VULNERABILITY ASSESSMENT OF COLORADO
AQUIFERS TO PESTICIDE CONTAMINATION

by

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ABSTRACT

Assessment of groundwater contamination from non-point sources has been an important subject of recent research due to the increasing number of detections of these contaminants. Agricultural chemicals fit into this class of non-point source contaminants, and therefore, must be monitored. The United States Environmental Protection Agency has required that each state produce a State Management Plan (SMP) to monitor and manage pesticide contamination. In partial fulfillment of this SMP, this research resulted in a vulnerability assessment for the state of Colorado. This assessment method is based on an equation that is derived from a steady-state solution to the Advection-Dispersion Equation. The vulnerability equation is a vadose-zone transport equation that includes various site-specific soil characteristics and pesticide properties. The depth to groundwater and various land-management factors have been incorporated into the vulnerability equation as multiplying factors. The assessment has been combined with a Geographic Information System (GIS) to display the assessment for the entire state. The method has been tested against groundwater data from Weld County, Colorado, and showed to be successful at predicting areas that are highly vulnerable to pesticide contamination. Due to the regulatory nature of this research, a User's Manual for the vulnerability assessment has also been constructed.

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CHAPTER 1 INTRODUCTION

1.1 Significance of Completed Research

Groundwater is a very important source of drinking water in the U.S. In order to assure the quality of the groundwater, many attempts have been made to assess and manage non-point source pollution. For example, the potential transport of pesticides through the vadose zone to groundwater is of great concern. Non-point pesticide contamination has resulted mostly from crop application and subsequent leaching to the groundwater (Flury, 1996). To control pesticide pollution, the United States Environmental Protection Agency (U.S. EPA) has proposed a regulation that will require each state to develop and implement a state management plan (SMP) to manage pesticide use and minimize potential for groundwater contamination. This plan will aid farmers, agricultural extension agents, and state regulators in making decisions on which pesticides are appropriate for a certain crop and/or land-management practice based on the site-specific hydrogeologic conditions. In order to construct an SMP, state administrators need to choose a vulnerability-assessment method that is appropriate for their needs. According to the U.S. EPA, a state should consider available soil, climate, and geographic data, along with land-management practices in choosing a vulnerability assessment technique (U.S. EPA, 1993).

Aquifer “sensitivity” is defined by the U.S. EPA as the relative ease with which a contaminant (in this case a pesticide) applied on or near the land surface can migrate to the aquifer of interest (U.S. EPA, 1993). According to the popular convention, aquifer sensitivity assessments include only hydrogeologic characteristics, whereas groundwater vulnerability assessments also include pesticide characteristics (Meeks and Dean, 1990) and sometimes agronomic management practices (Loague, 1991).

Assessment methods vary based on the factors that are considered. Hydrogeologic factors may include depth to water table, depth to bedrock, soil texture, vadose-zone hydraulic conductivity, aquifer hydraulic conductivity, well depths, parent materials, soil organic fraction (f_{oc}), amount of recharge, soil moisture content, and infiltration capacity. Pesticide characteristics that impact the partitioning and degradation of pesticides in the soil phase may include the aqueous solubility, organic carbon partition coefficient (K_{oc}), soil-water partition coefficient (K_d, where $K_d = f_{oc}K_{oc}$), Henry’s constant (K_H), and biochemical degradation rate ($t_{1/2}$). Hornsby *et al.* (1995) have compiled a comprehensive reference of pesticide properties that will be used in the vulnerability assessment for Colorado. While agronomic management practices have not typically been included in past assessments, it is logical that factors such as the type of crop, presence and type of irrigation, type of tillage, and method/amount of pesticide applied should be included. The relative importance of each factor in pesticide transport must also be considered when constructing an assessment method. For instance, the effect of depth to groundwater may greatly outweigh the importance of tillage type if the water table is over 100 feet below the surface.

Once a method is chosen, it can be used to develop the SMP, which then can be used to manage future contamination of the groundwater. This is especially important because 50% of the population of the United States currently relies on groundwater (Sun, 1986). The transport of pesticides also needs to be considered when conducting a vulnerability assessment. Charizopoulos *et al*. (1999) found pesticides in the groundwater in both rural and urban areas in Greece. Hopefully choosing an appropriate assessment method can prevent this from occurring in other areas in the future.

