Vulnerability of Ground Water to Atrazine Leaching in Kent County, Michigan

by D.J. Holtschlag and C.L. Luukkonen

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 96-4198

Prepared in cooperation with
Michigan Department of Agriculture

Lansing, Michigan
1997

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, *Director*

For additional information write to:

Chief, Michigan District
U.S. Geological Survey
Water Resources Division
6520 Mercantile Way, Suite 5
Lansing, MI 48911

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver Federal Center
Denver, CO 80225-0286

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS

Multiply	By	To Obtain
inch (in)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
cubic feet per second (ft^3/s)	0.02832	cubic meter per second
million gallons per day (Mgal/d)	0.04381	cubic meter per second

Temperature in degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) as follows: °C = 5/9 (°F - 32).

Sea Level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

VULNERABILITY OF GROUND WATER TO ATRAZINE LEACHING IN KENT COUNTY, MICHIGAN

By D.J. Holtschlag and C.L. Luukkonen

ABSTRACT

A steady-state model of pesticide leaching through the unsaturated zone was used with readily available hydrologic, lithologic, and pesticide characteristics to estimate the vulnerability of the near-surface aquifer to atrazine contamination from non-point sources in Kent County, Michigan. The modelcomputed fraction of atrazine remaining at the water table, *RM*, was used as the vulnerability criterion; time of travel to the water table also was computed. Model results indicate that the average fraction of atrazine remaining at the water table was 0.039 percent; the fraction ranged from 0 to 3.6 percent. Time of travel of atrazine from the soil surface to the water table averaged 17.7 years and ranged from 2.2 to 118 years.

Three maps were generated to present three views of the same atrazine vulnerability characteristics using different metrics (nonlinear transformations of the computed fractions remaining). The metrics were chosen because of the highly (right) skewed distribution of computed fractions. The first metric, $rm = RM^{\lambda}$ (where λ was 0.0625), depicts a relatively uniform distribution of vulnerability across the county with localized areas of high and low vulnerability visible. The second metric, $rm^{\lambda^{-0.5}}$, depicts about one-half the county at low vulnerability with discontinuous patterns of high vulnerability evident. In the third metric, $rm^{\lambda^{-1.0}}$ (*RM*), more than 95 percent of the county appears to have low vulnerability; small, distinct areas of high vulnerability are present.

Aquifer vulnerability estimates in the *RM* metric were used with a steady-state, uniform atrazine application rate to compute a potential concentration of atrazine in leachate reaching the water table. The average estimated potential atrazine concentration in leachate at the water table was 0.16 μg/L (micrograms per liter) in the model area; estimated potential concentrations ranged from 0 to 26 μg/L. About 2 percent of the model area had estimated potential atrazine concentrations in leachate at the water table that exceeded the USEPA (U.S. Environmental Protection Agency) maximum contaminant level of 3 μg/L.

Uncertainty analyses were used to assess effects of parameter uncertainty and spatial interpolation error on the variability of the estimated fractions of atrazine remaining at the water table. Results of Monte Carlo simulations indicate that parameter uncertainty is associated with a standard error of 0.0875 in the computed fractions (in the *rm* metric). Results of kriging analysis indicate that errors in spatial interpolation are associated with a standard error of 0.146 (in the *rm* metric). Thus, uncertainty in fractions remaining is primarily associated with spatial interpolation error, which can be reduced by increasing the density of points where the leaching model is applied.

A sensitivity analysis indicated which of 13 hydrologic, lithologic, and pesticide characteristics were influential in determining fractions of atrazine remaining at the water table. Results indicate that fractions remaining are most sensitive to the unit changes in pesticide half life and in organic-carbon content in soils and unweathered rocks, and least sensitive to infiltration rates.

The leaching model applied in this report provides an estimate of the vulnerability of the near-surface aquifer in Kent County to contamination by atrazine. The vulnerability estimate is related to water-quality criteria developed by the USEPA to help assess potential risks from atrazine to the near-surface aquifer. However, atrazine accounts for only 28 percent of the herbicide use in the county; additional potential for contamination exists from other pesticides and pesticide metabolites. Therefore, additional work is needed to develop a comprehensive understanding of the relative risks associated with specific pesticides. The modeling approach described in this report provides a technique for estimating relative vulnerabilities to specific pesticides and for helping to assess potential risks.

INTRODUCTION

Synthetic organic pesticides are routinely used in the United States to increase crop yields by controlling weeds, insects, and other organisms. Nationwide use of pesticides started in about 1952 and has grown from about 540 million pounds of active ingredient in 1964 to about 1.1 billion pounds in 1993 (U.S. Geological Survey, 1993). About 75 percent of this total is used for agricultural production.

Herbicides are applied to 98 percent of crop acreage and insecticides are used on 27 percent of the acreage (National Agricultural Statistics Service, 1994). In the United States, about 60 percent of all pesticide use occurs within 12 midwestern states (Koplin and others, 1995, p. 1125). An estimated 12.6 million pounds of herbicide are used annually in Michigan; atrazine, with an estimated application of 2.71 million pounds per year, is the herbicide used in the greatest quantity (Gianessi and Puffer, 1991).

Although increased pesticide use has resulted in increased food production, concerns about the potential adverse effects of pesticides on human health and the environment have also increased. In response to these concerns and available data on adverse impacts, the USEPA (U.S. Environmental Protection Agency, 1992) has established maximum contaminant levels (MCL) and health advisory levels for some pesticides in drinking water. For example, the MCL for atrazine is 3 micrograms per liter (μg/L). However, few standards for drinking water or limits for aquatic ecosystems have been established for pesticide metabolites, although some of these constituents also may adversely affect water quality.

The greatest potential for adverse effects of pesticides is through contamination of the hydrologic system. Water is the primary means by which pesticides are transported from their areas of application to other parts of the environment. Pesticides and their metabolites are commonly present at low concentrations in ground water beneath agricultural areas, but only seldom at concentrations that exceed water-quality standards. However, frequencies of detection of pesticides in ground water may also be substantial in non-agricultural settings such as golf courses, commercial and residential areas, rights-of-way, and timber production areas (U.S. Geological Survey, 1995a).

In a study of the distribution of pesticide contamination in the Midwest, Koplin and others (1995, p. 1131) detected pesticides or their metabolites in water samples from about 29 percent of 303 wells in near-surface aquifers. In particular, atrazine was detected in 20.8 percent of the 303 wells in a 1991 survey when the reporting level was 0.05 μg/L. Atrazine detection increased to 43 percent in resampling of 100 wells in 1992, when more sensitive analytical procedures were used with a lower reporting limit (0.003 μg/L). Any ground water determined to have entered the ground before 1953 on the basis of tritium analysis would predate significant wide-spread use of pesticides. Koplin and others (1995) report that pesticides were detected in only 15.8 percent of sampled wells containing pre-1953 water. In contrast, pesticides were detected in 70.3 percent of sampled wells containing post-1953 water.

Many other pesticides follow pathways through the hydrologic system similar to atrazine. That is, following detection of atrazine, there was an increased likelihood of detecting other pesticides or metabolites of pesticides (Koplin and others, 1995).

In order to provide a screening tool for estimating aquifer vulnerability, Michigan Department of Agriculture and U.S. Geological Survey entered into a cooperative agreement as part of the Michigan Groundwater Stewardship Program. This aggreement supported the analysis of aquifer vulnerability described in this report.

Purpose and Scope

The purpose of this report is to provide a method for estimating the vulnerability of near-surface aquifers to atrazine contamination from non-point sources by leaching through the unsaturated zone to the water table. An estimate of the potential concentration of atrazine in leachate at the water table is computed to help assess risk. Only those techniques that could be readily applied over county-sized areas with existing data were considered when developing this method. The variability of the vulnerability estimate is estimated with respect to uncertainty in hydrologic, lithologic, and atrazine characteristics and to spatial interpolation error. Sensitivity to uncertainty in leaching model parameters is also estimated.

This vulnerability estimate is not intended to be used to predict atrazine concentrations in ground water or vulnerability associated with small scale (less than 94.7 acres) hydrologic or lithologic features, or well construction characteristics. Prediction of pesticide concentrations in ground water would require additional information, including historical data on pesticide loading rates, application of an unsteady ground-water flow and transport model that would properly account for pesticide movement and transformation through both the saturated and unsaturated zones, and time series data of pesticide concentrations at numerous locations within the study area for model calibration. Other studies have shown only limited ability to predict pesticide concentrations on the basis of either vulnerability assessments or simulation models (U.S. Geological Survey, 1995b).

Acknowledgments

The authors gratefully acknowledge the assistance of Joe T. Ritchie, Crop and Soil Sciences, and Theodore L. Loudon, Agricultural Engineering, Michigan State University for providing information on soil properties, Shirley Businski, Michigan Department of Environmental Quality, for providing well log data in electronic format needed to implement the modeling procedure, and Mark Swartz, Michigan Department of Agriculture, for providing comments and suggestions that improved the analysis and the report.

Description of the study area and pesticide use

Kent County, which has an area of about 856 mi^2, is in the western part of the lower peninsula of Michigan (fig. 1). The population of Kent County in 1990 was 500,631; most of this population, 436,033, lives in the Grand Rapids metropolitan area, which is located in the southwestern part of the county (U.S. Department of Commerce, 1996). Surficial deposits are unconsolidated materials of glacial origin that generally range in thickness from about 10 to 400 feet. Deposits are primarily medium- and fine-textured till, outwash sand and gravel, and postglacial alluvium (Farrand and Bell, 1984).

In 1992, 241 mi^2 within the county were classified as cropland; about 77 percent of this cropland was harvested and 42 percent was treated with sprays to control weeds (U.S. Department of Census, 1994). The distribution of 575 mi^2 of cropland and pasture in Kent County (U.S. Geological Survey, 1992, fig. 2) provides a general indication of the location of agricultural areas in the county.

In 1990, an estimated 202,192 pounds of herbicides (table 1) were applied to crops in Kent County (Gianessi and Puffer, 1991). About 27.9 percent of herbicide applications were atrazine (56,382 pounds); only field corn and sweet corn receive direct applications of atrazine. In 1994, 65.6 mi^2 were planted in corn (Michigan Agricultural Statistics Service, 1995, p. 88). The next most commonly used herbicide, metolachlor, accounted for 14.2 percent (28,741 pounds) of the total amount of herbicides applied.

METHODS FOR ASSESSING AQUIFER VULNERABILITY

Assessment methods are commonly used in pesticide management to select sites for monitoring and to prioritize areas for enhanced protection. Assessment methods have been classified into two categories (U.S. Environmental Protection Agency, 1993, p. 27). Aquifer sensitivity methods provide assessments on the basis of hydrogeologic factors alone. Ground-water vulnerability methods provide assessments on the basis of pesticide and management factors as well as hydrogeologic factors.

Ground-water vulnerability methods have been subdivided into pesticide leaching methods,

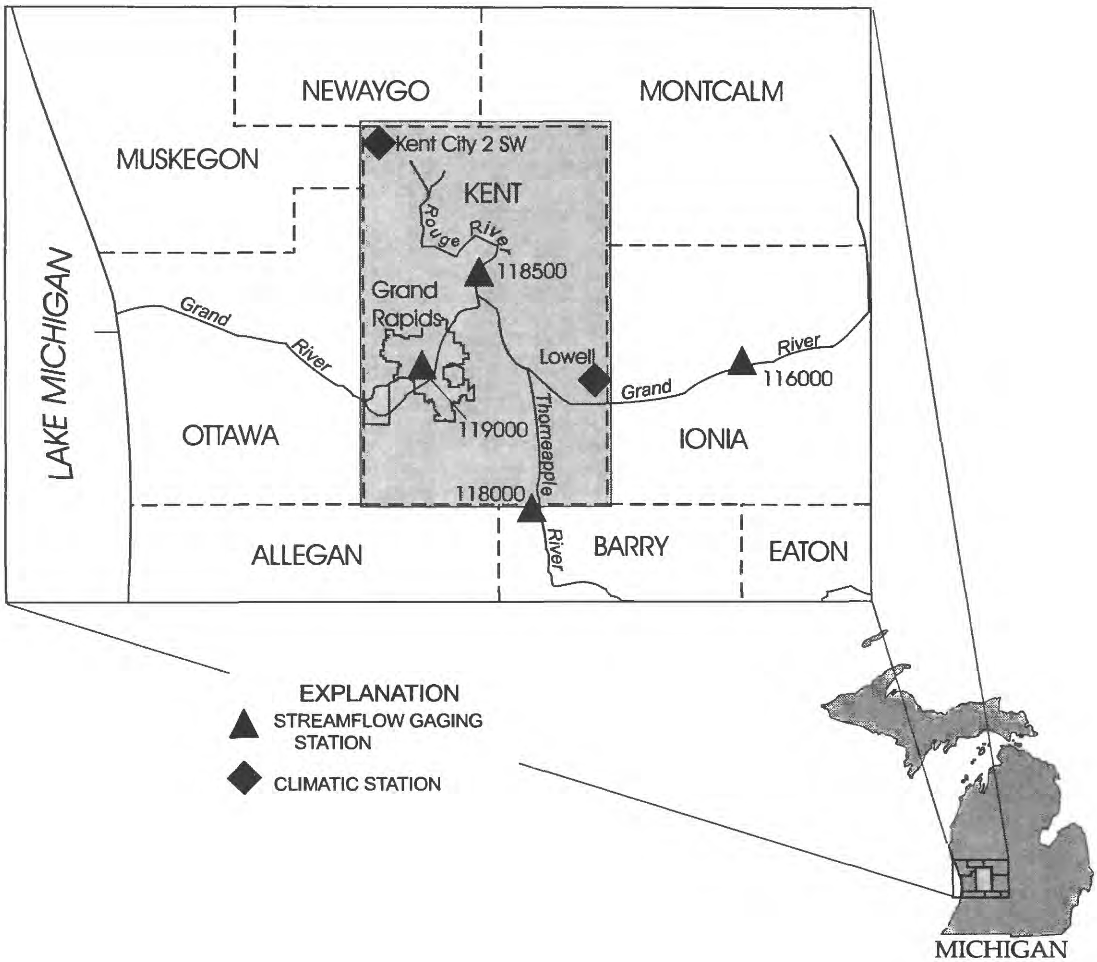
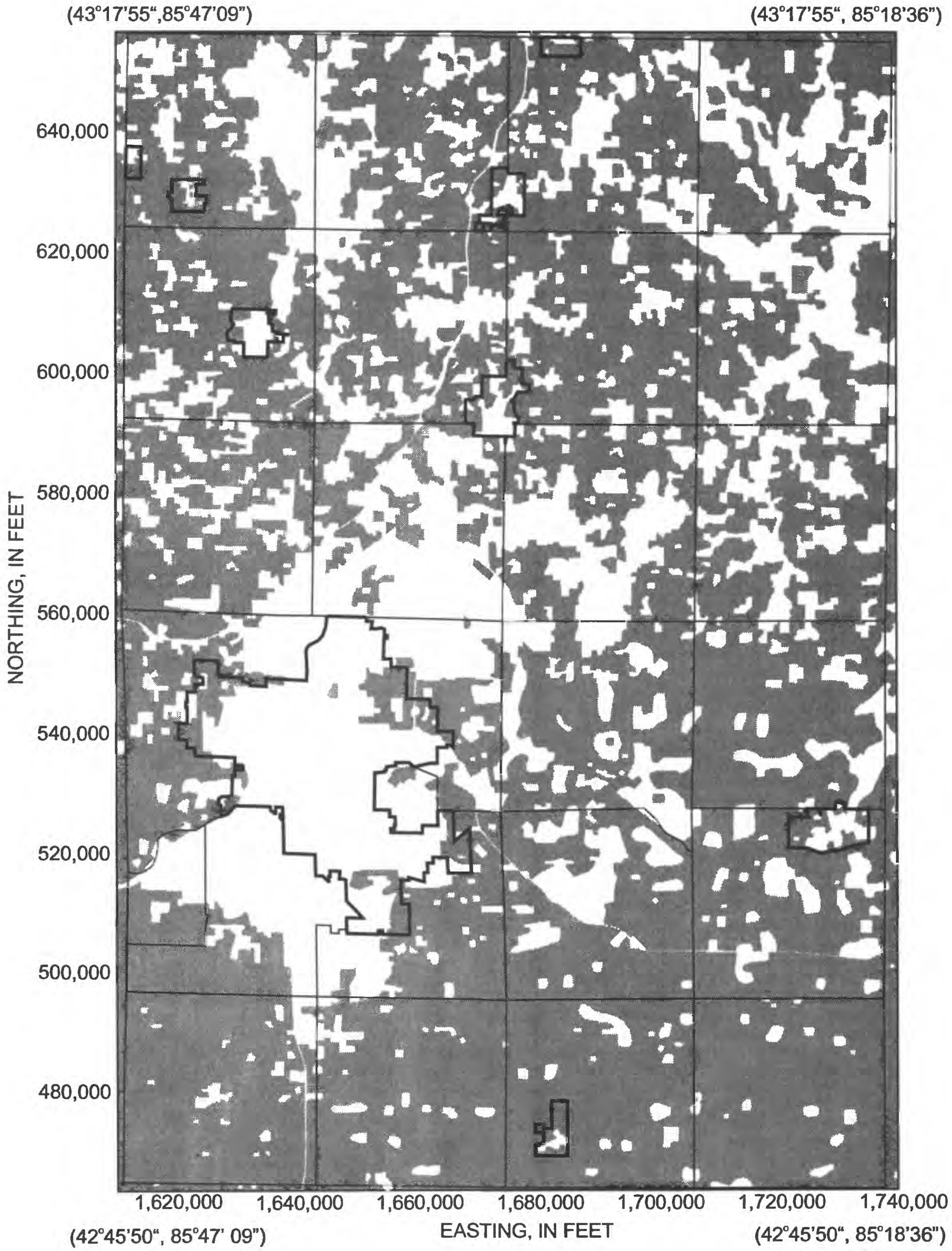


Figure 1. Location of Kent County, Michigan.



EXPLANATION

CROPLAND AND PASTURE (Anderson, J.R., Hardy, E.E., Roach, J.T., Witmer, R.E., 1976, A land use and land cover classification system for use with remote sensing data: U.S. Geological Survey Professional Paper 964).

OTHER

Figure 2. Distribution of cropland and pasture in Kent County, Michigan.

Table 1. Estimated annual agricultural use of herbicides in Kent County, Michiga

Herbicide	Annual Application by Crop (pounds)										
	Alfalfa	Apples	Field Corn	Cucumbers	Dry Beans	Pasture	Potatoes	Soybeans	Sweet corn	Other	Total
2-4-D	.	355	3,535	.	.	4,890	.	.	.	659	9,439
Alachlor	.	.	20,118	.	135	.	.	1,298	420	.	21,971
Atrazine	.	.	55,856	.	.	.	.	.	526	.	56,382
Bromoxynil	.	.	896	.	.	.	.	.	.	250	1,146
Butylate	.	.	18,854	.	.	.	.	.	.	.	18,854
Chloramben	.	.		.	2,423	.	.	.	.	595	3,018
Cyanazine	.	.	11,878	.	.	.	.	.	561	.	12,439
Dicamba	.	.	2,126	.	.	2,445	.	.	.	43	4,614
Diuron	.	1,065	.	.	.	.	.	.	.	110	1,175
EPTC	.	.	18,854	.	1,211	.	352	.	.	43	20,460
Glyphosate	.	1,420	1,768	.	7	1,467	29	25	.	234	4,950
Hexazinone	1,422	.	.	.	.	.	.	.	.	.	1,422
Metolachlor	.	.	25,643	.	1,077	.	408	1,149	421	43	28,741
Naptalam	.	.	.	1,007	.	.	.	.	.	.	1,007
Oryzalin	.	1,597	.	.	.	.	.	.	.	142	1,739
Paraquat	.	852	.	.	.	.	.	.	.	216	1,068
Simazine	1,422	4,259	.	.	.	.	.	.	.	941	6,622
Other	568	796	.	440	387	.	478	2,082	.	.	7,145
Total	3,412	10,344	159,528	1,447	5,240	8,802	1,267	4,554	1,928	5,670	202,192

pesticide loading methods, and simulation models. Pesticide leaching methods include hydrogeologic factors and factors affecting pesticide movement and metabolism; pesticide loading methods combine pesticide use and hydrogeologic factors. Neither pesticide leaching nor pesticide loading methods include management factors. Simulation models describe the transport and fate of pesticides in soil and aquifer systems by use of mathematical expressions related to physical and chemical processes (U.S. Environmental Protection Agency, 1993, p. 27).

