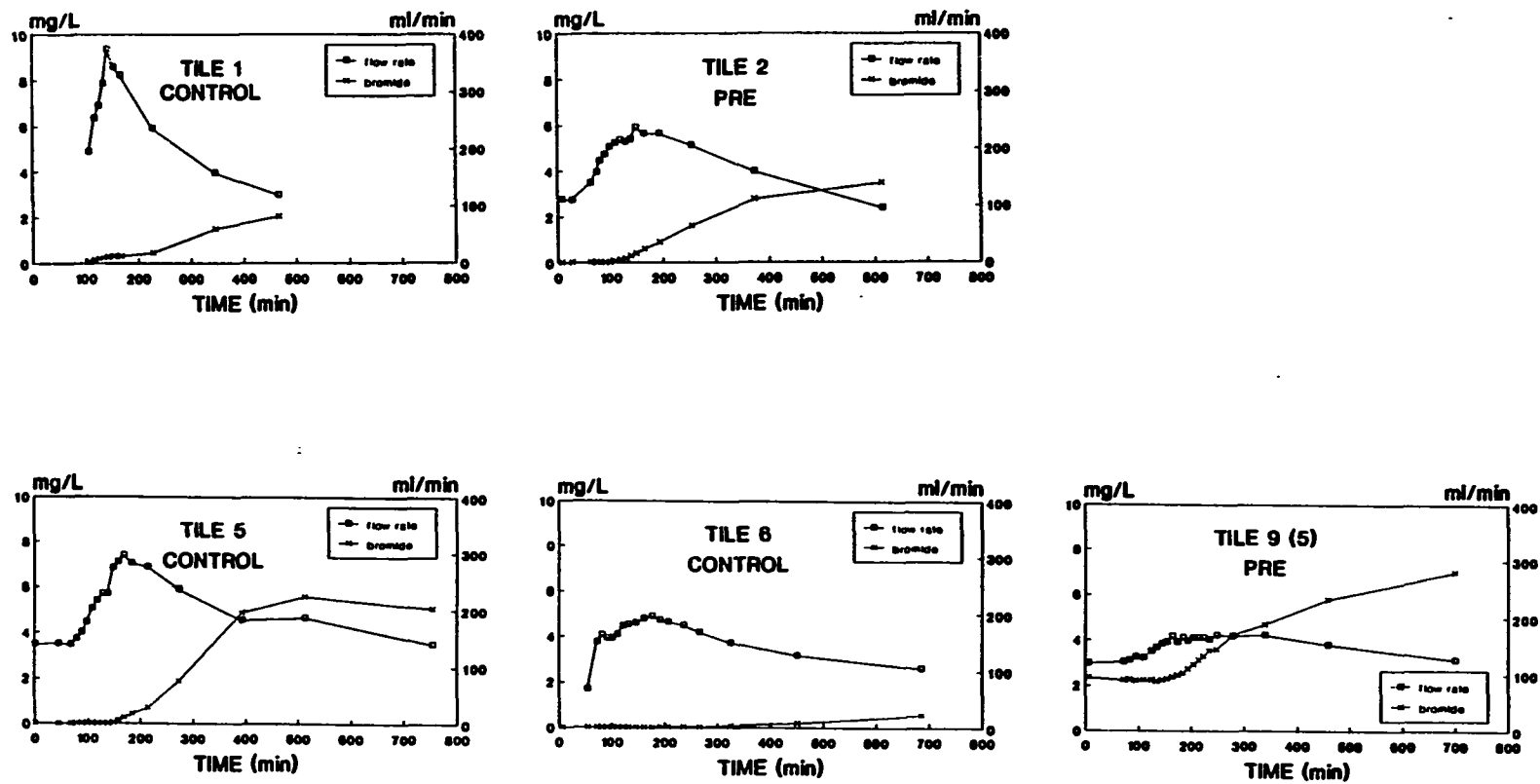


Figure II-3. Tile flow rates and bromide concentrations for sand backfill tiles in 1988 (Tile 9 (5) received a previous application of bromide)

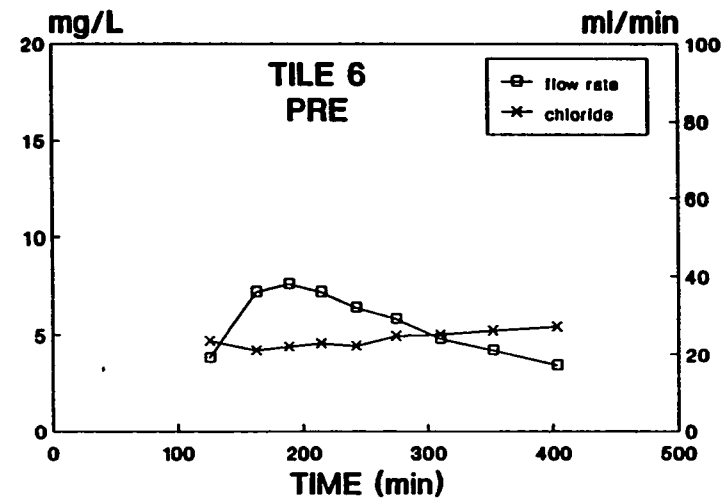
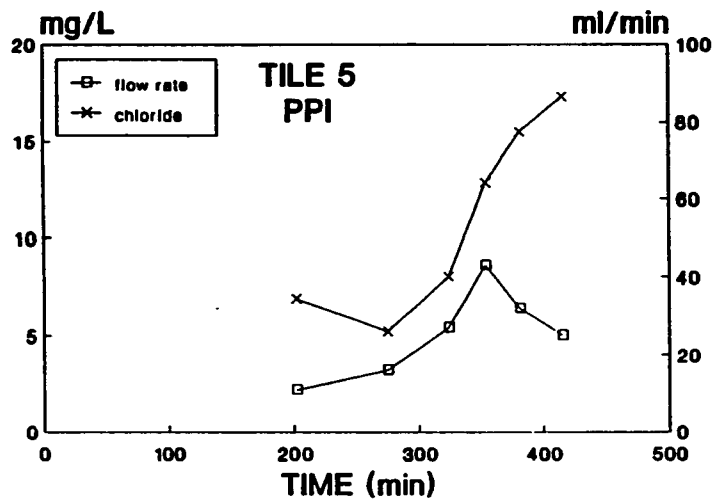
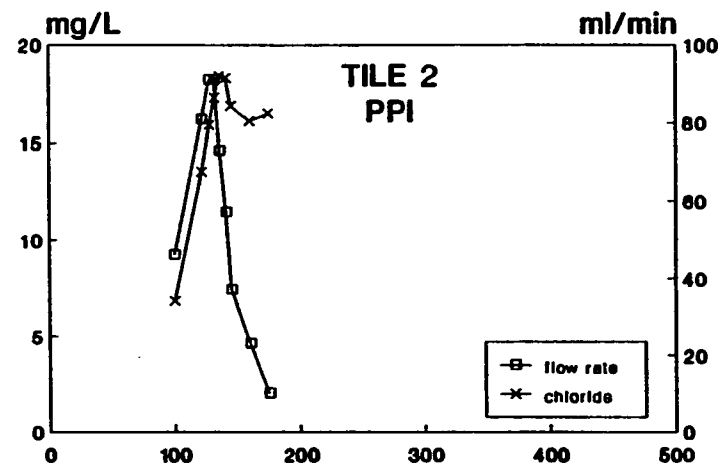
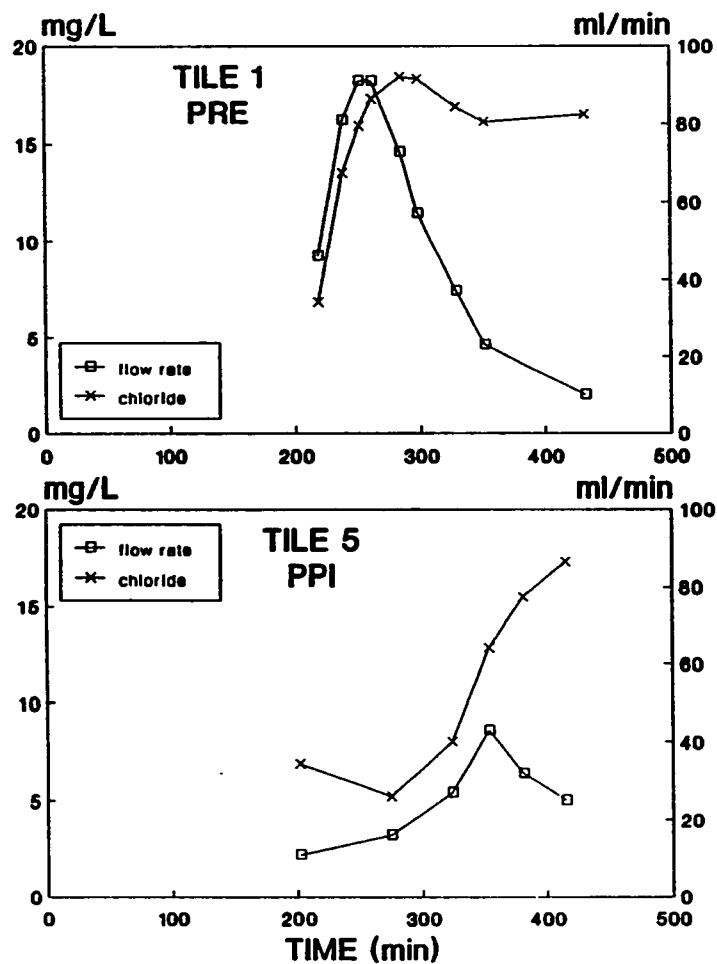


