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INFILTRATION, NITRATE AND CHLORIDE LEACHING, AND DICAMBA

FATE IN UNSATURATED SOIL BELOW TURFGRASS

A Thesis

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ABSTRACT

INFILTRATION, NITRATE AND CHLORIDE LEACHING AND DICAMBA FATE IN UNSATURATED SOIL BELOW TURFGRASS

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University of Guelph, 1998

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The leaching of pesticides and fertilizers applied to turfgrass will be affected by microbial and plant activity unique to this system. The objectives of this research were (i) to measure the degradation of dicamba in thatch and soil using a small-scale, laboratory, batch experiment; (ii) to investigate the effect of turfgrass on water flow and the leaching of nitrate, chloride and dicamba applied to field lysimeters packed with a sandy loam soil profile and topped with turfgrass, and (iii) to test the ability of the model LEACHM (within EXPRES) to simulate these processes. Degradation of dicamba was 5.9 to 8.4 times faster in thatch than in soil, with a half-life as low as 5.5 days. Drainage and leaching occurred primarily in autumn, being strongly controlled by evapotranspiration. LEACHM predictions mirrored the fluctuations in water contents, solute concentrations and drainage well, though the predicted values often differed from field measurements.

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Finally, I cannot understate the contribution of my family and Ellen in the completion of this research. Their love and faith sustain my aspirations and dreams.

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CHAPTER 1

Research Introduction

The leaching of pesticides and nitrate to groundwater poses a potential risk to

human health and local ecosystems. Fertilizers are an integral part of sod production and

turf management and, although non-chemical alternatives are being developed, the demand

for pesticides is still growing. Hay (1988) suggested that the development of weed

control systems and the incorporation of cultural and biological controls is a step towards

more ecologically friendly practices, but added that herbicides will undoubtedly form the

backbone of weed control for the foreseeable future. Therefore the need for a better

understanding of pesticide and nitrate transport will remain, if not increase, in order to

address environmental and health concerns.

Much of the previous work on pesticide and fertilizer nitrate transport has been

performed on bare soil or with agricultural crops such as corn and soybeans. However,

the turfgrass system is significantly different. During the year, turfgrass generally has a

longer period of biological activity than most crops and even deciduous forests. In fact,

recent studies (Branham et al., 1993; Gold and Groffman, 1993; Starrett et al., 1996) have

indicated an increased dissipation of pesticides in soils under turfgrass compared to other

conditions. Also, agricultural soil, unlike turf, is routinely disturbed and often left bare -

conditions that affect transport and the water balance (Gold and Groffman, 1993).

In his review on the state of knowledge of pesticide transport in soils, Flury (1996)

indicated that there are still limitations to the understanding of transport processes in soils.

Instances of contamination were occurring even when lab studies suggested leaching

would not occur. In response to these observations, an increase in studies performed in

the field has occurred over the past decade. Many researchers have found greater leaching than expected based on lab findings, a development that researchers have attributed to spatial variability and/or preferential flow pathways (including macropores) in the soil (Flury, 1996). These processes may be applicable to other solutes as well. Testing of our understanding of these processes and of the models developed to simulate them must be performed using field data to ensure proper predictions can be made in the future.

Boesten (1991) used a mathematical model to analyze the effect of different soil and climatic factors on pesticide leaching. The amount leached was most sensitive to the sorption variables and the transformation rate in soil. Weather conditions also influenced leaching, as did the effect of temperature on the transformation rate. The time of application, autumn versus spring, was very important for non-sorbing pesticides with short half-lives, such as dicamba. Plant uptake was important only for poorly sorbed pesticides (i.e., dicamba). A complete examination of the turfgrass ecosystem, with respect to pesticide and nitrate transport, and incorporating solute transport model predictions, is needed.

The main objectives of this research were i) to measure the degradation rate of dicamba in soil and thatch for various soil temperature and moisture conditions, using a simple, laboratory, batch experiment and modified analytical procedure; ii) to investigate water flow and transport of dicamba, nitrate and chloride through unsaturated, sandy soil under turfgrass in the field; and iii) to test the ability of the solute transport model LEACHM (Leaching Estimation and Chemistry Model), within EXPRES (Expert system for Pesticide Regulatory Evaluations and Simulations), to simulate water flow and solute transport in the turfgrass system.

In association with these objectives, I attempted to determine whether the leaching of dicamba applied to turf should be a greater concern for temperate climates, such as southern Ontario. The hypothesis was that a spring or autumn application of dicamba in such a climate, may be more susceptible to leaching due to lower microbial activity and higher water contents and water flux rates, effects associated with the lower temperatures and the slower growth of the turfgrass plants.

This research consisted of a two-year field study and supporting laboratory experiments, followed by model testing using the field observations. The laboratory experiments consisted of measuring the degradation rate of dicamba in the thatch of turfgrass and soil under a number of different temperature and moisture conditions, as well as measuring the hydraulic properties of the turf and the different soil layers. The measured values provided insight into the individual processes, and were also used in the modeling study.

The field experiment involved the application of dicamba, ammonium-nitrate fertilizer and potassium chloride to several soil-profile lysimeters installed at the Guelph Turfgrass Institute and Environmental Research Centre (GTIERC), 43° 32' 50" N latitude, 80° 13' 50" W longitude, Guelph, ON. Each lysimeter was constructed from a 118 litre cylinder of high density polyethylene, 43-cm diameter, 81-cm height, with an 18-cm deep conical bottom. This bottom, filled with pea gravel, trapped the leached soil solution and allowed for easier vacuum-suction removal. Each was packed with a three-horizon profile of Lisbon sandy loam from the Cambridge Research Site, near Cambridge, ON. Starrett et al. (1995) found considerable difference in flow between packed and intact soil columns, due to the disruption of preferential flow pathways during packing. It was concluded that

the use of disturbed columns may not reflect natural soil conditions. This should not be as important for sandy soil, especially since the lysimeters have been exposed to environmental and biological processes for some time. In the spring of 1995 they were covered with turf (Green Horizons Compact Sod) and placed even with the surrounding ground surface to ensure no unnatural runoff or ponding would occur.

The application scheduling and amounts of solutes applied are outlined in Table 1.1. Potassium chloride was added in amounts that, it was believed, would not produce concentrations much over 2000 mg L^{-1}, as Cordukes and Maclean (1973) observed no apparent effects of calcium chloride at this level on the quality of Kentucky bluegrass turf grown on sand or clay loam soil.

Table 1.1. List of application dates and amounts for ammonium-nitrate fertilizer, potassium chloride salt and dicamba herbicide.

Substance	Application Rate	Application Date	
		1996	1997
	kg ha^{-1}		
Fertilizer (N)	154	July 17	May 14
	154	October 29	July 25
	154	-	September 28
Salt (Cl^{-})	327.5	-	May 14
	327.5	-	September 28
Dicamba	0.60	-	May 14
	0.60	-	September 28
	0.60	-	November 27

The model tested was EXPRES (EXpert system for Pesticide Regulatory Evaluations and Simulations) (Mutch et al., 1993) which contains the model LEACHM (v.2) (Wagenet and Hutson, 1987), a research-oriented simulation model requiring a fairly extensive set of input parameters and variables describing site-specific soil, plant, and

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climatic conditions. EXPRES has incorporated a user-interface to make the model more accessible as a management tool, but has not been widely tested.

The style of this thesis is journal paper format; each of Chapter 3-6 resembles an individual paper, complete with abstract, introduction, methodology, results, discussion, conclusions and references. Following this introductory chapter, a literature review is presented in Chapter 2, covering water and solute transport equations, turfgrass, dicamba, nitrate and computer modeling. The order in which the results are presented in this thesis follows the model validation protocol outlined by Armstrong et al. (1996):

Stage 1 - Parameterisation of model using independently measured parameters;

Stage 2 - Hydrological validation (water movement and water content);

Stage 3 - Solute movement - for other solutes (Chloride, and then nitrate) first;

Stage 4 - Pesticide fate in soil (parameters ($t_{1 2}$, K_{oc}) derived from independent studies);

Stage 5 - Pesticide leaching (patterns and order of magnitude occurrence).

Chapter 3 describes and gives the findings of the dicamba degradation study, which also provides parameters for modeling of dicamba in the field, as outlined in Stage 1. Chapter 4 includes the laboratory-determined hydraulic values for the turf/soil system, furthering Stage 1 above, and the examination of water flow in the field lysimeters, as suggested by Stage 2. Chapter 5 mirrors Stage 3, focusing on solute transport, but only considering nitrate and chloride. Chapter 6 deals with the leaching of dicamba, and is a combination of Stages 4 and 5. General conclusions from the entire thesis and recommendations for future research are presented in Chapter 7.

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CHAPTER 2

Literature Review

2.1 Water and Solute Transport

Concerns of pesticide and fertilizer contamination focus on leaching, the downward transport of the solute through the vadose zone to groundwater. In the vadose zone, the soil is usually unsaturated, although the capillary fringe and temporary ponding, groundwater mounding, or perched water tables may result in zones of water saturated conditions above the water table. Therefore, the soil water or matric potential is usually negative. The vadose zone has also been described as a conduit for liquid and gas exchange between the surface and the water table (Nielson et al., 1986). The movement of water and solutes through the vadose zone has been described mathematically with linear and nonlinear partial differential equations (pde). Descriptions of the pde for water and solute transport are given in the following sections.

2.1.1 Buckingham-Darcy Flux Equation:

In 1856, Henry Darcy derived an empirical relationship which gives the flux of water through a saturated, homogeneous, isotropic, and rigid soil. In 1907, Edgar Buckingham modified Darcy's equation to include flow in the unsaturated zone:

$$J_w = -K(\psi) \frac{\partial H}{\partial z} \qquad [1.1]$$

where J_w is the volumetric water flux density, representing the volume of water flowing across a bulk cross-sectional area per unit time; $K(\psi)$ is the unsaturated hydraulic conductivity, H is hydraulic head in unsaturated soil and z is depth.

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The driving force for water flow is the gradient of hydraulic head; water moves from high head to low head. Head describes the potential energy of the water per unit weight of water (Hubbert, 1940). Hydraulic potential consists of water pressure, matric (how strongly the soil pores retain water), gravitational, osmotic, electrochemical, and perhaps more potentials, under isothermal conditions (Nielson et al., 1986). Air pressure differences can also affect water flow, especially if water ponds at the surface or if the soil is relatively impermeable (e.g. Horton, 1940). However, for sandy soils without ponded water, (as was the case for this study) hydraulic head is mainly the sum of matric and gravitational heads.

The hydraulic conductivity, which depends on the soil permeability and the fluid (water) density and viscosity, is a constant, K_s, at saturation. Buckingham (1907) determined that the hydraulic conductivity would decrease as the soil became unsaturated, with decreasing soil-water matric head, ψ. Since matric head is a function of water content, the unsaturated hydraulic conductivity can be written as a function of both matric head and water content.

2.1.2 Richards' Equation

Combining the Darcy-Buckingham equation with the soil water conservation of mass expression, that is:

$$\frac{\partial \theta}{\partial t} = -\frac{\partial J_w}{\partial z} + \Phi_w \qquad\qquad [1.2]$$

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where Φ_w is a water source or sink term, θ is soil water content, and t is time, results in

the Richards' equation (Richards, 1931) for water flow with either ψ or θ as the

dependent variable:

$$C(\psi)\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial z}(K(\psi)\frac{\partial\psi}{\partial z}) - \frac{\partial K(\psi)}{\partial z} + \Phi_w \qquad [1.3]$$

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}(D_w(\theta)\frac{\partial\theta}{\partial z}) - \frac{\partial K(\theta)}{\partial z} + \Phi_w \qquad [1.4]$$

where the water capacity function C (ψ) is $d\theta/d\psi$, and the water diffusivity function is

defined as, $D_w(\theta) \equiv K(\theta) d\psi/d\theta$.

The relationship between water content and matric head is nonlinear; therefore, the

value of C(ψ) is not constant. Also, the relationship between θ and ψ will be different

when measured during wetting and drying, a phenomenon termed hysteresis. This

hysteretic effect is caused by the presence of different contact angles during wetting, and

drying and by the geometry of single pores (ink-bottle effects) (Hillel, 1980). Hysteresis

also affects the K(ψ) function, but K is generally considered to be a single-valued function

of θ (Hillel, 1980).

Equation 1.3 represents flow in homogeneous or heterogeneous materials such as

layered soils; .iowever, equation [1.4] only applies to homogeneous soils. Both equations

consider only vertical flow; with the vertical space coordinate z positive downward. In

addition, the matrix and liquid are incompressible and the fluid density is independent of

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space and time. The equations describe water movement in soils under laminar flow conditions in the liquid phase.

Of note, these deterministic equations (i.e. 1.3 and 1.4) do not simulate water flow in two-domain media, often termed preferential flow (White, 1985, Nielson et al., 1986). The two domains consist of the soil matrix, where flow is conventional (i.e. Darcy-based), and a domain where flow is primarily influenced by gravity, such as one or more large and continuous voids, termed macropores. Preferential flow may also be initiated by wetting front instability and other processes (Glass et al., 1989).

Since more water can be channeled through the preferential flowpaths than the surrounding soil matrix, preferential flow may provide a faster conduit for solutes to reach the groundwater. The solute moving through the remaining soil matrix will travel slower than if no preferential flow were occurring, due to the decreased water content and lower hydraulic conductivity (Flury, 1996). It is generally more important in structured soils, such as clay and loam, where cracks between aggregates can occur. However, Kung (1990), observed the funneling of water and solutes into more permeable zones along horizontal heterogeneity in sandy soils. Preferential flow will also reduce the contact time and area between solutes and soil solids, potentially reducing sorption (Kung, 1993).

2.1.3 Solute Equation of State

In soil a solute can exist in up to three different phases: sorbed to a stationary solid, dissolved in a liquid or as a gas in the soil air. The total concentration of solute, C_T (mass solute / volume total), can be expressed as

$$C_T = \rho_b C_s + \theta C_l + a C_g \qquad\qquad [1.5]$$

where ρ_b is soil bulk density, (mass of dry soil / volume total); C_s is the concentration of

adsorbed solute, (mass solute / mass of dry soil); θ is the volumetric water content,

(volume soil water / volume total); C_l is the concentration of aqueous solute, (mass solute

/ volume soil water); a is the volumetric gas content, (volume soil gas / volume total); and

C_g is the concentration of gaseous solute, (mass solute / volume soil gas).

2.1.4 Convection-Dispersion Equation (CDE)

An analogy to Richards' Equation for water flow is the convection-dispersion

equation for solute transport. The CDE is an extension of Fick's first law of diffusion

because it accounts for solute movement due to convection and mechanical dispersion.

Classical theory of solute dispersion in porous media assumes that mechanical dispersion

and molecular diffusion are additive processes (Taylor, 1953; Aris, 1956). The processes

of diffusion and dispersion accompanied by water movement through soil are normally

combined into a single hydrodynamic dispersion coefficient (Elrick et al., 1979).

2.1.5 Development of the CDE Model: Translating Physics into Mathematics

The first step in developing the CDE is a statement of solute conservation of mass,

$$\frac{\partial C_T}{\partial t} = -\frac{\partial J_s}{\partial z} + \Phi_s \qquad\qquad [1.6]$$

where J_s is the solute flux and Φ_s is the solute source/sink term. The solutes studied in

this study are all relatively nonvolatile. Therefore, the following development of a

mathematical expression is for solute transport in the liquid and solid phases only. As

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discussed above, the CDE model includes the transport processes of convection, dispersion, and diffusion. Therefore the total mass flux density of solute, J_s, is

$$J_s = J_w C_l - D_{lh} \frac{\partial C_l}{\partial z} - D_{ld} \frac{\partial C_l}{\partial z} \qquad [1.7]$$

where the coefficients for mechanical dispersion and diffusion are D_{lh} and D_{ld}, respectively. The first term in equation [1.7] accounts for solute movement by convection. Convection describes the transport of the solute with the water on a macroscopic scale, that is, at the same average linear velocity of the pore water, V. However, on the microscopic scale, water velocity will vary due to the tortuosity of the pathways, different pore sizes and even the velocity profile within a single pore - accounted for by the second term. The third term in 1.7 accounts for solute movement due to molecular diffusion. Diffusion of the solute between pore domains of differing velocity will further impact solute transport. A two-pore domain model developed by van Genuchten and Wierenga (1976) assumes that diffusion is responsible for the exchange of solute between mobile and immobile soil water regimes. On a larger scale, soil properties will also vary spatially and directionally. These differences cause spreading of the solute front or pulse, an effect called hydrodynamic dispersion (term 3 in equation [1.7]). The hydrodynamic dispersion coefficient has often been observed to be proportional to the pore water content, and is dependent upon the scale of measurement (Elrick et al., 1979).

The flux due to dispersion has been given a mathematical form identical to Fickian diffusion (Bear, 1972), in which transport depends on a chemical gradient. In practice, the diffusion and hydrodynamic dispersion coefficients are combined into a single effective dispersion parameter, D_e. It is often measured as an empirical fitting parameter by

inversion procedures and may include solute spreading mechanisms not described in equation [1.7], such as anion exchange (Nielson et al., 1986). Therefore, equation [1.7] becomes

$$J_s = -D_e \frac{\partial C_l}{\partial z} + J_w C_l \qquad [1.8].$$

Assuming that the solute has a negligible vapour pressure, the CDE can be written as

$$\frac{\partial}{\partial t}(\rho_b C_s + \theta C_l) = \frac{\partial}{\partial z}(D_e \frac{\partial C_l}{\partial z}) - \frac{\partial J_w C_l}{\partial z} + \Phi_s \qquad [1.9]$$

which can be reduced for inert, non-sorbing solutes to

$$\frac{\partial C_l}{\partial t} = D \frac{\partial^2 C_l}{\partial z^2} - V \frac{\partial C_l}{\partial z} \qquad [1.10]$$

where $D = D_e/\theta$ and $V = J_w/\theta$.

2.1.6 Sorption of Solute

Sorption isotherms describe the relationship between the dissolved solute concentration, C_l, and the sorbed concentration C_s, at equilibrium. Solute sorption in soil can generally be described by the Freundlich isotherm,

$$C_s = K_f C_l^{(1-N)} \qquad [1.11]$$

where K_f and N are constants which determine the shape of the relationship between C_s and C_l. A special case is the linear isotherm, in which $N = 1$, and $K_f = K_d$, the distribution coefficient (Jury et al., 1991). The relationship

$$K_{oc} = \frac{K_d}{f_{oc}}$$ [1.12],

where K_{oc} is the organic carbon partition coefficient and f_{oc} is the fraction of organic carbon in the soil, was developed after many researchers reported that the sorption of many organic chemical, including pesticides, was primarily associated with the organic carbon content of the soil (Rao et al., 1988). The K_d values for a linear adsorption isotherm can be used to calculate the solute's retardation factor (e.g. Jury et al., 1983):

$$R = 1 + \frac{\rho_b K_d}{\theta}$$ [1.13].

The CDE can be rewritten for inert, adsorbing solutes using R, which eliminates the term containing C_s:

$$\frac{\partial C_l}{\partial t} = D_R \frac{\partial^2 C_l}{\partial z^2} - V_R \frac{\partial C_l}{\partial z}$$ [1.14]

where $D_R = D/R$ and $V_R = V/R$.

Application of the CDE to transport through repacked soil columns in lab tests, through relatively uniform soils, and for weakly reactive solutes has been fairly successful, but less successful for strongly adsorbing solutes and in naturally aggregated soils (Jury and Sposito, 1985). The simple approach outlined above does not take changes in geochemistry (i.e. pH and Eh) or nonequilibrium adsorption isotherms into consideration. Nielson et al. (1986) have reported that more advanced models can incorporate such effects. Some improvement has been observed when using two-site models, in which the adsorption term includes both equilibrium and first-order kinetic adsorption.

2.1.7 Sink Term

The loss of organic molecules from the soil-water system through microbial or chemical degradation in soil is the major contributor to the sink term. Extremely complex, these processes are affected by many environmental and soil conditions, as well as microbial growth and maintenance factors. However, as a first approximation, they can be described as a first-order decay process (Hamaker, 1972), in which loss is proportional to the mass of solute, M, or liquid concentration, C_l

$$dM/dt = - K_m \qquad [1.15]$$

$$dC_l/dt = -kC_l = \Phi_s \qquad [1.16]$$

Degradation does not affect convective transport, or therefore, average breakthrough time, but will shorten the end tail created by dispersion and diffusion since the solvent molecules at the tail have the longest time in which to be degraded. Plant uptake can also be combined into the sink term, but this is difficult to express mathematically because of the many environmental parameters and complex interactions involved in this process (Nielson et al., 1986).

2.1.8 Analytical Solutions to the CDE

Solving the CDE equation analytically, given an appropriate set of boundary and initial conditions, provides an exact solution for solute transport. Generally, only one-dimensional flow is considered since vertical transport is most common and of primary concern through the unsaturated zone. The dependent variable, C_l, can be expressed as a flux or resident concentration (Kreft and Zuber, 1978). The flux concentration is defined as the mass of solute passing through a cross-sectional area over an elementary time

interval; there must be flow of solute to calculate this concentration. It is an average concentration for the liquid collected by a porous cup solution sampler or measured using vertical TDR rods. In comparison, the mass of solute per unit volume of fluid contained in an elementary volume of the system, at an instant in time, is called the resident concentration. Dividing a soil core taken at an instant in time into discrete sections, and measuring the concentration in each section would provide the resident concentration.

For fertilizer or herbicide application, the solute is added at the surface as a narrow pulse. Solving equation [1.10] analytically for a spike of solute added over a very small time interval requires the use of the Dirac delta function, ($\delta(t)$). The Dirac delta function has properties of

$$\delta(t) = 0 \quad t \neq 0$$ [1.17]

and

$$\int_{-\infty}^{\infty} \delta(t)dt = 1$$ [1.18].

The initial and boundary conditions for the flux concentration include:

$$C_F(x,0) = 0 \text{ for} \qquad x > 0$$ [1.19]

$$C_F(0,t) = \frac{A}{Q}\delta(t)$$ [1.20]

$$\lim_{x \to \infty} C_F(x,t) = 0$$ [1.21]

where Q is the discharge (volume/time) of water crossing the surface area, A, upon which the solute is applied. For a semi-infinite medium the analytical solution of equation [1.10] is:

$$C_F(L, t) = \frac{(CT)L}{2\sqrt{\pi Dt^3}} \exp(-\frac{(L - Vt)^2}{4Dt})$$
[1.22]

where CT is the area under the C_F (z,t) curve and L is a specific depth (z) below the soil

surface where the flux concentration is measured. The equation can be written to include

sorption and degradation processes as well. The solution for the resident concentration is

a more complicated, 3-term equation first solved by Lindstrom and Boersma (1971).

2.1.9 Convolution for Layered Soils:

Vertical transport in a horizontally layered soil can be described by convolution

because equation [1.22] is linear (Shamir and Harleman, 1966; Jury and Roth, 1990). In

essence, the output from the bottom of the upper layer becomes the input function for the

next layer. Summing of the many spike inputs by a convolution integral at the boundary

between the two layers is required to account for all the solute passing the boundary over

time. Convolution provides a means of representing some heterogeneity in the soil, but

the soil and water conditions within a layer must still be constant.

Analytical solutions to the CDE provide a straightforward method for making

general predictions and answering simple questions related to solute transport. However,

the solutions are generally restricted to steady-state water flow conditions and certain

classes of heterogeneity which are rare in field situations. More complex, numerical

solutions based on these equations are required to simulate transport of solutes under

natural field conditions, as for the model LEACHM (e.g. Wagenet and Hutson, 1987)

used in this study. The analytical solutions are still useful in these instances for checking

the more rigorous, yet complicated numerical models.

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2.2 Turfgrass

Aside from agricultural applications, one of the major uses of pesticides and fertilizers is in turfgrass management, which includes lawns, golf courses, educational facilities, parks, cemeteries, and turf farms (Hodge, 1993). Turfgrass is valued for its aesthetic, recreational and robust properties. It provides low cost, safe, recreational surfaces for both sport and play. There has been a tremendous increase in turfgrass use over the past 40 years, spurred in part by the growing popularity of golf (Potter, 1993).

Turfgrass also has an important role in soil and water preservation. The high growth density greatly modifies overland flow, nearly eliminating runoff and promoting infiltration, which also reduces the flooding potential of sudden storms. It also increases evapotranspiration during the time it is biologically active (Fetter, 1994), which can reduce the amount of deep percolating water. The dense root system stabilizes the soil and thatch layer (accumulated dead grass material), providing ideal conditions for an active biological ecosystem. In return, the organisms living in the soil help create a healthier soil for turfgrass by increasing aeration, breaking down and mixing organic debris into the soil and degrading organic chemicals. The increased infiltration and biodegradation usually lead to increased amounts of clean water recharging the groundwater (Beard and Green, 1994).

One of the most important inhabitants of turfed soils is the earthworm; their burrowing increases aeration and water infiltration (Potter, 1993). These burrows, essentially single or interconnected macropores, can also act as primary flow conduits, providing rapid downward flow for solutes under ponded water conditions (Stehouwer et al., 1994). The material lining these burrows is enriched in organic carbon, and may significantly retard herbicide transport.

2.3 Dicamba

2.3.1 Pesticides in the Environment

A pesticide is a chemical that causes a toxicological effect in a biological organism, and generally has specificity toward a certain group of organisms. This allows people to restrict or eliminate undesirable species (pests) in favour of more desirable ones. Pesticides and fertilizers can also affect organic matter decomposition and nutrient recycling in turfgrass by altering primary production or impacting soil organisms (Potter, 1993). To remain beneficial, pesticides must stay on the plant or in the root zone; if they leave they can no longer perform their intended function (Flury, 1996). The loss of pesticide is a waste of money and resources, and can become an environmental and/or human health concern. Pesticide residue carried in runoff or in discharging groundwater can affect surface water species and their ecosystem. Groundwater contamination became a public issue in the late 1970's, but concern over pesticides in drinking water did not really begin until the early 1980's after several incidents of contamination from field applications were reported (Holden, 1986).

2.3.2 Pesticide Fate in Soil

Mobility and persistence, and factors that affect these two properties, will determine the potential of a pesticide to contaminate groundwater. Pesticides are applied to soil or turf as dilute solutions, as a solid that subsequently dissolves, or as a vapour phase. The fate of the pesticide once dissolved in soil water is depicted in Figure 2.1. Volatilization into the gas phase is rapid for a pesticide in a solid state, but slows once dissolved. Plant uptake can occur through the roots or the leaves; pesticides can be

subsequently stored, metabolized or exuded from the roots. They can also be broken

down into other compounds by microorganisms, via biodegradation, or through chemical

reactions. The process of sorption involves the attraction of a pesticide molecule to a soil

particle surface (adsorption) or inclusion into organic matter (absorption). It can be

permanent or a continuous process of adsorption and release. A portion of the pesticide

applied to the soil surface may leach with the infiltrating water to below the root zone

(Nash, 1988). All soils whether sandy, loamy, or clayey are susceptible to leaching,

though transport differs in each type of medium (Flury, 1996), based on the mode of water

movement and the pesticide-soil interactions outlined above.
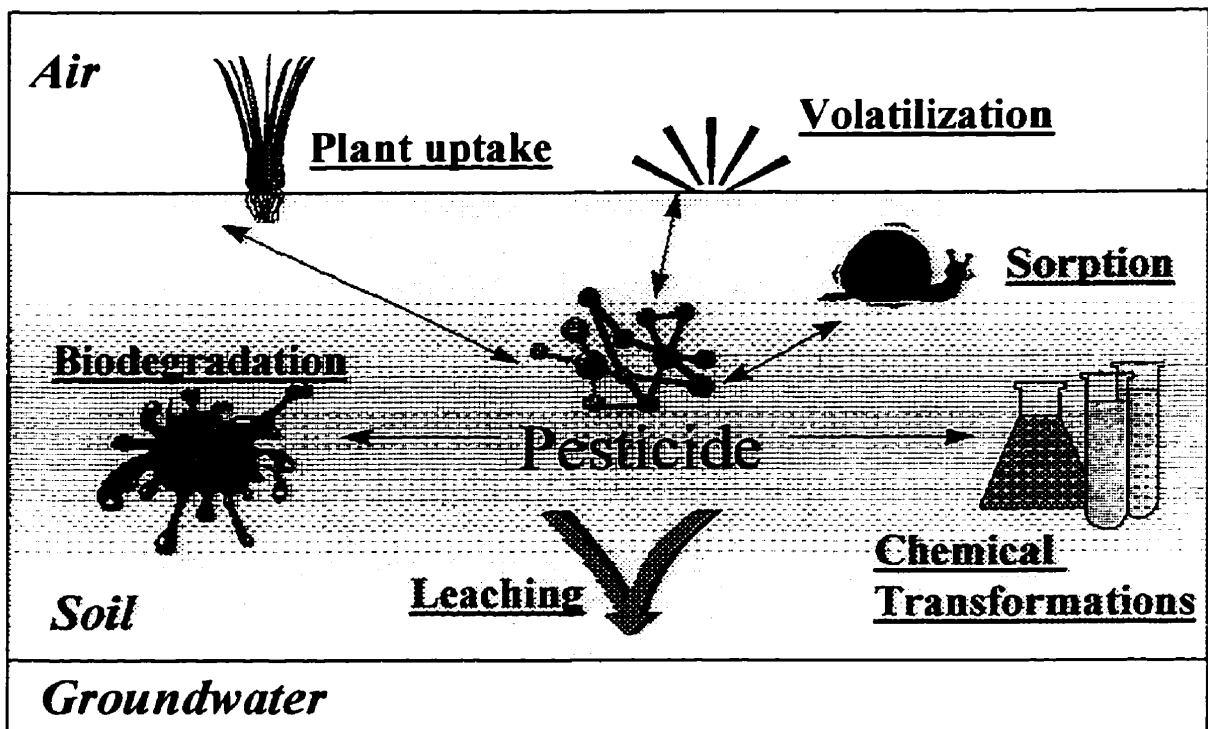
Fig. 2.1 A general diagram of the fate of a pesticide in soil. Bidirectional arrows indicate
processes where release back to the soil water is possible (adapted from Nash, 1988).

Dicamba is generally considered to have low persistence but high mobility under

normal soil-water conditions (Caux et al., 1993). The general trend for pesticides applied

to turf is a marked decrease in the amount leaving the root zone compared to bare or cropped soils, which suggests that mobility and/or persistence is reduced under turf.

2.3.3 Dicamba Properties

Dicamba, 2-methoxy-3,6-dichlorobenzoic acid, was introduced in the early 1960's as a postemergent herbicide specific to woody and broadleaf plants. It is synthesized from 1,2,4-trichlorobenzene, and generally exists as a water soluble alkali or amine salt. Structural formulas for dicamba and its primary metabolites are illustrated in Fig. 2.2;
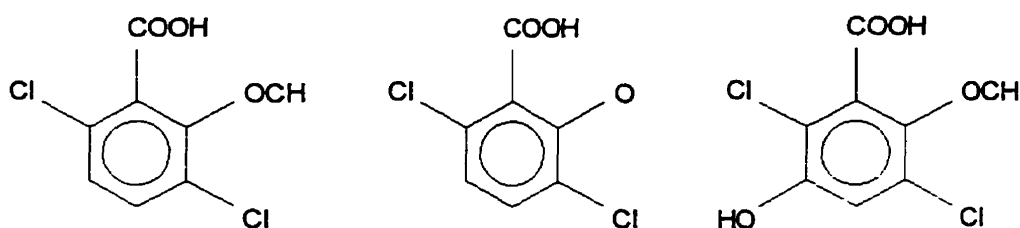
Fig. 2.2. Chemical structure of the herbicide dicamba, its primary metabolite in soil, 3.6-dichlorosalicylic acid (DCSA), and in plants, 5-hydroxydicamba (from left to right).

Table 2.1. Physical properties of dicamba as compiled by Caux et al. (1993).

Parameter	Value	Parameter	Value
Solubility	6.5 g L^{-1}	Henry's Law constant, K_h (20 and 25 °C)	0.12 and 0.154 mPa m^3 mol^{-1}
Molecular Weight	221.04 g mol^{-1}	Octanol-water partition coefficient, K_{ow}	2.2 - 3.0
Vapour Pressure (25 °C)	4.5 mPa	Organic carbon partition coefficient, K_{oc}	0.08 - 511 mL g^{-1}
Specific Gravity (25 °C)	1.57	Soil-water partition coefficient, K_d	0 - 0.9 mL g^{-1}
Melting Point	114-116 °C	Dissociation constant, pKa	1.95

many of its physical properties are listed in Table 2.1. Dicamba has a high solubility in water and exists as an anion in solution, so it will remain primarily in the water phase once in the soil, increasing the probability of transport through the soil profile. It is usually applied as a spray or in granular form. Upon application researchers believe it is rapidly absorbed by roots and foliar tissues, and translocated to other parts of the plant (Frear, 1976). It may be excreted from the roots in limited quantities. It is a plant growth regulator, as it resembles the natural plant growth hormone IAA (endogenous auxin), causing similar but uncontrolled growth (Ahrens, 1994). These reactions lead to abnormal growth and, subsequently, death. The selectivity of dicamba for certain plants is linked to the chemical's distribution within the plant, and in absorption, translocation and metabolism rates (Frear, 1976).