Selection of assessment methods is resource and problem dependent. On the basis of the need to provide a screening tool for estimating aquifer vulnerability over county-sized areas with limited information on pesticide loading and farm management practices, this report uses a vulnerability assessment based upon pesticide leaching methods.

PESTICIDE LEACHING MODEL

Model Description

In this report, pesticide leaching is described by a steady-state unsaturated-zone transport model developed by Rutledge and Helgesen (1991). The model calculates fraction of pesticide remaining and time of travel in the unsaturated zone as a function of depth. The model allows for multiple lithologic layers in the unsaturated zone, water-content variation with depth, pesticide retardation caused by partitioning, pesticide-decay rates that vary between layers, and root uptake of pesticides. The transport model contains numerous variables associated with hydrologic, lithologic, and pesticide characteristics that must be specified for model application.

The pesticide transport model contains the following assumptions: (1) water content in the unsaturated zone may be described as a static function of elevation above the water table; (2) water flux is steady, is downward, and is diminished linearly with depth in the root zone; (3) all water in the unsaturated zone transports pesticides; (4) water initially present in the profile is completely displaced downward by water entering from above; (5) pesticides are in aqueous phase or are absorbed; (6) adsorption is described by a linear, reversible equilibrium relation; (7) pesticide decay is an irreversible first-order reaction; (8) pesticides occur at concentrations small enough that the capacities for adsorption and decay of the pesticides by materials in the unsaturated zone are not exhausted; (9) pesticide loss in the root zone is proportional to root uptake of water and subsurface runoff, and (10) pesticides are applied at land surface at a constant rate, pesticide flux is steady state everywhere, and dispersion of pesticides is negligible. Although these assumptions may limit the applicability of the model results for quantitative estimation of concentrations of constituents in ground water, these limitations become less significant if model results are used in a comparative sense.

In this report, the criterion for vulnerability is the fraction of atrazine remaining at the water table. This fraction is affected by the attrition of the atrazine from root uptake, the movement of atrazine directly into surface-water bodies, the time of travel of atrazine through the unsaturated zone, and atrazine decay into metabolites.

In the leaching model, numerical integration is used to determine time of travel defined as

$$t_i = \int_0^{z_i} \frac{1}{v} dz , \qquad (1)$$

where t_i = time of travel (T, time) for transport of atrazine from land surface to z_i, and

z_i = the depth of interest below land surface (L, length);

v = the vertical velocity of water (LT^{-1}, length per time).

The vertical velocity can also be expressed as:

$$v = \frac{q}{\theta R} , \qquad (2)$$

where q = the volumetric water flux per unit surface area (LT^{-1}),

θ = the volumetric water content (dimensionless).

R = the retardation factor of pesticide transport, which is the ratio of the average velocity of water to the average velocity of atrazine.

Water flux (q) at the land surface ($z=0$) is set equal to the infiltration rate and, at the bottom of the root zone, is set equal to the rate of deep percolation. For all depths within the root zone, water flux is interpolated linearly between these two values. Water flux below the root zone is equal to the rate of deep percolation.

The model determines the volumetric water content at a given point as a function of the elevation of that point above the water table (h). The volumetric water content varies with the air-entry level (capillary rise, in feet), the residual moisture content (fraction), field capacity (fraction), and the porosity (fraction) (Rutledge and Helgesen, 1991, p. 3).

The retardation factor R is computed as

$$R = 1 + \frac{\rho_b K_d}{\theta}, \quad (3)$$

where ρ_b = bulk density (ML^{-3} for mass, M), and

K_d = distribution coefficient (L^3M^{-1}).

Bulk density and distribution coefficient are constant within any given layer but may vary from one layer to another. Bulk density is calculated from

$$\rho_b = \rho_s(1-\eta), \quad (4)$$

where ρ_b = density of the solid material in the unsaturated zone (ML^{-3}), and

η = porosity.

In this report, it is assumed that the bulk density ρ_s = 165 pounds per cubic foot. K_d is calculated for each layer from:

$$K_d = \frac{K_{oc} P_{oc}}{100}, \quad (5)$$

where K_{oc} = organic-carbon partition coefficient (L^3M^{-1}) of the pesticide, and

P_{oc} = percentage of organic carbon in the layer.

Combining equations 2, 3, and 4:

$$t_i = \int_0^{z_i} \frac{1}{q}[\theta + \rho_b K_d]\,dz. \quad (6)$$

The pesticide transport model (Rutledge and Helgesen, 1991) describes pesticide decay rates by use of a differential equation for irreversible first-order reactions as:

$$\frac{dC}{dt} = -kC, \quad (7)$$

where C = concentration of atrazine (ML^{-3}),

t = time of travel in the layer of interest (T), and

k = a constant.

After integrating, rearranging, and substitution, this equation can be written

$$RM = e^{-kt}, \quad (8)$$

where RM is the fraction of atrazine remaining after its transport through the layer. Because RM = 0.5 at t = half life of the pesticide, the equation can be rewritten:

$$RM = e^{-0.693\left(t/t_{\frac{1}{2}}\right)}, \quad (9)$$

where

$t_{\frac{1}{2}}$ = half-life of atrazine in the layer (T).

Equation 9 is solved for each lithology layer in the model. The amount of original pesticide applied to the land surface that remains after transport through all the layers is computed as the product of RM values for each layer. To account for decay and root uptake, the amount of pesticide remaining after decay and adsorption is multiplied by the ratio of the amount of water flux at the depth of interest to the infiltration rate.

Model Application

The pesticide transport model was applied to data available for 5,444 wells in Kent County, Michigan. Infiltration and deep percolation rates were estimated for each well on the basis of continuous precipitation data, gridded recharge data, and a water-budget analysis. Soil characteristics at each well were determined on the basis of county-level soil survey data (U.S. Department of Agriculture, 1986). Well logs were used to identify lithologic characteristics beneath the soil horizon and to determine the depth to the water table. Physical properties of lithologic materials were estimated on the basis of measurements for similar materials in the literature. Atrazine characteristics were determined from information in the USEPA's Pesticide Environmental One-Line Summary (USEPA, Environmental Fate and Effects Division, written commun., 1996). Model estimates of fraction of atrazine remaining at the water table were mapped to cells representing 94.7-acres (0.148 mi^2) across Kent County on the basis of their spatial covariance structure. The following paragraphs describe details of the procedure.

A grid was developed to discretize the heterogeneous hydrologic and lithologic properties of Kent County into more homogeneous blocks. The grid boundaries extend slightly beyond the county borders (fig. 3). The lower left corner of the grid has an easting of 1,610,000 feet and a northing of 464,000 feet, based on the state plane coordinate system; this point corresponds to about 42° 45' 50" north latitude and 85° 47' 09" west longitude. The upper right corner of the grid has an easting of 1,740,000 and a northing of 657,000; this point corresponds to about 43° 17' 55" north latitude and 85° 18' 36" west longitude. The grid partitions the study area into 95 rows and 64 columns of cells. Each cell is indexed by its i^{th} row number and j^{th} column number starting with $i=1$ and $j=1$ at the lower left hand corner of the grid. Cell dimensions are uniform within the study area. Each cell represents a land area of 2,031 feet on a side for a cell area of 94.7 acres. The total area represented by the grid is 900 mi^2.

Hydrologic Factors

Water budget

A water budget (fig. 4) analysis was used to estimate infiltration and deep percolation, which are used in the leaching model to compute the variation of water flux with depth, $q(z)$, from annual precipitation, recharge, and streamflow data. Water budget analysis was based on the following equation:

$$P - DSR = I = ET + SSR + D\bar{P} + \Delta S \qquad (10)$$

where P = Precipitation rate;

DSR = Direct Surface Runoff or runoff from precipitation that does not infiltrate the ground before discharging directly into streams from overland flow;

I = Infiltration of precipitation into the soil, $q(z=0)$;

ET = Evapotranspiration or water loss through evaporation from the soil surface and plant transpiration;

SSR = Subsurface Runoff or runoff from precipitation that infiltrates the soil but does not percolate to the water table before discharging into streams;

DP =Deep percolation or water moving below the plant root zone to the water table, $q(z>r)$, where r is the root depth; and

ΔS =Changeinstorageofwaterwithinthebasin. In the steady-state modeling approach used in this report, long-term changes in storage are assumed to be zero.

Average precipitation within Kent County varies from about 32 in/yr (inches per year) along the eastern half to 34 in/yr near the southwestern corner. Based on a minimum curvature interpolation (Keckler, 1994, p. 5-37) of precipitation isolines (Eichenlaub and others, 1990, p. 91), average precipitation rates were estimated for each cell in the model grid (fig. 5). Average precipitation within the study area is 32.6 in/yr; average precipitation estimates for individual

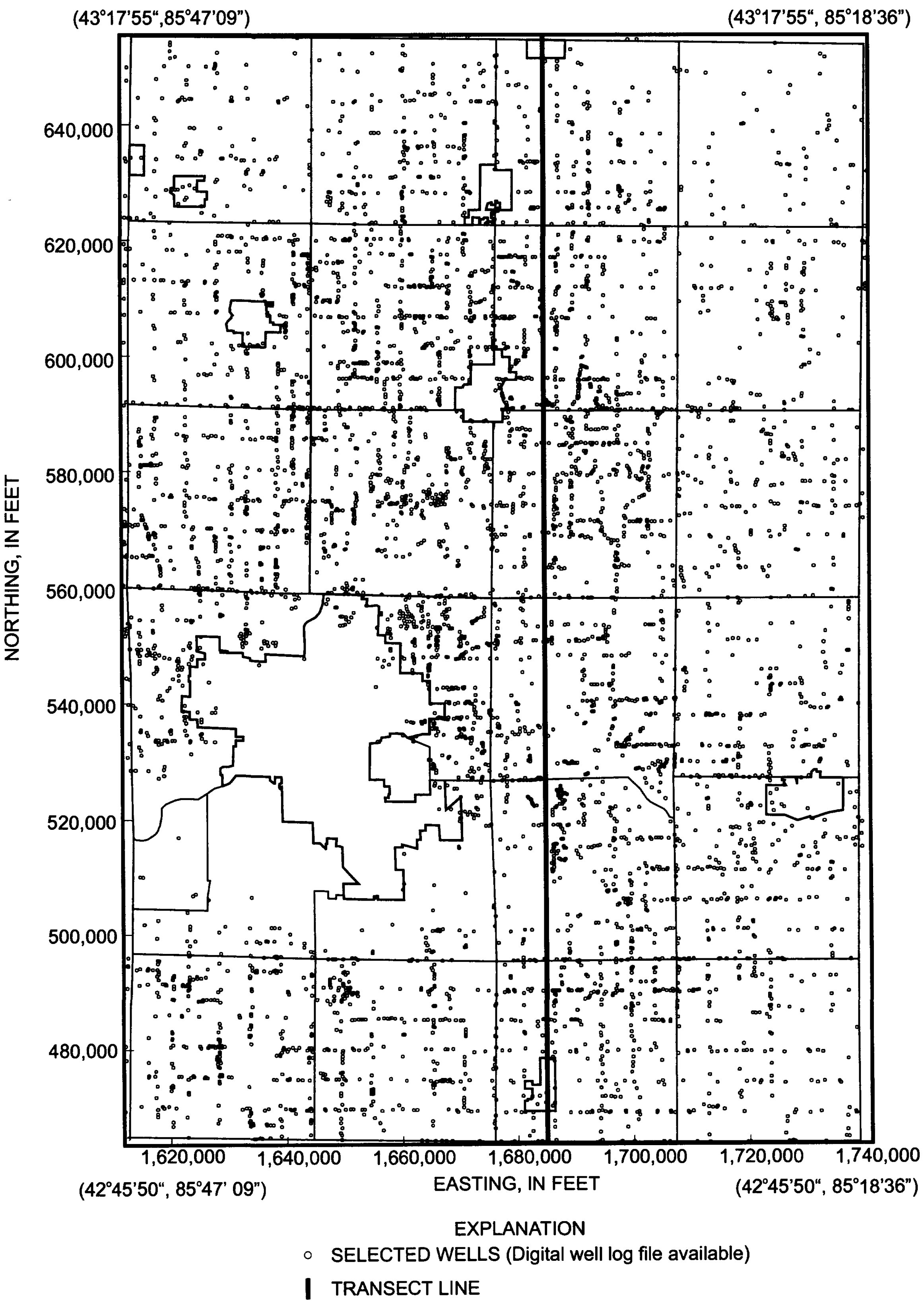


Figure 3. Location of model area in Kent County, Michigan.

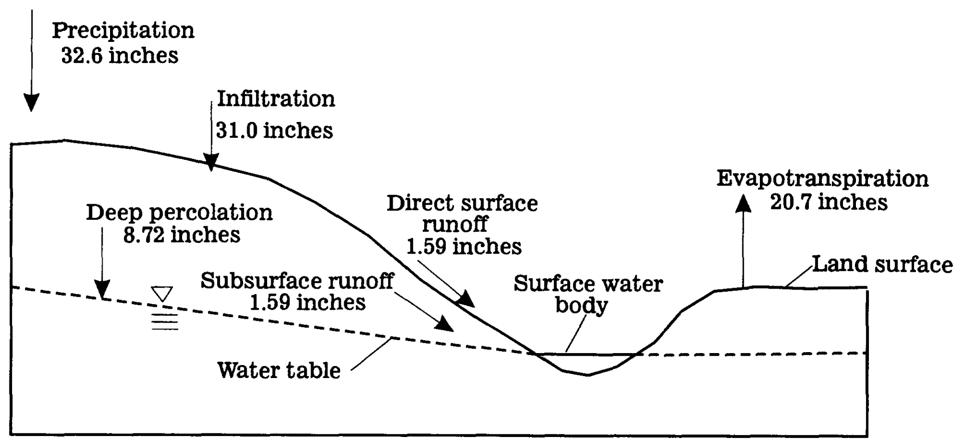


Figure 4. Generalized water budget for Kent County, Michigan.

model cells ranged between 31.9 and 33.5 in/yr.

Long-term climatological stations at Lowell, Michigan (Station Lowell, index number 4944) and Kent City, Michigan (Station Kent City 2 SW, index number 4320) (fig. 1) provide additional information on precipitation characteristics in Kent County. Average precipitation between 1952 and 1993 at the Lowell and Kent City stations was 34.6 and 34.3 in/yr, respectively. Variability of annual precipitation within Kent County was estimated as the variance of the average annual precipitation at the two climatic stations $(5.25 \text{ in/yr})^2$.

In this analysis, precipitation includes only natural precipitation; irrigation is not included. The 1992 Census of Agriculture indicates that 14.1 mi^2 were irrigated in Kent County (U.S. Department of Commerce, 1994). Preliminary results of a 1994 statewide irrigation survey (Ron Van Til, Michigan Department of Environmental Quality, written commun., 1996) documents 974 million gallons of water used for irrigation on 6.20 mi^2 in Kent County. This amount of irrigation, which averages 9 in/yr over irrigated areas, would likely affect the local movement of constituents from the land surface to shallow groundwater aquifers. However, because specific locations of irrigation are not available, irrigation water use can only be represented as an average of about 0.065 inches per year over the entire county. This component of the water budget is less than the uncertainty of other water budget components and was therefore not included as part of the water budget in this report.

Total streamflow (runoff), $RO = DSR + SSR + DP$, was determined by use of 35 years of common streamflow records between 1952 and 1993 from three USGS streamflow gaging stations. Total average runoff, $\overline{RO}$, of 11.9 in/yr within Kent County was estimated on the basis of the average runoff of 10.5 in/yr at Grand River at Grand Rapids, Mich. (station 04119000) (fig. 1) minus 11.4 in/yr of runoff from Thornapple River at Caledonia, Mich. (station 04118000) and 9.65 in/yr of runoff from Grand River at Ionia, Mich. (station 04116000). These reductions were made because Thornapple River at Caledonia, Michigan measures streamflow from counties that are south of Kent County and Grand River at Ionia, Michigan measures streamflow from counties that are east of Kent County. During approximately the same period, runoff averaged 13.9 in/yr from

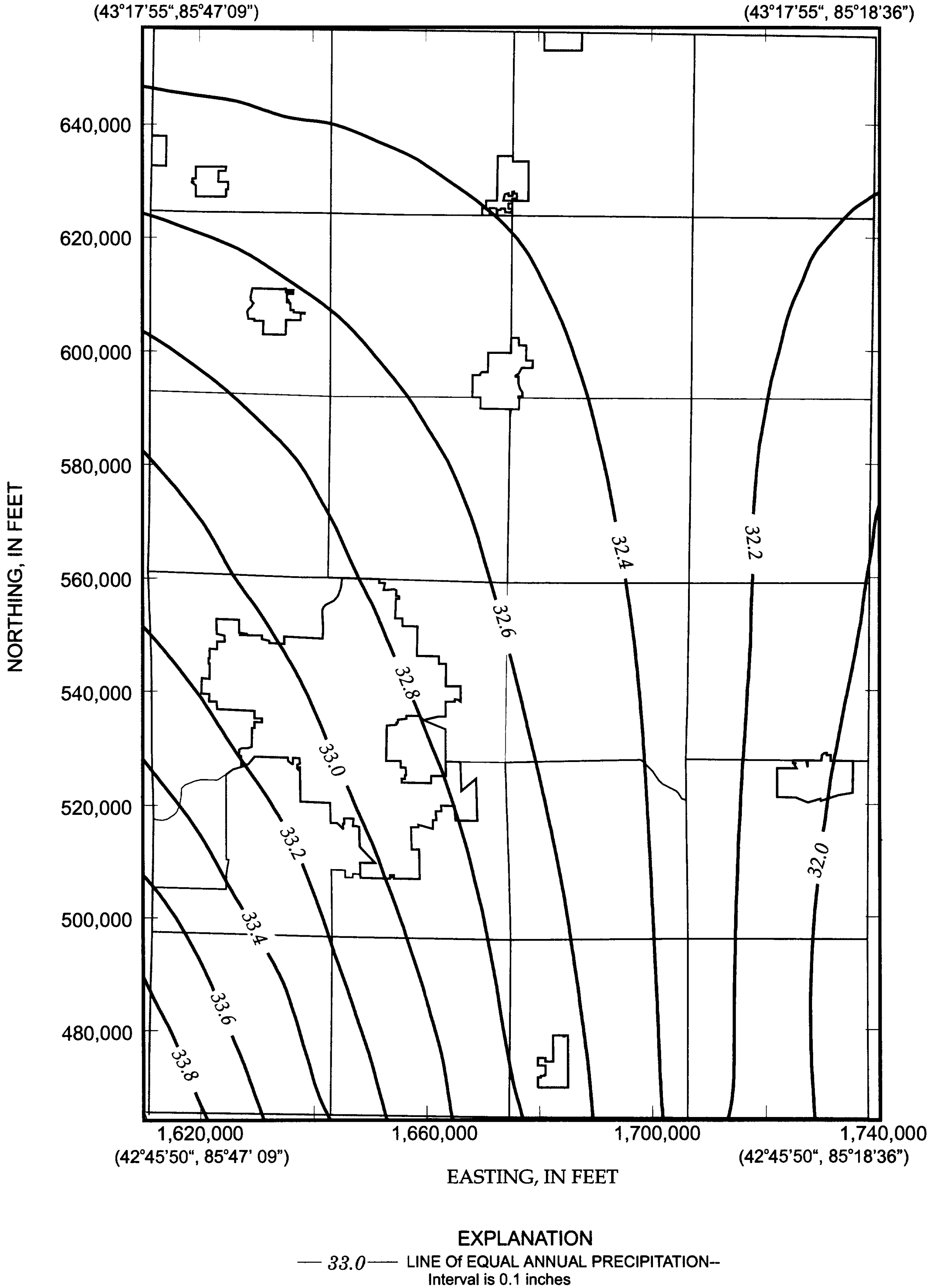


Figure 5. Spatial variation of average precipitation in Kent County, Michigan.

Rouge River near Rockford, Mich. (station 04118500). Runoff at Rouge River, which drains the northwestern part of Kent County, contributes to the higher average runoff in Kent County than the three gaging stations used in the computation of runoff. Among model cells, runoff ranged between 4.89 to 26.6 in/yr.