Figure II-4. Tile flow rates and chloride concentrations for sand backfill tiles in 1989

Table II-5. Total sampling time, drainage, and percent chloride and bromide loss from sand backfill tiles in 1988 and 1989

	Tile Number				
	1	2	5	6	9 (5) ^a
1988					
Total sampling time (min)	368.4	614.7	765.1	451.4	460.2
Total drainage (L)	76.8	101.4	142.6	68.9	70.1
Total bromide loss (%)	0.08	0.2	0.5	0.004	0.03
1989					
Total sampling time (min)	269.8	354.1	273.8	330.8	----
Total drainage (L)	10.1	23.6	5.8	8.6	----
Total chloride loss (%)	0.3	0.8	0.1	0.006	----

^a Tile 5 was used twice. The second time it is listed as tile 9 (5).

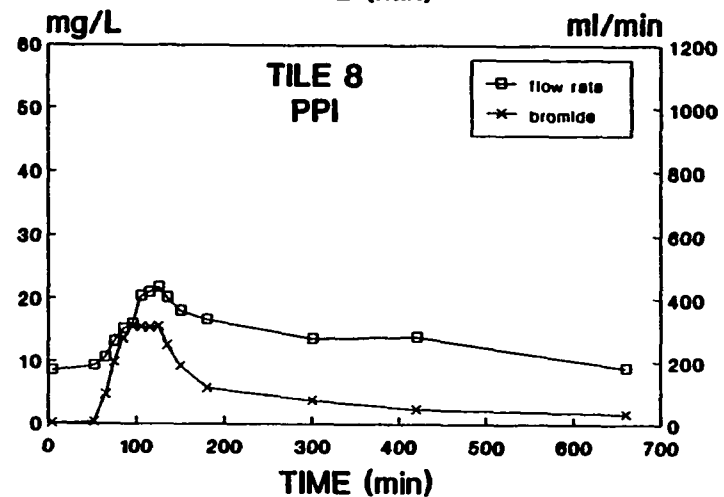
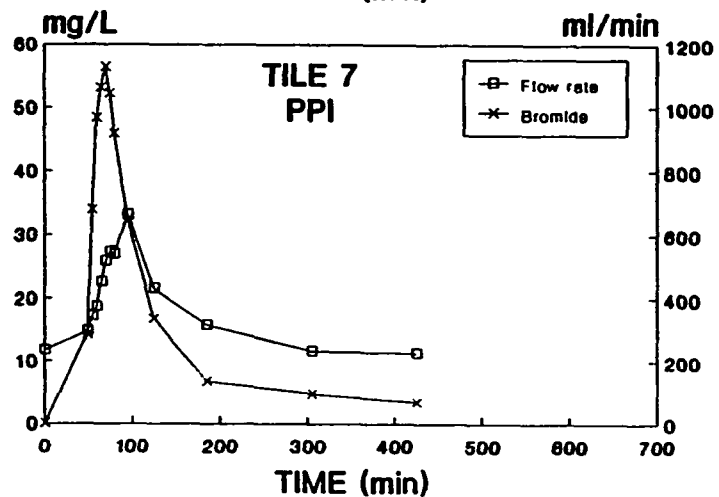
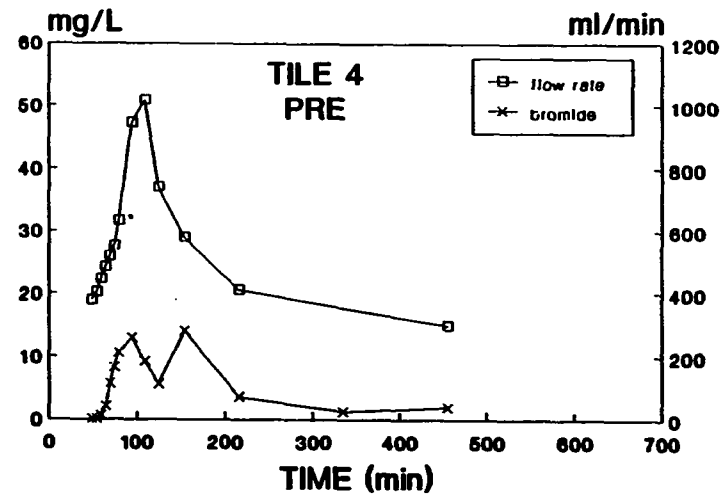
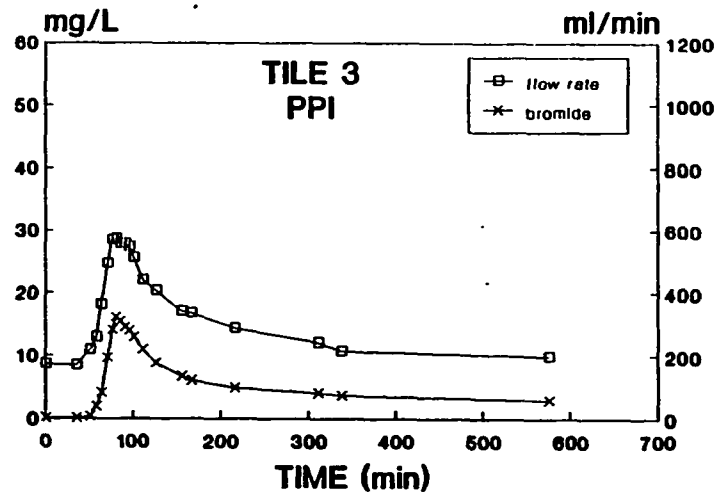


Figure II-5. Tile flow rates and bromide concentrations for soil backfill tiles in 1988

approximately 102 minutes after the start of the simulated rainfall, while time to peak bromide concentration averaged 85 minutes after the start of rainfall. The rapid movement of bromide to the 1.2 m tile depth must have occurred as a result of preferential flow. If preferential flow was not occurring, significantly higher amounts of water would have been required to displace the surface-applied bromide to the tile depth.

In tile 4, the initial bromide concentration peak occurred after 94 minutes, while a second bromide peak was measured 60 minutes later. This may be the result of a large dead-end macropore which finally emptied and released bromide accumulated from the soil surface. Alternatively, since this was an untilled plot, crop residue may have delayed bromide in reaching the soil surface.

Figure II-6 shows herbicide and dye concentrations as a function of time for the soil backfill tiles. Cyanazine, alachlor, and rhodamine WT quickly reached the 1.2 m tile depth, again suggesting preferential flow. The average time to reach peak initial concentration was 88 minutes for cyanazine, 90 minutes for alachlor, and 91 minutes for rhodamine WT. Similar to the tile 4 bromide data, a second herbicide and dye peak was also noted 154 minutes after the start of rainfall. Although herbicide concentration peaks were as high as $36 \mu\text{g L}^{-1}$ for tile 7, total loss did not exceed 0.23% of the amount applied (Table II-6).

