Assessment of Ground-Water Vulnerability to Atrazine Leaching in Kent County, Michigan: Review, Comparison of Results of Other Studies, and Verification

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

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS AND VERTICAL DATUM

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
acre (ac)	0.4047	hectare
cubic feet per second (ft^3/s)	0.02832	cubic meter per second
pounds (lbs)	0.454	kilograms (force)

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

Vertical datum: 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.

ASSESSMENT OF GROUND-WATER VULNERABILITY TO ATRAZINE LEACHING IN KENT COUNTY, MICHIGAN: REVIEW, COMPARISON OF RESULTS OF OTHER STUDIES, AND VERIFICATION

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

ABSTRACT

Model assumptions and parameters used in an earlier study of the vulnerability of ground water in Kent County, Michigan, to atrazine contamination were reviewed and compared with other studies. The review indicated that model assumptions are consistent with those used in other models and that the parameters assigned in the Kent County model are within the broad range commonly found in the literature. Model assumptions most likely to limit the accuracy of the previous study include those of uniform transport and steady-state flow. Simulation results are more sensitive to parameter estimates for atrazine half life, organic-carbon content, and organic-carbon partition coefficient than to other model parameters.

Potential atrazine detection probabilities and concentrations of atrazine reported in the previous Kent County Study were compared with data from other studies. Detection probabilities of 14 measurements of atrazine concentrations in ground water from shallow wells in the southern Lower Peninsula of Michigan were compared with detection probabilities based on potential atrazine concentrations computed for Kent County. Results indicate that the distribution of detection probabilities based on measured concentrations is similar to that based on adjusted potential concentrations. Potential concentrations were adjusted for effects of differences between sampling and modeling depths and for differences between the uniform application rate used for potential concentrations and the percentage of Kent County that is likely to be treated with atrazine. Potential concentrations of atrazine in the Kent County Study were within the wide range of concentrations measured in other states.

A stratified random sampling strategy was developed to verify expected atrazine concentrations in ground water within Kent County. The strategy helps identify strata, determine the optimum allocation of ground-water samples within defined strata, and project the sampling error. Implementation of the strategy was illustrated by use of potential atrazine concentrations computed in the previous Kent County Study. Once detailed information on historical application rates of atrazine is developed, expected atrazine concentrations can be computed by use of the vulnerability model and used to implement the sampling strategy. Sampling results may be used to verify the effectiveness of the vulnerability model and local estimates of historical atrazine application rates by use of analysis of variance.

INTRODUCTION

Holtschlag and Luukkonen (1997) utilized a steady-state model of pesticide leaching through the unsaturated zone to estimate the vulnerability of the near-surface aquifer to atrazine contamination from non-point sources in Kent County, Michigan. The model-computed fraction of atrazine remaining at the water table was used as the vulnerability criterion. In addition, the computed fraction of atrazine remaining was used with an assumed steady-state uniform application rate of 2 pounds per acre per year to compute a potential concentration of atrazine reaching the water table. Model assumptions, parameter values, and computed results developed by Holtschlag and Luukkonen (1997) are referred to as the "Kent County Study" in this report or "previous study" where the context is clear.

Purpose and Scope

This report was developed in cooperation with the Michigan Department of Agriculture to assess the vulnerability of ground water to atrazine contamination described in the Kent County Study. The assessment compares model assumptions and parameters used in the Kent County Study with those reported in the literature. In addition, the assessment compares potential atrazine concentrations computed in the Kent County Study with limited data on atrazine in Michigan and nearby states. Finally, a field sampling design is devised to verify

expected atrazine concentrations by direct measurements of atrazine within Kent County, Michigan. Expected atrazine concentrations can be computed on the basis of model- simulations, once detailed information on historical atrazine application rates become available.

Description of Study Area

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 people, 436,033, live in the Grand Rapids metropolitan area 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 ft. These deposits are primarily medium- and fine-textured till, outwash sand and gravel, and postglacial alluvium.

In 1990, an estimated 202,192 lbs of herbicides were applied to crops in Kent County (Gianessi and Puffer, 1991). About 27.9 percent of herbicide applications were atrazine, which is only directly applied to field corn and sweet corn. In 1994, 65.6 mi^2 were planted in corn (Michigan Agricultural Statistics Service, 1995, p. 88).

Review of Literature

Atrazine and Atrazine Metabolites

Atrazine is a synthetic, organic, pre-emergent pesticide that has been used routinely in Michigan and other parts of the United States following its development in 1953. Atrazine is primarily used to increase the yield of field corn by controlling weeds. In some areas, a small fraction of applied atrazine may move through the soil and underlying unsaturated zone into the ground water as an unavoidable consequence of routine applications carried out in accordance with generally accepted agricultural practices.

The primary concern about atrazine in ground water is associated with its potential adverse impact on the quality of water in aquifers that are sources of drinking-water supply. In response to these concerns and available data on adverse impacts, the

USEPA (U.S. Environmental Protection Agency) has established a maximum contaminant level (MCL) of 3 micrograms per liter (μg/L) of atrazine in drinking water (Nowell and Resek, 1994). Data from multistate surveys and from compilations of monitoring data indicate that atrazine concentrations have been below this MCL in more than 99 percent of the wells sampled in agricultural areas throughout much of the United States (Barbash and Resek, 1996, p. 406).

Although MCL criteria provide a useful standard, they have not been developed for all atrazine metabolites. These criteria are likely to be established and/or revised as more is learned about toxicities of atrazine parent and metabolites concentrations and about possible combined effects of multiple pesticides. A secondary concern about atrazine in ground water is that it will be a chronic source of low concentrations of the herbicide during periods of base flow to surface-water bodies, which support aquatic ecosystems and are also used as a source of drinking water in some areas (Squillace and Thurman, 1992, Squillace and others, 1993, Squillace and others, 1996).

Atrazine is degraded to its metabolites by both chemical and biological means. The primary chemical transformation is replacement of chlorine in atrazine with a hydroxol group to form hydroxyatrazine. Hydroxyatrazine is less phototoxic and is considered less of a threat to human health than the parent compound (Levy, 1993). And, although hydroxyatrazine is more water soluble than atrazine, it exhibits a substantially greater tendency to sorb to soils, particularly the clay fraction, than the parent compound and is therefore less mobile than atrazine (Adams and Thurman, 1991).

Biological transformations of atrazine are associated with soil microorganisms. In particular, dealkylation of atrazine gives rise to three chlorinated metabolites: deethyl atrazine (DEA), deisopropyl atrazine (DIA), and diamino-chloro-s-triazine (DIAM). Because of their toxicological similarity to atrazine and their widespread occurrence, data on concentrations of DEA and DIA are needed to obtain an adequate estimation of the true risk of using near-surface aquifers as sources for drinking water (Liu and others, 1996a). In Wiscon-
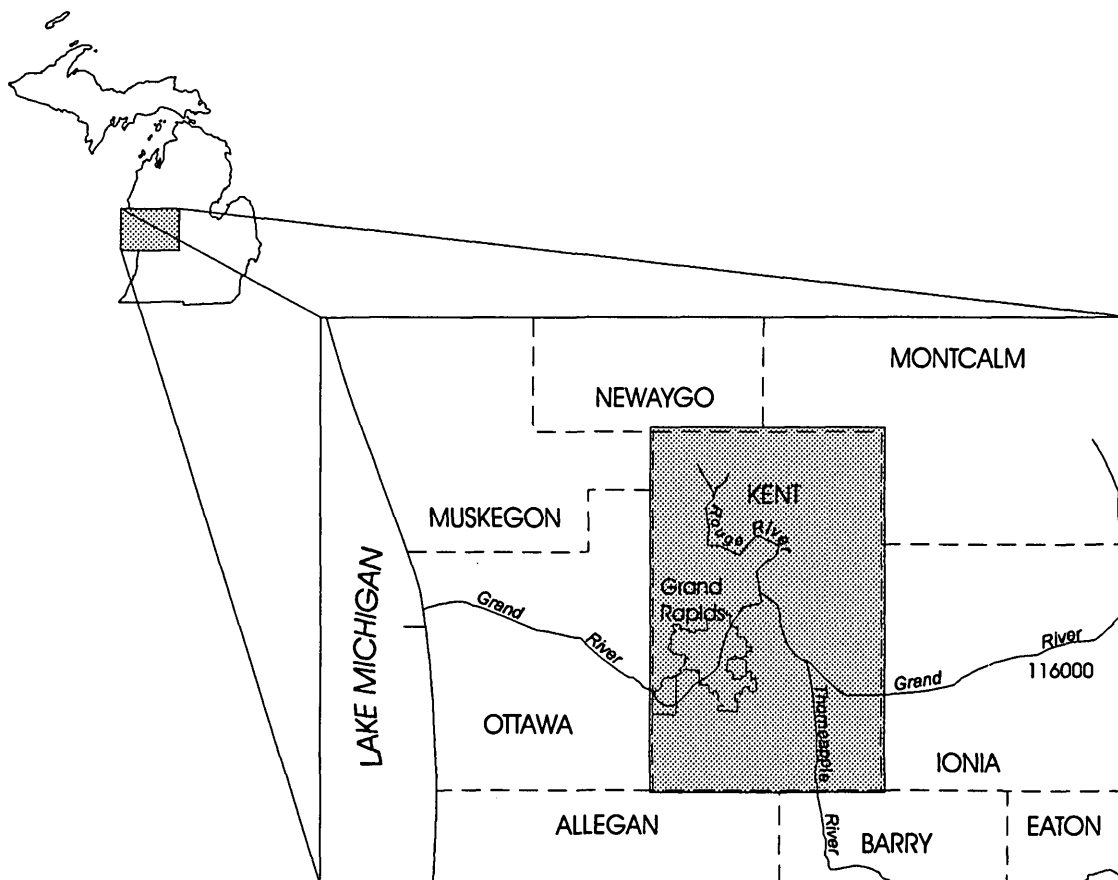
Figure 1. Location of Kent County, Michigan.

sin, the 3.0 ppb (part per billion[1]) enforcement standard and the 0.3 ppb preventative action level now apply to the sum of concentrations of atrazine, DEA, DIA, and DIAM (Levy, 1993, p. 329). Based on information on the soil partition coefficient, aqueous solubilities, and melting points, Mills and Thurman (1994) indicate that the DEA and DIA would likely move through the soil profile to ground water faster than the parent compound.

Distribution of Atrazine Concentrations in Ground Water

Over the past two decades, pesticides or their metabolites have been detected in ground waters of more than 43 states. At least 143 pesticides and 21 metabolites have been detected, including compounds in every major chemical class. For two of the multistate surveys -- the National Pesticide Survey (U.S. Environmental Protection Agency, 1990)

and the Midcontinent Pesticide Study (Koplin and others, 1995) -- the most frequently detected pesticide compounds were metabolites, rather than the parent compound (U.S. Geological Survey, 1995). Pesticides that have been detected most frequently include those that have been used most extensively, such as atrazine, simazine, alachlor, and metolachlor, and those for which sampling has been most extensive because of contamination problems, such as alicarb and its metabolites, and ethylene dibromide.

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. For the five multistate studies carried out to date, which focused mainly on agricultural areas (U.S. Environmental Protection Agency, 1990), the proportions of sampled wells with pesticide detections ranged from 4 percent (nationwide, rural domestic wells) to 62 percent (wells in corn and soybean areas of the

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1.At low concentrations, parts per billion is approximately equivalent to micrograms per liter (μg/L).

3

northern midcontinent, post-planting). Pesticide concentrations were 1 µg/L or less in more than 95 percent of the wells sampled during these studies (U.S. Geological Survey, 1995).

Herbicide compounds were prevalent in ground water across Iowa, which has some of the most intensive applications of herbicide in the United States. In a survey of 106 municipal wells in Iowa during the summer of 1995, herbicide compounds were detected in 70 percent of the wells sampled (Kolpin and others, 1997). Atrazine was detected at concentrations greater than 0.05 µg/L in 40.6 percent of the wells sampled and DEA was detected in 34.9 percent of the wells. However, the maximum concentration of atrazine measured was 2.13 µg/L, below the 3.0 µg/L MCL set for atrazine. The maximum concentration measured for DEA was 0.59 µg/L.