Pure dicamba is rarely applied. Generally a mix of herbicides and inert ingredients produces the best results for turf. The herbicide contents and brand names of some common mixes are listed in Table 2.2. Dicamba is added to 2,4-D mixes because of its ability to kill 2,4-D- tolerant weeds, especially knotweed, and its longer soil activity. In Ontario, these herbicide mixes are applied in the spring and in early autumn when weed growth is at its peak. It is recommended (Ontario Herbicide Committee, 1996) that the application be timed at least 3 - 6 hours before any rainfall and the turf not be irrigated, raked or mowed for at least 24 hours after application.

Dicamba has a moderate toxicity to mammals, with effects reported on the respiratory, neurologic, gastrointestinal, hepatic, urogenital and dermatologic systems

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Table 2.2. Some of the herbicide mixes containing dicamba are listed, including their contents and brand names (Ontario Herbicide Committee, 1996).

Ingredients	Brand Name
2,4-D, dicamba, mecoprop	KILLEX, TRICEP, KIL-MOR, PREMIUM 3-WAY TURF HERBICIDE, PAR III
dicamba	BANVEL 480, DYCLEER
dicamba, atrazine	MARKSMAN
dicamba, MCPA	DYVEL
dicamba, MCPA, mecoprop	TARGET

(Caux et al., 1993). The drinking water limits for dicamba are quite high for a pesticide, 200 μg L^{-1} set by the USEPA and 120 μg L^{-1} in Canada (Caux et al., 1993). Of the few tests done, none have shown indications of carcinogenicity (USEPA, 1989), though there is insufficient information available to be certain (Caux et al., 1993).

Widely used in the prairie provinces and Ontario, dicamba was one of the ten most highly used herbicides in Canada, as reported in 1988 (Caux et al., 1993). It is applied to both agricultural and noncropland (pastures, rangeland, forest lands, roadsides, railways and turf) areas.

Dicamba has been detected in a number of groundwater sampling studies. In the Delmarva Peninsula, northeast U.S.A., 100 wells were sampled in 1988-90; dicamba was one of the most common pesticides detected, though few samples exceeded 3 μg L^{-1} (Koterba et al., 1993). Additionally, dicamba contaminated groundwater has been reported in 17 states in the U.S.A. (Cox, 1994). In Europe, Funari et al. (1995) calculated (based on 7 data sets) that dicamba was found in groundwater in approximately 1 % of the

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analyzed samples. The mean concentrations were between 0.17 to 0.6 μg L^{-1}, with maximum values of 1.1 to 320 μg L^{-1}, averaging 6.9 μg L^{-1}. Based on studies in Canada, compiled by Caux et al. (1993), 8 % of the surface water and 2 % of the groundwater samples proved positive for dicamba. Broad groundwater monitoring schemes may not be the most reliable method of determining the extent of contamination from dicamba because it can be difficult to detect, due to the small mass added per area of soil surface. Specific to turfgrass, Cohen et al. (1990) tested the groundwater under various golf courses and detected dicamba in one of the sixteen monitoring wells.

2.3.4 Dicamba and Other Pesticides in Turf

In an experiment on golf green turfgrass, Smith et al. (1993), applied 2,4-D in a split application of 0.56+0.56 kg a.e. (acid equivalent) ha^{-1} over two weeks to lysimeters packed with a varied sand/peat mixture. The lysimeters received a daily irrigation of 0.625 cm and a weekly rain event of 2.54 cm. Only trace amounts (below 5 μg L^{-1}) of 2,4-D were detected in the effluent, collected 15 cm below the surface. More recently, Smith and Bridges (1996) applied 2,4-D, dicamba and mecoprop to lysimeters in a greenhouse and in the field (Georgia), again simulating golf green conditions. The highest concentrations of dicamba detected in the effluent were 3.6 μg L^{-1} and 2.6 μg L^{-1}, for indoor and outdoor conditions, respectively. Less than one per cent of the applied dicamba was collected in the leachate during the study period, though there was significant loss in runoff from the sloped site. Herbicide application took place in November for the first study, and in July for the second.

The leaching and dissipation of 2,4-D and dicamba from a suburban lawn were measured in field plots of silt loam or sandy loam, overlying highly permeable sand and gravel by Gold et al. (1988). Leachate was sampled at 0.2 m, where the soil texture changed. The herbicides were applied either three times (April, June, September) or once (just June) per year over two years at a dose of 1.1 and 0.11 kg ha^{-1} at each time for 2,4-D and dicamba, respectively. The plots received natural precipitation and either minimal irrigation, to avoid drought, or 37.5 mm per week. Generally, the herbicide concentrations in the leachate were low; for dicamba 95% of the samples were under 1 μg L^{-1}, but 2 % were over 10 μg L^{-1}. The plots receiving less irrigation and only the June application had the highest concentrations. These results may be explained by dilution from overwatering and microbial acclimation from more periodic application. There was also a tendency for higher concentrations to remain in the autumn, compared to the summer.

In an extension of the study outlined above, dicamba was found to dissipate more rapidly in home lawn turf than corn plots (Gold and Groffman, 1993). In a similar study conducted in growth chambers, Branham et al. (1993) observed a decreased persistence of isazofos in turf compared to the same soil without turf four weeks after application; 5% and 13% remained in each, respectively. Starrett et al. (1996) studied the fate of isazofos, chlorpyrifos, metalaxyl, and pendimethalin applied to turf in leachate and found 6.3, 0.5, 7.7 and 0.2 % of each herbicide, respectively, under heavy irrigation regimes and 0.4, 0, 0.2 and 0 % of each herbicide, respectively, under light irrigation. The calculated half-lives in turf were shorter than those reported in the literature for row crops. All three

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research groups attributed this difference to higher microbial activity under turfgrass conditions.

Relatively high concentrations of dicamba were reported in a runoff/percolate field study of pesticides and fertilizer on sloped turf over a clay topsoil (Harrison et al., 1993). Dicamba was applied at 0.28 kg ha^{-1} five times during the year: in July, August, September, October, and November over 2 years. The maximum concentration found in pan lysimeters at 15-cm depth coincided with the first major irrigation or rainfall events within a week after application. The mean concentrations for dicamba for these events were 11, 21, 22, 118, 57 μg L^{-1}, although the irrigation events were considered extreme. Runoff values were much smaller, with maxima of 24 to 4 μg L^{-1}.

The results of another study (Petrovic et al., 1994) add further support to the postulate of increased degradation occurring within turfgrass. The fungicide triadimefon was applied in the autumn to sandy, turfgrass lysimeter plots. The detection of the metabolite triadimenol in the leachate, and rarely the parent compound, suggests a high rate of degradation. However, its rapid appearance in the leachate and continued detection up until early June of the next year could indicate preferential flow through earthworm burrows and a decline in degradation and transport rates over the winter months.

2.3.5 Mobility in Soil

2.3.5.1 Water Flow

Since a dissolved solute, such as dicamba, must move with the water, those factors affecting water transport must be considered when addressing the problem of leaching.

The effect of the initial water content on pesticide transport seems dependent on soil

texture. From Flury (1996): "There is evidence that the effects of the water content

depend on soil texture: under dry soil conditions, sandy soils tend to show less leaching,

whereas loamy and clayey soils show more leaching when exposed to a strong rainfall

shortly after pesticide application." For loam and clay soils dryness can promote the

development of desiccation cracks and fissures in the soil.

The effect of precipitation on pesticide leaching is not straight forward either.

Increased leaching with increased precipitation has been observed by Troiano et al. (1993)

for atrazine in loamy sand, by Pearson et al. (1996) for dicamba in silt loam, but not for

dicamba in silty, clay loam (Hall and Mumma, 1994). Instead Hall and Mumma found that

the dicamba losses were related to individual precipitation events of a sufficient amount

and intensity to cause leaching, especially when they occurred soon after application. This

same effect was reported again by Harrison et al. (1993).

In a modeling exercise, Haan et al. (1994) used a weather simulation model,

WGEN (Weather Generator), to simulate possible weather sequences in order to

investigate the effects on solute transport. There was considerable variability in pesticide

travel times through the soil. Travel times were strongly affected by the sequence of

precipitation events and single daily events.

Preferential flow was evident in a pesticide leaching experiment with a clayey soil

(Tindall and Vencill, 1995) using atrazine, dicamba and 2,4-D. Each moved rapidly

through the soil and at the same rate, even though 2,4-D tends to adsorb more strongly

than the other two pesticides. In this same study, there was also an indication that

dicamba, adsorbed or trapped in dead-end pores of the matrix, may become mobile later

on, especially during flushing after large rainfall events. Hall and Mumma (1994) made similar observations, as dicamba was leached after large rainfall events even six months after application.

2.3.5.2 Sorption

Most studies have found that dicamba is not readily sorbed to soil particles, regardless of the soil type, during normal soil water conditions. Sorption is strongest at lower pH levels (4-6), and minimal above a pH of 6, primarily due to the dominance of negatively charged soil surfaces at higher pH values (Frear, 1976). Both Krzyszowska and Vance (1994) and Pearson et al. (1996) found that dicamba travel times were similar to non-adsorbing tracers. Batch and flow studies indicated no increase in dicamba sorption on the enriched organic content of earthworm burrow linings (Stehouwer et al., 1994). Pearson et al. (1996) also noted that, at the end of their experiment, dicamba was only found below 0.4 m, while the metabolite 3,6-dichlorosalicylic acid (3,6-DCSA) was found primarily in the top 0.2 m. Smith (1974), using soil slurry adsorptive studies, found at least 30 % of 3,6-DCSA sorbed to three different soil types, and fit a linear adsorption isotherm to the data.

The retardation factor for dicamba, measured in an experiment by Comfort et al. (1992), ranged from 1.03 to 1.18 in a variety of clay soils. The adsorption coefficients compiled by Caux et al., (1993) included 0.078, 2.0, 2.2, 3.8, 50 and 511 mL g^{-1} for K_{OC}, and 0, 0.08, 0.07, 0.9 and 0.11 mL g^{-1} for K_d, which are generally quite small, suggesting little sorption to soil. The exception involves the adsorption of dicamba to kaolinite clay, which has considerable anion adsorption capacity. Burnside and Lavy (1966) measured a

K_d value of 3.6 mL g^{-1} for pure kaolinite clay, at a pH of 4.7. The variability in K_{oc} could be the result of different experimental methods. Another possibility is the $K_{oc} = K_d / f_{OC}$ relationship may not hold under all conditions (Caux et al., 1993).

In two recent studies, researchers have investigated the sorption of dicamba in the thatch layer of turfgrass. Baskaran et al. (1997) looked at the sorption and movement of 5 pesticides (atrazine, chlorpyriphos, diazinon, dicamba and 2,4-D) applied to golf green materials (a sand/peat mixture and thatch). In the batch sorption study, dicamba sorbed the least (lowest K_d), and in the column leaching study it was the most mobile, moving at the same rate as the water. The calculated K_d was 0.54 mL g^{-1} for rooting material and 3.29 mL g^{-1} for thatch. Similarly, Raturi et al. (1997) found increased dicamba sorption to zoysia (*Zoysia japonica* Steud.) and hard fescue (*Festuca longifolia* Thuill) thatch compared to the soil below, using a modified batch/flow technique. Adsorption was greatest and fastest for hard fescue thatch, with 30.7 % of the herbicide adsorbed compared to 24.6% for Zoysia thatch and around 10 % for soil, possibly because of its lower pH or higher degree of decomposition. No significant difference between concentrations was observed. However, adsorption increased with greater residence times, taking up to 16 hours to reach equilibrium. The researchers suggest that sorption of dicamba may be more prevalent in turfed soils because of the adsorption to thatch.

2.3.6 Persistence in Soil

2.3.6.1 Volatilization

Although vapor pressures of most pesticides, including dicamba, are low, Behrens and Lueschen (1979) observed dicamba symptoms on soybean plants placed 60 m

downwind of a corn plot where dicamba was applied. Smith et al. (1993) noted that the loss of pesticide via volatilization and photo-oxidation can be enhanced if it is trapped in the turf canopy. Applying dicamba in solution rather than in solid, granular form may reduce this loss, however. Behrens and Lueschen (1979) observed reduced volatilization in the field after a rainfall event. In the laboratory they found that 1 mm or more of simulated rain nearly eliminated subsequent foliar injury to nearby soybean plants.

2.3.6.2 Degradation

The dissipation of dicamba in soil is largely due to microbial degradation (Burnside and Lavy, 1966; Smith, 1974). Dicamba is essentially stable, resisting oxidation and hydrolysis, under normal conditions (Ahrens, 1994). The main degradation product in soil is 3,6-dichlorosalicylic acid (3,6-DCSA), a less mobile and more persistent species (Smith, 1974; Pearson et al., 1996). Dicamba has also been found to degrade to 5-hydroxydicamba, mostly in plants, though both metabolites degrade to 2,5-dihydro-3,6-dichlorobenzoic acid and eventually to carbon dioxide (Caux et al., 1993).

The amount of degradation in soil is highly variable and depends on a number of factors, including application rate, soil moisture content, temperature, pH and organic matter content (Caux et al., 1993). These factors can affect the rate and type of microbial growth and activity (Table 2.3). Some microbial species utilize a contaminant as their sole carbon source, while others may produce enzymes for other food sources, but can also degrade the contaminant - a process called cometabolism (Atlas and Bartha, 1993). If the pesticide has been applied to the area in the past, biodegradation may be enhanced upon subsequent applications (Skipper et al., 1996). Based on a review of the literature,

Comfort et al. (1992) found dissipation rates for dicamba in soil varying from 2 to 12 weeks, which is in general agreement with the studies cited in this thesis.

The soil moisture content is important for microbial growth, as it determines the amount of water and air available. Starrett et al. (1996) observed that a light irrigation seemed to enhance degradation compared to a heavy irrigation. In a study on chlorpyrifos degradation, the highest percent mineralization occurred at field capacity (0.3 bar), with less degradation occurring at much drier (3 bar) and much wetter (0.03 bar) conditions (Cink and Coats, 1993).

Table 2.3. Half-lives of dicamba in soil, for various soil conditions, as reported in the literature.

Half-life (days)	Temperature (°C)	Soil Type(s)	Moisture‡	Study
17-32 (25 average)	24 day, 18 night	forest, grassland		Altom & Stritzke, 1973
<10	15, 25, 35	silty clay loam	80% f.c.	Burnside and
1 - 2 months	15	silt & sandy loams	" "	Lavy, 1966
<10	25,35		" "	
>4 months	15,25,35	silty clay loam	13 % f.c.	
23.5	28	clay soil	$0.255\ m^3 m^{-3}$	Comfort et al.,
38	20	" "	" "	1992
151	12	" "	" "	
13.5†	room (~23)	" "	" "	
31	25	Kenyon loam	unsaturated	Krueger et al.,
58	" "	" "	saturated	1991
10 - 17†		rangeland (Borollic Haplargids)		Krzyszowska and Vance, 1994
<21	25	heavy clay	f.c.	Smith, 1973
<1.5 weeks	25	silty clay, heavy clay & sandy loam	f.c.	Smith, 1974
16	20	clay & sandy loams	85% f.c.	Smith, 1984
50	" "	heavy clay		

† indicates a column study, the remainder being batch studies
‡ f.c. = field capacity

The effect of oxygen availability, and therefore, the degree of water saturation of the soil, on pesticide degradation is not clear. Krzyszowska and Vance (1994) determined that dicamba dissipation in soil was similar under saturated, $t_{1/2}$ = 15 days, and unsaturated, $t_{1/2}$ = 17 days, conditions. Whether the saturated columns were truly anaerobic remains a question. Krueger et al. (1991) compared anaerobic and aerobic conditions in batch systems for the study of dicamba degradation. Though metabolism was similar, the observed half-lives were 31 days and 58 days for aerobic and anaerobic conditions, respectively. The main metabolite was 3,6-DCSA, though low levels of 2,5-dihydro-3,6-dichlorobenzoic acid were also detected.

The amount and type of vegetative cover will have an effect on the microbial community in the soil. Dicamba was slightly less persistent in soil under grassland than under forest, even though the soil physical characteristics were similar (Altom and Stritzke, 1973). Many researchers (Gold and Groffman, 1993; Branham et al., 1993; Starrett et al., 1996) have reported increased degradation under turf compared to agricultural or bare soils, which may be related to increased microbial activity.

A decrease in degradation rate with depth, most significant between A and B horizons, and with decreasing temperature was observed by Veeh et al. (1996). It was also noted that the microbial population decreased with depth, which correlated with a decrease in the percentage of organic carbon. Temperature had a similar effect on dicamba degradation in a batch study by Comfort et al. (1992), with measured half-lives of 23.5 days at 28 C, 38 days at 20 C and 151 days at 12 C.

Abnormally high concentrations of pesticide can occur due to spillage. In the Schoen and Winterlin (1987) study of factors affecting pesticide degradation, pesticide

concentration was a more important factor than was soil type, pH, water content, percentage of organic matter and microbial activity. Similarly, concentration had the greatest effect on chlorpyrifos degradation in soil, as a high initial concentration reduced the degradation rate (Cink and Coats, 1993).

2.3.7 Plant Uptake

Plant uptake and metabolism can affect the movement and persistence of a herbicide, but there are indications that simulation models do not account for this process very well. Dicamba is rapidly absorbed by roots and foliar tissues and translocated to other parts of the plant, but the rate of these processes depends on the plant species (Frear, 1976). It can then be metabolized or exuded from the plant, via the roots or leaves (Caux et al., 1993). In soybeans for example, most of the ^{14}C-dicamba applied to the leaves was absorbed. Of the absorbed dicamba, most (about two-thirds) was exuded into the nutrient solution (Petersen et al., 1985).

Al Khatib et al. (1992) reported that pea, alfalfa, and grape plants absorbed between 65 to 95 % of the dicamba from solution. However, these same plants only absorbed 0.4 to 4.7 % of the herbicide from a soil treated with dicamba that was applied directly to the leaves. Absorption and translocation varied significantly between species, with no observable correlation between the processes. Morton et al. (1967) reported a half-life of two weeks in several grass species, but whether the loss of dicamba was due to metabolism or exudation was not determined.

The amount of pesticide absorbed by leaves will also be dependent on the amount of time it remains in contact with them. Wash-off from leaves by rain or irrigation can

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reduce absorption, delivering more of the pesticide to the soil surface. An average of 66 % of the dicamba applied to turfgrass at 0.6 kg ha^{-1} was present on foliage before a rainfall event 18 to 48 hours after application (Carroll et al., 1993). This reduction could be attributed to vaporization or absorption, assuming the plants intercepted all of the herbicide. Rainfall decreased retention by the leaves; 8 mm of rain removed half of the dicamba measured on the leaves, but nearly one-third still remained after 50 mm of rain. These results suggest that a significant amount of dicamba may not reach the soil, and that only a small amount of rainfall is necessary to wash off at least half of the herbicide remaining on the foliage.

2.3.8 Application Time

The time of year for application will likely have a strong effect on the leaching of dicamba in Canada. The distinctness of the seasons provides a wide continuum of environmental conditions, which, as described previously, will affect a pesticide's mobility and persistence. Precipitation, hours of daylight, wind, soil water content and temperature vary from season to season; this variability in turn will affect plant growth, microbial activity, and water transport. The burrowing effect of earthworms on the macropore network is also seasonal, as they are more active at the surface during the early spring and autumn (Potter, 1993).

Seasonal effects on leaching patterns from turfgrass have been observed, an effect attributed to reduced plant uptake and evapotranspiration when the grass is in a state of dormancy during the winter months. For example, in Sweden there are two main drainage periods consisting of late autumn/early winter and late winter/early spring, with very little

drainage at other times of the year (Bergström, 1996). In a modeling exercise, Boesten and Linden (1991), concluded that the season when the pesticide was applied had a large effect on the leaching of pesticides with low sorption and half-life, which accurately describes dicamba. For this type of pesticide, the model predicted the fraction leached to be 0.1 % following spring application and 20 % following autumn application.

2.3.9 Summary

Boesten (1991) used a mathematical model to analyze the importance of different factors to the process of pesticide leaching. The fraction of pesticide leached was most sensitive to the sorption variables (K_d and the Freundlich exponent N), as well as the transformation rate in soil. All are key factors of a pesticide's mobility and persistence. Leaching showed moderate sensitivity to the temperature effect on the transformation rate and the weather conditions, important considerations for the Canadian climate. Plant uptake was found only to be important for poorly sorbed pesticides, such as dicamba. The time of application, autumn versus spring, was very important for non-sorbing pesticides with short half-lives, such as dicamba. Due to the many factors involved, it is likely that the transport of dicamba applied to turf under Canadian conditions will be a complex matter, worthy of further research.

2.4 Nitrate

2.4.1. The Fate of Fertilizer N

Nitrogenous fertilizers are applied to turf to ensure that the lack of combined nitrogen, an essential nutrient, does not limit plant growth. The fate of the nitrogen when

applied to turfgrass is a function of plant uptake, atmospheric loss, soil storage, leaching and runoff. Since these other processes will control the amount of N available for leaching, some discussion of each is necessary. Petrovic (1990) made a thorough review of this subject, so I will only deal with his conclusions in this section.

Plant uptake of 5 to 74 % of the fertilizer nitrogen applied has been reported. It is highly dependent on the soil temperature and water content, the type of fertilizer, the available nitrogen pool, and the plant species. In addition, the percent recovery was observed to increase with an increasing application rate, up to an optimum level, before declining.

Ammonia volatilization and denitrification are the main pathways for atmospheric loss of nitrogen, and are affected by soil conditions such as temperature, pH, and water content. The application rate, type of fertilizer and its form at application (dry/wet) are also important factors. Losses from 0 to 93 % have been reported. The presence of thatch, which has substantial urease activity, can greatly increase ammonia volatilization from turf as long as the fertilizer remains in that layer.

After application, fertilizer N can also be stored in the soil in inorganic or organic form. Soil microbes must first convert organic nitrogen to an inorganic form before it can be taken up by plants or transformed to gaseous compounds, a process highly influenced by the form of the N, temperature and moisture. A key component of storage of N in the soil is incorporation into organic matter. The amount of storage is dependent on the size of the organic matter pool, which tends to increase under newly established turf, over a number of years, until equilibrium is reached. Thus, the soil has a limited capacity for fertilizer N storage.

Few researchers have investigated the loss of fertilizer in runoff from turfgrass, but generally very little runoff has been observed because of the high infiltration capacity of turfgrass soils. Leaching of 0 to 80 % of the applied N has been reported, though most values are below 10 %. The main factors influencing leaching of N are soil type, irrigation practices, N source, application rate and season of application. Nitrate leaching is a complex process however, with which researchers continue to grapple.

2.4.2. Nitrate Leaching

Nitrogenous fertilizers may contain nitrate (NO_3^-) or other simple, nitrogenous compounds, such as ammonium. Nitrate exists as an inorganic anion in solution and does not sorb to soil solids very readily, which is why it is often used in soil and groundwater studies as a conservative tracer. This means that it generally flows at the same rate as the water and will serve as an easy means of monitoring water flow. Ammonium exists as an inorganic cation in solution, and is more strongly held to soil surfaces. In the soil, the process of nitrification often occurs; aerobic bacteria convert ammonium (or other reduced forms of nitrogen) to nitrite, then nitrite to nitrate. Different types of bacteria perform each step, but the groups are so closely linked that nitrite rarely accumulates (Atlas and Bartha, 1993).

The potential for nitrate leaching following fertilizer application to turfgrass is an environmental concern. The loss of N from the root zone means a loss to growing plants, a waste of the energy used to produce the fertilizer, and possible groundwater contamination (Starr and DeRoo, 1981). Contaminated groundwater can discharge to surface waters, where nitrogen is a limiting nutrient, via springs or baseflow, and can

cause eutrophication. High nitrate levels in drinking water are also a human health threat, causing methemoglobinemia in infants less than 6 months of age, which can lead to death, and possibly promoting certain cancers (Canter, 1997). As a result, the maximum concentration limit (MCL) for drinking water was set at 10 mg L^{-1} nitrate-N (Spalding and Exner, 1993).

Currently, nitrate is the most ubiquitous chemical contaminant in the world's aquifers, and levels are increasing. The levels in groundwater exceed the MCL in several agricultural areas in southern Ontario (Gillham, 1988; Goss et al., in press). In a recent study of Ontario sod farms by Thurtell (1997), 10 of the 86 water samples taken from tile drains or piezometers contained nitrate-N at 10 mg L^{-1} or greater, with an overall average 3.74 mg L^{-1}. In the midwest U.S., of nearly 35,000 wells tested 3.4 % exceeded the MCL, 10.4 % ranged in concentration from 3-10 mg L^{-1}, and 23 % exceeded 1 mg L^{-1} (Richards et al., 1996). Unfortunately, the available treatment technology has limitations, so communities with contaminated drinking water are usually forced to find new sources of water (Spalding and Exner, 1993).

The levels of nitrate within the soil or in groundwater can be reduced naturally by soil or aquifer microorganisms that mediate the transformation to gaseous N compounds. This process occurs within anaerobic zones, where nitrate can be used as the terminal electron acceptor in place of oxygen (Atlas and Bartha, 1993). The two nitrate-reducing pathways are denitrification and dissimilatory nitrate reduction to ammonia (DNRA):

Denitrification:

Nitrate (NO_3^-) → Nitrite (NO_2^-) → Nitric Oxide (NO) → Nitrous oxide (N_2O) → Dinitrogen gas (N_2)

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<u>DNRA</u>:

Nitrate (NO_3^-) → Nitrite (NO_2^-) → Ammonia (NH_3)

The two pathways involve different groups of microorganisms, but generally only the denitrification process is significant in terrestrial soils (Nijburg et al., 1997). Conditions that control denitrification include the dissolved oxygen concentration and the electron donor availability (Spalding and Exner, 1993), and indirectly, the groundwater flow rate. In a laboratory study, Montgomery et al. (1997) observed reduced nitrate concentrations exiting a soil column when the flow rate was decreased. A low flow rate would allow for a longer residence time and greater oxygen depletion in the column, resulting in more nitrate reduction.

As stated previously, Petrovic (1990) found the degree of nitrate leaching to be highly variable. For example, Starr and DeRoo (1981) observed little leaching of nitrate to the saturated zone, 2 m below turf. Although the grass took up 20 - 35 % of the applied N in the first 2 to 3 weeks after application, the rate of uptake quickly dropped off. This suggests the remaining nitrate was either immobilized in the thatch and soil or transformed. Dowdell and Webster (1980) reported mean nitrate concentrations ranging from 4 to 16 mg-N L^{-1} in the leachate collected from lysimeters. The use of ^{15}N-labeled nitrate enabled the identification of fertilizer N, which made up the majority of N in the leachate. The amount of N leached varied considerably between lysimeters, possibly due to differences in grass uptake or infiltration amount.

In his review, Petrovic (1990) analyzed 12 studies from 1974 to 1988 on N leaching from turfgrass, and identified several factors that influence the degree of leaching: soil type, irrigation, N source, N rates, and season of application. As the conditions for

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each factor can be variable, and the effect of one factor alone on leaching may be dependent on the conditions of many other factors, it is often difficult to compare the results of different experiments or draw general conclusions from a single experiment. This complexity may be one reason why a full understanding of nitrate leaching from turf continues to be evasive.

2.4.3 Rate of Application

For matured turf, Brauen and Stahnke (1995) found the rate of application was the most significant factor for nitrate leaching after fertilization. The trend of increased leaching with increased application rates seems logical, but really only becomes significant when there is more nitrogen available than the grass can use. In a monitoring survey of sod farms, Thurtell (1997) noted the nitrate-N concentrations in soil solution at a 60-cm depth ranged from less than 2.5 to 22.7 mg L^{-1}, but only surpassed 10 mg L^{-1} when fertilized over the recommended rate for Ontario (160 kg-N ha^{-1} $year^{-1}$). In an associated field plot experiment, few samples at a 60-cm depth surpassed 10 mg L^{-1} for the recommended rate of application, but doubling the rate resulted in very high concentrations.

Similarly, Hardt et al. (1993) observed that the amount of nitrate in leachate samples was consistently low for the 20 and 40 g N m^{-2} yr^{-1} applications, but increased significantly at 80 g N m^{-2} yr^{-1} for organic and soluble fertilizers. Concentrations over 200 mg L^{-1}, up to 862 mg L^{-1}, were observed at this high rate. Duff et al. (1998) applied urea-N at 0, 10.3, 18 and 25.7 g m^{-2} yr^{-1} over 5 applications to established Kentucky bluegrass turf over a fine, silty loam. Again, only the highest rate resulted in concentrations over 10

mg L^{-1} at 60-cm depths. Increased leaching was even measured for slow-release sources

applied to Bermudagrass over a sand soil, as up to 5.5 % of the fertilizer leached (Snyder

et al., 1981).

2.4.4 Fertilizer Type

Generally, more nitrate leaching occurs when soluble organic and inorganic

fertilizers are used, compared to slow-release fertilizers, such as sulfur-coated urea (SCU).

Hardt et al. (1993) compared leaching from golf greens using slow release, organic and

soluble N-fertilizers. Leaching at 80 g N m^{-2} $year^{-1}$ from lysimeters was only significant

for horn meal and ammonium-sulfate fertilizers. Brown et al. (1982) observed much more

loss using ammonium nitrate than urea formaldehyde, Milorganite, and isobutylenediurea.

Similarly, in comparing soluble and slow-release sources on sand soil, Snyder et al. (1981)

reported that at a rate of 8 g N m^{-2} more nitrate leached using calcium nitrate, about 9.3 %

of applied, compared to slow-release fertilizers, at less than 5.5 % of applied. The slow-

release fertilizers generally produced better quality turf as well.

2.4.5 Soil Type

The texture of a soil can affect nitrate leaching from turfgrass because of its

influence on water flow, denitrification and ammonium adsorption (Petrovic, 1990).

Generally, course-textured soils such as sands are more prone to infiltration than fine-

textured soils, especially with regular rainfall or irrigation. Petrovic (1995) found that

only 2 of 1385 samples collected at 15 cm below the turf from sand, sandy loam and silt

loam soils, were over 10 mg L^{-1}, and those two were in sand.

Modifications to sand soils, such as the addition of peat for golf course greens, can alter the leaching process as well. Brauen and Stahnke (1995) observed that adding peat greatly reduced the total amount of N leached. However, greens composed of a sandy loam soil showed less leaching than even a modified sand (Brown et al., 1982). Approximately 23 % of the fertilizer leached from sand/peat greens compared to about 10 % for the sandy loam soil. The nitrate also took longer to reach tile drains from the soil green compared to the modified sand.

Indications of preferential flow influenced by soil type have also been observed. Webster and Dowdell (1984) measured greater losses of nitrate from clay loam than silt loam soils. The highest losses occurred when a drought was imposed for 4 weeks prior to fertilizer application, a condition favorable to crack formation.

2.4.6 Irrigation

Although some turfgrass species, such as Kentucky bluegrass, can go dormant in order to survive hot and dry conditions in the summer, maintaining the lush, green appearance of turf during these times requires irrigation. However, while maintaining the plants, irrigation water can also infiltrate below the rootzone, carrying nitrate along with it. Thurtell (1997) determined the water input rate to have a significant, positive effect on the amount of N leached below turfgrass in field plots. Leaching was also enhanced by the salinity of the irrigation water, and plant exacerbation by drought or heat stress. Such conditions increased leaching from 5 % of the applied N to 30-100 % in a study by Bowman et al. (1995). Irrigation of 640 mm during a 34 day study period, carried as much as 95 % of the ammonium-nitrate below the rootzone, to an average depth of 1.2 m

at the end of the study by Exner et al. (1991). High, uniform nitrate concentrations in the

unfertilized plot indicated that excessive irrigation alone could cause nitrate leaching.

2.4.7 Season/Time of Application

Dowdell and Webster, (1980), Hardt et al. (1993), Brauen and Stahnke (1995),

and Jabro et al. (1997) noted the trend of increased nitrate leaching from fertilizers in the

autumn and winter months, with lowest concentrations of nitrate in infiltrating water in the

summer. This effect has been attributed to changes in plant uptake and evapotranspiration

between summer and autumn/winter. However, Miltner et al. (1996) measured nitrate

levels in leachate rarely exceeding 1 mg L^{-1}, from both spring and autumn applications of

urea, while (Geron et al., 1992) recorded the highest concentrations from urea during late

summer and early autumn. While testing the effect of application rate, Duff et al. (1998)

observed greater nitrate concentrations in infiltrating water in the summer with a relatively

low urea application rate, although a greater percentage of the fertilizer-N leached in the

autumn. Climatic conditions also affected leaching on an annual basis. From the highest

application treatment, 7.5 % leached in the cool, wet year, while 20 % leached in the

warm, dry year. A higher transformation rate from urea to nitrate under the warmer

conditions, and decreased root uptake due to heat stress, were given as possible causes for

both observations.