Average evapotranspiration, $\overline{ET}$, was estimated as 20.7 in/yr based on the difference between average precipitation of 32.6 in/yr and total runoff of 11.9 in/yr. Records at the climatological stations nearest to Kent County, South Haven, Mich. (station 7690) and East Lansing, Mich. (station 2395), show 35.8 in/yr and 39.1 in/yr of April through October pan evaporation, respectively. Thus, 53-58 percent of the potential evaporation as indicated by pan evaporation data is estimated to occur as actual evapotranspiration. Little spatial variation in the average evapotranspiration rate could be predicted on the basis of average annual temperatures that vary only about 1°F from the 58 °F average within the county (Eichenlaub and others, 1990, p. 25). Therefore, the spatial variation in evapotranspiration was computed as the difference between precipitation and runoff. On this basis, the evapotranspiration ranged from 5.95 to 27.5 in/yr among model cells.

Deep percolation within Kent County was estimated on the basis of a report describing ground-water recharge in the Lower Peninsula of Michigan (Holtschlag, 1994). The recharge report discretizes the Lower Peninsula into a grid of square cells 1 kilometer (3,281 ft) on a side. Estimates of recharge to each cell are based on a statistical relation between land characteristics and the base flow component of the streamflow hydrographs. Recharge, as determined by Holtschlag (1994), is likely to differ from deep percolation by the amount of deep seepage of water below streams. However, the magnitude of deep seepage is expected to be small relative to other water budget terms. In this report, values from cells from the recharge report that are surrounding Kent County were used with minimum curvature interpolation (Keckler, 1994) to regrid the recharge estimates to deep percolation estimates, DP_{ij} (fig. 6). Based on this analysis, the average deep percolation, $\overline{DP}$, in Kent County is 8.72 in/yr; deep percolation values ranged from 1.18 to 22.0 in/yr among model cells.

The difference of 3.17 in/yr between average total runoff (11.9 in/yr) and average deep percolation (8.72 in/yr) represents the sum of average direct surface runoff, $\overline{DSR}$, and average subsurface runoff, $\overline{SSR}$. In this report, precipitation was reduced by DSR to represent infiltration in the model; SSR was included with evapotranspiration as a loss of water and pesticides within the plant root zone. Unfortunately, there is no reliable way to distinguish DSR from SSR with the available data. Therefore, DSR and SSR are assumed to be equally probable, which corresponds to an estimate of 1.59 in/yr for both $\overline{DSR}$ and $\overline{SSR}$.

The value of SSR is assumed to be proportional to the local deep percolation. Thus, areas of higher than average SSR are associated with areas of higher than average deep percolation. For each cell indexed by ij, SSR was computed as:

$$SSR_{ij} = \frac{DP_{ij}}{\overline{DP}} \frac{(\overline{RO}-\overline{DP})}{2}. \qquad (11)$$

Among model cells, SSR ranged from 0.21 to 4.00 in/yr.

To ensure a cell by cell water balance, the direct surface runoff was computed as

$$DSR_{ij} = \min\left\{k\frac{\overline{DP}}{DP_{ij}}\frac{(\overline{RO}-\overline{DP})}{2}, \overline{DSR}+\overline{SSR}\right\}, \qquad (12)$$

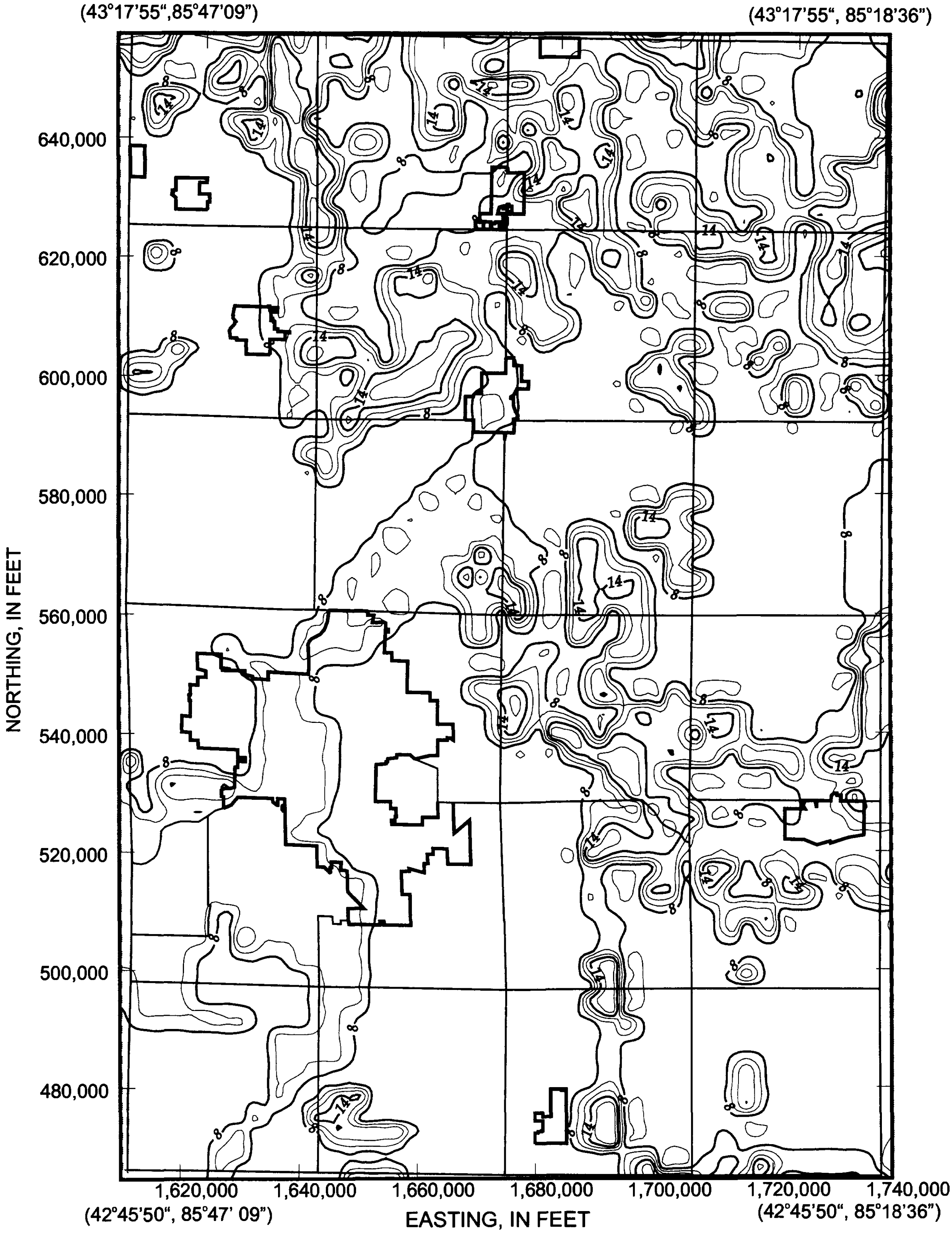
where $k = 0.924$ is a proportionality constant and is the minimum of the two values in the bracketed expression. Among model cells, DSR ranged from 0.58 to 3.50 in/yr.

Finally, values of infiltration were computed as

$$I_{ij} = P_{ij} - DSR_{ij}. \qquad (13)$$

Average infiltration was 31.0 in/yr; among model cells infiltration ranged between 28.9 to 32.3 in/yr.

Uncertainty in infiltration and deep percolation rates was represented by a bivariate normal probability distribution of the form:



EXPLANATION

—— 8 —— LINE Of EQUAL ANNUAL RATE Of DEEP PERCOLATION--
Interval is 2 inches per year

Figure 6. Spatial variation of average deep percolation rate within Kent County, Michigan.

$$\begin{bmatrix} I \\ DP \end{bmatrix} = \begin{bmatrix} q(z=0) \\ q(z>r) \end{bmatrix} \sim N\left[\begin{bmatrix} \mu_{z=0} \\ \mu_{z>r} \end{bmatrix}, \begin{bmatrix} \sigma^2_{z=0} & \sigma_{z=0}\sigma_{z>r} \\ \sigma_{z=0}\sigma_{z>r} & \sigma^2_{z>r} \end{bmatrix}\right] \quad (14)$$

where $\mu_{z=0}$ is the average infiltration rate at the soil surface (*z=0*) estimated locally as I_{ij};

$\mu_{z>r}$ is the average deep percolation rate below the root depth ($z > r$) estimated locally as DP_{ij};

$\sigma^2_{z=0}$ is the variance of infiltration estimated as $(5.25\ \text{in/yr})^2$ on the basis of the variance of precipitation;

$\sigma^2_{z>r}$ is the variance of deep percolation estimated as $(I_{ij}/DP_{ij})^2\ \sigma^2_{z=0}$; and

$\sigma_{z=0}\sigma_{z>r}$ is the covariance between infiltration and deep percolation. Based on the relation between precipitation and runoff (fig. 7), the covariance was scaled to equal $\sqrt{0.5}\sigma^2_{z=0}\sigma^2_{z>r}$ to produce a coefficient of determination that was similar to the relation between precipitation and runoff.

Depth to the water table

Within the leaching model, depth to the water table, *z=swl*, is used in the calculation of the volumetric water content, θ. Depths to the water table were based on reported static water levels, in feet below the land surface, for wells screened in the glacial deposits. Static water levels are routinely obtained by well drillers and recorded in the well log. Data on static water levels for 5,444 wells in Kent County used in the analysis were obtained from Michigan's Statewide Groundwater Data Base (Shirley Businski, Department of Environmental Quality, written commun., 1995).

Uncertainty in depths to the water table at each well was represented by normal distributions with a mean equal to the reported static water level, $rswl_i$, and relative uncertainty, *d*, equal to 25 percent. Reported static water levels were assumed to be within plus or minus 25 percent of their true levels 95 percent of the time. This assumption can be expressed as:

$$swl_i \sim N_i\left(rswl_i, rswl_i d\right) \quad (15)$$

Lithologic Factors

Lithologic factors include properties of soils and unweathered glacial deposits above the water table that affect the downward movement of atrazine. Information on lithologic factors were compiled at each of the 5,444 wells used in the analysis. Some properties, such as thickness of the root zone and density of the solid materials, were assumed to be constant for each point corresponding to a well. Other properties, such as porosity, air-entry level, residual moisture content, field capacity, and organic-carbon content, varied vertically by model layers. The vertical variations were grouped by common textural classes defined for soils and strata identified for unweathered lithologic materials. A detailed description of lithologic factors and their associated uncertainties follow.

Layer thickness

Vertical variations in the textural characteristics of soils are classified into distinct soil layers, which may contain one or more soil horizons. Thicknesses of these layers were determined from depth ranges for each soil series. For example, four soil horizons are contained in two layers described for the Oakville soil series (U.S. Department of Agriculture, 1986, p. 244). The first layer, which contains the *Ap* horizon, is described as a fine sand and has a depth range of 0-6 in. The second layer, which contains the *Bw*, *BC*, and *C* horizons, is described as a fine sand, sand, and a loamy fine sand and has a depth range of 6-60 in. In this report, where more than one textural description is provided for each layer, the primary description was used to assign physical properties to the layer for model computations.

In a manner analogous to methods used by soil scientists, well drillers identify strata or layers of materials having similar textural characteristics. Thicknesses and strata characteristics of these layers were obtained from well logs contained in Michigan's Statewide Groundwater Database. Thicknesses of layers for soils and unweathered lithologies were composited at points corresponding to the selected wells by substituting the upper most part of the well-log data with the more detailed soil data.

Thickness of the root zone

In this analysis, the thickness of the root zone was generally determined on the basis of rooting characteristics described for each soil horizon of each soil series (U.S Department of Agriculture, 1986, p. 112). The effective thickness of the root zone at the i^{th} soil series, r_i, was computed by use of thicknesses for zone 1 (r_{1i}) and root zone 2 (r_{2i}), where zone 1 rooting characteristics were described as "many roots", "many fine roots", or "common fine roots" plus one half the thickness of zone 2, where rooting characteristics were described as "few fine roots." The total thickness of soil horizons identified as the plowed layer, *Ap* horizon, or the undifferentiated *A* horizon, and the organic horizon, *O*, were always included as part of the root zone 1.

Uncertainty in the thickness of the root zone was represented by a normal probability distribution with a mean equal to the computed effective root zone thickness with a relative error d of 25 percent. This assumption is expressed as:

$$r_i \sim N\left(r_{1i} + 0.5r_{2i}, d\left(r_{1i} + 0.5r_{2i}\right)\right) \quad (16)$$

Density of solid material

Density of solid material refers to the mass (or weight) of a unit volume of soil solids and is called the particle density. Within Kent County, about 93.5 percent of the land area is composed of mineral soils as indicated by an organic matter content of less than 15 percent (U.S. Department of Agriculture, 1986, p. 165). Solid material density ρ_s of mineral soils generally range between the narrow limits of 2.60-2.75 g/cm^3 (grams per cubic centimeter) (Brady, 1974, p. 50). Given this narrow range of likely values, a constant density of 2.65 g/cm^3 was used in model computations for the density of minerals in both soils and unweathered lithologies.

Solid material density of organic soils is dependent on the source material, the condition of the layer, and the admixture of minerals. An estimate of solid material density for organic soils was computed on the basis of the limited information on bulk densities and porosity of organic materials. Rawls (1983, p. 123) applies an average bulk density value for organic material of 0.224 g/cm^3, which is consistent with the range of bulk densities (0.08-0.55 g/cm^3) for muck and mucky peat in Kent County reported in the State Soil Geographic (STATSGO) data base for Michigan (Bill Frederick, Natural Resources Conservation Service, written commun., 1995). Todd (1980, p. 28) provides a representative porosity for peat equal to 92 percent. The solid material density that corresponds to this bulk density and porosity data, computed by use of equation 4, is 2.8 g/cm^3, which is approximately equal to the upper limit of solid material density for mineral soils. In this report, there was insufficient data available to quantitatively estimate distinct values of solid material density for mineral and organic materials, therefore a single value of ρ_s = 2.65 g/cm^3 was used throughout.

Porosity

Porosity describes the fraction of void space occupied by air or water within lithologic materials. For soil layers, minimum and maximum porosity values, η, were computed from moist bulk density values, ρ_b, reported in the Kent County soil survey (U.S. Department of Agriculture, 1986, p. 253). For example, the maximum porosity was computed as:

$$max(\eta) = 1 - \frac{min(\rho_b)}{\rho_s} . \quad (17)$$

Minimum porosity values were computed in an analogous manner; intermediate porosities were computed using the average of minimum and maximum solid and bulk densities values.

Porosities of unweathered lithologic layers were computed from values available in the literature for similar lithologic classifications (Hausenbuiller, 1978, p. 90; Freeze and Cherry, 1979, p. 37;Todd, 1980, p. 28; Guymon, 1994, p. 22, and Brooks and others, 1991, p.89).

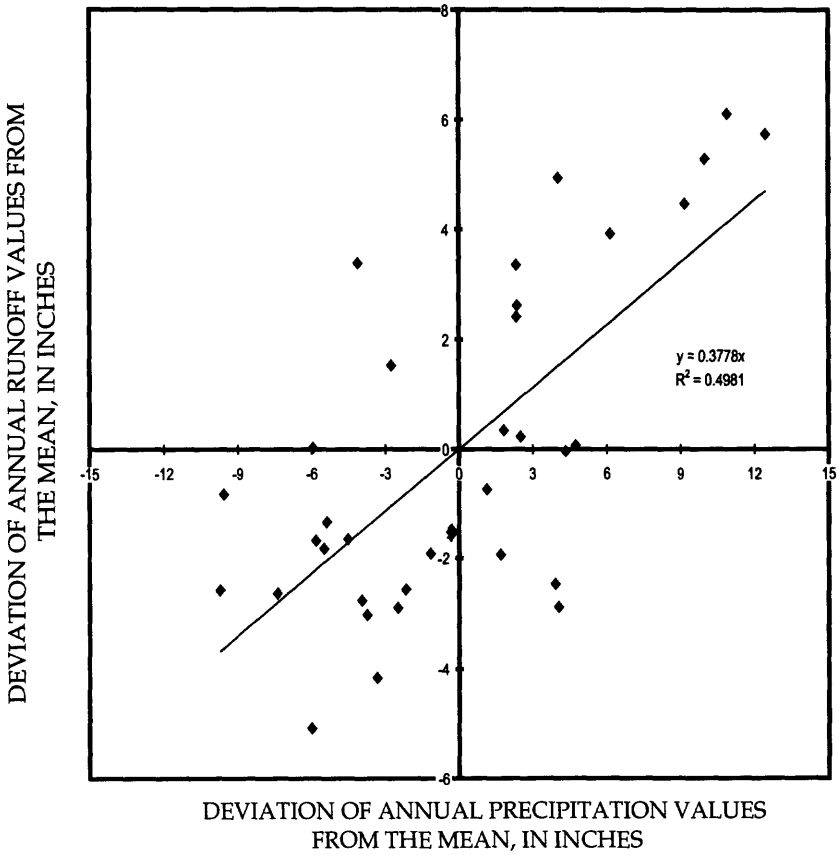


Figure 7. Relation between annual precipitation and annual runoff in Kent County, Michigan.

Intermediate values were used for those units for which literature values were not available (table 2). Uncertainties in porosity values were described by a triangular density function. A triangular density function, denoted as *triang*(min, max, mode), specifies a probability density that has zero density at the limits of the range, the minimum and maximum values of the random variable, and maximum probability at the most likely value (mode) of the random variable. Linear interpolation is used to estimate probability densities between the minimum and the mode and between the maximum and the mode.

Air-entry level

Air-entry level, *h*, is the height to which water rises above the water table by capillary action and is commonly referred to as the capillary fringe. Air-entry levels are not included in soil survey data. Therefore, in this report air-entry levels were estimated by relating air-entry levels identified for particle-size classes in the literature with particle-size compositions of soil-texture classes and strata characteristics.

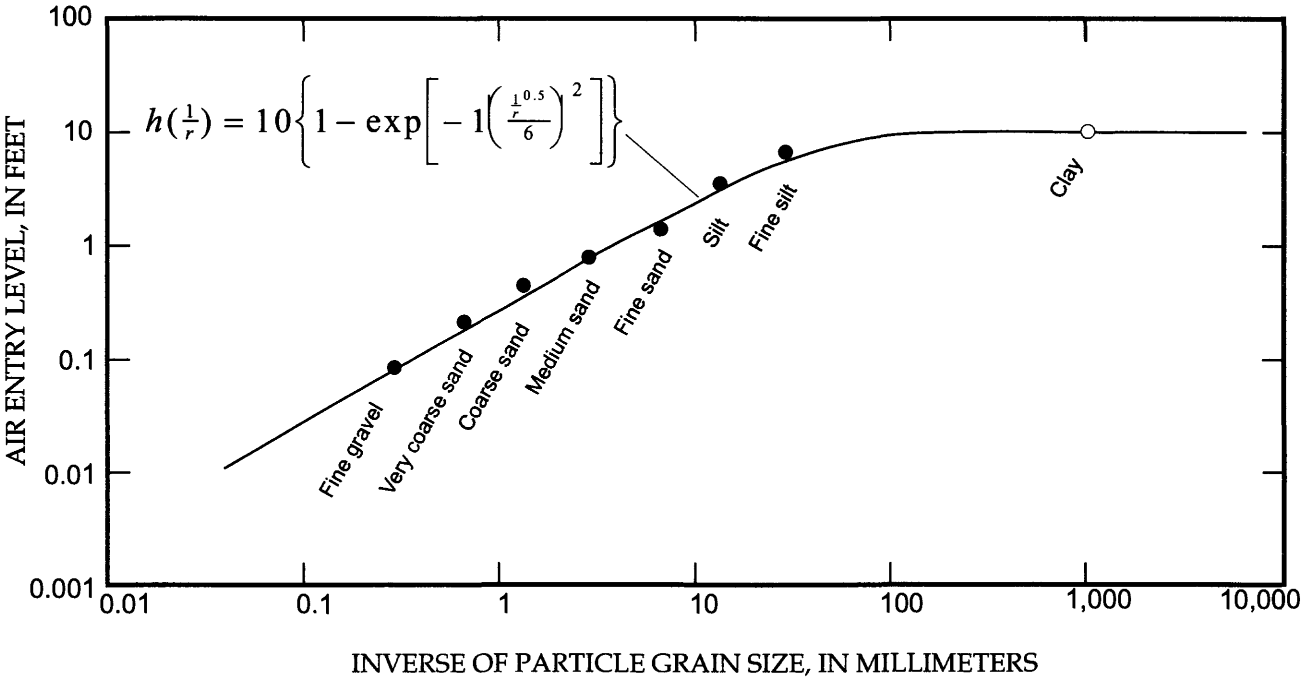
Empirical data relating air-entry level to particle diameter, *r*, are reported by Guymon (1994, p. 85). This data, which spans particle sizes from fine gravel to silt, was augmented with an estimated value for air-entry level of 10 ft for clay-sized materials. An equation was developed in this report to describe the relation between particle size and air-entry levels (fig. 8). Based on this relation, corresponding estimates of minimum and maximum air-entry levels were computed for a range of particle class sizes (table 3).

