PREDICTING PESTICIDE MIGRATION THROUGH SOILS OF THE GREAT LAKES BASIN

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INTRODUCTION

Pesticide contamination of ground water has traditionally been considered to be due primarily to spills, and to improper storage, disposal and application practices. There is increasing evidence, however, that 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). Although this type of contamination is usually well below Canadian drinking water guidelines, there are growing public concerns over potential health hazards related to long-term exposure to low levels of pesticides (Agriculture Canada, 1990). Consequently, there is a need to determine how important and widespread low-level non-point source pesticide contamination of ground water might be; what the controlling soil, land use and weather factors are; and which agricultural practices are required to mitigate and control this type of pollution at acceptable and sustainable 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 the pesticide movement in space and time with acceptable accuracy. Accordingly, the objectives of this study are: (i) to develop a methodology for predicting, characterizing and quantifying pesticide migration rates through the soil profile, and (ii) to conduct a test and evaluation of the methodology by applying it to atrazine migration through the soil profiles of the Grand River watershed in Southern Ontario, Canada.

The herbicide atrazine was chosen for study because it is the most commonly used pesticide for corn production in Southern Ontario; and because atrazine residues have been detected in the ground waters of many agricultural watersheds in the Great Lakes basin, particularly where there is some combination of high atrazine usage, intensive agriculture, high precipitation, coarse textured and other highly permeable soils, high water tables, and sloping topography (Millette and Torreiter, 1992). The watershed scale was chosen (rather than the field scale, for example) because it is a natural landscape unit; because the most readily available and complete soil and weather databases are applicable on the watershed scale; and because the watershed provides a convenient basis for estimating agrochemical loadings to the Great Lakes. The Grand River watershed (Fig. 1) was chosen as a test case because it is one of the largest in Southern Ontario (≈ 680,000 ha); it contains a large range of soil textures with a complexity of distribution that is typical for the region; the primary land use is field crop production using standard agricultural practices and "normal" rates of pesticide usage (Shelton et al., 1988); and it empties directly into the Great Lakes (Lake Erie). These features make this watershed ideal for testing and demonstrating the methodology. In addition, the results obtained for the Grand River watershed should be "characteristic" of the entire Southern Ontario region.

Ground water contamination in this study is defined as non-zero values of predicted annual mass loading of pesticide to the 90 cm depth in the soil. Non-zero mass loading was used, rather than pore water concentrations above a specified threshold, because of the need to estimate the quantities and distributions of all pesticide additions to ground water, not just the "high level" additions. The 90 cm depth was selected because it reflects the mean tile drain depth in Southern Ontario, as well as the primary rooting depth for most field crops. It was assumed that if a pesticde reached this depth, it would not be intercepted by tiles and roots, but continue to percolate downward and eventually enter the ground water.

METHODOLOGY

The methodology consists essentially of a water/solute transport model in combination with pedotransfer functions, geostatistical analyses and a geographic information system (GIS). It makes use of archived soil and weather data, and it accounts for many factors and processes which control pesticde migration. The main components of the methodology are outlined briefly below.

i) Water/Solute Transport Model

The transport model is an in-house modification of the well established and tested modelling package, LEACHM (Leaching Estimation And CHemistry Model, Hutson and Wagenet, 1989). The model 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 sorption, degradation, advection and dispersion; precipitation and evaporation; soil heat flow; and changes in water table elevation. LEACHM is a mechanistic model, which uses Richards' equation to predict water flow and the convection-dispersion equation to predict solute fluxes. Its 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. Only the LEACHW and LEACHP submodels are used in this study.

The LEACHW and LEACHP submodels required several modifications before they could be applied effectively on a watershed basis. The most important changes are outlined in Appendix A, with a full description given in Reynolds et al. (1994). Both submodels simulate water and solute movement in the vertical direction only, i.e. they are one-dimensional. Extension of the models to an areal basis required running them at a number of georeferenced locations distributed throughout the area, and then applying interpolation procedures that accounted 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.

ii) Soil and Weather Data

The National Soil Data Base (NSDB) was used to obtain the required soil input data for applying the LEACHW and LEACHP models to the Grand River watershed. The data were 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 a 3 million ha "map window" encompassing the Grand River watershed (Fig. 2). The map window was used (rather than the watershed alone) to increase the amount of data, 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 soil data for each landscape polygon were extracted for 3 soil layers (approximately A, B and C horizons), and included the upper and lower depths of the layer; sand, silt and clay contents; bulk density (BD); organic carbon content (OC); saturated hydraulic conductivity (K_s); 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. 2).