The time of application with respect to the establishment of turf is also an

important factor. Leaching from seeded turf was greater than leaching from sodded turf

for the first few months after planting in a lysimeter study by (Geron et al., 1992). After

developing a deeper and denser root system though, the seeded turf prevented leaching more effectively than the sodded turf.

2.4.8 Herbicide Interactions

Although herbicides are rarely concentrated enough to be toxic to soil microorganisms, they can adversely affect the soil microbial community (McColl, 1987). Using a forest soil, Amakiri (1977) illustrated that some herbicides can alter microbial growth patterns, causing both inhibition and stimulation as compared to a control. The effects were different between type and concentration of herbicides and the time of sampling after application. It is important to note that these effects describe the entire community and not individual microbial populations. However, in the same study, *Nitrosomonas* was observed to be more sensitive to the herbicides than *Nitrobacter*, though both were initially inhibited. Such an effect could have implications for nitrate leaching and nitrogen cycling within soil. In a review of the literature, (Dhanaraj, 1988) reported mixed results, finding that dicamba could inhibit, stimulate or have no effect on nitrification. Work with other pesticides has illustrated that the soil and climatic conditions are intricately involved in the type of response. No studies were reported on the impact of dicamba on denitrification, though high concentrations are required for most pesticides to elicit an effect.

2.4.9 Summary

The leaching of nitrate from fertilizers applied to turfgrass is a complicated issue because of the large number of factors that can influence this process. Generally, there is

little threat from fertilizing turfgrass if the timing and rate of application of a particular

fertilizer are managed properly for the specific conditions of a given site (Petrovic, 1990;

Hardt et al., 1993; Starrett and Christians, 1995; Duff et al., 1998). Continued research

into the long-term effects of various fertilizer programs is still required.

2.5 Modeling

A predictive approach is essential for preventative interventions. The need for

prevention and for predictive *a priori* approaches was recognized not only by the scientific

community, but also by politicians and legislators (Vighi and Di Guardo, 1995). The

complexity of predictive tools ranges from leaching indices based on pesticide properties,

which are simple to apply and interpret, e.g. GUS – Groundwater Ubiquity Score

(Gustafson, 1989), to computer models that attempt to consider all important processes

simultaneously, and integrate them through a modeling approach to simulate transport

through the soil, e.g. LEACH (Wagenet and Hutson, 1987). Predictive models are also

useful for enhancing the understanding of chemical transport behaviour and for guiding

further research efforts (Rao et al., 1988). The more complex models are less applicable

to large-scale problems though, due to the difficulty in obtaining precise input data over

large spatial scales, and due to varying environmental conditions. Simpler models require

fewer parameters and, therefore, give less precise results, but are more versatile over

larger, non-homogeneous areas. As the cost of experimentation has gone up, the cost of

computation has gone down, making computer models increasingly popular. However,

collecting data from the field is essential for the validation and improvement of the

predictive capability of environmental models, and is often lacking (Vighi and Di Guardo, 1995).

2.5.1 Screening Tests

Screening tests are the most basic tool used for determining the probability of pesticide contamination of groundwater. They are based upon pesticide physico-chemical characteristics that are common in the scientific literature or are easily determined in the lab. Screening tests provide a general indication of how the pesticide will react in soil. The Groundwater Ubiquity Score (GUS), developed by Gustafson (1989), is based on a graphical examination of a plot formed by two widely available pesticide properties: half-life in soil and the partition coefficient between soil organic carbon and water (K_{oc}). It is preferable if the values can be derived in the field, but lab measurements are often used. The plot area is separated into "leachers" and "nonleachers" and a transition zone. Those falling in the transition zone would need further review, while the leachers would require a more thorough investigation, such as a field test. Dicamba was determined to be in the transition between a leacher and nonleacher using this test (McRae, 1991).

A screening test devised by Jury et al. (1987), is based on mobility and persistence of the pesticide, but considers different soil conditions, one for high and one for low pollution potential. For example, the high potential scenario has low organic carbon, low water content, high water flow and a small zone of biodegradation. For dicamba, the residual mass leaching to 3 m below the ground surface was 3.84 % in 0.6 years for high pollution potential and 0 % in 3.5 years for low pollution potential conditions. These

results illustrate the importance of dicamba's fairly short half-life on its potential for groundwater contamination.

2.5.2 Computer Models

As for the choice of models, LEACHP (Wagenet and Hutson, 1987) seems to be the most popular among researchers, with PRZM (Carsel et al., 1984), CMLS (Nofziger and Hornsby, 1987), and GLEAMS (Leonard et al., 1987) also being used. All of these listed are deterministic models, which utilize a single set of model parameter values and produce a unique solution. The parameters are based on physical processes, so this type of model is well suited for attempting to understand transport processes. Stochastic models statistically account for the variability in model parameters based on a large number of observations. In the study by Pennell et al. (1990), many models were compared for their ability to describe bromide and aldicarb transport through a field soil. The models LEACHP, PRZM and CMLS all sufficiently predicted the maximum depth of leaching and total mass remaining, but no model gave accurate concentration distributions. In another field study, Costa et al. (1994) statistically determined that LEACHM was more successful in predicting bromide transport under unsaturated, steady-state conditions than the convection-dispersion equation, the continuous-time Markov process, or the transfer function model. Similarly, agreement with observed results was best for LEACHP, followed by PRZM-2, and then VARLEACH (UK), in a comparative study by Brown et al. (1996).

The predicted breakthrough curves (BTC) from LEACHM were significantly slower than the observed BTC for dicamba and 2,6-DFBA in a study by Pearson et al.

(1996). This difference may have been due to preferential flow in the field. Predicted soil

concentrations of dicamba and DCSA were also low, suggesting that the degradation of

these compounds was slower than the previously determined half-life of 13.5 days. Only

recently have researchers modeled the transport of solutes applied to turfgrass. The

GLEAMS model was tested for pesticide leaching under turf (Smith et al., 1993), and it

greatly overpredicted leaching. The LEACHM model predicted significantly higher

concentrations in leachate and longer travel times for dicamba transport under turf

(Watschke- personal communication), though it gave reasonably accurate predictions for

nitrate transport below Orchard grass (Jabro et al., 1997).

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CHAPTER 3

Degradation of Dicamba in the Thatch of Turfgrass and Soil

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Abbreviations: GTIERC, Guelph Turfgrass Institute and Environmental Research Centre; GC/MS, gas chromatography-mass spectrometry; TMP, 2,2,4-trimethylpentane; TP, 2,4,5-trichlorophenoxy propionic acid; HPLC, high pressure liquid chromatography; PE LC, Perkin Elmer liquid chromatography; GUS, Groundwater Ubiquity Score

ABSTRACT

The degradation of dicamba [2-methoxy-3,6-dichlorobenzoic acid] in a sandy loam soil and thatch removed from Kentucky bluegrass (*Poa pratensis*) was measured at 4 and 20°C and two different water contents, using a small-scale batch experiment and simplified analysis. Dicamba was applied at a rate equivalent to 0.6 kg a.i./ha to thatch and soil in 20 mL vials. Three replicate samples and one sterile control were taken 2, 9, 20, 40, 61, and 100 d after application. Dicamba was extracted with base, and methylated for analyses by gas chromatography-.nass spectrometry. Levels of dicamba in the samples were quantified from equations derived by linear regression (R^2 = 0.954 to 0.998) of samples spiked with known amounts of dicamba (100, 50 and 10 % of applied and a control). Degradation rates were derived by fitting a first-order kinetic equation to the experimental data. Under the same conditions, the degradation rate of dicamba in thatch was 5.9 to 8.4 times greater than in soil, with a calculated half-life as low as 5.5 d. An increase in temperature from 4 to 20°C resulted in an increase in the degradation rate ranging from 2.0 to 3.7 times. Arrhenius activation energies of 29.8 to 55.0 kJ mol^{-1} were similar to literature values, ranging from 35.9 to 110.9 kJ mol^{-1}, for other pesticides. The wide range of half-lives, 5.5 to 136 d, demonstrates the importance of measuring the degradation rate for individual site conditions when accurate predictions of pesticide fate are required.

INTRODUCTION

Leaching of pesticides through the soil to the groundwater is a concern since they may affect the quality of drinking water supplies and surface water ecosystems. Dicamba, a postemergent herbicide commonly used to control broadleaf weeds in turfgrass, has been detected in groundwater on numerous occasions (Koterba et al., 1993; Cox, 1994). From studies in Canada, compiled by Caux et al. (1993), 8 % of the surface water and 2 % of the groundwater samples were positive for dicamba. Specific to turfgrass, Cohen et al. (1990) tested the groundwater under various golf courses on Cape Cod (MA) and detected dicamba in one of the sixteen monitoring wells.

The dissipation of a pesticide in the soil will control the proportion available for leaching. The dissipation of dicamba in soil is largely due to microbial degradation (Burnside and Lavy, 1966; Smith, 1974). The main degradation product in soil is 3,6-dichlorosalicylic acid (3,6-DCSA), a less mobile and more persistent molecule (Smith, 1974; Pearson et al., 1996). The amount of dicamba degradation in soil is highly variable, with reported half-life values ranging from less than 10 d (Burnside and Lavy, 1966; Smith, 1974) to 151 d (Comfort et al., 1992). Pesticide degradation can be influenced by many factors, including application rate, soil moisture content, temperature, pH and organic matter content (Caux et al., 1993), which can affect microbial populations and the amount of pesticide they physically contact.

Field studies have shown a change in dissipation rates of pesticides applied to turfgrass with the seasons. This phenomena is likely associated with effects of different temperature and moisture conditions. In a study involving dicamba applications in April, June and September, Gold et al. (1988) observed higher concentrations of dicamba in soil

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during the autumn compared to the summer. Petrovic et al. (1994) suggested that the continued detection of the fungicide triadimefon {1-(4-chlorophenoxy)3,3-dimethyl-1-(1H-1, 2,4-triazol-1-yl)-2-(butanone)} and its metabolite until early June following a autumn application to turfgrass, indicates a decline in the rate of degradation during the winter months. Many researchers have shown the effect of temperature (Walker and Zimdahl, 1981; Parker and Doxtader, 1983; Comfort et al., 1992; Veeh et al., 1996) and soil moisture (Walker and Zimdahl, 1981; Parker and Doxtader, 1983; Krueger et al., 1991; Cink and Coats, 1993; Starrett et al., 1996) on pesticide degradation rates in soil using laboratory studies.

The vegetative cover also affects microbial activity in the soil. For example, dicamba was less persistent in soil under grassland than forest, even though the physical characteristics of both soils were similar (Altom and Stritzke, 1973). The dissipation of 2,4-D {(2,4-dichlorophenoxy) acetic acid} and dicamba from a lawn and corn crop were measured in field plots; dicamba was found to dissipate more rapidly under turf (Gold and Groffman, 1993). In both studies, it was suggested that increased dissipation under grass was the result of higher microbial activity.

Plant uptake and metabolism can also affect the persistence of a herbicide. Dicamba is rapidly absorbed by roots and foliar tissues, and translocated to other parts of the plant, but the rates of these processes depend on the plant species (Frear, 1976). Following uptake, dicamba can be metabolized or exuded from the plant via the roots or leaves (Caux et al., 1993). The importance of this process, in comparison to microbial degradation, in enhancing the dissipation of pesticides applied to turfgrass is not clear.

Increased dissipation of other pesticides in thatch versus soil has been observed.

Diazinon {O,O-diethyl-O-(2-isopropyl-6-methyl-4-primidinyl) phosphorothioate}

dissipated more rapidly in turfgrass with thatch than without thatch (Branham and

Wehner, 1985), as measured by diazinon recovery from soil cores and $^{14}CO_2$ release.

However, no distinction between chemical hydrolysis and microbial decomposition was

made. The rates of degradation of ^{14}C-benefin {N-butyl-N-ethyl-α,α,α-trifluoro-2,6-

dinitro-p-toluidine}and ^{14}C-DCPA {dimethyltetrachloroterephthalate} measured in a batch

experiment were significantly greater in thatch from a Kentucky bluegrass turf than in the

underlying soil (Hurto and Turgeon, 1979). Although degradation was most likely

biologically mediated, no controls were used to quantify the contribution of chemical

degradation. More recently, Liu and Hsiang (1996) measured the degradation of methyl

benzimidazol-2-ylcarbamate (MBC), a degradation product of benomyl, in thatch

collected from creeping bentgrass (*Agrostis stolonifera*). The determined half-life for

MBC was 2.5 weeks *in vitro*, with no significant degradation occurring in autoclaved

thatch samples. This half-life was much shorter than the previously reported half-lives of 3

to 6 months in turf and 6 to 12 months in bare soil.

In this laboratory study, our primary objective was to measure and compare the

biodegradation rates of dicamba in thatch and bare soil, as affected by soil temperature and

water content. Few researchers have incorporated a range of both temperature and water

content that can occur following a spring or autumn herbicide application in temperate

climates. The second objective was to determine whether a batch study using many small

samples and a simplified analytical procedure, may be used to estimate degradation rates

for a variety of possible environmental conditions.

MATERIALS AND METHODS

Chemical and Soils Preparation

Dicamba, >99 % purity, was obtained from BASF Chemical Corporation (Mississauga, ON). A 500.0 mg L^{-1} solution was prepared with 250.0 mg dicamba dissolved in deionized water in a 500 mL volumetric flask. All other dicamba solutions were made by appropriate serial dilutions of this stock solution. All solvents used were pesticide grade and distilled in glass. Tetrabutylammonium dihydrogen phosphate (98 % purity) was obtained from Sigma Chemical Co. (St. Louis, MO), and 1-methyl-3-nitro-1-nitrosoguanidine (97 % purity), used for the preparation of diazomethane, was obtained from Aldrich Chemical Co. (Milwaukee, WI).

Soil for this study was taken from the A Horizon at the Cambridge Research Station, near Cambridge, Ontario. This sandy loam soil is composed of about 73 % sand, 20 % silt, and 7 % clay. The soil, on average, also contains 1.2 % organic carbon and has a pH of 6.8. The thatch, a layer of fibrous organic material and soil, was collected from Kentucky bluegrass at the Guelph Turfgrass Institute and Environmental Research Centre (GTIERC), University of Guelph, Guelph, Ontario. It was 2.0 to 2.5 cm thick, had a 5.8 % organic carbon content and a pH of 7.2. The thatch may have been exposed to low applications of dicamba before the sod was brought to GTIERC, over two and a half years prior to sampling. Enhanced degradation from prior exposure is unlikely in this case, as it has not been reported for dicamba in the literature, and the effect with other pesticides is not long lasting without continued applications (Racke and Coats, 1987; Harvey, 1990; Roeth et al., 1990; Skipper, 1990).

Soil and thatch were collected about a week before the start of the experiment and stored at 4°C prior to sample preparation. The soil was passed through a 2 mm sieve. The thatch was trimmed to remove all green shoots and large, protruding roots. All remaining materials that would come in contact with the herbicide, thatch or soil were either flame-sterilized or autoclaved (121°C for 55 min.) before use to ensure aseptic initial conditions.

Degradation Experiment

The degradation experiment involved eight treatments, including two materials (soil and thatch), two temperatures (4 and 20 °C), and two volumetric water contents (approximately 0.28 and 0.21 m^3m^{-3} for thatch, and 0.25 and 0.18 m^3m^{-3} for soil).

The experimental design is a modification of that of Smith (1974). To 20 mL glass vials was added 10.0 g of soil or 5.0 g of thatch, and each was packed down to an equivalent volume (9 cm^3). Controls were sterilized by autoclaving (121°C for 55 min.) a total of three times, each spaced two days apart. To each sample was added 29.5 μg of dicamba, dissolved in either 1.30 or 0.65 mL of deionized/distilled water (two water contents), at an application rate of 0.6 kg ha^{-1}. The herbicide solution was dripped onto the surface of the soil/thatch using a pipettor. The vials were stoppered with glass wool to allow air circulation and then incubated in a sealed, black, plastic bag at either 4 or 20°C. Wet, sterile sponges were put in the bags to reduce evaporative water loss from the vials. Deionized water was added to the vials periodically to maintain steady water content conditions. It was found that water evaporated from the samples and condensed in the glass wool at 4°C. Therefore, these samples received more frequent additions of water.

Triplicate samples and a control from each treatment set were removed 2, 9, 20, 40, 61 and 100 days after application, capped and stored in a freezer at -20°C until analysis. Dicamba stability was monitored with dissolved ^{14}C-dicamba and no loss during storage was observed.

All the samples for each sampling date were analyzed simultaneously. In addition, new soil and thatch samples were prepared as described before, and fortified with a known amount of dicamba: 3, 15, and 30 µg, representing 0.1, 0.5, and 1.0 of the fraction of dicamba initially applied. In all cases a control (no dicamba) was also included. These samples, hereafter termed spikes, underwent the same extraction and analysis procedure as the samples used for the degradation experiment. The spikes were used to measure analytical efficiency and served as standards to quantify dicamba levels in the samples.

Gas Chromatography-Mass Spectrometry (GC/MS)

GC/MS analysis, including extraction, was modified from Clegg (1987) to accommodate the large number of samples and to reduce the volume of solvents used. Each soil sample received 10.0 mL and each thatch sample received 13.0 mL of 0.1 M NaOH. The vials containing these samples were capped, shaken manually for 30 seconds and allowed to sit overnight. The following day, 1.0 mL of the resultant solution was removed and placed in a scintillation vial. The basic sample was neutralized with 1.0 mL of 0.1 M HCl, and acidified with two or three drops of 6.0 M HCl, to a pH of 2 or less. Dicamba was partitioned into ethyl ether to prepare for GC/MS analysis. Either 5.0 or 10.0 mL of ethyl ether was added, the vials were capped, sealed with Parafilm, and shaken upright overnight on a rotary shaker.

To 5 mL glass test tubes was added 100 μL of 2,2,4-trimethylpentane (TMP), 20

μL of 10 mg L^{-1} 2,4,5-trichlorophenoxy propionic acid (TP, internal standard) and 1.0 mL

of the ethyl ether extracted sample. The mixture was mixed for 5 seconds, and blown

down to near dryness (approximately 50 μL) under air. The evaporated extracts were

methylated with 1 mL of diazomethane in ethyl ether, and allowed to react for 30 min.

Excess diazomethane and ether were evaporated under air to a final volume of 25 μL.

The methylated extracts were reconstituted with 1.0 mL of TMP, transferred to 1.5 mL

glass autosampler vials and capped.

A Saturn 4D GC/MS/MS was used for mass spectrometric detection of dicamba.

A 1.0 μL aliquot of sample was injected onto a DB-1 capillary column (30 m, 0.25 mm

i.d. x 0.25 μm thickness), with helium carrier gas pressure of 82.8 kPa (12 p.s.i.) and a

flow rate of 1.0 mL min^{-1}. The inlet temperature was 90°C and the detector temperature

was 280°C. A temperature gradient was used, starting at 90°C for 1 minute, increased to

150°C at 20 °C min^{-1}, and then increased to 280°C at 5 °C min^{-1}. The final temperature

was held for 5 minutes. Residues of dicamba and TP (internal standard) were determined

by reconstruction of selected ions 203 and 196, respectively. The analytical results for

dicamba in spikes and samples were standardized based on a single value of the internal

standard prior to quantification.

High Pressure Liquid Chromatography (HPLC) Analysis and Comparison

The analysis of dicamba by gas chromatography, unlike liquid chromatography,

does not discriminate between the parent compound and the primary metabolite in soil,

3,6-DCSA. The methylation step used in gas chromatography transforms both species

into the same compound, namely dicamba-methyl ester. However, 3,6-DCSA adsorbs more strongly to soil particles and, as a result, is more difficult to extract. To quantify the amount of 3,6-DCSA contributing to the concentration measured by GC/MS, a small number of samples underwent a comparative GC/MS and HPLC analysis, as outlined below.

A 1.0 mL aliquot of solution from the base-extracted samples was removed and added to 4 to 5 mL of HCl-acidified water, to a final pH less than 2. The solution was filtered through a 0.45 μm nylon membrane filter using a 5 mL syringe. Often a second filter was required for the thatch samples because of clogging. Following the procedure of Arjmand et al. (1988), the sample was first extracted using C18 solid phase extraction columns. The columns were positioned on a vacuum manifold and conditioned by passing 5 mL of methanol, followed by 5 mL of acidified water (pH<2) through each column, taking care that the columns never completely dried. The acidified sample was subsequently passed through the column, and the C18 cartridges were dried for 15 minutes by drawing air through them using the vacuum manifold. Adsorbed compounds were eluted from each column with 4.0 mL of methanol and split into two equal portions. one to be analyzed by HPLC and the other by GC/MS. The sample for GC/MS was blown down under air to approximately 50 μL and then methylated and analyzed as described previously. The sample for HPLC was blown down under air to 250 μL, added to a 300 μL microvial insert within a 1.5 mL glass vial and capped.

A Perkin Elmer liquid chromatography (PE LC) system was used that included a PE LC-95 UV/Visible Spectrophotometer Detector, a series 200 PE pump, a Millipore (Waters) radial-pak cartridge, and a Nova-Pak C18 column (4 μm particle size 8.0 mm

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i.d.). The detector was set at a wavelength of 210 nm. The mobile phase consisted of

methanol and water at 30/70 (v/v) for A and 52/48 (v/v) for B, with the ion-pairing

reagent tetrabutylammonium dihydrogen phosphate maintained at a concentration of 0.005

M. A gradient solvent program was used. After injection, the solvent balance was held at

50 % of A and 50 % of B, for 2 minutes. The balance was changed along a gradient, up

to 100 % of B through 10 minutes, and remained at this level for another 20 minutes. The

flow rate was 1.2 mL min^{-1}, and the injection volume was 20 µL.

Degradation Kinetics

The fraction of dicamba remaining was plotted as a function of sampling time (d).

The resulting degradation curves were interpreted and compared by fitting the first-order

degradation equation

$$CF = e^{-kt}$$
[3.1],

where CF is the fraction of the measured concentration at time t over the initial

concentration of dicamba; t is time (d) after the start of the experiment; and k is the first-

order rate constant (d^{-1}), to the experimental data. Half-lives were calculated using the

following relationship:

$$t_{1/2} = \ln(2)/k$$
[3.2]

where $t_{1/2}$ is the half-life (d). Fitting was accomplished with the Minerr function, which

uses a modified Levenberg-Marquardt least squares fitting method (More et al., 1980),

available in MathcadPLUS6.0 (1986-1995 Mathsoft, Inc.). Goodness of fit was measured

by the root mean square error

$$RMSE = \left[\sum_{i=1}^{n} (P_i - M_i)^2 / n \right]^{1/2}$$

[3.3]

where n is the number of samples; M_i are the measured values for CF; and P_i are the predicted values for CF.

The Arrhenius equation has been used extensively (Walker and Zimdahl, 1981; Parker and Doxtader, 1983; Boesten, 1991; Veeh et al., 1996) to describe the relationship between the degradation rate constant and temperature:

$$\ln k_T = -E_A/RT + A$$

[3.4]

where A is a constant related to soil chemical and other nonthermal factors, k_T is the rate constant of degradation at temperature T (K); R is the ideal gas constant (J mol^{-1} K^{-1}); and E_A is the activation energy (J mol^{-1}). It has been shown that this function is valid for temperatures below the optimum for microbial growth (Walker and Zimdahl, 1981; Parker and Doxtader, 1983). Previous degradation studies have indicated that the optimum temperature for dicamba degradation is greater than 20°C (Burnside and Lavy, 1966; Comfort et al., 1992), the highest temperature used in this experiment, so we assumed this function for the range of temperatures used.

RESULTS AND DISCUSSION

Degradation in Soil and Thatch

The half-lives of dicamba in thatch were 5.9 to 8.4 times shorter than those calculated using soil, at the same temperature and moisture conditions (Table 3.1). Furthermore, the half-lives were also shorter than those calculated by other researchers for soils under similar conditions (Smith, 1984; Comfort et al., 1992). These results support

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the hypothesis that the increased pesticide degradation under turf compared to agricultural

or bare soils observed by several researchers (Branham et al., 1993; Gold and Groffman.

1993; Horst et al., 1996; Starrett et al., 1996) is related to higher microbial activity.

Table 3.1. Dicamba degradation rate constants (k), half-lives (t $_{1/2}$) and root mean square error (RMSE), derived from fitting the first-order kinetics equation to the fraction of dicamba remaining in the sample.

Material	Temperature	Water Content	k	t $_{1/2}$	RMSE
	°C	m^{3}m^{-3}	d^{-1}	d	
Thatch	4	.21	0.0299	23.2	0.135
		.28	0.0621	11.2	0.091
	20	.21	0.1100	6.3	0.066
		.28	0.1261	5.5	0.048
Soil	4	.18	0.0051	136.1	0.197
		.25	0.0075	92.2	0.171
	20	.18	0.0183	37.9	0.146
		.25	0.0191	36.2	0.167

An increase in the degradation rate of 2,4-D and dicamba in soils with more

organic matter and microbial biomass was observed by Voos and Groffman (1997). The

thatch, with its high organic matter content compared to soil, may support a microbial

population different in both size and structure, leading to increased biodegradation.

Mancino et al. (1993) compared the microbial populations in soil and thatch under a

putting green, composed of a sand-peat mixture. Depending on the sampling date, they

found that the thatch contained 40 to 1600 times more bacteria, 500 to 600 times more

fungi and up to 100 times more actinomycetes than the soil. Furthermore, soils with a

plant root-zone (the rhizosphere) are generally enriched in sugars, amino acids,

microorganisms and more complex organic compounds (Holden and Firestone, 1997).

Microorganisms adapted to metabolizing a more complex compound derived from a plant may possess a biodegradative pathway for a structurally similar pesticide. It is suggested that these characteristics of the rhizosphere act to enhance biodegradation rates compared to bare soils and deeper soil layers (Holden and Firestone, 1997).

Sorption to organic matter may actually impair degradation, since the bound herbicide residue is not as accessible to microbes (Stott et al., 1983). Although negatively charged molecules such as dicamba generally do not sorb strongly to soil, recent research suggests that dicamba sorption to thatch is greater than to soil. Baskaran et al. (1997) determined that 42 % more dicamba sorbed to thatch than to a sand/peat mixture (calculated from K_d values). Raturi et al. (1997) reported 11 and 13 % more sorption to thatch than to soil for two types of turfgrass. The smaller half-lives for dicamba in thatch compared to soil in this study suggest that the qualities of thatch that boost degradation far outweigh the effect of increased sorption.

The decline in the fraction of dicamba remaining in the thatch was rapid (Fig. 3.1) for all temperature and moisture conditions. In comparison, there appears to be an initial acclimation period or slow phase, where the fraction of dicamba remaining stays around 1.0, for a number of the soil treatments (Fig. 3.2). The acclimation period appears to last at least 40 d for the 4°C treatment and about 10 d for the 20°C treatment. Parker and Doxtader (1983) suggest that the early slow phase results from the growth of a small population of herbicide degraders initially present in the soil. The lack of a slow phase in the thatch treatment, even at the lower temperature, suggests this population may be more substantial in the thatch. The presence of dicamba analogs, compounds of similar structure exuded by turfgrass roots, may also reduce the acclimation period since the

metabolic pathways of the microbes do not require extensive modifications before

degradation of the herbicide could commence.

Fig. 3.1. The fraction of dicamba remaining in thatch samples as a function of time: (a) 4°C and 0.21 water content, (b) 4°C and 0.28 water content, (c) 20°C and 0.21 water content, and (d) 20°C and 0.28 water content. The solid line indicates the curve described by eq. [1].

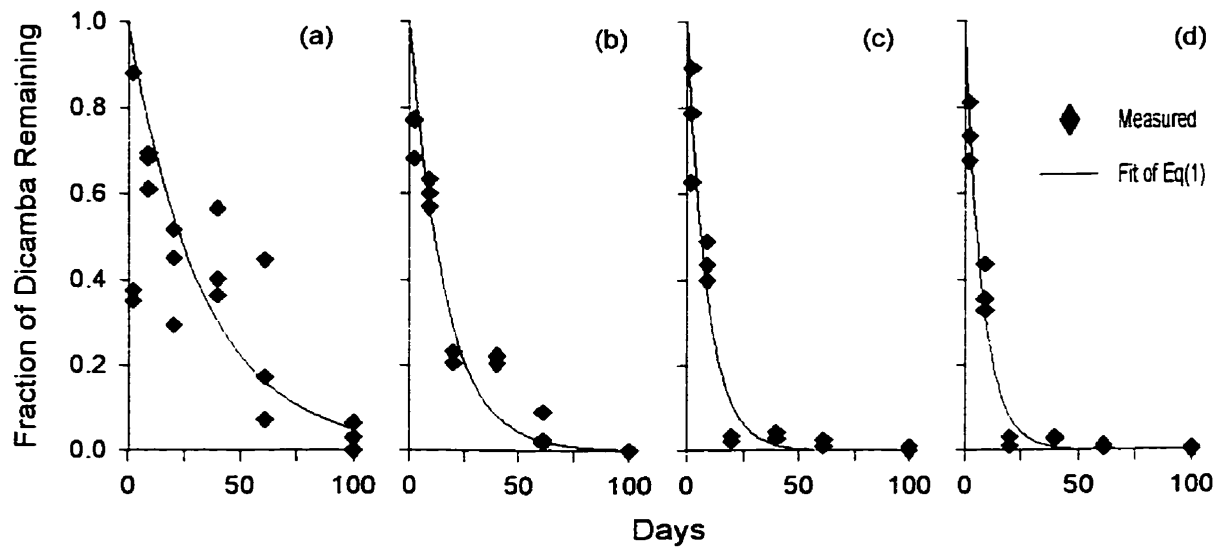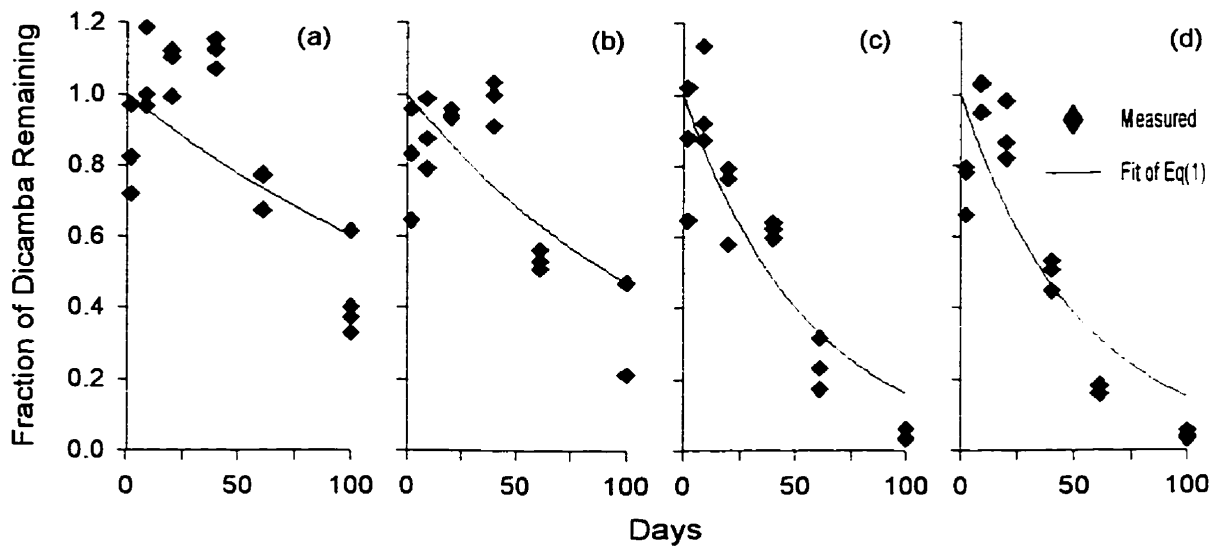Fig. 3.2. The fraction of dicamba remaining in soil samples as a function of time: (a) 4°C and 0.18 water content, (b) 4°C and 0.25 water content, (c) 20°C and 0.18 water content, and (d) 20°C and 0.25 water content. The solid line indicates the curve described by eq. [1].

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The acclimation period is a major cause of the poorer fit (larger RMSE values) between the measured values and the calculated curve for degradation in the soil (Table 3.1). Although the first-order kinetics equation [3.1] cannot reproduce an acclimation period, it is easily incorporated into computer models since it does not account for changes in microbial numbers or environmental conditions. The calculated half-life also provides a standard means of comparing the degradation process for a number of compounds or a variety of environmental conditions.

Temperature Effects on Degradation

An increase in temperature from 4 to 20°C resulted in a decrease of the half-life of dicamba ranging from 2.0 to 3.7 times (Table 3.1), with the greatest difference associated with the low water content. Complete dissipation was not observed at the lowest temperature, due to the long observation time required, which may be the cause of the larger RMSE values for the soil at 4°C (Table 3.1). Numerous research groups (Walker and Zimdahl, 1981; Parker and Doxtader, 1983; Veeh et al., 1996) have reported a decrease in the degradation rate of various pesticides with decreasing temperature. However, Parker and Doxtader (1983) observed an upper temperature limit at which the rate was no longer affected - the optimum temperature for biodegradation. In a batch study on dicamba degradation in clay, Comfort et al. (1992) measured half-lives of 23.5 d at 28°C, 38 d at 20°C and 151 d at 12°C. These values compare well with the half-lives for dicamba in soil measured in our study (Table 3.1).