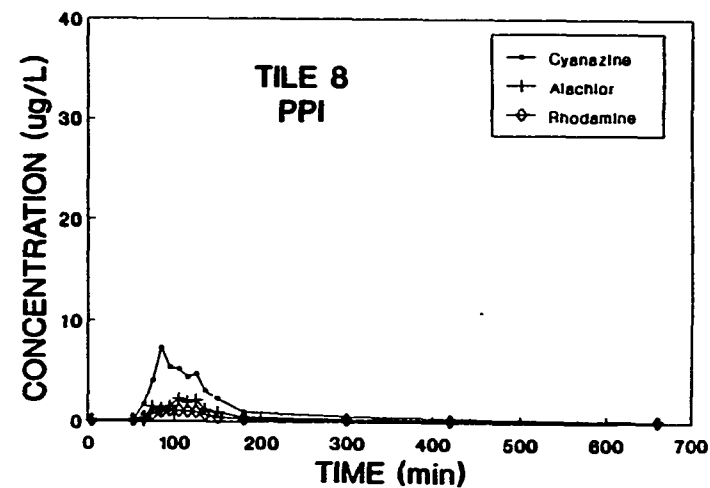
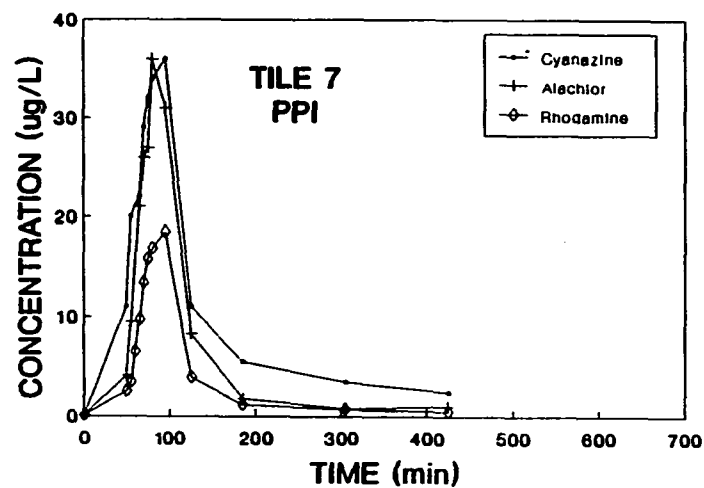
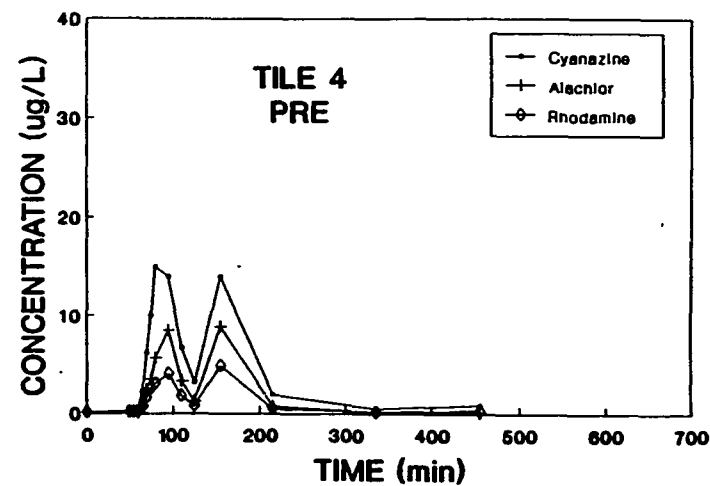
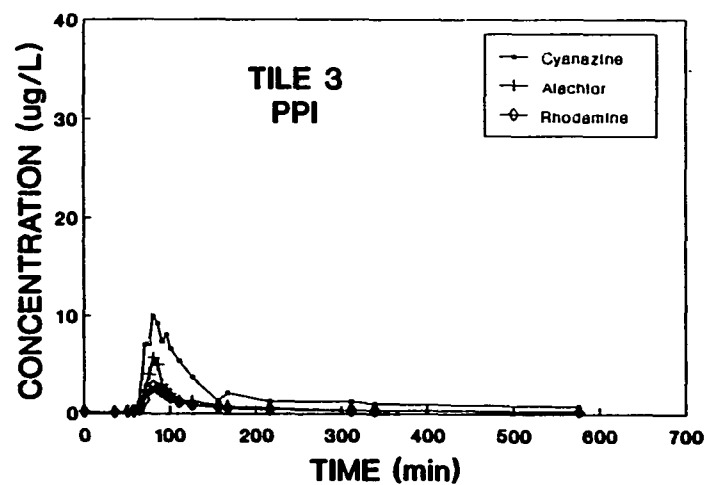


Figure II-6. Herbicide and rhodamine dye concentrations for soil backfill tiles in 1988

Table II-6. Total sampling time, drainage, and percent loss of applied herbicides, rhodamine dye, and bromide from soil-backfill tiles in 1988

	Tile Number			
	3	4	7	8
Total sampling time (min)	586.7	408.1	489.3	600.7
Total drainage (L)	143.7	189.8	175.2	147.7
Total loss (%)				
Bromide	1.0	1.4	4.1	0.9
Alachlor	0.009	0.04	0.2	0.005
Cyanazine	0.02	0.08	0.2	0.01
Rhodamine WT	0.007	0.02	0.1	0.003

1989 Experiment The preferential movement of a non-adsorbing tracer (chloride) to the 1.2 m tile depth was even more significant in 1989 (Figure II-7). Greater preferential flow may have occurred in 1989 because tiles had recently stopped draining before the start of rainfall simulation. As a result, there was less water in the soil profile to dilute the incoming solutes. While the first tile effluent sample was collected an average of 69 minutes after the start of rainfall, average peak chloride concentration was detected at 89 minutes. In addition, the highest chloride concentration reaching the 1.2 m tile depth in tile 7 was detected in the first sample, indicating that preferential flow mechanisms must be involved.

Preferential flow was also involved in the movement of alachlor, cyanazine, and rhodamine WT (Figure II-8). Concentration peaks occurred within 130 minutes following the start of rainfall. In contrast, pendimethalin was only identified in one sample, and at concentrations barely above the detection limit. Since pendimethalin has low water solubility and is tightly adsorbed to soil it did not leach significantly, even under extreme conditions.

In tile 7, the first sample collected contained $400 \mu\text{g L}^{-1}$ of alachlor and $570 \mu\text{g L}^{-1}$ cyanazine. A reddish color from rhodamine WT was clearly visible in the sample, which had a concentration of $112 \mu\text{g L}^{-1}$. Additional alachlor and

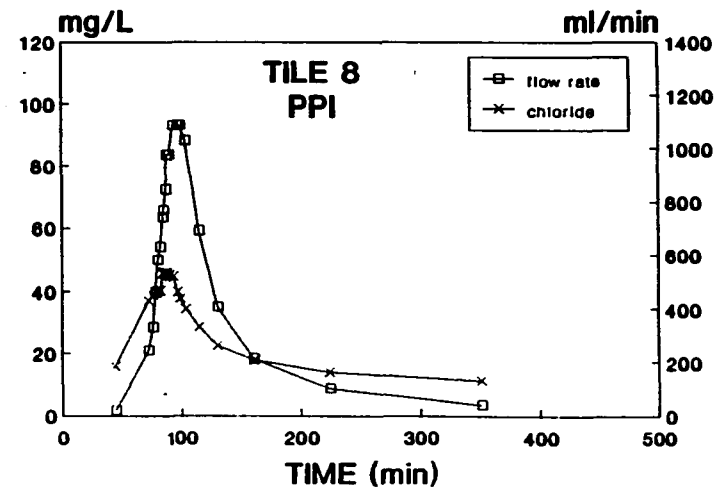
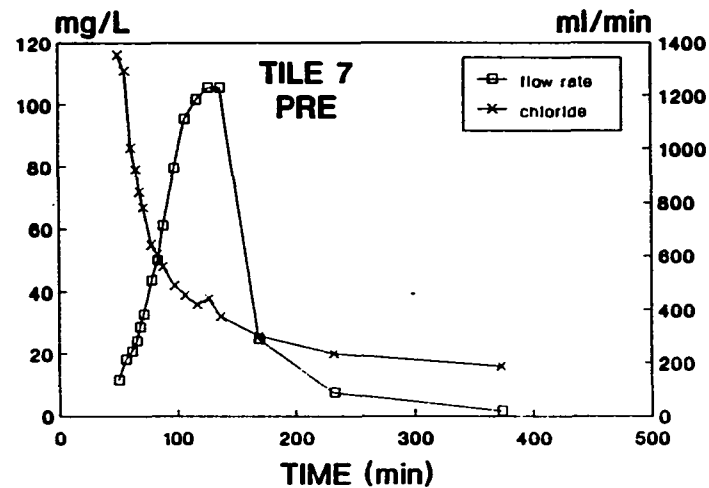
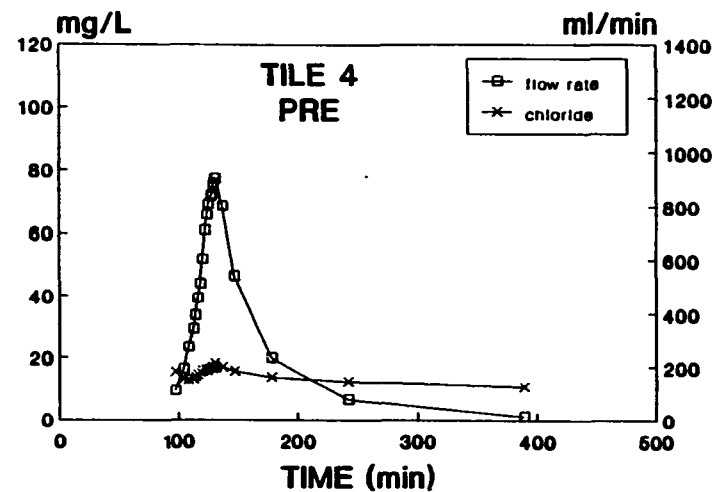
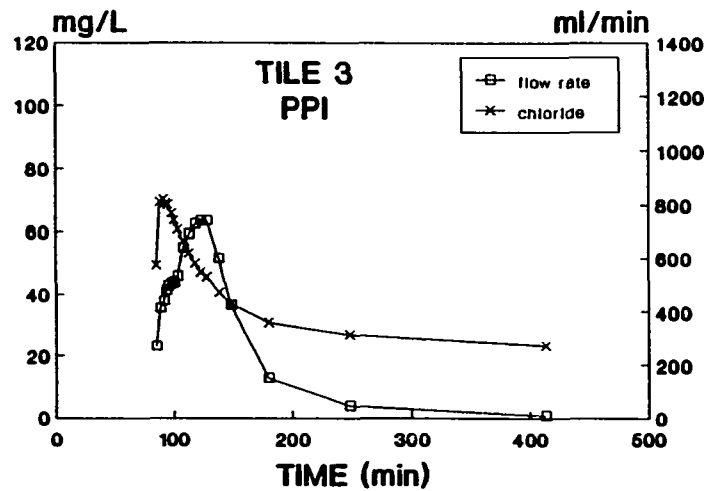