The required climate data for the Grand River watershed application were extracted from the Archived Weather Data Base (AWDB), and included the monthly 30 year normals (1950-1980) of maximum and minimum air temperature, precipitation, and days with precipitation. These data were assigned to each of the landscape polygon centroids within the map window, using the values from the nearest weather station. The monthly normals were converted to daily data (required by the models) using the procedures described by Brooks (1943) and Van Diepen et al. (1988). Potential evapotranspiration (also required by the models) was calculated according to Baier and Robertson (1965).

iii) Pedotransfer Functions

Data that were missing from the NSDB for the Grand River watershed application 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 content, for which there were no missing values in the NSDB. Bulk density was estimated using the Gupta and Larson (1979) model. The soil water characteristic, $\theta(h)$, was estimated using the model of McBride and Macintosh (1984), and then least squares fitted to the Van Genuchten (1980) function. Saturated hydraulic conductivity, K_s, was estimated using the model of Jabro (1992). The unsaturated hydraulic conductivity, $K(h)$, was estimated (Van Genuchten, 1980) using the $\theta(h)$ and K_s results. The estimated data, as with the available data, were all assigned to the appropriate georeferenced landscape polygon centroids.

iv) Model Simulations and Output

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 Appendix A. 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 values for the soil dispersivity, λ, and the atrazine partition coefficient, K_{oc}, were assumed for all soil types and depths in the soil profile (i.e. $\lambda = 15.5$ cm, obtained from the field measured chloride breakthrough curves; $K_{oc} = 160$ ml/g, Jury et al., 1984). Atrazine dissipation rate constants were determined using Table A1 (Appendix A). A constant water table depth of 120 cm was assumed because of inadequate water table data in the NSDB. As mentioned above, 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.

v) Geostatistical Analyses

A geostatistical technique known as kriging was 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 values or results at georeferenced locations. The weighting factors are determined from a semivariogram, which itself 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).

Kriging was used to convert the 119 irregularly spaced and highly variable point values of soil properties (texture, BD, OC, K_s), precipitation (spring, summer, fall, winter) and predicted atrazine loadings (mg atrazine/m^2/yr) into 7381 interpolated values extending throughout the map window on a 2 km x 2 km grid. These kriged interpolations provide the required extension from a point basis to an areal basis, but still retain the spatial variability characteristics of the original data sets. The kriged data also provide the spatial detail necessary for effective use of the GIS.

vi) Geographic Information System (GIS)

The main function of the GIS is to produce, quantify and overlay maps of the kriged soil, weather and agrochemical loading data. This allows estimation of the importance and distributions of agrochemical contamination of ground water, as well as determination of the soil, weather and land management factors that control the contamination. 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.

RESULTS AND DISCUSSION

i) Testing and Calibration of LEACHW and LEACHP

Laboratory and field studies were used to test and calibrate the LEACHW and LEACHP models. The laboratory studies tested the ability of the models to predict water content and pressure head profiles and chloride and atrazine breakthrough curves measured in columns of intact (undisturbed) soil. The field studies tested the ability of the models to predict in-situ measured water content profiles over an entire growing season, as well as the ability to predict in-situ measured chloride breakthrough curves under steady field-saturated and near field-saturated flow conditions. The field studies also provided in-situ measurements of soil hydraulic properties and dispersivity, which are required for field-calibration of the models. A complete description of the model testing and evaluation can be found in Reynolds et al. (1994).

Overall, the models were found to generally provide excellent predictions of water content and pressure head profiles (Average Relative Error, ARE, usually within ±20%, see Reynolds et al., 1994, for definition of ARE), good predictions of chloride transport behaviour (ARE usually within ±40 %), and adequate predictions of atrazine transport (ARE usually within ±200 %). In addition, all of the predictions satisfied 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 felt that the modified LEACHW and LEACHP models can be applied effectively within a pedotransfer function - geostatistics - GIS framework.

ii) The Grand River Watershed Application

Soil texture (sand, silt, clay content) and bulk density exhibited moderate to high variability across the watershed (CV = 8.1 to 85.1 %), but only modest changes with depth (Table 1). The high lateral variability in soil texture is also reflected in the surface texture map for the watershed (Fig. 3), which shows a wide range in soil types (sand to silty clay), as well as very complex spatial distributions. The soil texture semivariograms for the 3 soil horizons (not shown) are similar, with a small nugget (20 - 40 % of the variance) and a correlation distance (range) of about 60 km. The similarity between the semivariograms, coupled with the extreme and intricate lateral variability in soil texture, probably reflects the complex glacial origin of most soils in the watershed.