Table 2. Physical properties of unweathered lithologic materials in Kent County, Michigan

Strata code	Driller's lithologic descriptions	Porosity (percent)			Air-entry level (feet)			Residual moisture content (percent)			Field capacity (percent)		
		Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum
10	Clay, Clay fill	40.0	52.0	64.0	2.416	3.160	4.410	17.0	23.0	28.0	35.0	38.0	41.0
11	Hard clay	50.0	54.0	58.0	2.416	3.160	4.410	22.0	28.0	33.0	39.0	42.0	45.0
12	Soft clay	40.0	52.0	64.0	2.416	3.160	4.410	17.0	23.0	28.0	35.0	38.0	41.0
13	Sandy clay, Sandy silty clay	37.0	48.0	59.0	1.050	1.376	1.984	16.0	18.0	20.0	24.0	32.0	39.0
14	Fine sandy clay	40.0	52.0	64.0	1.787	2.295	3.196	17.0	23.0	28.0	35.0	38.0	41.0
15	Silt, Sandy silt	35.0	43.0	50.0	2.062	2.925	4.563	8.0	10.0	12.0	22.0	27.0	31.0
16	Clay and sand, Silty clay	37.0	48.0	59.0	0.998	1.313	1.904	16.0	18.0	20.0	24.0	32.0	39.0
17	Clay and gravel	27.0	41.0	55.0	0.113	0.149	0.222	7.0	8.0	9.0	25.0	28.0	29.0
18	Hardpan	27.0	41.0	55.0	2.416	3.160	4.410	7.0	8.0	9.0	25.0	28.0	29.0
19	Till	27.0	41.0	55.0	1.452	1.938	2.829	7.0	8.0	9.0	25.0	28.0	29.0
20	Sand, Sandy fill	25.0	38.0	50.0	0.582	0.770	1.133	2.0	4.0	6.0	8.0	11.0	13.0
21	Fine sand, Silty sand	25.0	38.0	50.0	2.628	3.589	9.939	2.0	4.0	6.0	8.0	11.0	13.0
22	Medium sand	250	38.0	50.0	0.582	0.770	1.133	2.0	4.0	6.0	8.0	11.0	13.0
23	Coarse sand	25.0	38.0	50.0	0.297	0.394	0.584	2.0	4.0	6.0	8.0	11.0	13.0
25	Sand and gravel	25.0	28.0	40.0	0.053	0.069	0.109	0.1	2.0	6.0	1.0	5.0	9.0
26	Sand with gravel	25.0	38.0	50.0	0.076	0.099	0.156	2.0	4.0	6.0	8.0	11.0	13.0
27	Sand and clay	31.0	40.0	49.0	0.998	1.313	1.904	4.0	6.0	7.0	13.0	17.0	20.0
28	Sand with clay	31.0	40.0	49.0	0.998	1.313	1.904	4.0	6.0	7.0	13.0	17.0	20.0
29	Water sand	25.0	38.0	50.0	0.285	0.378	0.561	2.0	4.0	6.0	8.0	11.0	13.0
30	Gravel	25.0	28.0	40.0	0.111	0.146	0.218	0.10	2.0	6.0	1.0	5.0	9.0
31	Gravel and clay	31.0	40.0	49.0	0.066	0.085	0.135	4.0	6.0	7.0	13.0	17.0	20.0

Table 2. Physical properties of unweathered lithologic materials in Kent County, Michigan

Strata code	Driller's lithologic descriptions	Porosity (percent)			Air-entry level (feet)			Residual moisture content (percent)			Field capacity (percent)		
		Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum
32	Gravel and sand	25.0	28.0	40.0	0.036	0.046	0.074	0.10	2.0	6.0	1.0	5.0	9.0
33	Fine gravel	25.0	28.0	40.0	0.042	0.056	0.083	.10	2.0	6.0	1.0	5.0	9.0
34	Medium gravel	25.0	28.0	40.0	0.021	0.027	0.043	.10	2.0	6.0	1.0	5.0	9.0
35	Coarse gravel	25.0	28.0	40.0	0.011	0.015	0.021	.10	2.0	6.0	1.0	5.0	9.0
36	Water gravel	25.0	28.0	40.0	0.005	0.007	0.011	.10	2.0	6.0	1.0	5.0	9.0
37	Gravel and cobbles	25.0	28.0	40.0	0.005	0.008	0.011	.10	2.0	6.0	1.0	5.0	9.0
38	Gravel and boulders	23.0	26.0	29.0	0.005	0.007	0.010	.0	.0	.0	0.10	2.0	4.0
39	Boulders	23.0	26.0	29.0	0.004	0.006	0.010	.0	.0	.0	.10	2.0	4.0
40	Top soil	27.0	41.0	55.0	1.123	1.505	2.228	7.0	8.0	9.0	25.0	28.0	29.0
41	Organic soil	30.0	40.0	50.0	1.123	1.505	2.228	2.0	6.0	10.0	16.0	21.0	26.0
42	Black dirt	30.0	40.0	50.0	1.123	1.505	2.228	2.0	6.0	10.0	16.0	21.0	26.0
44	Muck	35.0	43.0	50.0	1.986	2.612	3.702	8.0	10.0	12.0	22.0	27.0	31.0
45	Marl	35.0	43.0	50.0	1.986	2.612	3.702	8.0	10.0	12.0	22.0	27.0	31.0
49	Drift	27.0	41.0	55.0	2.423	3.253	4.720	7.0	8.0	9.0	25.0	28.0	29.0



$$h(\tfrac{1}{r}) = 10\left\{1 - \exp\left[-1\left(\frac{\frac{1}{r}^{0.5}}{6}\right)^2\right]\right\}$$

Figure 8. Relation between particl grain size and air-entry level.

Textures of lithologic materials indicate the relative proportions of sand, silt, and clay-sized particles in the matrix. In this study, percentages of clay, sand, and silt for each soil textural class was determined on the basis of the U.S Department of Agriculture soil textural classes (U.S. Department of Agriculture, 1986, p. 105) for soils and unweathered lithologic materials (tables 4 and 5), respectively. Air-entry levels for each texture and strata were then computed as the harmonic mean of the air-entry levels for each corresponding particle size weighted by the associated percent of material in that class (tables 6 and 2). Uncertainties in the air-entry values were represented by a triangular density function over the range of minimum and maximum air-entry levels with a maximum probability at the midpoint of the range.

<u>Residual moisture content</u>

Residual moisture content, RMC, is that soil moisture content corresponding to a soil moisture suction of about 15 bars. At RMC, no more water is available for plant growth and plants become permanently wilted. For soil layers, minimum, maximum, and intermediate residual moisture contents were assigned values reported by Ratliff and others (1983, p. 774) or by relating residual moisture contents to clay contents (table 6). Residual moisture contents of unweathered lithologic layers were assigned values available in the literature for similar lithologic materials (Fetter, 1988, p. 95; Hausenbuiller, 1978, p. 134; and Brooks and others, 1991, p. 59). Intermediate values were used for those units for which literature values were not available (table 2). The uncertainty of residual moisture content values was represented by a triangular probability density function over the range in residual moisture content values having maximum probability at the specified midpoint.

<u>Field capacity</u>

Field capacity, FC, is that moisture content of a soil after the gravitational, or free, water has drained away. It is typically represented by the moisture content of a soil, 2 or 3 days after a soaking rain. It is a dimensionless quantity that describes the water holding capacity of lithologic materials and is used in volumetric water content

Table 3. Relation between particle size classes and air-entry levels

Particle size	Particle size (millimeters)			Air-entry level (feet)		
	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum
Clay	0.0001	0.001	0.004	9.99	10.0	10.0
Silt	.004	.033	.062	3.61	5.69	9.99
Very fine sand	.062	.094	.125	1.99	2.56	3.61
Fine sand	.125	.187	.25	1.05	1.38	1.99
Medium sand	.250	.375	.50	.540	.714	1.05
Coarse sand	.50	.75	1.0	.274	.364	.540
Very coarse sand	1.0	1.5	2.0	.138	.183	.274
Very fine gravel	2.0	3.0	4.0	.069	.092	.138
Fine gravel	4.0	6.0	8.0	.035	.046	.069
Medium gravel	8.0	12.0	16.0	.017	.023	.035
Coarse gravel	16.0	24.0	32.0	.009	.012	.017
Very coarse gravel	32.0	48.0	64.0	.004	.006	.009

calculations in the leaching model. Field capacity is the sum of available water content (AWC) and residual moisture content (RMC).

Minimum and maximum available water contents are described for each soil layer in the soil survey for Kent County (U.S. Department of Agriculture, 1986, p.253). Estimates of residual moisture contents were based primarily on textural classifications (table 6). Uncertainty of field capacity values in the i^{th} soil layer was represented as $FC_i \sim triang(min(FC_i), max(FC_i), \text{mean}(FC_i))$. Field capacity values for the unweathered lithologic materials were obtained for specific textural classes from values reported in the literature (Hausenbuiller, 1978, p. 134; Fetter, 1988, p. 95; and Brooks, 1991, p. 59); estimates were developed for textural classes not explicitly reported (table 2). Within the i^{th} layer of the unweathered lithology, $FC_i \sim triang(min(FC_i), max(FC_i)$, and $mean(FC_i))$.

Organic-carbon content

Organic-carbon content is the percent organic carbon in a particular material. Average carbon content of soil organic matter is estimated at 58 percent, since carbon generally comprises a constant fraction of the organic materials contained in a wide range of soils (Hausenbuiller, 1978, p. 50). Organic matter contents in soil layers were obtained from data provided by Bill Frederick (Natural Resource Conservation Service, written commun., 1995). Organic matter contents in the unweathered lithologic materials were assumed to

Table 4. Percentage of selected particle-size classes associated with soil texture classes

Soil texture class	Particle size class							
	Clay	Silt	Very fine sand	Fine sand	Medium sand	Coarse sand	Fine gravel	Medium gravel
Clay	55.2	29.9	.	.	14.9	.	.	.
Clayey loam	32.6	37.6	.	.	29.8	.	.	.
Cherty-coarse sand	4.0	4.0	.	.	.	92.0	.	.
Coarse sand	4.0	4.0	.	.	.	92.0	.	.
Fine sand	4.0	4.0	.	92.0	.	.	.	.
Fine sandy loam	13.0	23.0	.	64.0	.	.	.	.
Gravely-loamy sand	5.0	10.0	.	.	75.0	.	10.0	10.0
Gravely sand	4.0	4.0	.	.	82.0	.	.	10.0
Gravely sandy loam	11.0	20.0	.	.	59.0	.	.	.
Loam	19.7	40.3	.	.	40.0	.	.	.
Loamy fine sand	6.0	13.0	.	81.0	.	.	.	.
Loamy sand	6.4	12.7	.	.	80.9	.	.	.
Loamy very fine sand	6.0	13.0	31.0	.	50.0	.	.	.
Muck	50.0	30.0	.	.	20.0	.	.	.
Sand	2.9	4.4	.	.	92.7	.	.	.
Sandy clay loam	27.4	18.3	.	.	54.3	.	.	.
Silty clay	46.3	47.6	.	.	6.0	.	.	.
Silty clay loam	33.2	59.2	.	.	7.6	.	.	.
Silty loam	18.5	64.9	.	.	16.6	.	.	.
Sandy loam	11.1	25.5	.	.	63.4	.	.	.
Stratified	33.0	33.0	.	.	34.0	.	.	.
Stratified very fine sand	4.0	4.0	.	.	.	.92.0	.	.
Variable	33.0	33.0	.	.	34.0	.	.	.
Very fine sand	4.0	4.0	92.0	.	.	.	.	.

Table 5. Percentage of selected particle-size classes associated with unweathered lithologic materials

Driller's lithologic description	Strata code	Particle size class									
		Clay	Silt	Very fine sand	Fine sand	Medium sand	Coarse sand	Fine gravel	Medium gravel	Coarse gravel	Very coarse gravel
Hard clay	11	55.2	29.9	.	.	14.9	.	.	.	.	.
Clay, Clay fill	10	55.2	29.9	.	.	14.9	.	.	.	.	.
Soft clay	12	55.2	29.9	.	.	14.9	.	.	.	.	.
Fine sandy clay	14	42.0	5.0	.	53.0	.	.	.	.	.	.
Sandy silty clay	13	41.0	11.5	.	.	47.5	.	.	.	.	.
Silty clay	16	35.0	15.0	.	.	50.0	.	.	.	.	.
Silt, Sandy silt	15	7.0	79.0	.	.	14.0	.	.	.	.	.
Muck	44	50.0	30.0	.	.	20.0	.	.	.	.	.
Marl	45	50.0	30.0	.	.	20.0	.	.	.	.	.
Clay and sand	17	50.0	10.0	.	.	10.0	.	30	.	.	.
Hardpan	18	55.2	29.9	.	.	14.9	.	.	.	.	.
Till	19	32.6	37.6	.	.	29.8	.	.	.	.	.
Top soil	40	18.0	41.0	.	.	41.0	.	.	.	.	.
Drift	49	32.6	37.6	.	.	14.9	.	.	.	.	.
Organic soil	41	18.0	41.0	.	.	41.0	.	.	.	.	.
Black dirt	42	18.0	41.0	.	.	41.0	.	.	.	.	.
Sand and clay	27	35.0	15.0	.	.	50.0	.	.	.	.	.
Sand with clay	28	35.0	15.0	.	.	50.0	.	.	.	.	.
Gravel and clay	31	35.0	15.0	.	.	25.0	.	.	25.0	.	.
Sandy fill	20	4.0	4.0	.	.	92.0	.	.	.	.	.
Fine silty sand	21	5.0	45.0	50.0	.	.	.	.	.	.	.

Table 5. Percentage of selected particle-size classes associated with unweathered lithologic materials

Driller's lithologic description	Strata code	Particle size class									
		Clay	Silt	Very fine sand	Fine sand	Medium sand	Coarse sand	Fine gravel	Medium gravel	Coarse gravel	Very coarse gravel
Medium sand	22	4.0	4.0	.	.	92.0	.	.	.	.	.
Coarse sand	23	4.0	4.0	.	.	.	92.0	.	.	.	.
Sand with gravel	26	4.0	4.0	.	.	72.0	.	.	20.0	.	.
Water sand	29	2.0	2.0	.	.	.	96.0	.	.	.	.
Sand and gravel	25	4.0	4.0	.	.	62.0	.	.	30.0	.	.
Gravel and clay	30	30.0	20.0	.	.	20.0	.	30.0	.	.	.
Gravel and sand	32	4.0	4.0	.	.	46.0	.	.	46.0	.	.
Fine gravel	33	4.0	4.0	.	.	10.0	.	82.0	.	.	.
Medium gravel	34	4.0	4.0	.	.	10.0	.	.	82.0	.	.
Coarse gravel	35	4.0	4.0	.	.	10.0	.	.	.	82.0	.
Water gravel	36	2.0	2.0	.	.	14.0	.	.	.	.	82.0
Gravel and cobbles	37	2.0	2.0	.	.	16.0	.	.	.	.	80.0
Gravel and boulders	38	1.0	1.0	.	.	10.0	.	.	.	.	88.0
Boulders	39	.	.	.	.	5.0	.	.	.	.	95.0

Table 6. Physical properties of soils used in the pesticide leaching model

Soil texture	Air-entry level (feet)			Residual moisture content (percent)			Field capacity (percent)		
	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum
Clay	2.42	3.16	4.41	21.0	22.0	23.0	28.0	30.0	32.0
Clayey loam	1.45	1.94	2.83	14.0	18.0	23.0	29.7	32.9	36.0
Coarse sand	0.30	0.39	0.58	4.0	7.0	10.0	9.0	10.0	11.0
Cherty-coarse sand	0.30	0.39	0.58	4.0	6.0	8.0	8.0	9.0	10.0
Fine sand	1.12	1.47	2.13	4.8	6.5	8.5	12.1	13.5	14.9
Fine sandy loam	1.46	1.93	2.80	4.9	7.6	10.3	17.9	21.1	24.4
Gravely-loamy sand	0.23	0.31	0.46	4.0	6.0	8.0	14.6	16.0	17.2
Gravely sand	0.13	0.18	0.27	4.0	5.9	7.8	7.9	8.9	9.9
Gravely sandy loam	0.14	0.18	0.29	8.0	9.0	11.0	20.0	21.0	22.0
Loam	1.15	1.54	2.27	7.0	11.0	16.0	26.7	29.6	31.9
Loamy fine sand	1.23	1.62	2.35	6.0	7.5	9.7	16.8	19.7	22.2
Loamy sand	0.65	0.86	1.27	2.0	6.0	10.0	13.4	15.0	17.1
Loamy very fine sand	0.89	1.18	1.90	6.0	8.0	10.0	16.0	16.0	17.0
Muck	1.99	2.61	3.70	5.0	5.0	6.0	40.0	45.0	50.0
Sand	0.58	0.76	1.13	2.0	4.0	6.0	8.1	9.8	12.0
Sand clay loam	0.92	1.22	1.78	13.0	18.0	23.0	31.2	33.8	36.4
Silty clay	3.43	4.64	6.58	15.0	22.0	28.0	29.4	35.4	42.0
Silty clay loam	2.96	4.10	6.07	17.0	21.0	24.0	31.9	33.9	36.8
Silty loam	1.98	2.74	4.14	9.0	15.0	21.0	33.6	35.5	37.7
Sandy loam	0.80	1.06	1.56	5.0	11.0	16.0	22.3	25.3	28.9
Stratified	1.33	1.76	2.57	5.3	9.9	14.4	20.2	23.2	26.9
Stratified-very fine sand	2.10	2.71	9.90	8.0	9.0	11.0	20.0	25.0	29.0
Variable	1.11	1.48	2.18	8.0	12.0	17.0	26.0	29.0	32.0
Very fine sand	2.10	2.71	9.90	5.0	7.0	10.0	13.0	18.0	23.0

be distributed as *triang* (0, 0.5, 0.1) percent.

Atrazine Characteristics

This report characterizes the vulnerability of the near-surface aquifer to atrazine contamination. Atrazine was selected to illustrate the use of the leaching model because atrazine has been the most intensively used herbicide for the last 30 years for weed control in corn. In addition, atrazine is one of the most frequently detected pesticides in ground water in the midwest (Koplin and others, 1995, p. 337).

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) slowly metabolizes into deethylatra-zine (DEA; 2-amino-4-chloro-6-isopropylamino-s-triazine) and then into deisopropylatrazine (DIA; 2-amino-4-chloro-6-ethylamino-s-triazine) (Koplin and others, 1995, p.336). These two metabolites are structurally and toxicologically similar to atrazine and they were detected in 22.8 and 10.2 percent, respectively, of the wells sampled by Koplin and others (1995, p. 338). However, the present configuration of the pesticide leaching model does not explicitly track metabolites. Therefore, areas delineated as having a relatively low fraction of atrazine remaining at the water table may still be vulnerable to one or more metabolites of atrazine or other pesticides.

Three characteristics of atrazine were estimated for model computations. These include the organic-carbon partition coefficient, pesticide half-life in the soil layers, and pesticide half-life in the layers representing the unweathered lithologic materials.

Organic-carbon partition coefficient

Dissolved constituents in ground water diffuse through and are adsorbed by the surrounding medium resulting in a retardation of constituent flow with respect to ground-water flow. Adsorption of trace organic constituents is primarily associated with solid organic compounds present in the lithology (de Marsily, 1986, p. 260). The adsorption characteristics, which are pesticide dependent, are described by the organic-carbon partition coefficient, K_{oc}. The K_{oc} is a dimensionless coefficient that is multiplied by the percentage of organic carbon to determine the distribution coefficient, K_d.

USEPA's Pesticide Environmental Fate One-Line Summary reports K_{oc} values for atrazine of 39, 70, 87, and 155 for sand, loam, clay, and sandy loam, respectively. Because these values do not show a consistent relation with textural characteristics, a single sampling distribution was used throughout the model area. Independent random samples were generated from the probability distribution *triang*(39,155,87.8), corresponding to the mean of values listed in the One Line Summary.