Atrazine has been detected in ground water in 25 states and is detected 10 to 20 times more frequently than the next most commonly detected pesticide (Belluck and others, 1991). Most detections of atrazine are at concentrations less than 2 µg/L. Whether point sources or non-point sources are responsible for most of ground-water contamination above MCLs is a subject of considerable debate (Barbash and Resek, 1996, p. 184). Low levels of atrazine concentrations in ground water likely originate from normal field use rather than from direct contamination of wells or point-source spills. Evidence indicating nonpoint-source origins include the widespread nature of detections, greater concentrations in shallow versus deep wells (as opposed to greater concentrations at depth due to back-siphoning), and greater concentrations down gradient from corn fields.

In 1991, the USGS (U.S. Geological Survey) undertook a study to determine the hydrological, spatial, and seasonal distribution of agricultural chemicals in near-surface aquifers of the Midcontinent region of the United States (Kolpin and others, 1994). A total of 303 wells in 12 states in the Midwest were selected for sampling. DEA and DIA concentrations were examined to determine if consideration of these metabolites substantially added to the understanding of the distribution of atrazine in ground water within the Midcontinent of the

United States. The mean atrazine-plus-metabolite concentrations were 53 percent greater than that of atrazine alone for those observations above the detection limit (> 0.05 µg/L). Furthermore, a regression analysis using atrazine plus metabolite concentrations (Liu and others, 1996b) revealed significant factors not identified when only atrazine concentrations were used.

Given the relatively long residence times of pesticides in shallow ground water (Levy, 1993), pesticide detections often reflect historic rather than current application patterns. This explains, in part, the continued detection in ground water of persistent compounds whose use has been discontinued. Several studies have reported detections of pesticides that were not used within the immediate vicinity of the sampled wells, but were used on nearby fields (Barbash and Resek, 1996, p. 141). These observations demonstrate the need to account for up-gradient use in ascertaining the sources of pesticides detected in individual wells, and in some cases, the applicability of solute-transport models to identify source areas or contributing areas of contamination.

Predicting Atrazine Occurrence in Ground Water

Three general categories of vulnerability assessment methods are available to predict the likelihood of pesticide occurrence in ground water without pre-existing data on atrazine concentrations. These are: computer simulations, scoring systems, and indicator solutes. The following overview provides a context for evaluating the vulnerability of ground water to atrazine leaching described in the Kent County Study, with respect to alternative techniques.

Computer simulations describe the transport and fate of constituents in ground water on the basis of mathematical equations related to the transport process, and attempt to account for pesticide use and agricultural management practices that may affect this process. Computer models vary widely in the level of detail with which transport processes are represented and simulated. A simplified transport model, which does not account for pesticide use or agricultural management practices, is referred to as a process-based model. Both simulation and process-based models represent physical

aspects of the transport process and minimize or avoid purely empirical parameters, even though some parameters may be adjusted so that simulated values more closely match measured constituents in ground water.

Attempts to simulate solute transport from the land surface to below the water table are relatively uncommon. Efforts to do so have typically involved coupling unsaturated- and saturated-zone models into a single code, such as SUTRA (Voss, 1984). Unfortunately, these modeling efforts have generally not been complemented to any degree by information on agricultural management practices (Delin and others, 1995) or atrazine formulations (Gish and others, 1991a), which can significantly affect pesticide movement.

Given the considerable effort invested in the development of computer models to simulate pesticide movement and fate in the subsurface, little testing of the predictions of these models has been conducted. Of 79 computer simulation studies of solute transport and fate through porous media reviewed by Barbash and Resek (1996, p. 367), only 40 compared their simulation results with pesticide concentrations measured in the field.

Among studies that have compared simulation results to pesticide distributions in the subsurface, models have been largely unable to successfully predict pesticide concentrations at specific locations. Several investigators have demonstrated this limited success even with widely used models (Eckhardt and Wagenet, 1996, Lafrance and Banton, 1995, Levy and Chesters, 1995, Loague and others, 1990, Persicani, 1995, and Persicani and others, 1995). The limited predictive ability of simulation models is associated with the common model assumption that the entire porous medium contributes equally to the sorption of constituents and that local equilibrium conditions exist. This assumption does not account for preferential transport (Ghodrati and Jury, 1992), a flow phenomenon that apparently is widespread in both the saturated and unsaturated zones. In addition, simulation models do not generally account for some physical, chemical, and biological processes that are known to affect transformation rates and pathways.

Process-based approaches, such as the steady-state leaching model applied in the Kent County Study, are a less computer-intensive method for estimating aquifer vulnerability than are simulation models. Meeks and Dean (1990) compared a process-based approach, Leaching Potential Index (LPI), with the observed distribution of DBCP (1,2-Dibromo-3-chloropropane) in ground waters near Stockton, California. Results indicate that the six LPI categories were statistically significant ($p = 0.066$) indicators of observed DBCP concentrations and that the coefficient of determination between LPI and DBCP ($r^2 = 0.52$) was one of the highest observed among 19 studies reviewed by Barbash and Resek (1996, p. 385).

Scoring systems are the most widely used approaches for assessing the susceptibility of ground water to contamination by pesticides or other agrichemicals. The DRASTIC system (Aller and others, 1987), which assigns scores on the basis of seven factors including: Depth to water; net Recharge; Aquifer media; Soil media; Topography; Impact of the unsaturated zone; and hydraulic Conductivity of the aquifer, is the most commonly used model in this class. The qualitative scoring in DRASTIC is not physically related to the transport process and neglects compound-specific properties of contaminants. Among the 10 qualitative scoring studies reviewed by Barbash and Resek (1996, p. 424), only three revealed significant positive correlations between predicted and measured contamination. The limited success of scoring systems may be associated with the use of inappropriate scoring factors, or with the use of county-wide input data for predicting contamination on a local scale. The limited ability of DRASTIC to predict pesticide concentrations in ground water, however, is not necessarily improved when the scale at which the vulnerability is assessed is sufficiently small. Koterba and others (1993) found DRASTIC scores to be unreliable predictors of pesticide contamination in ground water, even when they were computed for the 150 ac surrounding each well (an area that was close to the minimum of 100 ac recommended for these computations by Aller and others, 1987).

A third general approach for predicting the likelihood of atrazine occurrence is the presence of other solutes, particularly those that are either com-

monly available or inexpensively measured. Laboratory analysis of atrazine and individual metabolites are expensive, particularly with respect to some of the inorganic constituents, and are likely to remain so for the foreseeable future. Among solutes considered as possible indicators of pesticide contamination, the most prominent examples include nitrate and tritium.

Nitrogen fertilizers are commonly applied in conjunction with pesticides during cultivation of most crops. However, the preponderance of evidence (Barbash and Resek, 1996, p. 377) indicates that nitrate-nitrogen concentrations are generally an unreliable indicator of pesticide concentrations in ground waters. Klaseus and others (1988) present a particularly compelling demonstration of this lack of correlation between nitrate-nitrogen and atrazine concentration in 81 private wells in Minnesota ($r^2 <$ 0.01, in log-transformed units). Low correlation between nitrate-nitrogen and atrazine concentrations may be related to differences in migration rates for the two solutes. Whereas atrazine is slowed during transport due to sorptive interactions with soil organic matter, nitrate behaves as a conservative tracer under aerobic conditions. In addition, nitrate is depleted in ground waters where oxygen deficit occurs.

Despite the lack of correlation between concentrations of atrazine and nitrate-nitrogen, many studies have found that the likelihood of detecting pesticides in ground waters increases with increasing nitrate concentrations. This relation is thought to arise because both pesticide and nitrate occurrence exhibit inverse relations to the depth of sampling (Barbash and Resek, 1996, p. 380).

Atmospheric levels of tritium were elevated following atmospheric testing of nuclear weapons in the 1950s and the 1960s. Ground waters containing elevated concentrations of tritium have likely been recharged since pesticide use became wide spread in the early 1950s. Thus, tritium provides a valuable indicator for the potential, but not the guaranteed, presence of pesticides in ground water (Barbash and Resek, 1996, p. 382).

Kolpin and others (1995a) determined a relation between ground-water age, as determined by tritium dating, and the frequency of pesticide detec-

tion. In a survey of ground water in near-surface aquifers within the Midwestern United States, at least one pesticide or metabolite was detected in 15.8 percent of the samples of pre-1953 water and 70.3 percent of the samples of post-1953 water. Pre-1953 water is less likely to contain pesticides because it tends to predate the use of pesticides in the Midwest. Pre-1953 water was more likely be present in the near-surface bedrock aquifers (50.0 percent) than in the near-surface unconsolidated aquifers (9.1 percent) sampled.

While several chemical species have been investigated for use as indicators of pesticides in ground waters, all have considerable limitations. The desire to find such indicators has been driven largely by the need to avoid the high costs and time delays associated with most pesticide analyses. The recent advent of field-based enzyme-linked immunosorbent assay (ELISA) techniques, however, may eliminate the need for surrogates such as tritium. Provided that their limitations are fully recognized, ELISA methods appear to be the most convenient and affordable technology for screening ground waters for the presence of pesticide residues (Thurman and others, 1990).

GROUND-WATER VULNERABILITY TO ATRAZINE LEACHING IN KENT COUNTY

Review of the Vulnerability Evaluation Study

A simplified steady-state model of pesticide leaching through the unsaturated zone (Rutledge and Helgesen, 1991) was used to estimate the vulnerability of the near-surface aquifer to atrazine contamination from surface applications in the Kent County Study. Hydrologic data used as input to the model were obtained from precipitation and streamflow records and from recharge estimates for the area. Lithologic data were obtained from soil survey data for Kent County and from Michigan's statewide ground-water data base. The model was applied at 5,444 points in Kent County corresponding to locations of wells with known lithology. Geostatistical analysis was used to map point estimates at wells of the fraction of atrazine remaining at the water table to the rest of the county.

The model-computed fraction of atrazine remaining at the water table was used as a vulnerability criterion; time of travel to the water table was also computed. Simulation 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 among wells. For comparison, Wehtje and others (1983) estimate that about 0.05 percent of applied atrazine commonly leaches past the root zone into the subsoil. Time of travel of atrazine from the soil surface to the water table averaged 17.7 yrs (years) and ranged from 2.2 to 118 yrs. Assuming that atrazine applications began in 1953, sufficient time would have elapsed by 1998 for atrazine to move to the water table at 96.7 percent of the wells analyzed in Kent County.

Aquifer vulnerability estimates were used with a steady-state, uniform atrazine application rate of 2 lbs ai (active ingredient) per ac-yr (acre-year) to compute potential concentrations of atrazine in leachate reaching the water table. The average estimated potential atrazine concentration predicted in leachate reaching the water table was 0.16 μg/L (micrograms per liter); estimated potential concentrations ranged from 0 to 18.5 μg/L. About 2.6 percent of the points analyzed had an estimated potential atrazine concentration in leachate at the water table that exceeded the MCL of 3 μg/L.

Model Assumptions

Because of complexities and uncertainties in ground-water flow systems, model applications often require simplifying assumptions. Rutledge and Helgesen (1991) document assumptions in the pesticide leaching model that was applied in the Kent County Study. Results for a silt loam soil investigated by Eckhardt and Wagenet (1996), indicate that atrazine transport is directly related to the amount and timing of rain that follows spring applications of atrazine. Thus, the uniform, steady-state flow model assumption is of particular interest in attempting to verify model results with field measurements.

The uniform-transport assumption, which is shared by all widely-used solute-transport models, implies that all the sorptive capacity of soils and underlying earth materials is in immediate and continuous contact with fluids moving through the sub-

surface (Barbash and Resek, 1996, p. 191). In contrast, preferential transport involves the movement of water and solute through both dynamic and stagnant flow regions within a porous media. Dynamic regions are characterized by rapid, advection-dominated transport along preferred flow paths. Stagnant regions, in which solute transport is largely controlled by molecular diffusion, are present between preferred flow paths.

Evidence to support the widespread occurrence of preferential transport includes the detection of hydrophobic pesticides in ground water (which would normally be sorbed by organic matter), detection of pesticides with widely varying soil-organic-carbon partition coefficients (K_{oc}) migrating at virtually identical rates, and the detection of atrazine in leachate about 1.6 ft below the deepest point at which residues on soil were detected (Hall and Hartwig, 1978). Komor and Emerson (1994) suggest that preferential transport was responsible for detection of atrazine shortly after each application of irrigation water at Princeton, Minnesota, and for isolated concentrations of atrazine and bromide in soil well below the main masses of chemicals.