The natural log of the degradation rate was plotted against inverse temperature (K) to determine the Arrhenius activation energies, E_A. The calculated E_A values were 55.0

and 29.8 kJ mol^{-1} for thatch with low and high water content, respectively. Similar values were obtained for soil: 54.0 kJ mol^{-1} for the low water content, and 39.4 kJ mol^{-1} for the high water content, which may imply that there is a similarity between the microbial community in each material. The derived values were similar to those reported previously. From previously reported studies, Boesten (1991) calculated an average E_A value of 55 ±15 kJ mol^{-1} from some 50 measurements. In a batch study, the activation energy calculated at 17 % moisture content ranged from 45.4 to 51.1kJ mol^{-1} for atrazine {2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), 44.3 to 51.6 kJ mol^{-1} for metolachlor {α-chloro-6-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluide}and 35.9 to 37.4 kJ mol^{-1} for linuron {N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea} (Walker and Zimdahl, 1981). Veeh et al. (1996) derived E_A values for 2,4-D ranging from 43 kJ mol^{-1} to 63 kJ mol^{-1}, while those derived by Parker and Doxtader (1983) ranged from 51.9 to 110.9 kJ mol^{-1}. The observed decrease of E_A values with increasing moisture contents was also noted by Parker and Doxtader (1983).

Water Content Effects on Degradation

Increasing soil water content had a less dramatic effect on the rate of degradation of dicamba than did increasing temperature. At 4°C, the degradation rate ranged from 1.5 to 2.1 times faster for the higher water content (Table 3.1). The rates for the 20°C treatments were similar for both the high and low water contents. Slower degradation rates at lower water contents have been observed in batch studies (Burnside and Lavy, 1966; Walker and Zimdahl, 1981; Parker and Doxtader, 1983). The soil water content may influence microbial activity. Gaston and Locke (1996) suggested that differences in

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pesticide degradation rates in soil columns may correspond with soil aeration levels for aerobic biodegradation.

Water content will control the diffusion of the pesticide and nutrients to the microbes, and the chemical concentration in solution. By manipulating the water content and mass of 2,4-D in the soil, Parker and Doxtader (1983) determined that the increased concentration in solution had a greater effect on degradation kinetics than the moisture content. In this study, both water contents were fairly high so the concentration of dicamba in soil solution at the higher water content would be 70-80 % of the concentration at the lower water content.

Similar to the effect of temperature, there is also evidence of an optimum water content for microbial degradation of herbicides. In a column study, Starrett et al. (1996) observed that a light amount of irrigation (16, 6.4-mm applications) seemed to enhance degradation of pesticides compared to a heavy irrigation (4, 25.4-mm applications). In another study, soil moisture content had an effect on chlorpyrifos {O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate} degradation, with the highest percent mineralization under field capacity (0.3 bar), with less degradation for much drier (3 bar) and much wetter (0.03 bar) conditions (Cink and Coats, 1993). Anaerobic and aerobic conditions were compared in batch systems for the study of dicamba degradation by Krueger et al. (1991). Although metabolism was similar for both conditions, the half life of dicamba was 31 d for aerobic and 58 d for anaerobic conditions. An optimum point or plateau for water content may have been reached in this study, providing another possible explanation as to why the half-lives for the two water contents were so similar.

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Degradation Rates and Modeling

Dicamba was found to be in the transition zone between a leacher and a non-leacher, (McRae, 1991), using the Groundwater Ubiquity Score (GUS) model developed by Gustafson (1989). The GUS model is based on two pesticide properties: half-life in soil and the partition coefficient between soil organic carbon and water (K_{oc}). Using the same K_{oc} value (50 mL g^{-1}) as McRae, the degradation rates derived in this study would shift the designation to a leacher, for the 136 day half-life, or a non-leacher, for the 5 day half-life (Table 3.1). In a modeling study, Boesten and Linden (1991) determined that pesticide leaching was very sensitive to the degradation rate; changing it by a factor of two changed the fraction of pesticide leached typically by a factor of about 10. In our experiments, a change in degradation rate of 2 or greater was observed between soil and thatch, and the two temperatures.

Batch Study Evaluation

The small-scale, laboratory, batch study provided a reasonable assessment of the degradation of dicamba. The half-lives calculated for dicamba degradation (Table 3.1) in the sandy loam soil are similar to those compiled by Comfort et al. (1992). The general effects of the soil material, temperature and water content on the degradation rates observed in this study were consistent with past observations or theories. Considering the presence of an acclimation period in the soils, the RMSE for the best-fit lines are fairly low (Table 3.1). Variability between triplicate samples (Fig. 3.1 and 3.2) may be an artifact of the analytical procedure or may reflect the complexity of soil and microbial functions in the field. In either case, the trends for dicamba degradation under the different conditions

are clear. Often a precise value for a single set of conditions is not as valuable as having many values, for a range of conditions, when analyzing or modeling the fate of a pesticide in the field; the uncertainty involved in all the processes and their interactions is just too great.

Concerning the efficiency of the analytical procedure, the recovery of dicamba from the soil and thatch samples fortified with herbicide was acceptable (Table 3.2). The recovery from thatch was more variable, which the larger standard deviations indicate, reflecting some very high values for a single set of spikes. Matrix effects, probably caused by high levels of organic compounds in the samples, often produced non-zero values for dicamba in blanks. These values were subtracted from those of the other spikes. The samples were quantified using a linear equation, fitted by regression to the spike samples of soil and thatch, which served as a standard curve. The R^2 values for the spike curves on different sampling dates ranged from 0.954 to 0.998 for the soil, and from 0.978 to 0.997 for the thatch. The GC/MS-HPLC comparison (Fig. 3.3) indicates that there was little, if any, 3,6-DCSA extracted in the samples along with dicamba, since the GC/MS-derived concentrations are not much higher than those derived from HPLC. There was a minor difference between the GC/MS values for the different extraction methods.

Sterile controls can indicate if the loss of dicamba during the experiment was due to biodegradation or other processes such as volatilization, chemical degradation or immobilization by organic matter. The per cent of dicamba in the sterilized controls remained fairly constant, with a slight decline at later sampling dates (Table 3.3), which was especially noticeable in the thatch. To test for sterilization at the start of the experiment, 1.0 g samples of soil and thatch from extra controls were aseptically placed

into test tubes with 10.0 mL of sterile, nutrient broth and incubated at room temperature (Trevors, 1996). After 21 days, there was slight turbidity in the thatch controls, but none in the soils. Fresh material produced excessive turbidity after only 1 day. This suggests that the autoclaving process may not have been sufficient to destroy all microbial life in the thatch, possibly explaining the observations associated with the controls. However. the decline in extractable dicamba with time was most pronounced at the lower temperature for the thatch (not shown), which suggests the decline may be more related to immobilization of dicamba by organic matter than with biodegradation.

Table 3.2. The per cent recovery for gas chromatography analysis of soil and thatch spiked with known amounts of dicamba; mean and standard deviation calculated from n number of spikes.

Material	Mass	n	Mean	Standard Deviation
	µg		%	%
Soil	3	6	81.19	17.19
	15	6	81.15	18.90
	30	5	77.90	13.32
Thatch	3	6	91.42	22.51
	15	6	109.33	45.38
	30	5	110.91	41.36

Table 3.3. Measurement of the per cent recovery from sterile control samples; mean average and standard deviation (s.d.) calculated from n number of samples for each sampling date.

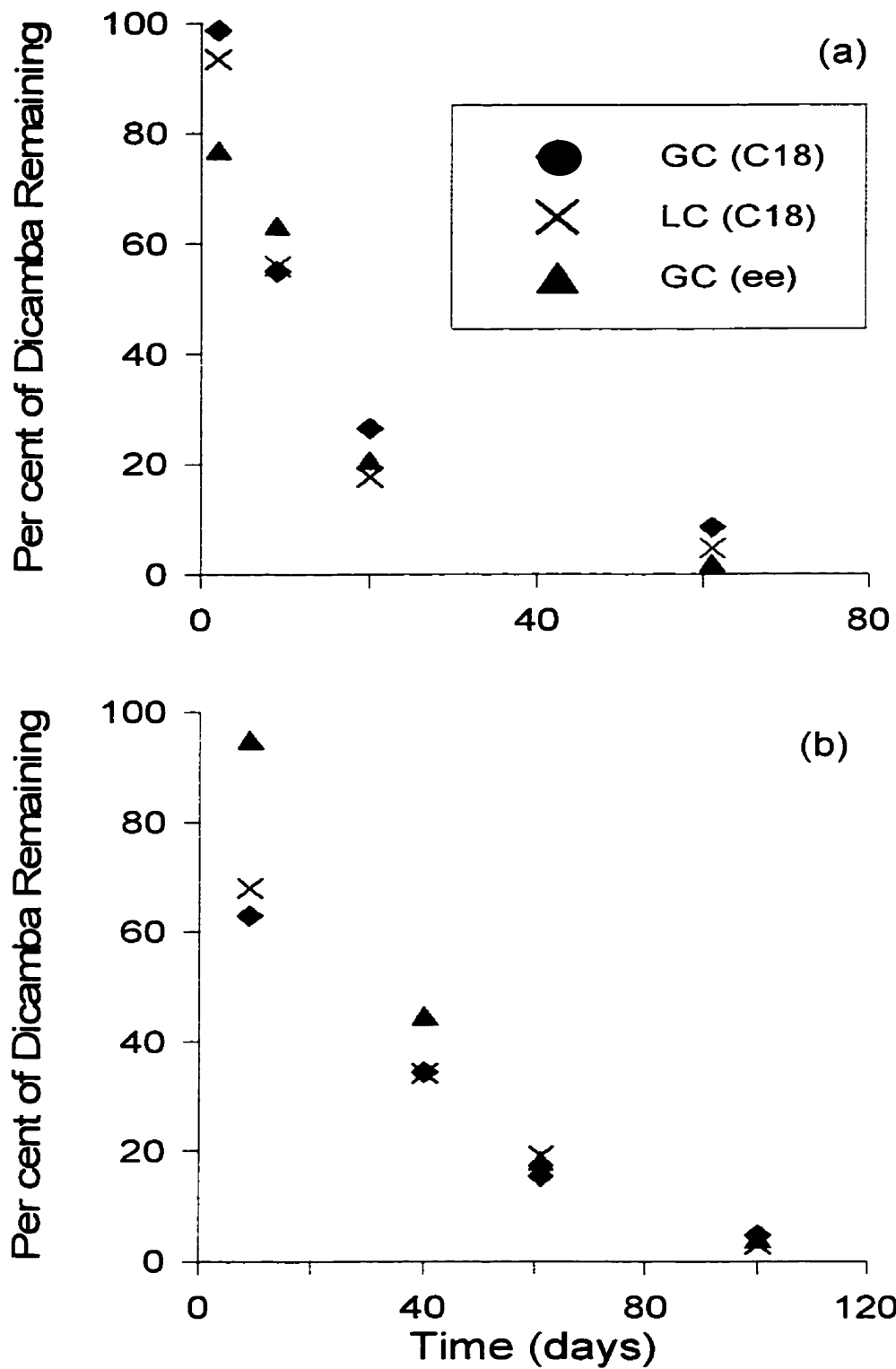| Day | Thatch | | | Soil | | |
	n	mean	s. d.	n	mean	s. d.
		%	%		%	%
2	4	102.51	17.26	4	108.07	6.90
9	4	90.27	11.60	3	108.26	16.85
20	4	104.47	9.62	4	106.93	12.74
40	4	77.63	5.50	4	109.43	5.33
61	4	84.75	12.94	4	87.44	4.40
100	6	76.80	29.62	4	95.59	23.07

Fig. 3.3. Comparison of identical samples, of (a) thatch and (b) soil, analyzed by gas chromatography (GC) and liquid chromatography (LC), using C18 cartridge extraction, and previous analysis of these samples by gas chromatography with ethyl ether (ee) extraction.

CONCLUSIONS

The more rapid degradation of dicamba in thatch may explain why there is less leaching of dicamba from turfgrass than agricultural soils. Higher temperature resulted in increased degradation in both thatch and soil, while water content had less of an effect on the degradation rate. The effect of each condition (i.e. temperature and moisture) on the degradation rate was also influenced by the other condition - the effect of temperature was more pronounced at the low water content; the effect of water content was greater at the low temperature. The wide range of half-lives measured in this study illustrates the dependence of biodegradation of dicamba on soil properties and environmental conditions. It is recommended that degradation rates be measured using local climatic and soil/crop conditions rather than using values obtained from the literature if accurate predictions of herbicide fate are required. The use of models that incorporate the effects of temperature and water content may also be beneficial.

Recent research into pesticide fate in soils has focused on measurements made in the field or using soil columns in the laboratory (Flury, 1996). However, the similarity between our results and those of others, with regard to degradation rates and Arrhenius activation energies, supports the claim that small-scale, laboratory studies can still provide effective, cost-efficient means of evaluating pesticide behavior while incorporating a number of different environmental conditions into the experimental design (Blumhorst, 1996). Field conditions at the Guelph Turfgrass Institute were simulated in the batch study because these degradation rates will be used for modeling dicamba transport in field lysimeters at this site.

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CHAPTER 4

Water Flow in Unsaturated Soil Below Turfgrass:

Observations and LEACHM (within EXPRES) Predictions

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Abbreviations: GTIERC, Guelph Turfgrass Institute and Environmental Research Centre; PET, potential evapotranspiration; AE, average error; ME, maximum error; RMSE, root mean square error; TDR, time domain reflectometry.

ABSTRACT

In cropped soils, water sustains the plants, affects the transport of nutrients within the root zone and controls the leaching of nutrients and chemicals to groundwater. The objectives of this study were (i) to investigate the effects of turfgrass on unsaturated water flow in sandy loam soil, and (ii) to test the ability of the model LEACHM (within EXPRES) to simulate water movement below turfgrass. Twelve field lysimeters were packed with a 3-horizon profile, topped with Kentucky bluegrass (*Poa pratensis*) sod and monitored for 2 years. The lysimeters became very dry during the summer, and only drained during the spring and autumn. Small peaks in water content at 85-cm depth during a dry period in 1997 indicated that some water from heavy rains may have been transmitted through the rootzone by preferential flow. Comparisons between observations and LEACHM predictions were based on soil water contents, soil water storage and drainage measured in lysimeters in the field. In general, the model predicted more drainage and less drying during the summer than was observed. Statistical analysis indicated that the model simulated infiltration well, but predicted water redistribution (gravity drainage and evapotranspiration) during the drying periods less well. The major inaccuracies of the model predictions appear to be associated with the bottom boundary condition, the snowfall/snowmelt routine, Campbell's soil hydraulic properties equation, and summer evapotranspiration calculations. The model seemed rather insensitive to the root distribution parameters, the initial water content and even the use of independently measured values for the turf layer hydraulic parameters.

INTRODUCTION

The water regime in cropped soils is important for the water needs of plants, the transport of nutrients within the root zone, and the leaching of nutrients and chemicals to groundwater. Turfgrass is a unique crop that requires unique management practices. It is valued for its aesthetic, recreational and robust properties, and is especially important in urban areas where lawns, parks, golf courses and recreational fields make up a considerable portion of unpaved land. Turfgrass can influence the water regime through plant uptake for evapotranspiration during the time it is biologically active (Fetter, 1994), changing hydraulic gradients in the process, and affecting the physical properties of the transport medium, due to thatch development and structural changes in the soil below. Turf's high growth density greatly modifies overland flow, nearly eliminating runoff in favour of infiltration. The overall effect is an increase in the amount of water entering the soil, which increases the water content and promotes solute transport (Beard and Green, 1994). The turfgrass system also has an abundance of earthworms; their burrowing increases aeration and water infiltration (Potter, 1993). These burrows, essentially single or interconnected macropores, can also act as primary flow conduits, providing rapid downward flow of solutes during ponded water conditions (Stehouwer et al., 1994).

Over the past decade, more attention has been focused on turfgrass with respect to solute transport in cropped systems, mainly due to the perceived threat of fertilizer and pesticide leaching from golf courses. However, only recently have researchers started to use computer models in this area (Franke, 1992; Smith et al., 1993; Jabro et al., 1997). Many models have been developed to simulate transport through the soil, including PRZM (Carsel et al., 1984), LEACHM (Wagenet and Hutson, 1987), and CMLS (Nofziger and

Hornsby, 1987). These deterministic models, which utilize a time invariant set of model parameters to produce a unique solution, are based on physical processes of water infiltration, redistribution and evaporation. Therefore, they are useful for testing our understanding of water flow or chemical transport behaviour and for guiding further research efforts (Rao et al., 1988). Models can also be used to develop better management practices based on site-specific conditions. The model EXPRES (Expert system for Pesticide Regulatory Evaluations and Simulations) (Mutch et al., 1993), developed as a management tool, combines the research models PRZM and LEACHM with a user-friendly interface. However, the testing of these models using data collected from the field is essential, and is often lacking (Vighi and Di Guardo, 1995). Eliminating inaccuracies, whether in the model or in the process of determining input parameters for the model, will help improve our understanding of water flow and the predictive capabilities of the models.

Our objectives were (i) to investigate the physical impact of turfgrass on water transport in unsaturated, sandy soil using large, field lysimeters topped with Kentucky bluegrass turf, and (ii) to test the ability of the model LEACHM (within EXPRES) to simulate the soil water processes in this system. The soil hydraulic properties of the turf layer were measured and simulations using LEACHM were used to identify its effect on water flow. Field measurements of soil water content, soil water storage and drainage from lysimeters were compared with LEACHM predictions. To date, testing of LEACHM has focused on the transport of solutes, particularly inorganic tracers (bromide or chloride), fertilizers and pesticides. Since water flow is generally the dominant process in solute transport it is essential that the model simulate it effectively.

MATERIALS AND METHODS

Lysimeter Set-up

Field lysimeters were constructed from 118 L, high-density polyethylene tanks (5 mm wall thickness) - 43-cm diameter, 81-cm long cylinders with an 18-cm deep conical bottom (CANBAR, Waterloo, ON). The tanks were filled with Lisbon sandy loam from the Cambridge Research Station (near Cambridge, ON), and with 0.63-cm (¼") diameter pea gravel in the conical bottom. The lysimeters were buried at the Guelph Turfgrass Institute and Environmental Research Centre (GTIERC), (43° 32' 50" N latitude, 80° 13' 50" W longitude) Guelph, ON, in the spring of 1995, placed even with the surrounding ground surface to prevent unnatural runoff or ponding. The entire site was then covered with Kentucky bluegrass sod. Cutting of the grass was performed with shears, to a minimum height of 5-cm, with the clippings left on the surface. The soil profile consists of a 5-cm thick turf layer, including about 2-cm of thatch (a layer of fibrous organic material and soil), a 25-cm thick A horizon (sandy loam) repacked to a dry bulk density of 1.55 g cm^{-3}, a 25-cm thick B horizon (loamy sand) repacked to a dry bulk density of 1.60 g cm^{-3} and a 31-cm thick C horizon (sand) repacked to a dry bulk density of 1.65 g cm^{-3}.

Each lysimeter was fitted with instrumentation prior to emplacement in the ground. A 1.27-cm (½") o.d. nylon tube was connected to the bottom of the conical portion of the tank to facilitate recovery of drainage water by a vacuum pump. A small plastic tube was inserted along the inner wall of each lysimeter to allow air inflow to the top of the pea gravel during pumping, preventing suction from being applied on the soil above. Pairs of 43-cm long TDR (time domain reflectometry) probes were placed horizontally to measure the volumetric soil water content (Topp et al., 1980) at depths of 7, 17.5, 29, 31, 42.5, 54,

56, and 85 cm below the surface (including thatch layer). The water contents were also used to calculate an approximate value for the temporal change in water storage for the whole lysimeter. In two lysimeters, horizontal tensiometers were installed, but these did not give reliable measurements, probably due to air entrapment in the horizontal portion of the tube.

Soil Hydraulic Properties

Air-dried soil for all three horizons was passed through a 2 mm sieve and packed in cores to the same bulk density as in the lysimeters. Cores from the turf, including the thatch, were collected *in situ* from an additional lysimeter at GTIERC. Measurements of the soil water retention curve, between 0 and -1500 kPa, via the pressure plate method (Klute, 1986) were made using 3-cm cores. The saturated hydraulic conductivity, Ks, was measured using 5 or 7-cm cores via the constant head permeameter (Klute and Dirksen, 1986). Particle size distribution was measured via the hydrometer method (Gee and Bauder, 1986). Soil pH and organic carbon content analyses were performed by Laboratory Services, University of Guelph, Guelph, ON.

To describe the water retention curve, LEACHM uses functions relating volumetric water content (θ) and matric potential (h) based on those proposed by Campbell (1974):

$$h = a \, (\theta / \theta_s)^{-b} \tag{4.1}$$

where θ_s is the volumetric water content at saturation, and a and b are empirical constants. Equation [4.1] was best-fit to the measured retention curve data by visual observation, as this method provided similar or better fits than those calculated by computer

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(MathcadPLUS6.0, 1986-1995 Mathsoft, Inc.). A more detailed look at the effect of the Campbell parameters is presented later in this paper.

Field Experiment

The study comprised two field seasons: the 1996 field season ran from July 19, 1996 to January 5, 1997 and the 1997 field season ran from May 11, 1997 to January 27, 1998. Twelve lysimeters were monitored in 1996 and eleven were monitored in 1997. Average values of water content, soil water storage and drainage were analyzed and used for model testing. The change in soil water storage reflected the balance between precipitation, drainage and evapotranspiration. Half of the 12 lysimeters received irrigation of 46.2 mm on July 25, and 53.8 mm on August 8, of 1996, so separate modeling runs were performed for both conditions. All 11 lysimeters were irrigated with 10 mm of water on August 5, 1997. In each year, only some of the lysimeters received nitrogen fertilizer, at 160 kg-N ha^{-1} on July 17 and October 29, 1996, and on May 14, July 25 and September 28, 1997.

The climate data required as input for LEACHM include air temperature, precipitation, and potential evapotranspiration (PET). Preliminary screening of several empirical models by Qian et al. (1996) revealed that the Penman-Monteith equation provided the most accurate estimate of turfgrass evapotranspiration for well-watered conditions; therefore, this equation was used, as described in Burman and Pochop (1994),

$$\lambda PET = \frac{\Delta}{\Delta + \gamma^*}(R_N + G) + \frac{1}{\Delta + \gamma^*}\frac{C_a}{r_a}(e_{S_a} - e_a) \qquad [4.2]$$

where λ (J kg^{-1}) is the latent heat of vaporization; Δ (Pa K^{-1}) is the slope of vapor pressure and temperature relationship; γ^* is assumed equal to γ (Pa K^{-1}), the psychrometric coefficient; R_N (W m^{-2}) is net radiation; G (W m^{-2}) is the soil heat flux, assumed equal to zero; C_a (J m^{-3} K^{-1}) is the volumetric heat capacity of air; the vapour pressure deficit is the difference between the saturated vapour pressure, e_{sa} (Pa), and the actual vapour pressure, e_a (Pa); and r_a (s m^{-1}) is the aerodynamic resistance to the turbulent diffusion of water vapour. The aerodynamic resistance to water vapour transport from the evaporating surface to the air layer above is defined as

$$r_a = (\ln\left[\frac{z_w - d}{z_{om}}\right])(\ln\left[\frac{z_h - d}{z_{oh}}\right]) / (k^2 u) \qquad [4.3]$$

where z_w (m) is the anemometer height; z_h (m) is the height of the humidity measurements; d (m) is the zero plane displacement height, equal to 2/3 of the crop height; z_{om} (m) is the momentum roughness length; z_{oh} (m) is the water vapour roughness length; k is the von Karman's constant (unitless) and u (m s^{-1}) is the wind velocity.

Hourly values of net radiation were obtained from the Elora weather station, Elora, ON, 15 km north of GTIERC. Hourly air temperature, wind speed at 10 m, and relative humidity were obtained from the GTIERC weather records. Any missing values at GTIERC were replaced with Elora weather data. Precipitation was also measured at GTIERC. Rainfall was determined with a tipping-bucket rain gauge, with a manual gauge for back up. Average snow depth was determined with a metered ruler and converted to depth of water using a snow density conversion of 0.10 cm liquid water per cm of solid snow (Dunne and Leopold, 1978). Observations of cumulative precipitation and irrigation versus potential evapotranspiration for the two field seasons are illustrated in Fig. 4.1.
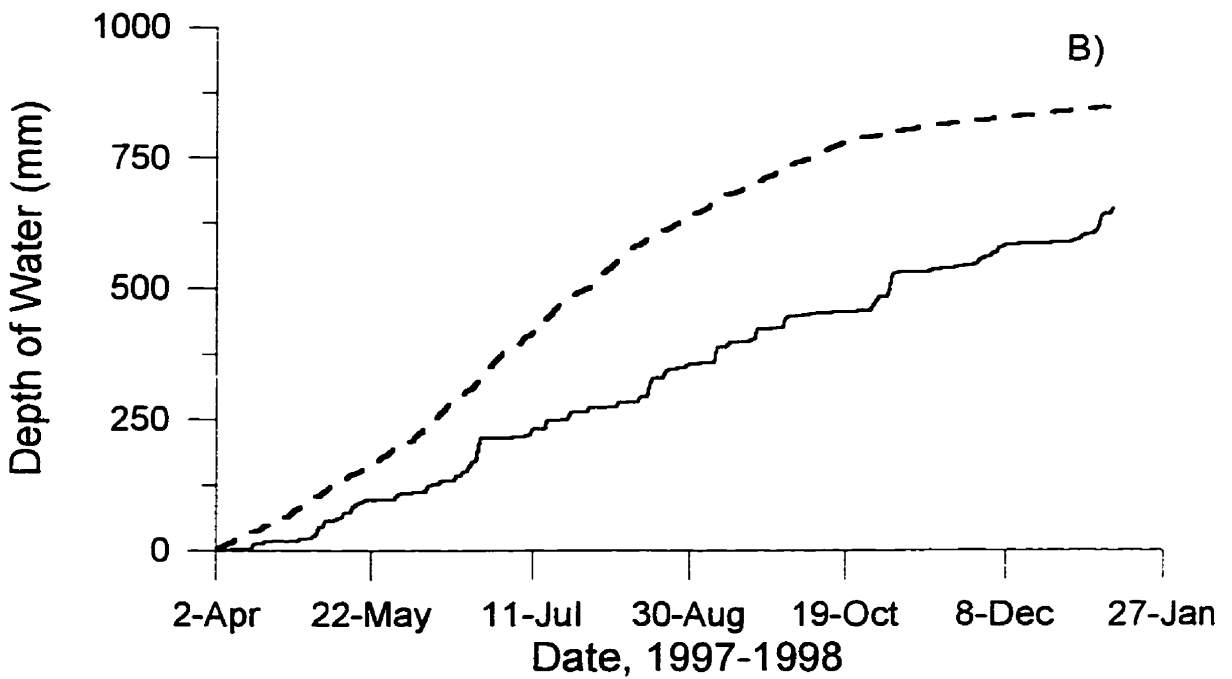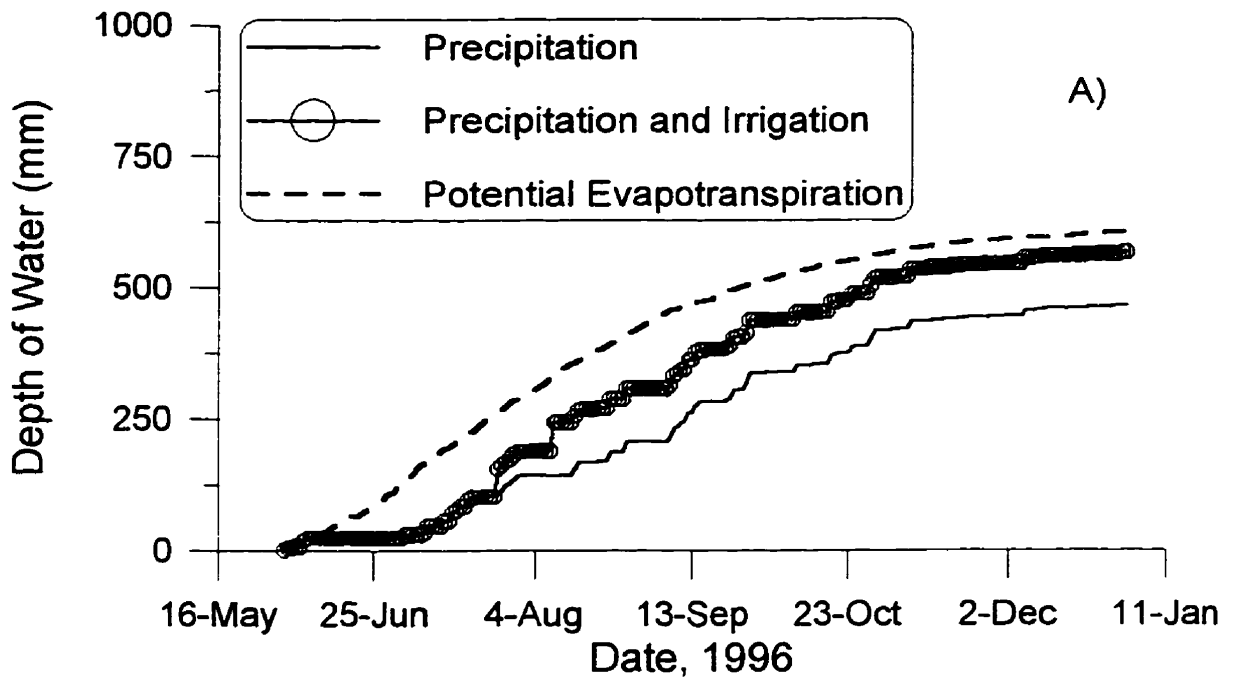
Fig. 4.1. Observations of precipitation and irrigation versus calculated potential evapotranspiration (Penman-Monteith equation [4.2]) for A) the 1996 field season: B) the 1997 field season.

Model Description

The computer model EXPRES (EXpert system for Pesticide Regulatory Evaluations and Simulations) (Mutch et al., 1993) contains a screening assessment and two mathematical simulation models, LEACHM and PRZM, coupled to a text/graphical user-system interface, and geographical and pesticide databases. The model LEACHM (v. 2) (Wagenet and Hutson, 1987) is a research-oriented simulation model requiring a fairly extensive set of input parameters and variables describing site-specific soil, plant, and climatic conditions. Modeling was performed with independently measured parameters or those reported in the literature, including the EXPRES manual (Mutch et al., 1993). No attempt was made to derive parameters using the model and inverse procedures.

The subroutine for water flow, WATFLO, solves the one-dimensional Richards' equation:

$$C(\psi)\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial z}[K(\psi)\frac{\partial\psi}{\partial z}] - \frac{\partial K(\psi)}{\partial z} + \Phi_w \qquad [4.4]$$

where C (ψ), the water capacity function, equals $\partial\theta/\partial\psi$; K($\psi$) is the hydraulic conductivity as a function of matric head, ψ; θ is volumetric water content; Φ_w is a water source/sink term; z is depth and t is time. See Wagenet and Hutson (1987) for more details.

This deterministic equation [4.4] does not simulate water flow in two domain media, often termed preferential or mobile-immobile flow (van Genuchten and Wierenga, 1976; White, 1985; Nielson et al., 1986). The two domains consist of the soil matrix, where flow is conventional (i.e. Darcy-based), and one or more large and continuous voids, termed macropores, where flow is primarily influenced by gravity. Water channeled

through preferential flowpaths can move more quickly than water flowing through the surrounding soil matrix.

EXPRES includes additional routines as well, one to simulate snowmelt based on the mean daily temperature, and another for surface runoff and losses of water and pesticide due to erosion. Table 4.1 contains a list of the parameters required by the model and their values, excluding the measured soil properties which are listed in Table 4.2. The Help feature in EXRES provided recommended values or lists of values to choose from based on the crop, for many of the parameters. Although no field measurements were taken, values of 35/60/5/0 (Troughton, 1957), representing a well-established turf, were used for the per cent root distribution for the Turf/A/B/C layers. The root distribution is important in determining from where in the profile water is removed by the turfgrass. To test the sensitivity of the model to this parameter set, a comparison with a distribution of 95/5/0/0, representing a freshly laid sod, was made. The peaks produced by infiltration water were very similar. Although the effect on the water cycle was not great, the shallow root system produced greater evapotranspiration, less drainage and lower water contents. which were especially noticeable from the middle of the A horizon to the middle of the B horizon. The difference in water content occurred mainly in the summer months. At this time, the shallow roots may have been able to remove more of the water, received from infrequent summer rains, which tended to remain in the turf and A horizon because the soil was so dry. Deeper roots would not have contributed much to evapotranspiration at these times.

Table 4.1. Parameter values used in the LEACHM simulation, excluding soil properties, with source of reference or brief explanation. See EXPRES manual for complete description (Mutch et al., 1993).