Figure II-7. Tile flow rates and chloride concentrations for soil backfill tiles in 1989

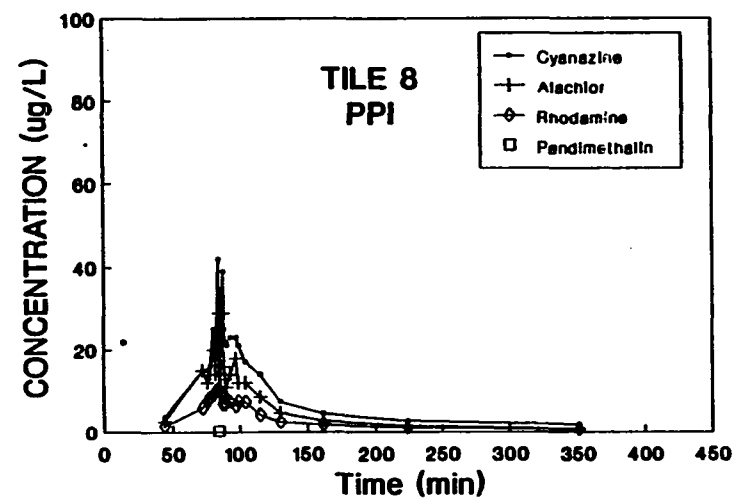
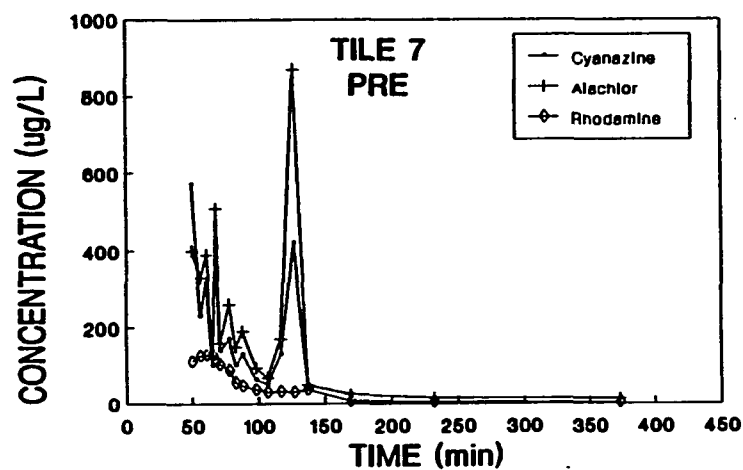
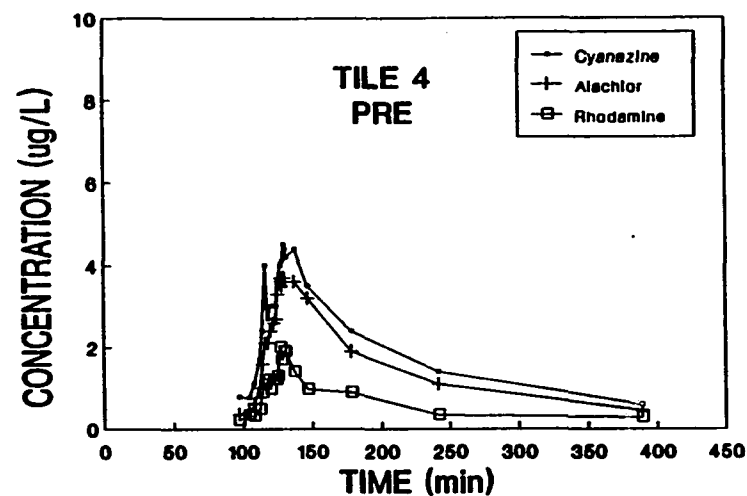
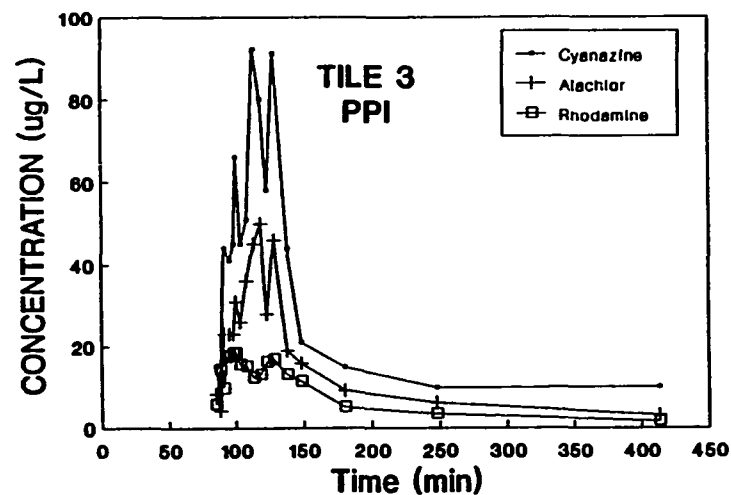


Figure II-8. Herbicide and rhodamine dye concentrations for soil backfill tiles in 1989 (NOTE: Tiles 4 and 7 are shown on a different scale)

cyanazine concentration peaks occurred 127 minutes after the start of rainfall.

Herbicide and dye breakthrough curves were more irregular in 1989 possibly indicating that the contribution of macropores to total flow was changing more often. Conversely, tiles were flowing in 1988 at the start of simulated rainfall, and water flow was more uniform. While chloride, herbicide, and dye concentrations were substantially higher in 1989, flow rate was lower (Table II-7). As a result, percent loss of alachlor, cyanazine, and rhodamine WT was similar to 1988 for all tiles except number 7.

Tillage effects In both years, the possible effects of tillage and chemical incorporation were masked by variation in tile flow rate. Although differences were not statistically significant, soil samples from untilled plots 4 and 7 reveal slightly higher levels of chloride remaining in the upper 15 cm of soil when compared to incorporated plots 3 and 8 (Figure II-9). After the rapid initial movement of chloride through macropores, subsequent rainfall may have bypassed chloride in the upper 15 cm of the soil matrix. There was also a trend for more total chloride to be retained in the soil profile for sand backfill tiles (1, 2, 5, and 6) when compared to soil backfill tiles (3, 4, 7, and 8). Chloride concentrations in soil background samples ranged from 3.4 to 7.9 mg kg⁻¹.