Water and solutes that move by preferential transport bypass much of the sorptive capacity of the soils and underlying earth materials. Also, the movement of water through dynamic regions may be sufficiently rapid so that insufficient time is available for equilibrium partitioning between atrazine in the aqueous phase and the subsurface materials. Thus, preferential transport would result in higher fractions of atrazine remaining at the water table than that indicated by a leaching model applied in the Kent County Study, which is based on the assumption of uniform transport.

The steady-state flow assumption contained in the leaching model does not account for seasonal variations or trends in pesticide concentrations in the near-surface aquifer. Results of a statewide survey in Iowa indicated that frequencies of pesticide detections range from 0 in January to about 42 percent in July; results of a statewide survey in Indiana showed frequencies of pesticide detection ranged from about 2 percent in the winter to about 7 percent in the spring (Barbash and Resek, 1996, p.

7

159). Seasonal variations in the occurrence and concentration of pesticides in ground water are largely attributed to the application of pesticides during the spring, but these variations are also influenced by seasonal changes in temperature and precipitation, coupled with the timing of agricultural practices such as irrigation and tillage. Trends in pesticide concentrations may be associated with systematic variations in atrazine application rates; however there is little field-scale documentation to support this possibility.

The leaching model applied in the Kent County Study does not account for spatial or temporal differences in management practices, such as conventional or reduced tillage operations. Reduced tillage promotes increased infiltration rates and causes less disruption of soil macropores than conventional tillage, which could provide additional conduits for preferential transport. Also, effects associated with pesticide application method (such as pre- versus post-emergence applications, single versus multiple annual applications, or broadcast versus narrow band placement) or formulation methods (such as encapsulation within a solid matrix to slow release) are not included in the model. Finally, the calculation of potential atrazine concentrations assumes a uniform, constant atrazine application rate even though actual application rates are uncertain, and are known to vary seasonally, temporally, and spatially.

Parameter Estimates and Model Sensitivity

The hydrologic, lithologic, and pesticide-specific parameters in the leaching model study of Kent County were based on reported values that vary widely under different laboratory and field conditions. Moreover, the availability of information on some model parameters is very limited, particularly for the unsaturated zone below the soil layer. A sensitivity analysis was used to identify factors associated with variations in model simulated fractions of atrazine remaining at the water table within Kent County, Michigan. Minimum and maximum estimates of model parameters used in the Kent County Study for computing fractions of atrazine remaining at the water table are shown in table 1. Model sensitivity was computed for selected parameters as the transformed[1] fraction of

atrazine remaining at the water table computed at the maximum estimate of the model parameter minus the transformed fraction of atrazine remaining at the water table computed at the minimum parameter estimate. The distributions of the model-computed fraction of atrazine (remaining at the water table) for the range of each parameter are shown on figure 2.

Simulation results indicate that fraction of atrazine remaining at the water table is highly sensitive to and positively associated with longer half lives of atrazine in the soil layers, and to a lesser extent, to atrazine half life in the unweathered zone. Half life represents the overall rate of depletion by several simultaneous chemical, biological, and physical process, including transformation, volatilization, and transport away from the site of measurement in either aqueous or gas phases by advection and molecular diffusion (Barbash and Resek, 1996, p. 36). Atrazine half life is an inherently site-specific, temperature-dependent parameter, reflecting the rate that the concentration decreases at a particular location within the unsaturated zone. In soils, atrazine degradation rates generally increase with increasing temperature, moisture content, and clay content. Atrazine degradation is relatively insensitive to pH (Hance, 1979). Interactions between these factors are complicated however, because chemical hydrolysis and microbial desalkylation are affected differently and sometimes inversely. Estimates of atrazine degradation rates in deeper soil horizons and in the saturated zone are rare, but indicate that atrazine may degrade slowly once it is leached beyond the root zone.

Levy (1993, Table I-3) cites 21 sources containing 88 estimates of atrazine half lives in various soils from laboratory experiments. Half lives used in the Kent County Study were generally within the

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1.The distribution of fractions of atrazine remaining at the water table computed for the Kent County Study was right skewed. That is, most of the computed fractions were near zero with relatively few values distributed at higher concentrations. A power transformation equal to 0.0625 was used to transform the computed fractions from a skewed distribution to a fairly symmetrical distribution.

Table 1. Ranges of parameters used in the atrazine leaching study for Kent County, Michigan.

Parameter	Minimums	Maximums	Units
Infiltration	1.75	3.42	feet per year
Root depth	1.46	2.42	feet
Deep percolation	0.48	0.96	feet per year
Water table depth	34.2	57.0	feet
Soil-organic-carbon partition coefficient (K_{oc})	39.0	155	dimensionless
Field capacity	19.0	25.0	percent
Residual moisture content	7.00	14.0	percent
Air entry level (Capillary rise)	1.10	2.14	feet
Porosity	35.0	49.0	percent
Organic carbon in soils	0.57	1.30	percent
Organic-carbon in unweathered materials	0.00	0.29	percent
Half life of atrazine in soils	6.00	181	years
Half life of atrazine in the unweathered materials	160	365	years

range of these estimates (fig. 3). Perry (1990) measured decreases in atrazine concentrations over a 2-yr period in an aquifer composed of thin lenses of fine to medium sand mixed with clay, and concluded that the decreases were due primarily to degradation rather than sorption or advection. On the basis of that assumption, a half life of 1000 days was estimated. Sinclair and Lee (1992) did not observe degradation over 150 days in unsaturated or saturated material from depths ranging from 3.8 to 12 m.

Results of the sensitivity analysis also indicate that computed fractions of atrazine at the water table are sensitive to and negatively correlated with percent organic matter, particularly in the unweathered deposits (fig. 2). Sorption of pesticides to soil organic matter constitutes the principal mechanism by which the migration of pesticides is slowed relative to the rate of water movement through the subsurface (Barbash and Resek, 1996, p. 36). Atrazine undergoes sorption when it develops a positive charge and becomes electrostatically bound to soil colloids. Increasing organic matter contents and clay mean increasing negatively charged and hydrophobic surfaces available for sorption. The organic-carbon content of soils tends to increase with increasing clay content because of the tendency for natural organic solutes to form surface complexes with clays (Barbash and Resek, 1996, p. 274). Dousset and others (1994), however, claim that adsorption of triazines is related to the degree of humification of the organic matter, rather than to clay or organic contents.

Atrazine sorption increases with increasing soil organic matter, clay content, and cation exchange capacity (Helling, 1971). Temperature has a negligible effect on atrazine sorption (Huang and others, 1984). In general, the range of organic-carbon content used in the Kent County Study was consistent with the range of organic-carbon content values described by 35 other investigators (Levy, 1993, Table I-1) (fig. 4).
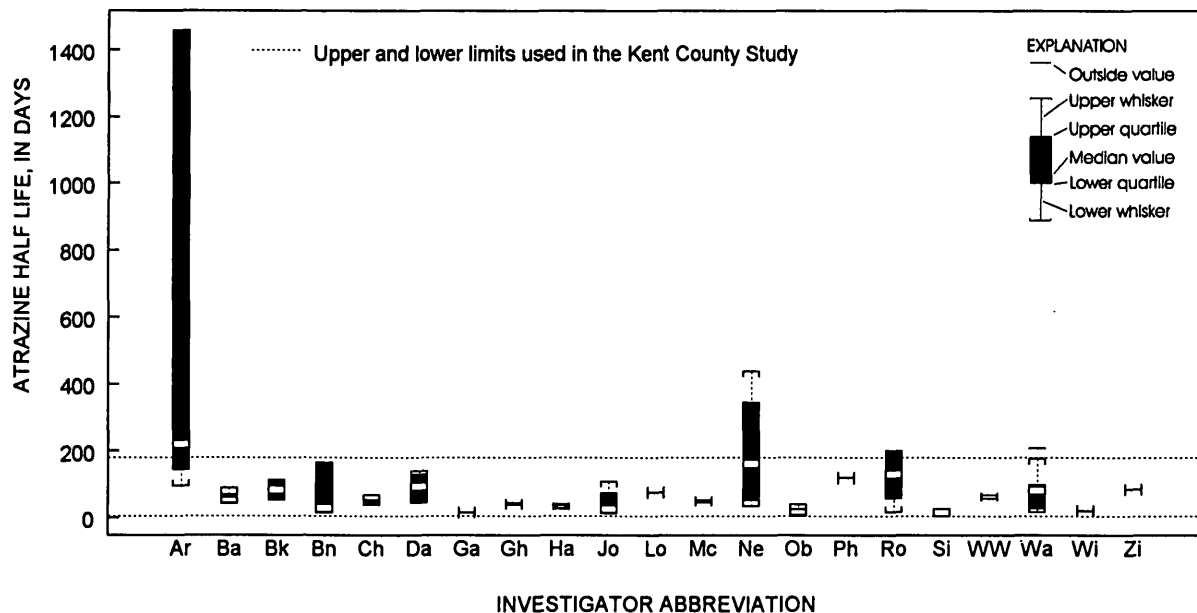
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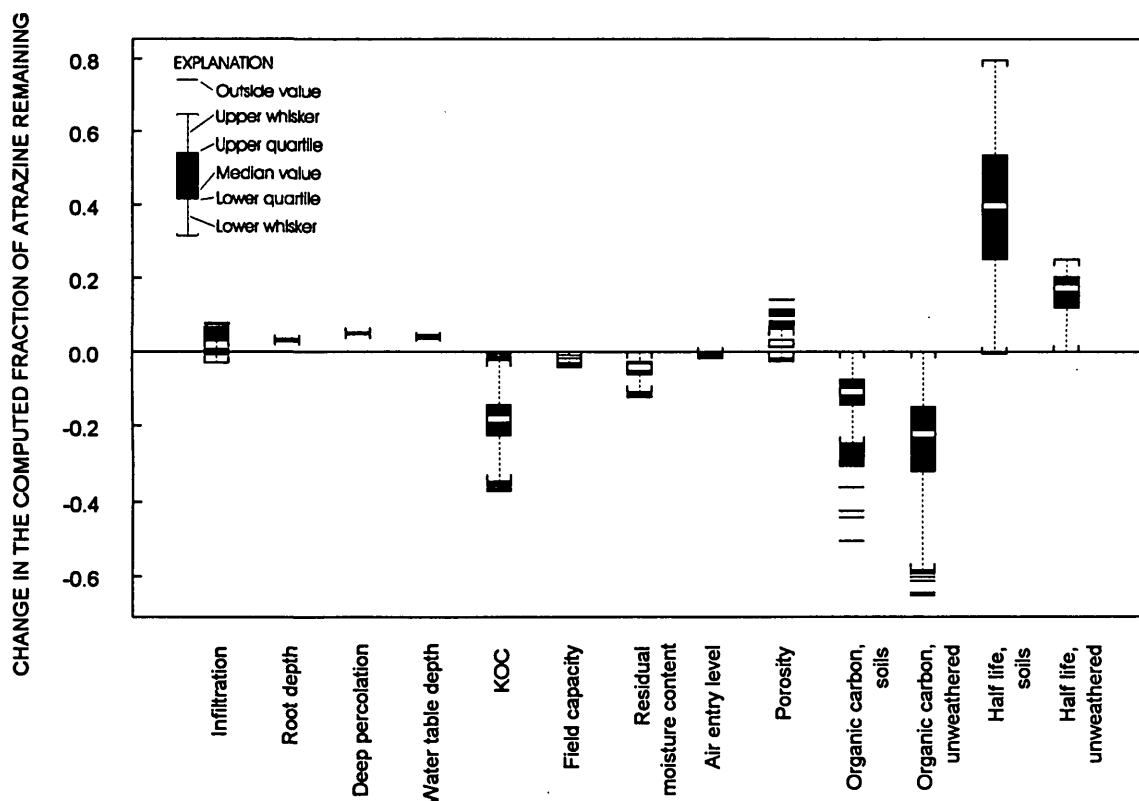
Figure 2. Model sensitivity to attributes and parameters used in the atrazine leaching study for Kent County, Michigan. (Whiskers show the range of values that fall within 1.5 times the difference between the upper quartile and the lower quartile.)