Parameter	Value(s)	Reference/Explanation
Maximum Interception Storage (cm)	0.1	EXPRES
Maximum Root Depth (cm)	50	Troughton, 1957
Crop cover fraction	0.99	EXPRES
Plant Density (m^{-2})	200	EXPRES
Curve Number	15	EXPRES
USLEC	0.01	EXPRES
Planting Date	day 1	must be at least 1 day apart
Emergence Date	day 2	
Root Maturity	day 3	
Plant Maturity	day 4	
Harvest Date	Dec-31	constant snow cover
Root growth condition		constant length
Minimum root water potential (kPa)	-3000	EXPRES
Maximum root water potential (kPa)	0	EXPRES
Root flow resistance factor	1.05	EXPRES
Maximum actual transpiration	1.1	EXPRES
Minimum depth of evaporation (cm)	15	EXPRES
Pan Evaporation coefficient	1	no pan, PET equation
Snowmelt Coefficient (cm/°C/day)	0.8	EXPRES
Root Fraction (Turf/A/B/C)	0.35/0.6/0.05/ 0	Troughton, 1957

Table 4.2. Measured values of soil properties required by LEACHM for the layers in the lysimeters.

Layer	Bulk Density	Organic Carbon	Sand	Silt	Clay	Hydraulic Conductivity (Ks) mean	Hydraulic Conductivity (Ks) st. dev.	Campbell's coefficients a	Campbell's coefficients b
	g/cm^3	—— % ——				—— mm/day ——		kPa	
Turf	0.90	5.8	52.5	20.5	27.0	330000	270000	-0.01	9.40
A	1.55	1.2	73.3	19.7	7.0	2600	230	-1.50	3.70
B	1.60	0.3	82.4	10.2	7.4	12000	1400	-1.10	3.10
C	1.65	3.0	96.8	2.0	1.2	83000	11000	-1.10	1.90

To accommodate layered soils, the soil profile in LEACHM can be divided into as many as fifty horizontal compartments of equal thickness, each with unique properties.

The depths for the model predictions of volumetric water content are within 1 cm (2-cm thick layers) of the actual depths of 7, 17.5, 29 (A horizon), 31, 42.5, 54 (B horizon), 56, and 85 (C horizon) cm below surface, measured by horizontal TDR.

To test the model's response to turf, a separate modeling run was made, where this 5-cm thick layer, with independently measured parameters, was changed to a 3-cm thick layer (2-cm thatch ignored completely) with parameter values identical to the A horizon. Ignoring the values for turf had very little effect on the water content values; they were slightly lower for all depths except 7 cm. The model also predicted slightly more drainage and evapotranspiration. Since the A horizon had lower hydraulic conductivity and higher bulk density values than the turf, it would generally have slower drainage from the surface layer, making water available for evapotranspiration longer. Also, having a low porosity, the A horizon soil would reach saturation more quickly, allowing for faster water flow after a large rain.

Error Analysis of LEACHM Predictions

The ability of LEACHM to predict volumetric water contents, drainage and change in soil water storage with time was characterized quantitatively using:

$$AE = \sum_{i=1}^{n} [P_i - M_i] / n \qquad [4.5]$$

$$ME = \max_{i=1}^{n} [P_i - M_i] \qquad [4.6]$$

$$RMSE = \left[\sum_{i=1}^{n} (P_i - M_i)^2 / n \right]^{1/2} \qquad [4.7]$$

where AE is the average error (or mean difference), ME is the maximum error between measured and predicted values within the study period, and RMSE is the root mean square error; i is the measurement date; n is the number of sampling dates; M_i are the measured daily averages for all the lysimeters; and P_i are the predicted values. The AE indicates how strongly the model overestimates (positive sign) or underestimates (negative sign) the measured values. The ME indicates the maximum deviation between the model predictions and the measurements, and whether it is an overestimate or underestimate. The RMSE quantifies the amount of scatter of the predicted and measured values about a 1:1 line. In each case, lower values reflect greater simulation accuracy. Smith and Skroch (1995), Jabro et al. (1995), Jabro et al. (1997) and others have found such statistical methods useful for evaluating model performance.

RESULTS AND DISCUSSION

Soil Hydraulic Properties

The saturated hydraulic conductivity, Ks, was much greater for turf than for the other horizons, even though the particle size distribution for the turf contained a larger percentage of fine particles (Table 4.2). This difference is likely due to the low bulk density of the thatch, along with the influence of macropores in the accompanying soil, created by rooting and worm burrowing action. Saturated hydraulic conductivity measurements were also more variable for the turf layer, as shown by the large standard deviation (Table 4.2), which may be due to the variability in thickness of the thatch layer, and the random occurrence and size of macropores.

As indicated earlier, the fit of Campbell's equation to the retention curve data was compared for visual inspection and computer fitting (MathcadPLUS6.0, 1986-1995 Mathsoft, Inc.). The computer and visually adjusted parameters differed the most for the curves representing the B and C horizon; each had a steep decline in water content at small matric head values, leading to a very low residual water content (not shown). The computer tended to fit either the near-saturated or residual end of the curve very well, but not both ends. Both sets of values resulted in similar RMSE for all depths in 1997, but the computer generated values resulted in much larger errors in 1996, especially for the irrigation simulation. Average 1996 RMSE, not including the 85-cm depth, were 0.0435 and 0.0464 m^3m^{-3} for the best fit by inspection, and 0.1175 and 0.0741 m^3m^{-3} for the computer best-fit, for irrigated and non-irrigated conditions, respectively. The AE were generally higher at all depths when using the computer-best fit parameters. Also, the computer generated values predicted less drainage and greater evapotranspiration, most likely linked to drainage from the C horizon.

Campbell's equation [4.1] was unable to describe the rapid decline in water content just below saturation, especially in the layers with higher sand content. The RMSE values were 0.017 m^3m^{-3} for the turf layer, 0.010 m^3m^{-3} for horizon A, 0.031 m^3m^{-3} for horizon B and 0.049 m^3m^{-3} for horizon C. The decline in the retention curve was very steep for the turf layer, which again suggests the presence of many large pores. It would be advisable for LEACHM (within EXPRES) to include the use of other equations to represent the retention curve, such as the van Genuchten functions which are sigmoidal in form and are capable of representing two-domain flow (e.g. Smith and Skroch, 1995).

Field Observations of Water Flow

Generally, there was very little drainage during the summer for each field season (Figs. 4.2 and 4.3), even from those lysimeters receiving irrigation in 1996. This dry period extended into November in 1997. The increase in standard deviation values for drainage in the autumn indicates water flow in the lysimeters was variable, possibly a result of preferential flow in some of the lysimeters. There was also less drainage from the lysimeters receiving fertilizer compared to those that did not (Fig. 4.4), especially noticeable in 1996. Although there are too few replicates for statistical analysis of the significance of this difference, the observations suggest an increase in evapotranspiration rates with fertilization. The effect is less pronounced in 1997, probably because the lysimeters remained dry for an extended period of time (Fig. 4.5B), so the rate of evapotranspiration would not matter. In addition, lysimeters receiving fertilizer tended to have lower water contents than those that did not (data not shown), a trend most noticeable in the B horizon during the summer when the soil was drying (August, 1996; June-July, 1997).

After an initial drop in early summer due to drainage, the water storage slowly declined, due to evapotranspiration during the summer, before rising more rapidly in the autumn (Fig. 4.5). Irrigation reduced the amount of decline in stored water but all the lysimeters had similar water storage by mid-autumn (Fig. 4.5A). The sharp fluctuations observed in the water storage (Fig. 4.5) and A horizon water contents (Fig. 4.6) suggest that rain water was taken up very quickly by the plants during the summer and even in the mild autumn of 1997. The water content occasionally dropped below $0.05 \text{ m}^3 \text{ m}^{-3}$; indeed, the grass was showing signs of senescence. A few small peaks in the water content at
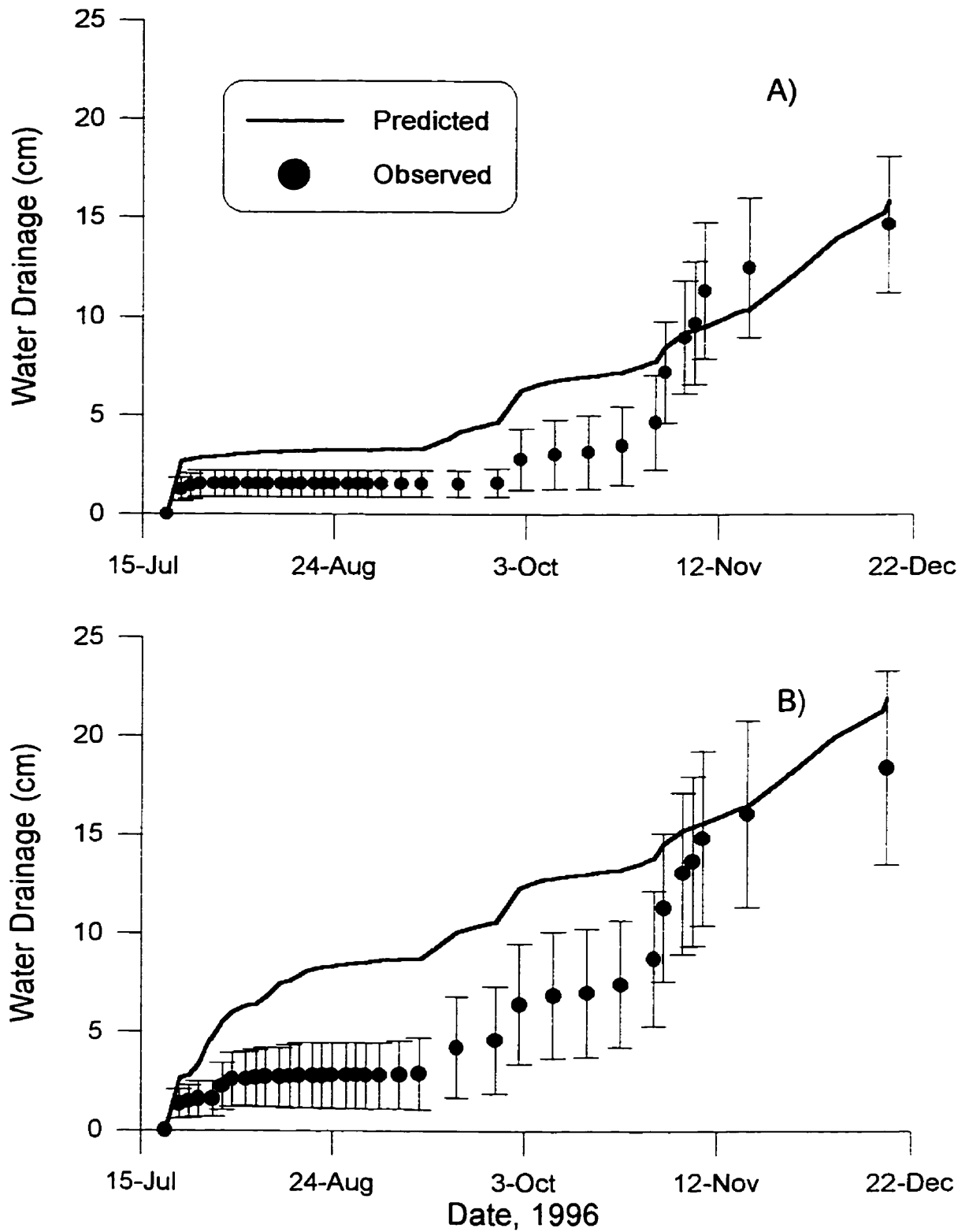
Fig. 4.2. Observed and predicted drainage for lysimeters for the 1996 field season A) without irrigation; B) with irrigation. Error bars indicate one standard deviation on either side of the mean.
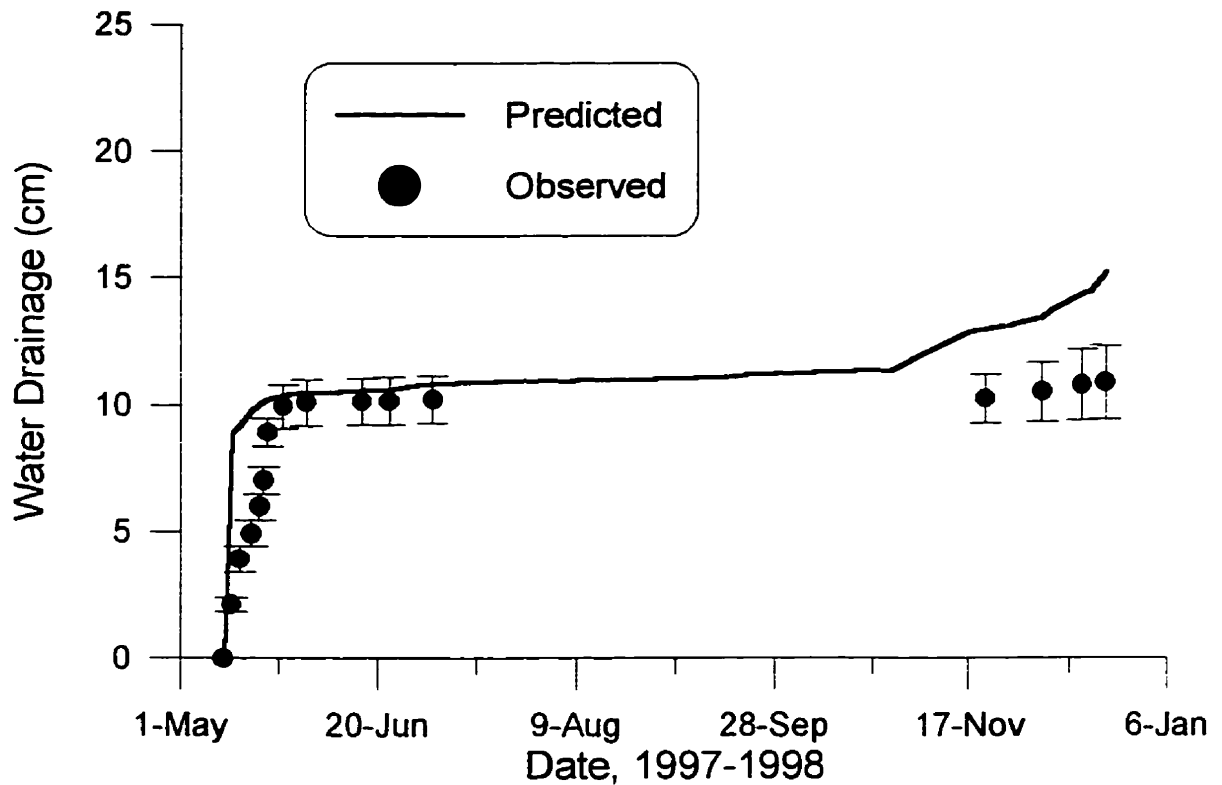
Fig. 4.3. Observed and predicted drainage for lysimeters for the 1997 field season. Error bars indicate one standard deviation on either side of the mean.

85-cm depth (Fig. 4.6) during the dry period in 1997 indicate that some water from heavy rains did leave the rootzone. The drainage, storage and water content observations suggest that the majority of infiltrating water reached the water table between the autumn and spring, but the intense drying of the soil over the summer occasionally promoted preferential flow following heavy rains.

The bottom boundary condition was that of zero pressure head, since the lysimeters were open to the atmosphere. This caused the build up of water at the bottom of the C horizon, as seen in the large water content values for the 85-cm depth (Fig. 4.6). High water contents remained, even after drainage had stopped for the summer in early
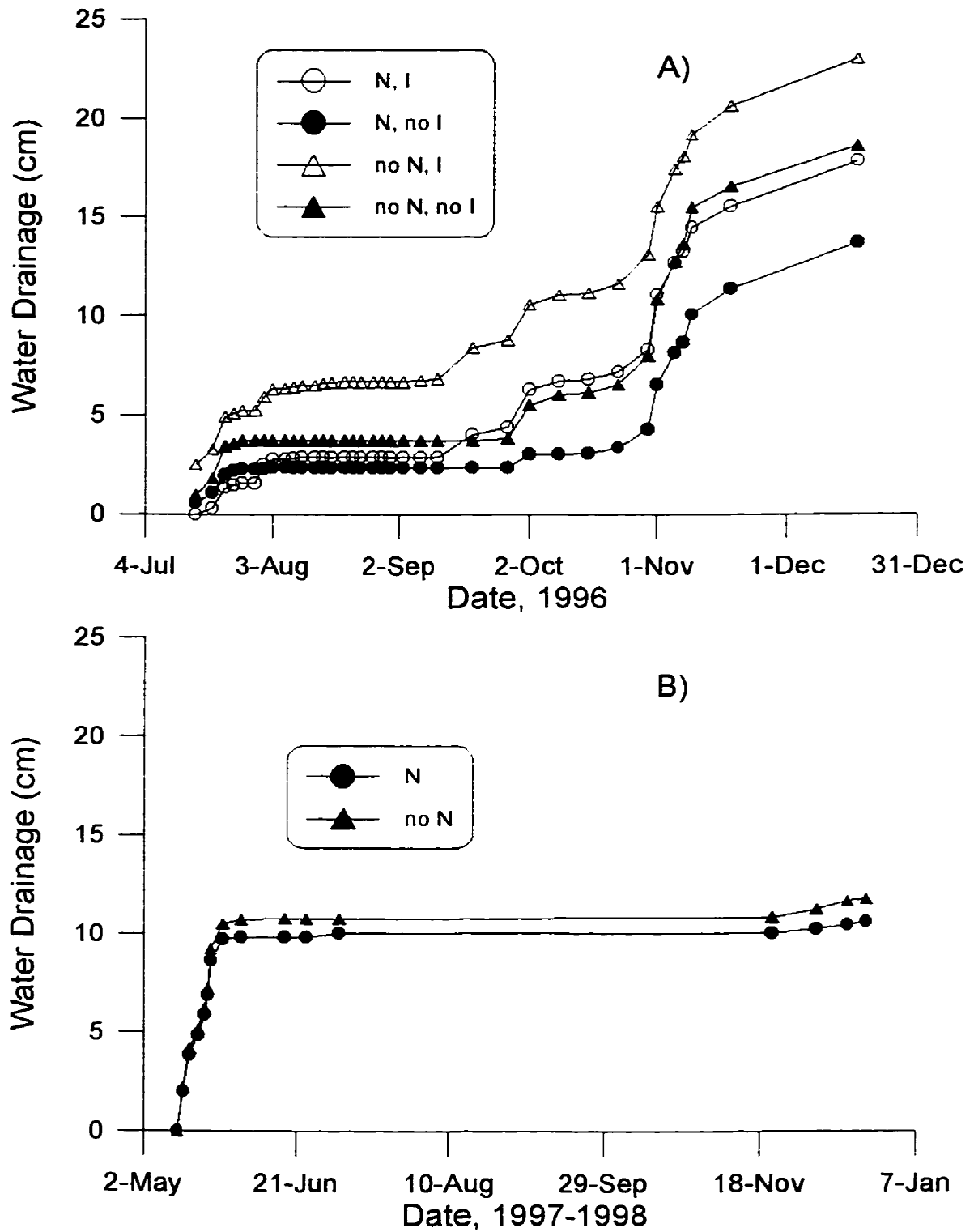
Fig. 4.4. Comparison of water drainage from lysimeters based on fertilization for A) the 1996 field season; B) the 1997 field season. [N - fertilized; no N - not fertilized; I - irrigated (1996); no I - not irrigated (1996)].
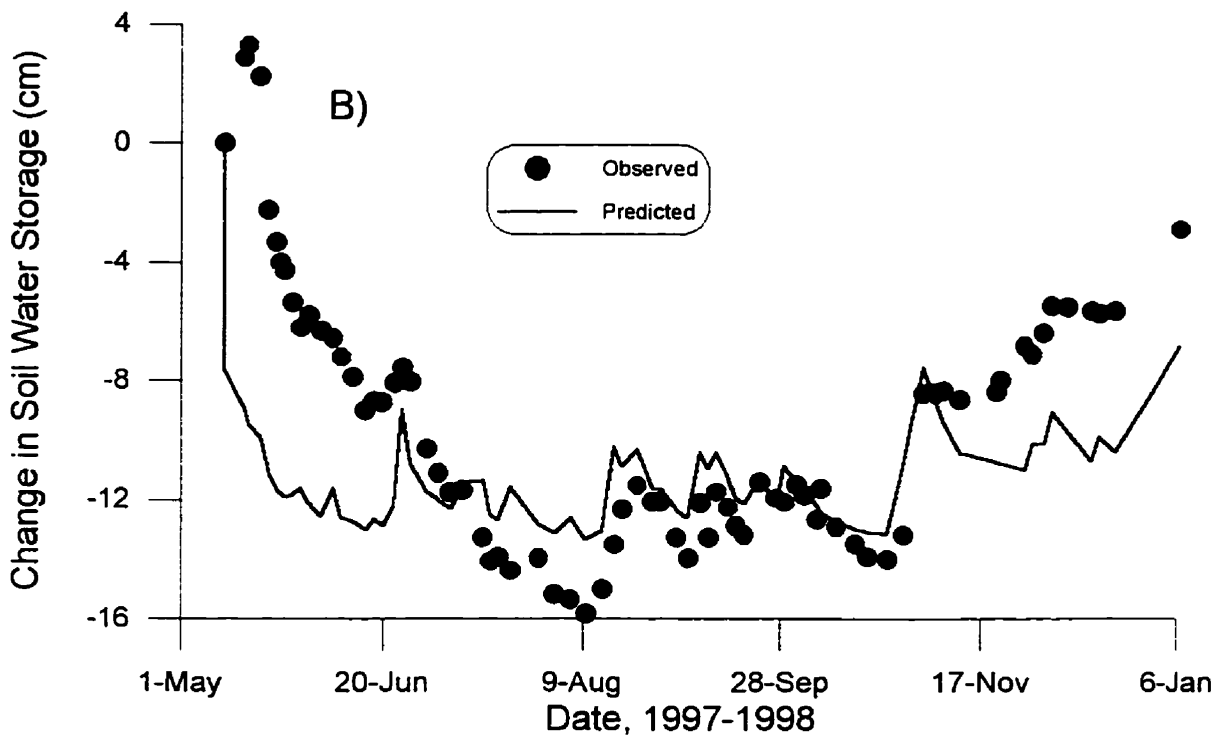
103
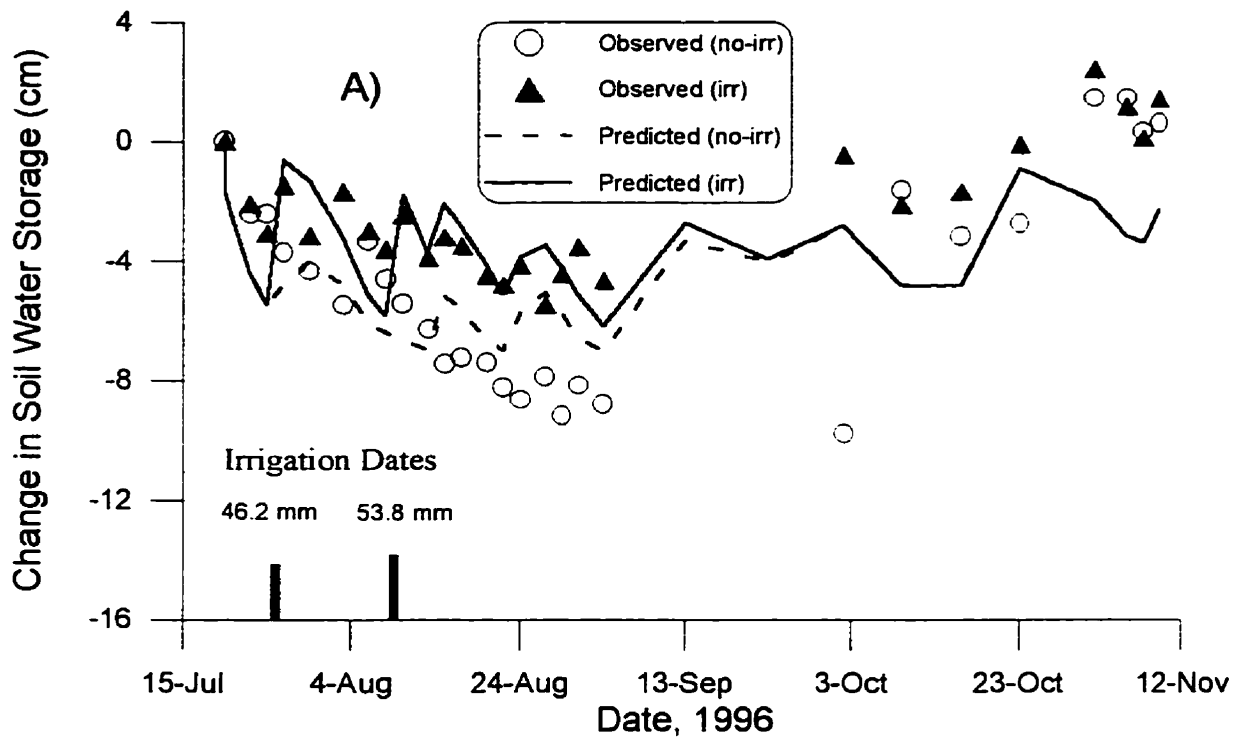
Fig. 4.5. Measured and predicted change in soil water storage for the lysimeters, for A) the 1996 field season; B) the 1997 field season.

July (Fig. 4.4B), and built up again before draining started in the autumn. This phenomenon would not be seen in the field unless the C horizon was underlain by a gravel layer. Horst et al. (1994) used porous ceramic plates under suction to simulate soil matric potentials at field capacity, and found that evapotranspiration was greater, while drainage of water and bromide was much less for columns without suction at the bottom. Therefore, the amount of drainage is probably less and the amount of evapotranspiration probably more for our study than would be seen in a field with a continuous,

Fig. 4.6. Observed volumetric water contents for the top of the A horizon (7 cm) and the bottom of the C horizon (85 cm), measured by TDR, for the 1997 field season.

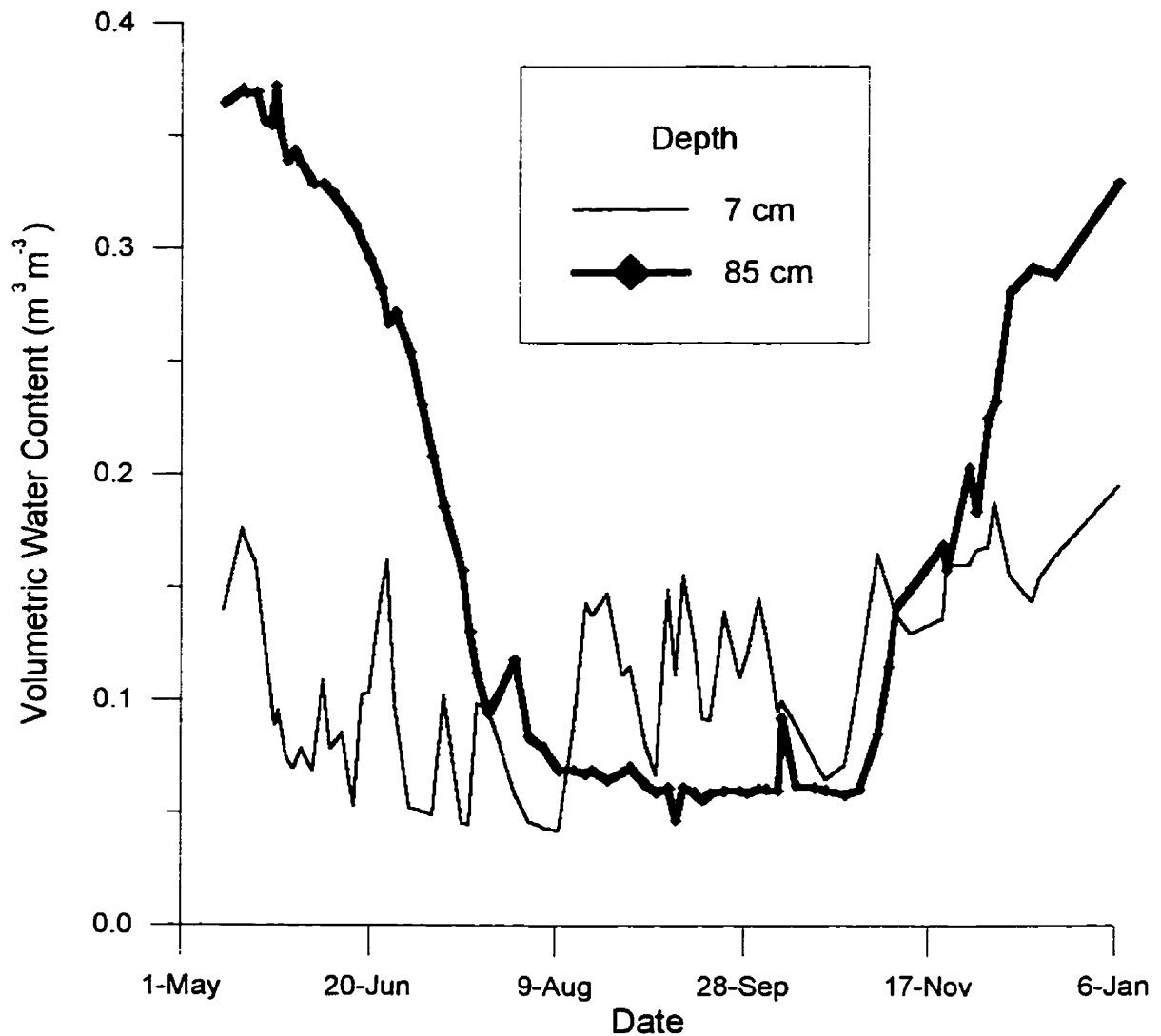homogeneous C horizon. In conjunction, the change in storage would drop more quickly in the spring and rise more slowly towards zero in the autumn.

LEACHM Predictions

In general, the predictions of drainage, change in water storage and soil water contents compared favourably with the measured averages, as indicated by statistical and visual analyses, with the largest deviations associated with soil wetting in the late summer or autumn. The LEACHM version in EXPRES could not simulate the zero tension lower boundary condition of the lysimeters; therefore, modeling was performed with a free drainage boundary (hydraulic potential gradient approximately unity) instead. This improper setting would help account for the earlier start to drainage in the late summer or autumn (Figs. 4.2 and 4.3) and the greater (more negative) change in storage predicted by the model (Fig. 4.5) in the spring and autumn. For both drainage and change in storage, the ME occurred either in the spring (1997) or the autumn (1996), the times most affected by the bottom boundary condition.

Another possible explanation for the poorer predictions in autumn could be the inaccuracy involved with snowfall measurements and the model simulation. Average snow depths were measured, though an uneven snowpack, blowing snow and uneven melting were all commonly observed conditions at GTIERC. The snowfall/snowmelt routine is based on the average daily temperature; precipitation is considered snowfall below 0 °C, and melting only occurs above this temperature. In late autumn we observed rain, as well as snow melting, on days with a daily average temperature below 0 °C, so the model

would underpredict infiltration on that day. Occasionally, there was also snow on days

with a daily average temperature above 0 °C.

Statistical analysis of the accuracy of prediction for the change in water storage is

given in Table 4.3. Generally, LEACHM predicted the lysimeters drier than they actually

were, as AE values tended to be negative. The RMSE values were under 4 cm for both

years. Considering the inaccuracy involved with the bottom boundary, these error values

indicate fairly good model predictions.

Table 4.3. Analysis of the accuracy of LEACHM predictions for drainage and change in soil water storage, using equations 4.5-4.7, average error (AE), maximum error (ME) and root mean squared error (RMSE).

	Year/Condition	RMSE	AE	ME	ME Date
		cm			
Change in	1996 - Irrigated	2.17	-1.203	-4.383	31-Oct
Storage	1996 - non-irrigated	2.668	-0.211	6.954	01-Oct
	1997	3.906	-1.918	-12.742	17-May
Drainage	1996 - Irrigated	4.525	4.53	6.028	26-Sep
	1996 - non-irrigated	1.995	1.94	3.831	15-Oct
	1997	3.413	2.595	6.774	13-May

Upon visual inspection, the model simulated reasonably well the general trend in

fluctuations for the change in water storage (Fig. 4.5), but occasionally shifted from wet to

dry or vice versa, earlier than the measurements. This may be an artifact of the method of

calculation of the observed change in storage, as the horizontal TDR measurements were

not able to pick up the infiltration front until it reached 7-cm depth. Without irrigation,

the soil dried up during the summer in 1996 more than was predicted, and remained drier

longer (Fig. 4.5A). Since there was very little drainage at this time, the discrepancy is

probably associated with the simulation of evapotranspiration.

Statistical analysis of the accuracy of prediction performed for drainage is given in Table 4.3. The model predicted more drainage than was observed (positive AE), with RMSE values ranging from 2 to 4.5 cm. Predicted drainage reacted similarly in terms of time, but often differed in the amount, although predicted values fell within one standard deviation in the summer of 1997 and the autumn of 1996. We observed a faster increase in drainage in late October-early November, 1996, than predicted (Fig. 4.2), following a few days of rain. At this time there was also a large increase in stored water and peaks in the water contents were measured at all depths. A similar event in 1997 produced the same observations for change in storage and water contents, but the observed increase in drainage was less than predicted. The quick infiltration of the rain water likely created a build-up of water at the bottom of the C horizon. In 1996, the water content at the bottom was already high, so water was released to drainage, whereas the build-up of water content at the bottom of the C horizon was just beginning in early November, 1997, preventing much drainage.

