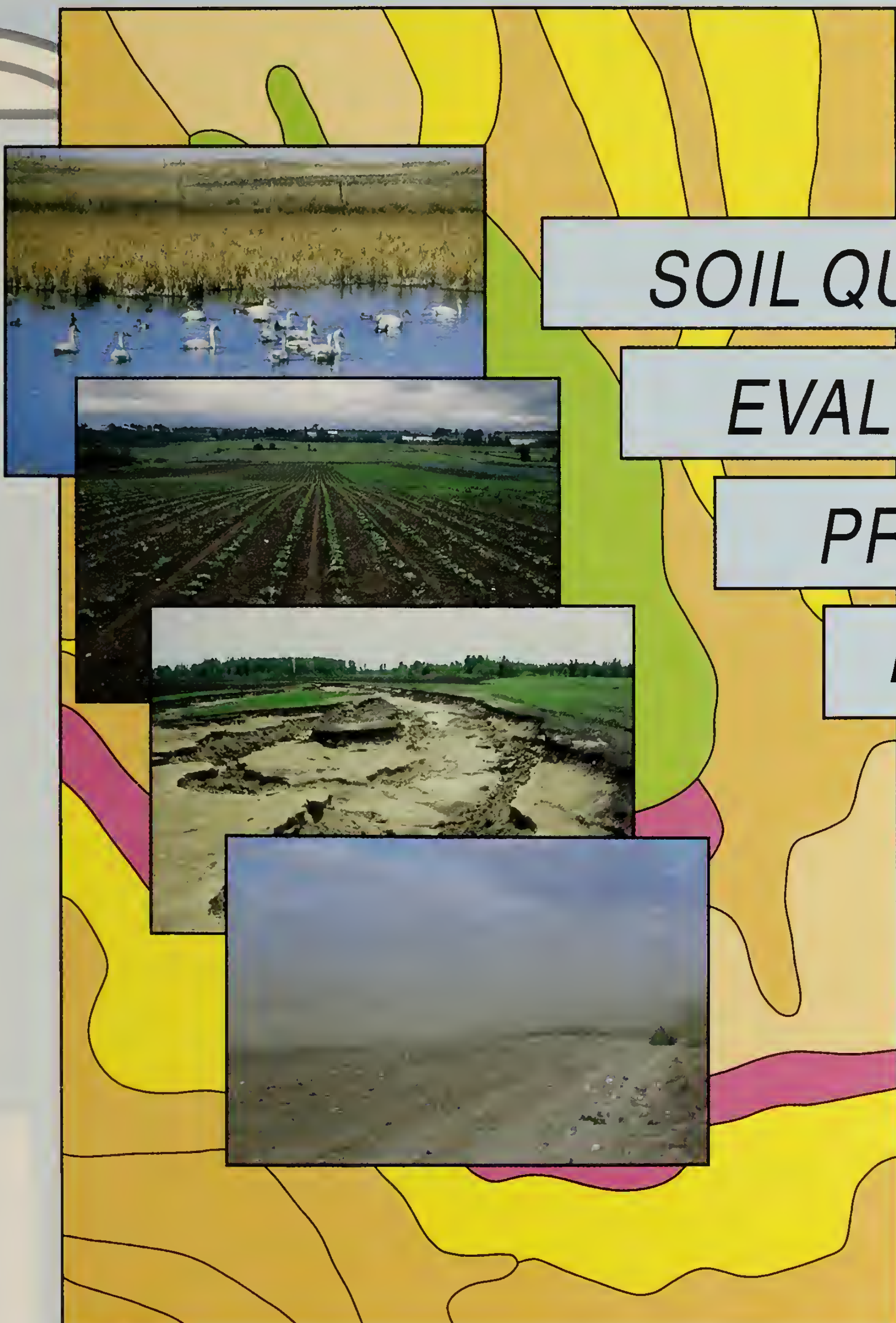
METHODOLGY for PREDICTING AGROCHEMICAL CONTAMINATION of GROUND WATER RESOURCES



SOIL QUALITY EVALUATION PROGRAM

Report 4

Agriculture Canada

Research Branch / Direction générale de la recherche

Canada

Methodology for predicting agrochemical contamination of ground water resources

Soil quality evaluation program technical report 4

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Funding for this study was provided by Agriculture and Agri-Food Canada through the Preservation Program of the Great Lakes Action Plan, and through the National Soil Conservation Program, under Federal-Provincial Agreements on Soil and Water Conservation and Development in Ontario.

Research Branch
Agriculture and Agri-Food Canada
1994

This publication may be cited as W.D. Reynolds, R. de Jong, S.R. Vieira and R.S. Clemente. 1994. Methodology for predicting agrochemical contamination of ground water resources, Soil Quality Evaluation Program Technical Report 4. Centre for Land and Biological Resources Research, Agriculture and Agri-Food Canada, Ottawa, ON. 51 pp.

Centre for Land and Biological Resources Research Contribution No. 94-51

Copies of this publication are available from:

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EXECUTIVE SUMMARY

Methodology was developed for the prediction and characterization of low-level non-point source contamination of ground water resources due to the migration of agrochemicals through the soil profile. Predictions of non-point atrazine contamination of ground water in the Grand River watershed of Southern Ontario are presented as a preliminary test and demonstration of the methodology.

The methodology consists of solute transport modelling applied in combination with pedotransfer functions, geostatistics and a geographic information system (GIS). The transport model, which is an in-house modification of LEACHM (**L**eaching **E**stimation **A**nd **CH**emistry **M**odel), integrates the major processes that occur in the soil profile, including soil horizonation, water flow, crop growth and transpiration, solute transport, soil heat flow, and changes in water table elevation. The pedotransfer functions are used to estimate, from available soil data, those soil attributes that are missing (unmeasured) but required as input to the model. The geostatistical analyses (kriging) are used to extend the model predictions of solute percolation behaviour from a point basis (LEACHM is 1-D) to an areal basis (e.g. watershed). The GIS is used to create maps of predicted solute movement, and to overlay these maps with those of soil attributes, weather, land use, etc. The maps and map overlays are then used to characterize and quantify ground water contamination resulting from the downward percolation of agrochemicals through the soil profile.

The methodology was applied to characterize and quantify non-point atrazine contamination of ground water in the Grand River watershed of Southern Ontario. Soil, weather and solute transport attributes required for the LEACHM model were obtained from archived soil and weather databases, and from in-situ measurements made at selected field sites. These data were assigned to the georeferenced centroids of the soil landscape polygons within an arbitrarily defined "map window" encompassing the Grand River watershed. Pedotransfer functions obtained from the literature were used to estimate missing soil hydraulic property data. The model was run at each of the 119 soil landscape polygon centroids within the map window for 10 consecutive simulation years, assuming initially atrazine-free soil, continuous corn cropping with the recommended atrazine application rate of 150 $mg/m^2/yr$, and 30 year normal weather. The predicted annual mass loading of atrazine at the 90 cm (average tile drain) depth in the soil profile at the end of the 10 year simulation was used as an indicator of ground water contamination. Kriging was used to interpolate the data at each polygon centroid onto a 2 km x 2 km grid. This resulted in 1657 georeferenced grid points within the Grand River watershed containing estimates of soil attributes, weather data and predicted annual atrazine loading. The geographic information system ("ILWIS") used these interpolations to produce maps and map overlays of atrazine loadings and concentrations.

The predicted atrazine loadings were highly variable spatially within the watershed (CV = 137%), and exhibited a frequency distribution that was skewed, flat and multimodal. The temporal (year to year) variability, on the other hand, declined to zero as the predicted annual loadings became constant at any particular location after about 5-8 simulation years. The predicted annual atrazine loadings after 10 simulation years were low, ranging from 0 to 2.5 $mg/m^2/yr$, with a mean value of 0.67 $mg/m^2/yr$. These values are less than 2% of the annual

application rate (150 mg/m^2/yr). The former Canadian drinking water guideline for atrazine (60 ppb) was never exceeded at the 90 cm depth; however, the corresponding USEPA standard (3 ppb) was exceeded on or before the 10th simulation year in about 27% of the watershed area. Correlations between atrazine loading and soil, weather and solute transport attributes were often statistically significant, but generally low in magnitude, suggesting that the loadings were determined by complex interactions among several soil, weather, crop management and solute transport factors. These predictions compare favourably with the results of the Ontario Farm Groundwater Quality Survey, Winter 1991/92 (Agriculture Canada, 1992).

It was concluded that the methodology, although still requiring further development and testing, is capable of providing useful predictions of agrochemical contamination of ground water on a watershed basis.

1.0 INTRODUCTION

This study is concerned with developing the capability to predict and characterize the downward percolation of agrochemicals (e.g. nutrients, pesticides) through the soil profile, taking into account spatial and temporal variability, water and solute transport mechanisms, agrochemical transformation and degradation processes, weather patterns, and crop management. Such a capability is essential for determining the impact of soil type, weather conditions and agricultural land use on agrochemical pollution of ground water resources. It is also essential for the development of agricultural practices and guidelines that maintain agrochemical inputs to the ground water at acceptable and sustainable levels.

As a first step, a methodology is being developed for predicting and characterizing the migration through the soil profile of the widely used herbicide, atrazine. This methodology is applicable on many scales (providing appropriate data are available), but the focus here is the watershed scale, with particular emphasis on the Grand River watershed in the Southern Ontario portion of the Great Lakes Basin (Fig. 1). The methodology makes use of archived soil survey and weather data, and it accounts for the many factors and processes controlling atrazine migration via the combined application of a sophisticated solute transport model, pedotransfer functions, geostatistical analyses, and a geographic information system.

2.0 RATIONALE AND OBJECTIVES

Although most pesticide contamination of ground water in the Great Lakes Basin is below current Canadian drinking water guidelines, there are growing public concerns in this region over potential health hazards related to long-term exposure to low levels of pesticides and their metabolites (Agriculture Canada, 1990). Pesticide residues, especially atrazine, have been detected in surface, ground and tile drainage waters of many agricultural watersheds in the Great Lakes Basin, particularly where there is some combination of high pesticide usage, intensive agriculture, high precipitation, irrigation, coarse and other highly permeable soils, high water tables, and sloping topography (Millette and Torreiter, 1992). For example, up to 49% of the water supply wells sampled between 1969 and 1984 in selected high pesticide usage areas of Southern Ontario contained detectable levels of pesticides (Frank et al., 1987a). In addition, several random water well surveys conducted between 1981 and 1987 in Southern Ontario obtained pesticide detection rates of 4 to 14% (Frank et al., 1987b, 1990), indicating that pesticide entry into the ground water is not restricted to only the areas of high pesticide usage. Of the approximately 17 pesticides that have been detected in Southern Ontario wells, atrazine is by far the most frequently occurring, with concentrations ranging between 0.2 and 34 ppb (Frank et al., 1990).

Pesticide contamination of ground water has traditionally been considered to consist of relatively isolated "hot spots" resulting from spills, and from improper storage, disposal and application practices (Agriculture Canada, 1990). There is increasing suspicion, however, that

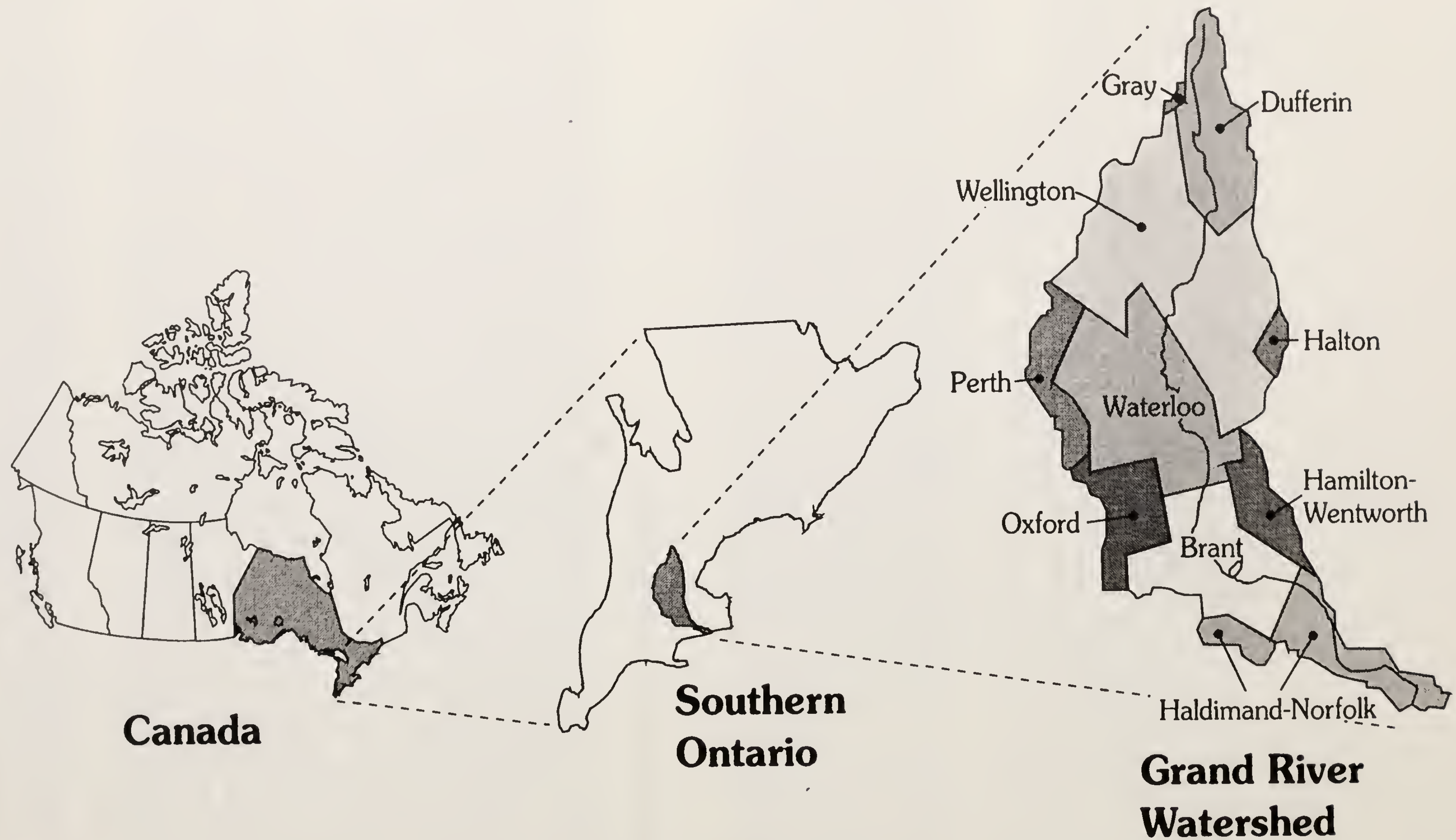

Fig. 1 Location map for the Grand River Watershed.

normal agricultural practices can also result in low-level, non-point source contamination of ground water via the downward migration of pesticides through the soil profile (Agriculture Canada, 1990). Consequently, there is a need to determine how important and widespread low-level non-point source pesticide contamination might be, what the controlling soil, land use and weather factors are, and what agricultural practices are required to maintain this type of pollution at acceptable levels. Essential steps in obtaining this information include, identification of the primary mechanisms controlling pesticide movement through the soil profile, and development of the capability to characterize and predict pesticide movement in space and time with acceptable accuracy. Accordingly, the objectives of this study are:

i) To develop methodology for predicting, characterizing and quantifying pesticide migration through the soil profile, taking into account "standard" field cropping practices, the primary solute transport mechanisms, and the spatial and/or temporal variability in soil and weather attributes.

ii) To conduct a preliminary test and evaluation of the methodology by applying it to atrazine migration through the soil profiles of the Grand River watershed in the Southern Ontario portion of the Great Lakes Basin.

3.0 DESCRIPTION OF METHODOLOGY

The methodology consists essentially of a solute transport model in combination with pedotransfer functions, geostatistical analyses, and a geographic information system (GIS). The transport model, which is an in-house modification of a well established and tested modelling package called, LEACHM (Hutson and Wagenet, 1989), integrates the major processes that occur in the soil-plant-atmosphere system, including: soil horizonation; saturated, unsaturated, steady and transient water flow; crop growth and transpiration; solute (e.g. atrazine) sorption, degradation, advection and dispersion; precipitation and evaporation; soil heat flow; and change in water table elevation. The pedotransfer functions are used to estimate from available soil data (e.g. soil texture, organic carbon content) those soil attributes that are required as input to the solute transport model (e.g. hydraulic conductivity function, soil water characteristic), but which are missing from the data set. The geostatistical analyses are used to extend the model predictions of solute percolation behaviour from a point basis (the model is one-dimensional) to an areal basis (e.g. plot, farmer's field, watershed, region), using procedures that take into account the inherent spatial variability of the area. The GIS is used to create maps of the geostatistically extended solute percolation behaviour, and to overlay those maps with maps of soil attributes, weather, cropping practices, etc. These maps and map overlays are the "end products" which can be used, to estimate the importance and distribution of ground water contamination by downward percolating pesticides; to determine the major soil, land use and weather factors controlling the contamination; and to predict the potential environmental impact of changes in land management practices.

In this study, "ground water contamination" is defined as non-zero values of predicted annual mass loading of pesticide (atrazine) to the 90 cm depth in the soil profile (units of mg atrazine/m^2/year). Non-zero mass loading was used, rather than pore water concentrations above a specified guideline value, because of the need to determine the quantities and distributions of all pesticide additions to ground water, not just the "high level" additions. Use of annual mass loading also allows convenient assessment of the total impact of an agrochemical on an area (e.g. watershed), as well as the total potential loading of the agrochemical to the Great Lakes. The 90 cm depth in the soil profile was chosen because it reflects the mean tile drain depth for Southern Ontario, as well as the primary rooting depth for most field crops. It was assumed that if an agrochemical reached the 90 cm depth, it would probably not be intercepted by tiles, roots, etc., but continue to percolate downward and eventually enter the ground water supply zone.

