A GIS–Based Ground Water Contamination Risk Assessment Tool for Pesticides

by Michael G. Sinkevich Jr., M. Todd Walter, Arthur J. Lembo Jr., Brian K. Richards,
Natalia Peranginangin, Sunnie A. Aburime, and Tammo S. Steenhuis

Abstract

A process-based preferential flow transport model was implemented in a geographic information system to locate areas in the landscape with high risk of contamination by agrochemicals, especially pesticides. Protecting ground water resources necessitates a reliable ground water quality monitoring strategy. It is valuable to be able to focus monitoring on areas with the highest risk of contamination because monitoring ground water is an expensive activity, especially at the landscape scale. The objective of this project was to develop a tool that quantifiably estimates distributed ground water contamination risk in order to develop reliable, cost-effective ground water observation networks. The tool is based on a mechanistic model of chemical movement via preferential flow and uses land cover data, information about chemical properties, and modeled recharge to estimate the concentration of chemical reaching the ground water at each point in the landscape. The distributed risk assessment tool was tested by comparing the model-predicted risk with observed concentrations from 40 sampling wells in Cortland County, New York, for atrazine (pesticide) and nitrate, the latter assumed to be an indicator of agricultural pollution. The tool predictions agreed well with observed nitrate concentrations and pesticide detections. An Internet-based version of this tool is currently being developed for ready application to New York State.

Introduction

Ground water is an important natural resource that should provide drinking water for future generations. However, in recent decades ground water pesticide contamination from agriculture has become a problem that requires monitoring. Because such monitoring is expensive—especially for ground water over large areas of agriculturally dominated landscapes—reliable and flexible tools are needed to identify potential hazard areas in the landscape so that monitoring strategies can focus on the highest risk areas. By focusing monitoring activities on the highest risk areas, fewer observation wells are needed and the potential cost and detection effectiveness of the monitoring is improved. The goal of this project was to develop a distributed landscape-scale, physically based ground water risk assessment tool that can be implemented with readily available open-access data.

While landscape-scale water quality risk assessment has been revolutionized by the advent of geographic information systems (GIS), most, if not all, risk assessment tools regularly used by water quality professionals employ logical factor- or index-based rubrics for assessing risk that are only loosely linked to physical processes and fail

to predict actual chemical concentrations. This is especially true for ground water (e.g., Grayman 1977; Hamlett et al. 1992; Nizeyimama et al. 1996; Peterson et al. 1996). Traditional mechanistic predictions of ground water risk are generally only applied at a single point in the landscape and assume that pesticide leaching through soils is accurately characterized by the convective-dispersive equation, which neglects preferential flow phenomena. The reliable, mechanistic or physically based models developed to predict the ground water contamination from land-applied chemicals that meaningfully consider preferential flow (e.g., Wagenet and Hutson 1986; Ramos and Carbonell 1991; Steenhuis et al. 1987; Steenhuis and Parlange 1991; Nguyen et al. 1998; Kim et al. 2005) have not been incorporated into GIS to assess contamination risks at a landscape scale, probably because they require either a copious amount of input data or data that are not readily available.

Perhaps the most important transport process to be included in ground water risk assessment is preferential flow, the rapid nonuniform transport of solutes via these flowpaths, which can result in contaminants reaching the ground water before they degrade or can be adsorbed by the soil (e.g., Stagnitti et al. 1994; Camobreco et al. 1996). Indeed, the surprise discovery of pesticide contamination of the Long Island aquifers in the early 1980s clarified that ground water contamination by toxic chemicals cannot be

reliably characterized by the convective-dispersive equation, which assumes relatively uniform water flow throughout the soil matrix (Parlange et al. 1988). The Long Island findings stimulated interest in preferential flow; since then, the occurrence and effect of preferred flowpaths on water quality have been widely researched (e.g., Steenhuis et al. 1990; Steenhuis et al. 1994; Pivetz and Steenhuis 1995; Geohring et al. 1999; Logsdon 2002; Gazis and Feng 2004). Several preferential flow mechanisms have been identified: (1) macropore flow, which is common in well-structured soils (e.g., Quisenberry and Phillips 1976; Beven and Germann 1982); (2) fingered flow, which generally occurs in unstructured soils and water repellent soils due to unstable wetting fronts (e.g., Hill and Parlange 1972; Bauters et al. 1998); and (3) funnel flow, which occurs at some textural interfaces in the soil profile (Kung 1990; Walter et al. 2000; Heilig et al. 2003). It is widely accepted that preferential flow is not an exception but a rule when dealing with solute flow through field soils (Dekker and Ritsema 1994, Vanclooster et al. 2000), and therefore it is extremely important that it be included when trying to accurately model the distribution of potential well water contamination.

The objective of this project was to employ a mechanistic model of preferential flow within a GIS to generate maps of distributed ground water contamination risk. We modified the Generalized Preferential Flow Model (GPFM) proposed by Kim et al. (in press) that is based on work by Darnault et al. (2004) and field tested by Peranginangin (2003); modifications included including chemical degradation factors appropriate for the deeper soil profile and incorporating the model into a GIS. As an example, we applied the distributed model to Cortland County, New York, and compared model-generated risk predictions to field observations for atrazine and nitrate. We cannot report specific sample locations and concentrations due to a confidentiality agreement signed at the beginning of this study, and therefore data will be presented in a generalized fashion through graphical methods.

Model Description

The Generalized Preferential Flow Transport Model

The GPFM describes solute transport between the land surface and the ground water. Figure 1 shows the conceptualization of the soil profile used to develop the GPFM, which is divided into two zones: a near-surface distribution zone and a deeper transmission zone (Jarvis et al. 1991; Steenhuis et al. 1994; Ritsema and Dekker 1995; Shalit and Steenhuis 1996; Kim et al. 2003; Steenhuis et al. 2001). In the distribution zone, water and solutes are funneled into preferential flowpaths, which transport the solutes through the transmission zone. The thickness of this distribution zone depends on land use or geomorphology, e.g., plow depth in cultivated land. The model uses the assumption that percolating water and solutes mix uniformly in the distribution zone and the zone behaves as a linear reservoir, resulting in an exponential loss of solutes (Steenhuis et al.
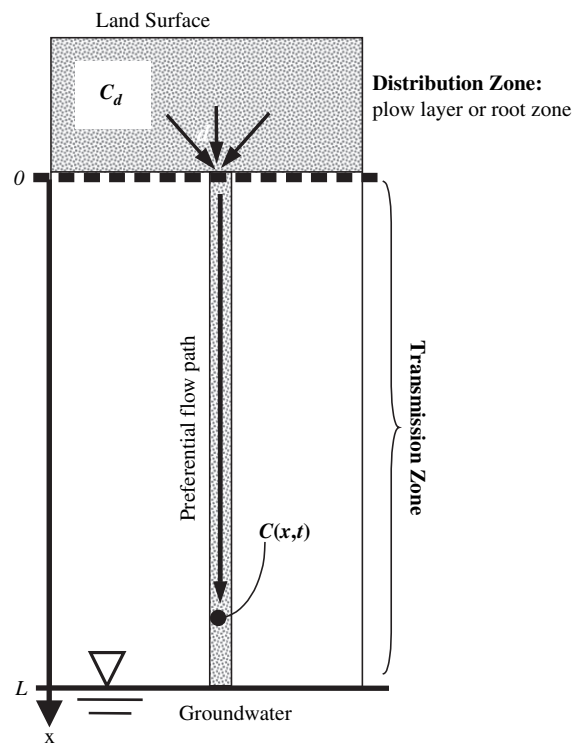

Figure 1. Schematic diagram of the preferential solute transport process in the vadose zone.