Table 1. 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.

Param.	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
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
K_s	cm/s	$1.2E^{-4}$	153.4	$1.2E^{-7}$	$8.2E^{-4}$	3.217	12.76
LAYER 2							
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
K_s	cm/s	$6.5E^{-5}$	79.7	$1.2E^{-7}$	$1.6E^{-4}$	0.418	1.95
Atrazine Load	$mg/m^2/yr$	0.50	136.9	0.0	1.88	0.956	2.30

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 also decrease substantially in mean value with increasing depth (Table 1). 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 simulated atrazine loadings across the watershed (Table 1) 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. 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. 4). The constant predicted annual atrazine loadings appear to be a consequence of reusing the same 30 year normal weather for each "simulation" year.

It should also be noted from the example soils in Fig. 4 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 expected 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. 4), contribute increasing quantities of atrazine with time until a plateau is reached after about 5-8 simulation years. These constant final loadings are somewhat soil dependent, increasing with coarser textures; but exceptions are frequent. For example, Fig. 4 shows that the annual atrazine loading is initially greater in the Fox sand (year 2 → 4) than in the Guelph loam, which is consistent with the much higher sand content of the Fox soil (≈ 80 % sand in Fox sand; ≈ 35 % sand in Guelph loam). After 5 years, however, the trend reverses, and the Guelph loam contributes a greater final annual atrazine loading (by about 14 %)than the Fox sand.

An ILWIS - generated map of kriged atrazine loading throughout the Grand River watershed is given in Fig. 5. It confirms, both the high variability and the complex spatial distribution of loadings indicated in Table 1. Visual comparison of this map with the surface texture map (Fig. 3) and the summer (June, July, August) precipitation map (Fig. 6) shows that the lowest atrazine loadings (0 - 0.1 $mg/m^2/yr$) tend to correlate 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 soil and weather attributes, but the magnitudes of these correlations are low. This supports the indication in Fig. 4 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.

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. 5) 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 1, because the kriging interpolations take into account the LEACHP - simulated loadings at all 119 polygon centroids in the map window (Fig. 2), 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 relative to 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 concentrations of atrazine in the soil water at the 90 cm depth are 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, 1987) was exceeded, however, on or before the 10th simulation year in about 27 % of the watershed area (Fig. 7). The areas where this occurs also have predicted annual atrazine loadings that fall within the top half of the range (0.5 - 2.5 $mg/m^2/yr$, Fig. 5), which suggests that atrazine concentration and loading rates are related, but this relationship is by no means direct or simple. It also suggests that the areas where the 3 ppb concentration is exceeded (Fig. 7) represent regions of potentially significant low-level non-point source contamination of ground water by the downward migration of atrazine through the soil.

ASSESSMENT OF THE GRAND RIVER WATERSHED PREDICTIONS

A 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.

i) Comparison to Ground Water Survey Data

The Grand River watershed predictions are consistent with the results of a recent survey of ground water quality in Southern Ontario (Agriculture Canada, 1992). The survey, which included over 1000 farm water supply and monitoring wells (approximately 110 of these wells fell within the Grand River watershed), found that non-point atrazine contamination of ground water was infrequent, highly variable spatially, and generally low-level. Atrazine and d-ethyl atrazine were detected in < 7 % of the wells, with maximum concentrations of ≤ 18 ppb and mean concentrations ≤ 1.1 ppb. The survey also found that the former Canadian drinking water guideline for atrazine (60 ppb) was never exceeded; that the USEPA drinking water standard (3 ppb) was exceeded only occasionally (≈ 1 % of the atrazine detections were above the 3 ppb concentration); and that the contamination was not strongly related to soil type or land use, implying control by many interacting soil, weather and land use factors rather than one or two dominant factors (see Reynolds et al., 1994 for further detail). This lends credibility to the LEACHM-Kriging-GIS methodology, notwithstanding that more extensive comparisons with field data are required before definite conclusions can be drawn.

ii) 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 consists of an approximately 7400 ha section of Haldimand-Norfolk county falling within the watershed. 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 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.

CONCLUSIONS

Although the LEACHM - pedotransfer function - geostatistics - GIS methodology is still under development, the results of this study are encouraging. The required input data 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 small map scales and a high percentage of missing data. Predictions of potential ground water contamination by atrazine for the Grand River watershed are plausible and compare favourably with recent ground water survey results. It is consequently felt that this methodology will prove very useful in the development of agricultural practices and guidelines that maintain agrochemical inputs to the groundwater at acceptable and sustainable levels.