Pesticide half-life

The rate at which atrazine decays within the unsaturated zone into transitional products is described by its half life. The half life of atrazine within the soil varies between 6-181 days with a mean of 160 days (Estella Waldman, USEPA Environmental Fate and Effects Division, written commun., May 6, 1996). The uncertainty in the value of this parameter was represented as *triang*(6,181,160).

Little information is available on the half life of atrazine in the unweathered lithology. Rutledge and Helgesen (1991) used a range of half lives in the unweathered materials that were 2 to 6 times the half lives in the soil layer. In this report, sample values of atrazine half lives in the unweathered lithology were drawn from a *triang*(160, 365, 320).

VULNERABILITY OF GROUND WATER TO ATRAZINE LEACHING

Point Estimates of Aquifer Vulnerability

The leaching model was used to compute fractions of atrazine remaining at the water table and corresponding times of travel for each of the 5,444 wells selected for analysis. These estimates are referred to as point estimates because they were computed by setting each parameter associated with specific hydrologic, lithologic, and pesticide characteristics, to its most likely value. The resulting estimates are the most likely fractions of atrazine remaining at the water table, given the assumptions associated with the leaching model and the uncertainty in the model parameters.

Computed fractions of atrazine remaining at the water table ranged from 0 to 3.6 percent; however 95 percent of the fractions remaining were less than 0.2 percent (fig. 9-a). The mean fraction remaining was 3.88×10^{-2} percent; the median was 2.59×10^{-5} percent. The nearly three orders of magnitude difference between the parametric (mean) and nonparametric (median) measures of central tendency reflects the (right) skewness of the probability density of fractions remaining. The tendency for skewness in this distribution may be partly accounted for by the theory of successive random dilutions (Ott, 1995, p. 218), which states that a concentration undergoing a series of independent random dilutions tends to be lognormally distributed. Spatial dependencies in successive dilutions may help explain why the skewness in the distribution is not as extreme as a lognormal distribution.

Nonlinear transformations are commonly applied to data from skewed probability densities so that the probability density under the transformation, the transformed metric, will be nearly symmetrical. Then, mathematical models are estimated in the transformed metric so that all observations are weighted similarly in determining model parameters and so that model errors are more likely to be normally distributed. Model predictions or estimates are compared with measured values, when available, in both the transformed and the original metrics.

Simple power transformations, of the form $rm = RM^{\lambda}$, are nonlinear transformations that have the effect of expanding the scale of one part of the range and contracting it in another (Box and Draper, 1987, p. 268). In general, a λ value of 1 corresponds to no transformation, a value of 0.5 to the square-root transformation, and a value of 0 to the logarithmic transformation. In this analysis, a power transformation parameter, λ, value of 0.0625, equal to $\left(\frac{1}{4}\right)^2$, was chosen for transforming fractions of atrazine remaining at the water table to a symmetrical probability density by inspection of the corresponding histograms (fig. 9a-c).

For the 5,444 selected wells, computed time of travel between the soil surface and the water table ranged from 2.2 to 118 years; the mean time of travel was 17.7 years (fig. 10a). Assuming that atrazine applications began in 1952, by 1997 sufficient time had passed for atrazine to move to the water table at 96.7 percent of the selected wells (fig. 10b).

Fractions of atrazine remaining at the water table generally decrease with increasing travel times to the water table (fig. 11). Part of this decrease is associated with the half life of atrazine, in which atrazine metabolizes to DEA and DIA, and the other part is associated with sorption on the lithologic materials. This relation between travel time and fraction remaining appears to be bounded on the right by the half life of atrazine; values that plot to the left of this limit reflect additional removal of atrazine by sorption on lithologic materials.

Mapping Aquifer Vulnerability Estimates

Mapping aquifer vulnerability requires spatial interpolation of point estimates of aquifer vulnerability that were computed at selected wells. In this report, estimates of aquifer vulnerability were interpolated to the center of each grid cell. The interpolation was based on a weighted average of values computed for wells up to 15,000 ft from the grid center; estimates were not computed for cells where no point estimates of aquifer vulnerability were available within 15,000 ft of the grid center. Weights were assigned so that the resulting estimates would be the best linear unbiased estimates available (Cressie, 1991, p. 163).

Weights were determined on the basis of the spatial correlation structure of the fraction of atrazine remaining at the water table, following transformation to the 0.0625 power. Variogram analysis (Cressie, 1991, p. 69) was used to quantify the spatial correlation structure. An empirical variogram was developed by computing separation distances, Δ, between all pairs of wells and corresponding (positive) differences between the fraction of atrazine remaining at the water table. Separation distances between 0 and 20,000 ft were grouped into intervals 200 feet wide, and the average difference between fractions, $\tilde{\gamma}(\Delta)$, were

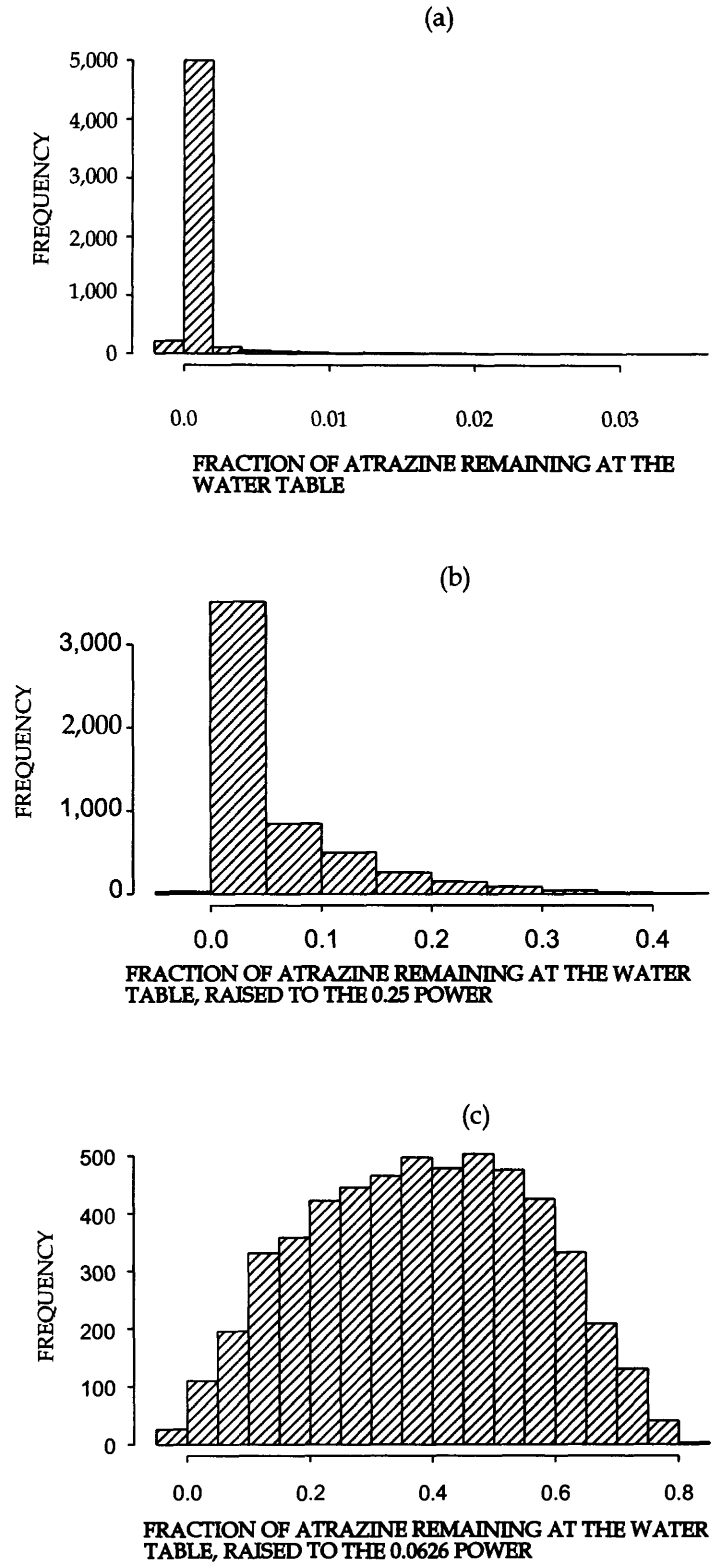


Figure 9. Fraction of atrazine remaining at the water table for selected wells in Kent County, Michigan.

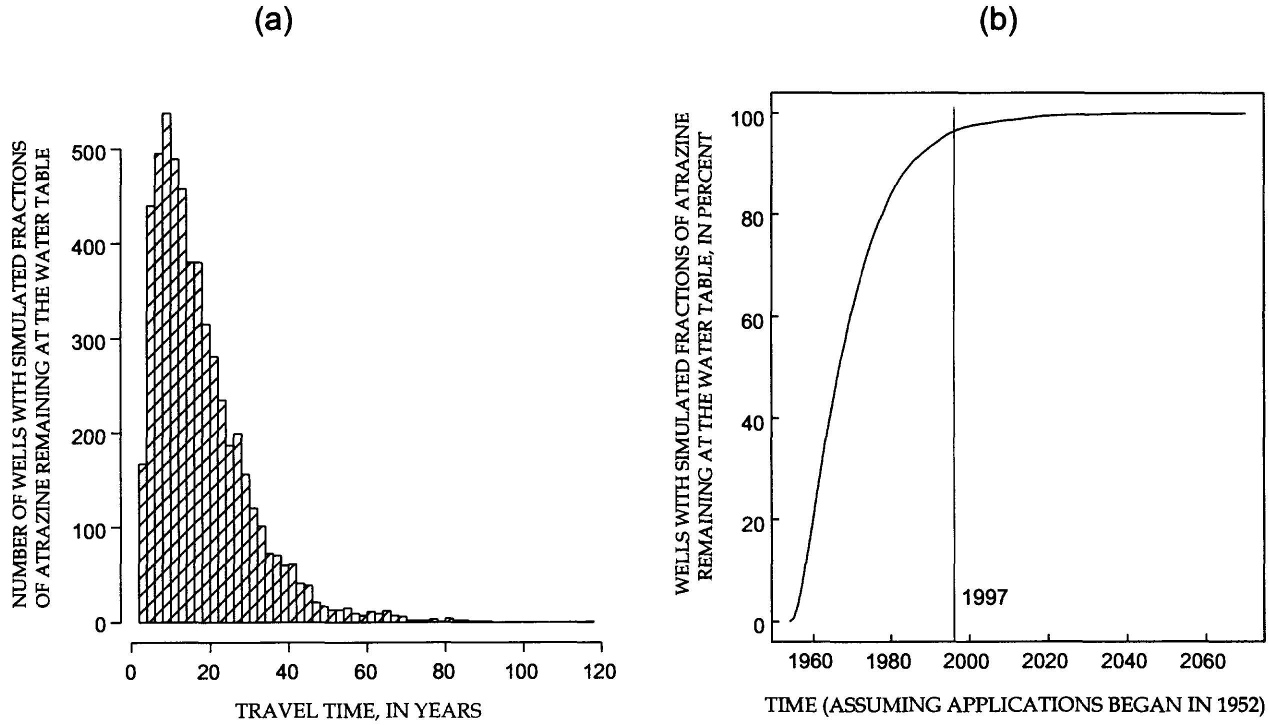


Figure 10. Distribution of travel times of atrazine to the water table for selected wells in Kent County, Michigan.

plotted for each group; to facilitate computation of weights, a model variogram, $\hat{\gamma}(\Delta)$, was fit to the empirical variogram (fig. 12). The weights for wells in proximity of grid centers, which are inversely proportional to $\hat{\gamma}(\Delta)$, were used within ordinary kriging equations (Cressie, 1991, p. 121) to compute estimates of the fraction of atrazine remaining at the water table, raised to the 0.0625 power.

Three images of the kriged surface were generated in different metrics to depict aquifer vulnerability to atrazine contamination in Kent County, Michigan. The *rm* metric (RM^{λ}) (fig. 13), which was used in variogram model development and kriging estimation, shows a fairly uniform distribution of gray tones, indicating vulnerability, mottling the study area. Relative differences among vulnerabilities in this metric appear small and localized. Figure 14 shows the $rm^{\lambda^{-0.5}}$ ($RM^{1/4}$) metric, which is midway, in terms of power transformations, between the *rm* and the original *RM* metrics. In this metric, about half of the study area appears to have low vulnerability; discontinuous patterns of vulnerability are evident. Finally, figure 15 shows the $rm^{\lambda^{-1.0}}$ (*RM)* metric, which corresponds to the untransformed fractions of atrazine remaining at the water table computed by use of the leaching model. In this metric, more than 95 percent of the study area appears to have low vulnerability; vulnerable areas appear highly localized. The frequency density of gray tones in each of the figures is similar to the frequency density of the fraction of atrazine remaining at the water table in corresponding histograms (fig 9-c, b, a).

<u>Potential Concentrations of Atrazine in Leachate</u>

Aquifer vulnerability estimates were used with a steady-state, uniform atrazine application rate to compute potential concentrations of atrazine in leachate reaching the water table. Potential

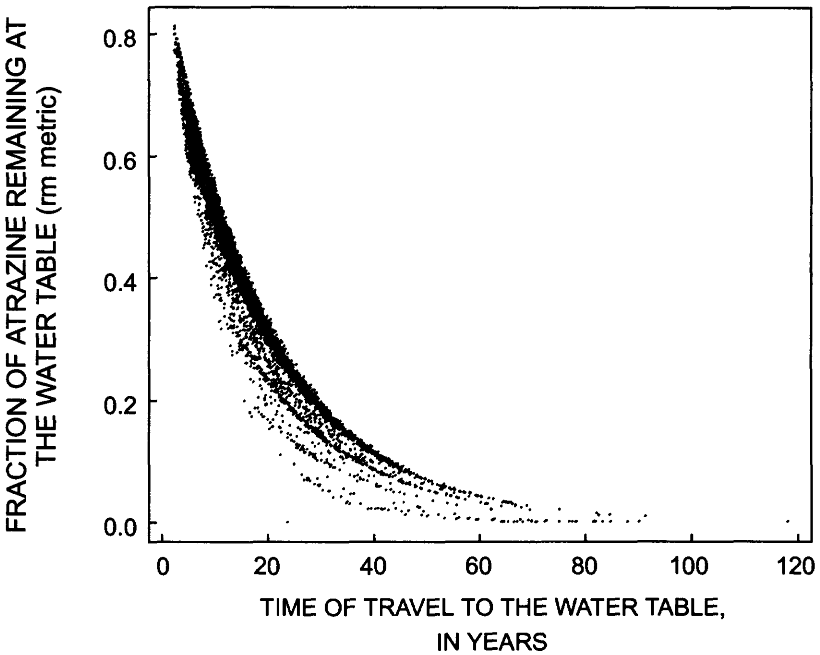


Figure 11. Relation between time of travel and fraction of atrazine remaining at the water table for selected wells in Kent County, Michigan.

concentrations were computed as

$$\hat{a}_{i,j} = C_0 \frac{A}{DP_{i,j}} RM_{i,j} \qquad (18)$$

where:

$\hat{a}_{i,j}$ = the potential concentration of atrazine in leachate at the water table in ij^{th} cell, in micrograms per liter;

A = a specified steady-state, uniform atrazine application rate of 2 pounds per acre per year;

DP_{ij} = the deep percolation rate in the ij^{th} cell, in inches per year;

RM_{ij} = the estimated fraction of atrazine remaining in the ij^{th} cell at the water table; and

C_0 = a coefficient equal to 4,413 used to convert units from pounds per acre-inch to micrograms per liter.

The specified application rate of 2 pounds per acre per year is intended to represent a long-term average rate since about 1952. Recent data, from the first half of the 1990s, indicate an annual application rate of about 1.34 pounds per acre based on an estimated 56,382 pounds of atrazine applied (table 1) on corn acreage of about 41,984 acres (Michigan Agricultural Statistics Service, 1995, p. 88). However, improvements in pesticide management and in the efficiency of pesticide delivery systems are thought to have reduced recent application rates from those representing the long-term average rate, so a somewhat higher than 1990s application rate was used to represent long-term average.

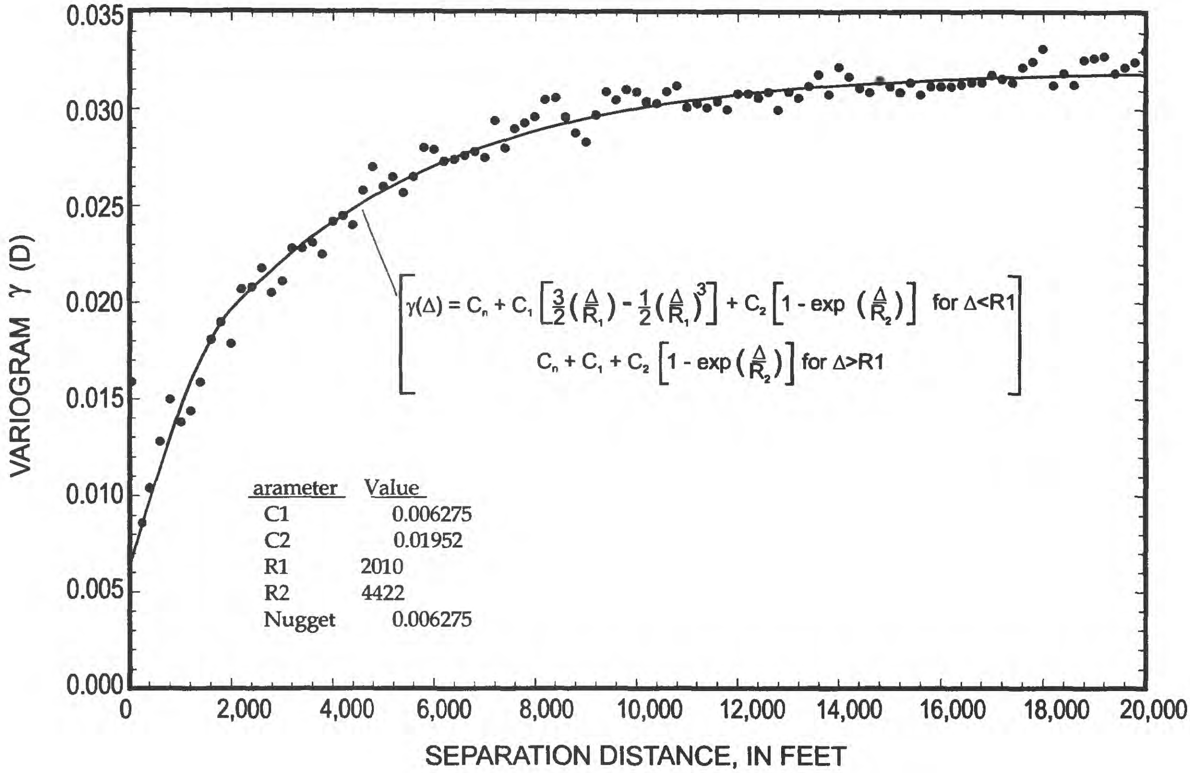


Figure 12. Variogram of the fraction of atrazine remaining at the water table in Kent County, Michigan (Fraction raised to the 0.0625 power).

A uniform application rate was used because detailed information on the spatial distribution of past atrazine applications was unavailable. However, atrazine is directly applied only to areas planted in corn, and corn acreage was reported as only 7.7 percent of the area in the county (Michigan Agricultural Statistics Service, 1995). Therefore, the potential concentration map likely identifies some areas as having leachate concentrations above the maximum contaminant level when, in fact, there is little likelihood of contamination resulting from direct application of atrazine. Detailed information on the spatial distribution of atrazine applications over time would be needed to estimate the concentrations of atrazine in leachate reaching the water table.

For the 5,444 wells analyzed, the average potential atrazine concentration in leachate at the water table was 0.28 μg/L; potential concentrations ranged from 0 to 18 μg/L. About 2.6 percent of the wells analyzed had potential concentrations of atrazine in leachate at the water table that exceeded the USEPA maximum contaminant level of 3 μg/L (fig. 16). The spatial distribution of potential atrazine concentrations in leachate was similar to the distribution of estimated aquifer vulnerability, owing to the assumption of a uniform application rate of atrazine. No data on leachate water quality near the water table were available to compare with the potential concentrations.