1994; Shalit and Steenhuis 1996). At $t = 0$, $C_d = C_o$ (e.g., Kim et al. in press):

$$C_d = C_o \exp[-(\lambda + \beta)t] \tag{1}$$

where C_d is the solute concentration in the distribution layer, λ and β represent the rates of loss due to leaching and biochemical degradation, respectively $[T^{-1}]$, and t is time $[T]$. C_o is the initial dissolved chemical concentration $[ML^{-3}]$ and can be written as:

$$C_o = \frac{M}{W} \tag{2}$$

and M = the mass of pollutant applied per unit area of land $[ML^{-2}]$ and W is the apparent water content of the distribution zone and incorporates chemical adsorption and is calculated (Shalit and Steenhuis 1996) as:

$$W = d(\theta_S + \rho_b k) \tag{3}$$

where d [L] is the depth of the distribution zone, θ_S $[L^3 L^{-3}]$ is the saturated moisture content, ρ_b $[ML^{-3}]$ is the soil dry bulk density, and k $[L^3 M^{-1}]$ is the sorption partition coefficient.

Solute degradation in the distribution zone (β) due to chemical and microbial breakdown is characterized by the chemical half-life, $t_{1/2}$ [T]:

$$\beta = \ln\left(\frac{2}{t_{1/2}}\right) \tag{4}$$

Half-life values are widely available in the literature for common pollutants, e.g., DelVecchio and Haith (1993). The leaching of solute from the distribution zone is

characterized by the ratio of the average percolation rate, R [LT^{-1}], to apparent soil water content, W [L], i.e.,

$$\lambda = \frac{R}{W} \tag{5}$$

Water and pesticides are released to the transmission zone via preferential and matrix flows. Because preferential flowpaths are the most relevant with respect to water quality, we assume that all water moves through the preferential flowpaths at an average characteristic velocity, v (Kim et al. in press), through the transmission zone. This transport via the preferential flowpaths of the transmission zone can be described with the convective-dispersive equation with a sink term for pesticide degradation (e.g., Peranginangin 2003):

$$D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} - \beta^* C \tag{6}$$

where C [ML^{-3}] is the chemical concentration in the preferential flowpaths at depth x and time t, D [L^{2}T^{-1}] is the dispersion coefficient, v [LT^{-1}] is the velocity of the solute, x [L] is the vertical axis with the origin at bottom of the distribution layer (positive downwards), and β^* [T^{-1}] is the first-order chemical degradation rate in the transmission zone. D/v is assumed to be constant with values in the range of 1 to 4 (Walter 1974). Pesticide degradation in the transmission zone is lower than in the more microbially and biogeochemically active distribution zone (Federle et al. 1986; Brockman et al. 1992; Kruger et al. 1997; Van der Heyden et al. 1997; Shaw and Burns 1998; Accinelli et al. 2001; Mbuya et al. 2001). Integrating Equation 6 using Laplace transforms with the initial condition $C = 0$ for $x > 0$ and $t = 0$ and a solute concentration at upper boundary condition at $x = 0$ for $t > 0$ is given by Equation 1, the concentration in the distribution zone can be written as for $4D(\lambda + \beta - \beta^*)/v^2 < 1$, (Toride et al. 1995; Darnault et al. 2004):

$$C = \frac{1}{2}C_{\text{o}}\exp(-(\lambda + \beta)t)\left[\exp\left(\frac{vx}{2D}(1 - a)\right)\text{erfc}\left(\frac{x - vta}{2\sqrt{Dt}}\right)\right.$$

$$\left. + \exp\left(\frac{vx}{2D}(1 + a)\right)\text{erfc}\left(\frac{x + vta}{2\sqrt{Dt}}\right)\right] \tag{7}$$

where: $a = \sqrt{1 - \frac{4D(\lambda + \beta - \beta^*)}{v^2}}$

At $x = L$, the depth of the ground water, Equation 7 gives a value for pollutant concentration in the ground water at time t after the application of the chemical. When x or t is sufficiently large, such that $(x + vta)/(4Dt)^{1/2} > 3$, then the last term of Equation 7 is negligible, i.e.,

$$\exp\left(\frac{vx}{2D}(1 + a)\right)\text{erfc}\left(\frac{x + vta}{2\sqrt{Dt}}\right) \approx 0$$

GPFM (Equation 7) has been successfully tested with both lab and field experiments; e.g., Figure 2 shows the agreement between model predictions and field observations of chloride and atrazine collected below the root zone (Peranginangin 2003), and Figure 3 shows results comparing model predictions and time-series field measures of tritium (H^3) radiation in picocuries (Aburime et al. 2002) collected at 60 and 120 cm over an ~1-year period. Tritium differs from most agrochemicals in that it has a long half-life (12.5 years) and a sorption partition coefficient, k, of zero.

Landscape–Scale Risk Assessment Model

To develop a ground water contamination risk assessment tool, we implemented the GPFM in a GIS using spatially distributed estimates of average percolation velocity, v, and depth to the ground water, x. Ground water depth typically varies throughout the year, but for the purposes of risk assessment, the soil survey or SURRGO/STATSGO minimum ground water depths sufficiently capture the distributed water table depths for the purposes of pollutant risk assessment. The percolation or transport velocity depends on the propensity for preferential flow; we used a conservative estimate for the fraction of area participating in preferential solute transport, A_{f}, proposed by Selker et al. (1996):

$$A_{\text{f}} = \frac{I_{\text{max}}}{K_{\text{S}}} \tag{8}$$

where I_{max} is the maximum annual daily precipitation [LT^{-1}] and K_{S} is the saturated hydraulic conductivity of the soil [LT^{-1}], usually the surface layer. The velocity of the solute can be expressed as:

$$v = \frac{R}{(\theta_{\text{S}} + k\rho_{\text{b}})(A_{\text{f}})} \tag{9}$$

where R is the ground water recharge, same as in Equation 5 [LT^{-1}], θ_{S} is the saturated moisture content [L^{3}L^{-3}], k is the sorption partition coefficient [L^{3}M^{-1}], and ρ_{b} is the bulk density [ML^{-3}]. The inclusion of the sorption in Equation 9 retards the velocity of chemicals prone to soil adsorption relative to the water velocity. This is similar to the equation that would be used in traditional matrix flow situations except for the fractional area term in the denominator, which makes the preferential flow velocity typically
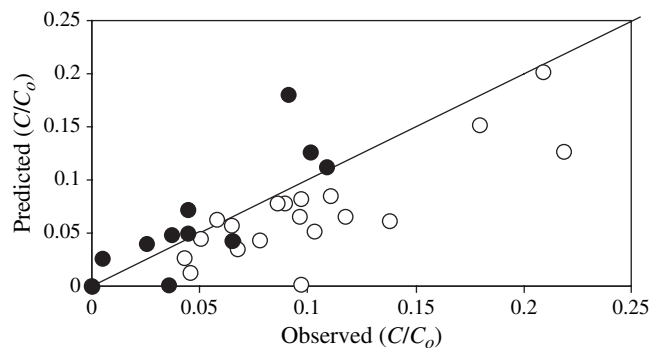