Other researchers have reported successful use of LEACHM for predicting drainage from cropped soils. Jemison et al. (1994) studied bromide leaching in the field from a well-structured, silt loam soil planted with corn. LEACHM simulated drainage from lysimeters (1.2 m depth) fairly well, with good correlation (r = 0.73 - 0.83) between predictions and observations for the three years of study. Their AE values, based on monthly drainage, reached 3.96 cm. In a related study of nitrate leaching, using the same conditions but for 5 years, Jabro et al. (1995) reported fairly accurate predictions of water drainage, with a maximum AE value of -0.97 cm. The AE values from our study are in a similar range (Table 4.3) as these two studies. More recently, LEACHM provided

accurate annual predictions of drainage below a depth of 1 m for 23 field lysimeters

containing a moderately-structured, silt loam soil planted with Orchardgrass (Jabro et al.,

1997). The RMSE for the two years were 3.38 and 2.08 cm, again a range similar to this

study (Table 4.3). Difficulties with snow accumulation and frozen soils, as well as

macropore flow, were given as prime causes for underpredictions in the winter and spring,

while poor simulation of evapotranspiration and crop growth were blamed for

overpredictions in the summer. In our study, snow accumulation and evapotranspiration

may be the sources of similar prediction errors.

Not including the 85-cm depth, RMSE values are below 0.068 m^3m^{-3} for 1996

(Table 4.4) and 0.074 m^3m^{-3} for 1997 (Table 4.5). In comparison, Clemente et al. (1994)

used water content profiles to compare 3 models, including LEACHW, for their ability to

simulate water flow in a sandy loam planted with soybeans and a clay soil planted with

grass hay. They concluded that the accuracy of the LEACHM predictions was acceptable,

with AE all below 0.039 m^3m^{-3} and RMSE all below 0.048 m^3m^{-3}.

Table 4.4. Analysis of the accuracy of LEACHM predictions for volumetric water contents for the 1996 field season (July 19 - November 8), using equations 4.5-4.7, average error (AE), maximum error (ME) and root mean squared error (RMSE).

Depth (horizon)	Irrigated $m^3 m^{-3}$				Non-irrigated $m^3 m^{-3}$			
	RMSE	AE	ME	ME Date	RMSE	AE	ME	ME Date
7 (A)	0.068	0.056	0.145	29-Jul	0.052	0.036	0.132	29-Jul
17 (A)	0.060	0.053	0.114	26-Aug	0.068	0.062	0.123	26-Aug
29 (A)	0.059	0.055	0.093	26-Aug	0.063	0.058	0.099	26-Aug
31 (B)	0.020	0.001	0.034	26-Aug	0.025	0.006	0.045	28-Aug
43 (B)	0.024	-0.016	-0.040	08-Oct	0.025	-0.011	-0.037	19-Jul
53 (B)	0.022	-0.009	-0.051	31-Oct	0.029	-0.016	-0.049	31-Oct
57 (C)	0.052	-0.044	-0.139	31-Oct	0.063	-0.055	-0.150	31-Oct
85 (C)	0.220	-0.218	-0.278	04-Nov	0.214	-0.208	-0.270	04-Nov

The best fit between predicted and measured water contents was for the B horizon as indicated by the smaller ME and RMSE values (Tables 4.4 and 4.5). This is not surprising, since it would be less directly affected by both the grass and the bottom boundary condition at the lysimeter bottom. In general, LEACHM predictions of water content, based on AE values (Tables 4.4 and 4.5), were high for the A horizon, slightly low for the B horizon, and low for the C horizon. The ME occurred in summer for the A horizon, but in spring (1997) and autumn (1996) for the rest of the profile.

Table 4.5. Analysis of the accuracy of LEACHM predictions for volumetric water contents for the 1997 field season (May 11 - December 20), using equations 4.5-4.7, average error (AE), maximum error (ME) and root mean squared error (RMSE).

Depth (horizon)	RMSE	AE	ME	ME Date
		$m^3 m^{-3}$		
7 (A)	0.034	0.018	0.115	14-Jul
17 (A)	0.049	0.043	0.102	14-Jul
29 (A)	0.051	0.044	0.125	16-Aug
31 (B)	0.027	-0.003	0.078	16-Aug
43 (B)	0.040	-0.013	-0.145	17-May
53 (B)	0.052	-0.006	-0.194	17-May
57 (C)	0.074	-0.049	-0.268	17-May
85 (C)	0.170	-0.129	-0.311	25-May

LEACHM tended to overpredict water contents in summer for a clay soil growing grass hay (Clemente et al., 1994). The researchers concluded that the inaccuracies of the predictions were possibly due to hysteresis and preferential flow. It may also be that grasses maintain a higher rate of evapotranspiration, even when the soil is drying, than is calculated.

Pearson et al. (1996) made similar findings while testing LEACHM for predicting tracer transport in silt loam, soil columns in the laboratory. Although the model produced

good predictions of water content for fallow conditions, predictions were frequently higher than observed for cropped soils. They attributed this problem to inaccuracies of the root distribution function. In this study, the root distribution was not measured directly, but as mentioned earlier, two different values for this parameter resulted in similar predictions.

A visual comparison of predicted versus measured water contents at shallow depths shows that often LEACHM predicted larger peaks in response to rain than observed (Fig. 4.7). Such large responses may indicate that the model is predicting greater drainage from the turf layer to the A horizon. Smith and Skroch (1995) reported that Ks values were larger from measurements performed on soil cores (5 cm) than *in situ* soil columns, and attributed the difference to macropores short circuiting flow in the smaller core samples. Therefore, the Ks value we measured for the turf layer may have been too large. The noticeable disagreement following irrigation on August 7, 1997 (Fig. 4.7), is likely a result of a high irrigation intensity combined with a low K(ψ) value due to the dry soil, causing ponding conditions and runoff, which led to lower infiltration in the field.

Smith and Skroch (1995) found LEACHM gave reasonably accurate predictions of water content and pressure head profiles, but was substantially more accurate when water retention curve values were derived using *in situ* measurements from intact soil columns rather than soil cores. They found that soil cores gave only the static, main drainage limb and were biased towards overprediction of water contents, as happened in this study for the A horizon. The effect of hysteresis and air entrapment would likely be less for the lower horizons with higher sand content.
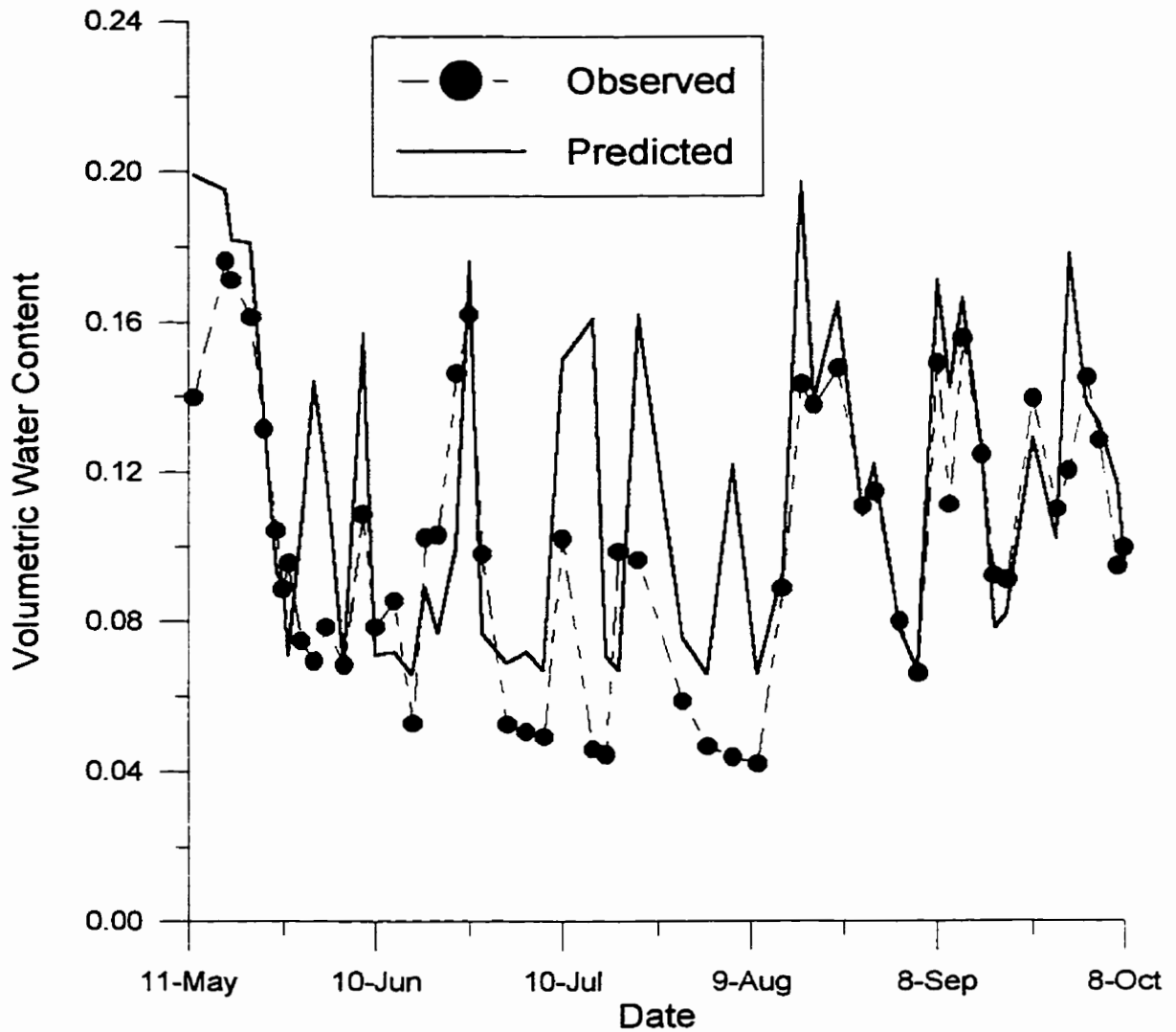
Fig. 4.7. Observed and predicted volumetric water contents at 7-cm depth. measured by TDR. for the 1997 field season.

An accurate retention curve and associated Campbell parameters are essential when using this type of model, as they affect drainage, the unsaturated hydraulic conductivity and the extent of plant evapotranspiration. In the model, plant evapotranspiration is limited by the water content at the permanent wilting point, -1500 kPa, and the movement of water to the roots, which is related to the unsaturated hydraulic conductivity. The higher water contents predicted in the A horizon may indicate the soil's

ability to retain water has changed since packing occurred, with the formation of a greater number of larger pore sizes. This could be attributed to rooting or freeze-thaw action.

With respect to the C horizon, the lower free drainage boundary condition compared to the actual zero pressure head condition is likely a key reason for the lower water contents predicted by LEACHM. In addition, Clemente et al. (1994) reported that LEACHM consistently underpredicted water contents for a sandy soil. The limited fit to the retention curve using Campbell's equation [4.1], as described previously, and the overprediction of water contents in the A horizon may also have disrupted the C horizon predictions.

CONCLUSIONS

Saturated hydraulic conductivity, measured on cores, was much greater and more variable for turf than soil. The moisture retention curve for turf also had a much steeper drop in water content at low applied head than soil. Both characteristics are likely due to the low bulk density of the thatch, along with the influence of macropores in the soil below, created by rooting and worm burrowing.

Field observations from the two-year study suggest that the majority of drainage below the root zone occurs in the spring and late autumn, but the intense drying of the soil over the summer may promote preferential flow following heavy rains. Observations of drainage and water contents also suggest there may be an effect of fertilization on the evapotranspiration rate of the turfgrass. Horizontal TDR probes provided insight into the change of water content with depth and the differences between the horizons, but only a rough estimate of the change in water storage of the entire soil profile could be calculated.

(Vertical TDR probes are now being installed in the lysimeters at GTIERC to remedy this problem.)

Although the Campbell parameters had a major effect on the water regime, the model seemed rather insensitive to the root distribution, the initial water content and even the use of independently measured values for the turf layer parameters. The effect of the turf layer may be more apparent for solute flow. The impact of turfgrass on enhancing or reducing macropore flow in structured soils would be an interesting topic for further research.

Statistical analysis, using RMSE, AE and ME, indicates that LEACHM simulated the water processes in soil reasonably well, with error values for drainage and water contents similar to other studies on bare soils or other crops. The best fit was for the B horizon, which was not surprising since it would be least affected by the bottom boundary condition and the grass. Visual inspection of water content predictions indicate that they follow the observed fluctuations well, reacting similarly to rainfall events for wetting, but less so for drying. This suggests LEACHM generally predicted water flow well, but had some difficulty with water redistribution during the drying periods (gravity drainage and evapotranspiration). The major limitations and inaccuracies in the EXPRES (LEACHM) simulation of the water regime for turf appear to be associated with the bottom boundary condition, the snowfall/snowmelt routine, the retention curve/Campbell parameters and evapotranspiration in the summer. The problem with evapotranspiration may be linked to the Campbell parameters through the limit of the permanent wilting point. Although the user-interface system incorporated into EXPRES makes LEACHM more accessible as a

management tool, the large amount of data required, including some parameters that are difficult to measure, may be an inhibitory aspect of using this model.

ACKNOWLEDGEMENTS

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CHAPTER 5

Transport of Nitrate and Chloride applied to Turfgrass:

Observations and LEACHM (within EXPRES) Predictions

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Abbreviations: GTIERC, Guelph Turfgrass Institute and Environmental Research Centre; TDR, time domain reflectometry

ABSTRACT

The leaching of surface-applied solutes, such as nitrate, to groundwater is an environmental concern. Computer simulation models are useful in designing management practices to address this problem and to further our understanding of solute transport processes. The objectives of this study were (i) to measure the leaching of nitrate and chloride applied to turfgrass, and (ii) to test the ability of the model LEACHM (within EXPRES) to simulate the transport of nitrate and chloride below turfgrass. Twelve lysimeters were packed with a three-horizon profile of a sandy loam soil, topped with Kentucky bluegrass (*Poa pratensis*) sod and monitored for 2 years in the field. Leaching of both nitrate and chloride occurred mainly in late autumn and winter, coinciding with lysimeter drainage patterns. Based on soil water samples taken from suction samplers placed at depths of 10, 17, 29, 43, 54, 64 and 85 cm, part of the solute from spring/summer applications remained in the soil during the very dry summers, and was later transported downward with the ensuing infiltration front in autumn. Observed variability between lysimeters may be linked to summer irrigation and/or the effects of past fertilization on turf rooting. For the most part, predictions by LEACHM of solute concentration profile were similar to field measurements. However, predicted and measured solute concentration values often differed significantly. Model errors in predicting plant uptake and the duration of soil storage of nitrogen are likely responsible for the differences in concentrations. Predictions of mass leached in drainage were too high. There were also a few indications of preferential flow with sharp peaks in solute concentration measured at depths much sooner than predicted.

INTRODUCTION

The potential for nitrate leaching following nitrogen fertilizer application to

turfgrass is an environmental concern. The leaching of nitrogen from the root zone means

a nutrient loss to growing plants, a waste of the energy used to produce the fertilizer, and

possible groundwater contamination (Starr, 1981). Currently, nitrate is the most

ubiquitous chemical contaminant in groundwater, and levels are increasing (Spalding and

Exner, 1993). The levels in groundwater exceed the Maximum Concentration Limit in

several agricultural areas in southern Ontario (Gillham, 1988; Goss et al., in press). In a

recent study of Ontario sod farms, 10 of the 86 water samples taken from tile drains or

piezometers contained nitrate-N at a concentration greater than or equal to 10 mg L^{-1}.

with an overall average of 3.74 mg L^{-1} for the 57 sites (Thurtell, 1997).

The fate of nitrogen applied to turfgrass is a function of plant uptake, atmospheric

loss, soil storage, leaching and runoff. Petrovic (1990) analyzed 12 studies undertaken

from 1974 to 1988 on N leaching from turfgrass, and identified several factors that

influence the degree of leaching, including soil type, amount and timing of irrigation, N

source, N application rates, and season of application.

In this study, the influence of rate and time of year for fertilizer application on the

amount of nitrate leaching were of primary interest. Dowdell and Webster (1980), Hardt

et al. (1993), Brauen and Stahnke (1995), and Jabro et al. (1997) all noted the trend of an

increase in nitrate leaching in the autumn and winter months, with lowest concentrations

of nitrate in infiltrating water in the summer. This effect has been attributed to a reduction

in plant uptake and evapotranspiration from summer to autumn/winter. In terms of the

effects of application rate, Thurtell (1997) noted that the average nitrate-N concentrations

at 60-cm depth only surpassed 10 mg L^{-1} when fertilized over the recommended rate for Ontario (160 kg N ha^{-1} $year^{-1}$ - Anonymous, 1994).

Although trends relating such factors to the amount of nitrate leaching observed in the field have been identified, there is still a lack of detailed understanding. The variability in the leaching process is apparent when comparing the measured travel times for ^{15}N-labeled fertilizer leaching in the following two studies. Branham et al. (1995) applied a total of 200 kg N ha^{-1} of urea in 5 applications to turf on a sandy loam soil; one application contained ^{15}N-labelled urea. It took nearly 2.5 years for the ^{15}N-labelled nitrate to appear in leachate collected from 1.2 m deep lysimeters. Approximately 33 % was found in the clippings during the 3 years. In contrast, Webster and Dowdell (1984) fertilized turf on clay loam and silt loam soils, using calcium nitrate at 400 kg N ha^{-1} $year^{-1}$, split into 4 applications, with ^{15}N-labelled nitrate applied in the first year. The drainage from monolith lysimeters, 1.35 m deep, contained 20.7 to 38 kg N ha^{-1} in the first year, of which the ^{15}N-labelled fertilizer contributed 48-69 %. In each study nitrate leaching was quantified at a single depth below the rootzone; in our study, we expect that sampling for nitrate at many depths within the soil profile may provide greater insight into the leaching process.

The testing of transport simulation models using data collected from the field is essential, and is often lacking (Vighi and Di Guardo, 1995). A validated transport model can be used to develop better management practices for nitrogen use-efficiency based on site-specific conditions. The modeling process itself is also useful for testing our understanding of chemical transport processes and for guiding experimental design and further research efforts (Rao et al., 1988). A number of researchers have indicated that

LEACHM (Wagenet and Hutson, 1987) has simulated solute transport in unsaturated soil as well or better than PRZM and CMLS (Pennell et al., 1990), the steady-state, convection-dispersion equation, the continuous-time Markov process, the transfer function model (Costa et al., 1994), PRZM-2 and VARLEACH (UK) (Brown et al., 1996). The model EXPRES (Expert system for Pesticide Regulatory Evaluations and Simulations) (Mutch et al., 1993), developed as a management tool, combines the research models PRZM and LEACHM with a user-friendly interface.

Only recently have researchers included model testing in leaching studies on turfgrass. The GLEAMS model was tested for pesticide leaching under turf (Smith et al., 1993), and it greatly overpredicted leaching. LEACHM predicted significantly higher concentrations in leachate and longer travel times than measured for dicamba transport under turf (T.L. Watschke - personal communication), though it gave reasonably accurate predictions for nitrate transport below Orchard grass (Jabro et al., 1997).

Our objectives were (i) to measure the leaching of nitrate and chloride in unsaturated, sandy soil using large, field lysimeters topped with Kentucky bluegrass turf, and (ii) to test the ability of the model LEACHM (within EXPRES) to simulate the transport processes in this system. The timing of ammonium-nitrate and potassium chloride applications followed the general fertilization practices of local sod farmers. Larger than normal fertilization rates, each equivalent to the yearly recommended rate, were used to ensure measurable nitrate concentrations and total mass leached for comparison to model predictions.

MATERIALS AND METHODS

Field Experiment

A description of the field lysimeters used in this study at the Guelph Turfgrass Institute and Environmental Research Centre (GTIERC), Guelph, ON, is given in Chapter 4. In addition to the TDR probes and drain tube, the lysimeters were fitted with suction samplers, each with a 1 bar, porous, ceramic cup, placed horizontally at 10, 17.5, 29, 42.5, 54, 70 and 84 cm below the thatch surface to enable extraction of soil water for analysis.

The application times of fertilizer correspond roughly to the practices of local sod farmers, though each application was equivalent to the recommended yearly rate. Granular, ammonium-nitrate fertilizer (Brussels Agromart Limited, Brussels, ON) was applied at 154 kg N ha^{-1} on July 17 and Oct. 29 of 1996, and May 14, July 25, and Sept. 28 of 1997. Potassium chloride dissolved in water was applied only in 1997, at 328 kg Cl ha^{-1}, on May 14 and Sept. 28. Six lysimeters received fertilizer in 1996, six did not. Half of each set received irrigation of 46.2 mm on July 25, and 53.8 mm on August 8, of 1996, so separate modeling runs were performed for both conditions. In 1997, 9 lysimeters were monitored: 4 received fertilizer, 4 received chloride and one control lysimeter did not receive either solute. Soil solution samples were only taken from two of the four lysimeters receiving chloride, however. All 9 lysimeters were irrigated with 10 mm of water on August 5 and 6.7 mm on September 28, 1997.

Chemical Analysis

Solution samples taken from suction samplers or the drain tube were stored in vacutainers at 4 °C prior to analysis. A Technicon TRAACS 800 auto analyzer system

was used to determine concentrations of nitrate and ammonium (Tel and Heseltine,

1990b) and chloride (Tel and Heseltine, 1990a). Mass of solute leached was calculated by

multiplying the concentration in samples taken from the drain by the volume of drainage

water collected.

Model Description

The computer model EXPRES (EXpert system for Pesticide Regulatory

Evaluations and Simulations) (Mutch et al., 1993), as described in Chapter 4, contains the

model LEACHM (v. 2) (Wagenet and Hutson, 1987) for simulation of water flow and

solute transport. The subroutine for solute (pesticides and conservative tracers) transport,

SOLP, solves the one-dimensional convection-dispersion equation (CDE) :

$$\frac{\partial}{\partial t}(\rho_b C_s + \theta C_l) = \frac{\partial}{\partial z}(D_e \frac{\partial C_l}{\partial z}) - \frac{\partial}{\partial z}(J_w C_l) - \Phi_s \qquad [5.1]$$

where C_s is the concentration of solute adsorbed to solid particles; C_l is the concentration

of solute in solution; D_e is the effective diffusion-dispersion coefficient; J_w is the water flux

density; θ is volumetric water content; ρ_b is the dry soil bulk density; Φ_s is a solute

source/sink term; z is depth; and t is time. This equation does not account for flow

through macropores or other forms of preferential flow. See Wagenet and Hutson (1987)

for more details.

In this study, the nitrate and chloride anions were considered conservative tracers,

eliminating sorption from the transport process. The only sink term, plant uptake by mass

flow (in the evapotranspiration stream) was not included. As EXPRES only contains the

LEACHM subroutines for pesticide transport, we were not attempting to simulate the

complicated transformations involved in the nitrogen cycle, but atmospheric losses or

immobilization in the soil may be apparent in the differences between observed and

predicted concentrations. The model simulation really represents a worst-case scenario in

terms of the amount of nitrate leaching. A list of parameters with values required by the

model was given in the previous chapter on water flow; additional parameters required for

solute transport are listed in Table 5.1. Two different values of dispersivity were

compared because of uncertainty in the appropriate value to use. As well, two root

fraction distributions investigated in the previous chapter were also compared.

Table 5.1. Parameter values for solute transport used in the LEACHM simulation, excluding those given in the previous chapter for water flow, with source of reference or brief explanation. See EXPRES manual (Mutch et al., 1993) for a complete description.

Parameter	Value(s)	Reference/Explanation
Solubility $(mg\ L^{-1})$ - NH_4NO_3	11830	Weast, 1985
- KCl	3440	Weast, 1985
K_{oc} $(L\ kg^{-1})$ - NO_3^-	0	inorganic anion
- Cl^-	0	inorganic anion
Molecular Diffusion Coefficient $(mm^2\ day^{-1})$	164	average - Weast, 1985
Dispersivity (mm)	13.8	equation in Fetter, 1994
	3.2	Pearson et al., 1996
Diffusion Coefficient in Air $(mm^2\ day^{-1})$	0	not volatile
Barometric Enhancement $(mm^2\ day^{-1})$	0	not volatile
Vapour Density $(mg\ L^{-1})$	0	not volatile
Root Fraction Distribution (Turf/A/B/C)	35/60/5/0	Troughton, 1957
	95/5/0/0	estimated for comparison study

Since the nitrate and chloride tend to move through the soil as a slug or peak,

gradually spreading out during transport down through the soil profile, it is difficult to

perform a statistical analysis on the model predictions versus measured values. For

instance, predicted peaks may reflect the shape and maximum concentration of

observations, but if shifted slightly in time large error values would result. Therefore, a qualitative analysis of the model simulation performance was undertaken.

RESULTS AND DISCUSSION

Nitrate Leaching Observations

The maximum concentration of nitrate in drainage water was 70 mg L^{-1} in 1996 and 600 mg L^{-1} in 1997. Leaching of ammonium was minimal for all lysimeters whether they were fertilized or not. Drainage losses of nitrate from unfertilized lysimeters was negligible, generally 10 % of that from fertilized lysimeters, and concentrations were always below 3 mg L^{-1}.

Even with the large fertilizer application rate there was very little, if any, leaching of nitrate from the lysimeters in the subsequent months following spring or summer applications (Figs. 5.1 and 5.2A). However, up to 13 % of the nitrogen applied in 1996 leached out of the lysimeters by January 6, 1997 and nitrate levels over 10 mg L^{-1} still remained in the C horizon at that time. During the 1997 field season the lysimeters lost up to 21 % of the nitrogen applied through leaching as measured in the drainage water. Of note, the concentrations of nitrate were over 200 mg L^{-1} on the last sampling date (January 29, 1998), suggesting even more leaching probably would have occurred during the winter.

It was not unexpected that the majority of leaching occurred in the late autumn and into the winter months. The seasonal trend of nitrate leaching has been attributed to changes in plant uptake and evapotranspiration. Higher evapotranspiration rates in the
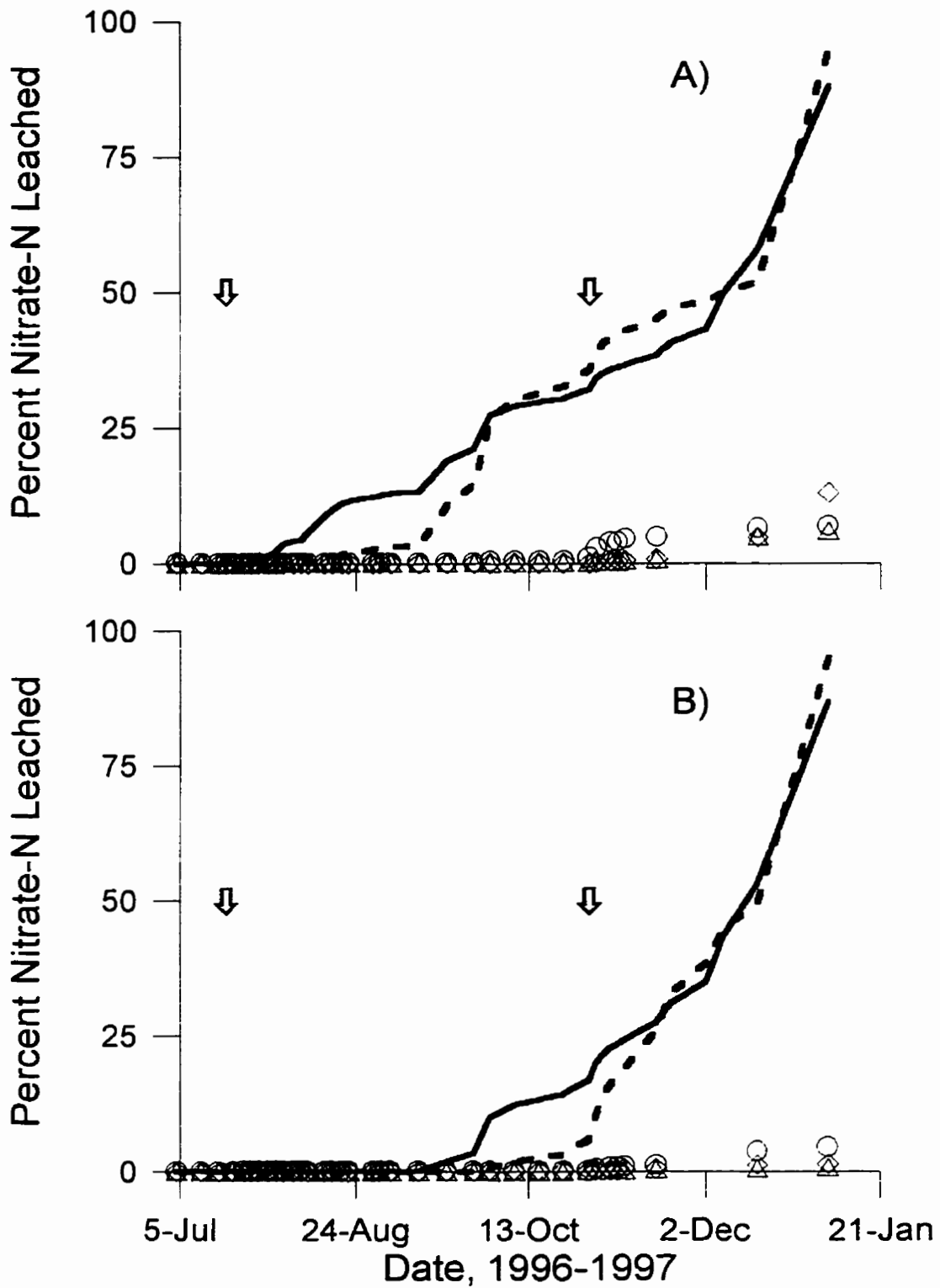
126

Fig. 5.1. Percent of applied nitrate-N leached from lysimeters for the 1996 field season for A) summer irrigation and B) no summer irrigation. Symbols represent measured field data from individual lysimeters; lines represent predictions (solid - high dispersivity; dashed - low dispersivity), arrows indicate application dates.
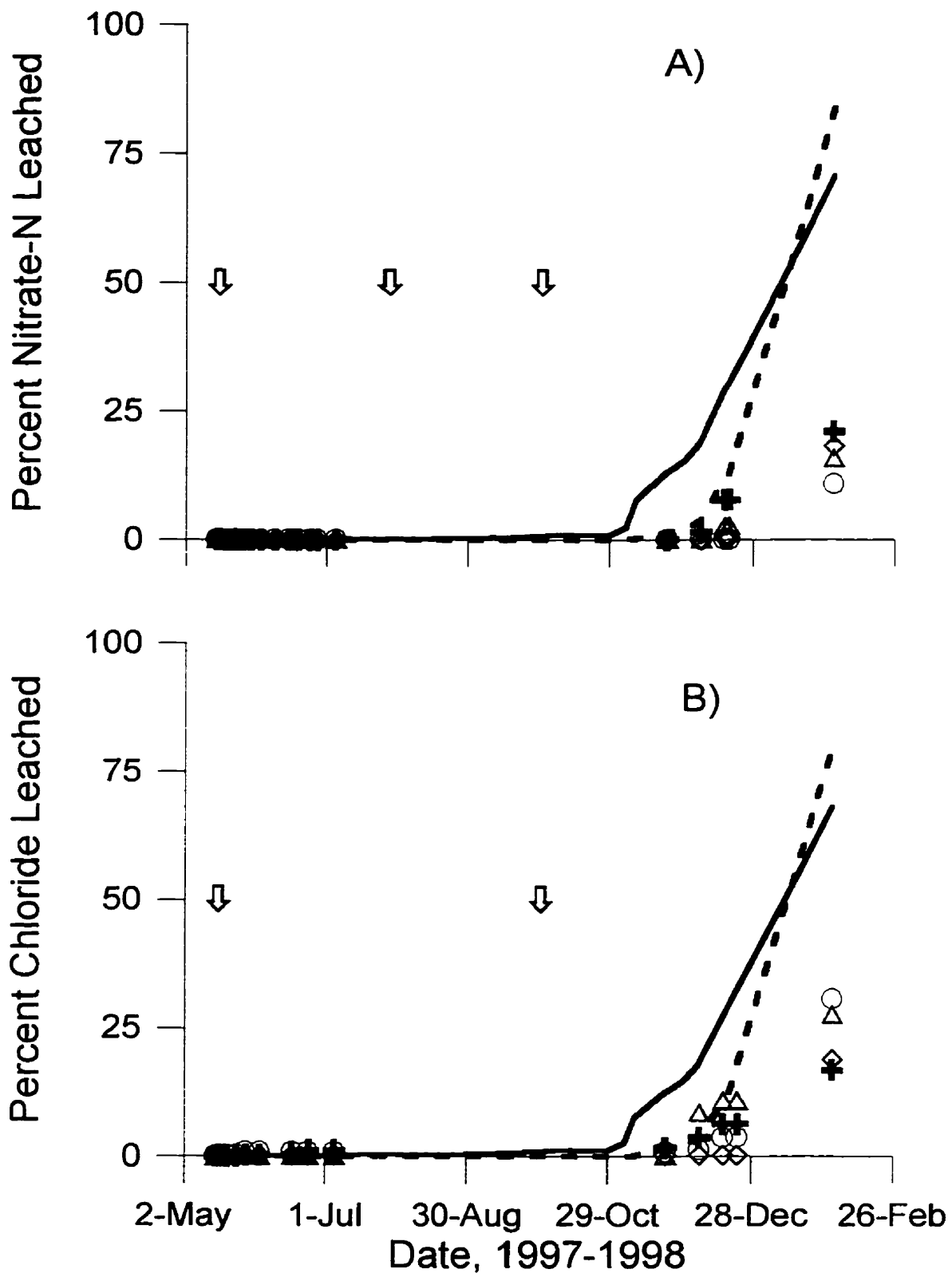
Fig. 5.2. Percent of applied A) nitrate-N and B) chloride leached from lysimeters for the 1997 field season. Symbols represent measured field data from individual lysimeters; lines represent predictions (solid - high dispersivity; dashed - low dispersivity), arrows indicate application dates.

summer (precipitation was similar between summer and autumn) resulted in virtually no drainage during the summer. Leaching during the summer never exceeded 0.5 % of the spring application, and was similar to that of the unfertilized lysimeters. Nitrate leaching followed soon after, or coincided with, the start of water drainage in the autumn in both years. Although the nitrate concentrations in the soil water at various depths were often larger in the autumn than the summer (Fig. 5.3), changing water contents and the mixing of nitrate from different applications make it difficult to attribute this effect to plant uptake.