Table II-7. Total sampling time, drainage, and percent loss of applied herbicides, rhodamine dye and chloride from soil-backfill tiles in 1989

	Tile Number			
	3	4	7	8
Total sampling time (min)	386.8	329.6	353.7	346.0
Total drainage (L)	56.6	54.9	110.3	72.8
Total loss (%)				
Chloride	4.0	1.3	6.7	3.3
Alachlor	0.12	0.01	1.9	0.06
Cyanazine	0.23	0.02	1.2	0.09
Pendimethalin	----	----	----	----
Rhodamine WT	0.06	0.005	0.38	0.03

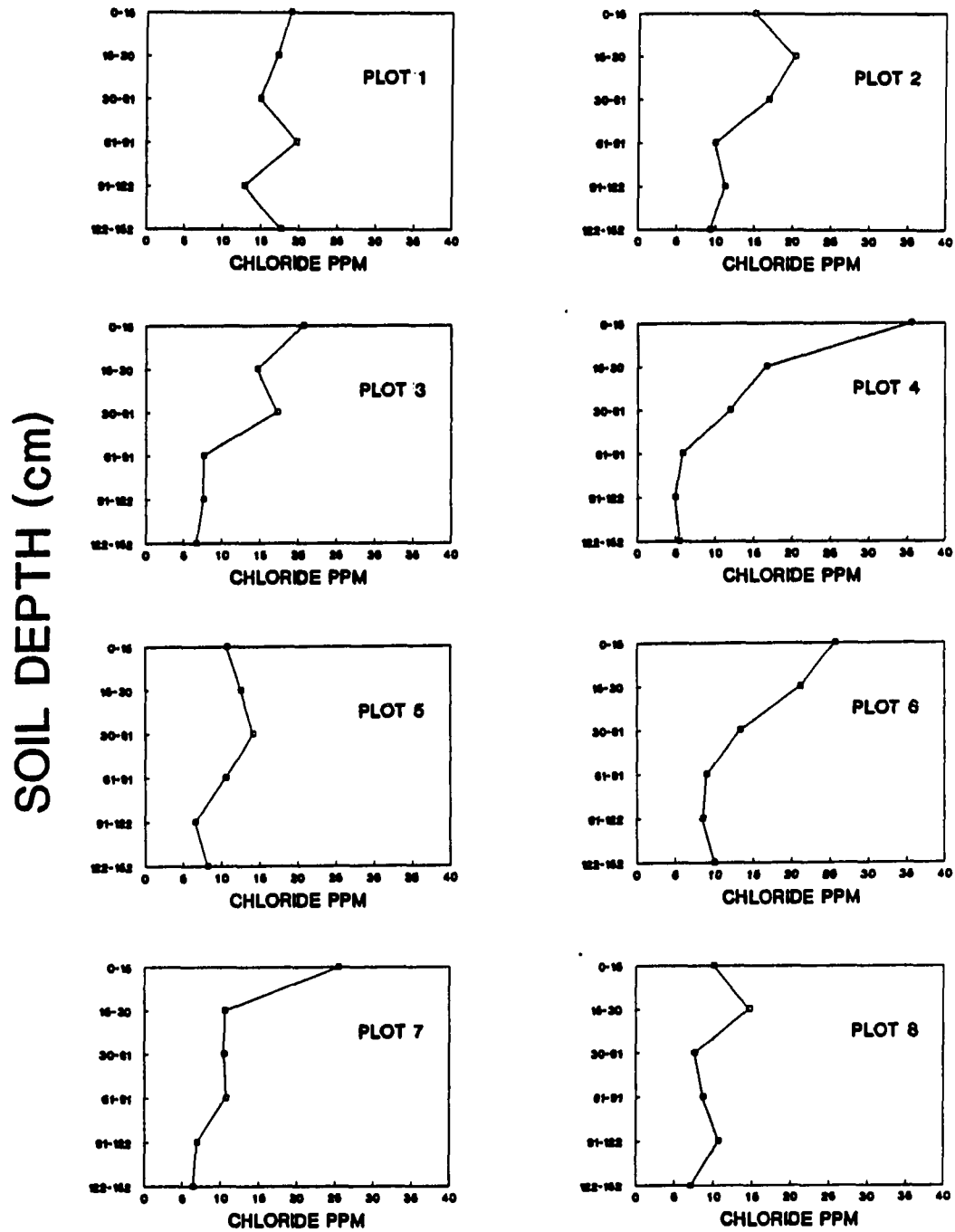


Figure II-9. Soil chloride concentrations over depth, one day following rainfall simulation in 1989

CONCLUSIONS

The rapid movement of herbicides, dye, and halides to the 1.2 m tile depth suggests that preferential flow is an important mechanism affecting solute movement through structured soils. In both years, peak concentrations occurred within 130 minutes following the start of a simulated heavy rainstorm, which lasted either 60 or 90 minutes. Breakthrough curves for one plot reflect extensive preferential flow paths, although no large holes were visible at the soil surface. In 1989, chemical concentrations were higher, but flow rates were lower resulting in similar percent losses. Differences in tile flow rates had a large impact on the extent of chemical movement and prevented significant tillage effects from being measured.

Even under extreme leaching conditions, pendimethalin was only detected in one tile sample, barely above the detection limit. Although preferential flow is an important mechanism affecting water and solute movement in the field, pesticide characteristics such as water solubility and soil affinity can be equally important.

Rhodamine WT was useful as a tracer to study the movement of alachlor and cyanazine in soil. In all tile effluent samples containing rhodamine WT above 0.2 ug L^{-1} , alachlor and cyanazine were also detected. Total loss of applied rhodamine WT was less than alachlor and cyanazine, indicating that it is

a conservative tracer for herbicides with a moderate leaching potential. Since rhodamine WT is significantly more soluble in water and is less tightly adsorbed to soil than pendimethalin, it was less useful as a tracer for a herbicide with a low leaching potential.

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**SECTION III. HERBICIDE AND TRACER MOVEMENT IN SOIL COLUMNS
CONTAINING AN ARTIFICIAL MACROPORE**

INTRODUCTION

The impact of agricultural chemicals on groundwater quality continues to be a concern. Since herbicides are used on approximately 98% of the corn and soybean hectares in Iowa (Wintersteen and Hartzler, 1987), movement under field conditions is of major interest. Specifically, the role of preferential water and solute movement through structured soils has received considerable attention (Thomas and Phillips, 1979; Beven and Germann, 1982; White, 1985; Priebe and Blackmer, 1989, Everts et al., 1989).

Intact or undisturbed soil columns have been widely used for solute leaching studies (Kluitenberg and Horton, 1990; White et al., 1986; Smith et al., 1985; Isensee; 1990, Weber et al., 1986). Although intact soil cores maintain much of the natural soil structure, large variation between cores has been noted. Priebe and Blackmer (1989) used six undisturbed columns (20 cm diameter, 50 cm height) to measure preferential movement of isotopically labeled water and nitrogen. Total amounts of labeled nitrogen in the leachate varied among columns from 0.2 to 70 mg, while total amounts of labeled water ranged from 0.2 to 191 g.

Alternatively, some investigators have used artificial or simulated macropores to study preferential water and solute movement. Kluitenberg and Horton (1989) used a modified column to demonstrate the importance of a small continuous

crack on preferential solute movement through clay liners used in hazardous waste sites. The time of first chloride breakthrough was 3 minutes for the modified column compared to 18.8 hours for the soil column without a crack.

Bouma and Anderson (1977) drilled 0.5 cm diameter holes through the center of soil columns to simulate macropores in two different soil types. They concluded that identical macropores had different hydraulic functions in a clay loam soil compared to a sandy loam soil.

Parker (1984) created an artificial macropore by first packing a column with a 1.7 mm diameter wire passing axially through its center. After saturating the column for several days, the wire was removed and a stable pore established. Rapid breakthrough of a bromide tracer was observed in column effluent.

Phillips et al. (1989) simulated macropores by placing hollow, straight-walled glass tubes against a porous fritted-glass plate. They demonstrated that water under negative pressure can enter simulated macropores after first establishing a film of water on the macropore walls.

Pesticide mobility studies, required by the EPA to support product registration, include soil-thin layer chromatography, soil column studies, or batch equilibrium (sorption/desorption) tests (Environmental Protection Agency, 1982). Little emphasis is placed on the role of preferential

flow through structured soils. A standardized soil column containing an artificial macropore should be useful in herbicide screening to assess potential field movement. This represents a potential worst case scenario for preferential flow, and could be used to supplement current pesticide mobility studies.

The objectives of this study were to 1) develop a soil column containing artificial macropores for preferential flow experiments with a silty clay loam soil, and 2) compare the movement of alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide), cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile), pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6 dinitrobenzenamine), and chloride among packed soil columns with either a continuous macropore, a macropore initiating 4 cm below the soil surface, or without a macropore.

MATERIALS AND METHODS

Since one objective of this study was to develop a modified soil column for preferential flow experiments on fine-textured soils, laboratory techniques will be described in detail. Soil from the surface 30 cm was collected at the Northern Iowa Research Center in Kanawha, Iowa. The area is mapped as an Okoboji series (Fine, montmorillonitic, mesic Cumulic Haplaquoll). A partial list of soil properties is shown in Table III-1.

Due to large amounts of montmorillonite clay and the high organic carbon content of the soil, traditional column packing techniques were not effective in producing a suitable soil column. Columns could not be packed to a high enough bulk density using methods described by Weber et al. (1986). Further, upon wetting of the columns, soil pulled away from the column wall, creating an unacceptable boundary layer.