1.2 Study Area

Cretaceous and Tertiary sedimentary rocks dominate the surface geology of Weld County with overlying Quaternary sediments in fluvial areas (Tweto, 1979). Tertiary rocks are exposed in the northern third of the county. The formations present include the Ogallala Formation in the far north and the White River Formation just south of the Ogallala. The Ogallala Formation is loose to well-cemented sand and gravel, while the White River Formation is composed of ashy claystone and sandstone. Cretaceous Laramie Formation forms the majority of the area under the rest of the county. This formation is a shale, sandstone, and claystone with major coal beds. Eolian deposits cover the southeast corner of Weld County. Various alluvial deposits can be found throughout the county along and around the South Platte River and its tributaries.

Two major aquifers underlie portions of Weld County. The Ogallala aquifer lies under the northern-most areas of the county. The Denver Basin aquifer system underlies the southern quarter of the county. The extensive alluvial deposits along the South Platte River are a major source of irrigated water use in Weld County. The dry climate (average precipitation is 30 cm/year) owes to the necessity of irrigation systems, which vary from sprinkler to flood or furrow irrigation systems.

Agriculture is prevalent in Weld County, and the numerous detections of pesticides throughout the county create an ideal environment for a vulnerability assessment to be completed. There are a wide variety of crops grown in Weld County: corn, alfalfa, grass hay, barley, wheat, sugar beets, potatoes, onions, and other vegetables (Colorado Agricultural Statistics, 2000).

Pesticides are commonly used throughout Weld County. Some of the more commonly used pesticides are atrazine, cyanazine, alachlor, metolachlor, terbufos, EPTC, butylate, chlorpyrifos, 2,4-D, and Dicamba (Dubois, 1993).

1.3 Objectives

The main objective of this research was to create a vulnerability-assessment method that will accurately predict groundwater vulnerability for site-specific areas throughout the state of Colorado. Several steps were required to complete this objective. The first step was to conduct an extensive literature review to review how other researchers have created vulnerability assessments. Another purpose of this step was to aid in choosing a preliminary assessment method that would be appropriate for Colorado. The next step was to complete a model-sensitivity analysis of the chosen method. This purpose of this analysis was to aid in evaluating the importance of measuring various input parameters versus estimating others. The chosen assessment method was then modified to fit the needs and information available for Colorado. This newly revised method was then incorporated into a GIS. The next step was to incorporate land-management effects in the method. The land management practices were to be included as multiplying factors to the assessment method calculation. A field test of the method against well data from Weld County was the last step. If the field test showed the method to be insufficient for regulatory purposes, other possible methods would be evaluated. A User's Manual for the chosen assessment method was also created.

CHAPTER 2 LITERATURE REVIEW

2.1 Theory of Pesticide Transport

In order to understand the vulnerability of groundwater to pesticides, one must first understand the relevant contaminant transport processes (Corwin *et al.*, 1999). Pesticides are exposed to many transport and transformation processes during and after application. Some of these processes include transportation with soil water, removal with surface runoff, plant uptake, volatilization, sorption to the soil, biochemical degradation below the surface, and dilution in the infiltrating water (Flury, 1996). Contaminant transport is traditionally represented by the reactive advection-dispersion equation (ADE)

$$D_L \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} - \left(\frac{\partial C}{\partial t}\right)_{rxn} = R \frac{\partial C}{\partial t} \tag{2.1}$$

Equation 2.1 is the one-dimensional form of the ADE (Fetter, 1999). D_L is the longitudinal hydrodynamic dispersion coefficient [L^2/T], C is the concentration of solute [M/L^3], v_z is the component of velocity in the z-direction [L/T], R [unitless] is the retardation of the pesticide due to interphase mass transfer, z is the distance in the z-direction [L], and t is time [T] (Fetter, 1999). The ADE assumes a homogeneous, isotropic porous media as well as Darcy flow. The dispersion and retardation terms differ for saturated porous media or unsaturated porous media. In most ADE applications in the vadose-zone, water content is assumed to be constant. Otherwise, this parameter would appear in the ADE. Some assessment methods use this equation as the basis for a vulnerability model (e.g. Carsel *et al.*, 1985; Meeks and Dean, 1990; Rao *et al.*, 1985; Freissinet *et al.*, 1999; Soutter and Musy, 1998, Hantush *et al.*, 2000). Several of the methods above use calculated indices such as an attenuation factor or a leaching potential index that are based on *R* or on simple solutions to the ADE (Meeks and Dean, 1990; Rao *et al*., 1985; Freissinet *et al.*, 1999; Soutter and Musy, 1998). These methods typically do not include land-management and pesticide-use factors because they are difficult to quantify in a mathematical model.