Figure 2. Predicted relative concentrations compared to observed relative concentrations taken from field data (Peranginangin 2003), with $R^2 = 0.6$. Chloride is represented with the open circles, and atrazine with the dark circles.
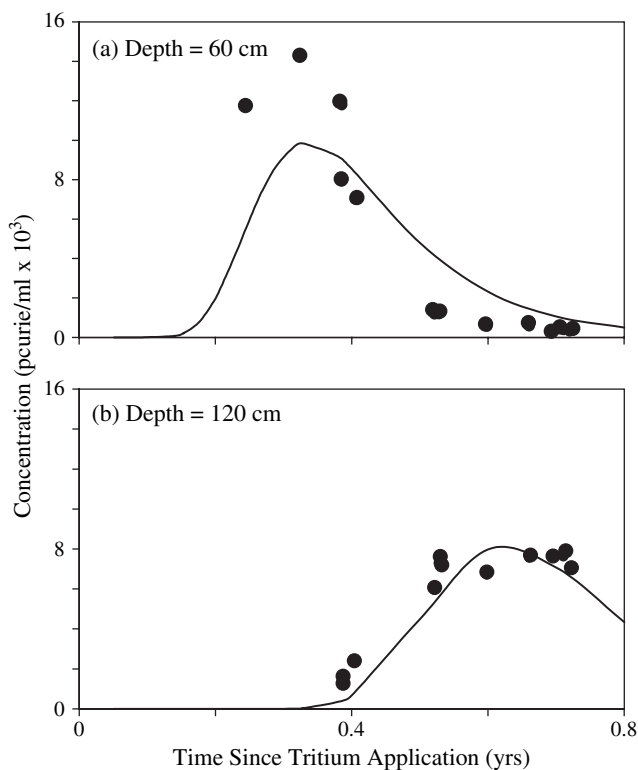
Figure 3. Comparison of the generalized preferential flow predictions (lines) to field data (symbols) for tritium at depths of (a) 60 cm and (b) 120 cm (Abumine et al. 2002).

>1 order of magnitude greater than that of matrix flow. The saturated moisture content θ_S in Equation (9) can be obtained through open-access soil data or, when unavailable, can be estimated from other commonly available soil data as follows (Fetter 2001):

$$\theta_S = 1 - \left(\frac{\rho_b}{(\rho_m(1 - Om)) + (\rho_o(Om))} \right) \quad (10)$$

where Om is the percent organic matter content in the soil, ρ_m is the mineral particle density (≈ 2.65 g/cm^3), and ρ_o is the organic soil particle density (≈ 1.00 g/cm^3) (Boelter 1969; Boelter and Blake 1964). Adsorption/desorption partition coefficients for many pollutants are published (e.g., Bailey et al. 1974; Baker et al. 1978; Davidson et al. 1975; Haan 1971; Helling et al. 1971; Smith et al. 1978); for pesticides, k can be estimated using the percent organic carbon, Oc, and the pesticide organic carbon adsorption coefficient, K_{oc} (DelVecchio and Haith 1993):

$$k = K_{oc} \left(\frac{Oc}{100} \right) \quad (11)$$

Little organic matter exists in the subsoil, and k tends toward zero in the transmission zone. Although ground water recharge, R in Equations 5 and 9, may be spatially variable, for small areas with reasonably homogenous climate it is commonly calculated as an average distributed flux using a Thornthwaite-Mather (1955) water balance (e.g., Steenhuis and Van der Molen 1986; Varni and Usunoff 1999). This procedure uses soil available water

capacity data, precipitation data, and estimated potential evapotranspiration (PET) to estimate recharge (see Steenhuis and van der Molen (1986) for a complete description).

The health risk of ground water contamination due to pesticides can be estimated using the hazard ratio (Steenhuis and Naylor 1987):

$$H = \frac{C^*}{h} \quad (12a)$$

$$C^* = \frac{\int_0^t CR d\bar{t}}{\int_0^t R d\bar{t}} \quad (12b)$$

where C is the pesticide concentration at depth L as estimated by the distributed GPFM (Equation 7) [ML^{-3}], C^* is the average concentration of pollutant in the ground water [ML^{-3}] over time t, R is the percolation rate or, alternatively, the ground water recharge [LT^{-1}], and h is the maximum safe drinking water concentration as determined by the U.S. EPA [ML^{-3}]. Values of H near or greater than 1 indicate potential concern for drinking water safety.

Model Application

Site Description

We applied our risk assessment model to Cortland County in central New York State because much of the area relies on ground water from the region's glacial aquifers and because its range of different soils types and land uses provided substantial spatial distribution for this case study. Additionally, a GIS-based assessment done within our research group in 2003 (Richards and Sinkevich, unpublished data) found that Cortland County had the greatest relative risk of pesticide contamination of ground water, based on land use, population ground water use, and aquifer characteristics. The shallow depth to the water table and the high permeability of these aquifers make them highly vulnerable to contamination. The aquifer system in Cortland County consists of an unconfined sand and gravel aquifer 10 to 25 m thick and a lower confined sand and gravel aquifer that is 1 to 50 m thick. The two aquifer systems are separated by a lacustrine and till stratum that is anywhere from 1 to 50 m thick. The two aquifers are hydraulically connected in some areas near valley walls where the confining layer is thin or absent (Miller et al. 1998). Land cover types in Cortland County are primarily agriculture (28%), forest (62%), and urban (8%) (Figure 4). Agriculture is fairly evenly distributed throughout the rural parts of the county. Cortland County has diverse topography that ranges from flat valley bottoms to steep valley walls and hillsides; elevations range from ~1100 to 2000 feet above mean sea level.

Cold winters, with an average temperature of 1°C, and dry summers, with an average temperature of 17°C, climatically characterize Cortland County, as well as much of upstate New York. Lake Ontario, which is 70 km north, moderates air temperatures and supplies moisture to the cold air masses during the winter. The average annual precipitation is 100 cm, and the average annual temperature is 9°C.
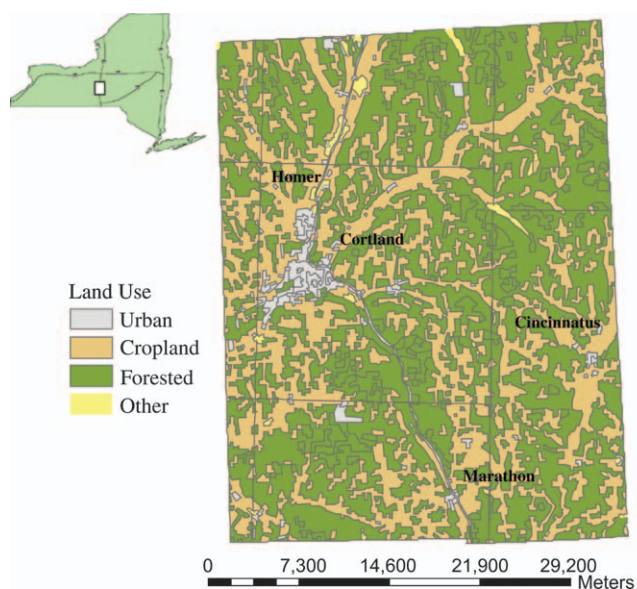
Figure 4. Land use (LULC) broken up into the three major land cover types in Cortland County, New York (forested, urban, and crop land).