Soil with a field moisture content of 16 to 18 percent was ground and sieved through a 2 mm screen. It was then added in twelve equal increments to a 15.2 cm diameter by 18 cm high PVC column. Soil was leveled after the addition of each layer, and compacted after every two layers for a total of six compactions per column. A modified Proctor rammer method (ASTM, 1988) was used to create a bulk density of 1.2 g cm^{-3} . The 2.49 kg rammer was dropped 30 times per layer from a height of 7.6 cm. After each compaction, the soil surface

Table III-1. Soil properties of an Okoboji silty clay loam from Kanawha, Iowa

	Soil Depth (cm)	
	0 - 15	15 - 30
Texture (%)		
Sand (2-.05 mm)	19.8	20.5
Coarse Silt (50-20 μm)	17.8	18.5
Fine Silt (20-2 μm)	27.6	27.5
Clay (<2 μm)	34.8	33.5
Bulk density (g cm^{-3})	1.24	1.17
pH	6.6	6.9
Organic carbon (%)	4.39	4.34

was scratched to help break up pressure faces.

Packed columns were then saturated from the bottom over a 24 hour period with a 0.0075 M calcium sulfate solution. Saturated hydraulic conductivity (K_{sat}) was measured by passing 2.5 to 3 pore volumes of calcium sulfate solution through each column. This also served to reduce background chloride concentrations. After saturation, some soil swelling was noted and column height increased by 2.8 percent. Final height was used to calculate bulk density. The nine columns were then grouped into three blocks (A, B, or C) based on K_{sat} values. Within each block, one of three treatments (continuous macropore, partial macropore, or no macropore) was randomly assigned to each column (Table III-2.).

A continuous macropore (treatment 1) was created by removing a vertical core from the center of individual columns. A straight-walled 6 mm diameter copper tube was used to remove the soil core. This represented a potential worst-case scenario for a continuous preferential flow path extending the entire length of the column. Partial macropores (treatment 2) were created by removing a 6 mm diameter vertical core from the bottom of the soil column, but stopping 4 cm from the top of the column. This simulated a macropore initiating below the soil surface or a macropore which had been partially destroyed by tillage. Lastly, one column in each block was not modified and served as a control containing

Table III-2. Dimensions and physical properties of soil columns (Mean particle density was determined to be 2.53 g cm^{-3})

Column ^a (trt)	Ksat ^b (cm hr^{-1})	Length (cm)	Bulk Density (g cm^{-3})	Total Porosity	Pore Volume (cm^3)
A-1	2.04	18.5	1.17	.54	1800
A-2	1.56	18.0	1.18	.53	1740
A-3	2.19	18.5	1.17	.54	1800
B-1 ^c	3.83	18.9	1.14	.55	1880
B-2	3.46	18.5	1.17	.54	1800
B-3	3.21	18.5	1.17	.54	1800
C-1	4.52	18.6	1.16	.54	1830
C-2	3.78	18.5	1.17	.54	1800
C-3	4.96	19.0	1.16	.54	1850

^a Column treatment: 1 = continuous macropore, 2 = partial macropore, 3 = no macropore.

^b Ksat measurements taken before columns were modified.

^c B-1 was substituted for a column with lower Ksat after the macropore in that column collapsed.

no macropore (treatment 3). The columns were stored at 5 C until they were used for leaching experiments.

Individual columns were resaturated with a 0.0075 M calcium sulfate solution over a 5 hour period, and then allowed to drain for 16 hours. The solution draining from each column was collected and analyzed for background chloride concentrations. Preliminary experiments revealed that continuous macropores collapsed during saturation. The resulting chloride breakthrough curve (data not shown) was similar to columns containing no macropore. To insure that pores remained functional, columns containing a continuous macropore were cored a second time prior to chemical application. No effort was made to recore columns containing a partial macropore.

A mixture of alachlor at the 1.5 kg ha⁻¹ rate, cyanazine at the 0.4 kg ha⁻¹ rate, and pendimethalin at a rate of 0.8 kg ha⁻¹ was applied dropwise to the soil surface. Herbicide properties are shown in Table III-3 (WSSA, 1989; Becker et al., 1989). A calcium chloride solution equal to 175 kg ha⁻¹ of Cl was then applied in a similar way. The average number of drops per column was 151 for the herbicide mixture and 191 for the calcium chloride solution. After application, columns were covered for 24 hours to prevent chemical volatilization.

A 0.0075 M calcium sulfate solution was applied through a drip irrigation head positioned 8 cm above the soil surface to

Table III-3. Herbicide characteristics

	alachlor	cyanazine	pendimethalin
Molecular weight (g)	269.8	240.7	281.3
Water solubility (ppm)	242	171	0.5
Soil half-life (days)	15	14	90
Soil sorption Koc	170	190	24,300
Leaching potential	Medium	Medium	Small

simulate rainfall. The solution was applied at an average rate of 9.5 ml min^{-1} , which corresponded to a rainfall intensity of 31.5 mm hr^{-1} . The simulated rainfall continued for two hours and all of the column discharge was collected in fractions. Samples were refrigerated immediately after collection. Chloride concentration was determined using constant potential coulometry (Haake Buchler Digital Chloridometer). Herbicide concentrations were determined at the Iowa Hygienic Laboratory, Iowa City, Iowa (methylene chloride extraction, and analysis using a gas chromatograph equipped with an N-P detector). Herbicide detection limits ranged from 0.3 to $0.5 \text{ } \mu\text{g L}^{-1}$.

RESULTS AND DISCUSSION

Chloride concentration breakthrough curves for blocks A, B, and C are shown in Figure III-1. Initial chloride breakthroughs for unmodified columns (Treatment 3) and those containing partial macropores (Treatment 2) were similar and occurred when 0.3 to 0.4 pore volumes had passed through. This was consistent regardless of initial hydraulic conductivity. This also indicated that boundary flow down the column wall was not occurring to any great extent.

In contrast, initial chloride breakthrough for columns containing a continuous macropore (Treatment 1) was largely dependent on the saturated hydraulic conductivity of the surrounding soil matrix. Both the speed of initial chloride breakthrough and initial concentration measured were highest in column A-1, which had a low initial saturated hydraulic conductivity before modification (Table III-3). Some ponding of the simulated rainfall away from the macropore was noted. Surface-applied solutes were apparently carried rapidly through the area of high conductivity.

Preferential transport through a continuous macropore became less pronounced as the conductivity of the surrounding soil matrix increased as seen in column B-1. Although some chloride was rapidly leached, the breakthrough peak was not as sharp. Finally, a continuous macropore had the least effect on chloride breakthrough when surrounding soil