No particularly satisfactory method has been developed for precisely determining the quantity of organic matter directly. The usual procedure is to multiply the mass fraction of organic carbon, which can be measured accurately, by 1.7 (Brady, 1974, p. 154). Site-specific values of organic carbon were based on organic matter reported in the Kent County soil survey (U.S. Department of Agriculture, 1986) and limited information in the unsaturated zone.

Organic-carbon content of soils is so directly related to soil permeability and textural characteristics that it is difficult to determine their separate influences. Studies in Minnesota, Wisconsin, and the Delmarva Peninsula (Barbash and Resek, 1996, p. 275) have all observed higher frequencies of pesticide detection beneath coarse-grained soils, which usually have low f_{oc} (mass fraction of organic carbon in soil or, commonly, organic-carbon content), than beneath finer grained soils, which usually have high f_{oc}. Other large-scale monitoring studies, how-

ever, have not detected consistent relations between pesticide occurrence in ground water and organic-carbon content or soil permeability (Barbash and Resek, 1996, p. 275).

Finally, the sensitivity analysis indicates the leachate model is sensitive to organic-carbon partition coefficient, K_{oc}. K_{oc} is a compound-specific coefficient that describes the partitioning of organic solutes between organic matter and water. Because of the relatively nonspecific nature of soil organic matter as a sorbent for most hydrophobic or weakly hydrophilic compounds, values of K_{oc} for individual compounds are widely applied across a broad range of different types of soils and aquifer solids. The product of the fraction organic matter and K_{oc} is used to compute the linear distribution coefficient (K_d), which is used to estimate the degree of partitioning between the solid and aqueous phase. K_{oc} values used in the Kent County Study were generally within the range of K_{oc} values (fig. 5) reported by other investigators (Levy, 1993, Table I-1).
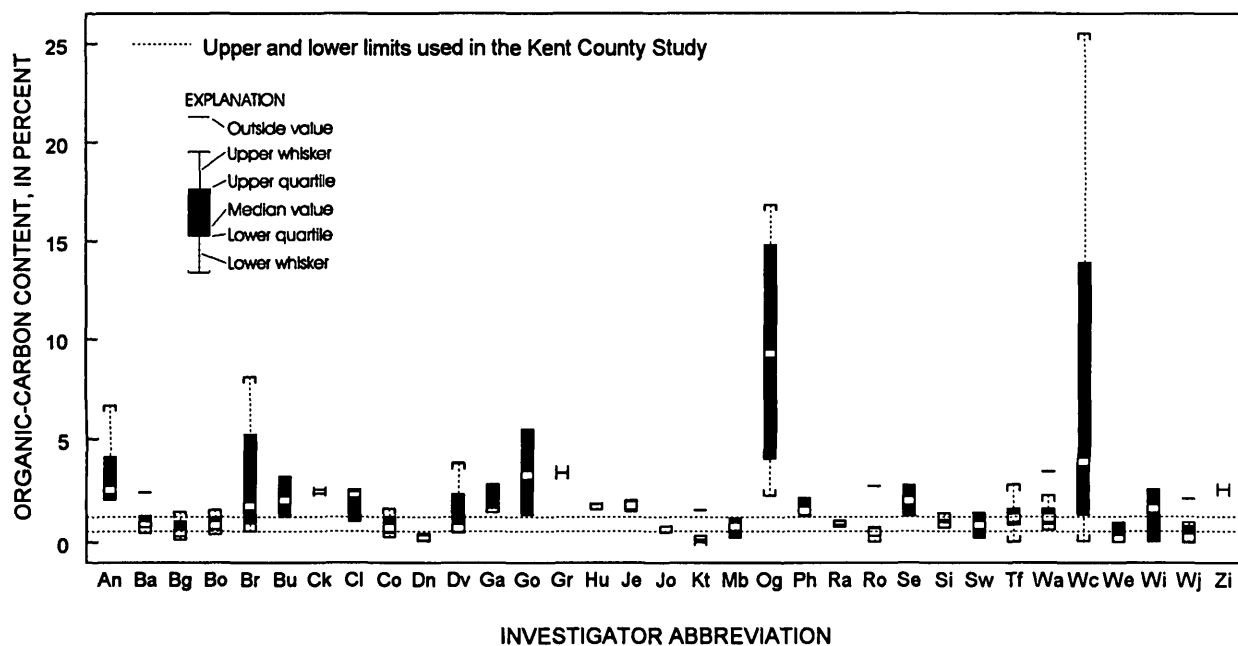
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Figure 3. Range of atrazine half lives used in the atrazine leaching study for Kent County, Michigan, and values reported by other investigators[3]. (Whiskers show the range of values that fall within 1.5 times the difference between the upper quartile and the lower quartile.)

[3]Investigator abbreviation and reference as cited by Levy (1993, Table I-3, p. 555-557): Ar–Armstrong and others, 1967; Ba–Bacci and others, 1989; Bk–Burkhard and Guth, 1981; Bn–Burnside, 1965; Ch– Chesters and others, 1989; Da–Dao, 1977, Ga–Gamerdinger and others, 1991; Gh-Ghardiri and others, 1984; Ha–Hance, 1979; Jo–Jones and others, 1982; Lo–Lopez-Avila and others, 1986; Mc–McCormick and Hiltbold, 1966; Ne–Nearpass and others, 1978; Ob–Obien and Green, 1969; Ph–Phogat and others, 1984; Ro–Roethe and others, 1969; Si–Sinclair and Lee, 1992, WW–Walker and Welch, 1991; Wa–Walker, 1978; Wi–Winkelmann and Klaine, 1991a; and Zi–Zins and others, 1991.

Neither the proportions of individual pesticides residing in the aqueous phase nor those associated with soils were found to be significantly correlated with K_{oc} (Barbash and Resek, 1996, p. 190). The relative movement of different pesticides in the subsurface has been found to increase with decreasing K_{oc} values, but these effects may be masked by preferential transport. This lack of correlation also may result from inaccurate determinations of K_{oc} that are based only on solution concentrations, without considering the sorbed phase (Singh and others, 1990). The extent to which interactions with solid-phase organic matter retard the movement of a pesticide through the subsurface is directly related to the K_{oc} of the solute and the f_{oc} of the porous media. Sorption to natural organic carbon tends to dominate retardation by sorption to mineral surface for $f_{oc} > 0.001$.

Levy (1993) conducted sorption and degradation experiments on unsaturated surface soils in Wisconsin. Results indicate that sorption values might reasonably be extrapolated to deeper aquifer materials; however, half lives in deeper aquifer materials are likely to be much longer than half lives in soils because of differences in microbial populations. Levy (1993) estimated atrazine half life in soil as 115 to 178 days, which is consistent

11

Figure 4. Range of organic-carbon content used in the atrazine leaching study for Kent County, Michigan, and values reported by other investigators[4]. (Whiskers show the range of values that fall within 1.5 times the difference between the upper quartile and the lower quartile.)

[4]Investigator abbreviations and references as cited by Levy (1993, Table I-1, p. 547-553): An–Anderson and others, 1980; Ba–Basile and others, 1990; Bg–Borggaard and Streibig, 1988; Bo–Bowman, 1990; Br–Brouwer and others, 1990; Bu–Burkhard and Guth, 1981; Ck–Clay and Koskinen, 1990a, 1990b; Cl–Clay and others, 1988; Co–Colbert and others, 1975; Dn–Daniel and others, 1989; Dv–Davidson and others, 1980; Ga–Gamerdinger and others, 1990, 1991; Go–Green and Obien, 1969; Gr–Green and others, 1968; Hu–Huang and others, 1984; Je–Jernlas, 1990; Jo–Jones and others, 1982; Kt–Konopka and Turco, 1991; Mb–Mueller and Banks, 1991; Og–Obien and Green, 1969; Ph–Pignatello and Huang, 1991; Ra–Raman and others, 1988; Ro–Roethe and others, 1969; Se–Seibert and Fuhr, 1984; Si–Swain, 1981; Sw–Swanson and Dutt, 1973; Tf–Talbert and Fletchall, 1965; Wa–Walker, 1972; Wc–Walker and Crawford, 1968; We–Wehtje and others, 1984; Wi–Weidner, 1974; Wj–Wolf and Jackson, 1979; and Zi–Zins and others, 1991.

with the 160-day average used in the Kent County Study. He also estimated a half life for atrazine of 1,980 days in ground water by model calibration.

Literature values for soil half lives and K_{oc} are unreliable as predictors of pesticide occurrence in ground water. Results using both NPS (National Pesticide Survey) (U.S. Environmental Protection Agency, 1990) and (MCPS) (Midcontinent Pesticide Study, Kolpin and others, 1995b) data indicate that the distributions of detected and nondetected pesticides among half-lives and K_{oc} are virtually random (Barbash and Resek, 1996, p. 270). Logistic regression analysis of NPS data indicate that the

likelihood of detecting individual pesticides in sampled wells was correlated ($\alpha=0.05$) with half life, but not significantly correlated with K_{oc}.

The limited utility of soil dissipation half-lives and K_{oc} values for predicting ground-water contamination by pesticides arises from a number of factors. These include: (1) the potentially significant influence of preferential transport on pesticide movement; (2) the substantial variability among literature values for soil dissipation half-life and K_{oc} for any compound; (3) the inherent uncertainties associated with the use of dissipation half-lives to predict pesticide fate; and (4) the spatial variability

Figure 5. Range of organic-carbon partition coefficients used in the atrazine leaching study for Kent County, Michigan, and values reported by other investigators[5]. (Whiskers show the range of values that fall within 1.5 times the difference between the upper quartile and the lower quartile.)
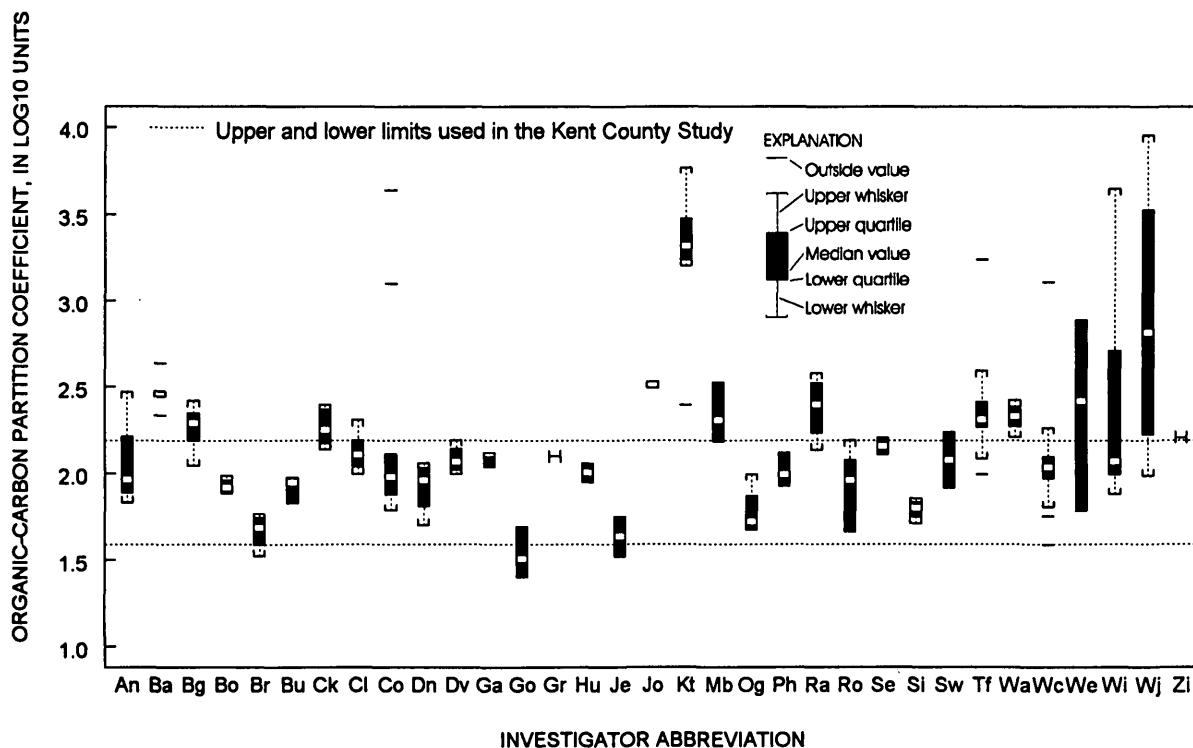
[5]Investigator abbreviations and references as cited by Levy (1993, Table I-1, p. 547-553): An–Anderson and others, 1980; Ba–Basile and others, 1990; Bg–Borggaard and Streibig, 1988; Bo–Bowman, 1990; Br–Brouwer and others, 1990; Bu–Burkhard and Guth, 1981; Ck–Clay and Koskinen, 1990a, 1990b; Cl–Clay and others, 1988; Co–Colbert and others, 1975; Dn–Daniel and others, 1989; Dv–Davidson and others, 1980; Ga–Gamerdinger and others, 1990, 1991; Go–Green and Obien, 1969; Gr–Green and others, 1968; Hu–Huang and others, 1984; Je–Jernlas, 1990; Jo–Jones and others, 1982; Kt–Konopka and Turco, 1991; Mb–Mueller and Banks, 1991; Og–Obien and Green, 1969; Ph–Pignatello and Huang, 1991; Ra–Raman and others, 1988; Ro–Roethe and others, 1969; Se–Seibert and Fuhr, 1984; Si–Swain, 1981; Sw–Swanson and Dutt, 1973; Tf–Talbert and Fletchall, 1965; Wa–Walker, 1972; Wc–Walker and Crawford, 1968; We–Wehtje and others, 1984; Wi–Weidner, 1974; Wj–Wolf and Jackson, 1979; and Zi–Zins and others, 1991.