Although the methodology can be applied to virtually any landscape unit (e.g. plot, field, watershed, region, etc.), the focus in this study is on the watershed. The watershed scale was chosen because it is a manageable natural landscape unit in Southern Ontario, it is compatible with the scale and density of the most readily available and complete soil and weather databases, and it provides a convenient basis for estimating agrochemical loadings to the Great Lakes. As mentioned above, the Grand River watershed is used in a preliminary test and demonstration of the methodology.

The remainder of this section includes a description of the LEACHM modelling package and the modifications made to it (Section 3.1, 3.2), a discussion of the testing and calibration of two of the submodels (Section 3.3), and an outline of how the modelling package is being applied within the pedotransfer function - geostatistics - GIS framework (Section 3.4).

3.1 Description of the LEACHM Modelling Package

LEACHM is a general acronym (**L**eaching **E**stimation **A**nd **CH**emistry **M**odel) that refers to four submodels of a large and comprehensive computer simulation package that describes the one - dimensional storage, transmission and dissipation of water and solutes within the soil profile. These submodels include LEACHW, which describes soil water flow only; LEACHP, which describes sorption, migration and degradation of pesticides; LEACHN, which describes nitrogen transport and transformations; and LEACHC, which describes the movement of inorganic salts. The submodels consider a variety of processes that occur in the plant root zone, including transient fluxes of water, solutes and heat; alternating periods of rainfall and evapotranspiration; and variable soil conditions with depth. All submodels utilize similar numerical solution schemes, based on procedures developed in several earlier models (Bresler, 1973; Nimah and Hanks, 1973; Tillotson et al., 1980). Only the LEACHW and LEACHP submodels are used in this study. The reader is referred to Hutson and Wagenet (1989) for a more detailed discussion of the entire LEACHM package.

3.1.1 LEACHW (Water Storage and Transmission Submodel)

The equation for transient vertical soil water flow, derived from Darcy's law and the continuity equation, is described by:

$$C_w(\theta)\partial h/\partial t = (\partial/\partial z)[K(\theta)(\partial H/\partial z)] - U(z,t) \quad (1)$$

where $C_w(\theta) = d[\theta(h)]/dh$ is the differential water capacity relationship $[L^3L^{-3}L^{-1}]$, $\theta(h)$ is the soil water characteristic $[L^3L^{-3}]$, θ is volumetric water content $[L^3L^{-3}]$, $H = h - z$ is hydraulic head [L], h is the pore water pressure head [L], z is depth below the soil surface [L], $K(\theta)$ is the hydraulic conductivity relationship $[LT^{-1}]$, U is a sink term representing water uptake by plant roots $[T^{-1}]$, and t is time [T].

Empirical functions characterizing the soil water characteristic, $\theta(h)$, and the hydraulic conductivity, $K(\theta)$, relationships (i.e. soil hydraulic properties) are required in LEACHW. A combined parabolic - power function relationship is currently used to describe $\theta(h)$ (Clapp and Hornberger, 1978; Hutson and Cass, 1987). The parabolic component is given by:

$$h = \frac{[1 - (\theta/\theta_s)]^{1/2}\,(\theta_i/\theta_s)^{-b}}{[1 - (\theta_i/\theta_s)]^{1/2}} \quad ; \qquad h_i \leq h \leq 0 \tag{2}$$

and the power function component by:

$$h = a(\theta/\theta_s)^{-b} \; ; \qquad -\infty \leq h \leq h_i \tag{3}$$

where $h_i = a[2b/(1+2b)]^{-b}$, $\theta_i = 2b\theta_s/(1+2b)$, θ_s is volumetric water content at saturation $[L^3L^{-3}]$, and a [L] and b are empirical constants. The point, (h_i,θ_i), locates the intersection of the parabolic and power function segments. The corresponding hydraulic conductivity relationship is given by (Campbell, 1974):

$$K(\theta) = K_s(\theta/\theta_s)^{2+(2+p)/b} \; ; \qquad h \geq h_i \tag{4}$$

$$K(h) = K_s(a/h)^{2+(2+p)/b} \; ; \qquad h < h_i \tag{5}$$

where K_s $[LT^{-1}]$ is the value of $K(\theta)$ at saturation (i.e. $\theta = \theta_s$) and p is an empirical pore interaction parameter.

Equation (1) is solved using finite difference techniques (Hutson and Wagenet, 1989) to obtain estimates of h at each depth interval (node) into which the soil profile has been subdivided. Water contents and hydraulic conductivities are calculated at each node using Eq. (2)-(5). Water flux densities between each node, q $[LT^{-1}]$, are calculated using:

$$q = K(\theta)(\Delta H/\Delta z) \tag{6}$$

The θ and q values are used in the LEACHP submodel for the simulation of solute (pesticide) transport.

3.1.2 LEACHP (Pesticide Transport, Sorption and Dissipation Submodel)

Solute (pesticide) transport through the soil profile is described in LEACHP using the convection - dispersion equation (CDE) written in the form:

$$(\partial C/\partial t)(\rho K_d+\theta+\varepsilon K_H) = (\partial/\partial z)[\theta D(\theta,q)(\partial C/\partial z) - qC] \pm \phi \tag{7}$$

where C is solute concentration in solution (i.e. soil pore water) $[ML^{-3}]$, ρ is soil bulk density $[ML^{-3}]$, K_d is the distribution coefficient $[L^3M^{-1}]$, ε is air filled porosity $[L^3L^{-3}]$, K_H is Henry's Law constant for solute volatilization [dimensionless], $D(\theta,q)$ is the apparent diffusion coefficient $[L^2T^{-1}]$, and ϕ represents sources and sinks of solute $[ML^{-3}T^{-1}]$ such as dissolution and degradation. The apparent diffusion coefficient is defined by:

$$D(\theta,q) = D_m(q) + D_p(\theta)/\theta + D_{og}K_H/\theta \tag{8}$$

where $D_m(q)$ is the hydrodynamic dispersion coefficient $[L^2T^{-1}]$, $D_p(\theta)$ is the effective solute diffusion coefficient in the liquid phase $[L^2T^{-1}]$ and D_{og} is the solute diffusion coefficient in the gaseous phase $[L^2T^{-1}]$. $D_m(q)$, which represents mechanical mixing of solute as a result of local variations in pore water velocity, is calculated from:

$$D_m(q) = \lambda(q/\theta) \tag{9}$$

where λ [L] is the porous medium dispersivity and the q/θ ratio is the average linear pore water velocity. D_p and D_{og} are estimated from empirical equations given by Bresler (1973) and Jury et al. (1983), respectively.

Solute sorption reactions, which assume instantaneous local equilibrium between the dissolved and sorbed phases of the solute, are described by:

$$S = K_d\, C \tag{10}$$

where S is the concentration of sorbed solute $[MM^{-1}]$, and the K_d values are determined using (Rao and Davidson, 1980):

$$K_d = K_{oc}F_{oc} \tag{11}$$

where K_{oc} is the organic carbon partition coefficient $[L^3M^{-1}]$, and F_{oc} [dimensionless] is the organic carbon fraction in the soil [F_{oc} = OC/100, where OC (%) is the soil organic carbon content]. K_{oc} is assumed constant in LEACHP, while F_{oc} can vary with depth.

Degradation and transformation of organic chemicals (e.g. atrazine) is accounted for using:

$$\phi = -C\,(k_1+k_2)\,(\theta+\rho K_d+\varepsilon K_H) \tag{12}$$

where ϕ represents the source/sink of the chemical $[ML^{-3}T^{-1}]$, and k_1 and k_2 $[T^{-1}]$ are first order kinetic rate constants for degradation (k_1) and transformation (k_2) in the liquid (θ), sorbed (ρK_d) and gaseous (εK_H) phases. As most rate constant data do not distinguish between degradation and transformation, k_1 and k_2 are usually replaced in the model by a lumped "dissipation" rate constant, k $[T^{-1}]$, where $k = k_1 + k_2$. Rate constant data also do not usually distinguish between the liquid, sorbed and gaseous phase chemical, although a flag is provided in the LEACHP input file which allows specification of whether the dissipation rate constant applies to all phases of the chemical or to the solution phase only. The transport and fate of degradation products (e.g. d-ethyl atrazine) are not tracked in LEACHP, however, their amounts are included in the total mass balance of the parent compound (e.g. atrazine).

LEACHP can simulate the fate of several chemical species simultaneously (up to five in the version used in this study), with each chemical having its own specified K_d, K_H, k_1 and k_2 values. The chemicals are all transported, however, according to the water flow regime determined by LEACHW. Flags in the program determine if the transformation products of some chemicals form sources for other chemicals.

3.1.3 Other Submodels

Water uptake by plants, the U(z,t) term in Eq. (1), is represented by (Nimah and Hanks, 1973):

$$U(z,t) = \frac{[h_{eff} + (1 + r_c)z - h(z) - h_0(z)]\ R_{df}(z,t)\ K(h)}{\Delta z\ \Delta x} \tag{13}$$

where h_{eff} is an iteratively determined effective root water pressure head [L] that allows the amount of water extracted over the rooting depth to equal the potential transpiration, $1+r_c$ is a root resistance term [dimensionless], h_0 is the osmotic pressure head [L], $R_{df}(z,t)$ is a root distribution function [dimensionless] that describes the proportion of total active roots in depth increment Δz at time t, and Δx = 1 cm is the assumed distance between the root and measurement location of U(z,t). Calculations of $R_{df}(z,t)$ and potential transpiration are made within the submodels GROWTH and POTET, respectively, as explained by Hutson and Wagenet (1989).

Simulation of soil temperatures (required for correction of the dissipation rate constant, k, see Sections 3.2.4, 3.2.5) is accomplished by solving the heat flow equation for specified initial and boundary conditions (Tillotson et al., 1980). The required soil thermal properties are estimated from bulk density, soil textural components and predicted soil water contents.

3.1.4 Model Operation

In solving for the water and pesticide distributions with depth and time, LEACHW and LEACHP proceed through a series of discrete time steps to estimate $\theta(z,t)$, q(z,t) and C(z,t) at each node in the soil profile. LEACHW first solves Eq. (1) and (6) to obtain $\theta(z,t)$ and q(z,t), then LEACHP solves Eq. (7) to obtain C(z,t). Bypass of the plant related and heat flow submodels is possible if plant growth and heat flow are not important. Model output at specified time intervals includes the amount of material (water and chemicals) initially in the soil profile; the amount of material currently in the soil profile; the simulated change, additions and losses of material; and composite material balance errors. A summary by depth (node) of predicted θ, h, q, C, and plant extraction of water and solute is also provided at specified time intervals.

3.1.5 Input Requirements for LEACHW and LEACHP

The principal input data requirements for LEACHW and LEACHP include:

i) LEACHW
- soil profile characteristics (e.g. depth; layers)
- soil hydraulic properties (e.g. $\theta(h)$ and $K(\theta)$ functions)
- weather data (e.g. daily precipitation and air temperature; weekly pan evaporation)
- lower boundary conditions (e.g. water table depth; free-draining profile)
- crop data (e.g. planting, emergence, maturity and harvest dates; canopy growth; rooting and transpiration characteristics)

ii) LEACHP
- soil profile characteristics (e.g. dispersivity; bulk density; organic carbon content; soil, air and water thermal properties)
- solute (pesticide) chemical properties (e.g. partition coefficient; solubility; vapour pressure; dissipation rate constant; speciation)
- chemical (pesticide) applications (e.g. dates and amounts of chemical applied)

The LEACHM user's manual (Hutson and Wagenet, 1989) should be consulted for a complete and detailed listing of all inputs.

For a homogeneous soil profile, only single values for bulk density (ρ), the coefficients a, b and p in Eq. (2)-(5), and the saturated hydraulic conductivity (K_s) are required to describe the soil hydraulic properties, K-θ-h. For a heterogeneous profile, however, these values must be entered for each of the soil layers, as indicated in the LEACHM users manual.

Temperature data and soil thermal properties are not required when it is assumed that pesticide dissipation is independent of soil temperature.

3.2 Modifications Made to LEACHW and LEACHP

3.2.1 Soil Hydraulic Properties

The $\theta(h)$ and $K(\theta)$ relationships used in LEACHW (Eq. 2-5) poorly reflect the often observed rapid decrease in water content and hydraulic conductivity at pore water pressure heads (h) between 0 and -0.2 kPa (see e.g. Topp et al., 1980). The K-θ-h relationships proposed by Van Genuchten (1980), on the other hand, usually give a better representation of the observed behaviour. Consequently the Van Genuchten functions were incorporated into LEACHW as an optional alternative to Eq. (2)-(5). The Van Genuchten $\theta(h)$ relationship is given by:

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^{[1-(1/n)]}} \qquad ; \theta_r \leq \theta \leq \theta_s \qquad (14)$$

where α [L^{-1}] and n [dimensionless] are empirical parameters which determine the shape of the $\theta(h)$ curve, and θ_r refers to the residual or air-dry volumetric water content of the soil [L^3L^{-3}]. The Van Genuchten K(h) relationship has the form:

$$K(h) = K_s \frac{[(1 + |\alpha h|^n)^{[1-(1/n)]} - |\alpha h|^{(n-1)}]^2}{[1 + |\alpha h|^n]^{[1-(1/n)](L+2)}} \tag{15}$$

where L = 0.5 is usually assumed.

The K-θ-h relationships currently in LEACHW cannot be used to calculate $C_w(\theta)$ for $h \geq 0$ (i.e. saturated flow) due to numerical overflow problems. As $C_w(\theta) = 0$ for $h \geq 0$, then an upper limit on h (h_u) is simply specified which yields $C_w(\theta)$ sufficiently close to zero to maintain solution accuracy. For the Campbell (1974) K-θ-h equations (Eq. 2-5), h_u = -0.002 kPa. For the Van Genuchten (1980) equations (Eq. 14, 15), $h_u = -10^{-23}$ kPa is required because of the high sensitivity of these relationships at near-zero h.

3.2.2 Lower Boundary Conditions

The original boundary condition options in LEACHW do not allow for a variable water table depth. It is well established, however, that the annual variation in water table depth can be as much as 3 m in humid regions, such as the Great Lakes Basin. A typical humid region cycle is: a rapid rise in water table elevation to near the soil surface during spring thaw; then a falling water table during the late spring through summer; then a rapid rise again in the fall to near the soil surface; and finally, a falling water table during the winter. LEACHW was therefore modified to include a fluctuating water table depth as an additional option for the bottom boundary condition. Daily water table depth data are required to use this option.

3.2.3 Water Extraction by Plants

Preliminary runs with LEACHW indicated that in wet soil profiles (i.e. pore water pressure heads greater than -10 kPa), the Nimah and Hanks (1973) water extraction function (Eq. 13) would predict unrealistic (oscillating) water uptake patterns. An alternative U(z,t) function, based on the work of Feddes et al. (1978), was therefore added as an option. This function has the form:

$$U(z,t) = R_{df}(z,t)\ [\beta(h_1,h_2,h_3,h_4)S_{max}] \tag{16}$$

where R_{df} is the root distribution function [dimensionless], $[\beta(h_1,h_2,h_3,h_4)S_{max}]$ is an empirical root water uptake function [$LT^{-1}L^{-1}$], and $h_1 \rightarrow h_4$ are prescribed pore water pressure heads [L]. The S_{max} parameter represents the maximum possible rate at which plant roots can extract water from the soil, and is given by:

$$S_{max} = PT / Z_r \tag{17}$$

where PT is the potential transpiration rate [LT^{-1}] and Z_r [L] is the rooting depth. When the LEACHW - calculated h value (pore water pressure head) in the root zone is non-optimal for plant growth, the rate of root water uptake is reduced from the maximum value (S_{max}) according to $\beta(h_1,h_2,h_3,h_4)$. For $h \geq h_1$ (oxygen deficiency) and $h \leq h_4$ (wilting point), $\beta = 0$ and no water is taken up by plant roots (i.e. $U(z,t) = 0$). For $h_2 \leq h < h_1$ and $h_4 < h \leq h_3$, β varies linearly between 0 and 1, and describes reduced rates of water uptake. For $h_3 < h < h_2$, $\beta = 1$ which represents optimal soil water conditions for water extraction by plant roots, i.e. $U(z,t) = R_{df}(z,t)S_{max}$. The value of h_3 changes with the evaporative demand of the atmosphere (and therefore PT) between prescribed crop dependent limits, i.e. $h_{3min} \leq h_3 \leq h_{3max}$.

The R_{df} function used (in Eq. 13 or 16) for the Grand River watershed application was developed by Tillotson et al. (1980), with the provision that Z_r increased linearly from 5 cm depth at planting to 90 cm depth at root maturity (see Section 3.2.8). The values of $h_1 \rightarrow h_4$ were adapted from Dierckx et al. (1988) and Veenhof (1993): h_1 = -1 kPa, h_2 = -2 kPa, h_{3min} = -60 kPa, h_{3max} = -40 kPa, h_4 = -1500 kPa.

3.2.4 Dissipation Rates

The dissipation rate constant, k, of most pesticides (including atrazine) is known to exhibit a substantial dependence on soil water content and temperature. Empirical water content and temperature corrections for k were therefore added to LEACHP. The water content correction has the form (Walker, 1978):

$$k_w = \ln 2 \; / \; A \; (100\;\theta)^{-B} \quad ; \quad \theta_r < \theta < \theta_s \tag{18}$$

where k_w is the water content corrected dissipation rate constant [T^{-1}], and A and B are empirical constants. The temperature correction, T_{cf} [dimensionless], is given by:

$$T_{cf} = Q_{10}^{\,0.1(t-tbase)} \quad ; \quad 0\ ^\circ C < t < 35\ ^\circ C \tag{19}$$

where Q_{10} [dimensionless] is the factor by which k changes over a 10 °C temperature interval, t [°C] is soil temperature, and tbase [°C] is the base temperature from which the temperature correction is determined. The water content - temperature corrected dissipation rate constant, k_{wt}, is then calculated as:

$$k_{wt} = k_w T_{cf} \tag{20}$$

For the Grand River watershed application, practical constraints dictated that Eq. (18) and (19) could be calibrated to atrazine only for the 3 predominant soil textures in the watershed (Table 1). Consequently, every soil in the watershed was assigned one of the 3 calibrated k_{wt} functions on the basis of which predominant soil texture they were the most similar to.