Ground Water Quality Data Collection

During the spring and summer of 2003, we collected ground water samples at 40 locations throughout the county from private residences, farms, small businesses, monitoring wells, and public water supplies. This data collection was done during model development, i.e., prior to generating any risk predictions, and thus sampling bias was avoided. Permission to sample was granted voluntarily. The Cortland County Soil and Water Conservation District (CCSWCD) and USGS cooperated in selecting the sampling sites. Approximately 60 locations were initially identified, selected in part based on the CCSWCD's intuitions about where there might be an elevated risk of pesticide contamination due to factors such as proximity to likely pesticide application, areas down slope of pesticide application, presence of a high water table, permeable soils that allow leaching, and cooperative land owners. The ground water samples were tested for atrazine and nitrate; the latter was included because elevated NO_3-N concentrations in ground water have been used as an indicator of the presence of pesticides (e.g., Panno et al. 2002; Panno and Kelly 2004).

The nitrate was analyzed at the Cornell Nutrient Analysis Laboratory by ion chromatography (Dionex DX-100 with AS4A-SC anion column, minimum detection limit (mdl) $= 1 \times 10^{-3}$ µg/L). Atrazine was analyzed at the Cornell Soil and Water Laboratory using Strategic Diagnostics Inc.'s RaPID Assay Atrazine Test Kit, which uses an enzyme-linked immunosorbent assay for the determination of atrazine (mdl $= 0.01$ µg/L).

Model Parameterization

Land Use

Land use influences the spatial distribution of pesticide or other potential contaminant use. We used Land Use and Land Cover (LULC) data files (www.webgis.com), which describe the vegetation, water, natural surface, and cultural features on the land surface. These were obtained from the USGS' National Mapping Program and from the EPA. Land use is always changing, especially in upstate New York where farms are constantly going out of business and residential areas are rapidly expanding; thus, the most current data were used, i.e., 1995 (Figure 4). Because it constitutes such a large amount of the area, agricultural land use is the primary concern with respect to pesticide contamination. We assumed for risk assessment purposes that all agricultural lands are in use and that these cropped fields receive the pesticide for which risk predictions are to be determined.

Pesticide Parameters

This study focused on atrazine and assumed pesticide application rates recommendations posted by the USDA (www.usda.gov/nass/). For this study, we followed one complete pesticide pulse, which is 1 year's worth of pesticide application because atrazine is generally applied only once in the early spring. Table 1 summarizes the atrazine parameters used in this study.

Soils

Currently, all of New York State's soil information is compiled in the soil survey database, STATSGO (www.essc.psu.edu). This database contains digitized maps of soil parameters needed to implement the GPFM in a GIS, namely, bulk density, organic matter content, and saturated moisture content. It also provides estimated average high water table information, which was used to

Table 1
Pesticide Parameters for Atrazine

Parameter	Value	Source
Pesticide organic adsorption coefficient (K_{oc}[1])	160 cm³/g	DelVecchio and Haith (1993)
Half-life ($t_{1/2}$)	60 d	DelVecchio and Haith (1993)
EPA drinking water standard (H)	3 mg/L	http://www.epa.gov/safewater/mcl.html#mcls
Application rate (M)	1.45×10^{-4} g/cm²	http://www.usda.gov/nass/

[1]K_{oc} is used in Equation 11 to solve for k with Om from STATSGO (see Soils section).
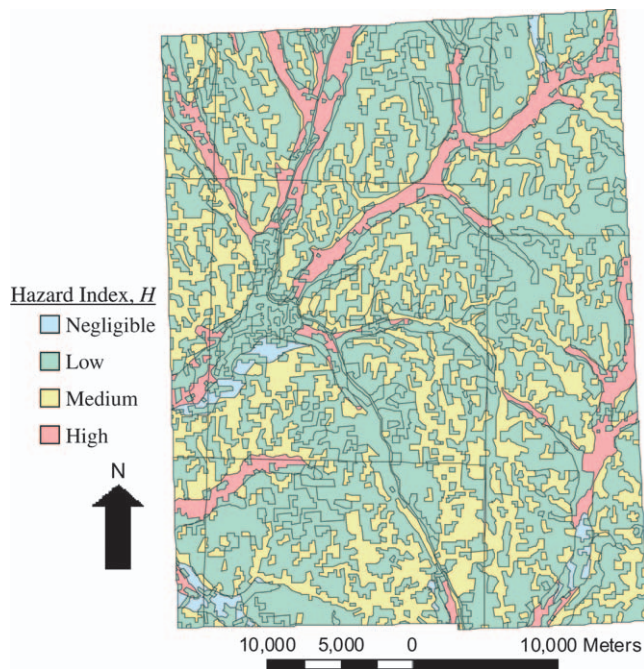
Figure 5. This is a risk assessment map for potential ground water contamination due to the pesticide atrazine leaching through the soil in Cortland County, New York. Light blue, dark blue, yellow, and red correspond to negligible, low, moderate, and high risk for that specific area, respectively.
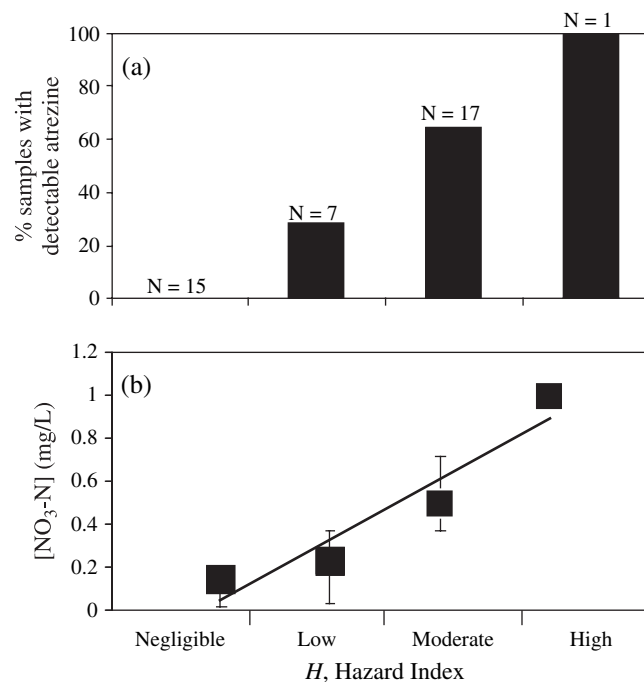

Figure 6. Comparisons between predicted atrazine hazard indices (H) and observed ground water quality with respect to (a) atrazine and (b) nitrate. Graph a shows the percent of samples "N" collected within each hazard class (negligible, low, moderate, and high) that had detectable concentrations of atrazine. Graph b shows the average nitrate concentration in groundwater for each hazard class; the error bars represent the 90% confidence interval of the observed values, and the line is a linear regression ($R^2 = 0.90$) emphasizing the relationship.

parameterize ground water depth for our model. These data were compared to USGS field measurements of water table depth over a small portion of Cortland County, and the relative distributions of STATSGO water table depth compared well with the field measurements (Sinkevich 2004).