Uncertainty Analyses

Numerous factors give rise to uncertainty in the maps of fractions of atrazine remaining at the water table in Kent County, Michigan. These factors include: (1) simplifying assumptions in the leaching model, (2) uncertainties in hydrologic, lithologic, and pesticide characteristics used in the leaching model, (3) uncertainties in spatial interpolation from points of measured characteristics to grid cell centers of unmeasured characteristics, and (4) the assumption that estimates at grid cell centers represent the average

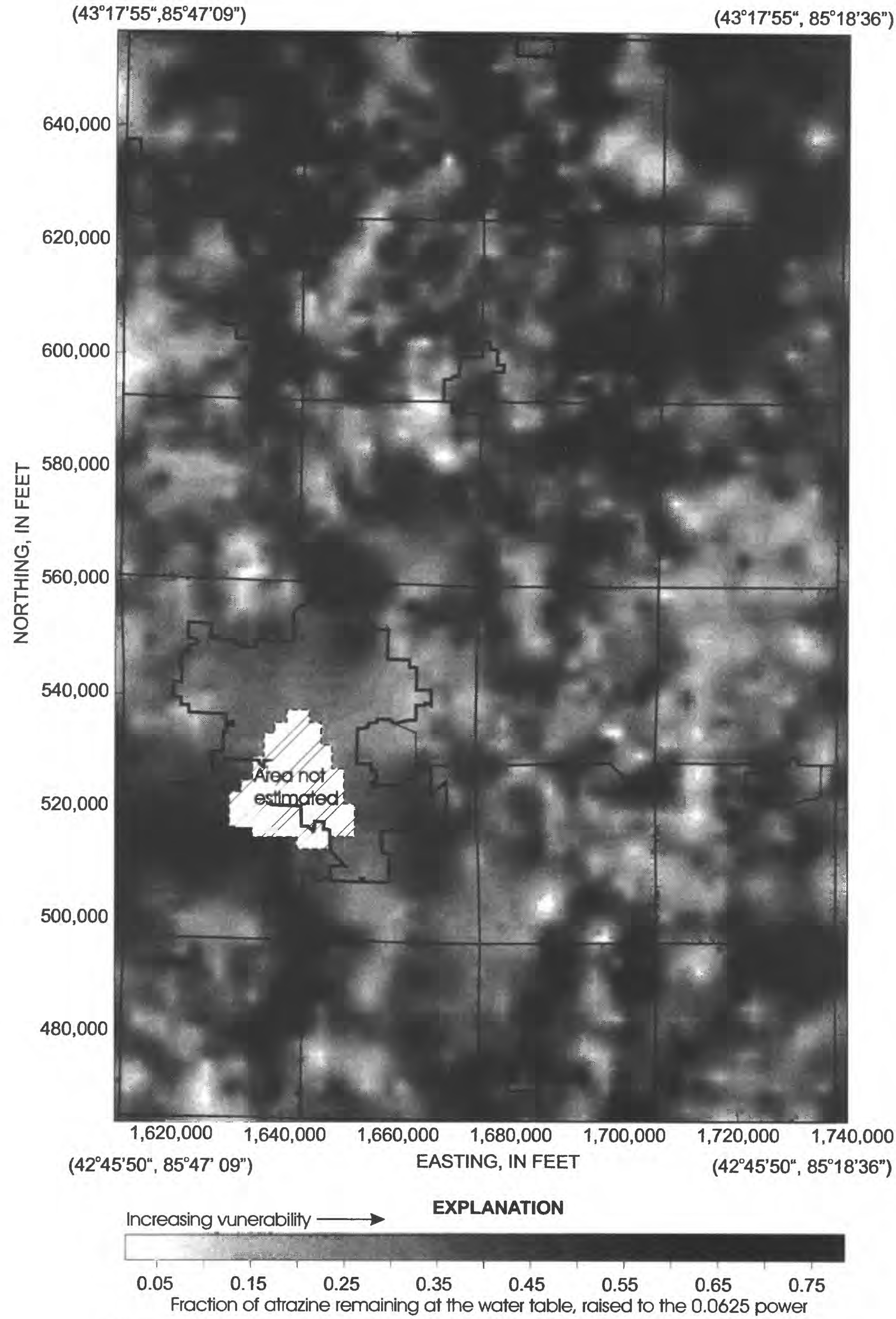


Figure 13. Estimated fraction of atrazine remaining at the water table, raised to the 0.0625 power, in Kent County,Michigan.

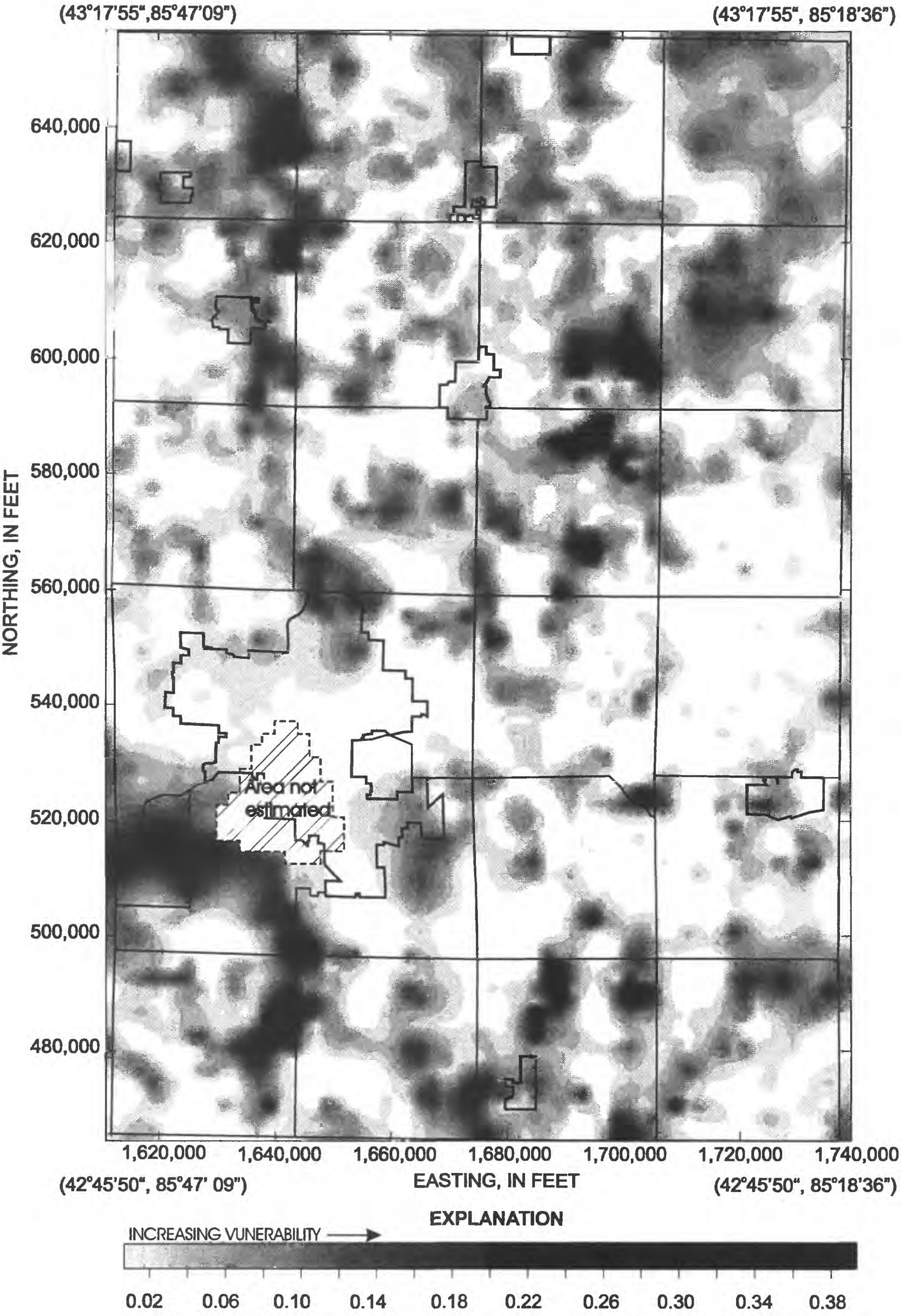


Figure 14. Estimated fraction of atrazine remaining at the water table, raised to the 0.25 power, in Kent County, Michigan.

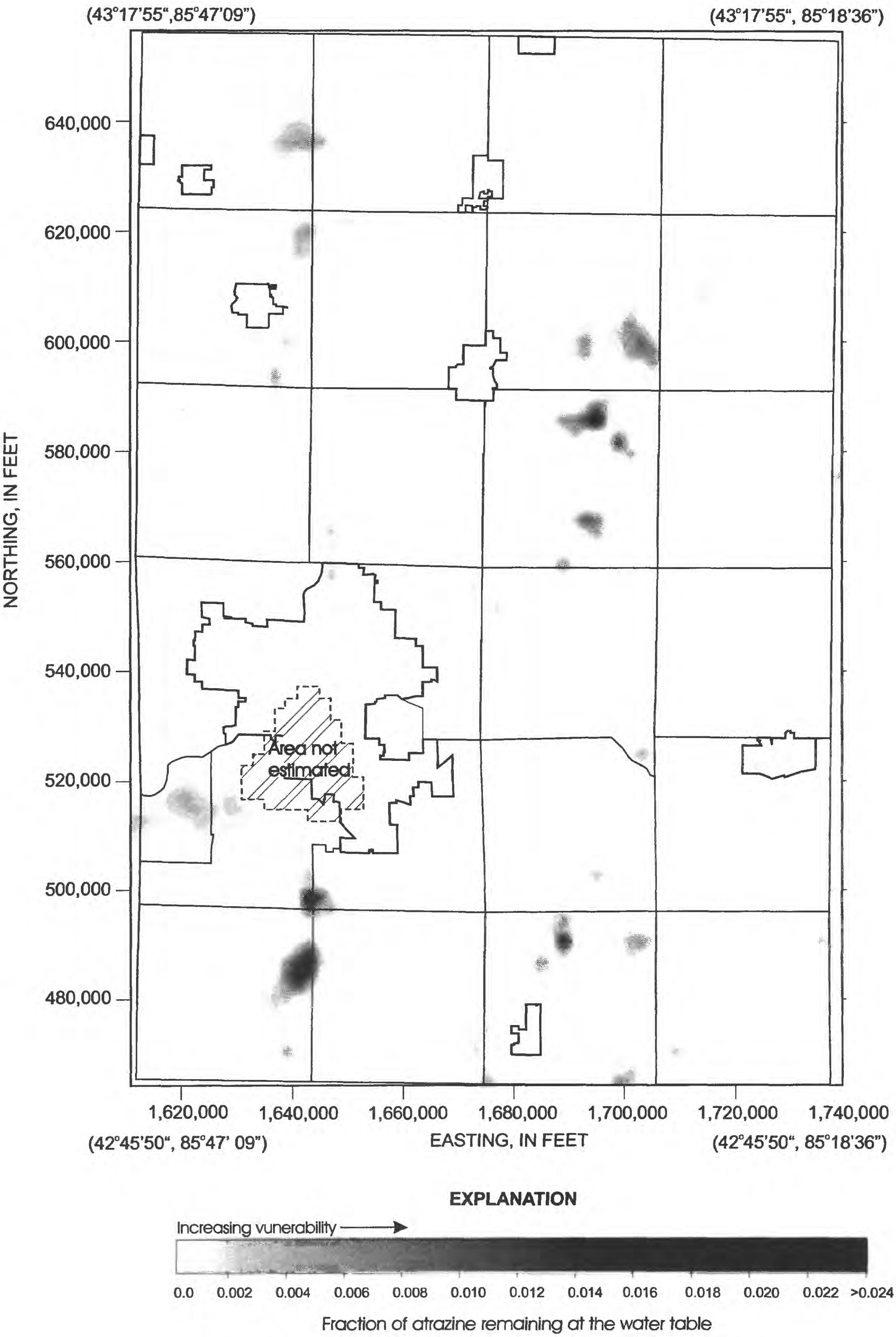
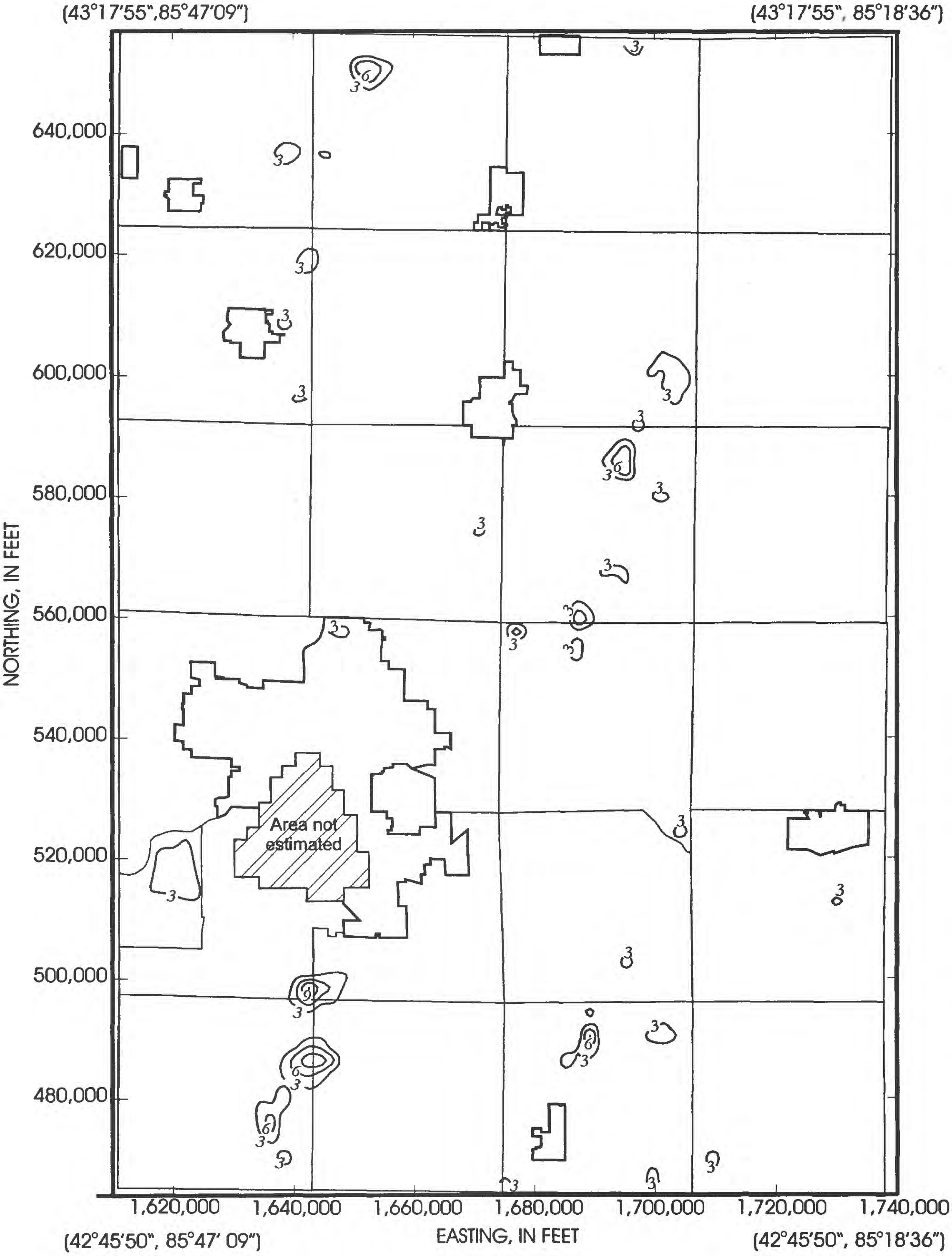


Figure 15. Estimated fraction of atrazine remaining at the water table in Kent County, Michigan.



EXPLANATION

—3— ESTIMATED POTENTIAL CONCENTRATION OF ATRAZINE IN LEACHATE AT THE WATER TABLE--Contour interval 3 micrograms per liter

Figure 16. Estimated potential concentration of atrazine in leachate at the water table in Kent County, Michigan.

value within a nonhomogeneous grid cell.

Uncertainty associated with factor 1 is potentially highly significant, but difficult to quantify based on available information. Rutledge and Helgesen (1991, p. 1) indicate that the leaching model is intended as a screening tool for the regional assessment of aquifer vulnerability from non-point sources. They indicate that model assumptions may limit the applicability of model results, although the limitations become less significant if model results are used in a comparative sense. Therefore in this analysis, rather than attempting to quantify the uncertainty associated with factor 1, the numerical estimates of aquifer vulnerability are not considered precise quantitative estimates.

A sample estimate of uncertainty associated with factor 2 was developed by use of Monte Carlo simulation techniques. Specifically, 100 wells were selected along a north-south transect at an easting of 1,685,900 ft through Kent County, Michigan (fig. 3). For each well location, 2,500 random samples were generated from probability distributions representing uncertainties in corresponding hydrologic, lithologic, and pesticide characteristics at that point. Each sample was simulated with a slightly modified version (only effecting input and output formats) of the original leaching model (Appendix I) to determine the effect of parameter uncertainty on the computed fractions of atrazine remaining at the water table. The probability density of the fractions of atrazine remaining at individual wells (fig. 17) were used to infer effects of parameter uncertainty. In particular, the standard deviation of the Monte Carlo simulations at each well, s_{mc}, was used as the measure of uncertainty.

Variability in the computed fraction of atrazine remaining at the water table resulting from uncertainty in model parameters is depicted by an interval equal to plus or minus one s_{mc} about the mean (fig. 17). Under a normal approximation, this interval contains about 68 percent of the simulated values. Similar intervals were developed for all 100 wells without inclusion of the full histogram (fig. 18); however, all intervals were constrained to range between 0 and 1. In the 100 wells selected, the mean fraction remaining (*rm*) was 0.227 and the mean value of s_{mc} was 0.0875. The widths of the intervals for the 100 wells ranged between 0.00714 to 0.280; the average width of the interval was 0.174.

Uncertainty in sample estimates of fractions, *f*, are commonly estimated as $s_f = \sqrt{f\frac{(1-f)}{n}}$, where *n* is the sample size. This estimate is based on the assumptions that the population being sampled is of infinite size and that the fractions are normally distributed. For the 100 locations used in the Monte Carlo simulation, s_f and s_{mc} are nearly proportional (fig. 19). This relation provides a mechanism for estimating the variability of the fraction of atrazine remaining at the water table that is associated with parameter uncertainty, based only on information about the estimated fraction.

Uncertainty associated with spatial interpolation, factor 3, was estimated on the basis of the kriging standard errors, s_k (de Marsily, 1986, p 300.). Values of s_k were computed for each of the 100 wells along the selected transect based on the variogram model and the proximity of nearby wells. The mean value of s_k for the 100 wells (in the 0.0625 metric) was 0.146. Thus, the effect of error in spatial interpolation was about 1.7 times greater than the effect of uncertainty in parameters in determining the uncertainty of the fraction of atrazine remaining at the water table (in the 0.0625 metric), as measured by the standard error.

A combined uncertainty was computed as:

$$s_c = \sqrt{\left(s_{mc}^2 + s_k^2\right)} \qquad (19)$$

assuming that the errors associated with parameter uncertainty were independent of the errors associated with spatial interpolation. A second set of intervals was calculated as the mean fraction of atrazine simulated plus or minus one standard deviation of the combined standard deviation (figs. 17, 18); again, the minimum and maximum of all intervals were constrained to the interval from 0 to 1. The widths of the 100 intervals ranged from 0.129 to 0.420; the average width of the interval was 0.240.