Table 1. Rate constants, k^*, Q_{10} values, and A and B constants for atrazine dissipation (Eq. 18 and 19). (Data provided by E. Topp and W.N. Smith, CLBRR, Agric. Canada, Ottawa, ON.)

Parameter	Soil Type		
	[1]Clay Loam	[2]Loam	[3]Sandy Loam
$^+k^*$ (d^{-1})	0.0468	0.0217	0.0215
Q_{10}	4.896	3.715	3.687
A (d)	686.9	122.9	198.4
B	1.061	0.369	0.514

$^+k^*$ is a "reference level" dissipation rate constant (determined at tbase = 25 ^{0}C and $\theta = 0.70\theta_s$) which is required for the calculation of Q_{10}, A and B.
[1] obtained near Woodslee, Ontario.
[2] obtained near Ottawa, Ontario.
[3] obtained near Alliston, Ontario.

3.2.5 Soil Temperature

The original lower boundary condition in the soil temperature subroutine of LEACHP was either a constant temperature or zero heat flux at the deepest node in the soil profile. As neither of these options are appropriate for shallow soil profiles (< 150 cm depth), the source code of LEACHP was modified to accept monthly 30 year normal soil temperature data (Phillips and Ashton, 1979). The monthly values are converted internally within LEACHP to daily values using a sine-wave interpolation procedure (Brooks, 1943) and these daily values are then assigned to the deepest node at the appropriate time in the simulation.

3.2.6 Bypass Flow

It is well established that preferential, or bypass, flow in macropores (i.e. cracks, worm holes, root channels, etc.) and "finger" zones can cause rapid movement of water and solutes through the soil profile and into the ground water (e.g. Thomas and Phillips, 1979; Beven and Germann, 1982; Hendrickx and Dekker, 1991). As a result, many attempts have been made to incorporate bypass flow into the traditional mechanistic water and solute transport models (e.g. LEACHM), which neglect this phenomenon. Most of the representations employ a dual flow domain system (Beven, 1991); one domain being the soil matrix where classical transport processes are assumed (i.e. Eq. 1, 7), and the other domain being the preferential flow zones where some form of specialized transport occurs (e.g. film flow, Poiseuille flow, storage-discharge flow, etc.). There have also been a number of purely statistical representations, such as the transfer function approach (e.g. Jury and Roth, 1990), as well as several combined mechanistic-statistical representations (e.g. Germann and Beven, 1986).

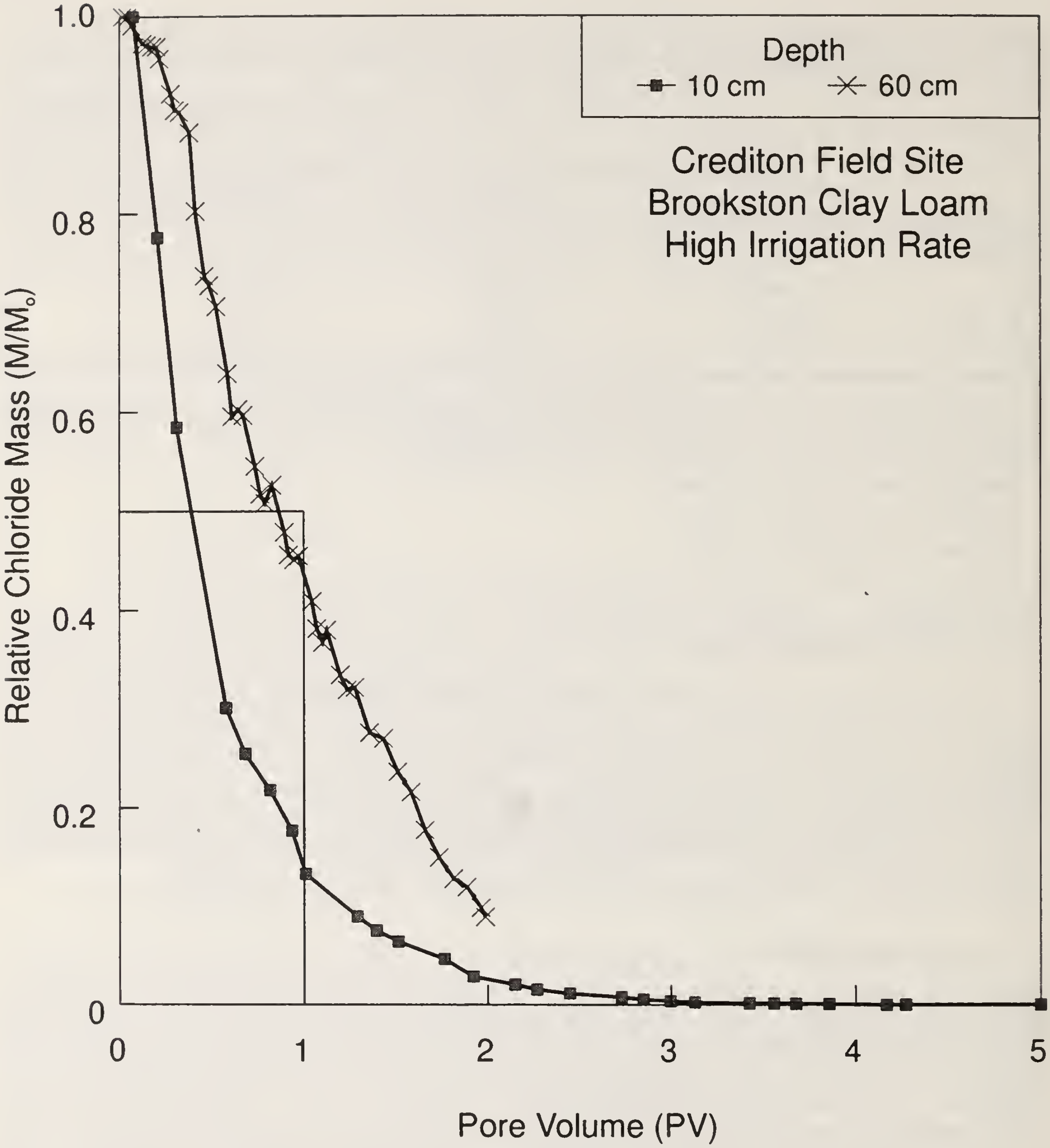

Fig. 2 Example of field-measured chloride breakout curves (BOC) exhibiting bypass flow through late-time tailing and the occurrence of the 0.5 M_o chloride mass at less than 1 pore volume (PV).

As all of these representations have serious limitations (Beven, 1991), a simplistic, but measurement based, approach to bypass flow was adopted for this work. The chloride tracer breakthrough and breakout curves obtained for testing and calibrating LEACHW and LEACHP (Section 3.3) often showed extensive tailing and the occurrence of $0.5M_0$ (M_0 = input mass of chloride) before one pore volume (PV) of soil water was eluted (see e.g. Fig. 2). This is indicative that some of the water in the soil profile was bypassed by the chloride solute (White, 1985; Bouma, 1991). The proportion of soil water bypassed by solute was determined using:

$$F = [1 - (\theta_T/\theta)] = (1 - PV_{0.5}) \ ; \theta_T \leq \theta \ ; 0 \leq F < 1 \qquad (21)$$

where F is a "bypass flow" factor [dimensionless], θ_T is the amount of soil water that participated in solute transport [L^3L^{-3}], and $PV_{0.5}$ [dimensionless] is the number of pore volumes at which the $0.5M_0$ tracer mass occurred. An F value of zero (i.e. F = 0) consequently means that none of the soil water was bypassed by the solute, while F = 0.3 (for example) means that 30% of the water was bypassed. The bypass flow factor was incorporated into the advection and mechanical mixing terms of Eq. (7), i.e.:

$$qC \rightarrow qC/(1 - F) \qquad (22)$$

$$D_m(q) = \lambda(q/\theta) \rightarrow \lambda q/[\theta(1 - F)] \qquad (23)$$

which implies that all of the soil water (θ) participates in solute sorption, dissipation and diffusion, but only a fraction of the water (specified by 1 - F) participates in advection and mechanical mixing. The effect of F on Eq. (7) is to increase the average velocity with which solute migrates through the soil profile relative to the average linear pore water velocity (q/θ), which in turn causes the predicted $0.5M_0$ mass of a nonreactive solute (e.g. chloride) to occur at less than one PV (i.e. $PV_{0.5} \leq 1$).

Bypass flow factors (F) were determined from field measured chloride breakout curves collected in Southern Ontario for several soil types, water contents and depths in the soil profile (Section 3.3.2). The F values were highly variable (CV = 168%) and did not show any consistent patterns with soil texture, water content, pore water flux, or depth in the soil profile. Consequently, the mean value of F = 0.2 (n = 56) was used in the simulations to represent bypass flow unless otherwise noted.

3.2.7 Multiple Year Simulations

LEACHW and LEACHP must be able to run over a number of consecutive years to determine if the annual pesticide mass loading at a specified depth becomes constant with time, continuously increases or decreases with time, or changes erratically from year to year. To accomplish this, new programs were written to prepare multiple year weather and crop management input files, with modifications to account for over - winter water redistribution and solute dissipation in the soil profile; snow accumulation during winter; and spring runoff.

It is assumed that during the "winter" (defined as when the weekly mean air temperature is less than 0 °C), the soil surface is frozen and there is no water flux across the atmosphere/soil interface. The result of this is that the existing water and solutes in the soil profile slowly redistribute during the winter via gravity drainage. Precipitation during the winter period is assumed to occur as snow, and it accumulates with the assumption that 30% is lost due to blowoff, evaporation and sublimation (H. Hayhoe, 1994, personal communication). The remaining 70% is distributed between infiltration and snowmelt runoff during the first seven days of "spring" (defined as when the weekly mean soil surface temperature is greater than 0 °C). Runoff is calculated with the USDA Soil Conservation Service (1972) curve number method. Soil surface temperatures are calculated using the data and procedures in Section 3.2.9.

3.2.8 Crop Management

The crop management routine in LEACHP was modified to take into account crop type, soil hydraulic conductivity and air temperature when determining the dates for pesticide application, planting, emergence, maturity and harvest. For the Grand River watershed application, corn (Zea mays L.) was planted in soils with intermediate surface hydraulic conductivity (100 mm/d $\leq K_s \leq$ 250 mm/d) when the mean air temperature reached 12.8°C (Brown, 1976). Relative to this date, planting was advanced seven days on soils with high surface conductivity ($K_s >$ 250 mm/d), and delayed seven days on soils with low surface conductivity ($K_s <$ 100 mm/d). Emergence was assumed to take place seven days after planting, and atrazine was applied two weeks after emergence. Crop maturity (full crop cover and maximum root depth) was assumed to occur when 1250 corn heat units were accumulated since planting. The crop was harvested in the fall when either the mean air temperature dropped below 12°C, or the minimum air temperature dropped below -2°C.

3.2.9 Weather Data

LEACHW requires daily precipitation including the time when an infiltration event starts, the average weekly soil surface temperature and its amplitude, and daily potential evapotranspiration. As these data are not consistently available for many locations (see Section 3.4.1), they were estimated using monthly 30 year normal values (which are consistently available) of precipitation, days with precipitation, and maximum and minimum air temperatures. The daily precipitation values were estimated from the normals using the procedure of Van Diepen et al. (1988), and it was assumed that an infiltration event starts at midnight. The sine-wave interpolation technique of Brooks (1943) was used to estimate daily air temperatures; and from these values, weekly soil surface temperature and its amplitude were calculated, assuming that air and soil surface temperature are equal for predominantly crop covered soil. Daily potential evapotranspiration, PE [mm], was estimated using (Baier and Robertson, 1965):

$$PE = -8.18 + 0.087Tmax + 0.088(Tmax - Tmin) + 0.0046Q_o \tag{24}$$

where Tmax and Tmin [°F] are the daily maximum and minimum air temperatures, respectively, and Q_o [cal/cm^2] is the latitude-dependent daily solar energy at the top of the atmosphere.

3.3 Testing and Calibration of LEACHW and LEACHP

An essential step in the development and application of a solute transport model is to verify its ability to simulate the main water and solute transport processes with acceptable accuracy. This was done for the modified LEACHW and LEACHP submodels using a laboratory column study and several field studies.

3.3.1 Column Study

Highly controlled and detailed laboratory column experiments were conducted to evaluate the abilities of the modified LEACHW and LEACHP models to predict measured water content and pressure head profiles (LEACHW), and measured chloride and atrazine breakthrough curves (LEACHP).

Duplicate 20.1 cm inside diameter by 65 cm long intact cores of Dalhousie loam soil were collected from an alfalfa field near Ottawa which had not received atrazine during the previous 7 years. The vertical columns were instrumented in 10 cm increments (starting at 10 cm below the soil surface) with a horizontal TDR probe (Topp, 1993) for measuring volumetric water content (θ), a tensiometer for measuring pore water pressure head (h), and two soil water solution samplers (installed on opposite sides of the columns) for measuring chloride and atrazine breakthrough curves (BTC). Each column therefore contained a total of 6 TDR probes, 6 tensiometers and 12 soil solution samplers. The bottom end caps of the columns were designed to allow leachate collection under both positive and negative pressure head conditions. Peristaltic pumps feeding into a 1 cm thick layer of 3-5 μm glass spheres were used to apply steady, uniformly distributed water and solute fluxes to the soil surface in the columns. The columns were maintained at 25 ± 0.5 °C throughout the experiments.

The $\theta(h)$ and $K(h)$ relationships required by LEACHW were determined for each 10 cm increment along the columns by fitting the Van Genuchten relationships (Eq. 14 and 15; De Jong, 1993) to θ-h data obtained from the TDR probes and tensiometers during the bottom-up saturation of the columns; and to K_s data obtained from,

$$K_s = q(\Delta z/\Delta H), \tag{25}$$

where q is a steady saturated flux through the column ($h \geq 0$) imposed by the peristaltic pump [LT^{-1}], and ($\Delta z/\Delta H$) is the inverse of the hydraulic head gradient between adjacent pairs of tensiometers. Dispersivities (λ), required by LEACHP, were obtained by fitting an analytical solution of Eq. (7) (Kirkham and Powers, 1972, Eq. 8-75, p.405) to chloride BTC data collected from the soil solution samplers. The chloride BTCs were also used to determine average linear tracer velocities, V_T (V_T = rate of migration of the BTC peak [LT^{-1}]), as well as bypass flow factors, F (Eq. 21). A water content - temperature corrected dissipation rate constant (k_{wt}, Eq. 20) for atrazine in Dalhousie loam (the loam soil in Table 1) was obtained from incubation experiments conducted on laboratory flasks and 20 cm diameter by 20 cm long intact soil cores (Topp et al., 1994). Organic carbon content (OC) profiles, required for calculating atrazine K_d's (Eq. 11), were obtained by sectioning the columns (5 cm increments) at the end of the experiments. An atrazine K_{oc} of 160 ml/g (Jury et al., 1983) was assumed in the LEACHP simulations.

The column experiments were conducted under steady saturated flow (q = 540 mm/d) and steady near-saturated flow (q = 22 mm/d) conditions . This allowed the predictive abilities of the models to be evaluated when all of the soil pores can potentially participate in water and solute transport (saturated flow conditions), and when the soil macropores are largely air-filled and inoperative (near-saturated flow conditions). The chloride tracer was added to the soil surface in the columns as a square wave pulse (25 or 50 ml) of concentrated KCl solution (M_0 = 2.2 g Cl^-). The atrazine was sprayed onto the soil surface as a concentrated spike (M_0 = 9.56 mg atrazine) dissolved in 9 ml of methanol. Further detail on the column experiments can be found in Smith et al. (1994).

The ability of the models to predict the measurements was characterized using (Ambrose and Roesch, 1982):

$$AE = \sum_{i=1}^{n} (P_i - M_i)/n \tag{26}$$

$$RE = AE/|M| \tag{27}$$

where AE is the average prediction error, RE is the relative average prediction error, P_i is the value predicted by the model (i.e. θ, chloride concentration, etc.), M_i is the corresponding measured value, $|M|$ is the magnitude (absolute value) of the mean measured value, and n is the number of values. These parameters are useful for evaluating model performance because their magnitudes indicate the average extent to which the model predictions deviate from the measurements (the larger the magnitude the greater the average deviation); and their sign indicates whether the model tends to underestimate the measured values (negative AE and RE), or overestimate the measured values (positive AE and RE).

The AE and RE values for the LEACHW predictions of the steady water content and pressure head profiles, $\theta(z)$ and h(z) respectively, are given in Table 2. In both columns, the $\theta(z)$ profiles were underpredicted (underestimated) for near-saturated flow (q = 22 mm/d) and overpredicted (overestimated) for saturated flow (q = 540 mm/d). The average degree of deviation is quite small, however (AE within ±0.013; RE within ±3.31%); and the maximum deviations were only 0.014 cm^3cm^{-3} (column 1, q = 540 mm/d) to 0.032 cm^3cm^{-3} (column 2, q = 22 mm/d). The average and maximum prediction errors for h(z) are somewhat larger (AE within ±2.1 cm; RE within ±20.0%; maximum deviation ≤ 10.0 cm); but they are still quite small, considering the generally low precision of near-zero h measurements (i.e. the measured h values for near-saturated flow ranged from -22 cm to -10 cm, while those for saturated flow ranged from -9 cm to 0 cm). It is also noted that the AE and RE values are about the same magnitude for both saturated and near-saturated flow, suggesting that water flow through macropores (many were observed when the columns were sectioned) did not substantially affect the ability of LEACHW to predict steady $\theta(z)$ and h(z) profiles. It is consequently concluded that the modified LEACHW model can accurately simulate steady $\theta(z)$ and h(z) profiles from intact laboratory columns, regardless of whether the soil macropores are largely operative (saturated flow) or largely inoperative (near-saturated flow).