of initial pesticide concentrations in soil water following application during a given study, in relation to detection limit (Barbash and Resek, 1996, p. 272).

While numerous studies have been conducted on leaching of atrazine, those examining the transport of its metabolites are more limited. Winkelmann and Klaine (1991b) measured half lives of 21, 26, 17, 19, and 121 days for ^{14}C-labeled atrazine, DEA, DIA, DIAM, and hydroxyatrazine, respectively, for a silt loam soil incubated at 25° C. They warn however, that failure to account for bound residues results in overestimation of degradation rates.

After 180 days, the bound residues accounted for 43, 60, 58, 29, and 28 percent of the applied ^{14}C for atrazine, DEA, DIA, DIAM, and hydroxyatrazine, respectively (Levy, 1993, p. 12).

Comparison with Other Studies

Three multistate monitoring studies have analyzed ground water in Michigan for atrazine. These include the Midcontinent Pesticide Study (MCPS), (Kolpin and others, 1995b), the National Pesticide Survey (NPS) (U.S. Environmental Protection Agency, 1990), and the National Alachlor Well Water Survey (Kline, 1997). In addition, two

nationwide data compilations have been completed: (1) the Pesticides in Ground Water Database[1] (PGWDB) (U.S. Environmental Protection Agency, 1992), and the 1988 Survey of State Land Agencies (Parsons and Witt, 1989, as referenced by Barbash and Resek, 1996). Of the two compilations, the PGWDB, with data for pesticide analytes in 68,824 wells in 45 states, is the more comprehensive with respect to the range of compounds studied and geographic coverage.

Probabilities of Detecting Atrazine in Ground Water

No spatial pattern in statewide detection frequencies of pesticides in the United States is apparent on the basis of the PGWDB; neither is there a statistically significant correlation between total statewide pesticide use and probabilities of detection (Barbash and Resek, 1996, p. 125). Although detection rates generally are low in areas of low pesticide use, high pesticide use is not necessarily associated with high rates of pesticide detection because of mitigating influences of climate, soils, hydrogeologic setting, and agricultural practices, as well as study design.

Consistent with the pattern observed for statewide data, atrazine detection rates are relatively low in counties with low atrazine use, but atrazine detection rates range widely in counties with high atrazine use (Barbash and Resek, 1996, p. 128). Perhaps most significant among the difficulties in relating pesticide use to detection frequencies in ground water is that county-level data--the smallest scale at which consistent information is available for large areas--may not accurately reflect pesticide use near individual wells. For both community water systems and rural domestic wells, pesticides that were not reported to have been used nearby were detected more frequently than those that had been used within the general vicinity of the well (Barbash and Resek, 1996, p. 147). The generally low correlation between pesticide use and detections in ground water may be related to surveys that were unable to control variations associated with well construction and from uncertainties in actual

pesticide use (particularly from non-agricultural sources) near the wells prior to the survey.

Direct correlations between the frequency of pesticide detection and pesticide use have been reported by a few state and local monitoring studies. Kross and others (1990, as referenced by Barbash and Resek, 1996) observed lower frequencies of atrazine detection in wells on Iowa farms where herbicides had not been applied during the most recent growing season (4 percent), compared with farms where they had been applied (10 percent). They also documented a significant correlation between the percentage of a region treated with atrazine and the frequency of atrazine detection in ground water beneath various regions in Wisconsin. The ability to detect this correlation is thought to be associated with relatively uniform well construction techniques and the use of the extent of the area treated rather than amount of atrazine applied as the measure of pesticide use (Barbash and Resek, 1996, p. 148). Data from process and matrix-distribution studies support a direct correlation between pesticide applications and their subsequent concentrations in the subsurface (Barbash and Resek, 1996, p. 152).

The National Alachlor Well Water Survey sampled 1,430 wells in 89 counties in 26 states between June 1988 and May 1989 (Klein, 1997). The survey deliberately over-sampled wells in areas where higher levels of alachlor (and perhaps other herbicides) might be expected. In addition to alachlor, analyses were conducted for atrazine, simazine, and metolachlor. Atrazine was the most commonly detected herbicide in the survey and occurred in about 12 percent of the sampled rural wells. In comparison, the survey estimates that simazine, metolachor, and alachlor are expected to be present in about 1.5, 1.0, and 0.8 percent, respectively, of the rural wells. Only 0.02 percent of the private wells are expected to exceed the MCL for alachlor.

Results of multistate studies may be inconsistent with results obtained by more local investigations. For example, although herbicides were not detected at several sites in south-central Wisconsin by the MCPS in 1991 or 1992 (Kolpin and others, 1994, 1997), this region was found during two suc-

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1.The Pesticides In Ground Water Database PGWDB specifically excludes data from the National Pesticide Survey (NPS).

cessive statewide surveys to exhibit the highest frequency of atrazine detections in Wisconsin (LeMasters and Baldock, 1997), despite the use of a higher detection limit (0.15 µg/L) than that employed for the MCPS (0.05 µg/L in 1991, 0.005 µg/L in 1992). The reasons for this discrepancy are unclear, but may be related to the much lower spatial density of sampling that characterizes the large-scale studies (Barbash and Resek, 1996). The likelihood of detecting pesticides in ground water increases with increasing proximity to cropped areas, increasing intensity of nearby agricultural activity, and increasing proportions of agricultural land within the surrounding area (Barbash and Resek, 1996, p. 268).

Pesticide detection frequencies observed beneath coarse-grained (and usually low f_{oc}) soils are commonly higher than beneath finer-grained (and usually higher f_{oc}) soils. In some large-scale monitoring studies, however, no clear association between soil properties and pesticide detections in ground water have been observed, particularly in relation to the triazine herbicides (Barbash and Resek, 1996, p. 275). One explanation for the absence of clear relations between soil texture and pesticide occurrence in ground water is that the soil texture in the immediate vicinity of a well is not necessarily the same as that in the area contributing recharge. Delin and Landon (1996) indicate that even small variations in topography can redirect recharge to lowland areas.

Effects of variations in soil properties on pesticide movement to ground water may be overshadowed by uncontrolled variation in well construction characteristics or other factors. In Iowa, a statewide effort to assess ground-water susceptibility to agrichemical contamination explicitly excluded consideration of varying soil types in all areas, except for those underlain by alluvial aquifers (Barbash and Resek, 1996, p. 275). On the basis of the relatively narrow range of soils found across much of Iowa, the Department of Natural Resources staff suggested that because the soil cover in most of the state is such a small part of the overall aquifer or well cover, processes that take place in the top few inches of soil are relatively similar and are insignificant in terms of relative susceptibilities to ground-water contamination. At the field scale, most pro-

cess and matrix-distribution studies have failed to detect consistent relations between soil properties and pesticide occurrence, concentrations, or persistence (Barbash and Resek, 1996, p. 152).

Of the 39 agricultural chemicals analyzed in water samples from 240 private wells in Illinois, only atrazine and nitrate were detected at concentrations above their maximum contaminant levels (Mehnert and others, 1995). Atrazine was detected in 11 samples at concentrations above the minimum reporting level of 0.15 µg/L; measured concentrations ranged from 0.15 to 3.8 µg/L. Occurrence of one or more analytes was greater in large-diameter wells and dug wells than in small diameter drilled wells. For small diameter wells, the frequency of occurrence of one or more analytes generally decreased as the depth to the uppermost aquifer increased. In addition, depth to the uppermost aquifer could be used to predict the occurrence of atrazine and nitrate.

Pesticides were detected in 20 of 50 water samples from springs and in 9 of 50 water samples from wells in the Ozark Plateaus Region of Arkansas, Kansas, Missouri, and Oklahoma (Adamski and Pugh, 1996). Of the 47 pesticides and metabolites which were analyzed, atrazine was present most commonly with detections in 14 wells; measured concentrations ranged from 0.001 to 0.015 µg/L of atrazine. The presence of atrazine in ground-water samples from the Ozark Plateaus is somewhat surprising because field corn constitutes a small percentage of land use in the study area (Adamski and Pugh, 1996). The significantly higher percentage of detections in springs rather than wells is thought to be associated with differences in source areas. Recharge to springs is derived primarily from sinkholes and losing streams, whereas recharge to wells is from more diffuse sources.

In the White River Basin of central Indiana, Fenelon and Rhett (1996) analyzed water samples from 94 shallow wells for 21 herbicides and 11 insecticides. The most frequently detected pesticides were DEA (15 percent at a minimum reporting level (MRL) of 0.007 µg/L), atrazine (8.5 percent at a MRL of 0.017 µg/L), and metolachlor (7.5 percent at a MRL of 0.009 µg/L); no insecti-

cides were detected. Most detections of atrazine and DEA were in agricultural areas overlying fluvial deposits; concentrations were less than 0.1 µg/L.

The results discussed above indicate that pesticide contamination of ground water may be detected more commonly beneath coarse, highly permeable, organic-carbon-poor soils than beneath fine-textured, less permeable, organic-rich soils. Such effects may be difficult to discern however, in areas that exhibit substantial variations in other factors, such as well construction, intensity of agricultural activity, pesticide application rates, or pesticide concentrations in soils. Frequencies of detection are significantly higher in unconsolidated aquifers than in bedrock. Inverse relations between well depths and pesticide detection frequencies or concentrations have been documented in many locations (Barbash and Resek, 1996, p. 290). Deeper wells exhibit lower frequencies of contamination than shallow ones. The relation between the depth to the water table below land surface and potential atrazine concentration for the Kent County Study is shown on figure 6.

In a Kansas field study conducted on corn in clay- and silt-loam soil receiving 3.4 kg/ha (3.0 lb/ac) of atrazine, Adams and Thurman (1991) determined that DEA was the primary chlorinated metabolite of atrazine in soil water and in soil cores. DEA appeared to enter the aquifer underlying the experimental plot at a soil-water concentration of 5.0 µg/L with a corresponding atrazine concentration of 4.1 µg/L. DIA was found in significantly lower concentrations than DEA throughout the study.

Ground-water-quality data collected directly from lysimeters and tile lines, or indirectly from springs and streams at base flow do not provide consistent or comparable indications of pesticide occurrence in water withdrawn from shallow wells (Barbash and Resek, 1996, p. 310). Further study is required to ascertain the degree to which each of these media is representative of shallow ground-water chemistry.