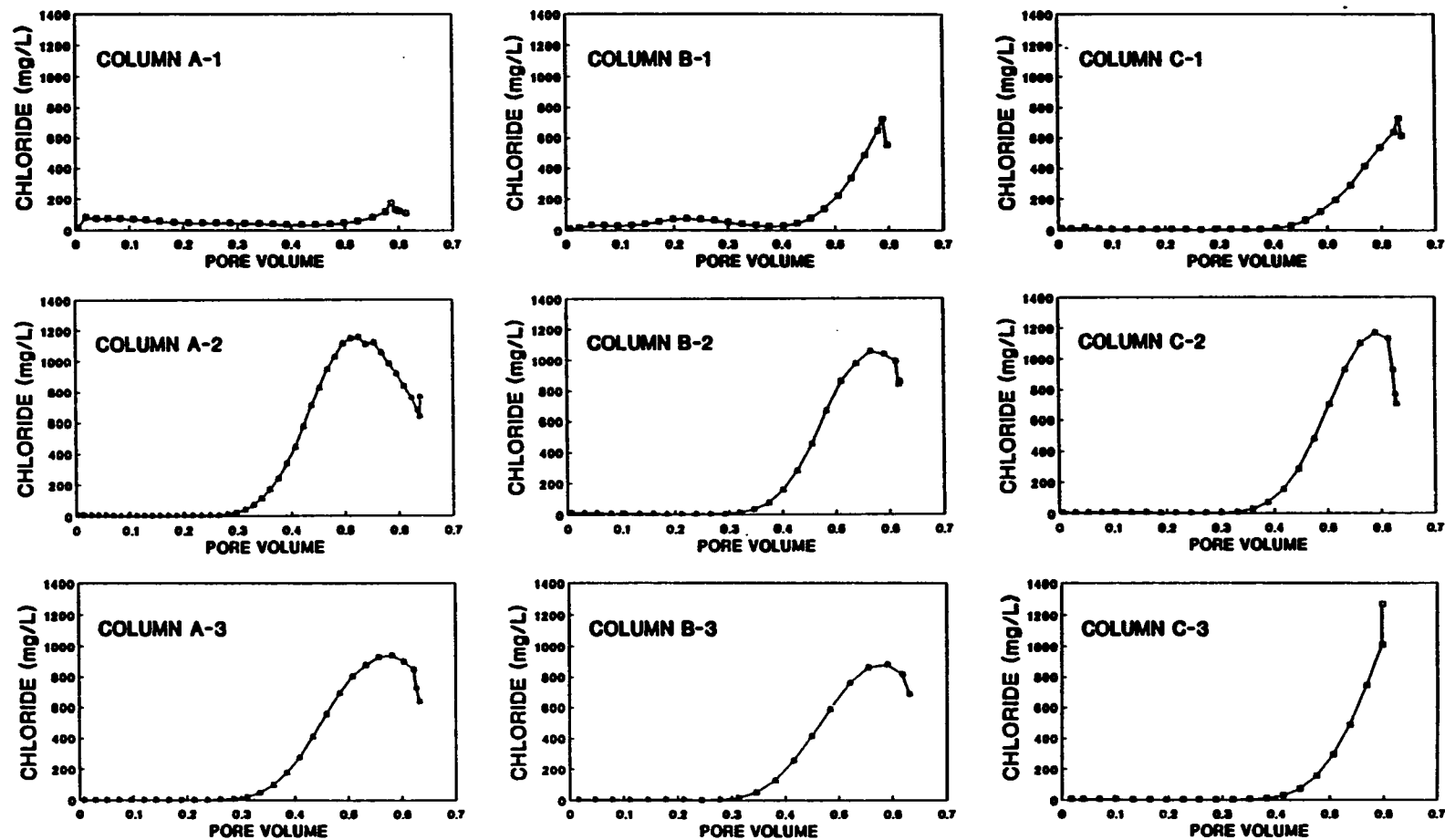


Figure III-1. Chloride concentrations in column drainage (1 = continuous macropore, 2 = partial macropore, and 3 = no macropore)

conductivity was highest (column C-1). Infiltration of simulated rainfall was high and ponding did not occur in this column. As a result, the continuous macropore had only a slight effect on initial solute movement, probably related to chloride close to the macropore opening.

Figure III-2 shows cumulative amounts of chloride drained from each of the nine columns. Total chloride leached was lowest in columns containing a continuous macropore, while highest chloride amounts were recovered from columns containing a partial macropore. It is difficult to determine if this is a treatment effect, or simply the result of differences in hydraulic conductivity among columns. In columns without a macropore, total chloride appeared to decrease as saturated hydraulic conductivity increased.

Analysis of variance indicated that treatment had a significant effect on the total amount of chloride leached ($P > F = 0.0318$). Analysis of covariance, however, did not show a significant treatment effect when total chloride was adjusted for differences in initial column hydraulic conductivity (K_{sat}). Similarly, no significant correlation was found between total amount of chloride leached and K_{sat} .

Initial chloride breakthrough was rapid in two columns containing a continuous macropore, but subsequent rainfall may have moved down the macropore, thus bypassing chloride which had diffused into the soil matrix. Column A-1, for example,

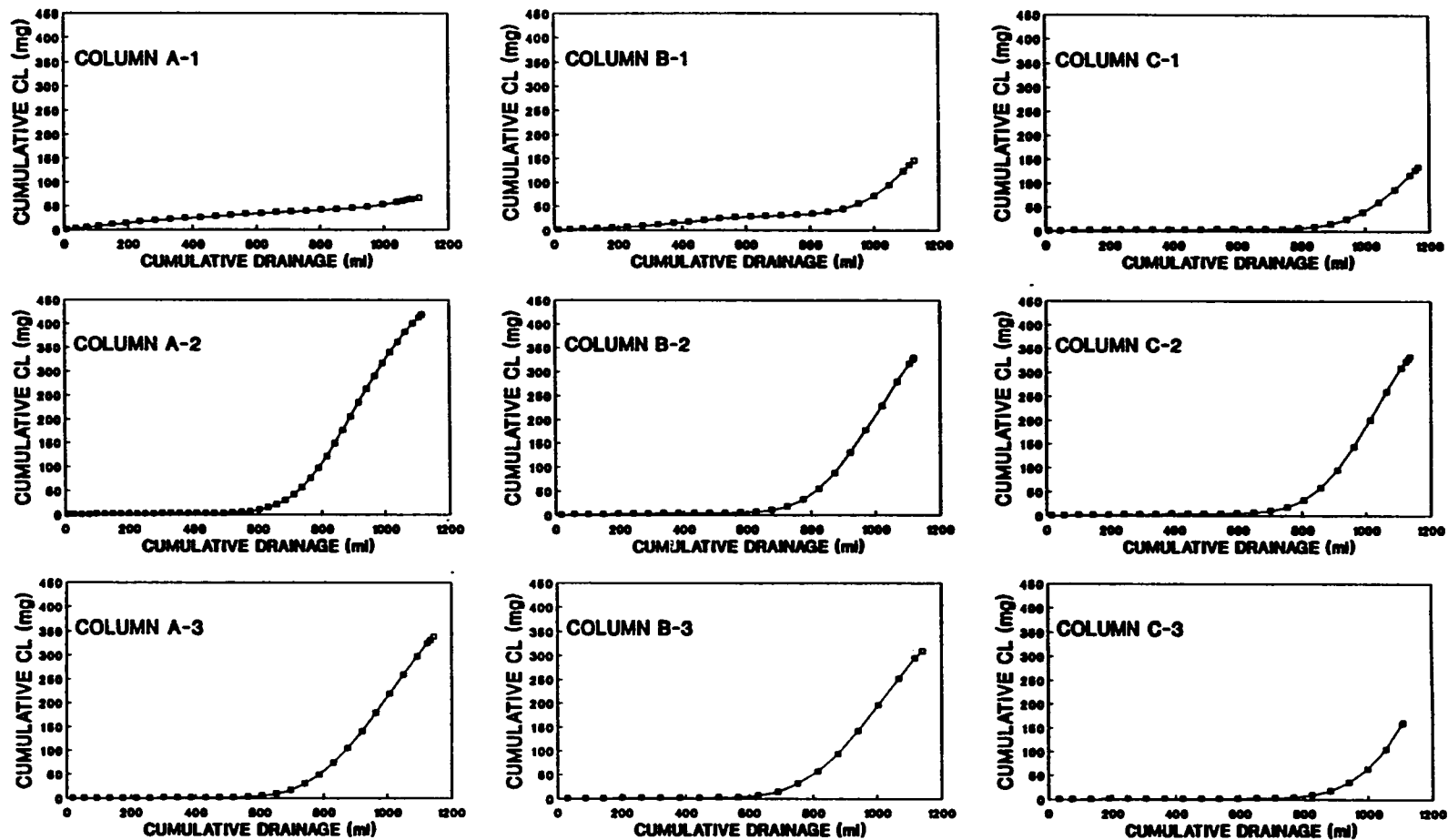


Figure III-2. Cumulative chloride recovered from column drainage (1 = continuous macropore, 2 = partial macropore, and 3 = no macropore)

had the highest initial chloride breakthrough, but the lowest total amount of chloride drained of all nine columns.

As ponding occurred in columns with low initial saturated hydraulic conductivity, more total chloride was leached. In contrast, simulated rainfall infiltrated much quicker in columns with high conductivity and had less time to interact with solute away from the point of raindrop impact.

Figure III-3 shows herbicide concentrations in drainage from soil columns with a continuous macropore. Alachlor, cyanazine, and pendimethalin were identified in column drainage, with highest concentrations occurring in the first 1 to 2 samples. The rapid breakthrough suggests that herbicides moved through the continuous macropore. Herbicide concentrations decreased in subsequent samples as surface-applied chemicals may have moved into the soil matrix, where they would be less vulnerable to preferential flow. Pendimethalin has low water solubility and is strongly adsorbed to soil, but it was also able to move the length of the 18.5 cm column.

In contrast, alachlor, cyanazine, and pendimethalin were not detected in drainage from any column with either a partial macropore or no macropore. In the absence of a continuous macropore, adsorbed solutes were retained in the soil column and breakthrough did not occur, above the $0.5 \mu\text{g L}^{-1}$ detection limit.