For near-saturated flow ($q = 22$ mm/d), both the water transport parameters (q/θ, θ) and the tracer transport parameters (V_T, λ, θ_T, F) were very similar between columns (Table 3), with the discrepancies ranging from zero (λ, F) to only 3.3% (θ_T). In addition, the average linear chloride velocities (V_T) fell within 3.6% of the average linear pore water velocities (q/θ); the dispersivities were relatively small ($\lambda = 8.9$ cm); and the bypass flow factors were not different from zero ($F = -0.03$). The measured chloride BTCs were also found to be reasonably similar in shape between columns, between the two sides of the columns, and with depth in the columns (data not shown). These results indicate that under near-saturated flow conditions, the two columns were similar and reasonably homogeneous with respect to water and chloride tracer transport. The results also indicate that no bypass flow of chloride occurred during near-saturated flow, when soil macropores are largely inoperative.

For saturated flow ($q = 540$ mm/d), the column averaged water transport parameters (q/θ, θ) remained very similar between columns (within 0.8%), but the tracer transport parameters (V_T, λ, θ_T, F) were very different (Table 3). The V_T, λ and F values were higher (by 29%, 330% and 389%, respectively), and the θ_T values were lower (by 38%), for column 2 relative to column 1. In addition, the V_T values were considerably larger in both columns than the corresponding q/θ values (by factors of 2.2 and 2.8 for columns 1 and 2, respectively); and the F values were greater than zero ($F = 0.09$ for column 1; and $F = 0.44$ for column 2). It was also observed that the chloride BTCs usually exhibited extreme tailing, as well as erratic changes in shape between columns, between the two sides of the columns, and with depth in the columns (data not shown). These results suggest that the chloride movement was very complex during saturated flow; and that substantial bypass of the soil water occurred, presumably due to preferential flow through the numerous and circuitous biopores that were observed in the columns when they were sectioned (Smith et al., 1994).

Table 2. Average and relative prediction errors, AE and RE respectively, for the LEACHW predictions of steady water content, $\theta(z)$, and pressure head, $h(z)$, profiles in the column experiments

Column Replicate Number	Flux Density (mm/d)	n	Water Content		Pressure Head	
			AE (cm^3/cm^3)	RE (%)	AE (cm)	RE (%)
1	22	6	-0.013	-3.21	-2.08	-13.02
2	22	6	-0.013	-3.31	+0.65	+ 4.33
overall	22	12	-0.013	-3.26	-0.70	- 4.60
1	540	6	+0.008	+1.79	+0.67	+10.26
2	540	6	+0.008	+2.00	+0.67	+20.00
overall	540	12	+0.008	+1.92	+0.67	+13.60

The F values further suggest that about 9% of the soil water was bypassed in column 1 (F = 0.09), and about 44% of the soil water was bypassed in column 2 (F = 0.44). The dispersivities and tailing in the BTCs reflect the bypass flow results in that λ is small (λ = 9.0 cm) and BTC tailing is reduced (although still substantial) when bypass flow is small (F = 0.09) (Table 3); while λ is large (λ = 38.7 cm) and BTC tailing is extreme when bypass flow is extensive (F = 0.44).

Table 3. Water and solute transport parameters from the column experiments

Column Replicate Number	Flux Density (mm/d)	(q/θ) (mm/d)	$^{*}V_T$ (mm/d)	λ (cm)	θ (cm^3/cm^3)	$^{+}\theta_T$ (cm^3/cm^3)	F
1	22	60.7	61.8	8.9	0.364	0.377	-0.03
2	22	62.1	62.9	8.9	0.356	0.365	-0.03
1	540	1395.4	3061.0	9.0	0.388	0.351	+0.09
2	540	1404.4	3958.4	38.7	0.385	0.216	+0.44

$^{*}V_T$ = average linear tracer velocity as determined from the rate of migration of the chloride BTC peak.

$^{+}\theta_T = q/V_T$, where q is the flux density (mm/d) set by the peristaltic pump.

The LEACHP model tended to slightly overpredict the chloride BTCs for near-saturated flow (column averaged AE $\leq$ 14.21 ppm; column averaged RE $\leq$ 10.53%), and to moderately underpredict the BTCs for saturated flow (column averaged AE $\geq$ -23.96; column averaged RE $\geq$ -25.36%) (Table 4a). The underprediction was due primarily to underestimation of the tails in the measured BTCs, which almost always occurred in both the saturated and near-saturated flow regimes. The net overprediction for near-saturated flow was caused by overestimation of the leading limb and/or peaks of the measured BTCs, which outweighed the consistent underestimation of the tails. The larger negative prediction errors for saturated flow are not surprising, as significant bypass of chloride tracer occurred for this flow condition (Table 3). As already mentioned, bypass flow usually causes extensive tailing in tracer BTCs (White, 1985). Use of the appropriate bypass flow factors from Table 3 usually worsened the saturated flow predictions, suggesting that a more sophisticated representation of bypass flow may be required (see Section 3.3.2 for further discussion).

Although some limitations are evident in the ability of LEACHP to simulate chloride transport through large columns of intact soil, RE values within ±25% are still considered to be acceptable, and the model is thus deemed to have predicted chloride tracer transport adequately.

Assuming no bypass flow (F = 0), the LEACHP prediction errors (AE and RE) for atrazine transport (Table 4a) were consistently positive, slightly larger in magnitude than the corresponding chloride transport values for saturated flow (q = 540 mm/d), and considerably larger than the corresponding chloride values for near-saturated flow (q = 22 mm/d). These overpredictions were caused primarily by overestimation of both the peak and the tail of the measured BTCs, i.e. LEACHP generally predicted higher atrazine concentrations in solution than were actually measured (data not shown). This overestimate was much more extreme for near-saturated flow than for saturated flow, hence the considerably larger AE and RE values. Incorporation of the measured bypass flow factors for the saturated flow condition (i.e. F = 0.09 for column 1, F = 0.44 for column 2; Table 3) reduced the atrazine prediction errors only marginally (Table 4b), which suggests that the overpredictions are not substantially related to preferential flow. This implies, as a consequence, that the overpredictions are related to the LEACHP representations of atrazine sorption and/or dissipation.

An underestimate of atrazine sorption (i.e. an underestimate of the actual atrazine K_d) would produce an overestimate of the atrazine concentration in solution. However, this would also tend to cause the predicted atrazine BTC peaks to occur before the measured peaks (i.e. at earlier time), which is generally not the case. Instead, the predicted and measured peaks tend to correspond reasonably well, with the predicted peaks usually appearing after the measured peaks (i.e. at greater time) rather than before the measured peaks (the column averaged AE for the time at which the BTC peaks occurred was +4.2 days for near-saturated flow, and +0.18 days for saturated flow). The representation of atrazine sorption in LEACHP (Eq. 10 and 11) and the value selected for K_{oc} (160 ml/g) therefore appear to be adequate (at least for the column experiments).

Table 4. Average and relative prediction errors, AE and RE respectively, for the LEACHP predictions of chloride and atrazine breakthrough curves (BTC) in the column experiments. F = bypass flow factor.

Column Replicate Number	Flux Density (q) (mm/d)	F	Chloride BTC			Atrazine BTC		
			+n	*AE (ppm)	*RE (%)	+n	*AE (ppb)	*RE (%)
(a) No Bypass Flow (F=0)								
1	22	0	99	+14.21	+10.53	124	43.21	206.92
2	22	0	102	+ 7.53	+ 3.88	124	85.78	364.31
1	540	0	70	-23.96	-25.36	63	26.78	36.07
2	540	0	28	-16.93	-21.54	30	36.72	26.04
(b) Bypass Flow (F > 0)								
1	540	0.09				63	26.51	35.71
2	540	0.44				30	35.49	25.16

+n includes all data points, all solution samplers and all depths.
*AE and RE are averaged over all solution samplers and all depths.

An underestimate of the overall atrazine dissipation rate by LEACHP would also produce an overestimate of the atrazine concentration in solution. The current representation of atrazine dissipation in LEACHP (Eq. 12,18,19,20) assumes first order kinetics with a rate constant (k) that depends only on water content and temperature (Section 3.2.4). Recent work suggests, however, that atrazine dissipation kinetics can be of variable kinetic order, particularly over time periods exceeding one month, and that the overall atrazine dissipation rate can increase through time due to a gradual increase in atrazine biodegradation (E. Topp and W. Smith, 1994, personal communication). In addition, some researchers have found effective dissipation rate constants from constant flux column experiments to be substantially greater than those obtained from corresponding static incubation experiments (e.g. Comfort et al., 1992). It is therefore quite possible that LEACHP underestimated the effective atrazine dissipation rates in the column experiments.

Underestimation of atrazine dissipation rates by LEACHP would also explain why the prediction errors were substantially different for saturated and near-saturated flow. Under saturated flow conditions, the atrazine BTCs pass all six sampling depths within 10 days. This leaves little time for dissipation, and consequently even a substantial underestimate in the overall dissipation rate would not greatly increase the prediction errors. Under near-saturated flow conditions, however, the atrazine BTCs require over 50 days to pass the deepest sampling depth (60 cm). Thus for near-saturated flow, even a relatively modest underestimate in dissipation rate could produce substantial overestimates in the amount of atrazine in solution, and thereby result in large prediction errors. Further investigations are required before definite conclusions regarding effective dissipation rate constants can be drawn.

Although some of the LEACHP simulations of atrazine transport produce large prediction errors (i.e. for near-saturated flow: RE = +207% for column 1; RE = +364% for column 2; Table 4a), the model still compares well to many other models that have not been "fitted" in some way to measured pesticide transport data (e.g. Melancon et al., 1986; Sauer et al., 1990). In addition, the LEACHP prediction errors are conservative (i.e. it tends to predict higher atrazine solution phase concentrations than measured), which adds an extra "margin of safety" to predictions of environmental impact and contamination. It is consequently concluded that LEACHP can be used effectively in its present form for predicting and characterizing atrazine contamination.

3.3.2 Field Studies

i) Field measurement of transport parameters

Six field experiments were conducted in Southern Ontario to measure water and solute transport parameters required to model the movement and fate of agrochemicals. The sites (Table 5) were chosen in areas of intensive agricultural production, and they were widely spaced geographically in an attempt to obtain an impression of the range of water and solute transport parameters that might be encountered in the Southern Ontario region. The soil types at these sites are typical of the region and include a highly structured Rideau silty clay (Ottawa), a structureless Tioga fine sand (Alliston), a well structured Brookston clay loam (Crediton), a moderately structured Guelph loam (Brantford), a poorly structured Brady sandy

Table 5. Dispersivities (λ) and profile averaged $PV_{0.5}$ values calculated from field measured breakout curves. Note that $F = 1 - PV_{0.5}$ (Section 3.2.6)

Site, Latitude and Longitude	Depth (cm)	Dispersivity, λ		$PV_{0.5}$ (Profile Averaged)	
		Low Irrigation Rate (cm)	High Irrigation Rate (cm)	Low Irrig. Rate (95% Confidence Limits)	High Irrig. Rate (95% Confidence Limits)
Ottawa	25	4.01	6.82		
Latitude = 45.4°	50	5.91	5.24	0.975	0.987
Longitude = 75.7°	75	6.49	5.33	(0.950-1.045)	(0.942-1.032)
Alliston	20	4.68	4.31		
Latitude = 44.2°	40	5.73	8.92		
Longitude = 79.9°	60	7.50	10.19	0.779	1.050
	80	11.54	13.02	(0.739-0.819)	(0.991-1.109)
	100	10.43	13.43		
Brantford	20	7.73	8.23		
Latitude = 44.0°	30	5.93	12.82		
Longitude = 79.6°	40	5.05	12.59	1.011	0.940
	60	8.71	10.98	(0.948-1.074)	(0.883-0.997)
	80	15.30	17.49		
Crediton	10	6.68	4.90		
Latitude = 43.3°	20	12.34	12.71		
Longitude = 81.5°	30	28.05	14.08	0.621	0.611
	40	24.85	22.08	(0.557-0.685)	(0.536-0.686)
	60	35.20	23.55		
Thamesville	20	16.70	5.45		
Latitude = 42.6°	30	22.32	17.46		
Longitude = 82.0°	40	63.10	38.45	0.838	0.961
	60	122.13	21.29	(0.694-0.982)	(0.827-1.095)
	80	149.18	60.60		
Woodslee	10	3.61	8.00		
Latitude = 42.2°	20	14.62	8.89		
Longitude = 82.7°	30	14.35	21.68	0.255	0.442
	40	14.25	25.47	(0.231-0.279)	(0.346-0.538)
	50	13.57	34.00		

loam (Thamesville), and a Brookston clay loam that exhibits extensive shrinkage cracking in the plough layer (Woodslee). The water and solute transport parameters measured included the soil water characteristic, $\theta(h)$, the hydraulic conductivity relationship, $K(h)$, dispersivity, λ, the $PV_{0.5}$ value, and the bypass flow factor, F.

The $\theta(h)$ and $K(h)$ relationships were obtained for the A, B and C horizons at each field site using intact soil cores. At the Ottawa, Thamesville and Woodslee sites, triplicate 10 cm diameter by 50-100 cm long cores were extracted, instrumented in the A, B and C horizons with horizontal TDR probes and tensiometers, and $\theta(h)$ and $K(h)$ determined using profile drainage measurements and the Van Genuchten relationships (Eqs. 14 and 15; De Jong, 1993). At the Alliston, Brantford and Crediton field sites, triplicate 7.6 cm diameter by 7.6 cm long intact cores were collected for each soil horizon because large cores could not be obtained without excessive soil disturbance. Tension table and pressure plate apparatus (Topp et al., 1993) were used in combination with the Van Genuchten relationships to obtain $\theta(h)$ and $K(h)$ from these cores.

The λ, $PV_{0.5}$ and F parameters were obtained via in-situ constant flux miscible displacement (breakthrough curve) experiments. At each field site, six replicate 1 m^2 plots were instrumented with time domain reflectometry (TDR) probes to simultaneously measure volumetric water content (θ) and monitor the movement of chloride tracer (Kachanoski et al., 1992). The TDR probes were vertically inserted from the soil surface to five different depths in the soil profile. The probe depths varied at each site to accommodate the particular soil horizonation and water table conditions at the site (Table 5). Each probe depth was replicated five times to produce a total of 30 replicate measurement points at each depth for each field site. A rainfall simulator was used to uniformly apply a steady flux of water to each plot. Two steady irrigation rates were chosen: a high rate to produce field-saturated flow through the profile, and a low rate (equal to 50% of the high rate) to produce "near" field-saturated flow. This was done to assess the effects of soil macrostructure on water and solute transport. Each plot was initially irrigated until a steady water content profile, $\theta(z,t)$, was obtained as determined by TDR measurements. A known mass (M_0) of Cl^- tracer (low irrigation rate, $M_0 = 38$ g Cl^-/m^2; high irrigation rate, $M_0 = 57$ g Cl^-/m^2) was then quickly and uniformly applied to the plot surface as a spike of concentrated KCl solution, and then the constant rate irrigation resumed. TDR measurements were then used to monitor the movement of chloride mass (M) past the end of each TDR probe. Chloride "breakout curves" (BOC), were then obtained by plotting M/M_o as a function of pore volumes (PV) of eluted soil water, where

$$PV = q_i t \,/\, \theta_{TDR} D \ , \qquad (28)$$

q_i is the applied irrigation flux [LT^{-1}], t is time [T], θ_{TDR} is the volumetric water content measured by the TDR probe [L^3L^{-3}], and D is the length (depth) of the TDR probe [L]. As the BOC describes movement of tracer mass past the end of the TDR probe, then a BOC is simply one minus the corresponding BTC (i.e BOC = 1 - BTC). Under ideal conditions (i.e. homogeneous, isotropic structureless soil; steady soil water flux), the BTC and BOC have a nearly symmetric sigmoid shape due to dispersion, and the $M = 0.5M_0$ mass occurs at PV = 1 (White, 1985). Extensive tailing of the BTC or BOC and the occurrence of $M = 0.5M_0$ at PV < 1 indicates (as mentioned in Section 3.2.6 and shown in Fig. 2) that a proportion of the soil water is bypassed by the solute (White, 1985; Bouma, 1991). Displacement of the $M = 0.5M_0$ mass to $PV > 1$, on the other hand, indicates adsorption or retention of the solute by the soil. The λ values were determined by least squares fitting the Ogata and Banks (1961) analytical solution of Eq. (7) to the measured BOCs. The F values were determined using Eq. (21) and the $PV_{0.5}$ values obtained from the measured BOCs. Further detail on the field studies can be found in Environmental Soil Services (1991, 1992, 1993).

Dispersivity (λ) values for the various depths and field sites are given in Table 5. Only three of the five depths were usable at the Ottawa site due to high water table conditions. It can be seen in Table 5 that λ is highly variable (CV = 82%, range = 3.61-149.18 cm), but tended to increase with depth and irrigation rate, as is often observed (e.g. Jury and Utermann, 1992; Burr and Sudicky, 1994). The trends with depth and flux are not consistent, however; and moreover, there is no clear relationship between λ and soil texture or soil structure. Consequently, the average λ for both irrigation rates and all sites and depths (i.e. $\lambda = 15.5$ cm) was used in the LEACHP simulations for the Grand River watershed.

The PVs at which the $M = 0.5M_0$ chloride mass occurred in the BOCs ($PV_{0.5}$) were averaged over all depths at each field site, and the 95% confidence limits calculated (Table 5). As expected, statistically significant bypass flow (i.e. $PV_{0.5} < 1$; $F > 0$) was observed in the cracking Brookston clay loam at the Crediton and Woodslee sites (e.g. Fig. 2). However, neither the highly structured Rideau silty clay (Ottawa) nor the moderately structured Guelph loam (Brantford) showed clear evidence of bypass flow. In addition, significant bypass flow was observed in the structureless (single grain) Tioga fine sand (Alliston) and the poorly structured Brady sandy loam (Thamesville) at the low irrigation rate, but not at the high irrigation rate.