NEW TECHNOLOGIES AND BENEFITS

A new methodology, which consists of solute transport modelling in combination with geostatistical analyses and a geographic information system, was developed for predicting, characterizing and quantifying non-point source contamination of ground water due to the migration of agrochemicals through the soil profile. The methodology can be used to develop inventories of "pollution potential" and to develop agricultural land use practices and guidelines that mitigate and control agrochemical inputs to the ground water at acceptable and sustainable levels. It can also be used to predict the impact of changes in land management practices and land use, using so-called "what if" scenarios. The methodology can be applied to a range of agrochemicals, and to virtually any landscape unit (e.g. plot, field, watershed, region), providing the necessary data are also available at that scale.

IMPLICATIONS FOR THE GREAT LAKES ECOSYSTEM

Predictions were made of atrazine migration through the soil profiles of a "representative" agricultural watershed within the Great Lakes Basin (the Grand River watershed, Southern Ontario). The results indicate that potential non-point atrazine contamination of ground water is highly variable spatially, generally low level, and determined by complex interactions among several soil, weather, crop and solute transport factors. Continuous corn cropping with annual applications of atrazine is predicted to produce a low, but steady, loading of atrazine to the ground water, and hence to the Great Lakes.

TECHNOLOGY TRANSFER POTENTIAL

Although the solute transport modelling-geostatistics-geographic information system methodology still requires further development and testing, the preliminary results indicate that it should be useful for: pesticide licensing and usage guidelines; land use planning and management; and the development of agricultural practices that control agrochemical pollution of ground water. Consequently, potential users of the methodology include scientists, planners, managers and policy makers.

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 (Eq. 5-7, Appendix A) is simplistic and may be inadequate in soils where extensive bypass flow occurs (e.g. see Table 8, Woodslee field site, Reynolds et al., 1994). 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 studies suggest that the current form of LEACHP may overestimate the concentration of atrazine in solution, possibly due to an underestimate of effective atrazine dissipation rates (see Reynolds et al., 1994 for details). 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. Major sources of uncertainty that require further investigation include:

i) NSDB database.

As mentioned above, 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 which is known to have a strong impact on soil hydraulic properties. Consequently, the accuracy and/or precision of some of these functions may be rather low.

iii) Use of 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. 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, 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 water content profiles, 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 before they are used as management, regulatory or policy making tools.

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APPENDIX A

The LEACHW and LEACHP submodels required several modifications before they could be applied effectively within the pedotransfer function - geostatistics - GIS framework. The most important changes are outlined below; a full description is given in Reynolds et al. (1994).

i) Soil Hydraulic Properties

The soil hydraulic property functions used in LEACHW poorly reflect the often observed rapid decrease in water content and hydraulic conductivity at pore water pressure heads between 0 and -0.2 kPa (see e.g. Topp et al., 1980). The functional relationships between pressure head (h), soil water content (θ) and hydraulic conductivity (K) proposed by Van Genuchten (1980), on the other hand, usually give a more accurate representation of the observed behaviour. Consequently the Van Genuchten functions were incorporated into LEACHW as an optional alternative.

ii) 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, U(z,t), would predict unrealistic (oscillating) water uptake patterns. An alternative function based on the work by Feddes et al. (1978) was therefore added as an option. This function has the form:

$$U(z,t) = R_{df}(z,t)\ \beta(h)\ PT / Z_r \qquad (1)$$

where R_{df} is a root distribution function [dimensionless] which is already calculated within a submodel called GROWTH, β(h) is a dimensionless sink term variable, ranging from zero to 1 as a prescribed function of soil water pressure head, PT is the potential transpiration rate [LT^{-1}] and Z_r [L] is the rooting depth. Root water uptake is adjusted to reflect non-optimal conditions using the β function and specified pressure head limits, h_1, h_2, h_3 and h_4 (see Feddes et al., 1978). In the Grand River watershed application, the values of $h_1 \rightarrow h_4$ were adapted for corn: h_1 = -1 kPa, h_2 = -2 kPa, h_{3min} = -60 kPa, h_{3max} = -40 kPa, h_4 = -1500 kPa.