Analysis of Atrazine Detection Probabilities

In the Midcontinent Pesticide Study (MCPS) (Kolpin and others, 1994, 1997), water samples were collected during the spring and summer of 1991 from 303 wells penetrating the near-surface unconsolidated and bedrock aquifers. The number of wells selected in each of the 12 states within the Midcontinent of the United States was allocated in proportion to the area of near-surface aquifer and the number of acres of corn and soybeans. Selected wells were completed in a near-surface aquifer where at least 25 percent of the land use in a 2-mi radius had been planted in corn or soybeans during the previous growing season. To obtain a vertical distribution of wells in each aquifer class, about 50 percent of the wells selected were completed in the upper one-half of the near-surface aquifer and about 50 percent were completed in the lower one-half of the near-surface aquifer.

As part of the MCPS in Michigan, 14 wells were sampled in unconsolidated aquifers in the southern Lower Peninsula, including one well (MI_{10}) in Kent County, Michigan. Of these 14 Michigan wells sampled in the spring and summer, only 2 samples exceeded the detection limit of 0.05 µg/L for atrazine. Both of these detections, having concentrations of atrazine of 0.09 and 0.11 µg/L, were obtained from the same well (MI_{13}) during spring and summer samplings, respectively. In addition to atrazine, detectable concentrations (≥ 0.05 µg/L) of chlorinated atrazine metabolites, including 0.05 µg/L DEA were measured in the spring, and 0.09 and 0.05 µg/L of DEA and DIA, respectively, were measured during the summer at well MI_{13}.

Two analyses of atrazine detection probabilities were conducted to facilitate comparison of limited MCPS data in Michigan with potential atrazine concentrations computed in the Kent County Study. The analyses were based on random sampling experiments that describe the distribution of atrazine detection probabilities in ground water. The results of the experiments were analyzed statistically to determine whether the distributions of detection probabilities from the MCPS data and the Kent County Study were similar.

For the MCPS data, wells were identified as MI_1, MI_2, ..., MI_{14}, with corresponding concentrations C_1, C_2, ..., C_{14}. Because only well, MI_{13}, had a concentration that exceeded the analytical detec-
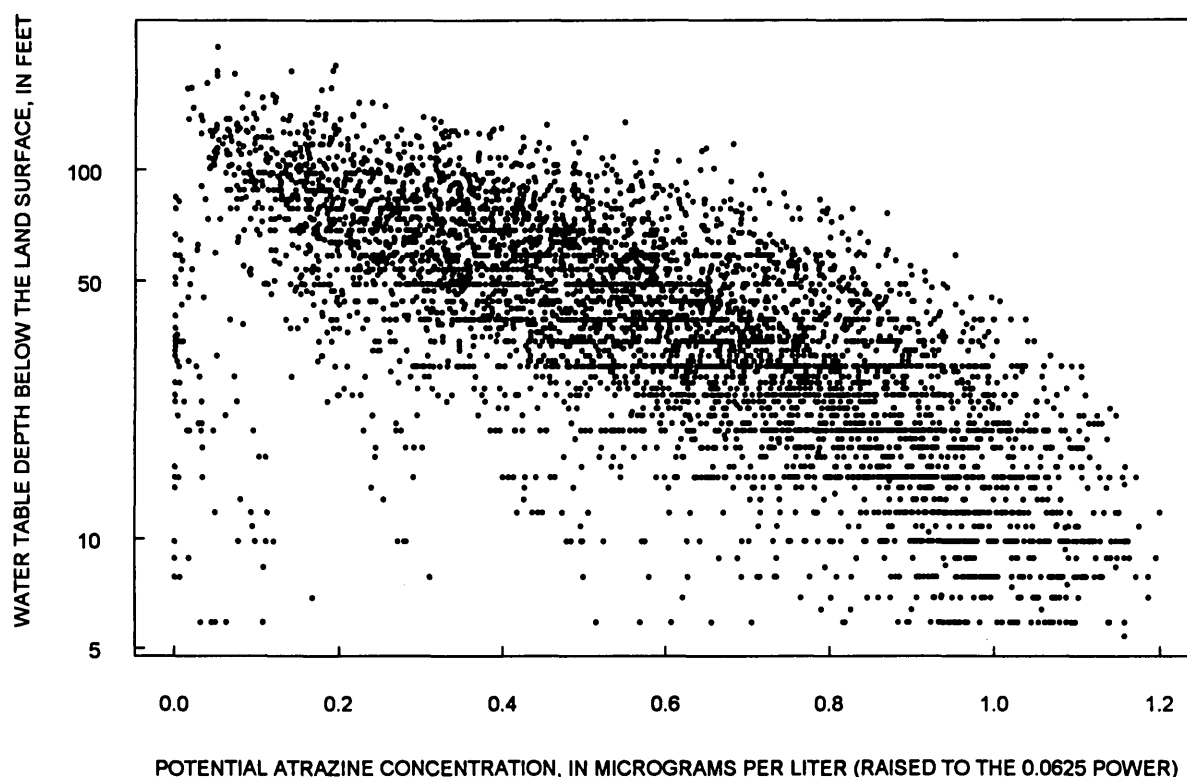
Figure 6. Relation between water table depth below the land surface and potential atrazine concentration computed for the atrazine leaching study for Kent County, Michigan.

tion limit, concentrations could not be used directly. Instead, the MCPS data were represented by an indicator vector identifying the well at which the atrazine concentration exceeded the detection limit with a 1; other elements contained zeros as: [0 0 0 0 0 0 0 0 0 0 0 0 1 0].

In each trial, 14 independent samples were randomly drawn from this vector representing the 14 MCPS wells sampled in Michigan. Thus, it was possible to select the same element more than one time in each trial. This strategy is commonly referred to as sampling with replacement. (Sampling without replacement would have provided only one unique outcome). In sampling with replacement in this situation, an outcome of 14 "ones" would occur with a theoretical probability 8.99×10^{-17}. This outcome corresponds to the event that in a random sample of 14 wells from a population of wells with the same probability of atrazine detection as the MCPS wells in Michigan, all 14 wells would exceed the detection limit. Similarly,

an outcome of 14 zeros, corresponding to the event that water from none of the 14 sampled wells exceeded the detection limit, would occur with theoretical probability 0.354. Sampling experiments used to describe the distribution of the likely number of detections of atrazine in samples of 14 wells with atrazine detection probabilities similar to those of the MCPS wells (fig. 7) consisted of 5,000 trials. Results indicate that the maximum likelihood of detection of 0.376 corresponds to 1 detection in 14 samples. Obtaining from 0 to 2 detections has an total empirical probability of 0.927.

Sampling experiments were conducted in a similar manner by use of the potential atrazine concentrations computed in the Kent County Study. Potential concentrations were determined for 5,444 wells as a function of a hypothetical long-term atrazine application rate and computed fractions of atrazine remaining at the water table. Here, a vector of length 5,444 was formed with ones again representing wells at which potential concentrations

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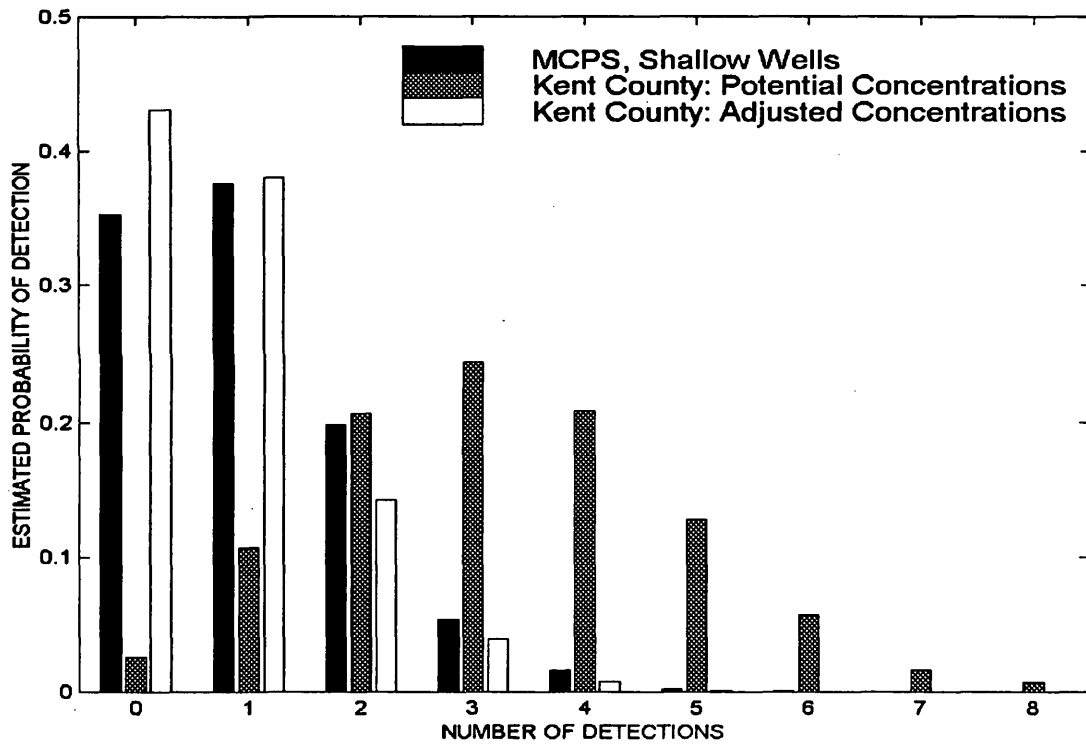
Figure 7. Estimated probability of detecting atrazine in ground water of near-surface aquifers within Michigan from 14 random samples.

exceeded a detection limit and zeros representing other wells. Fourteen random samples were selected, this time without replacement, from among the 5,444 vector elements representing individual wells in Kent County. The likely distribution of the number of detections in 14 samples was again determined on the basis of 5,000 trials.

Of the 5,444 wells considered in Kent County, 1,266 had potential concentrations of atrazine at the water table that exceeded 0.05 µg/L. A sampling experiment indicated that the maximum probability (0.243) corresponds to obtaining 3 detections in samples at 14 wells (fig. 7); obtaining from 2 to 4 detections corresponds to a total probability of

0.658. Obtaining only 1 detection, as with the Mid-continent data, has a probability of only 0.107.

Pearson's chi-squared statistic (X^2) was computed to test the similarity between the empirical distributions of detections in the MCPS data and the Kent County Study as:

$$\chi^2 = \sum_{bins} \frac{(O_i - E_i)^2}{E_i} \quad [1]$$

where *bins* are the magnitudes of detection. In this analysis, 6 bins were used: 0, 1, 2, 3, 4, and 5

18

through 8 detections. The 5th through 8th counts were combined so that each bin would have a minimum of 5 expected counts from the 5,000 trials.

O_i is the observed probability in the ith bin.
    Observed probabilities were based on frequency of detections in random sampling trials of 5,444 well locations in Kent County, Michigan.

E_i is the expected probabilities in the ith bin.
    Expected probabilities were based on frequencies of detections in random sampling trials of the Midcontinent data for wells in Michigan.

The chi-squared statistic (X^2) for potential atrazine concentration detections at the water table in Kent County and in near-surface aquifers of Michigan from MCPS wells was 19.8 with 5 degrees of freedom, where the degrees of freedom are the number of bins minus one. On the basis of the X^2 probability distribution, discrepancies in the distributions of detections this size would be expected with a probability of 0.0014. Thus, potential atrazine concentrations at the water table in Kent County would likely have greater detection probabilities than atrazine concentrations in near-surface wells represented by the MCPS data. Differences likely arise because the water table is closer to the source of atrazine than wells sampled by MCPS in the upper or lower portion of the near-surface aquifer, and because potential atrazine concentrations were computed on the basis of a uniform application of atrazine across the entire county, which is unrealistic as only about 65.6 mi^2 (7.7 percent) of Kent County was planted in corn (potentially treated with atrazine) in 1994 (Michigan Agricultural Statistics Service, 1995).