The reasons for these sometimes inconsistent results are not understood. The expectation was that the amount of bypass flow would be consistently large (i.e. $PV_{0.5} << 1$; $F >> 0$) for field-saturated flow (high irrigation rate) through the well structured soils (i.e the Rideau, Brookston and Guelph soils). Under these conditions, water and solutes should move rapidly through macropores and thereby bypass much of the soil matrix. Bypass flow was also expected to decrease as flow changed from field-saturated (high irrigation rate) to "near" field-saturated (low irrigation rate). The largest macropores should be empty (i.e. air-filled) under near field-saturated flow conditions, and thus not participate in the conduction of water and solutes. Finally, structureless and poorly structured soils, such as the Tioga fine sand (at Alliston) and the Brady sandy loam (at Thamesville), were expected to exhibit virtually no bypass flow (i.e. $PV_{0.5} \approx 1$; $F \approx 0$) due to the apparent absence of macropores.

In view of the many unexpected results, it was decided to simply use a constant "representative mean" F value in the LEACHP simulations. For the Grand River watershed application, $F = 0.2$ was used (i.e. 20% of the soil water is bypassed by solute), which was obtained using Eq. (21) and the average $PV_{0.5}$ for all sites and irrigation rates in Table 5.

ii) Field evaluation of LEACHW

LEACHW was evaluated for its ability to simulate in-situ measured soil water content profiles, $\theta(z,t)$, obtained from several short term miscible displacement experiments [described above in subsection 3.3.2 (i)], and from two long term water balance studies conducted near Simcoe and Ottawa, Ontario.

The Simcoe water balance study was conducted during the 1974 growing season on a free-draining Caledon sandy loam soil, planted to soybeans. The water content was measured in-situ (neutron probe method) on a daily basis at 0-25, 25-50 and 50-100 cm depth. The $\theta(h)$ and $K(h)$ relationships were obtained by fitting Eq. (2)-(5) to $\theta(h)$ data collected from intact soil cores. K_s values were estimated for the appropriate textural class using the method of Clapp and Hornberger (1978).

The Ottawa water balance study was conducted during the 1982 growing season on a well structured Rideau clay cropped to grass hay. Volumetric water content was measured in-situ (TDR method) on a weekly basis at 0-15, 15-30, 30-50, 50-80 and 80-120 cm depth. The $\theta(h)$ and $K(h)$ relationships were obtained by fitting Eq. (14) and (15) to $\theta(h)$ data collected from intact soil cores taken from each of the five depths. The $K(h)$ functions were matched to K_s values measured in-situ at each depth using the Guelph permeameter method (Reynolds, 1993) and the analysis procedures of Vieira et al. (1988).

Daily precipitation was measured in both water balance studies using an on-site recording rain gauge; potential evapotranspiration was estimated using the Priestley and Taylor (1972) approach. Rooting depths and distributions were derived from values reported by Allmaras et al. (1975) (Simcoe site) and De Jong et al. (1992) (Ottawa site). Further details on these studies can be found in Bailey and Davies (1981) and De Jong et al. (1992).

The average prediction errors (AE) and the average relative prediction errors (RE) for the miscible displacement experiments are given in Table 6, where the data for the low and high irrigation rates are combined (hence n = 10). It is seen that the AE and RE values are quite small (AE within ± 0.011 cm^3 cm^{-3}; RE within $\pm 2.6\%$), despite considerable heterogeneity in $\theta(h)$ and $K(h)$ within the soil profiles (data not shown). The LEACHW model therefore appears quite capable of accurately predicting short term $\theta(z,t)$ profiles in the field.

Table 6. Average and relative prediction errors, AE and RE respectively, for the LEACHW predictions of steady water content profiles, $\theta(z)$, in the field-based miscible displacement experiments

Statistic	Ottawa	Alliston	Brantford	Crediton	Thamesville	Woodslee
n	7	10	10	10	10	10
AE (cm^3/cm^3)	+0.005	+0.011	+0.002	+0.001	-0.010	+0.009
RE (%)	+1.0	+2.6	+0.5	+0.1	-2.6	+2.0

The AE and RE values for the longer term water balance studies appear in Table 7. At the Simcoe site, LEACHW consistently underpredicted the measured $\theta(z,t)$ throughout the growing season, with RE ranging from -8.1% to -28.5%. At the Ottawa site, $\theta(z,t)$ was alternately overpredicted and underpredicted during the growing season; but the prediction errors were generally smaller ($-3.6\% \leq RE \leq +8.1\%$), which is probably due, at least in part, to the use of in-situ measured K_s data and the Van Genuchten K-θ-h relationships (Eq. 14 and 15). The prediction errors are attributed primarily to limitations in LEACHW's representation of the soil-plant-atmosphere system, particularly its lack of account for hysteresis and bypass flow (only LEACHP considers bypass flow). From the point of view of predicting $\theta(z,t)$ over a growing season, however, RE values within ±30% are considered quite acceptable (Clemente et al., 1994), and LEACHW is thus judged to have performed well for these water balance studies.

iii) Field evaluation of LEACHP

LEACHP was tested for field conditions by evaluating its ability to predict the field measured chloride BOCs in subsection 3.3.2 (i). The AE and RE values in Table 8 quantify the discrepancies between the measured and predicted BOCs for the deepest measurement depth at each field site. When F = 0 (no bypass flow), the prediction error is seen to be smallest for the high irrigation rate at the Brantford site (AE = -0.006; RE = -1.1%); and largest for the low irrigation rate at the Woodslee site (AE = +0.225; RE = +186.1%). The large prediction error at the Woodslee site is attributed, at least in part, to inaccurate M/M_0 measurements resulting from high background electrical conductivities in that soil. The prediction errors (for F = 0) are also noted to be consistently larger for the low irrigation rate experiments than for the high rate experiments, which is unexpected and unexplained. As mentioned above, less bypass flow, and hence lower prediction errors, were expected for the near field-saturated flow conditions produced by the low irrigation rates.

Table 7. Average and relative prediction errors, AE and RE respectively, for the LEACHW predictions of water content profiles, $\theta(z,t)$, in the Simcoe and Ottawa water balance studies

Site	Depth (cm)	n	AE (cm^3/cm^3)	RE (%)
Simcoe	0 - 25	67	-0.009	- 8.10
	25 - 50	67	-0.039	-28.50
	50 - 100	67	-0.021	-18.99
	Overall	201	-0.023	-19.26
Ottawa	0 - 15	22	+0.012	+ 3.52
	15 - 30	26	+0.006	+ 1.57
	30 - 50	26	+0.005	+ 1.32
	50 - 80	26	+0.033	+ 8.11
	80 - 120	26	-0.017	- 3.63
	Overall	126	+0.008	+ 1.94

Positive prediction errors (i.e. AE and RE positive) were usually reduced substantially by using the profile averaged bypass flow factor obtained from the measured BOCs (i.e. the values relating to F > 0 in Table 8). The Crediton and Woodslee sites, high irrigation rate, are the only exceptions. Negative prediction errors, on the other hand, were increased by the use of F > 0 (Brantford and Thamesville sites, high irrigation rate). The rather simplistic manner in which bypass flow was conceptualized (Eq. 21) and incorporated into LEACHP (Eqs. 22 and 23), and/or inadequate representations of water and solute transport mechanisms, are probably responsible for this behaviour. It was noted, for example, that the use of a constant, profile averaged F value usually decreases the prediction error at some depths in the soil profile, but increases it at other depths (data not shown). This probably indicates that a bypass flow "function" should be developed which varies with soil, solute transport and other properties.

Despite the above problems in predicting field measured BOCs, the AE and RE values for F > 0 are still relatively small (neglecting the low irrigation rate results at Woodslee); and all of the predictions satisfy the criterion for model acceptance set by the Prediction Exposure Assessment Workshop (Hedden, 1986), which states that a model should be able to replicate field-based solute transport data within a factor of 2 (±200%) for site-specific applications. It is therefore concluded that the modified LEACHP model can adequately predict steady vertical movement of nonreactive solutes (e.g. chloride) under field conditions.

Although the above testing and calibration of the modified LEACHW and LEACHP models is not entirely comprehensive (practicalities precluded that), the column and field studies indicate nonetheless that these models are generally capable of providing excellent predictions of water content and pressure head profiles (RE usually within ±20%), good predictions of chloride transport behaviour (RE usually within ±40%), and adequate predictions of atrazine transport (RE usually within ±200%). It is consequently felt that the modified LEACHW and LEACHP models can be applied effectively within a pedotransfer function - geostatistics - GIS framework.

3.4 Application of LEACHW and LEACHP within the Pedotransfer Function - Geostatistics - GIS Framework

The LEACHW and LEACHP models simulate water and solute movement in the vertical direction only, i.e. they are one-dimensional. Extension of the models to an areal basis requires running them at a number of georeferenced locations distributed throughout the area, and then applying interpolation procedures that account for the inherent spatial variability within the area. This was accomplished using archived soil survey and weather databases, pedotransfer functions, geostatistical analyses, and a GIS. The main elements of the procedure are given below. Further detail can be found in Vieira (1993).

3.4.1 Soil Survey and Weather Data

As indicated in Section 3.1.5, the input requirements of the LEACHW model include (among other things) soil physical and hydraulic properties, and weather data. When the model is being applied to large areas, such as watersheds, the main sources of these data (in Canada)

Table 8. Average and relative prediction errors, AE and RE respectively, for the LEACHP predictions of field measured breakout curves, assuming bypass flow (F > 0) and no bypass flow (F = 0)

Site	F	Low Irrigation Rate			High Irrigation Rate		
		n	AE	RE (%)	n	AE	RE (%)
Ottawa	0.00 0.10	21 21	+0.188 +0.146	+41.3 +31.9	20 21	+0.167 +0.125	+37.5 +28.5
Alliston	0.00 0.1[illegible]	18 18	+0.154 +0.102	+26.9 +17.9	15 15	+0.054 +0.006	+ 9.7 + 1.0
Brantford	0.00 0.10	16 16	+0.056 +0.022	+ 9.7 + 3.8	16 16	-0.006 -0.031	- 1.1 - 5.6
Crediton	0.00 0.30	21 21	+0.086 +0.026	+16.4 + 4.9	23 22	+0.041 -0.066	+ 7.5 -12.5
Thamesville	0.00 0.18	14 14	+0.024 -0.020	+ 5.7 - 4.8	19 19	-0.016 -0.053	- 3.9 -13.1
Woodslee	0.00 0.77	15 15	+0.225 +0.162	+186.1 +134.1	11 11	+0.038 -0.050	+ 9.1 -12.0

are the National Soil Data Base (NSDB) and the Archived Weather Data Base (AWDB). The NSDB is an amalgamation of soil survey data collected over a number of years and on a variety of map scales. It is reasonably complete to the 1 m depth with respect to soil classification (soil series name and type), soil texture (sand, silt, clay content) and organic carbon content. It is not complete, however, for the required soil physical and hydraulic properties. These properties were estimated using pedotransfer functions (Section 3.4.2). The most readily and widely available climate data in the AWDB are georeferenced monthly 30 year normals of maximum and minimum air temperatures, precipitation, and days with precipitation. These values were converted to the data required by LEACHW using the procedures in Section 3.2.9.

3.4.2 Pedotransfer Functions

Pedotransfer functions are empirical relationships that estimate required, but unavailable (i.e. not measured), soil properties from the soil properties that are available (Vereecken, 1992). These functions are calibrated for a particular study area and/or range of soil types by least squares fitting to a set of measured values. The functions are then used to estimate the required data where these data have not been measured.

Pedotransfer functions are being used in this study to estimate from available soil texture and organic carbon content data (from the NSDB data base), the bulk density, soil water characteristic and hydraulic conductivity data which are required as input to the LEACHW model. The specific pedotransfer functions used for the Grand River watershed are described in Section 4.1.

3.4.3 Geostatistical Analyses

A geostatistical technique known as kriging is used to account for spatial variability when extending the soil and weather input data and model predictions from a point basis to an areal basis (e.g. watershed). Kriging is essentially a weighted moving-average technique for interpolating between known data values at georeferenced locations. The kriging equation, in its most simple form, is given by (Davis, 1973):

$$Z_i = \sum_{j=1}^{n} a_j X_j \qquad (29)$$

where Z_i is the interpolated (kriged) value at grid location i, X_j are the known values (e.g. a measured weather attribute such as precipitation) at various locations surrounding Z_i, n is the number of X_j values used in the average, and a_j [dimensionless] are weighting factors where,

$$\sum_{j=1}^{n} a_j = 1. \qquad (30)$$

The values of a_j are determined from the semivariogram of the known values within the area of concern. The semivariogram characterizes the spatial variability of the known values by defining both the maximum distance over which the values are related to each other (i.e. the range of the semivariogram), and the functional nature of this relationship (i.e. the shape of the semivariogram) (Davis, 1973). Semivariograms are often scaled by dividing each calculated semivariance value by the variance of the entire data set. This allows the variability structure of different data sets to be compared (e.g. texture vs. bulk density vs. K_s). The main advantages of kriging over other interpolation techniques are: it works particularly well when the known values are sparse, irregularly spaced and highly variable; it provides interpolation estimates that are statistically unbiased with minimum possible estimation variance; and it can provide a measure of the probable error associated with each of the interpolation estimates (Davis, 1973).

Kriging is used here to convert the relatively small number of irregularly spaced and highly variable point values of soil properties, weather attributes and predicted agrochemical loadings, into a large number of interpolated values that extend throughout the area of interest on a regular, fine-mesh grid. The interpolations provide the required extension from a point basis to an areal basis, and also retain the spatial variability characteristics of the original data sets. The interpolations also provide the spatial detail necessary for effective use of a geographic information system.

3.4.4 Geographic Information System (GIS)

A GIS is essentially any system (usually computer based) that accomplishes the input, storage/retrieval, manipulation/ analysis, and output of georeferenced (spatial) data (Aronoff, 1989). It is used primarily for the collection and storage of different types of georeferenced data, production of maps, quantification of various map attributes, and for overlaying different types of maps to detect and characterize interrelationships among map attributes.

In this study, the main function of the GIS is to produce, quantify and overlay maps of the kriged soil, weather and agrochemical loading data. This will allow estimation of the importance and distribution of agrochemical contamination of ground water, as well as determination of the soil, weather and land management factors that control the contamination. The GIS should also be useful for the eventual development of agricultural practices and guidelines that maintain agrochemical contamination of ground water at acceptable levels.

The GIS used in this study is the Integrated Land and Water Information System (ILWIS, version 1.3), developed at the International Institute for Aerospace Survey and Earth Sciences (ITC), Enschede, The Netherlands. ILWIS was developed specifically to handle land and water information (as suggested by its name), including that obtained by satellite imagery. In addition, it is microcomputer-based; it can handle remote sensing data, tabular data, raster maps and vector files; and it can communicate with several other GIS systems including ARC/INFO.

4.0 APPLICATION OF METHODOLOGY TO GRAND RIVER WATERSHED

The Grand River watershed (Fig. 1) was chosen because it is one of the largest in Southern Ontario (≈ 680,000 ha); it contains a large range of soil textures (i.e. sand to loam to silty clay) with a complexity of distribution that is typical for the region; the primary land use is field crop production (≈ 75% of total land area) using standard agricultural practices and "normal" rates of pesticide usage (Shelton et al., 1988); it empties directly into the Great Lakes (Lake Erie); and there is the "usual" amount and quality of soil and climate data available for the area in the NSDB and AWDB. These features make the watershed fairly ideal for testing and demonstrating the methodology, and the results obtained should be "characteristic" of the Southern Ontario region.

4.1 Details of Grand River Watershed Application

A large (≈ 3 million ha), arbitrarily defined, "map window" encompassing the Grand River watershed was actually used for the application, rather than just the watershed alone (Fig. 3). This was done to increase the amount of data available, and thereby precision, of the geostatistical calculations; and to eliminate inaccuracies in the geostatistical and GIS calculations along the watershed boundaries due to border effects.

The required soil input data for the map window was identified and extracted from the NSDB on the basis of the dominant soil type in the 1:1 million scale soil landscape polygons

(Soil Landscapes of Canada, Shields et al., 1991) that fell within the window (Fig. 3). The data for each polygon were extracted for 3 soil layers (approximately the A, B and C horizons), and included the layer thickness; sand, silt and clay content; bulk density; organic carbon content; saturated hydraulic conductivity; and 2-4 points on the soil water characteristic. The data were assigned to the georeferenced centroids of the polygons. A total of 119 landscape polygon centroids fell within the map window, 18 of these falling within the Grand River watershed (Fig. 3).

Data that were missing from the NSDB included bulk density (61% missing), the soil water characteristic (61% missing), saturated hydraulic conductivity (91% missing), and the unsaturated hydraulic conductivity function (100% missing). These were estimated using pedotransfer functions based on soil texture and organic carbon (OC) content, for which there were no missing values in the NSDB. Bulk density (BD) was estimated using the Gupta and Larson (1979) model which is based on random particle size packings. The soil water characteristic, $\theta(h)$, was estimated using the model of McBride and Macintosh (1984), and then least squares fitted to Eq. (14) (De Jong, 1993) to obtain the α, n and θ_r values ($L = 0.5$ assumed). Saturated hydraulic conductivity, K_s, was estimated using the model of Jabro (1992). The unsaturated hydraulic conductivity relationship, $K(h)$, was derived from $\theta(h)$ and K_s using Eq. (14) and (15). The estimated data, as with the available data, were assigned to the appropriate georeferenced landscape polygon centroids (Fig. 3).

The climate data for the map window were extracted from the AWDB, and included the monthly 30 year normals (1950-1980) of maximum and minimum air temperatures, precipitation, and days with precipitation. These data were assigned to each of the 119 landscape polygon centroids within the window, using the values from the nearest weather station. The monthly normals were converted to the daily values required by LEACHW using the procedures in Section 3.2.9.