The dry conditions of summer and early autumn in 1997 may have enhanced the leaching of the autumn application. Webster and Dowdell (1984) observed greater leaching of nitrate when drought was introduced 2 weeks before and after fertilization, or 4 weeks prior to fertilization. Drought may have decreased plant uptake and microbial denitrification, and promoted crack development (preferential flow pathways) in the soil. However, in that study, lysimeters which had drought imposed also received more irrigation in the subsequent two weeks, which could also have boosted nitrate leaching.

The use of solution samplers installed at seven depths in the soil profile provided more information about the leaching of nitrate from different applications than if only the drain samples were used. In 1996, nitrate from the summer application reached or passed the bottom of the B horizon, where it remained until it leached out in early November (data not shown). The late autumn application of 1996 had reached the middle of the B horizon by mid-December. In 1997, no fertilizer nitrate was detected below the 10-cm depth (Fig. 5.3A,B) during the spring or early summer. After the summer application, a plug containing high levels of nitrate moved down into the B horizon, where it remained
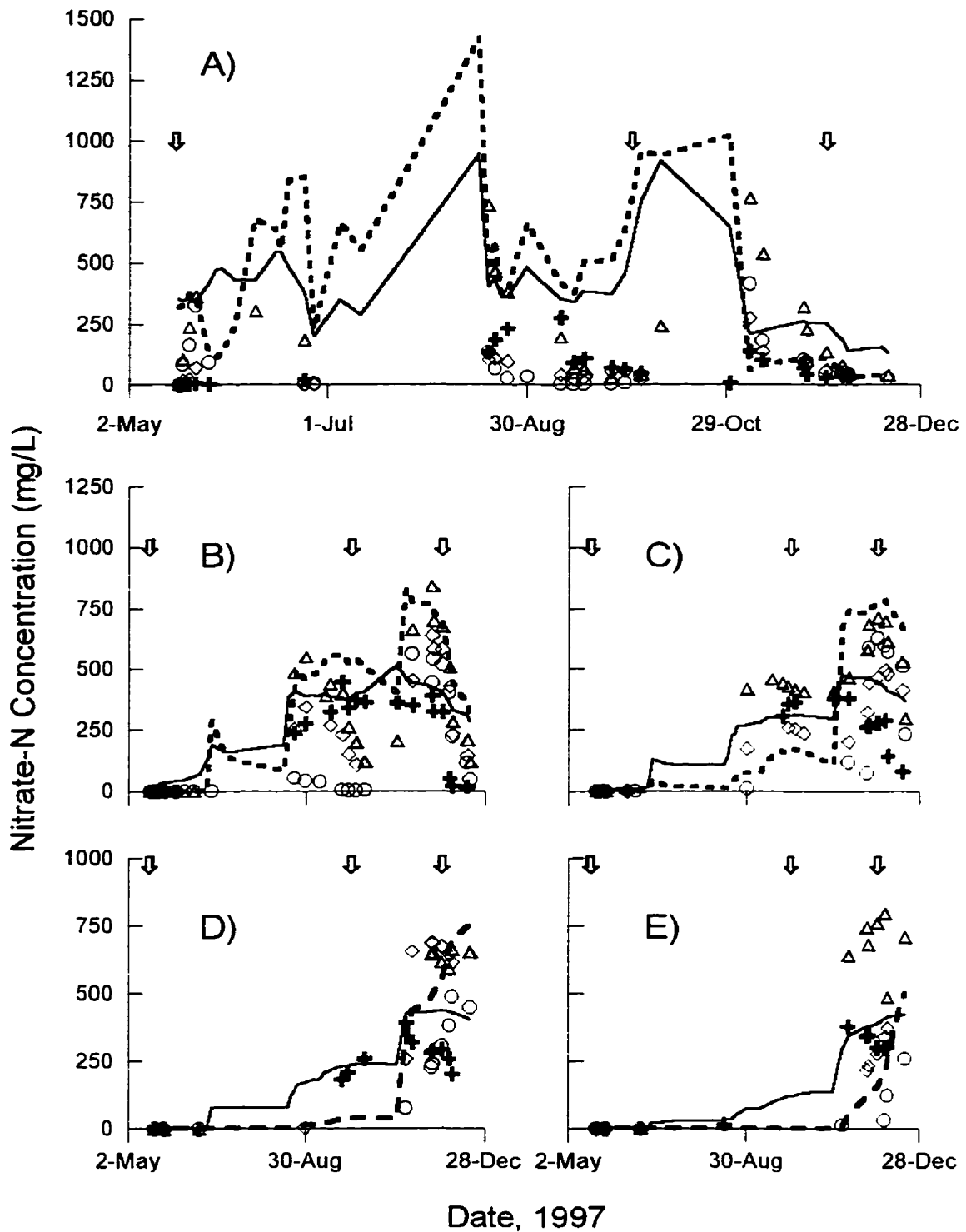
Fig. 5.3. Nitrate concentrations within the soil profile at A) 9. B) 29. C) 43. D) 53 and E) 85-cm depth below the turf surface, for the 1997 field season. Symbols represent field observations (obtained with suction samplers) from four lysimeters; lines represent predictions (solid - high dispersivity; dashed - low dispersivity). Arrows indicate fertilization dates. For clarity, scales are not the same on all graphs.

until the wetting front, initiated in the autumn of that year, arrived carrying nitrate from the autumn application (Fig. 5.3C). Within the C horizon, in early November, peaks in concentration from the different applications became indiscernible (Fig. 5.3D,E). It appears that during a very dry summer, unused fertilizer nitrogen may move and remain below the A horizon and, potentially, the turfgrass root system. This nitrogen can be subsequently leached when the soil wets up in the autumn. The high concentrations of nitrate in the drainage water could indicate the build-up of the solute slug as the resident nitrate was collected and carried in front of the passing infiltration front. This phenomenon is similar to the plane of separation model of solute transport and water flow by Elrick et al. (1987). The timing and amount of nitrogen leached from spring and summer fertilizations seem strongly controlled by drying of the soil profile via evapotranspiration.

It is apparent that tripling or doubling the recommended fertilization rate will result in a large amount of N leaching. These results corroborate the findings of Thurtell (1997) of an increase in nitrate leaching from sod receiving fertilizer at greater than the recommended rate. Solution sampler measurements show that a significant amount of nitrogen from the summer application was transported out of the rootzone (Fig. 5.3). In a similar study in Texas, a single application of ammonium-nitrate at 163 kg N ha^{-1} to golf greens on sandy loam soil resulted in leaching losses of 9.8 % of that applied, with nitrate peaks of 170 mg L^{-1} (Brown et al., 1982).

Variability

Although one would expect solute transport in repacked sandy loam soil to be fairly uniform, there was some variability in the travel times, the spreading of peaks and the peak concentrations between lysimeters. These differences became more pronounced with depth. For example, the maximum penetration depth of the nitrate peak from the summer application of 1996, before summer drying, ranged from the top to past the bottom of the B horizon (data not shown). The time when the nitrate peak reached the drain in the autumn varied between lysimeters by a few weeks, and the amount removed in the drainage water by January 6, 1997, ranged from around 1 to nearly 13 percent of applied N (Fig. 5.1). For the 1997 field season, the breakthrough time of nitrate in drainage waters differed by up to one month, and the amount leached by January 29, 1998, varied from 11 to 21 percent of applied N (Fig. 5.2A).

The irrigation of half of the lysimeters in the summer of 1996 may have produced some of the variability illustrated in Fig. 5.1. The average amount of nitrate leached by January 6, 1997, was 8.6 % of applied N from the irrigated lysimeters and 2.2 % for the non-irrigated lysimeters. Even though leaching did not occur until the autumn, the irrigation water likely transported the nitrate from the summer fertilization deeper into the soil, making it less available to the plants. These observations are in agreement with Thurtell (1997), who determined that the water input rate had a significant, positive effect on the amount of nitrogen leached below turfgrass in field plots.

Another possible cause of the variability in nitrate leaching may be fertilization history. For example, nitrate arrived at the bottom of the lysimeters fertilized the previous year sooner than those not fertilized the previous year. In addition, the lysimeters

receiving fertilizer the previous year generally had higher peak concentrations and faster

breakthrough times of nitrate in the soil profile. Nitrogen from the previous applications,

stored in organic matter, may have been released to infiltrating water in the spring, with

nitrification producing the extra nitrate. Hansen and Djurhuus (1996) suggested that

although the soil inorganic-nitrogen contents were similar at harvest, the increased

leaching with increased application rate (spring fertilization) was caused by greater

mineralization of organic residues, mainly in autumn. Past fertilization may have also

affected the rooting pattern of the turf, as high fertilization loading leads to shallower root

systems (Beard, 1973), which could limit plant uptake of nitrate.

Chloride Leaching Observations

Chloride moved through the A horizon very quickly in the spring (data not

shown), compared to nitrate, likely due to the formation of water ponding conditions

during the application of chloride in solution. A slower application rate was used to

reduce the chance of ponding for the autumn application. At lower depths the peak

concentration of chloride moved similarly to nitrate, as the chloride remained in the profile

until the autumn infiltration front pushed it to greater depths. Breakthrough of chloride

from the bottom of the lysimeter occurred with the start of drainage, as did nitrate (Fig.

5.2B). Since, on average, only 23.5 % of the applied chloride had been collected in the

lysimeter drainage by January 29, 1998, there must still have been a large portion of the

pulse remaining within the soil. The average percent of nitrate leached was lower (17 %)

than for chloride; the difference is likely due to nitrogen removal, such as by the plants or

microbial transformations. This also suggests that the nitrate removed with the drain

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water was probably only from the spring and/or summer applications, with the autumn application N still in the soil profile.

LEACHM Simulation - Percent Loss in Drainage

Measurements and LEACHM predictions of the percent of applied nitrate leached out the bottom of the lysimeters is illustrated in Fig. 5.1 for the 1996 field season, and for nitrate and chloride in Fig. 5.2 for the 1997 field season. The model did not predict significant leaching during the summer, as was observed. However, LEACHM predicted that autumn leaching would begin earlier than was actually observed. In the previous chapter, we noted that the prediction of water drainage was earlier than observed as well, and that the difference was likely related to the bottom boundary condition and possibly lower than predicted evapotranspiration losses during the summer. Although chloride did not exit the bottom of the lysimeter until the middle of November at the earliest, it had reached the bottom of the C horizon in early November, the same time leaching was predicted to begin.

The field-measured leached losses of nitrate and chloride generally were lower than the amounts predicted, especially for the 1996 field season (Figs. 5.1 and 5.2). Based solely on the drainage data, it is uncertain whether the cause of the larger discrepancy between observations and predictions for 1996 is due to slower leaching through the profile, or greater removal of nitrogen prior to or during transport. Further discussion on this matter will occur in the next section.

An increase in model dispersivity will cause more solute spreading, so leaching from the lysimeter will begin sooner, but the percent leached will increase more gradually.

The build-up of water at the bottom of the C horizon (Chapter 4) distorts the data by delaying both drainage and solute breakthrough. Therefore, it is difficult to determine which of the two model dispersivity values tested more closely represents the value in the field.

Irrigation had a much larger effect on the predictions of solute transport than in reality. The start of leaching differed by one month based on LEACHM simulations (Fig.5.1, A vs. B), when in actuality, the measured start of leaching was very similar for all the lysimeters, irrigated or not (Fig. 5.4). The evapotranspiration losses during the summer were probably higher than was calculated by the model, so most of the irrigation
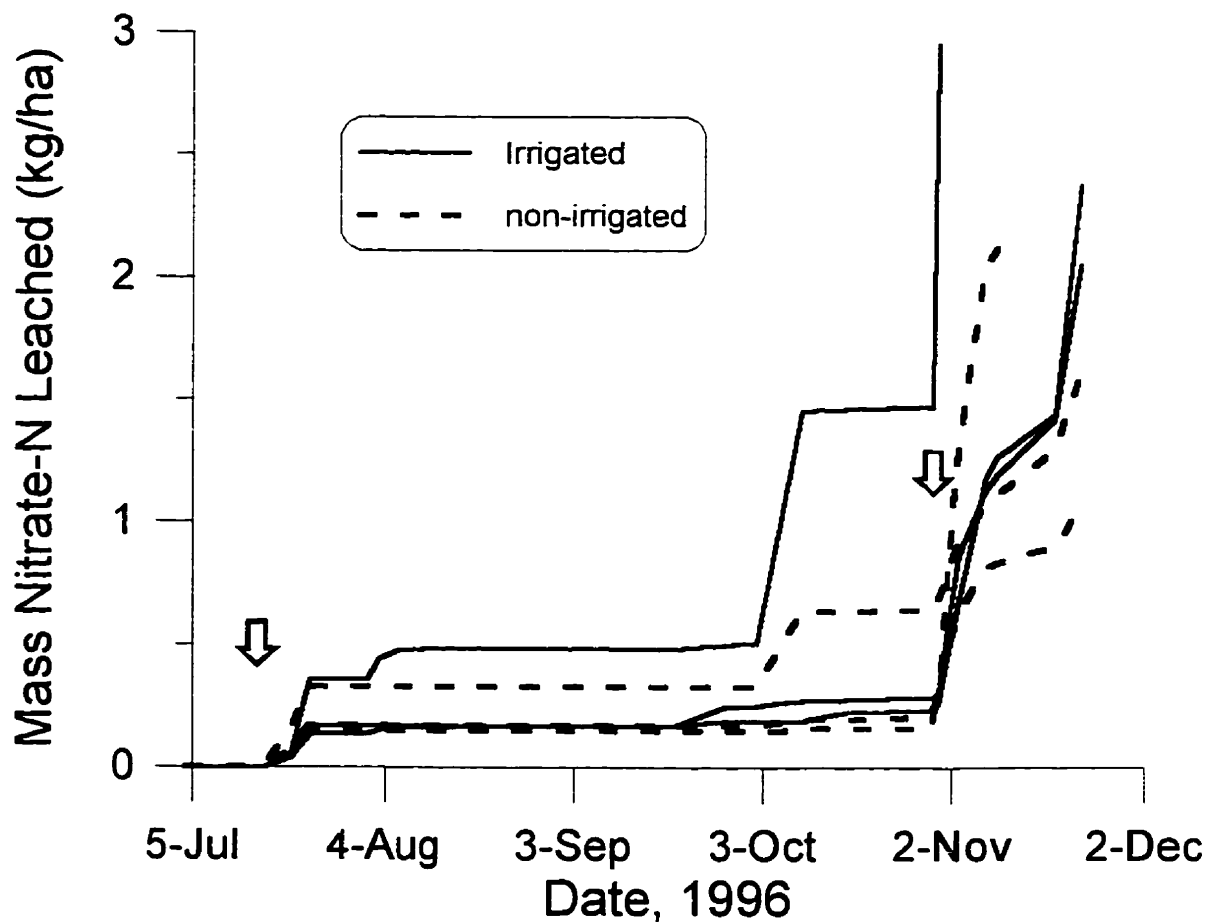

Fig. 5.4. Details of measured cumulative mass of nitrate-N leached out of the bottom of the six lysimeters receiving fertilizer (arrows represent application dates) from July to November, 1996.

water remained near the surface and was used by the plants before it could considerably affect the solute distribution.

LEACHM Simulation - Concentration Profiles

Although model simulations did not always match exactly with the measurements of solute concentrations within the soil profile, they did capture the major trends given by the field data. In general, the timing of transport was simulated well, but the solute concentrations were simulated less well. Even when there was variability in breakthrough times between lysimeters, the predictions often reflected the average travel times (Fig. 5.3E - dashed line). The only time period in which the predictions of solute breakthrough did not resemble measurements was in the autumn of 1996 (data not shown). Greater drying in the field due to increased evapotranspiration in the summer slowed transport of nitrate at depth from the June application. However, nitrate from the autumn application moved faster, and as a sharper peak than predicted, for late autumn. The inaccuracy of the snowfall/snowmelt routine, explained in the previous chapter, may have essentially slowed infiltration in the model simulation by predicting snow on the surface when in reality none was present.

The model predictions using the two dispersivity values were fairly similar; variability between lysimeter observations was of the same magnitude as the difference in predictions with the two dispersivity values (e.g. Fig. 5.3E).

Predicted concentrations more closely resembled the measured solute concentrations for the 1997 field season, being much larger than the 1996 field season levels. Similar findings were made based on the amount of nitrate collected in the

drainage water. These findings suggest that more nitrogen was removed from the soil

water in the first field season, through ammonia volatilization, denitrification, plant uptake

or soil organic matter storage. Plant uptake of 5 to 74 % of the applied fertilizer nitrogen,

and atmospheric losses from 0 to 93 % have been reported for turf (Petrovic, 1990).

Indeed, Webb (1997) measured higher N_2O emissions from turf at GTIERC in 1996,

apparently from denitrification, which suggests that N_2 losses may also have been higher.

The drier conditions of 1997 may have impaired microbial activity, reducing the

production of nitrogenous gases, and restricted plant growth. A key component of

storage of nitrogen in the soil is incorporation into organic matter. The amount of storage

is dependent on the size of the organic matter pool, which tends to increase under newly

established turf over a number of years until an equilibrium is reached (Petrovic, 1990).

Thus, the soil has a limited capacity for fertilizer nitrogen storage. Since there was one

more fertilizer application in 1997, the immobilization of nitrogen in soil would likely

show less of a decrease in the fraction leached.

LEACHM Evaluation

A sensitivity analysis was performed to investigate the effect on solute transport of

root fraction distribution. The two values used in the modeling exercise were given in

Table 5.1. The resultant curves of concentration versus time were compared for 9, 43 and

85-cm depths. Changing the root fraction distribution created only minor differences in

nitrate concentrations and the spread of the peaks (data not shown), with differences most

likely due to the lower water contents and less drainage associated with the shallower root

system. The effect of the rooting fraction on nitrate movement tended to be more

prominent when using the lower dispersivity value; likely a larger portion of the mass remained in the rooting zone for a longer time.

The transport of nitrate through the soil was sometimes very rapid. Measured nitrate concentration peaks generally reached the 10-cm depth within days to a week following spring and autumn applications. Peaks occasionally passed consecutive sampling depths within a day or two. Since the model also predicted these peaks at these times, they do not represent preferential flow. However, there were some possible indications of this phenomenon. In July 1996, a small amount of nitrate was leached from the lysimeter less than a week after application (Fig. 5.4), while leaching was only predicted (not shown) a week later for the irrigated plots and two months later for the non-irrigated ones. In May 1997, the spring application of chloride reached the B horizon almost immediately after application. However, the dissolved potassium chloride was applied with 1 cm of water in about 1 minute, so some ponding may have occurred leading to macropore flow. On two occasions in June, very high concentrations (nearly 1000 to 3900 mg L^{-1}) of chloride were measured at the bottom of the lysimeter and in drainage water, indicating the occurrence of preferential flow (data not shown).

Pennell et al. (1990) presented the following criteria for evaluating transport simulation models: the predicted solute travel times should be within 50 % of the observed values. In this study, it was difficult to determine the exact travel time in the lysimeters due to a lack of samples during dry periods, changing water contents, and mixing of nitrate from different applications. However, based on a visual inspection of LEACHM predictions and field observations, we would argue that this criteria is met for NO_3^- and Cl^-

breakthrough measured by solution samplers, except perhaps for the indications of preferential flow, which as previously outlined, the model does not include.

CONCLUSIONS

Nitrate levels in drainage water were much larger in the fertilized lysimeters, with maximum concentrations reaching 70 mg L^{-1} in 1996 and 600 mg L^{-1} in 1997, than in control lysimeters. Both nitrate and chloride leaching mainly occurred in late autumn and winter, with losses in 1997 averaging 23.5 % of applied chloride and 17 % of applied nitrate by February, 1998. The concentrations in drainage water were still high when sampling was stopped for the winter. It is possible that a significant amount of nitrate from the fertilizer would have reached the groundwater at this site given the application rates used and the local climatic conditions.

Using suction samplers to obtain water samples within the soil profile, it was observed for both 1996 and 1997 that nitrate and chloride from spring/summer applications remained in the unsaturated soil below the rootzone during the very dry periods, and were carried along with the infiltration front during wetting in the autumn.

Variability between lysimeters in nitrate concentrations, solute spreading and breakthrough times was observed, even though similarly-packed lysimeters were used. Breakthrough times from the bottom of the different lysimeters often varied by a few weeks. Summer irrigation and/or the effects of past fertilization on turf rooting, likely altered the amount of infiltrating water and soil water contents, affecting solute flow velocities.

Predictions by LEACHM were good for the timing of nitrate and chloride transport, with breakthrough times judged to be within 50 % of those observed. The predictions differed more from observations in terms of solute concentrations. The LEACHM model predicted a higher percentage of the applied chloride and nitrate leached, especially for the 1997 field season. Predicted breakthrough times in drainage were also faster than was measured. The predictions were affected by various solute sinks we did not attempt to include (e.g. denitrification), and water flow inaccuracies, including summer evapotranspiration losses and the bottom boundary condition. Predicted concentrations were much more similar to observations from the 1997 field season than for 1996. The spring application of solute, applied only in the second season, likely provided nitrogen well in excess of soil storage limits, and the dry conditions may have limited microbial activity, reducing atmospheric losses, and also plant uptake. There were also a few indications of preferential flow, with sharp peaks observed at depths much sooner than predicted, especially when the solute was applied with irrigation water.

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CHAPTER 6

Leaching of Dicamba from Turfgrass: Observations and LEACHM (within EXPRES) Predictions

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Abbreviations: GTIERC, Guelph Turfgrass Institute and Environmental Research Centre; TDR, time domain reflectometry; ELISA, enzyme-linked immunosorbent assay; PBS, phosphate-buffered saline; USGA, United States Golf Association.

ABSTRACT

The leaching of surface-applied herbicides, such as dicamba [2-methoxy-3,6-dichlorobenzoic acid], to groundwater is an environmental concern. Computer simulation models are useful in designing better management practices and in furthering our understanding of solute transport processes. The objectives of this study were (i) to investigate the leaching of dicamba applied to turfgrass, and (ii) to test the ability of the model LEACHM (in EXPRES) to simulate the transport and degradation processes in this system. Four field lysimeters, packed with a 3-horizon profile of sandy loam soil and topped with Kentucky bluegrass (*Poa pratensis*) sod, were monitored after receiving 3 applications of dicamba. Concentrations of dicamba over 1 mg L^{-1} were detected in soil water using suction samplers, though drying of the soil during the summer prevented leaching out of the A horizon. Lower temperatures and increased infiltration allowed greater leaching of the November application; high concentrations were maintained in the B horizon at the end of the year. In general, LEACHM predictions were similar to observed concentration profiles, though there were some indications of preferential flow in the field following application in September. Dicamba peaks at 10-cm depth tended to be sharper, with higher concentrations than predicted, for the May and November applications. Differences between predictions and observations were likely caused by lower predicted evapotranspiration in summer, inaccuracy of the snowfall/snowmelt routine, and the model's inability to modify degradation rates with changing climatic conditions. A further modeling exercise indicated that increased degradation in the turf layer can significantly reduce dicamba leaching.

INTRODUCTION

Leaching of pesticides through the soil to the groundwater is a concern since these chemicals may affect the quality of drinking water supplies and surface water ecosystems. Dicamba, a postemergent herbicide commonly used to control broadleaf weeds in turfgrass, has been detected in groundwater on numerous occasions (Koterba et al., 1993; Cox, 1994). The drinking water limit for dicamba is 200 μg L^{-1} in the U.S., and 120 μg L^{-1} in Canada (Caux et al., 1993). Based on numerous studies in Canada, Caux et al. (1993) calculated that 8 % of the surface water and 2 % of the groundwater samples had detectable amounts of dicamba. Specific to turfgrass, Cohen et al. (1990) tested the groundwater under various golf courses on Cape Cod (MA) and detected dicamba in one of the sixteen monitoring wells.

In a turfgrass system, herbicides with low volatility can be taken up by plants, sorbed to soil particles or organic matter, degraded, and/or leached. Dicamba is rapidly absorbed by plant roots and foliar tissues, and translocated to other parts of the plant (Frear, 1976), after which it can be metabolized or exuded via the roots or leaves (Caux et al., 1993). However, Snyder and Cisar (1997) recovered very little of the applied dicamba in turfgrass clippings from a golf green. Baskaran et al. (1997) studied sorption of dicamba to golf green materials – a sand/peat mixture and thatch. In their batch-sorption experiment, the adsorption coefficient, K_d, was low: 0.54 mL g^{-1} in soil and 3.29 mL g^{-1} in thatch. In their column leaching experiment, dicamba moved at the same rate as water. Dicamba is readily degraded by microorganisms, with the main degradation product in soil, 3,6-dichlorosalicylic acid (3,6-DCSA), being a less mobile and more persistent species (Smith, 1974; Pearson et al., 1996b). This degradation process is influenced by

environmental conditions such as temperature and soil water content. In both soil and the thatch of turfgrass, an increase in temperature from 4 to 20°C resulted in an increase in the degradation rate of dicamba ranging from 2.0 to 3.7 times (Chapter 3).

Most studies of dicamba on turf have measured only very low levels in infiltrating water and low total mass leached. The leaching and dissipation of 2,4-D and dicamba from a suburban lawn were measured in field plots of silt loam or sandy loam, overlying highly permeable sand/gravel (Gold et al., 1988). Leachate was sampled at 0.2 m, at the top of the sand/gravel. Dicamba was applied either in April, June, or September at 0.11 kg ha^{-1}. Generally the herbicide concentrations in the leachate were quite low, with 95% of the samples under 1 µg L^{-1}, 2 % over 10 µg L^{-1} and a maximum concentration of 38 µg L^{-1}.

More recently, Smith and Bridges (1996) applied 2,4-D, dicamba (maximum rate of 0.28 kg ha^{-1}) and mecaprop in November and July to lysimeters (0.15 m deep) in a greenhouse and in the field (Georgia), simulating conditions on a golf green. The highest concentrations of dicamba detected in the effluent were 3.6 µg L^{-1} and 2.6 µg L^{-1}, for indoor and outdoor conditions, respectively. Less than one per cent of the applied dicamba was collected in the leachate during the study period, though there was significant loss in runoff because of the sloped conditions.

Snyder and Cisar (1997) applied dicamba and 2,4-D to USGA-type greens in spring and late summer. The turf received 0.06 kg ha^{-1} twice, a week apart, each time. Soil cores showed noticeable peaks of concentration in soil and thatch shortly after application, which rapidly declined over the following two weeks. Samples taken at 0.10 m depth with a lysimeter percolate collection apparatus had an average concentration of

2.5 μg L^{-1} from the spring application and 1.7 μg L^{-1} from the summer application, with total recovery of 9.7 % and 10.8 % of applied.

Relatively high concentrations of dicamba were reported in a runoff/percolate field study of pesticides and fertilizer on sloped turf over a clay topsoil (Harrison et al., 1993). Dicamba was applied at 0.28 kg ha^{-1} in July, August, September, October, and November over 2 years. Pan lysimeters at 0.15 m depth were used to collect leachate samples. The peaks in concentration coincided with the first major irrigation or rainfall within a week after application, although the irrigation events were considered extreme. The mean concentrations (3 replicates) for dicamba for these events were 11, 21, 22, 118, 57 μg L^{-1}.

We suggest that for spring and autumn applications of dicamba in temperate climates, the effect of lower temperatures, causing reduced plant uptake and microbial activity, may permit greater leaching losses than commonly observed.

The testing of transport simulation models using data collected from the field is essential, and is often lacking (Vighi and Di Guardo, 1995). A validated transport model can be used to develop better management practices for herbicide application based on site-specific conditions. The modeling process itself is also useful for testing our understanding of chemical transport processes and for guiding experimental design and further research efforts (Rao et al., 1988). A number of researchers have indicated that LEACHM (Wagenet and Hutson, 1987) has simulated solute transport in unsaturated soil as well or better than PRZM and CMLS (Pennell et al., 1990), the steady-state convection-dispersion equation, the continuous-time Markov process, and the transfer function model (Costa et al., 1994), PRZM-2 and VARLEACH (UK) (Brown et al., 1996). The model EXPRES (Expert system for Pesticide Regulatory Evaluations and

Simulations) (Mutch et al., 1993), developed as a management tool, combines the research models PRZM and LEACHM with a user-friendly interface.

Only recently have researchers modeled the transport of solutes applied to turfgrass. The GLEAMS model was tested for pesticide leaching under turf (Smith et al., 1993), and it greatly overpredicted leaching. LEACHM predicted significantly higher concentrations in leachate and longer travel times for dicamba transport under turf (Watschke - personal communication).

Our objectives were (i) to investigate the leaching of the herbicide dicamba in unsaturated, sandy soil using large, field lysimeters topped with Kentucky bluegrass turf, and (ii) to test the ability of the model LEACHM (in EXPRES) to simulate the transport and degradation processes in this system. Dicamba was applied three times during the year with samples taken at various depths and from the lysimeter drain. Comparisons between these field observations and LEACHM predictions are based on soil-water concentrations and total mass leached from the lysimeters.

MATERIALS AND METHODS

Field Experiment

A description of the field lysimeters used in this study at the Guelph Turfgrass Institute and Environmental Research Centre (GTIERC), Guelph, ON, is given in Chapter 4. In addition to the TDR probes and drain tube, the lysimeters were fitted with suction samplers, each with a 1 bar, porous, ceramic cup, placed horizontally at 10, 17.5, 29, 42.5, 54, 70 and 84 cm below the thatch surface to enable extraction of soil water for analysis.

Soil temperature, required to calculate degradation rates, was monitored with thermocouples.

Banvel (480 g L^{-1} of dicamba) was obtained from Sandoz Agro Canada Inc. (ON). It was applied at a rate equivalent to 0.6 a.i. kg ha^{-1}, the maximum recommended rate for turf (Ontario Herbicide Committee, 1996), using a push-cart sprayer mounted with a line of 4 nozzles, on May 5, September 28, and November 27, 1997. Filter papers were placed on the grass around the lysimeters to quantify the actual amount of dicamba reaching the turfgrass. The measured amounts received at the surface for each application were 0.05 to 0.60 kg ha^{-1} (May); 0.10 to 0.48 kg ha^{-1} (September); 0.11 to 0.45 kg ha^{-1} (November). Therefore, the actual amount received by each lysimeter may be different, though likely not more than the desired rate. Each lysimeter was irrigated with 10 mm of water on August 5, and 6.7 mm on September 28, 1997.

Dicamba Analysis

Soil-water samples taken from suction samplers or the drain tube were stored in vacutainer vials at -20 °C prior to analysis. Dicamba stability was monitored with dissolved ^{14}C-dicamba; no loss during storage was observed. The concentration of dicamba in samples was measured using indirect ELISA (enzyme-linked immunosorbent assay) (Hall et al., 1989), which gives a general estimate of the herbicide concentration. A brief description of the analysis follows.