Two adjustments to the potential atrazine concentrations at the water table in Kent County were applied to facilitate comparison with ground water in the near-surface aquifer. First, the threshold for detection of atrazine at the water table was increased from 0.05 μg/L to 0.10 μg/L to partially account for vertical differences in the distribution of atrazine between the water table and the average value in the near-surface aquifer. Increasing the threshold decreased the number of detections from 1,266 (23.3 percent) to 1,047 (19.2 percent). Second, the number of detections (1,047) was multi-

plied by 0.306 (0.077/0.25) to account for the amount of land in Kent County that would be classified as susceptible by MCPS standards. That is, the fraction (7.7 percent) of Kent County that was planted in corn was divided by 0.25 to meet the MCPS requirement that at least 25 percent of the land use in a 2 mi radius around selected wells was planted in corn or soybeans. The number of detections used in the second sampling experiment for the Kent Count Study was 320 (5.87 percent).

Analysis of this sampling experiment indicates that the maximum probability (0.430) corresponds to obtaining 0 detections in a sample of 14 wells (fig. 7); obtaining from 0 to 2 detections corresponds to a total probability of 0.953. Obtaining only 1 detection, as in the MCPS, corresponds to a probability of 0.380. The chi-squared statistic of 0.0432, computed by use of equation 1, corresponds to a p-value of greater than 0.999. Thus, there is no substantial evidence against the similarity of distributions in the adjusted potential atrazine detection probabilities for ground water in Kent County with results obtained in for MCPS data in Michigan.

Concentrations of Atrazine Reported in Other Areas

Concentrations of atrazine in ground water measured by other investigators are presented to provide a basis for comparing potential concentrations computed for the Kent County Study. Analysis of results for the Kent County Study indicated that model-computed fractions of atrazine remaining at the water table of as little as 0.34 percent, when associated with a uniform, steady-state application rate of 2 lbs of atrazine active ingredient per ac-yr, would result in a potential leachate concentration at the water table exceeding the MCL of 3 μg/L. For a model to accurately predict the arrival of 0.34 percent of the mass of an applied compound, however, it must be able to account for the movement and fate of the remaining 99.66 percent. No transport model has yet demonstrated such accuracy. In fact, Nicholls (1988) argues that "concentrations of pesticide in water entering subsoils cannot be reliably simulated to an accuracy of better than an order of magnitude because the complex patterns of water flow (including preferential transport) and the slow diffusion processes of the pesticide are insufficiently understood."

Smith and others (1990) investigated atrazine movement in the soil profile and shallow ground water with surface applications of atrazine on a sandy soil underlain by an impermeable clay layer. Concentrations of atrazine moved rapidly through the soil on the study site. Concentrations of atrazine in the soil water at a depth of 0.61 m reached 350 μg/L 19 days after application. Detectable concentrations of atrazine reached the water table two months after application. Atrazine concentrations as high as 90 μg/L were observed in the shallow ground water nearly six months after application.

Atrazine contamination is greatest in areas of shallow depths to ground water, coarse-textured soils, areas continuously planted in corn, and areas undergoing intense irrigation. Wehtje and others (1984) reported concentrations of 2 μg/L in 1.5 m (4.9 ft) deep monitoring wells beneath fields with such characteristics. For similar conditions in the lower Wisconsin River valley, atrazine was detected in ground water at 25 of 35 sites; concentrations exceeding 0.35 μg/L were detected at 19 sites, and concentrations exceeding 3.5 μg/L were detected at 8 sites (Wisconsin Department of Agriculture, Trade, and Consumer Protection, 1991, as referenced in Levy, 1993). The highest concentration detected was 35 μg/L. In comparison, the highest potential atrazine concentration computed at the water table in the Kent County Study, based on the assumption of a steady-state uniform application rate of 1 lbs/ac-yr, was 18.5 μg/L.

Pesticide concentrations or detection frequencies in ground water vary during the course of the year. Typically, detection frequencies and median concentrations in shallow ground water are lowest during the winter, and reach peak value during the late spring and early summer (Barbash and Resek, 1996, p. 156). Results from the MCPS reflect this pattern over a large scale; Burkart and Kolpin (1993) found the frequencies of herbicide detection in ground waters for the pre-planting period in March and April to be significantly lower (20.4 percent) in their 12-state area ($\alpha = 0.05$) than those observed during the post-planting period (27.8 percent) in July and August of 1991. The seasonal variability of pesticide detection frequencies in shallow ground water may be sufficient to mask long-term changes in detection frequencies over multi-year

periods. Seasonal variations in pesticide occurrence in ground waters are largely attributed to the application of pesticides coupled with spring recharge. These variations are also influenced by seasonal changes in temperature and precipitation, coupled with the timing of agricultural practices such as irrigation and perhaps tillage. The temporal variability of pesticide concentrations in ground water generally decreases with increasing depth. Such observations are consistent with general principles of solute transport, dispersion, sorption, and degradation in porous media. As pesticides (or any other surface-derived solutes) move downgradient, away from their source areas, temporal variations in their input concentrations dampen out due to hydrodynamic dispersion (Barbash and Resek, 1996, p. 158).

Ghodrati and Jury (1992) similarly identified considerable transport of atrazine through the unsaturated zone to a depth of 150 cm (4.92 ft). However, they did not identify consistent effects of irrigation methods, pesticide formulation, or tillage practices. When averaged over all treatments, 18.8 percent of the recovered atrazine was found between 30 cm (0.984 ft) and 150 cm. Moreover, investigated pesticides were highly mobile in the surficial 30 cm regardless of the soil's adsorption coefficient. The authors conclude that fine preferential pathways occur within the soil matrix that allow solution to move but may block particles.

Eckhardt and Wagenet (1996) simulated potential atrazine transport in a Kansas silt-loam soil. Simulations were based on the LEACHM model (Hutson and Wagenet, 1992), a transient-state unsaturated flow and advective-dispersive solute transport model. Results for a 22-yr simulation period were summarized in a concentration-frequency analysis. The analysis indicates that, for annual application rates of 1.5 kg/ha (1.3 lb/ac), the estimated frequency of atrazine concentrations that exceed 1 μg/L is negligible. When application rates are doubled to 3.0 kg/ha (2.7 lb/ac), the frequency of concentrations that exceed 1 μg/L increases to 7 percent. The leaching potential at the Kansas site was considered low, mainly because the degradation rate for atrazine in the soil is rapid and because the hydraulic conductivity is low relative to other Midwestern soils. Atrazine can leach below the root zone at this site, however, and the simulation results

show that periodic leaching is most probable when heavy spring rain coincides with atrazine in the soil. Below the soil layer, atrazine concentrations in leachate would be further diminished by degradation, dispersion and dilution as water moves downward through underlying deposits. Measured atrazine concentrations in the Kansas River valley are typically much lower than values indicated by simulation results, somewhat invalidating the model results.

At a research site operated by the USDA (U.S. Department of Agriculture) Pesticide Degradation Laboratory, Gish and others (1991) monitored pesticide concentrations in a shallow perched water zone located approximately 1 m below the soil surface. Between 1986 and 1988, water quality was monitored in 16 wells at two plots under conventional tillage practices and in 19 wells at two plots under no-till cultivation. Atrazine, formulated as a wettable powder, was applied at the rate of 1.34 kg/ha (1.20 lb/ac) following corn planting in the spring. Samples of ground water were obtained monthly and after rainfall events exceeding 9 mm/day (0.03 ft/day). As a result, 110, 459, and 647 samples were collected in 1986, 1987, and 1988, respectively. Data for relatively dry conditions prevalent in 1986 and 1987 indicate that atrazine concentrations were generally well below 3 μg/L. However, during a wet period following atrazine application in 1988, average atrazine concentrations in the shallow ground water were about 57 μg/L in the conventionally tilled areas and about 238 μg/L in the no-till areas. Concentrations of atrazine remained elevated above 3 μg/L for the remainder of year. No chlorinated metabolites of atrazine were monitored in the study.

Delin and others (1995) analyzed the effects of 1992 farming systems[1] on ground-water quality below cropped and buffer areas at the Management Systems Evaluation Area (MSEA) near Princeton, Minnesota. Atrazine was detected in 58 percent of the 361 ground-water samples. Most detections were at trace levels, between the detection limit of 0.01 μg/L and the reporting limit of 0.04 μg/L.

Atrazine concentrations beneath the cropped areas were generally indistinguishable from background concentrations because none of the atrazine detections below cropped areas exceeded the 0.14 μg/L maximum concentration in the buffer areas. A source unrelated to the MSEA farming systems is the most likely origin of atrazine detected beneath the cropped areas. DEA was detected at higher frequencies (78 percent) and in greater concentrations (median 0.07 μg/L; range <0.03 to 0.77 μg/L) than atrazine or any other herbicide or metabolite. DIA was detected in 13 percent of the 361 samples collected during 1992.

Verification by Measurement of Atrazine Concentrations in Water from Shallow Wells

Direct verification of the vulnerability estimate developed in the Kent County Study with field measurements of atrazine concentrations in ground water is not possible. This is because concentrations of atrazine in ground water are determined both by aquifer vulnerability and by atrazine application rates. It is possible, however, to field verify estimates of the expected atrazine concentrations at the water table. These estimates could be developed on the basis of the fraction of atrazine remaining at the water table computed in the Kent County Study, provided that information on long-term average rates of atrazine application were available.

At the time this report was being completed, long-term average rates of atrazine application were not available for Kent County at a resolution (100 ac) that is consistent with the computed fractions of atrazine remaining at the water table. However, a method for verifying the expected atrazine concentrations at the water table was developed and is illustrated using the potential atrazine concentrations. Potential concentrations were computed in the Kent County Study on the basis of the computed fractions remaining and an assumed uniform application rate of 2 lbs/ac-yr throughout the county. Once reliable estimates of the long-term atrazine application rates become available, they can be used to revise the computations to reflect expected concentrations and a field sampling program can be implemented.

1.Three farming systems were evaluated: (1) corn-soybean rotation with ridge-tillage, (2) sweet corn-potato rotation, and (3) continuous field corn.

Table 2. Potential atrazine characteristics in shallow wells within sampling strata

Stratum (h)	Stratum (Defined by Quantiles of Potential Atrazine Concentrations)		Concentration characteristics of stratum (micrograms per liter)				Number of wells in stratum (N_h)
	Lower	Upper	Mean	Minimum	Maximum	Standard deviation ($S_{m(h)}$)	
1	0.000	0.500⁻	0.000031	0	0.000409	0.000074	2133
2	0.500	0.750⁻	.0104	0.000409	.0443	.0115	1067
3	0.750	0.850⁻	.118	.0443	.242	.0574	427
4	0.850	0.900⁻	.383	.242	.585	.101	213
5	0.900	0.950⁻	.949	.585	1.52	.278	213
6	0.950	0.975⁻	2.24	1.52	3.22	.505	107
7	0.975	1.000	6.31	3.22	18.5	3.20	107

In the Kent County Study, potential atrazine concentrations at the water table ranged from 0 to 18.5 μg/L. This range can be divided into subintervals to form corresponding land areas that have less variable atrazine concentrations than the county as a whole. These subareas are referred to as strata. In this report, individual stratum are indexed by h from $h=1$ to L, where L is the number of statum. One possible set of $L=7$ stratum, based on unequally-spaced quantiles of the potential atrazine concentration distribution, is shown in table 2.

Strata are used to increase the efficiency of probability sampling in a design referred to as stratified random sampling (Cochran, 1977, p. 89). In stratified random sampling, the total number of samples n available (as determined by cost or other constraints) are distributed among individual stratum n_h so as to minimize the variability of the estimate of the expected atrazine concentration in the county. In general, more samples are allocated to larger and more variable stratum. The distribution of samples among stratum that minimizes this variability is referred to as the optimum allocation.