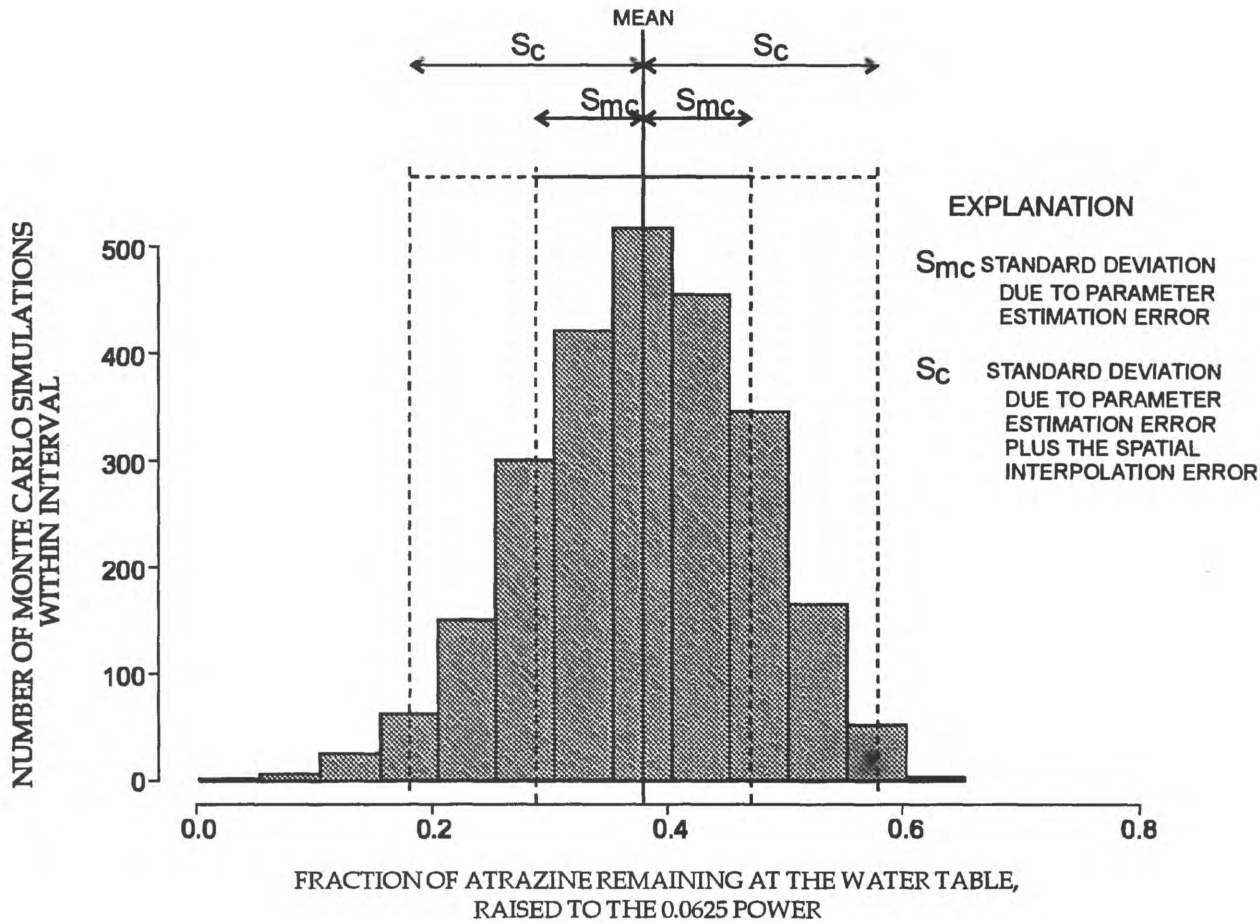


Figure 17. Effect of parameter uncertainty and spatial interpolation error on the uncertainty of the fraction of atrazine remaining at the water table at a selected well. (Results shown for the well with minimum northing along selected transect.)

Sensitivity Analysis

Analyses were conducted to determine the local sensitivity of the estimated fractions of atrazine remaining at the water table to changes in 13 selected model parameters. The sensitivity coefficients, which are applicable within the range of parameters specified, describe changes in the fraction remaining with unit changes in the parameters. Local sensitivity coefficients were computed as:

$$s_{kl} = \frac{\left(RM_{kl}^{\lambda}(+) - RM_{kl}^{\lambda}(-)\right)}{b_{klm}^{+} - b_{klm}^{-}}, \qquad (20)$$

where

s_{kl} equals the sensitivity coefficient of the k^{th} parameter at the l^{th} well;

$RM_{kl}^{\lambda}(+/-)$ is the fraction of atrazine remaining at the l^{th} well that was associated with a high (+) value or a low (-) value of the k^{th} parameter, and λ is the power transformation parameter equal to 0.0625;

b_{klm} is the value of the k^{th} parameter at the l^{th} well in the m^{th} layer.

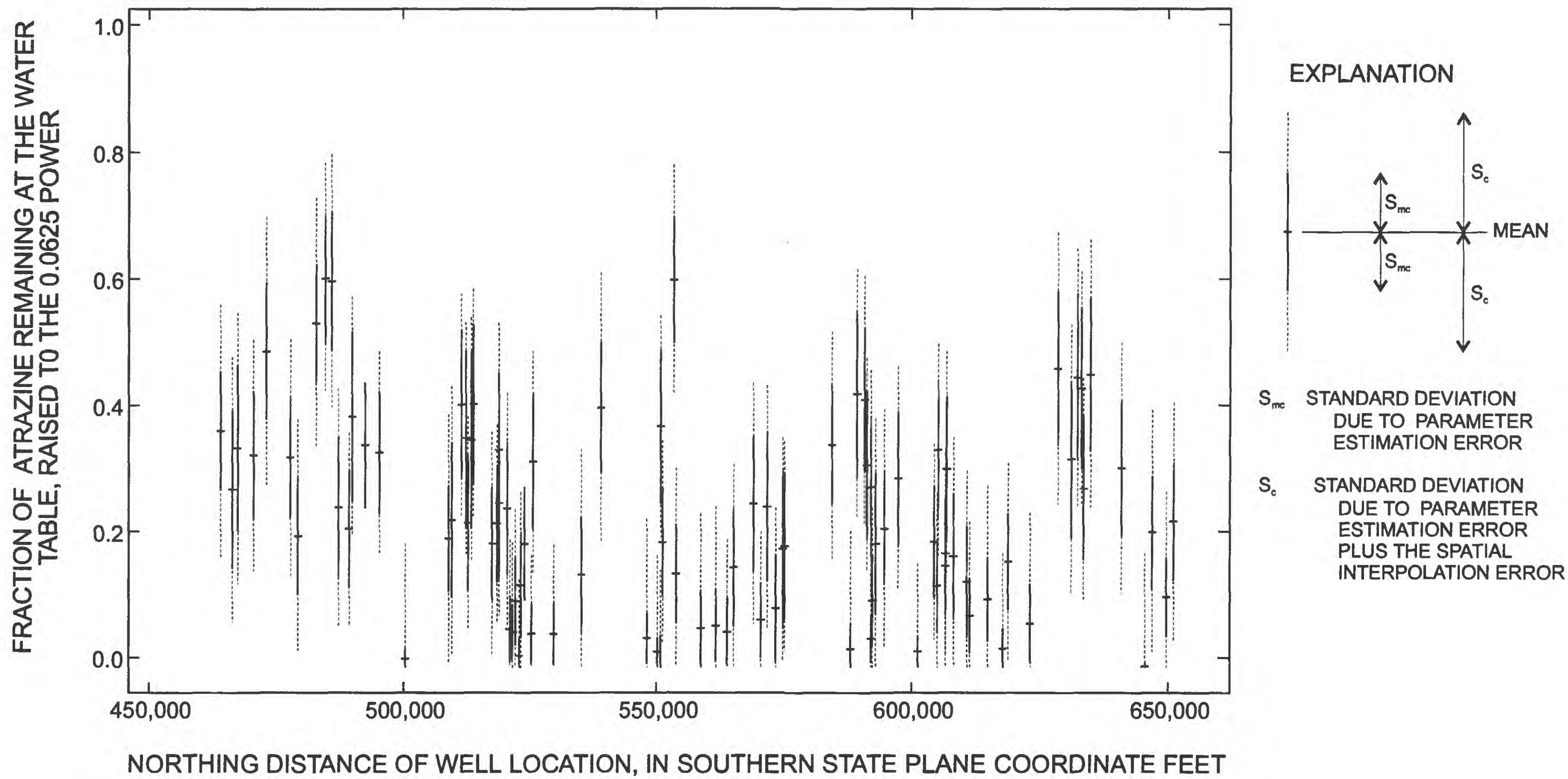


Figure 18. Effects of parameter uncertainty and spatial interpolation error on the uncertainty of the fraction of atrazine remaining at the water table at wells along the north-south transect of Kent County, Michigan. (Fractions raised to the 0.0625 power.)

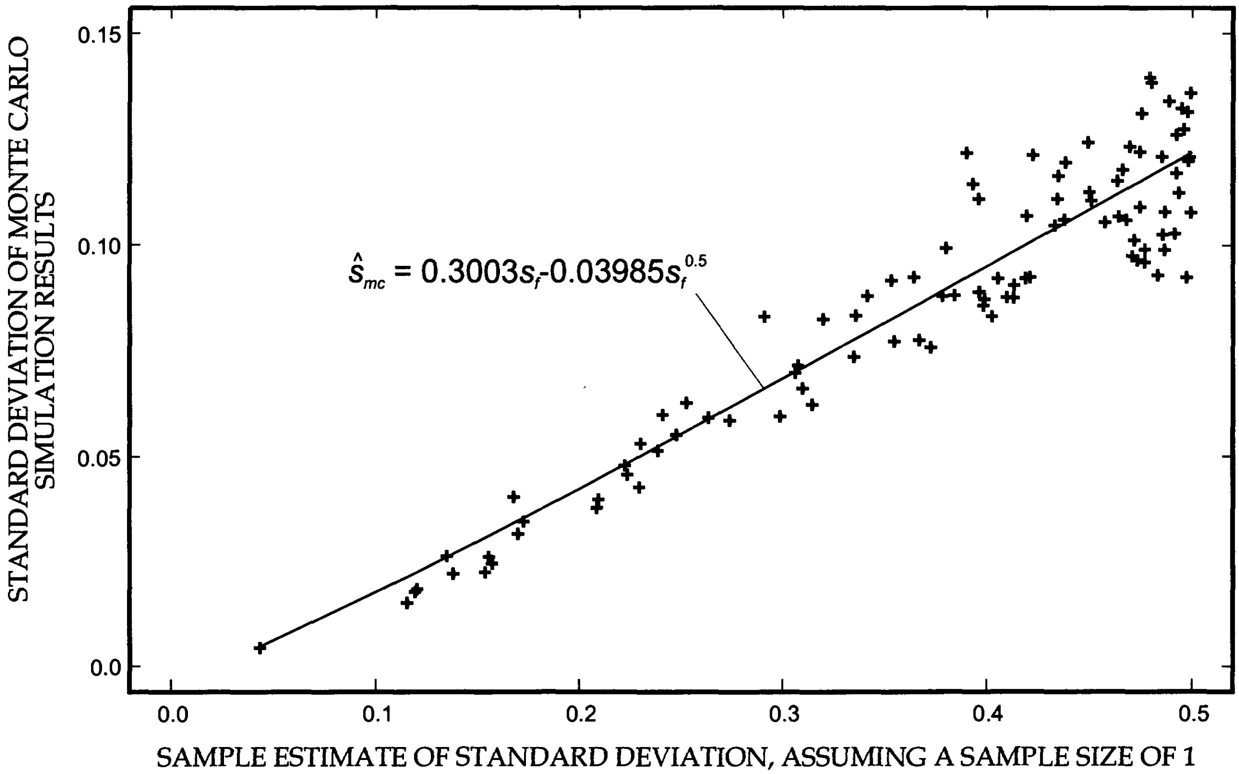


Figure 19. Relation between fraction of atrazine remaining at the water table and parameter uncertainty in Kent County, Michigan. (Fractions raised to the 0.065 power).

Sensitivity coefficients varied among parameters and wells (fig. 20). Most parameters had a consistent effect on fractions of atrazine remaining. Fractions remaining were consistently positively associated with root depth, deep percolation, and pesticide half life; fractions remaining were consistently negatively associated with K_{oc}, field capacity, residual moisture content, air-entry level, and organic carbon content. Infiltration was both positively and negatively associated with fractions remaining at the water table at about equal numbers of wells. The mixed effects for infiltration may result from higher than average levels of infiltration causing higher than average losses of pesticides to plants in some areas and higher than average infiltration increasing the velocity of pesticide movement through the soil zone. Although mixed results occurred for water table depth and porosity, effects tended to be dominately positive or negative. Sensitivities were generally greatest for parameters describing half-life of atrazine and organic carbon content of soils and unweathered lithologies; sensitivity was lowest for infiltration.

Discussion

Three maps are presented in this report showing the estimated relative vulnerability of the near-surface aquifer to contamination by atrazine from non-point sources. The maps present three views of the same vulnerability characteristics under different metrics. The three metrics are analogous to three digital filters from a continuous range of power transformations determined by the parameter λ.

Choice of λ represents a trade-off between resolution and noise that varies with the magnitude of the computed fraction. For λ equal to 0.0625, small differences between low computed fractions (less than 0.2 percent) of atrazine remaining at the

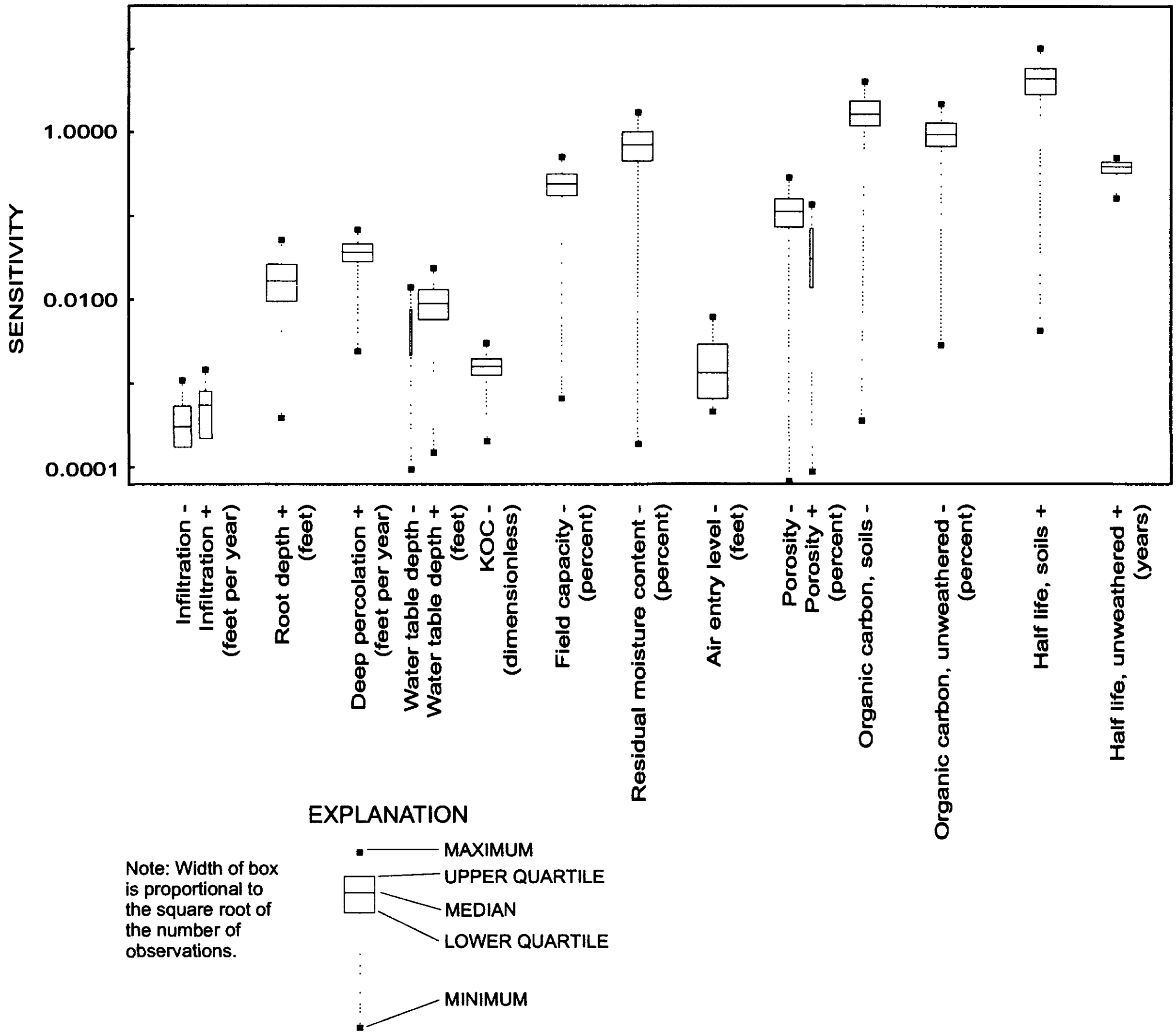


Figure 20. Sensitivity of the computed fractions of atrazine remaining at the water table to variations in selected parameters (Fractions raised to the 0.0625 power).

water table are apparent; thus resolution of small differences in frequent (more than 95 percent of selected wells), low vulnerability areas is higher than at larger λ values. At the same time, the additional resolution in low vulnerability areas masks larger differences in less frequent, high vulnerability areas. Thus, if differences between low- and high-vulnerability areas are of primary interest, resolution of small differences among low vulnerability areas might be associated with unwanted noise. Three maps are presented in this report to provide the reader with information about both frequent, small differences among low-vulnerability areas and infrequent, large differences in vulnerability.

Concentrations of atrazine potentially reaching the water table were computed on the basis of a steady-state, uniform atrazine application rate of 2 pounds per acre per year. A uniform application rate was used because detailed information on the historical application rates of atrazine is unavailable. This estimate of potential concentrations of atrazine in leachate reaching the water table is intended to provide a context for relating aquifer vulnerability estimates to water-quality criteria developed by the USEPA. Potential concentrations almost certainly differ systematically from actual leachate concentrations, in part, because of differences between the uniform atrazine application rate used in the computation and actual application rates. No data on atrazine concentrations in the leachate were available to assess the accuracy or utility of the computed potential concentrations.

Although leachate-water quality directly effects ground-water quality in the saturated zone, the relation between leachate-water quality at the water table and water-quality in the near-surface aquifer is complex. Under steady-state conditions, average concentrations of atrazine in the aquifer would likely be lower than average concentrations in leachate due to dilution, sorption of atrazine, and transformation of atrazine to metabolites in the saturated zone. However, the magnitude of this change is uncertain. In addition, minimum and maximum concentrations of atrazine in leachate and in the saturated zone may not be co-located due to the lateral movement of ground water in the saturated zone. Additional analysis beyond the scope of this report would be required to estimate leachate-water quality and to relate leachate-water quality to water quality in the saturated zone.

The leaching model applied in this report provides an estimate of the vulnerability of the near-surface aquifer to contamination by atrazine. The vulnerability estimate is related to water-quality criteria developed by the USEPA to help assess potential risks from atrazine to the near-surface aquifer. However, atrazine accounts for only 28 percent of the herbicide use in the county (table 1); additional potential for contamination exists from other pesticides and pesticide metabolites. Therefore, additional work is needed to develop a comprehensive understanding of the relative risks associated with specific pesticides within the county. The modeling approach described in this report provides a technique for estimating relative vulnerabilities to specific pesticides and for helping to assess potential risks.

Uncertainty in vulnerability estimates arises due to spatial interpolation from point estimates of computed vulnerability and from uncertainty in hydrologic, lithologic, and pesticide characteristics used in leaching-model computations. In this report, uncertainty associated with spatial interpolation was a larger component of variability in vulnerability estimates than uncertainty associated with model parameters. Uncertainty in spatial interpolation could be reduced by increasing the density of wells used in the analysis. In addition, for areas with detailed information on depths to the water table, the uncertainty associated with the spatial interpolation could be limited to that uncertainty associated with spatially interpolating the loss of pesticide in the unweathered lithologic materials, because soils data is available as a continuous coverage. With respect to parameter uncertainty, leaching model computations are most sensitive to uncertainties in parameters describing atrazine half life and organic carbon content of soils and unweathered lithologic materials. Additional research refining estimates of these parameters would likely reduce model uncertainty to the greatest extent.

The pesticide leaching model developed by

Rutledge and Helgesen (1990) provides an objective, physically-based model for estimating the relative vulnerability of the near-surface aquifer to pesticide leaching through the unsaturated zone from non-point sources. The model uses readily available hydrologic, lithologic, and pesticide characteristics in developing estimates. Increased density of point estimates of aquifer vulnerability would reduce spatial interpolation error; reduced uncertainty of selected parameters would improve model estimates of aquifer vulnerability.

SUMMARY

A physically-based model was used to estimate relative vulnerability of the near-surface aquifer to pesticide leaching from non-point sources in Kent County, Michigan. Model input data, which included hydrologic, lithologic, and pesticide characteristics, were readily obtained from existing sources.