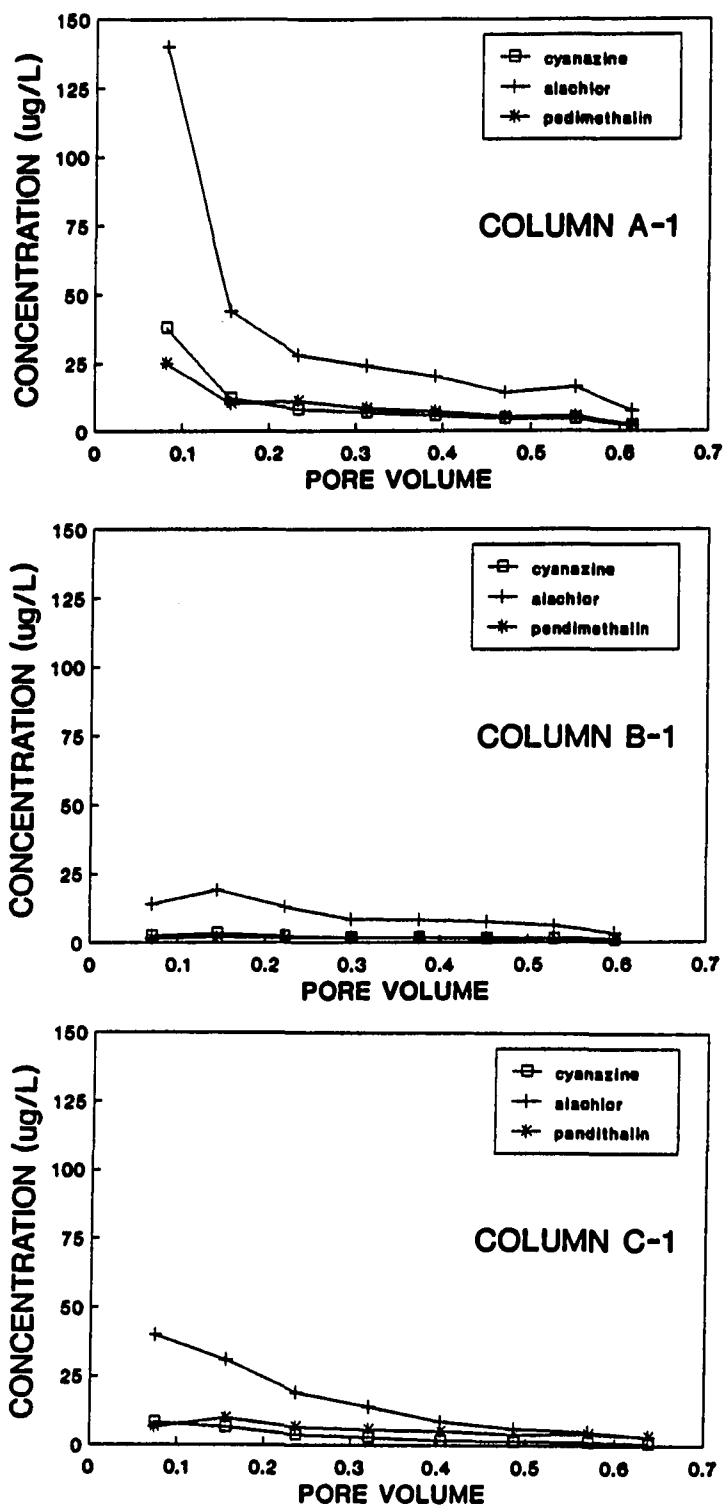


Figure III-3. Herbicide concentrations recovered from columns with a continuous macropore

CONCLUSIONS

The importance of a continuous macropore for solute transport depended largely on the conductivity of the surrounding soil matrix. Bouma and Anderson (1977) demonstrated that identical macropores can have different hydraulic functions depending on soil type. These data indicate that the contribution of a macropore to water and solute movement is further governed by the hydraulic conductivity of the surrounding soil matrix, within a given soil type.

The movement of adsorbed and non-adsorbed solutes was similar in columns containing a continuous macropore. Chloride, alachlor, cyanazine, and pendimethalin leaching were greatest when the hydraulic conductivity of the surrounding soil was lowest. As column conductivity increased, macropores became less important for solute transport.

Surface-applied solutes can move rapidly through a continuous macropore, but total solute movement is a function of both preferential and matrix flow. A large, continuous macropore does not guarantee excessive leaching of surface-applied chemicals. Rather, under certain conditions, it may allow rainfall to bypass some of the solute contained in the soil profile.

For chloride, which is not adsorbed, total loss was less in columns containing a continuous macropore than for columns

with either a partial or no macropore. At the start of rainfall, small quantities of chloride on the soil surface traveled through the continuous macropore, while the remainder of applied chloride moved into the soil matrix. In columns without a continuous macropore, rainfall interacted with all the chloride on the soil surface moving it as a more concentrated front.

In contrast, the movement of three herbicides was effectively reduced in columns without a continuous macropore. Alachlor, cyanazine, and pendimethalin, which are adsorbed to soil, were restricted from moving through the soil matrix. Herbicides were not detected in column drainage under the boundary conditions considered.

Herbicide leaching through a packed soil column can significantly underestimate the extent of field movement through a structured soil. Pesticide leaching experiments using a soil column with an artificial macropore may provide a more realistic estimate of field behavior. A modified soil column could be useful to study the impact of preferential flow on chemical movement.

Although this experiment was conducted using a single rainfall application rate, rainfall intensity would also be expected to significantly influence macropore contribution to total solute movement. As rainfall intensity exceeds infiltration rate, macropores should become more important.

Lastly, the artificial macropore used in this experiment more closely resembles solute movement through a soil crack rather than a wormhole or root channel. There is some evidence to suggest that organic matter remaining in biologically-derived macropores may slow the movement of adsorbed chemicals through the root zone compared to cracks without organic matter residues (Edwards et al., 1990).

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GENERAL SUMMARY

Preventing groundwater contamination is an important issue facing production agriculture. In order to select management practices which do not adversely affect water quality, it is first necessary to understand pesticide and fertilizer movement under field conditions. Monitoring field drainage tiles is one method for measuring chemical movement and offers several advantages over other sampling techniques. Drainage tiles integrate spatial variability, but maintain secondary soil structure which may be important for water and solute movement.

The detection of herbicides in tile effluent immediately after a natural rainfall suggests that chemicals can move through preferential flow paths and possibly contaminate deeper groundwater. This occurs through natural soil cracks, root channels, and worm holes, collectively referred to as macropores. The timing and duration of the first significant rainfall following chemical application can have large effects on the preferential movement of pesticides and fertilizers. Herbicide and tracer movement to field drainage tiles was readily apparent when a heavy, simulated rainfall occurred 24 hours after chemical application. Rapid breakthrough of herbicides, dye, bromide, and chloride was observed under these conditions. Chemical concentrations peaked within two

hours following the start of rainfall and then decreased rapidly. These studies indicate that pesticide sampling done immediately after significant rainfall events should record peak chemical concentrations. Preferential flow had the greatest impact on chemical movement initially, while matrix flow becomes more important over time.

Laboratory experiments indicated that macropores can influence chemical movement in several ways. Initial chloride concentrations were higher in columns with a continuous, artificial macropore compared to columns without a continuous macropore. Total chloride loss, however, was less in columns with the intact macropore. Further, macropore contribution to solute transport was largely governed by the hydraulic conductivity of the surrounding soil matrix.

Packed soil columns have been traditionally used for herbicide leaching experiments, but often underestimate chemical movement under field conditions. Alachlor, cyanazine, and pendimethalin were recovered in drainage from columns with a continuous macropore, while no herbicides were detected in drainage from columns without a continuous preferential flow path. A modified soil column with an artificial macropore may provide a more realistic estimate of pesticide movement in structured soils. This type of column could be useful in herbicide screening to assess leaching under worst-case situations.

It was difficult to draw many conclusions concerning the effect of tillage on chemical leaching to drainage tiles. Field studies were complicated by variability in tile flow rate, and the fact that tillage treatments at Kanawha were only in place for a single year. Differences between no-till and conventional tillage on chemical movement may take several years to become evident. The establishment of a field hydrology laboratory at the Northeast Iowa Research Center should provide considerable insight to pesticide behavior in long-term tillage plots.

Laboratory experiments suggested that the presence of a continuous macropore does not always increase leaching losses of non-adsorbed chemicals. Continuous macropores are more common in no-till systems, partly due to increased earthworm activity. Initially, surface-applied chemicals can move rapidly through the root zone, but intact macropores may allow subsequent rainfall to bypass solutes contained in the soil matrix.

Herbicide movement in column drainage was only observed when a continuous macropore was present, and preferential flow was most evident when conductivity of the surrounding soil matrix was low. The worst case for herbicide leaching may occur if continuous macropores are present, but surrounded by a compacted zone with low hydraulic conductivity. This would allow herbicides on the soil surface to readily move with

preferential water flow, but would slow herbicide movement into the soil matrix.

Both field studies at the Kanawha site and column experiments indicated that preferential water flow is an important mechanism in structured soils. The contribution of preferential flow to chemical and tracer movement, however, is more complicated. Boundary conditions such as rainfall timing and intensity, timing of chemical application, pesticide properties, initial soil moisture content, and soil hydraulic conductivity all influence the extent of leaching.

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