Once the sampling strata are determined, the number of possible sampling locations in the county, N, are determined for each stratum. The number of possible sampling locations within each stratum is denoted as N_h. If existing shallow wells are selected as the set of possible sampling locations, costs associated with boring to the water table and possible risks of aquifer contamination can be avoided. This strategy also focuses sampling resources in areas that serve as potential sources of drinking water. Alternatively, obtaining water samples at the water table will provide information that corresponds more closely with vulnerability estimates computed at the water table in the Kent County Study. Water quality in shallow wells may differ significantly from water quality at the water table due to transport, sorption, diffusion, and degradation processes occurring in the saturated zone.
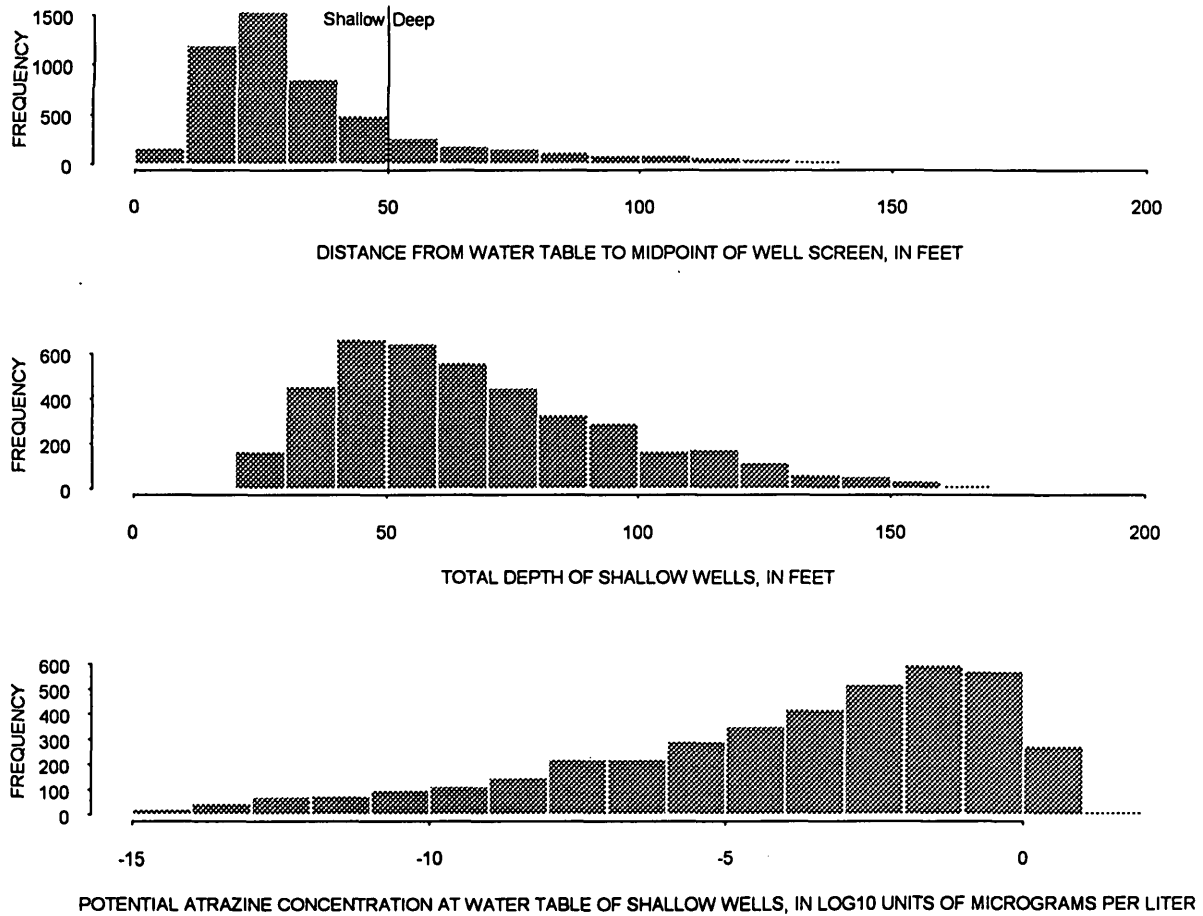
Figure 8. Frequency distributions of shallow well characteristics in the atrazine leaching study for Kent County, Michigan.

For the purpose of illustrating the sampling design, existing shallow wells were selected as the set of possible sampling locations. In this report, shallow wells are defined with respect to the distance between the water-table and the midpoint of the screened interval, rather than the total well depth. This convention was used because the leaching model accounts for the fraction of atrazine throughout the unsaturated zone, regardless of its depth below the surface; model extrapolation occurs only in the saturated zone. The distribution of distances within the saturated zone (water table to the midpoint of the screened interval) is shown on figure 8. Of the 5,444 wells used in the Kent County Study, 4,267 (78.4 percent) have a water-table to mid-screen distance of less than or equal to 50 ft and are classified here as shallow wells. The distribution of total well depths for the shallow wells and associated potential atrazine concentrations also are shown on figure 8.

Optimum allocation of a fixed number of samples in a stratified random sampling design is determined by the application of the following formula (Cochran, 1977, p. 98):

$$n_h = n\frac{W_h S_h}{\sum W_h S_h}, \qquad [2]$$

where n_h is the number of samples in the hth stratum,

n is the total number of samples available,

W_h is the relative weight of the hth stratum,

and

S_h is the standard error of the hth stratum.

23

The relative weight of the hth stratum, W_h, is associated with the land area within the corresponding stratum. In this report, land area within each stratum was assumed to be proportional to the number of shallow wells in the stratum. Formally, shallow wells were assumed to be distributed randomly with respect to potential atrazine concentrations. The number of shallow wells within each stratum is shown in Table 2.

The standard error of each stratum S_h (or its square, referred to as the error variance, S_h^2) is assumed to arise independently from two sources: the model error variability ($S_{m(h)}^2$) and the random error variability ($S_{e(h)}^2$). That is, $S_h = \sqrt{S_{m(h)}^2 + S_{e(h)}^2}$. For this report, $S_{m(h)}^2$ was estimated as the variance of potential atrazine concentrations in each stratum, corresponding to the squared standard deviations shown in table 2. After reliable historical atrazine application rates become available and expected atrazine concentrations are computed, new strata can be developed and their corresponding $S_{m(h)}^2$ substituted into equation 2.

The second component of the error variance, $S_{e(h)}^2$, arises due to model simplifications including uniform flow, uncertainty in model parameters, and uncertainty in the spatial distribution of historical atrazine application rates. Although no direct estimate of the magnitude of $S_{e(h)}^2$ is available, the relative magnitude of the $S_{e(h)}^2$ may be estimated on the basis of the predictive ability of similar models in other locations. Thus, where reliable estimates of historical atrazine application rates exist, $S_{e(h)}^2$ can be assigned to areas that have lower atrazine application rates and are less vulnerability than areas that have higher application rates and greater vulnerability. In this analysis, the assumption of a uniform distribution of atrazine prevents this distinction; therefore, all stratum are assigned the same random error component ($S_e^2 = S_{e(h)}^2$ for all h). A range of likely $S_{e(h)}^2$ values were evaluated to show their impact on sample allocation.

Results of optimum sample allocation analysis for a hypothetical sample size of $n = 100$ and uniform atrazine applications indicate that about 1 to 2 percent of the samples would be randomly distributed among the least vulnerable strata and about 10 to 50 percent of the samples distributed to the most

vulnerable stratum (table 3), depending on the assumed magnitude of the random error component. Optimum allocation of sample sizes other than 100 can be distributed in proportion to those shown for 100; corresponding error variances (rather than standard errors) are inversely proportional to the sample size. The minimum error of the mean atrazine concentration estimate corresponding to the sample allocation shown in table 3 was computed as:

$$S_{min}(\bar{y}_{st}) = \frac{\sum W_h S_h}{\sqrt{\sum n_h}}. \qquad [3]$$

Following field sampling and water-chemistry analysis, the reliability and utility of the leaching model and local estimates of historical atrazine application rates can be assessed on the basis of an analysis of variance. Should the analysis of variance show no significant differences in atrazine concentrations among defined strata, it may be concluded that the leaching model and estimates of historical atrazine application rates are ineffective. Otherwise, the utility of the model and application rate estimates may be considered verified to the extent that the analysis of variance indicates a consistent relation between expected and sampled concentrations of atrazine. The analysis of error will also provide an estimate of the random error component for comparison with the value used in the sampling design.

SUMMARY AND CONCLUSIONS

This report overviews and assesses results of a study of ground-water vulnerability to atrazine leaching in Kent County, Michigan. That study established the simulated fraction of atrazine remaining at the water table as a criterion for vulnerability. This fraction, along with an assumed uniform, steady-state application rate of 2 lbs of atrazine (active ingredient) per ac-yr, was used to compute a potential atrazine concentration at the water table. This assessment reviews model assumptions, examines parameter values and model sensitivity, compares atrazine detection probabilities and concentrations in the previous study with

24

Table 3. Optimum allocation of 100 samples among strata for alternate random error components

Random error component (S_e)	Optimum number of randomly selected wells in each stratum (n_h) (Percent of existing wells in each stratum)							Standard error of the strata mean $S_{min}(y_{st})$
	Stratum							
	1	2	3	4	5	6	7	
0.00	0.031 (0.001)	2.39 (0.224)	4.77 (1.12)	4.17 (1.96)	11.5 (5.41)	10.5 (9.82)	66.6 (62.3)	0.012
.05	15.8 (0.741)	8.12 (0.761)	4.82 (1.13)	3.55 (1.67)	8.92 (4.18)	8.04 (7.52)	50.7 (47.4)	.016
.10	24.8 (1.16)	12.5 (1.17)	5.72 (1.34)	3.51 (1.65)	7.31 (3.43)	6.40 (5.98)	39.8 (37.2)	.020
.25	36.8 (1.72)	18.4 (1.72)	7.55 (1.77)	3.96 (1.86)	5.49 (2.58)	4.16 (3.88)	23.7 (22.1)	.034
.50	43.2 (2.03)	21.6 (2.03)	8.71 (2.04)	4.40 (2.07)	4.94 (2.32)	3.08 (2.88)	14.0 (13.1)	.058
1.00	47.0 (2.02)	23.5 (2.02)	9.42 (2.21)	4.71 (2.21)	4.87 (2.28)	2.64 (2.47)	7.90 (7.38)	.106

those in other investigations, and develops a strategy for using field sampling to verify expected atrazine concentrations. Expected atrazine concentrations can be computed by use of the vulnerability model developed in the Kent County Study, once detailed information on historical atrazine application rates becomes available.

Model assumptions that most likely limit the accuracy of the previous study include uniform transport and steady-state flow. The uniform transport assumption, which is common to most transport models, does not account for preferential flow. Solutes transported along preferential flow paths bypass much of the soils and underlying earth materials where sorption can occur and reaches the saturated zone faster than under uniform transport, thereby reducing the time available for natural degradation. Thus, preferential transport can result in higher fractions of atrazine remaining at the water table than computed under the uniform-transport assumption. The steady-state flow assumption does not account for seasonal variations in atrazine concentrations, which have been documented in the literature, or for possible trends in atrazine concentrations.

Analysis of parameters used in the evaluation indicates that the model is most sensitive to variations in input values for atrazine half life, organic carbon content, and organic-carbon partition coefficient. Comparison with other investigations indicates that the ranges of model parameters used in the Kent County Study are consistent with the broad range of parameter values reported in the literature. Given the highly site-specific nature of these parameters, however, and the wide range of reported values, significant uncertainty in the modeled fractions of atrazine remaining could be associated with parameter uncertainty.

A sampling experiment compared atrazine detections in 14 shallow wells in the southern Lower Peninsula of Michigan monitored as part of

Midcontinent Pesticide Study with potential atrazine concentrations computed in the Kent County Study. Unadjusted detection probabilities for potential concentrations were modified to improve comparability with likely detection probabilities for shallow wells. Modifications involve adjustments for differences in detection probabilities between ground water at the water table and ground water in wells, and adjustments for differences caused by the uniform atrazine application rate used to compute potential concentrations and lower average application rates that are applicable in Kent County. Following these adjustments, results indicate that the distribution of detection probabilities from wells was similar to the detection probabilities indicated by the aquifer vulnerability evaluation. Also, the range of potential atrazine concentrations computed in the evaluation was consistent with the range of values reported in other areas, including Wisconsin and Minnesota.

Verification of the vulnerability model for Kent County by use of direct measurements of atrazine concentrations in ground water alone is not possible. However, a stratified random sampling strategy is developed for verifying expected atrazine concentrations in ground water. Expected atrazine concentrations can be determined on the basis of vulnerability model simulation results and detailed estimates of historical atrazine application rates. The strategy is illustrated, with alternate random error components, by use of the potential atrazine application rates computed for the Kent County Study. Should the sampling strategy be implemented, analysis of variance could be used to simultaneously evaluate the effectiveness of the vulnerability model and estimates of historical atrazine application rates.

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