The LEACHW - LEACHP simulations were conducted for all 119 soil landscape polygon centroids in the map window, using the appropriate soil and weather input data at each centroid. The simulations were run for 10 consecutive "simulation" years, assuming an initially atrazine - free soil profile and repeating the 30 year normal weather each year. Corn (Zea mays L.) was grown every year over the entire map window using the crop management scheme described in Section 3.2.8. Atrazine was applied each year at the recommended rate of 150 mg/m^2 (Ontario Ministry of Agriculture and Food, 1993), 3 weeks after planting. Representative mean soil dispersivity ($\lambda = 15.5$ cm, see Section 3.3.2) and atrazine partition coefficients ($K_{oc} = 160$ ml/g, Jury et al., 1984) were assumed for all soil types and depths in the profiles. Atrazine dissipation rate constants were determined using Table 1 and the procedures in Section 3.2.4. A constant water table depth of 120 cm was assumed because of inadequate water table data in the NSDB. As mentioned in Section 3.0, the predicted annual mass loading of atrazine at the 90 cm depth at the end of the 10 year simulation was used as an estimate of ground water contamination.

Scaled semivariograms of soil properties (texture, BD, OC, θ_s, θ_r, K_s, α, n), precipitation (spring, summer, fall, winter) and predicted atrazine loadings (mg atrazine/m^2/yr) were calculated using the 119 locations in the map window. The data were then kriged

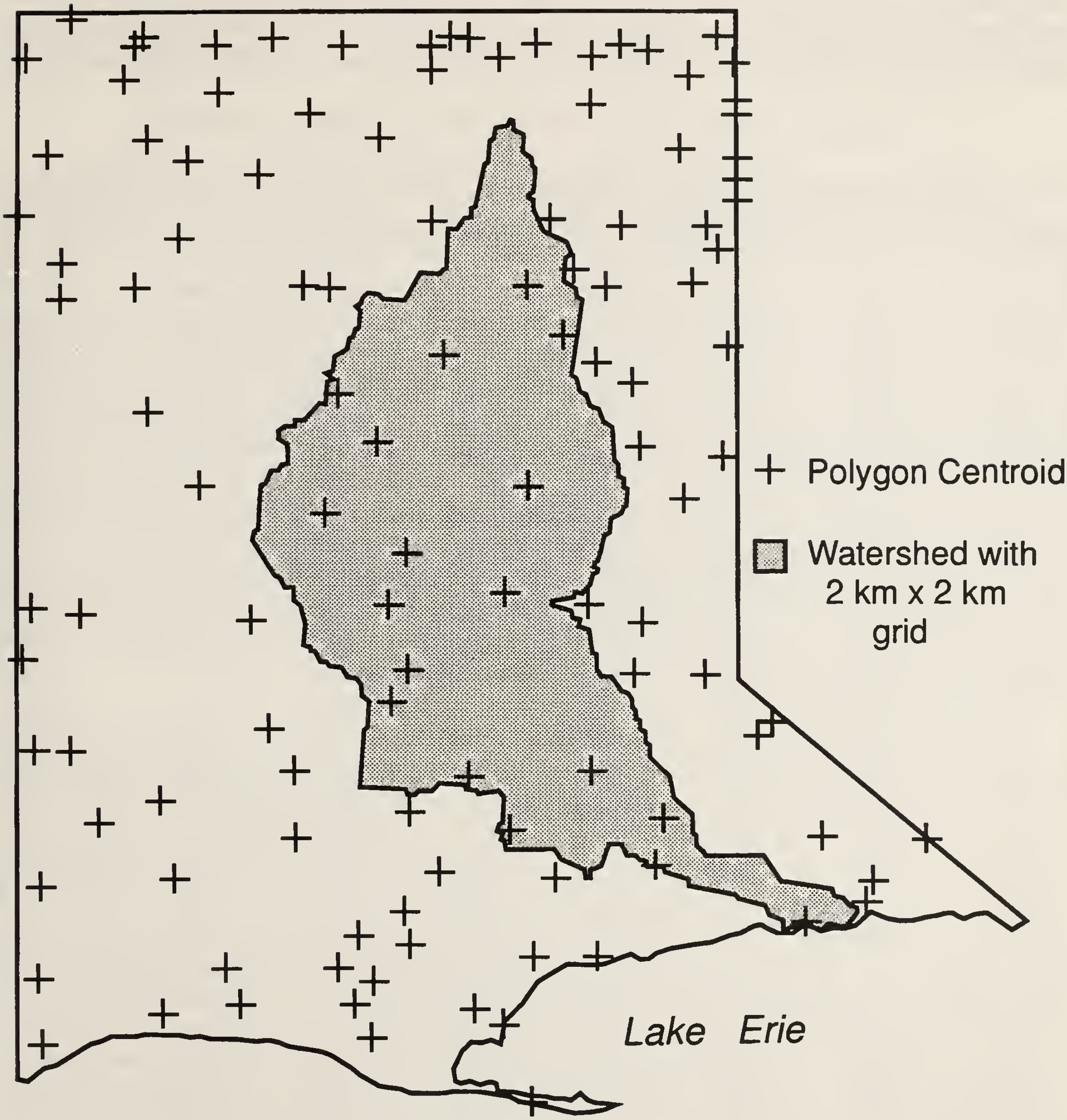

Fig. 3 Map window encompassing the Grand River watershed with locations of soil landscape polygon centroids.

(interpolated) on a 2 km x 2 km grid to produce a total of 7381 georeferenced grid points (1657 within the watershed) containing estimates of soil hydraulic properties, precipitation and predicted atrazine loading. These kriged data formed the input to ILWIS for GIS analysis.

4.2 Results and Discussion of Grand River Watershed Application

The soil texture (sand, silt, clay content), bulk density (BD), θ_s and the Van Genuchten parameters (α, n, θ_r) exhibit moderate to high variability across the watershed (CV = 7.1 to 85.1%), but only modest changes in mean value with depth (Table 9). The statistical distributions of these attributes are moderately, but not consistently, skewed (i.e. -1.732 $\leq$ skewness $\leq$ +1.017), somewhat flatter than a normal distribution (kurtosis generally less than 3), and usually have several histogram classes with no values (data not shown). This implies complex spatial distributions for these attributes within the watershed, and possibly multimodal populations as well. The soil surface texture map for the watershed (Fig. 4) supports these statistical results, showing a wide range of soil types as well as very complex spatial patterns. The soil texture semivariograms are similar for the 3 soil horizons (A horizon shown in Fig. 5), with a small nugget (20 - 40% of the variance) and a correlation distance (range) of about 60 km. The similarity between these semivariograms, coupled with the extreme and intricate lateral variability in soil texture, probably reflects the complex glacial origin of most soils in this watershed. The variability statistics (Table 9) and semivariograms for the Van Genuchten parameters (not shown) are similar to those for soil texture, which is not surprising since they were derived to a large extent from texture - based pedotransfer functions.

The OC and K_s values are moderately to extremely variable across the watershed (36.0% $\leq$ CV $\leq$ 64.0% for OC; 79.7% $\leq$ CV $\leq$ 156.7% for K_s) at any particular depth, and they decrease substantially in mean value with increasing depth (Table 9). The K_s distributions for soil layers 1 and 2 also have very large positive skewness and kurtosis values (2.537 $\leq$ skewness $\leq$ 3.217; 9.22 $\leq$ kurtosis $\leq$ 12.76), indicating that many low K_s values exist close to the mean value, many large K_s values exist far above the mean value, and relatively few K_s values fall in between. The decrease in mean OC and K_s with increasing depth is not surprising because of the usual decrease in biological activity and soil structure with depth. The extreme K_s distributions may reflect the combined effects of three dimensional changes in soil texture, structure and organic matter content throughout the watershed. The decrease in K_s with increasing depth may favour reduced atrazine contamination of ground water by decreasing the pore water velocity (q/θ), thus allowing more time for degradation, adsorption, etc. This may be largely offset, however, by an accompanying decrease in atrazine sorption with depth due to the rapid decrease in OC, and hence K_d (Eq. 10 and 11).

The atrazine loadings across the watershed (Table 9) are highly variable (CV = 136.9%) and form a statistical distribution that is positively skewed (skewness = +0.956) and flat (kurtosis = 2.30), which indicates that many high loading values exist far above the mean value. The loading distribution also appears to be multimodal, as several peaks occur in the loading histogram and many of the histogram classes contain no values (data not shown). In contrast to this extreme and complex spatial variability, is the temporal (year to year) variability which declines to zero as the predicted annual atrazine loadings become constant at any particular location after about 5-8 simulation years (example given in Fig. 6). Evidently,

Table 9. Basic statistics for the Grand River watershed application, based on the 18 landscape polygon centroids within the watershed. Thick = layer thickness; rest of parameters defined in text

Parameter	Unit	Mean	CV	Min. Val.	Max. Val.	Skewness	Kurtosis
				LAYER 1			
Thick	cm	14.4	33.3	5.0	25.0	0.204	2.60
Sand	%	32.9	68.9	11.0	75.0	0.901	2.13
Silt	%	43.8	32.9	17.0	64.0	-0.682	2.13
Clay	%	23.2	54.1	8.0	45.0	0.345	1.75
BD	g/cc	1.34	11.8	1.0	1.57	-0.433	2.11
OC	%	1.83	36.0	0.5	3.10	-0.218	2.18
α	cm^{-1}	0.020	28.5	0.0070	0.026	-1.128	2.70
n	--	1.46	7.1	1.35	1.71	0.659	2.56
θ_r	%	17.0	32.3	6.1	25.1	-0.470	1.82
θ_s	%	49.5	13.9	40.0	63.0	0.227	1.80
K_s	cm/s	5.8E-4	156.7	2.7E-5	3.8E-3	2.537	9.22
				LAYER 2			
Thick	cm	16.7	48.3	5.0	30.0	0.525	1.79
Sand	%	34.5	72.5	4.0	80.0	0.693	2.07
Silt	%	38.8	34.7	15.0	62.0	-0.361	2.16
Clay	%	26.7	65.0	5.0	61.0	0.422	1.98
BD	g/cc	1.45	9.0	1.25	1.70	0.311	1.98
OC	%	1.21	47.4	0.17	1.91	-0.306	1.63
α	cm^{-1}	0.022	31.7	0.0024	0.028	-1.732	4.81
n	--	1.47	9.1	1.36	1.73	0.885	2.15
θ_r	%	19.0	42.9	5.8	31.0	-0.406	1.71
θ_s	%	45.7	11.2	35.9	56.2	-0.116	2.50
K_s	cm/s	1.2E-4	153.4	1.2E-7	8.2E-4	3.217	12.76
				LAYER 3			
Thick	cm	88.3	11.2	70.0	100.0	-0.213	1.67
Sand	%	33.9	85.1	3.0	87.0	0.766	2.00
Silt	%	32.1	43.9	9.0	64.0	0.206	2.61
Clay	%	34.1	65.1	4.0	64.0	0.015	1.33
BD	g/cc	1.50	8.1	1.30	1.71	-0.143	2.31
OC	%	0.62	64.0	0.10	1.72	0.977	3.90
α	cm^{-1}	0.030	33.0	0.0074	0.050	0.072	3.02
n	--	1.46	9.5	1.36	1.76	1.017	2.21
θ_r	%	23.2	46.6	5.6	36.7	-0.327	1.59
θ_s	%	42.1	11.1	35.5	53.0	0.779	2.92
K_s	cm/s	6.5E-5	79.7	1.2E-7	1.6E-4	0.418	1.95
Atrazine Loading	$mg/m^2/yr$	0.50	136.9	0.0	1.88	0.956	2.30

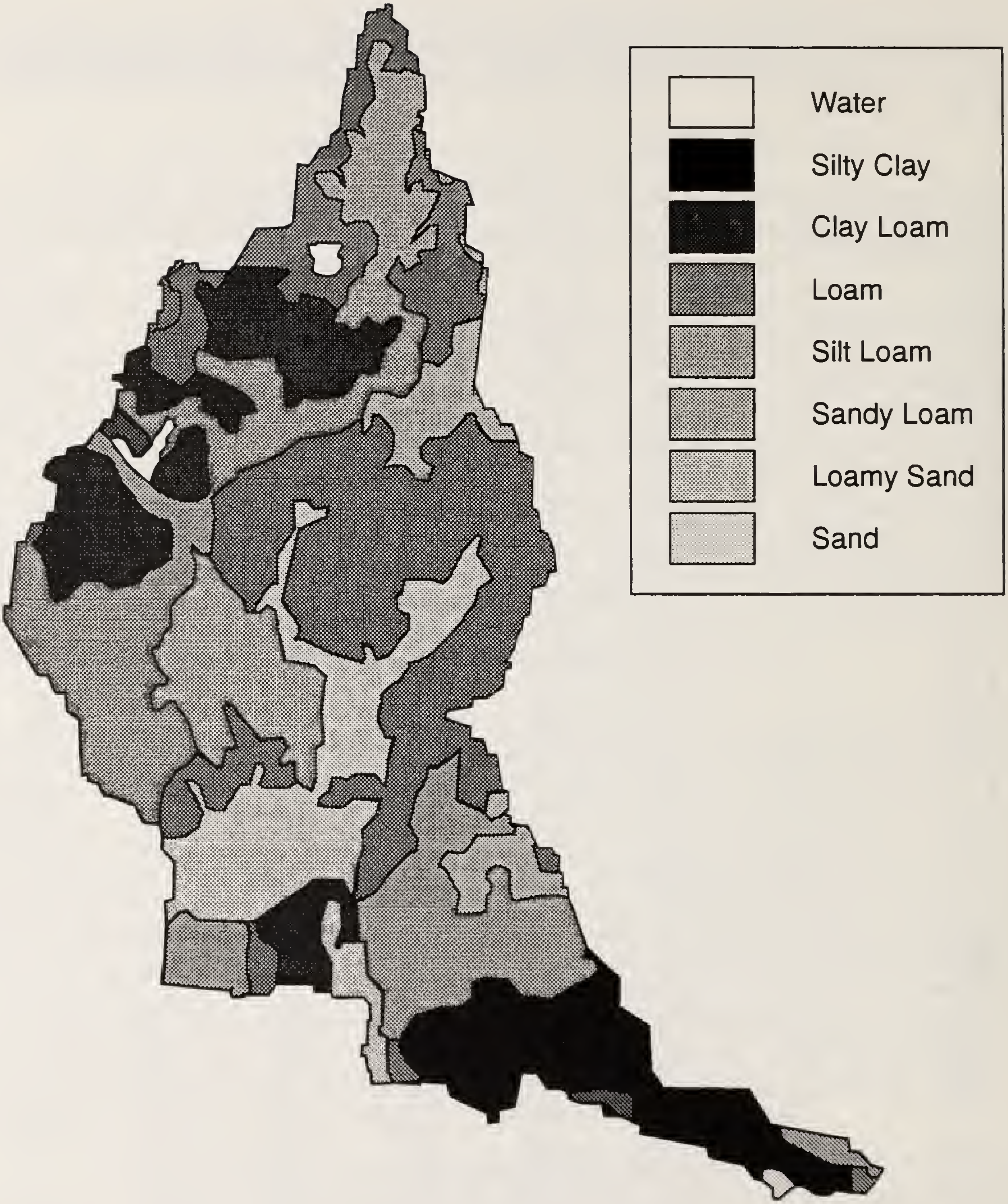

Fig. 4 Soil surface texture map of the Grand River watershed

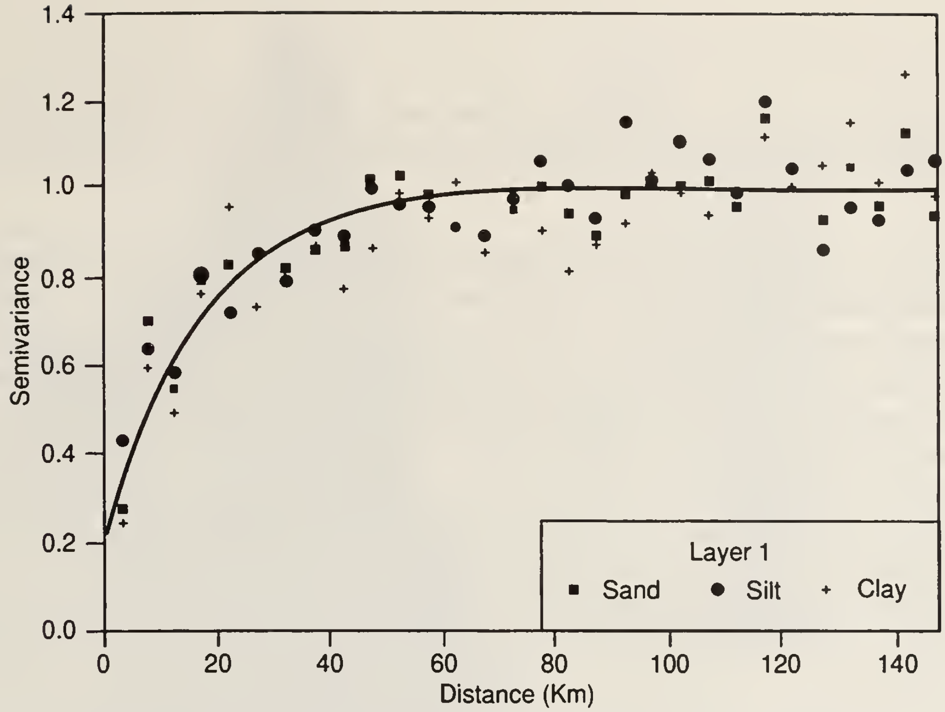

Fig. 5 Semivariogram for the A horizon soil texture in the Grand River watershed, scaled according to variance. Nugget = 0.2, range = 60 km, model = exponential with fitting parameter = 0.8.