Ground Water Recharge

The Thornthwaite-Mather (1955, 1957) method, as described by Steenhuis and van der Molen (1986), was used to estimate annual ground water recharge, R. This procedure for calculating recharge was chosen because of its modest data requirements and ease of calculation. The Thornthwaite-Mather method requires the soil available water capacity, daily precipitation, and daily PET. PET was estimated using the Priestly-Taylor (1972) equation. We used average daily precipitation and temperature over >30 years with data obtained from the weather station in Cortland, New York. Using these weather data, average annual ground water recharge, R, was calculated as 40.4 cm/year.

The Preferential Flow Parameter

The fraction of soil participating in preferential solute transport, A_f, is not well known. We used $A_f = 0.3$ based on field studies in which we dyed macropores, images available at the Cornell Soil and Water Lab Web site (SWL— Preferential Flow Website 2005). We checked this value against Equation 8 using I_{max} equal to average intensity of the 1-year 24-h rainfall in Cortland ($I_{max} = 2$ cm/h— United States Department of Commerce, Weather Bureau 1961) and an average K_S from the local soil survey. Values of K_S ranged over several orders of magnitude, but

reasonable "average" values yielded $A_f = 0.2$ to 0.4, which agreed with our own field studies.

Hazard Index Mapping

The hazard index map was created using the spatial datasets for land use (LULC) and soils (STATSGO), as well as the nonspatial aspects solved for in Equations 2 through 12. Using ESRI's ArcGIS (any GIS that allows vector and raster processing would work), the LULC data were joined with the STATSGO data. An attribute table containing the necessary land use and soils data was imported to a spreadsheet program to solve Equations 7 through 12, and the results were imported back into a GIS to display a map of H. For a step-by-step procedure using ArcGIS, see Sinkevich (2004). Although Equation 12 is shown for a general case, here we used long-term average R and replaced the integrals with monthly summations. For simplicity, we assumed no temporal variation in R.

Results and Discussion

Figure 5 shows the atrazine hazard index map for Cortland County, New York, divided up into four major risk groups: negligible, low, moderate, and high. Negligible-risk areas, $H = 0$, correlate almost exclusively to areas that do not receive pesticides, i.e., areas that are not cropland, and/or areas with deep water tables, generally >8 m

deep. The low-risk areas indicate some potential pesticide leaching, $0 < H \leq 0.05$, but at concentrations well below the EPA standard. The moderate areas were predicted to have concentrations up to 1.5 µg/L, i.e., $0.05 < H \leq 0.5$, which indicates substantial potential pesticide leaching that is nevertheless still below the EPA standard for ground water contamination by atrazine. The high-risk areas are all locations with a potential atrazine leaching risk index of $H > 0.5$. Note that the high-risk areas constitute only a small portion (5%) of the watershed; focusing ground water monitoring on these areas would be substantially more cost effective than implementing an evenly distributed county-wide program. Most of the areas are actually at negligible to low risk, >70%, which corresponds to the fact that 70% of the county is forest or urban areas that do not typically receive atrazine and for which a low intensity monitoring strategy would probably suffice.

Figures 6a and 6b show the comparison between our atrazine hazard indices and field measurements of atrazine and nitrate, respectively. Because the scope of sampling was limited, our sample set unfortunately only included one well from a high-risk area, although this sample contained atrazine and the highest-observed concentration of nitrate. Out of the 40 samples, 14 had detectable levels of atrazine (i.e., >0.005 µg/L); all samples had low concentration (<0.2 µg/L). Assuming that the propensity of atrazine detection is a good indicator of pesticide contamination risk, we found a good correlation between atrazine detection frequency and our risk predictions (Figure 6a). We used nitrate as a general agrochemical tracer for which we could detect a larger range of concentrations than we found for atrazine, and, as shown in Figure 6b, the concentration

of nitrate correlated well with the atrazine risk indexes, i.e., higher-risk areas correlated to higher nitrate concentrations. Although nitrate is a better indicator of overall ground water recharge from agricultural areas than preferential flow per se, these tests corroborate the reliability of our risk assessment tool's ability to predict ground water contaminant hot spots.

To illustrate the importance of considering preferential flow in ground water risk assessment, Figure 7 shows the risk predictions with preferential flow removed, i.e., $A_f = 1$ (Equation 8). Interestingly, in the absence of preferential flow, there is very little predicted risk of ground water contamination by atrazine. Traditional leaching models typically ignore preferential flow and assume uniform, convective-dispersive transport like that used to generate Figure 7. Figure 8 replicates the analyses shown in Figure 6 but without preferential flow transport; note the propensity for detectable levels of atrazine in negligible-risk and low-risk areas (Figure 8b) as well as high nitrate concentrations for negligible-risk and low-risk areas.

To evaluate the role of chemical degradation in contaminant risk, we used our tool to create a hazard index map for Cortland County, New York, with respect to 2,4-D (Figure 9), which has a decay rate four to eight times faster than that of atrazine (Hamaker 1972). For 2,4-D, the maximum contaminant levels in drinking water are 70 µg/L (EPA), the sorption partition coefficient is spatially distributed but remains around 20 cm^3/g, the application rate is 2.24×10^{-5} g/cm^2, and $t_{1/2}$ is 10 d. The hazard map is
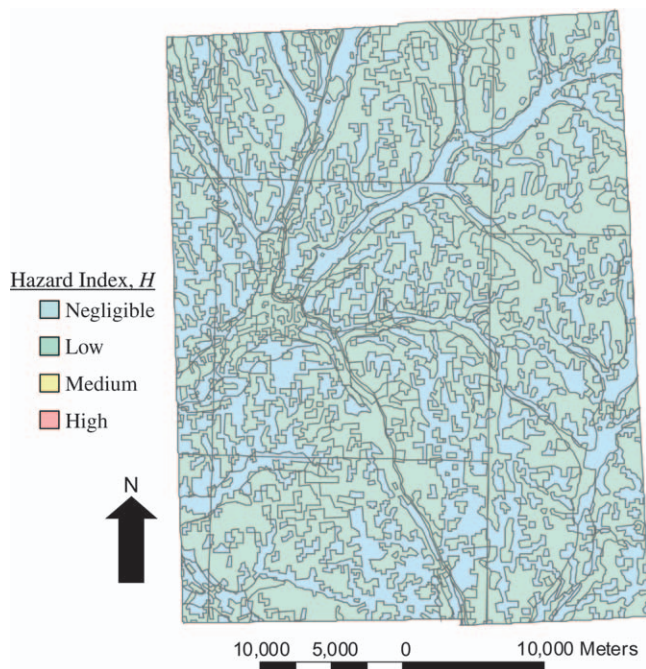