Immulon #4 flat-bottomed plates were coated with coating conjugate (dicamba linked to OVA diluted to 1:1000 in PBS) at 100 μL per well and incubated at 4° C overnight. The plates were washed three times with phosphate-buffered saline (PBS)

containing 0.05 % (v/v) Tween 20 and dried. Sites not containing coating conjugate were blocked by adding 200 μL per well of 0.1 % gelatin in PBS (w/v). After a 20 minute incubation the plates were washed and dried, as described previously. Samples or dicamba standards were mixed 1:1 with the anti-dicamba antibody (diluted to 1:50 in PBS); after one hour the mixture was added to the plates at 100 μL per well. The plates were incubated at room temperature for one hour, before being washed and dried. A secondary antibody linked with a colour indicator, goat anti-rabbit horse radish peroxidase (diluted to 1:5000 in PBS), was added at 100 μL per well. Substrate, 1 mg mL^{-1} (approximately) ABTS (2,2'-azino-bis [3-ethylbenzthiazoline 6-solfonic acid] diammonium; Sigma Chemical Co. (St. Louis, MO)) with 1 mg mL^{-1} urea hydrogen peroxide (Sigma Chemical Co. (St. Louis, MO)) in citrate buffer (pH 5.0), was added to react with the indicator. The light absorbance (405 nm), measured via mass spectroscopy after one hour, is inversely proportional to the concentration of dicamba, which was quantified using standard concentrations in water.

The ELISA for dicamba is just newly developed, and provides a fast and inexpensive method of analysis. However, currently the detection limit is fairly high compared to gas or liquid chromatography methods (e.g. Clegg, 1987; Arjmand et al., 1988); the linear range was from ~ 0.2 to 1.0 mg L^{-1}, so values below 0.2 mg L^{-1} are questionable. There was not enough sample volume to concentrate those below 0.2 mg L^{-1}, but samples with measured concentrations above the linear range were diluted with deionized water and analyzed again.

Computer Model Description

A brief description of the computer model EXPRES (Expert system for Pesticide

Regulatory Evaluations and Simulations) and the subroutine for pesticide transport in

LEACHM, within EXPRES, is presented in Chapter 5. See Wagenet and Hutson (1987)

and Mutch et al. (1993) for more details.

A list of parameters with values required by the model was given in Chapter 4 on

water flow; additional parameters required for dicamba transport are listed in Table 6.1.

Table 6.1. Parameter values for dicamba transport used in the LEACHM simulation, excluding those given in the previous chapter for water flow, with source of reference or brief explanation. See EXPRES manual (Mutch et al., 1993) for complete description.

Parameter	Value(s)	Reference/Explanation
Solubility (mg L^{-1})	6500	Caux et al., 1993
K_{oc} (L kg^{-1})	2	Caux et al., 1993 (middle value)
Washoff factor	0.99	worst case
Degradation Half-life (days) - thatch	14	chapter 3
- soil	83	
Molecular Diffusion Coefficient (mm^2 day^{-1})	43	EXPRES
Dispersivity (mm)	3.2	Pearson et al., 1996a
Diffusion Coefficient in Air (mm^2 day^{-1})	0.43	EXPRES
Barometric Enhancement (mm^2 day^{-1})	0	not highly volatile
Vapour Density (mg L^{-1})	0.045	EXPRES

Note that the choice of the maximum 0.99 for the washoff factor represents a

worst-case scenario. Although turfgrass leaves can retain a significant portion of the

applied dicamba (Carroll et al., 1993), a rain or irrigation soon after will wash much of the

herbicide off the leaves. In this study, there was rain (more than 4.4 mm) the evening or

morning after herbicide application, but there was no observable runoff. Degradation

rates were determined from the accompanying laboratory study (Chapter 3). The

Arrhenius equation [3.4] was used to derive degradation rates for the measured soil temperatures based on the calculated values from the laboratory degradation study (Chapter 3), for the low water content at 4 and 20° C. Since the model requires only one degradation rate value per layer, an average temperature of 10° C, measured for the soil in the month following the spring and early autumn applications, was used to derive degradation rates, which likely do not represent the late autumn application as well. Plant uptake (mass flow) was not included, except to test the effect on model predictions in general.

Due to the limited number of samples, and for reasons outlined in the previous chapter, only a qualitative analysis of the model simulation accuracy was undertaken.

RESULTS AND DISCUSSION

Observations

Concentrations of dicamba over 1 mg L^{-1} were detected in the A and B horizons, down to a depth of 43 cm, using solution samplers (Figs. 6.1 and 6.2). These levels are much higher than have been reported in other studies on turf (e.g. Gold et al., 1988; Harrison et al., 1993; Smith and Bridges, 1996; Snyder and Cisar, 1997) as described earlier. Although the application rates were lower in these studies than in our experiment (0.6 kg a.i. ha^{-1}), our observed concentrations are still proportionally higher. Gold et al. (1988) used a rate of 0.11 kg ha^{-1}, nearly 6 times lower, and reported a maximum concentration of 38 μg L^{-1}. Smith and Bridges (1996) detected a maximum concentration of 2.6 μg L^{-1} using a rate of 0.28 kg ha^{-1}, over 2 times lower. Harrison et al. (1993) also used this same application rate, but observed a maximum concentration of 118 μg L^{-1}.
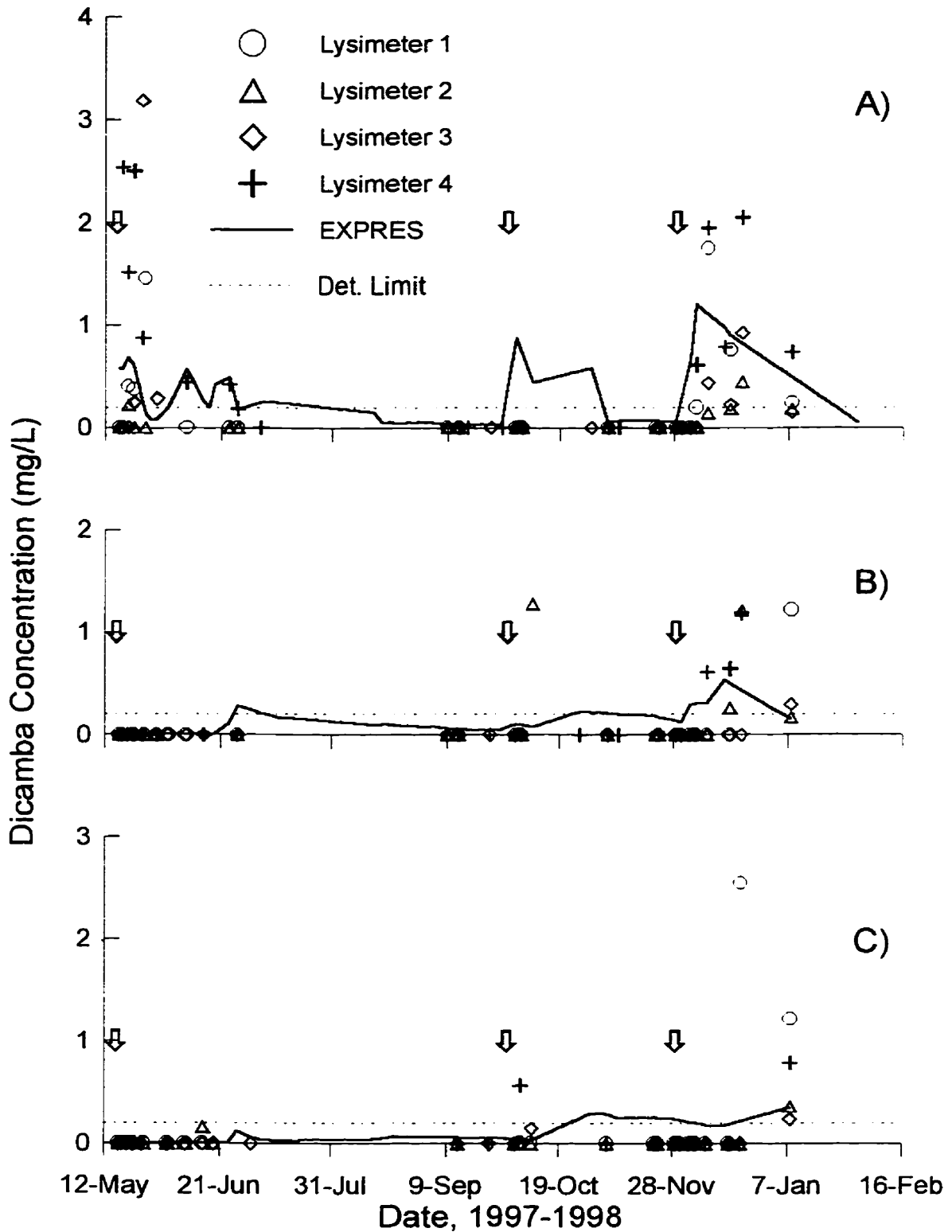
Fig. 6.1. Dicamba concentrations within the A horizon at A) 9, B) 17 and C) 29-cm depth below the turf surface, for the 1997 field season. Symbols represent field observations (obtained with suction samplers) for 4 lysimeters; line represents LEACHM prediction; arrows indicate application dates. Approximate detection limit is 0.2 mg L^{-1}.
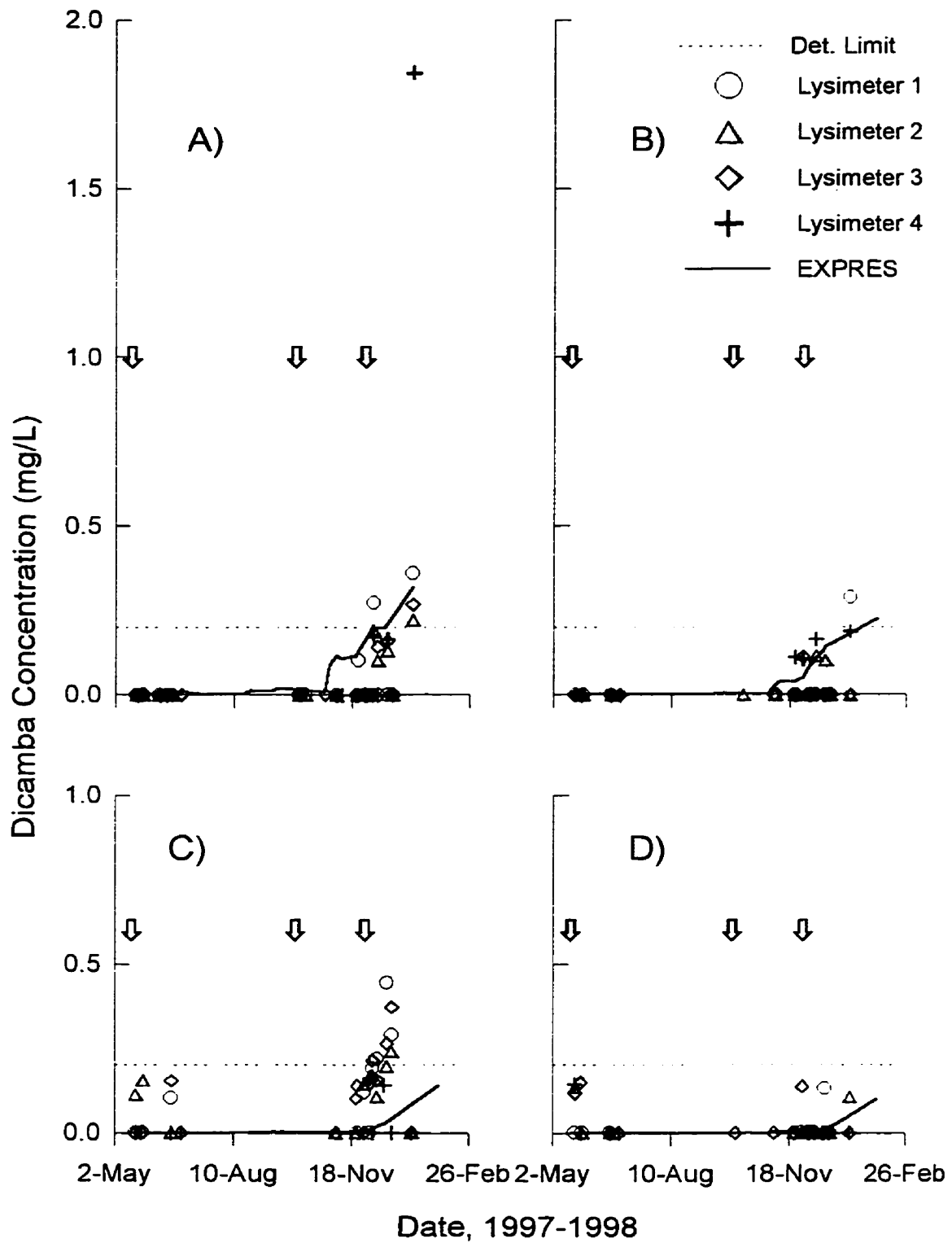
Fig. 6.2. Dicamba concentrations within the B and C horizons at A) 43, B) 54, C) 69 and D) 85-cm depth below the turf surface, for the 1997 field season. Symbols represent field observations (obtained with suction samplers) for 4 lysimeters; line represents LEACHM prediction; arrows indicate application dates. Approximate detection limit is 0.2 mg L^{-1}.

The higher concentrations observed in this study may be a result of the higher

application rate or less dilution in soil water, as the turf in the other studies was usually

irrigated. More than likely, the increased levels can also be attributed to lower

degradation rates, less plant uptake or faster transport into the soil, all factors related to

climatic conditions.

Similar to nitrate (Chapter 5), the downward movement of dicamba applied in the

spring was limited by the dry conditions of the soil. Further leaching of dicamba in the

summer and early autumn was prevented by the low water contents (Chapter 4), a result

of a high evapotranspiration rate. Degradation likely eliminated most of the dicamba

remaining in the soil during these periods of minimal water infiltration, as there were no

measurable levels of dicamba in water samples collected from the drain (0.85 m) during

the monitoring period (data not shown). However, the measurable concentrations in the B

and C horizons in November may indicate that degradation was not complete. Both Hall

and Mumma (1994) and Tindall and Vencill (1995) observed low dicamba levels leaching

from agricultural soil following heavy rainfalls several months after application - an

indication that dicamba, adsorbed or trapped in dead-end pores of the matrix, may

eventually become mobile. Such low levels could not be detected in this study due to the

high limit of detection of the ELISA analysis.

Observed leaching patterns following the late autumn application differed from the

earlier applications. Dicamba concentrations remained high throughout the A horizon

(Fig. 6.1). The dicamba concentrations measured in the B horizon soon after the

November application (Fig. 6.2) may have come from the earlier applications or may

indicate very fast transport of dicamba applied in November. In either case, high

concentrations of dicamba were still detected in the soil profile on January 6, 1998 (Figs. 6.1 and 6.2). Since degradation generally declines with depth and temperature (Veeh et al., 1996), it is likely that similar high levels would have reached the drain during the winter or early spring.

The lack of a peak in dicamba concentration at the 10-cm depth following the September application was somewhat surprising, considering the large concentrations detected soon after the other two applications (May and December - Fig. 6.1A). It was windy on the day of application (September 28), so the lysimeters may not have received the full dose of herbicide, and the dicamba that reached the surface may have been lost via volatilization later that day. In addition, only a few water samples were obtained during October because the soil was very dry. The passing dicamba peak may have been missed, especially if preferential flow was occurring. The two large peaks at 17 and 29-cm depths detected in two of the lysimeters (Fig. 6.1) may be an indication of preferential flow.

Variability between observations from different lysimeters may be due to the method of application - there was a sizable range (0.05 to 0.60 kg ha^{-1}) in the amount of herbicide measured on filter papers laid alongside the lysimeters during application. Differences in water flow patterns related to fertilization, noted in Chapter 5, may have contributed as well. Even though the lysimeters were packed similarly, some natural variability in the soil had likely developed during the two years since packing was done.

LEACHM Simulation - Comparison

Based on a visual inspection of Figures 6.1 and 6.2, the model produced good predictions for dicamba travel times, generally being within 50 per cent of the observed

values, a criteria for model testing suggested by Pennell et al. (1990). There were however, a few indications of preferential flow. Although there was no evidence of the early autumn application at 10-cm depth in any lysimeter, in two lysimeters large peaks of dicamba at 17 and 29-cm depths (Fig. 6.1) were detected much sooner than predicted, within 10 days of application. Preferential flow is suspected as the lysimeters received more than 1 cm of rain within 24 hours after application.

Larger concentrations of dicamba were observed than predicted at a 10-cm depth after the spring application (Fig. 6.1). It appears that the dicamba moved through the turf layer very quickly and as a sharp peak. There may also have been less degradation than predicted based on the batch study (Chapter 3), as the soil was cooler than the $10°$ C average used to calculate the soil and thatch degradation rates, the week following application.

Dicamba from the late autumn application reached the bottom of the A (31 cm) to the middle of the B horizon (43 cm) by early January (Figs. 6.1 and 6.2), which was faster than predicted and with concentrations greater than predicted. As outlined in Chapter 4, the snowfall/snowmelt routine may have delayed predicted infiltration, and therefore solute transport. The colder and fluctuating temperatures in December likely impaired microbial activity, reducing degradation losses that would have lowered the predicted concentrations. The degradation rates used by the model were based on a temperature of $10°$ C, and would have been too large for the final application.

Observations and predictions of dicamba leaching from the lysimeters were mostly in agreement, with no leaching losses in either case by the end of the year.

LEACHM Evaluation

Having simulated the leaching of dicamba fairly well, LEACHM was used to test

the effect of the higher degradation rate in thatch, described in Chapter 3, and herbicide

uptake via mass flow by the grass plants, on dicamba leaching. Figure 6.3 shows the

effects of ignoring the increased degradation of the thatch layer (dashed line) - greater

dicamba leaching from turfgrass. Although the initial peaks are similar, plant uptake

(dotted line) quickly reduces the dicamba concentrations below that predicted without

plant uptake (original - solid line). Comparing the original predictions with the altered

predictions described above at a 54-cm depth (Fig. 6.3B), the increased degradation seems

to play a more significant role in reducing dicamba leaching than plant uptake via mass

flow. The predicted concentrations for the different conditions are more similar to each

other at the 10-cm depth following the late autumn application. It is likely that the water

and herbicide are moving quickly through the turf layer at this time, so neither the

enhanced degradation nor the uptake of dicamba by plants can have as great an effect the

amount of dicamba leached.

CONCLUSIONS

Concentrations of dicamba over 1 mg L^{-1} were observed in the A horizon

following herbicide application in May, September and November. These levels are much

higher than those reported in previous studies, potentially due to the higher application

rate, lower water contents and/or decreased degradation and plant uptake. Drying of the

soil via evapotranspiration inhibited leaching from spring until late autumn, which allowed
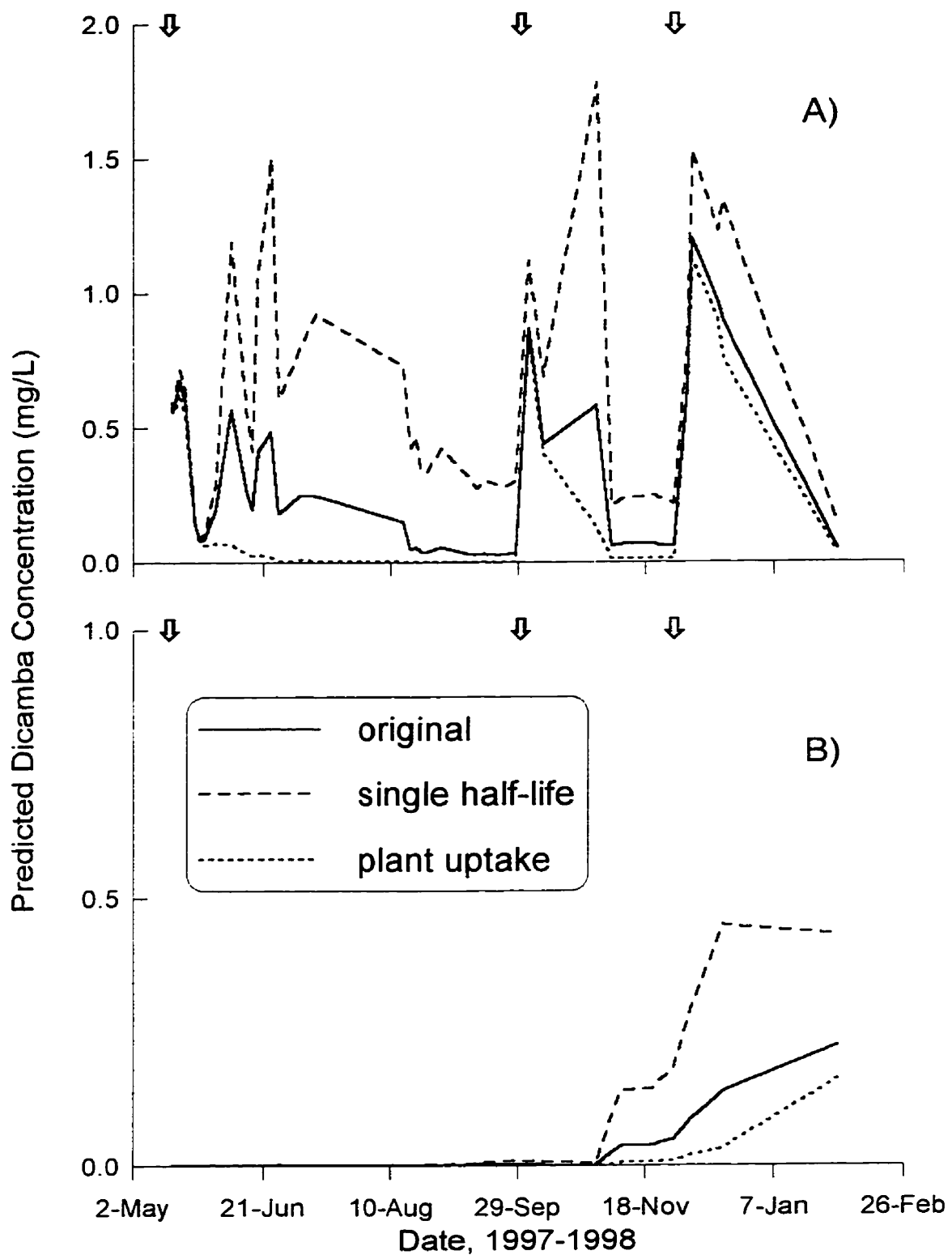
Fig. 6.3. Predictions of dicamba concentration in soil water at A) 10 and B) 54-cm depths. for the original simulation of no plant uptake and increased degradation in the turf layer (solid line). along with separate predictions including plant uptake (dotted line). and ignoring the increased degradation (dashed line). Arrows indicate application dates.

more of the herbicide to be degraded before it could move deeper. There were measurable concentrations in the B and C horizons, however, suggesting that some of the dicamba from spring or early autumn applications may not have been degraded and continued to leach later in the autumn. High concentrations of dicamba from the November application reached or passed the bottom of the A horizon by early January, suggesting that there is potential for significant amounts of dicamba to leach under conditions of low temperature and increased water infiltration. In temperate climates, it would be advisable for pesticide managers to adjust spraying schedules in the spring or autumn based on local weather conditions.

Similar to the findings for nitrate and chloride in Chapter 5, LEACHM simulated the timing of dicamba transport fairly well. There were some signs of preferential flow in the field measurements following the September application, and faster transport of dicamba below the A horizon following the November application. Observed concentrations were higher than predicted, especially at 10-cm depth, which is likely due to quicker movement through the turf and/or a slower degradation rate than predicted. The most likely causes of differences between observations and predictions are the inaccuracies of water flow simulation (bottom boundary condition, evapotranspiration in summer, the snowfall/snowmelt routine) and the inability of the model to modify degradation rates with changing climatic conditions.

A modeling exercise with LEACHM indicated that increased degradation in turf can significantly restrict dicamba leaching, while plant uptake via mass flow quickly reduces the concentrations. However, both processes have less of an impact when infiltration is rapid, as was observed in late autumn. It is recommended that degradation

rates be measured using local climatic and soil/crop conditions, and for individual layers
within the soil profile to provide accurate predictions of herbicide fate.

ACKNOWLEDGEMENTS

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CHAPTER 7

CONCLUDING REMARKS

Some of the key results obtained through this thesis research include the following:

i) The degradative loss of dicamba in the thatch from turfgrass was faster than in soil, probably due to biodegradation, and not chemical degradation.

ii) Drainage occurred mainly in the spring and autumn (late autumn in 1997), with nitrate and chloride leaching from the lysimeters strongly associated with the drainage period in autumn. The high evapotranspiration of the turfgrass during the summer and early autumn limited leaching.

iii) Some of the nitrate from the spring or summer application remained in the rootzone during the dry period, but was later flushed to greater depths and out with the drainage water in the autumn. Large concentration peaks were created at the head of the infiltration front

iv) High concentrations, over 1 mg L^{-1}, of dicamba were measured at and below 10-cm depth in the soil profile, following herbicide applications in May, September and November. These levels are much higher than have been reported in previous studies, though the application rate used in this study was 2 to 6 times greater as well. There was more substantial leaching from the November application, with less degradation losses.

v) The model LEACHM simulated water flow and solute transport fairly well. Although predictions did not always match exactly with the measurements of water contents, drainage or solute concentrations within the soil profile, they did follow the major trends given by the field data.

vi) There were only a few indications of preferential flow, identified by faster water or solute transport in the field compared to the model predictions, and these generally occurred during the dry periods of summer and early autumn.

It is quite apparent from these conclusions that the threat of both fertilizer and pesticide leaching is greatest in the early spring and autumn, when temperatures are low and infiltrating water is moving down out of the rootzone. However, this is not to say that preventing applications during this time will remedy the situation entirely, as nitrate from spring and summer applications remained in the soil profile until it was flushed out in the autumn.

Previously reported observations of reduced dicamba leaching under turf compared to bare or agricultural soils are likely associated with the increased degradation in thatch versus soil illustrated in the batch study. However, the reduction in the amount of deep percolating water, caused by high evapotranspiration rates of the grass plants, is also a probable cause.

A recurring theme throughout Chapter 3 to 6 was that of spatial and temporal variability in all the processes. Degradation was strongly influenced by temperature, and moderately affected by the soil water content. The hydraulic conductivity of the turf layer varied considerably compared to those for the packed soil of the A, B, and C horizons. Even water flow and solute transport patterns differed between lysimeters, though they were all packed similarly. There were indications that past fertilization and summer irrigation were influential factors. However, it is also likely that natural variation in soil structural development and plant growth, along with snow accumulation and melting, led to some of the observed variability.

All the factors involved in the leaching process and the variability that occurs in the field clearly demonstrate how difficult it is to make useful observations and to attempt to understand these complicated processes. I did find that the measurements provided by the solution samplers at various depths within the soil profile were very helpful in determining the fate of the applied solute, especially since solute from different applications tended to mix, becoming a single large slug by the time it reached the drain in autumn.

The EXPRES model performed quite well; its ease of use and the accuracy of the LEACHM simulation of water flow and solute transport make it a useful model. The strong dependence of solute transport on water flow, observed in this study, suggests that the accurate simulation of water flow should probably receive more emphasis in future model testing. Many researchers appear to gloss over this area, focusing on the transport of their chosen solute. A more in-depth examination of water flow and water content, which can be monitored easily with TDR (time domain reflectometry) in the field, could help elucidate the causes of inaccurate model simulations.
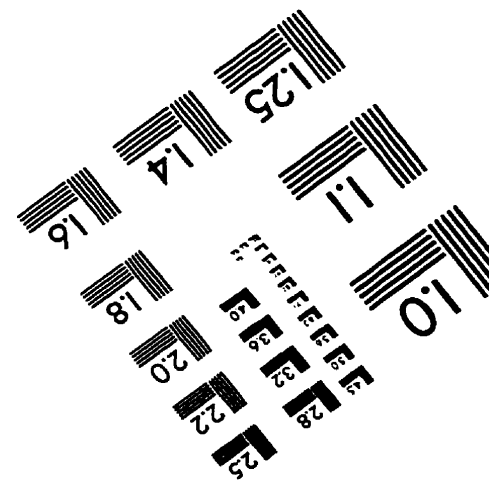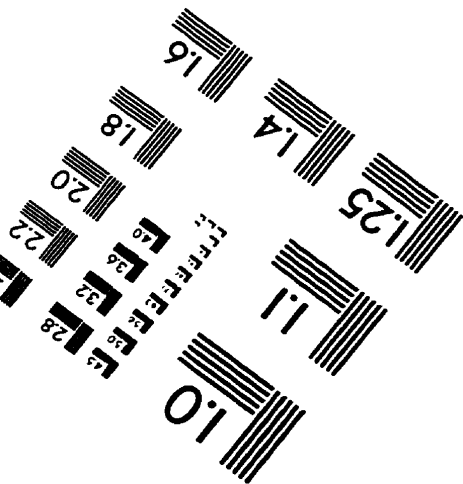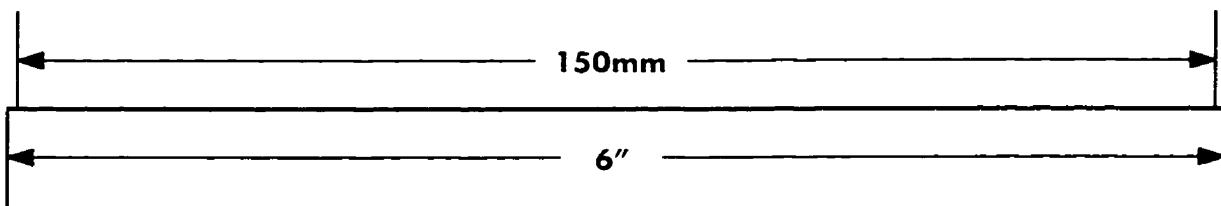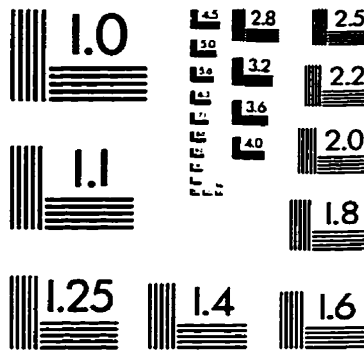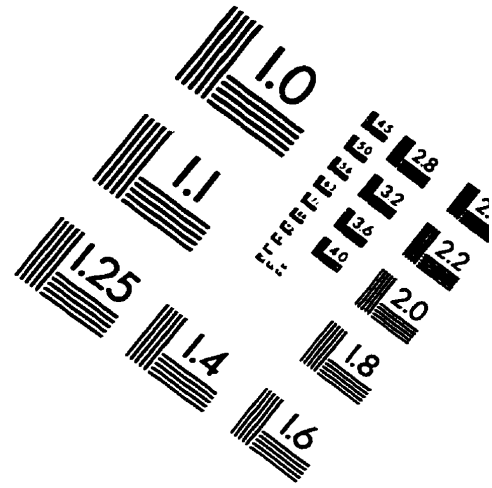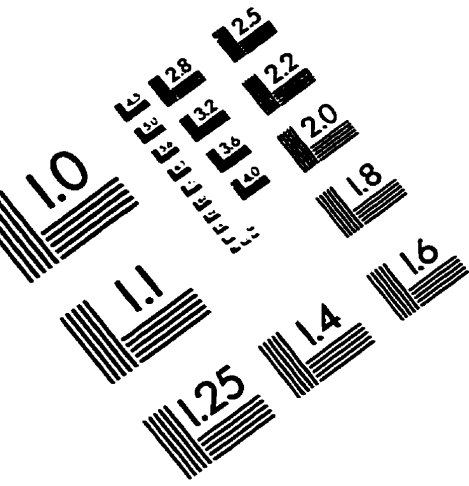
There are some areas where improvements could be made to current models of solute transport. As more attention is brought to flow in heterogeneous systems, researchers are attempting to divide flow into different domains and increasingly separate layers. In dealing with the thatch layer of turf, root channels or worm holes, it would be advantageous to be able to input separate sorption values for these components. For pesticides, some researchers are attempting to incorporate the Arrhenius equation in to their models to accommodate the temperature dependence of biodegradation in soils. Further work in developing functions that consider temperature, water content, and even organic matter content effects on the degradation rate is required. Considering the

common observations of acclimation periods and enhanced degradation with subsequent pesticide applications, the ability to modify the degradation rate based on the past history of pesticide contact would likely help improve future pesticide fate models.

As for the EXPRES model itself, the inclusion of a greater selection of bottom boundary conditions and functions to represent the water retention curve (e.g. van Genuchten equations) would make the model more applicable to a wider variety of conditions. The snowfall/snowmelt routine is really a necessity when modeling solute transport in temperate climates, as the times of greatest leaching coincide with the months when snow often falls and/or melts. This routine still needs some work, however, to better simulate actual conditions.

Having reviewed this research on water flow and solute transport, a few suggestions for future research endeavours can be made. The large amount of nitrate leaching with the large application rates observed in this study, suggests that the leaching of nitrate from turf after an autumn application of ammonium-nitrate at the recommended rate may still be a concern, especially when cool temperatures and large amounts of water infiltration from rains or melting snow soon follow application. Dicamba applied in the autumn may also be a leaching concern, considering the large concentrations of dicamba observed at depth following the November application. Such a study should focus on small time periods involving cool spells in the autumn, with substantial rains or irrigation following application. Lastly, it would also be interesting to determine whether the establishment of turf on a soil would affect (increase or decrease) the potential for preferential flow.

IMAGE EVALUATION
TEST TARGET (QA-3)

150mm

6"