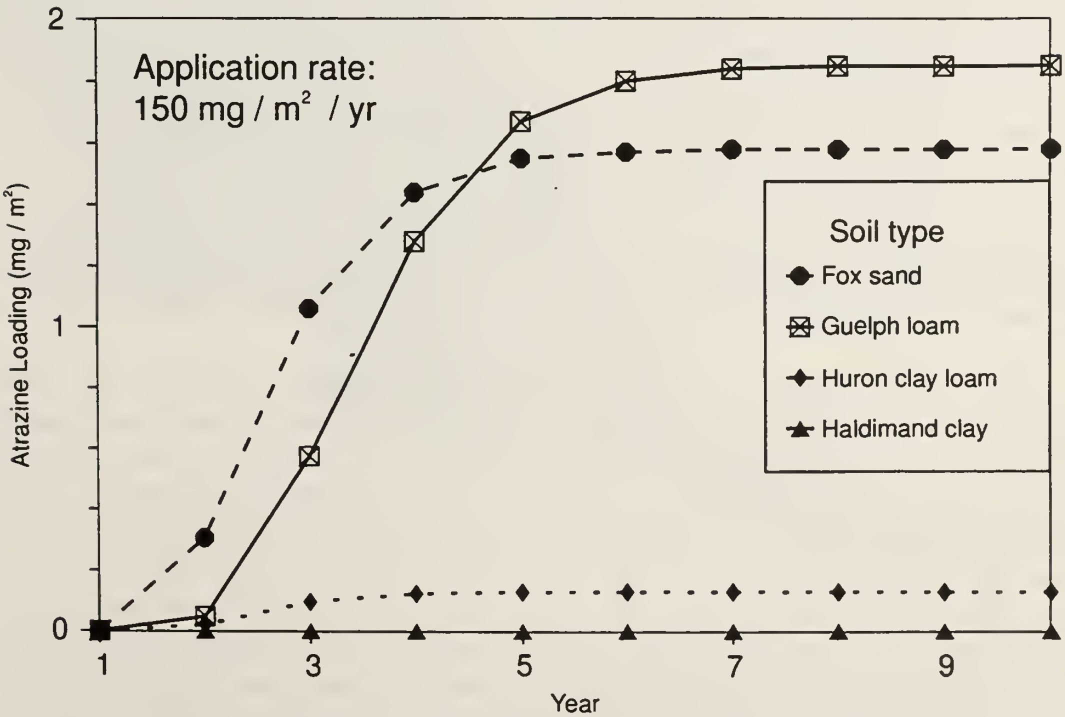

Fig. 6 Predicted annual atrazine loading (mg/m^2) versus time (yr) at 90 cm depth for Fox sand, Guelph loam, Huron clay loam and Haldimand clay.

the spatially and/or temporally distributed weather and soil attributes interact in such a way as to enhance the spatial variability, but eliminate the annual variability, of atrazine loading at the 90 cm depth.

It should also be noted from the example soils in Fig. 6 that the rate and path by which atrazine loading stabilizes, as well as the final loading value, appear to be determined by complex interactions among weather, soil properties and solute transport mechanisms. The predicted atrazine loadings all start at zero, reflecting the fact that initially atrazine-free soil profiles were assumed. For a few soils (e.g. Haldimand clay), the loadings stay at zero for the entire 10 year simulation, which implies that the atrazine applied to these soils is either degraded entirely, or sufficiently retarded in its movement, that it does not reach the 90 cm depth after 10 simulation years. It is assumed in this work that these soils will never contribute significant quantities of atrazine to the ground water. The majority of soils, however (e.g. Fox sand, Guelph loam, Huron clay loam; Fig. 6), contribute increasing quantities of atrazine with time until a plateau is reached after about 5-8 simulation years, whereupon the loadings remain constant.

The constant final atrazine loadings are seen in Fig. 6 to be somewhat soil dependent, increasing with coarser textures (e.g. final loading for Haldimand clay < Huron clay loam < Guelph loam). Exceptions are frequent, however. For example, Fig. 6 shows that the annual atrazine loading is initially greater in the Fox sand than in the Guelph loam (years 2-4), which is consistent with the much higher sand content of the Fox soil ($\approx$ 80% sand for the Fox sand; $\approx$ 35% sand for the Guelph loam). After 4-5 years, however, the trend reverses, and the Guelph loam contributes a greater final annual atrazine loading than the Fox sand (years 8-10). This can be explained in terms of interacting water and solute transport properties. The average atrazine migration velocity at field capacity (h = -10 kPa) in the top 90 cm of the soil profile [which depends on q, K(h), θ(h), BD, K_d, F, etc.] is about 3 times greater in the Fox sand than in the Guelph loam. Atrazine therefore reaches the 90 cm depth sooner in the Fox sand. However, the concentration of atrazine in solution is greater in the Guelph loam than the Fox sand, due to an approximately 22% lower average atrazine K_d for Guelph loam. The final annual atrazine loading is consequently greater (by about 14%) for the Guelph loam soil.

An ILWIS - generated map of kriged atrazine loading throughout the Grand River watershed is given in Fig. 7. It confirms, both the high variability and the complex spatial distribution of loadings indicated in Table 9. Visual comparison of this map with the surface texture map (Fig. 4) and the summer (June, July, August) precipitation map (Fig. 8) shows that the lowest atrazine loadings (0-0.1 mg/m^2/yr) tend to correlate (albeit imperfectly) with clayey soils and low summer precipitation; and the intermediate to high loadings (0.5-2.5 mg/m^2/yr) tend to correlate with sandy to loamy soils and moderate to high summer precipitation. Correlation analysis shows further that atrazine loading is significantly correlated with many of the soil and weather attributes, but the magnitudes of these correlations are low (data not shown). This supports the indication in Fig. 6 that atrazine loading tends to be determined by complex interactions among several soil, weather, crop management and solute transport factors, rather than by one or two dominant factors.

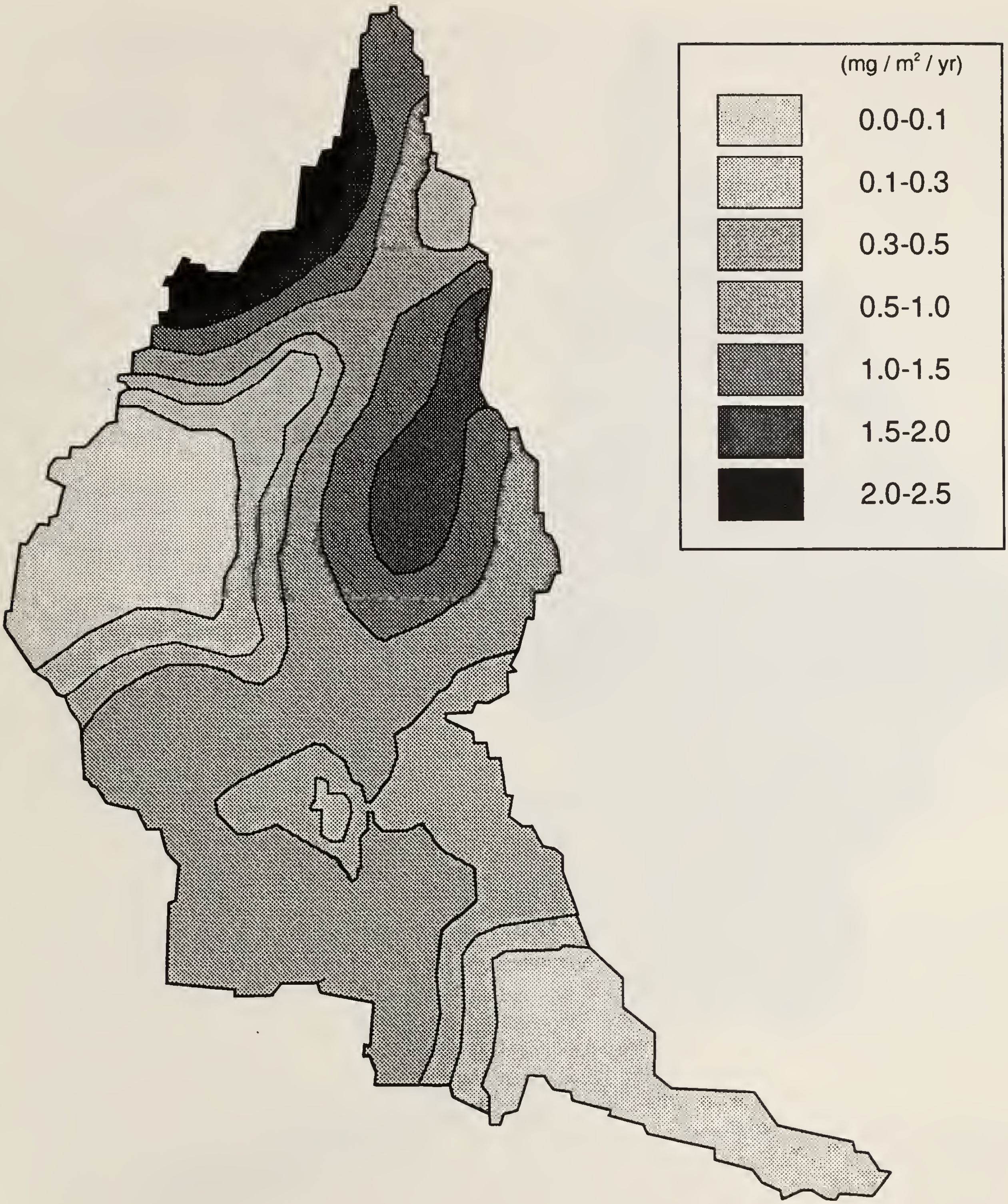

Fig. 7 Predicted annual atrazine loading ($mg/m^2/yr$) at the 90 cm depth for the Grand River watershed.

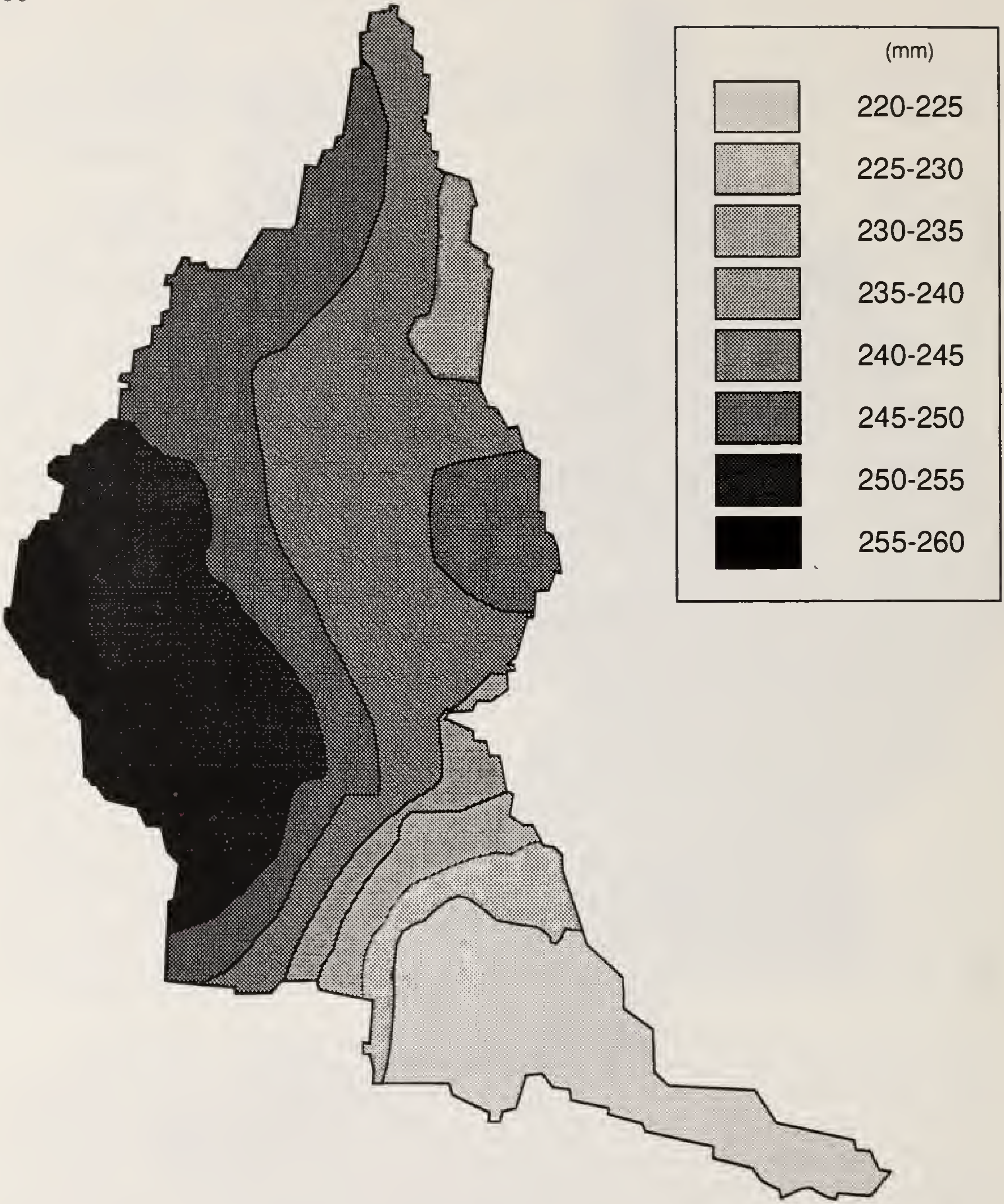

Fig. 8 Thirty year normal (1950-1980) summer precipitation (June, July, August) for the Grand River watershed.

The predicted atrazine loading to the ground water in the Grand River watershed, based on the ILWIS compilation of the 1657 kriged loading values, ranges from 0 to 2.5 mg/m^2/yr (Fig. 7) with a mean value of 0.67 mg/m^2/yr. The maximum and mean loadings given here are somewhat higher than those in Table 9 (by 33% and 34%, respectively) because the kriging interpolations take into account the LEACHP - simulated loadings at all 119 polygon centroids in the map window (Fig. 3), several of which are considerably higher than the loadings for the 18 centroids within the watershed. (The maximum LEACHP - simulated loading in the map window was 8.29 mg/m^2/yr.) Both the mean and maximum predicted atrazine loadings for the watershed (i.e. 0.67 mg/m^2/yr and 2.50 mg/m^2/yr, respectively) are quite low and less than 2% of the application rate of 150 mg/m^2/yr, suggesting that atrazine sorption and dissipation are extensive within the soil profile. The total predicted atrazine loading to the ground water (90 cm depth) for the watershed is estimated via ILWIS to be 4500 kg/yr, which is only 0.44% of the total specified surface application of 1.02 million kg/yr.

The concentration of atrazine in the soil water at the 90 cm depth was also predicted to be generally low throughout the watershed. The former 60 ppb Canadian drinking water guideline for atrazine (Canadian Water Quality Guidelines, 1989) was never exceeded at the 90 cm depth during the 10 year simulation. The 3 ppb USEPA standard (USEPA, 1978) was exceeded, however, on or before the 10th simulation year in about 27% of the watershed area (Fig. 9). The areas where this occurs also have predicted annual atrazine loadings that fall within approximately the top half of the loading range (0.5-2.5 mg/m^2/yr, Fig. 7), which suggests that atrazine concentration and loading rates are related (as one might expect), but this relationship is by no means direct or simple. It also suggests that the areas where the 3 ppb concentration is exceeded (Fig. 9) represent regions of potentially significant low-level non-point source contamination of ground water by the downward percolation of atrazine through the soil profile. Figure 9 may thus demark regions in the watershed where more detailed investigation and monitoring are warranted.

4.3 Assessment of Grand River Watershed Predictions

Comprehensive assessment of the accuracy and validity of the predictions is not possible due to a lack of appropriate field measurements. There are, however, sufficient field data available to get a general indication of the plausibility of the predictions; as well as an indication of the sensitivity of the predictions to the quality and quantity of input data.