Figure 7. This is a risk assessment map for potential ground water contamination due to the pesticide atrazine leaching through the soil in Cortland Country, New York, neglecting preferential flow ($A_f = 1$). Color scheme is the same as Figure 5.
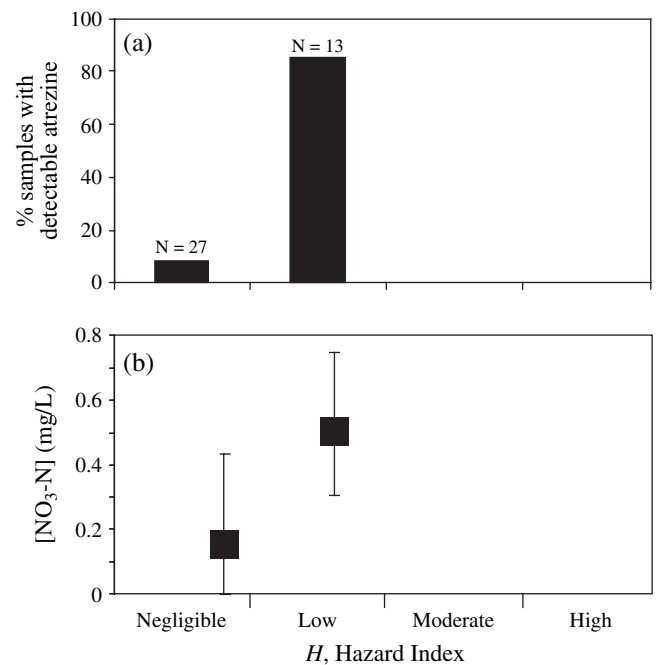

Figure 8. Comparisons between predicted atrazine hazard indices (H) ignoring preferential flow and observed ground-water quality with respect to (a) atrazine and (b) nitrate. Graph a shows the percent of samples "N" collected within each hazard class (negligible, low, moderate, and high) that had detectable concentrations of atrazine. Graph b shows the average nitrate concentration in ground water for each hazard class; the error bars represent the 90% confidence interval of the observed values.
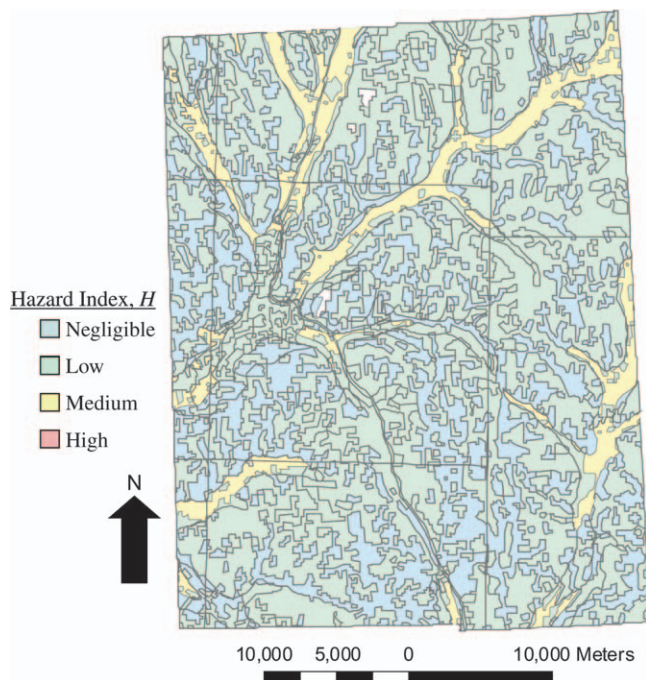
Figure 9. This is a risk assessment map for potential ground water contamination due to the pesticide 2,4-D leaching through the soil in Cortland County, New York.

scaled proportionally the same as for the atrazine analysis, e.g., high risk corresponds to $H > 0.5$. Notice that the risk of 2,4-D contamination is considerably less than for atrazine (Figures 9 and 5, respectively). Most of the areas are negligible to low risk, 70% and 25% of the county, respectively. Because of the fast degradation rate of 2,4-D, there are actually no areas of high risk for water contamination in Cortland County, and the moderate-risk areas only represent ~5% of the county. This is in agreement with many survey studies that find atrazine concentrations in drinking water wells but find little to no 2,4-D concentrations (Tindall and Vencill 1995; Franklin et al. 1994).

Summary and Conclusions

We developed and tested a risk assessment tool to assist in developing reliable and cost-effective well sampling strategies. Our tool is based on a spatially distributed version of the GPFM that accounts for the preferential flow of pesticides downward through the soil, acknowledging that degradation rates may be lower at depth than in the root zone, i.e., the distribution and transmission zones, respectively. Our risk assessment tool translates the GPFM-predicted concentrations into hazard indexes that show the degree of potential ground water contamination by pesticides across a landscape. We applied our model to Cortland County, New York, and found good agreement between risk predictions and field measurements of atrazine and nitrate. Our GIS-based risk assessment tool can be parameterized entirely with open-access data and published information on agrochemical characteristics. The next goal of this project is to implement our tool on the Internet so that water quality professionals have easy access to it.

References

Aburime, S.A., J.C. Seaman, J. Singer, and E. Galligan. 2002. Tritium dynamics in the vadose zone of MWMF tritium phytoremediation site. Project #DOE/ERDA 00–133. U.S. EPA, Washington D.C.

Accinelli, C., G. Dinelli, A. Vicari, and P. Catizone. 2001. Atrazine and metolachlor degradation in subsoils. *Biology and Fertility of Soils* 33, no. 6: 495–500.

Bailey, G.W., A.P. Barnett, W.R. Payne, and C.N. Smith. 1974. Herbicide runoff from four coastal plain soil types. EPA 660/2-74-017. U.S. EPA, Washington, D.C.

Baker, J.L., J.M. Laflen, and H.P. Johnson. 1978. Effect of tillage systems on runoff losses of pesticides, a rainfall simulation study. *Transactions of the ASAE* 21, no. 5: 886–892.

Bauters, T.W.J., D.A. DiCarlo, T.S. Steenhuis, and J.-Y. Parlange. 1998. Preferential flow in water-repellent sands. *Soil Science Society of America Journal* 62, no. 5: 1185–1190.

Beven, K., and P. Germann. 1982. Macropores and water flow in soils. *Water Resources Research* 18, no. 5: 1311–1325.

Boelter, D.H. 1969. Physical properties of peats as related to degree of decomposition. *Soil Science Society of America Proceedings* 33, no. 4: 606–609.

Boelter, D.H., and G.R. Blake. 1964. Importance of volumetric expression of water contents of organic soils. *Soil Science Society of America Proceedings* 28, no. 2: 176–178.

Brockman, F.J., T.L. Kieft, J.K. Fredrickson, B.N. Bjornstad, S.-M.W. Li, W. Spangenburg, and P.E. Long. 1992. Microbiology of vadose zone paleosols in south-central Washington state. *Microbial Ecology* 23, no. 3: 279–301.

Camobreco, V.J., B.K. Richards, T.S. Steenhuis, J.H. Peverly, and M.B. McBride. 1996. Movement of heavy metals through undisturbed and homogenized soil columns. *Soil Science* 161, no. 11: 740–750.

Darnault, C.J.D., T.S. Steenhuis, P. Garnier, Y.-J. Kim, M.B. Jenkins, W.C. Chiorse, P.C. Baveye, and J.-Y. Parlange. 2004. Preferential flow and transport of Cryptosporidium parvum oocysts through the vadose zone: Experiments and modeling. *Vadose Zone* 3, no. 2: 262–270.