Meeks and Dean (1990) emphasized the importance of including the chemical characteristics in selecting an assessment method. Some of these properties include soil-water partition coefficient (K_d), organic carbon partition coefficient (K_{oc}), volatilization half-life, and biochemical degradation half-life. If a pesticide is strongly sorbed to the soil particles or organic matter, it will be held up in the soil, and thus will be retarded in its transport to the water table. Longer transport times may allow more biochemical degradation before the contaminant reaches groundwater. Loll and Moldrup (2000) report that the importance of biological processes is equal to that of hydraulic and meteorologic processes. Volatilization and evaporation are the loss of the chemical to the gas phase at the soil surface and in the soil gas. A very short or very long volatilization half-life can greatly affect the amount of pesticide that will reach the groundwater, as can the degradation half-life.

The theory of transport of specific pesticides has been reported in many journals and is reviewed by Flury (1996). In the same review, Flury discussed the effects of macropore, or preferential, flow. Preferential flow is thought to increase the depth that pesticides reach in the vadose zone. Some soil types are thought to be more susceptible to preferential flow than others. For example, Kelly and Pomes (1998) suggest that claypan soils are very susceptible to preferential flow through desiccation cracks, worm burrows, and root channels. Van den Bosch *et al.* (1999) found that in a water-repellent sandy soil the occurrence of preferential flow was related to the thickness of the A-horizon in the soil profile and the type of vegetation cover. Thicker A-horizons reduce the fingering of the wetting front, as does dense, uniform vegetation.

2.2 Importance of Land-Management Factors

Land-management factors have been proposed to be an important component of a groundwater vulnerability assessment (Loague, 1991). These factors include style of irrigation, style of tillage, application method, and formulation of the pesticide during application. Each of these land-management factor is discussed in detail below. Table 2.1 is a summary of literature reported effects for each land-management factor.

Table 2.1 Reported effects of various land-management practices.

Factor	Increase Vulnerability	No Difference	Decrease Vulnerability
Irrigation		Ghodrati and Jury, 1992; Ren *et al.*, 1996	
Flood	Nachabe *et al.*, 1999		
Furrow	(Compared to Basin) Troiano *et al.*, 1993; Loague, 1991		
Basin	(Compared to Sprinkler) Troiano *et al.*, 1993		
Tillage			
Conventional Tillage		Starr and Glotfelty, 1990; Steenhuis *et al.*, 1990; Gaynor *et al.*, 1992; Ghodrati and Jury, 1992; Ritter *et al.*, 1994; Gaynor *et al.*, 1995; Weed *et al.*, 1995; Shang and Arshad, 1998 (clay soil); Miller *et al.*, 1999; Schwartz *et al.*, 1999; Turpin *et al.*, 1999	
Conservation (No Till)	Dick *et al.*, 1989; Hall *et al.*, 1989; Pivets and Steenhuis, 1989; Andreini and Steenhuis, 1990; Isensee *et al.*, 1990; Gish *et al.*, 1991; Helling and Gish, 1991; Locke and Harper, 1991; Sadeghi and Isensee, 1994; Isensee and Sadeghi, 1995; Myers *et al.*, 1995; Isensee and Sadeghi, 1996; Sadeghi *et al.*, 2000		Gish *et al.*, 1995; Shang and Arshad, 1998 (sandy loam)
Formulation			
Aqueous	(Deeper movement) Ghodrati and Jury, 1992	Gückel *et al.*, 1974; Furmidge, 1984	
Granular	(Less uniform distribution) Furmidge, 1984		
Controlled-release		Fleming *et al.*, 1992	Gish *et al.*, 1991; Schreiber *et al.*, 1993; Buhler *et al.*, 1994

The type of irrigation is an important consideration. Nachabe *et al.* (1999) recommend that using sprinkler irrigation rather than flood irrigation can reduce macropore flow because water must be ponded at the soil surface before significant macropore flow can occur. The study also showed that sprinkler irrigation was more efficient matching crop water needs and reducing leaching below the root-zone. Flury's (1996) review suggested that there is still some controversy as to whether the type of irrigation has an effect on leaching potential.