4.3.1 Comparison to Ground Water Survey Data

A survey of rural ground water quality in Southern Ontario was recently completed by Agriculture and Agri-Food Canada under the Federal - Provincial Environmental Sustainability Initiative (Agriculture Canada, 1992). Between October 1991 and March 1992, approximately 900 farm water supply wells across Southern Ontario and 144 specially designed multilevel water monitoring wells were sampled for nitrate-nitrogen, total and faecal coliform bacteria, petroleum derivatives, and five common herbicides including atrazine plus d-ethyl atrazine, alachlor, metolachlor, metribuzin and cyanazine. The farm wells were selected in areas of intensive agriculture on the most common soil types, and on farms using the most common agricultural practices. Within these areas, the distribution of selected wells was kept as random and uniform as possible. Approximately 100 of the farm wells fell within the Grand River

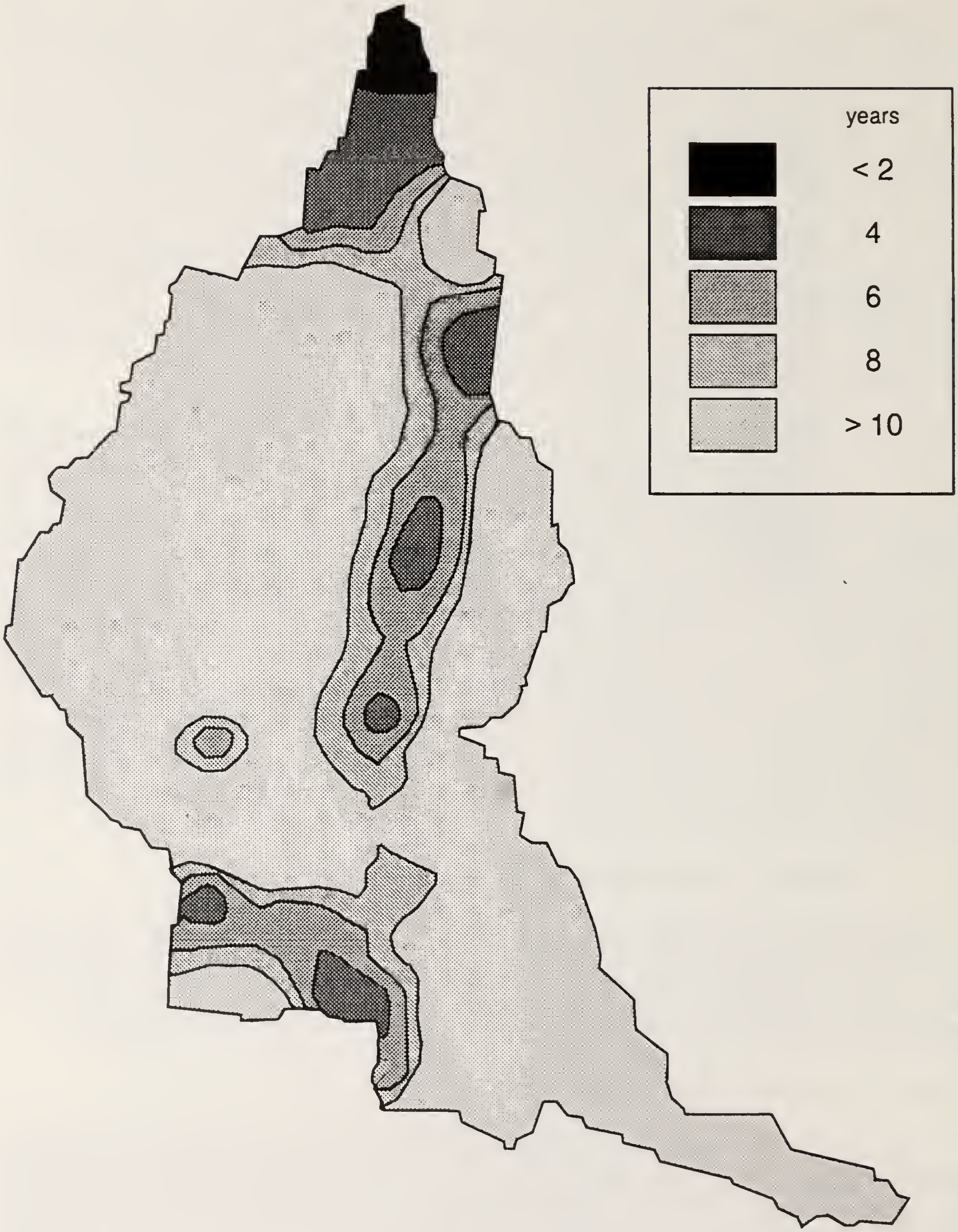

Fig. 9 Predicted time (yrs) for atrazine to reach 3 ppb at the 90 cm depth in the Grand River watershed.

watershed. The multilevel monitoring wells were installed adjacent to sampled farm wells in areas where non-point contamination of ground water was anticipated to be most likely, i.e. in areas of intensive agriculture on permeable sandy soils. Approximately 11 of the monitoring wells fell within the Grand River watershed.

The rate of detection of atrazine and d-ethyl atrazine in the farm wells was 6.7% and 4%, respectively, while that for the monitoring wells was 4% for atrazine plus d-ethyl atrazine. For the farm wells, the maximum, mean and median detected concentrations of atrazine and d-ethyl atrazine were, respectively, 18 ppb (atrazine) and 4.4 ppb (d-ethyl atrazine), 1.1 ppb (atrazine) and 0.5 ppb (d-ethyl atrazine), and 0.4 ppb (atrazine) and 0.35 ppb (d-ethyl atrazine). The maximum detected concentrations of atrazine and d-ethyl atrazine in the monitoring wells was 3.1 ppb and 1.9 ppb, respectively. The former Canadian drinking water guideline for atrazine (60 ppb) was never exceeded in any of the wells; however, the USEPA standard (3 ppb) was exceeded about 1% of the time in the farm wells, and "many" times in the monitoring wells. The monitoring wells further indicated that herbicide contamination occurred primarily in the shallow ground water. Detection of atrazine (or any of the other herbicides) was highly scattered spatially, and did not appear to be strongly related to land use (e.g. crop rotation, tillage practices, etc.) or soil type.

These results are very consistent with the predictions for the Grand River watershed, and thereby lend credibility to the methodology. Both studies indicate that non-point atrazine contamination of ground water is infrequent and low level. Both studies found that the former Canadian drinking water guideline is never exceeded, but the USEPA standard is exceeded occasionally. Finally, both studies conclude that atrazine contamination of ground water is highly variable spatially and not strongly related to soil type, suggesting that the contamination is controlled by many interacting factors.

4.3.2 Effect of Scale and Missing Data

The effects of map scale and missing soil hydraulic properties on the predicted atrazine loadings were briefly assessed using a subregion of the Grand River watershed where the soil data were more complete and available at a much more detailed scale. The subregion consisted of an approximately 7400 ha section of Haldimand-Norfolk county that fell within the watershed (Fig. 10). The subregion contained 359 soil polygon centroids at 1:45,000 scale, and 15 different soil types. For 13 of the 15 soils, values of sand, silt and clay content, OC, BD, K_s, θ_s and 2-3 points on the soil water characteristic were available for 4 soil layers extending to 100 cm depth. Consequently, much less estimation of data via pedotransfer functions was required, and distances between polygon centroids were much smaller, than for the original 1:1 million scale data. The subregion was kriged on a 200 m x 200 m grid to produce 1781 georeferenced grid points of soil, weather and atrazine loading data.

The 1:45,000 scale data yielded a mean atrazine loading of 0.035 mg/m^2/yr, a range of 0-0.781 mg/m^2/yr and a CV of 323%. The original 1:1 million scale data within the subregion gave a mean loading of 0.041 mg/m^2/yr, a range of 0.037-0.044 mg/m^2/yr and a CV of 4.1%. The closeness of the two mean loadings (within 17%) suggests that the methodology can still give reasonable overall predictions when map scales are coarse and substantial amounts of data must be estimated. The much smaller range and CV of the 1:1 million scale results indicate, however, that considerable detail is lost when coarse scales are used.

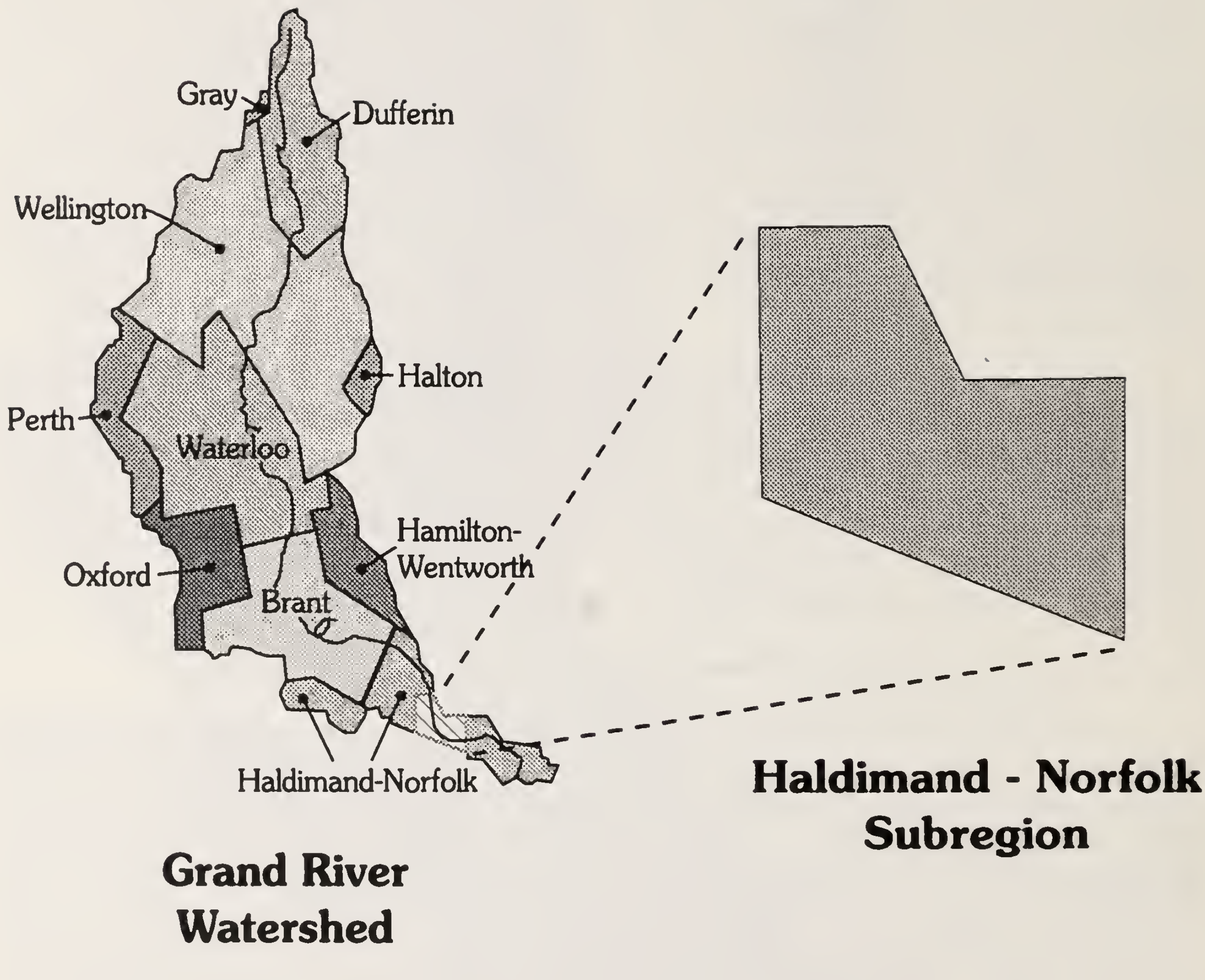

Fig. 10 Location of the Haldimand-Norfolk subregion in the Grand River watershed.

5.0 SUMMARY AND CONCLUSIONS

5.1 Grand River Watershed Study

i) Predicted annual loadings and pore water concentrations of atrazine at the 90 cm depth were low. The annual mass loading ranged from 0 - 2.5 mg/m^2/yr with a mean value of 0.67 mg/m^2/yr. These values are less than 2% of the specified annual atrazine application rate of 150 mg/m^2/yr. The total predicted annual mass loading of atrazine for the watershed (at 90 cm depth) was about 4500 kg/yr, which is only 0.44% of the total specified annual surface application of 1.02 million kg/yr. The predicted atrazine concentration in the pore water never exceeded the former Canadian drinking water guideline of 60 ppb during the 10 year simulation.

ii) The spatial variability in predicted annual mass loadings of atrazine was extreme and complex within the watershed, as indicated by a high CV (CV = 137%), and a frequency distribution that was skewed (skewness = 0.956), flat (kurtosis = 2.30) and multimodal (Table 9). The temporal (year to year) variability, on the other hand, declined to zero as the predicted annual loadings became constant at any particular location in the watershed after about 5-8 simulation years. Spatially and/or temporally distributed weather and soil attributes apparently interact to enhance the spatial variability, but eliminate the annual variability, of atrazine loading at the 90 cm depth.

iii) The distribution in predicted atrazine loadings across the watershed (Fig. 7) were significantly correlated with many of the soil and weather attributes, but the correlation coefficients were generally low in magnitude. This suggests that atrazine loading on a watershed basis is determined by the interaction of several soil, weather, crop management and solute transport factors, rather than by one or two dominant factors.

iv) Predicted atrazine solution phase concentrations at the 90 cm depth exceeded the 3 ppb USEPA drinking water standard in about 27% of the watershed area (Fig. 9). The areas where this occurred also have predicted annual atrazine loadings (at 90 cm depth) in approximately the top half of the loading range (0.5-2.5 mg/m^2/yr). These areas may therefore represent regions of potentially significant low-level non-point source contamination of ground water by the downward percolation of atrazine through the soil profile.

v) The predicted non-point atrazine contamination of ground water (i.e. at the 90 cm depth) compared favourably with recent ground water survey results (Agriculture Canada, 1992). In both cases, the contamination was highly variable but low-level, the former Canadian drinking water guideline (60 ppb) was never exceeded, the USEPA drinking water standard (3 ppb) was exceeded occasionally, and the contamination was not strongly related to soil type.

5.2 Overall Performance of Methodology

Although the LEACHM-Kriging-ILWIS methodology still requires further development and testing, the preliminary results are very encouraging. The modified LEACHW and LEACHP models appear generally capable of simulating both laboratory- and field- measured transport of water, chloride and atrazine with acceptable accuracy (Section 3.3). The input data required for the models was extractable, or derivable (via pedotransfer functions), from information archived in the NSDB and AWDB databases. The pedotransfer function, kriging and ILWIS manipulations were effective and sufficiently robust to accommodate coarse map scales and fairly high percentages of missing data. Application of the methodology to predict, characterize and quantify atrazine migration through the soil profiles of the Grand River watershed produced plausible results that were in general agreement with the limited amount of field data available. It is consequently felt that this methodology will ultimately prove very useful in the development of agricultural practices and guidelines that maintain agrochemical inputs to the ground water at acceptable and sustainable levels.

6.0 REQUIREMENTS FOR FURTHER DEVELOPMENT AND TESTING

Several important factors were not considered in the Grand River watershed application, including land use patterns, crop rotations, annual variation in water table depth, topography, and the simultaneous transport of several agrochemicals and metabolites. These factors are likely to be important in the Great Lakes Basin, and should be taken into account. Most watersheds, especially those in the Great Lakes Basin, have substantial non-agricultural areas (e.g. ≈ 25% of the Grand River watershed is used for non-agricultural activities) and this will obviously affect the amounts and distributions of agrochemical inputs to the ground water. Land use and crop rotations not only affect water movement and water content distributions in the soil profile (through crop water use), but also determine the type, amount, timing and frequency of application of fertilizers and pesticides. In humid regions, the depth to the water table can vary from virtually zero at spring thaw to 3 m or more in late summer. Thus, the distance agrochemicals must travel to enter the ground water varies substantially throughout the year. Run-off and run-on of water, solutes and sediment due to variations in topography have a strong impact on the amount and spatial distribution of water and agrochemical entry into the soil. Any particular agricultural practice (e.g. continuous corn cropping) is likely to contribute a variety of agrochemicals and metabolites to the ground water (e.g. fertilizer nitrate, atrazine plus its main metabolite d-ethyl atrazine, metolachlor, etc.), rather than a single chemical. Except for topography, the methodology in its present form can account for all of the above factors through adjustments and additions to the various input data files. A run-off - run-on based routine that accounts for topography has not been developed.

The representation of "bypass flow" of solute in LEACHP (Section 3.2.6) is simplistic and may be inadequate in soils where extensive bypass flow occurs (e.g. Table 8, Woodslee field site). Improved, soil property based, representations of bypass flow should be developed and added to LEACHP so that early arrival of agrochemicals to the water table can be detected.

The laboratory column study (Section 3.3.1) suggests that the current form of LEACHP may overestimate the concentration of atrazine in solution, possibly due to an underestimate of effective atrazine dissipation rates. Further investigations of pesticide - soil interactions should therefore be conducted so that more accurate representations of pesticide transformation and dissipation can be incorporated into LEACHP.

Only a very cursory assessment of the accuracy and uncertainty of the predictions has thus far been attempted (Section 4.3). Major sources of uncertainty that require further investigation include:

i) NSDB database.

As mentioned in Section 4.1, many of the required soil data for the Grand River watershed were missing from the NSDB. In addition, many of the values that are present (e.g. K_s) are estimates made by soil survey personnel, rather than actual measurements. Consequently, the use of the NSDB database may be limited in some watersheds and for certain applications.

ii) Accuracy and precision of the pedotransfer functions.

The accuracy and precision of pedotransfer functions should be clearly established before they are used. For example, the largely texture - OC based relationships used in the Grand River watershed application do not account for soil structure. As soil structure is known to have a strong impact on soil hydraulic properties, the accuracy and/or precision of some of these functions may be rather low.

iii) Use of only the dominant soil type in the landscape polygons.

Only the dominant soil in the landscape polygons was used for the LEACHW and LEACHP simulations because the distribution of soil types within the polygons was not available. However, the subdominant soil, which can occupy up to 30% of the polygon area, may strongly influence, or even control, water and agrochemical movement. Consequently, procedures should be developed to account for both the dominant and subdominant soils when determining the solute transport characteristics of a polygon.

iv) Effect of map scale.

The 1:1 million map scale was used for the Grand River watershed predictions because that scale is compatible with the majority of the NSDB data. This scale may not be appropriate for certain applications, however, because it is too coarse to yield the required detail in soil properties and chemical transport behaviour. Criteria should be developed for matching the appropriate map scale to the intended use of the predictions.

Obtaining the required input data, and validation of the predictions, are important and difficult aspects of applying the LEACHM-Kriging-ILWIS methodology. Appropriate, high quality, field measured input data (e.g. soil hydraulic properties, water table depths, dispersivities, partition coefficients, dissipation rate constants) are very scarce; and appropriate data for ground truthing the predictions (e.g. soil profile water contents, agrochemical concentration profiles) are even more scarce. A catalogue of all such data should be compiled so that this and similar methodologies can be calibrated, tested and assessed as much as possible before they are used as management, regulatory or policy making tools.

7.0 ACKNOWLEDGEMENTS

We gratefully acknowledge the capable assistance of W. Smith and Dr. E. Topp in the laboratory column studies, Dr. M. Hares in the modification of LEACHM, and W. Greidanus in the GIS analyses. Special thanks to Drs. J.L. Hutson and R.J. Wagenet, Cornell University, for generously providing a copy of the LEACHM model and advice on its application. The field investigations were conducted by Environmental Soil Services, Guelph, Ontario under contract to Agriculture and Agri-Food Canada. The skilful and timely production of the figures for this report by the Cartographic Design and Reproduction Unit, CLBRR, Agriculture Canada is greatly appreciated.

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