Davidson, J.M., G.H. Brusewitz, D.R. Baker, and A.L. Wood. 1975. Use of soil parameters for describing pesticide movement through soils. EPA 660/2-75-009. U.S. EPA, Washington, D.C.

Dekker, L.W., and C.J. Ritsema. 1994. Fingered flow: The creator of sand columns in dune beach sands. *Earth Surface Processes and Landforms* 19, no. 2: 153–164.

DelVecchio, G.M., and D.A. Haith. 1993. Probabilistic screening of ground-water contaminants. *ASCE Journal of Environmental Engineering* 119, no. 2: 287–299.

Federle, T.W., D.C. Dobbins, and J.R. Thornton-Manning. 1986. Microbial biomass, activity, and community structure in subsurface soil. *Ground Water* 24, no. 3: 365–374.

Fettr, C.W. 2001. *Applied Hydrogeology*, 4th ed. Upper Saddle River, New Jersey: Prentice-Hall Inc.

Franklin, R.E., V.L. Quizenberry, B.J. Gossett, and E.C. Murdock. 1994. Selection of herbicide alternatives based on probable leaching to groundwater. *Weed Technology* 8, no. 1: 6–16.

Gazis, C., and X.H. Feng. 2004. A stable isotope study of soil water: Evidence for mixing and preferential flow paths. *Geoderma* 119, no. 1–2: 97–111.

Geohring, L.D., P.E. Wright, T.S. Steenhuis, and M.F. Walter. 1999. Subsurface drain water quality impacts from manure applications. NABEC Paper No. 9905 presented at NE Agricultural/Biological Engineering Conference, Lancaster, Pennsylvania.

Grayman, W.M. 1977. Geographic information system for hydro-logic-simulation and analysis. *Transactions of the American Geophysical Union* 58, no. 8: 383.

Haan, C.T. 1971. Movement of pesticides by runoff and erosion. *Transactions of the ASAE* 14, no. 3: 445–449.

Hamaker, J.W. 1972. Decomposition: Quantitative aspects. In *Organic Chemicals in the Soil Environments* (in two volumes), ed. C.A.I. Goring and J.W. Hamaker, 253–340. New York: Marcel Dekker Inc.

Hamlett, J.M., D.A. Miller, R.L. Day, G.W. Peterson, G.M. Baumer, and J. Russo. 1992. Statewide GIS-based ranking of watersheds for agricultural pollution prevention. *Journal of Soil Water Conservation* 47, no. 5: 399–404.

Heilig, A., T.S. Steenhuis, M.T. Walter, and S. Herbert. 2003. Funneled flow mechanisms in layered soil: Field investigation. *Journal of Hydrology* 279, no. 1-4: 210–223.

Helling, C.S., P.C. Kearny, and M. Alexander. 1971. Behavior of pesticides in soils. In *Advances in Agronomy*, vol. 23, ed. N.C. Brady, 147–240. New York: Academic Press.

Hill, D.E., and J.-Y. Parlange. 1972. Wetting front instability in layered soils. *Soil Science Society of America Proceedings* 36, no. 5: 697–702.

Jarvis, N.J., P.E. Jansson, P.E. Dik, and I. Messing. 1991. Modeling water and solute transport in macroporous soil: 1. Model description and sensitivity analysis. *Soil Science* 42, no. 1: 59–70.

Kim, Y.-J., C.J.G. Darnault, N.O. Bailey, J.-Y. Parlange, and T.S. Steenhuis. 2005. An equation for describing solute transport in field soils with preferential flow paths. *Soil Science Society of America Journal*. 69, no. 2: 291–300.

Kruger, E.L., P.J. Rice, J.C. Anhalt, T.A. Anderson, and J.R. Coats. 1997. Comparative fates of atrazine and deethylatrazine in sterile and nonsterile soils. *Journal of Environmental Quality* 26: no. 1: 85–101.

Kung, K.-J.S. 1990. Preferential flow in a sandy vadose zone: 2. Mechanisms and implications. *Geoderma* 46, no. 1-3: 59–71.

Logsdon, S.D. 2002. Determination of preferential flow model parameters. *Soil Science Society of America Journal* 66, no. 4: 1095–1103.

Mbuya, O.S., P. Nkedi-Kizza, and K.J. Boote. 2001. Fate of atrazine in sandy soil cropped with sorghum. *Journal of Environmental Quality* 30, no. 1: 71–77.

Miller, T.S., D.A. Sherwood, P.M. Jeffers, and N. Mueller. 1998. Hydrology, water-quality, and simulation of ground-water flow in a glacial aquifer system, Cortland County, New York. USGS Water-Resources Investigations Report 96–4255. NY USGS, Washington, D.C. 84 pages.

Nguyen, H., J. Nieber, P. Oduro, C. Ritsema, L. Dekker, and T.S. Steenhuis. 1998. Modeling solute transport in a water repellent soil. *Journal of Hydrology* 215, no. 1-4: 188–201.

Nizeyimama, E., G.W. Peterson, M.C. Anderson, B.M. Evans, J.M. Hamlett, and G.M. Baumer. 1996. Statewide GIS/census data assessment of nitrogen loadings from septic systems in Pennsylvania. *Journal of Environmental Quality* 25, no. 2: 346–354.

Panno, S.V., and W.R. Kelly. 2004. Nitrate and herbicide loading in two groundwater basins of Illinois' sinkhole plain. *Journal of Hydrology* 290, no. 3–4: 229–242.

Panno, S.V., W.R. Kelly, C.P. Weibel, I.G. Krapac, and S.L. Sargent. 2002. Water quality and agrichemical loading in two groundwater basins of Illinois' sinkhole plain. Environmental Geology Report. Champaign, Illinois: Illinois State Geological Survey.

Parlange, J.-Y., T.S. Steenhuis, R.J. Glass, T.L. Richard, N.B. Pickering, W.J. Waltman, N.O. Bailey, M.S. Andreini, and J.A. Throop. 1988. The flow of pesticides through preferential paths in soils. *New York's Food & Life Science Quarterly* 18, no. 1: 20–23.

Peranginangin, N. 2003. A simple model for predicting the fate of preferentially moving pesticides in a structured soil. Unpublished doctoral thesis, Dept. of Biological and Environmental Engineering Cornell University, Ithaca, New York.

Peterson, G.W., J.M. Harmlett, S. Harrison, S.R. Messier, B.M. Evans, G.M. Baumer, and M.C. Anderson. 1996. *GIS Pesticide Vulnerability Assessment Procedure for Pennsylvania Public Water Systems*. University Park, Pennsylvania: Penn State Environmental Resources Research Institute.

Pivetz, B.E., and T.S. Steenhuis. 1995. Soil matrix and macropore biodegradation of 2,4-D. *Journal of Environmental Quality* 24, no. 4: 564–570.

Priestly, C.H.B., and R.J. Taylor. 1972. On the assessment of surface heat flux and evaporation using large-scale parameters. *Monthly Weather Review* 100, no. 2: 81–92.

Quisenberry, V.L., and R.E. Phillips. 1976. Percolation of surface-applied water in the field. *Soil Science Society of America Journal* 40, no. 4: 484–489.