The pesticide leaching model was used to estimate the fraction of atrazine remaining at the water table, *RM*, as a measure of vulnerability. Point estimates of the fraction remaining were computed at 5,444 wells distributed throughout Kent County. The probability density of the estimated fractions was skewed to the right. A power transformation of the form $rm = RM^{\lambda}$, where the power transformation parameter, λ, equals 0.0625, was used to develop a metric of vulnerability, *rm*, that was symmetrically distributed. The transformed metric was used in a geostatistical analysis to identify the spatial correlation structure. The spatial correlation structure and *rm* values at individual wells were used with the ordinary kriging equations to estimate the average fraction of atrazine remaining, in the transformed metric, at the center of each cell representing 94.7 acres, in a regular grid over the county. Maps of relative vulnerability were generated for the *rm* metric, an intermediate inverse transform, $rm^{\lambda^{-0.5}}$, and for the inverse transform $rm^{\lambda^{-1.0}}$ (*RM*). For the 5,444 selected wells, estimated time of travel between the soil surface and the water table ranged from 2.2 to 118 years; the mean time of travel was 17.7 years. Assuming that atrazine applications began in 1952, by 1997 sufficient time will have passed for atrazine to move to the water table at 96.7 percent of the selected wells.

The three maps present three views of the same vulnerability characteristics under different metrics. Vulnerability in the *rm* metric depicts a relatively uniform distribution of vulnerabilities across the county with localized areas of high and low vulnerabilities visible. The $rm^{\lambda^{-0.5}}$ metric depicts about one-half the county as low vulnerability with discontinuous patterns of high vulnerability evident. In the $rm^{\lambda^{-1.0}}$ metric, more than 95 percent of the county appears to have low vulnerability; areas of high vulnerability are distinct. Choice of the metric to depict vulnerability is application dependent. Land-use information on the distribution of cropland aids the interpretation of the vulnerability maps by indicating areas likely to be affected by pesticide applications.

Aquifer vulnerability estimates (*RM* metric) were used with a steady-state, uniform atrazine application rate to compute a potential concentration of atrazine in leachate reaching the water table. The average estimated potential atrazine concentration in leachate at the water table was 0.16 µg/L in the model area; estimated potential concentrations ranged from 0 to 26 µg/L. About 2 percent of the model area had estimated potential atrazine concentrations in leachate at the water table that exceeded the USEPA maximum contaminant level of 3 µg/L. The spatial distribution of estimated potential atrazine concentrations in leachate followed the distribution of estimated aquifer vulnerability, owing to the assumption of a uniform application rate of atrazine. The computed potential concentration of atrazine in leachate is not intended as an estimator of leachate-water quality or water quality in the saturated zone.

The leaching model provides an estimate of the vulnerability of the near-surface aquifer to contamination by atrazine. However, the assessment does not account for vulnerability to metabolites of atrazine, in particular DEA (deethylatrazine) and DIA (deisopropylatrazine), which are structurally and toxicologically similar to atrazine or to vulnerability from other pesticides. By extension to other pesticides and pesticide metabolites, the type of vulnerability assessment described in this report

could be used to develop a more comprehensive understanding of the vulnerabilities and relative risks associated with other major pesticides.

Uncertainty analysis was used to quantify the variability in aquifer vulnerability estimates to uncertainties in parameters and spatial interpolation errors. For this analysis, 100 wells were selected along a north-south transect through the county east of Grand Rapids, Michigan. At each well, 2,500 samples of 13 parameters were randomly drawn from their corresponding probability densities. Samples were used in a Monte Carlo simulation of the leaching model to determine the variability in aquifer vulnerability estimates. Results indicate that the parameter uncertainty introduced a variability in the computed fraction of atrazine remaining at the water table of 0.0875 (in the *rm* metric), as measured by the average standard error of the Monte Carlo simulations, s_{rm}. In comparison, the average kriging standard error, s_k, associated with errors in the spatial interpolation, was 0.146. Thus in this report, uncertainties in spatial interpolation had a greater effect than uncertainties associated with parameters in increasing variability in estimated fractions of atrazine remaining at the water table. Uncertainties in spatial interpolation can be reduced by increasing the density of wells in the mapping area.

Sensitivity analysis was used to determine how unit changes in parameter values affected estimated fractions of atrazine within the range of parameters specified. Results indicate that most parameters had a consistent effect on fractions of atrazine remaining. Fractions remaining were consistently positively associated with root depth, deep percolation, and pesticide half life; fractions remaining were consistently negatively associated with K_{oc} (organic-carbon partition coefficient), field capacity, residual moisture content, air-entry level, and organic carbon content. Infiltration was both positively and negatively associated with fractions remaining at the water table at about equal numbers of wells. Among parameters, sensitivities were generally greatest for half life and organic carbon content of soils and unweathered lithologies; sensitivity was lowest for infiltration. Additional research refining estimates of pesticide half-life and organic-carbon content is needed to reduce parameter uncertainty.

REFERENCES CITED

Box, G.E.P., and Draper, N.R., 1987, Empirical model-building and response surfaces: New York, John Wiley, 669 p.

Brady, N.C., 1974, The nature and properties of soils: New York, Macmillian Publishing, 639 p.

Brooks, K.N., Ffolliot, P.F., Gregersen, H.M., and Thames, J.L., 1991, Hydrology and the Management of Watersheds: Iowa State University Press, Ames, Iowa, 392 p.

Cressie, N.A., 1991, Statistics for spatial data: John Wiley, New York, 900 p.

Eichenlaub, V.L., Harman, J.R., Nurnberger, F.V., and Stolle, H.J., 1990, The climatic atlas of Michigan: The University of Notre Dame Press, Notre Dame, Indiana, 165 p.

Fetter, C.W., 1988, Applied hydrogeology: New York, Macmillan Publishing.

Farrand, W.R., and Bell, D.L., 1984 (reprinted), Quaternary geology of Michigan with surface-water drainage divides, Michigan Department of Natural Resources, Geological Survey Division, 2 maps.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, New Jersey: Prentice Hall, 604 p.

Gianessi, L.P. and Puffer, Cynthia, 1991, Herbicide use in the United States: Washington, D.C., Resources for the Future, December 1990 (revised April 1991), 128 p.

Guymon, G.L., 1994, Unsaturated zone hydrology: Englewood Cliffs, New Jersey, Prentice Hall, 210 p.

Holtschlag, D.J., 1994, A Generalized Estimate of Ground-Water Recharge Rates in the Lower Peninsula of Michigan: U.S. Geological Survey Water-Supply Paper 2437 (in press), 59 p.

Hausenbuiller, R.L., 1978, Soil science: W.C. Brown Company, Dubuque, Iowa, 611 p.

Keckler, Doug, 1994, User's Guide: Surfer for Windows: Golden Software, Golden Colorado, 446 p.

Koplin, D.A., Goolsby, D.A., and Thurman, E.M., 1995, Pesticides in near-surface aquifers: An assessment using highly sensitive analytical methods and tritium: Journal of Environmental Quality, v. 24, no. 6, November-December.

Michigan Agricultural Statistics Service, 1995, Michigan Agricultural Statistics: Michigan Department of Agriculture, Lansing, Michigan, 105 p.

Ott, W.R., 1995, Environmental statistics and data analysis: Lewis Publishers, Ann Arbor, Mich., 313 p.

Ratliff, L.F., Ritchie, J.T., and Cassel, D.K., 1983, Field-measured limits of soil water availability as related to laboratory-measured properties: Journal of the Soil Science Society of America, vol. 47, p. 770-775.

Rawls, W.J., 1983, Estimating soil bulk densities from particle size analysis and organic matter content: Soil Science, v. 135, no. 2, Note, p. 123-125.

Rutledge, A.T., and Helgesen, J.O., 1991, A steady-state unsaturated-zone model to simulate pesticide transport: U.S. Geological Survey Water-Resources Investigations Report 90-4164, 13 p.

Todd, D.K., 1980, Groundwater hydrology, 2nd ed.: New York, John Wiley, 535 p.

U.S. Department of Agriculture, 1986, Soil Survey of Kent County, Michigan: U.S. Department of Agriculture, Soil Conservation Service, 263 p.

U.S. Department of Commerce, 1994, Census of agriculture, 1992--Final county file: U.S. Department of Commerce, Bureau of the Census, [machine-readable data file].

U.S. Department of Commerce, 1996, 1990 US Census Data: URL: http:///www.census.gov/cdrom/lookup, database: C90STF3A, Summary Level: State--Urbanized Area, Grand Rapids, Michigan, April 17.

U.S. Environmental Protection Agency, 1992, Drinking water regulations and health advisory: USEPA, Office of Water, Washington, DC.

_____,1993, A review of methods for assessing aquifer sensitivity and ground water vulnerability to pesticide contamination: Office of Water (WH-550) contract number 813-R-93-002, Washington, D.C., U.S. Government Printing Office, 147 p.

U.S. Geological Survey, 1990, USGeoData 1:250,000 and 1:100,000 scale land use and land cover and associated maps digital data: U.S. Geological Survey, ftp://nmdpow9.er.usgs.gov/public/lulcguide.

_____, 1995a, Pesticides in the atmosphere: Current understanding of distribution and major influences: U.S. Geological Survey Fact Sheet FS-152-95, 4p.

_____, 1995b, Pesticides in ground water: Current understanding of distribution and major influences: U.S. Geological Survey Fact Sheet FS-244-95, 4 p.

APPENDIX I.

Listing of FORTRAN program used in the analysis of atrazine leaching

```
      PROGRAM PestLeach
C
C ***************************************************************************
C  * PestLeach is an adaptation of the pesticide leaching model originally     *
C  * developed by Rutledge, A.T., and Helgesen, J.O., 1991, A steady-state     *
C  * unsaturated-zone model to simulate pesticide transport: U.S. Water-      *
C  * Resources Investigations Report 90-4164, 13 p.                           *
C  *                                                                          *
C  * PestLeach produces identical results to the original program. Changes   *
C  * primarily affect the input format of data to facilitate analysis of     *
C  * large numbers of wells in a single model run and capabilities to        *
C  * conduct Monte Carlo simulation.                                          *
C ***************************************************************************
C
      REAL D(20), AEXL(20), aexi(20), aexh(20), aes(20),
     1        RMCXL(20), rmcxi(20), rmcxh(20), rmcs(20),
     2        FCXL(20), fcxi(20), fcxh(20), fcs(20),
     3        PORXL(20), porxi(20), porxh(20), pors(20),
     4        OCXL(20), ocxi(20), ocxh(20), ocs(20),
     5        HALFL(20), halfi(20), halfh(20), halfs(20),
     6        tlayer(20)
c
      REAL ae, rmc, fc, poroc, bulk, sdens, oc
      REAL LBACRE, KOC, H, Q, KD, Z, ZSOIL, ZGLAC, zwt
      INTEGER NUMPTS, ANS, TIME, ns, ng, nl, modrun
      character fnameo*60, rdstr*40
c
      print *, 'PestLeach is an adaptation of the pesticide leaching  '
      print *, 'model orignially developed by Rutledge, A.T., and     '
      print *, 'Helgesen, J.O., 1991, A steady-state unsaturated-zone '
      print *, 'model to simulate pesticide transport: U.S. Geological '
      print *, 'Water-Resources Investigations Report 90-4164, 13 p.  '
      print *, ' '
      print *, 'Two input files area required.  The point data file   '
      print *, 'contains data that is constant for each point of      '
      print *, 'estimation.  The lithology data file contains         '
      print *, 'properties that change with each model layer.         '
      print *, ' '
      print *, 'Point data filename? '
      read (*,'(a60)')  fnameo
      OPEN (9, FILE= fnameo, STATUS= 'OLD')
c
      print *, 'Enter number of points (or 0 to read until the eof)   '
      read (*,'(i10)') numpts
      if (numpts.le.0) then
        numpts = 10000
        print *, 'Computing up to 10,000 points.'
      end if
c
      print *, 'Lithology data filename? '
```

```
      read (*,'(a60)') fnameo
      OPEN (10, FILE=  fnameo, STATUS= 'OLD')
c
      print *, 'Output filename? '
      read (*,'(a60)') fnameo
      OPEN (12, FILE=  fnameo, STATUS= 'NEW')
c
    2 print *, 'Enter "0" w/o parenthesis for point estimation or      '
      print *, '      "1"                for Monte Carlo simulation  '
      print *, '(Note: Monte Carlo simulation requires that the        '
      print *, ' lithology data file have three entries)              '
      read (*,'(i10)') modrun
      if (modrun.eq.0) then
        print *, 'Point Estimation in Progress...'
      else if (modrun.eq.1) then
        print *, 'Monte Carlo Simulation in Progress...'
      else
        print *, 'Simulation characteristics unknown. Stopping. '
        stop
      end if
c
      READ (9,13,end=999) rdstr,RAIN,RETURN,ROOT,zwt,KOC,SDENS,NS,NG
      nl = ns + ng
      print *, 'ns=',ns,' ng=',ng,' nl=',nl
      WRITE(12,*) ' Rain    Return    Root    ZWT     KOC   SDENS
     1   AE     RMC     FC     POROC  Halflife   Time   Remain'
C
c     Read in the lithology data
c
      if (modrun.eq.0) then
c     Read in single line of layer data for each estimation point
        do 6 l=1,nl
          READ (10,16) D(L),AEXI(L),RMCXI(L),FCXI(L),PORXI(L),OCXI(L),
     $        HALFI(L)
          OCXi(L)= OCXI(L)/100.0
    6   continue
      else if (modrun.eq.1) then
c     Read in three line set of layer data for Monte Carlo simulation
        DO 8 L=1,NL
          READ (10,16) D(L),AEXL(L),RMCXL(L),FCXL(L),PORXL(L),OCXL(L),
     $        HALFL(L)
          OCXl(L)= OCXL(L)/100.0
          READ (10,16) D(L),AEXI(L),RMCXI(L),FCXI(L),PORXI(L),OCXI(L),
     $        HALFI(L)
          OCXi(L)= OCXI(L)/100.0
          READ (10,16) D(L),AEXH(L),RMCXH(L),FCXH(L),PORXH(L),OCXH(L),
     $       HALFH(L)
          OCXh(L)= OCXh(L)/100.0
        print *, NL, L
    8   CONTINUE
      else
        print *, 'Unrecognized modrun number. '
        goto 2
      end if
c
```

```
      ZSOIL = D(NS)
      ZGLAC = D(NL)
c
      DO 140 K = 1,NUMPTS
      Z = 0.0
      ET = RAIN - RETURN
      RAIN= RAIN/12.0
      ET= ET/12.0
      Z = zwt
c  30 continue
C
C SET LIMITS AND "CONSTANTS" FOR EACH SOIL ZONE, SO THAT INTEGRATION
C CAN BE PERFORMED SEPARATELY FOR EACH ZONE:
C
      START= 0.0
      DO 100 L= 1,NL
       IF(Z.LE.START) THEN
           TLAYER(L)= 0.0
           GO TO 100
       END IF
       if (modrun.eq.0) then
        AEs(L)   = AEXi(L)
        RMCs(L)  = RMCXi(L)
        FCs(L)   = FCXi(L)
        PORs(L)  = PORXi(L)
        OCs(L)   = OCXi(L)
       else
        call trisam(AEXL(L), AEXi(L), AEXh(L), AEs(L))
        call trisam(RMCXL(L),RMCXi(L),RMCXh(L),RMCs(L))
        call trisam(FCXL(L), FCXi(L), FCXh(L), FCs(L))
        call trisam(PORXL(L),PORXi(L),PORXh(L),PORs(L))
        call trisam(OCXL(L), OCXi(L), OCXh(L), OCs(L))
       end if
c
       AE    = AEs(L)
       RMC   = RMCs(L)
       FC    = FCs(L)
       POROC = PORs(L)
       BULK  = SDENS * (1.0-POROC)
       KD    = OCs(L) * KOC
C
C PERFORM NUMERICAL INTEGRATION TO CALCULATE TIME OF TRANSPORT THROUGH
C                 THIS SOIL ZONE:
       STOP = D(L)
       IF (Z.LE.STOP) THEN
          STOP= Z
          END IF
       X= START - 0.005
       NUMX = INT( 0.5 + (STOP-START)/0.01 )
       TLAYER(L)= 0.0
       DO 80 I=1,NUMX
        X= X + 0.01
        H = zwt - X
        CALL CONTENT (AE,RMC,FC,POROC,H,WC)
        CALL DISCHARG (RAIN,ET,ROOT,X,Q)
```

```
        Y= (WC + (BULK*KD))/Q
        TLAYER(L) = TLAYER(L) + (Y*0.01)
   80   CONTINUE
       START= D(L)
  100 CONTINUE
      TTOTAL= 0.0
      DO 110 L=1,NL
  110 TTOTAL= TTOTAL + TLAYER(L)
      T=TTOTAL * 365.25
C
      H =  zwt - Z
      CALL CONTENT (AE,RMC,FC,POROC,H,WC)
      CALL DISCHARG (RAIN,ET,ROOT,Z,Q)
C
C CALCULATE AMOUNT LEFT AFTER DEGRADATION:
C
      REMAIN= 1.0
      DO 120 L=1,NL
       if (modrun.eq.0) then
        HALFs(L) = HALFI(L)
       else
        call trisam(HALFL(L),HALFi(L),HALFh(L),HALFs(L))
       end if
       REMAIN= REMAIN * EXP(-0.693*TLAYER(L)*365.25/HALFs(L))
  120 continue
C
C ALLOW FOR LOSS OF PESTICIDE DUE TO ROOT UPTAKE:
C
      REMAIN= REMAIN * Q / RAIN
      write (12,18) rdstr,rain*12.,return,root,zwt,koc,sdens,
     1         ae,rmc,fc,poroc,halfs(nl),T/365.25,REMAIN
C
c     Read in new point data
      READ (9,13,end=999) rdstr,RAIN,RETURN,ROOT,zwt,KOC,SDENS,NS,NG
      nl = ns + ng
c     Test need to read in new layer data
      if (modrun.eq.0) then
       do 136 l=1,nl
        READ (10,16) D(L),AEXI(L),RMCXI(L),FCXI(L),PORXI(L),OCXI(L),
     $        HALFI(L)
        OCXi(L)= OCXI(L)/100.0
  136  continue
      end if
  140 CONTINUE
c
   12 FORMAT (I11, I6, 8F10.2, 1I10)
   13 format (a37,6f10.0,2i10)
   14 FORMAT (80X)
   15 FORMAT (a37, F8.1, f10.3, 2e14.6)
   16 FORMAT (7f10.0)
   17 FORMAT (6F10.0)
   18 format (a37,6f9.3,f10.4,f9.4,f9.4,f9.4,f8.2,f10.4,e13.5)
   19 format (6f10.4,e14.6)
c
```

```
999  continue
     CLOSE ( 9, STATUS= 'KEEP')
     CLOSE (10, STATUS= 'KEEP')
     CLOSE (11, STATUS= 'KEEP')
     CLOSE (12, STATUS= 'KEEP')
     print *, 'Done.'
     STOP
     END
c
     SUBROUTINE CONTENT(AE,RMC,FC,POROC,H,WC)
     REAL POROC, H
C    THIS ROUTINE GIVES WATER CONTENT OF UNSATURATED ZONE AS A FUNCTION
C    OF HEIGHT ABOVE WATER TABLE AND 4 PROPERTIES OF THE LITHOLOGIC TYPE:
C    AIR ENTRY HEIGHT(FT), RESIDUAL MOISTURE CONTENT, FIELD CAPACITY
C    WATER CONTENT, AND POROCITY (FRACTIONS)
     IF (INT(10*H).GE.34) THEN
       WC= RMC + (3.4228*(FC-RMC)/H)
     ELSEIF (INT(100*H).GE.INT(100*AE)) THEN
       WC= POROC + ((FC-POROC)*(H-AE) / (3.4-AE))
     ELSE
       WC= POROC
     ENDIF
     RETURN
     END
c
     SUBROUTINE DISCHARG(RAIN,ET,ROOT,Z,Q)
     REAL Q
C    GIVES VOLUMETRIC WATER FLUX ("DARCY VELOCITY") IN UNSATURATED ZONE AS
C    FUNCTION OF DEPTH BELOW LAND SURFACE:
     IF(INT(100*Z).LE.INT(100*ROOT)) THEN
      Q= RAIN - (ET*Z/ROOT)
     ELSE
      Q= RAIN - ET
     ENDIF
     RETURN
     END
c
     subroutine trisam(xa, xc, xb, sample)
     real xa, xb, xc, sample, ranval, xsc
c    Generate a sample from a triangular distribution
     ranval = ran(12345)
     xsc = (xc - xa)/(xb - xa)
     if (ranval.le.xsc) then
       sample = sqrt(xsc * ranval)
     else
       sample = 1.0 - sqrt((1.0 - xsc)*(1.0 - ranval))
     end if
     sample = xa + (xb - xa)*sample
c    print *, 'xa=',xa,' xc= ',xc,' xb= ',xb
c    print *, 'ranval=',ranval,' sample=',sample
     return
     end
```