iii) Dissipation Rates

The dissipation rate constant, k, of most pesticides (including atrazine) exhibits 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):

$$k_w = \ln 2 / A\,(100\,\theta)^{-B} \tag{2}$$

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:

$$T_{cf} = Q_{10}^{\,0.1(T-Tbase)} \quad ; \quad 0\ {}^{0}C < T < 35^{\circ}C \tag{3}$$

where Q_{10} [dimensionless] is the factor by which k changes over a 10 ^{0}C temperature interval, T [^{0}C] is soil temperature, and Tbase [^{0}C] is the base temperature from which the temperature correction was determined. The combined water content-temperature corrected dissipation rate constant, k_{wt}, is calculated as:

$$k_{wt} = k_w T_{cf} \tag{4}$$

For the Grand River watershed application, practical constraints dictated that Eqs. (2)-(4) could be calibrated to atrazine only for the 3 predominant soil types in the watershed (Table A1). Consequently, every soil in the watershed was assigned one of the 3 calibrated k_{wt} functions on the basis of which predominant soil type they were the most similar to.

Table A1. Rate constants, k^*, Q_{10} values, and A and B constants for atrazine dissipation (Eq. 2 and 3). (Data provided by E. Topp and W.N. Smith, CLBRR, Agric. Canada, Ottawa, Ont., Canada).

	Soil Type		
Parameter	[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°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.

iv) Bypass Flow

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. White, 1985). Many attempts have been made to incorporate this type of flow into the traditional mechanistic water and solute transport models; however, all of these representations have serious limitations (Beven, 1991). Consequently, a simplistic, but measurement based, approach to bypass flow was adopted for this work.

The proportion of soil water bypassed by the solute was defined in terms of:

$$F = 1-(\theta_T/\theta) = 1-PV_{0.5}\,; \qquad \theta_T \le \theta;\ \ 0 \le F < 1 \qquad (5)$$

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 of soil water at which the $0.5C_0$ concentration of solute tracer occurred (C_0 = input concentration of tracer). This factor was incorporated into the advection and mechanical mixing terms of the convection-dispersion equation, i.e.:

$$qC \rightarrow qC/(1-F) \qquad (6)$$

$$D_m(q) = \lambda q/\theta \rightarrow \lambda q/[\theta(1-F)] \qquad (7)$$

where q [LT^{-1}] is water flux density, C [ML^{-1}] is solute solution concentration, D_m [L^2T^{-1}] is the mechanical mixing component of the hydrodynamic dispersion coefficient and λ [L] is the soil dispersivity. Equations (6) and (7) imply that all soil water 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 the convection-dispersion equation is to increase the average velocity with which solute migrates through the soil profile relative to the average linear pore water velocity (q/θ). This in turn causes the predicted $0.5C_0$ concentration of a nonreactive solute (e.g. chloride) to occur at less than one PV (i.e. $PV_{0.5} \le 1$). Further details on F and its determination are given in Reynolds et al. (1994).

Bypass flow factors (F) were determined from field measured chloride breakthrough curves for several soil types, water contents and depths in the profile. These measurements were made at six field sites distributed across Southern Ontario (see Reynolds et al., 1994). The F values were highly variable (CV = 168 %) and did not show any consistent patterns with site location, soil texture, water content, pore water flux, or depth in the soil profile (Reynolds et al., 1994). Consequently, the mean value of F = 0.20 (n = 56) was used in the simulations to represent bypass flow in the Grand River watershed application.

v) Multiple Year Simulations

LEACHW and LEACHP were modified 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. The modifications included various program changes, and the development of multiple year weather and crop management input files, to account for: over-winter redistribution and/or dissipation of water and solutes in the soil profile, snow accumulation during winter, and spring runoff.

It was assumed that during the "winter" (defined as when the weekly mean air temperature is less than 0 ^{0}C), the soil surface is frozen and there is no water flux across the atmosphere/soil interface. Consequently, the existing water and solutes in the profile slowly redistribute during the winter via gravity drainage, and solutes continue to dissipate. Precipitation during the winter period is assumed to occur as snow which accumulates with the assumption that 30% is lost due to blowoff, evaporation and sublimation. The remaining 70% is distributed between infiltration and snow melt runoff during the first seven days of "spring" (defined as when the weekly mean soil surface temperature is greater than 0 ^{0}C). Runoff is calculated with the USDA Soil Conservation Service (1972) curve number method. Soil surface temperatures were assumed to equal air temperatures.

vi) Crop Management

The crop management component of 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 < K_s < 250 mm/d) when the mean air temperature reached 12.8^{0}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) occurred when 1250 corn heat units had accumulated since planting. The crop was harvested in the fall when either the mean air temperature dropped below 12^{0}C, or the minimum air temperature dropped below -2^{0}C.

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