Ramos, C., and E.A. Carbonell. 1991. Nitrate leaching and soil-moisture prediction with the LEACHM model. *Fertilizer Research* 27, no. 2–3: 171–180.

Ritsema, C.J., and L.W. Dekker. 1995. Distribution flow—A general process in the top layer of water repellent soils. *Water Resources Research* 31, no. 5: 1187–1200.

Selker, J.S., T.S. Steenhuis, J.-Y. Parlange. 1996. An engineering approach to fingered vadose pollutant transport. *Geoderma* 70, no. 2-4: 197–206.

Shalit, G., and T.S. Steenhuis. 1996. A simple mixing layer model predicting solute flow to drainage lines under preferential flow. *Journal of Hydrology* 183, no. 1–2: 139–150.

Shaw, L.J., and R.G. Burns. 1998. Biodegradation of 2,4-D in a noncontaminated grassland soil profile. *Journal of Environmental Quality* 27, no. 6: 1464–1471.

Sinkevich, M.G. Jr. 2004. A GIS interpretation of a hazard index for pesticide contamination in groundwater. Unpublished master's thesis, Dept. of Biological and Environmental Engineering, Cornell University, Ithaca, New York.

Smith, C.N., R.A. Leonard, G.W. Langdale, and G.W. Bailey. 1978. Transport of agricultural chemicals from small upland Piedmont watersheds. EPA-600/3-78-056. Athens, Georgia: U.S. EPA and Agricultural Research Service, USDA.

Stagnitti, F., J.-Y. Parlange, T.S. Steenhuis, B. Nijssen, and D. Lockington. 1994. Modeling the migration of water-soluble contaminants through preferred paths in the soils. In *Groundwater Quality Management*, ed. K. Kovar and J. Soveri, 367–379. IAHS Publication No. 220. IASH, Wallingford, U.K.

Steenhuis, T.S., J. Boll, G. Shalit, J.S. Selker, and I.A. Merwin. 1994. A simple equation for predicting preferential flow solute concentrations. *Journal of Environmental Quality* 23, no. 5: 1058–1064.

Steenhuis, T.S., Y.J. Kim, J.-Y. Parlange, M.S. Akhtar, B.K. Richards, K.-J.S. Kung, T.J. Gish, L.W. Dekker, C.J. Ritsema, and S.A. Aburime. 2001. An equation for describing solute transport in field soils with preferential flow paths. In *Preferential Flow, Water Movement and Chemical Transport in the Environment, Proceedings of the ASAE 2nd International Symposium*, Honolulu, Hawaii, January 3–5, 2001, ed. D.D. Bosch and K.W. King, 137–140. St. Joseph, Michigan: ASAE.

Steenhuis, T.S., and L.M. Naylor. 1987. A screening method for preliminary assessment of risk to groundwater from land-applied chemicals. *Journal of Contaminant Hydrology* 1, no. 1: 395–406.

Steenhuis, T.S., S. Pacenka, and K.S. Porter. 1987. MOUSE: A management model for evaluating groundwater contamination from diffuse surface sources aided by computer graphics. *Applied Agricultural Research* 2, no. 4: 277–289.

Steenhuis, T.S., and J.-Y. Parlange. 1991. Preferential flow in structured and sandy soils. In *Proceedings of the National ASAE Symposium on Preferential Flow*, Chicago, Illinois, 12–21. ASAE, St. Joseph, Michigan.

Steenhuis, T.S., J.-Y. Parlange, and M.S. Andreini. 1990. A numerical model for preferential solute movement in structured soils. *Geoderma* 46, no. 1-3: 193–208.

Steenhuis, T.S., and W.H. van der Molen. 1986. The Thornthwaite-Mather procedure as a simple engineering method to predict recharge. *Journal of Hydrology* 84, no. 3–4: 221–229.

SWL—Preferential Flow Website. 2005. www.bee.cornell.edu/swlab/SoilWaterWeb/Research/pfweb/.Accessed March 2003.

Thornthwaite, C.W., and J.R. Mather. 1955. The water balance. Laboratory of Climatology, No. 8. Centerton, New Jersey.

Tindall, J.A., and W.K. Vencill. 1995. Transport of atrazine, 2,4-D, and dicamba through preferential flow paths in an unsaturated claypan near Centralia, Missouri. *Journal of Hydrology* 166, no. 1–2: 37–59.

Toride, N., F.J. Leji, and M.T. Van Genuchten. 1995. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.0. Research Report 137. Riverside, California: U.S. Salinity Lab.

United States Department of Commerce, Weather Bureau. 1961. Rainfall frequency atlas of the US for durations from 30 minutes to 24 hours and return periods from 1 to 100 years. Technical Paper #40. U.S. Weather Bureau, Washington, D.C.

Vanclooster, M., J.J. T. I. Boesten, and M. Trevisan. 2000. Mathematical modeling for assessing pesticide leaching in agricultural soils at the field scale. In *Pesticide/Soil Interactions: Some Current Research Methods*, ed. J. Cornejo and P. Jamet, 407–430. Paris, France: Institut National De La Recherche Agronomique (INRA).

Van der Heyden, V., P. Debongnie, and L. Pussemier. 1997. Accelerated degradation and mineralization of atrazine in surface and subsurface soil materials. *Pesticide Science* 49, no. 3: 237–242.

Varni, M.R., and E.J. Usunoff. 1999. Simulation of regional-scale groundwater flow in the Azul River basin, Buenos Aires Province, Argentina. *Hydrogeology Journal* 7, no. 2: 180–187.

Wagenet, R.J., and J.L. Hutson. 1986. Predicting the fate of nonvolatile pesticides in the unsaturated zone. *Journal of Environmental Quality* 15, no. 4: 315–322.

Walter, M.F. 1974. Movement of nitrogen in cool climates. Unpublished Ph.D. thesis, Department of Agricultural Engineering, University of Wisconsin, Madison.

Walter, M.T., J.-S. Kim, T.S. Steenhuis, J.-Y. Parlange, A. Heilig, R.D. Braddock, J. Selker, and J. Boll. 2000. Funneled flow mechanisms in sloping layered soil: Laboratory investigation. *Water Resources Research* 36, no. 4: 841–849.

Biographical Sketches

Michael G. Sinkevich Jr is a Graduate Student, M.S. at the Department of Biological and Environmental Engineering, Cornell University, Ithaca, New York.

M. Todd Walter, corresponding author, is an Assistant Professor at the Department of Biological and Environmental Engineering, Cornell University, Ithaca, New York; (607) 255-2488; fax (607) 255-4080; mtw5@cornell.edu.

Arthur J. Lembo Jr is a Senior Extension Associate at the Department of Crops and Soil Science, Cornell University, Ithaca, New York.

Brian K. Richards is a Senior Research Associate at the Department of Biological and Environmental Engineering, Cornell University, Ithaca, New York.

Natalia Peranginangin is a Graduate Student, Ph.D. at the Department of Biological and Environmental Engineering, Cornell University, Ithaca, New York,

Sunnie A. Aburime is a Professor at the Department of Engineering, Clark Atlanta University, Atlanta, GA 50314.

Tammo S. Steenhuis is a Professor at the Department of Biological and Environmental Engineering, Cornell University, Ithaca, New York.