The type of tillage has also been reported to influence the transport of pesticides, but current literature has shown that no consensus exists on this topic. Many researchers report that no-till, or conservation tillage, increases vulnerability to pesticides (Dick *et al.*, 1989; Hall *et al.*, 1989; Pivetz and Steenhuis, 1989; Andreini and Steenhuis, 1990; Isensee *et al.*, 1990; Gish *et al.*, 1991; Helling and Gish, 1991; Locke and Harper, 1991; Sadeghi and Isensee, 1994; Isensee and Sadeghi, 1995; Myers *et al.*, 1995; Isensee and Sadeghi, 1996; Sadeghi *et al.*, 2000). Preferential flow is thought to be the cause of the increased vulnerability under this type of tillage because the soils are allowed to remain intact over long periods of time allowing macropores to develop. Other researchers, however, found no differentiation in the vulnerability owing to tillage practice (Starr and Glotfelty, 1990; Steenhuis *et al.*, 1990; Gaynor *et al.*, 1992; Ghodrati and Jury, 1992; Ritter *et al.*, 1994; Gaynor *et al.*, 1995; Weed *et al.*, 1995; Shang and Arshad, 1998; Miller *et al.*, 1999; Schwartz *et al.*, 1999; Turpin *et al.*, 1999). These researchers have reported that either the effect is not significantly large or over longer periods of time the effect of tillage type is negligible. Certainly, it is possible that the potential influence of tillage is strongly dependent on soil and climate factors. However, the current literature does not include the data required to verify this hypothesis.

The mode of application can also influence whether a pesticide will reach groundwater. Pesticides may be applied to the foliage or to the bare soil before crop emergence. Application at intermediate stages of emergence would result in pesticide application to both foliage and the soil surface. Pesticide application to plant leaves can greatly decrease the amount of pesticide that will reach the soil and hence the groundwater. Pesticides may be lost to evaporation, photolysis, or incorporation into the plant material. This decreases the portion of pesticide applied that reaches the soil surface, thus decreasing the amount of pesticide available for transport to the water table.

Pesticide formulation is also thought to have an effect on leaching potential. Granular applications are often less uniform, which may contribute to leaching (Flury, 1996). Timing of release has brought about mixed results according to the literature. Slow-release formulations include pesticides that are starch-encapsulated to be released when the soil conditions are appropriate. For example, temperature or soil moisture may control the timing of the release. Flury (1996) discusses many studies that describe both suspected effects and actual field results and contends that the same amount of pesticide is being released to the soil in slow-release pesticide formulations; it just takes longer for the contaminant to reach the water table. The net effect of the pesticide is still the same. Beltman *et al.* (1996) showed theoretically that the pesticide-application method and frequency could impact the pesticide concentrations in groundwater for hypothetical sinusoidal frequencies. However, it would be difficult to assess the impact of this factor for actual application patterns. Incorporating this factor is deemed impractical for planning and management at the county scale or greater, which is the focus of this study.

2.3 Types of Assessments

There are a number of published assessment methods currently in use. The first method reviewed is a sensitivity method. Recall that sensitivity assessments include only hydrologic characteristics, while vulnerability assessments also include pesticide properties and may incorporate land-management practices. Because sensitivity studies are simpler and perhaps more frequently used, a review of such studies is relevant to this research.

2.3.1 Colorado Sensitivity Assessment

In 1996, Maurice Hall, in collaboration with the Colorado State University Cooperative Extension, the Colorado Department of Agriculture (CDA), and the Colorado Department of Public Health and Environment (CDPHE) developed a method to assess the sensitivity of Colorado aquifers to nitrate contamination (CDA, 1996; Hall, 1998). The study has also been used as an initial assessment of pesticide contamination.

Hall chose four hydrogeologic characteristics to include in the sensitivity analysis: presence of a productive aquifer, depth to groundwater, availability of recharge, and infiltration capacity of overlying soil material. Each characteristic was assigned a value of zero (not sensitive) to four (highly sensitive) for various sub-areas in the state. The results were overlaid using a Geographic Information System (GIS) to obtain the final ranking of sensitivity.

For the presence of aquifer factor (AQU), locations were assigned a value of one if there was an underlying high conductivity aquifer and a value of zero if no such aquifer was present. Depth to groundwater (WTD) values ranged from one to three; one corresponding to a depth greater than 50 feet, two for a depth between 20 and 50 feet, and three if the aquifer was less than 20 feet below the surface. Values for recharge (RCH) were either zero (no recharge from irrigation) or one (irrigation). The semi-arid climate of Colorado generally results in evapotranspiration greater than precipitation, resulting in little recharge. The infiltration capacity of overlying soil (SOIL) was determined based on the hydrologic group provided in the State Soil Survey Geographic Database (STATSGO) (NRCS, 1994). Soils were assigned values between one (Hydrologic Group D) and four (Hydrologic Group A).

The overall sensitivity range was calculated using the equation:

$$\text{SENS-range} = \text{AQU} \times \text{RCH} \times \{(2 \times \text{WTD}) + \text{SOIL}\} \tag{2.2}$$

WTD was weighted with a multiplier of 2 based on data confidence and the perceived importance of this factor (Hall, 1998). The equation gives values that range from zero to ten. For easier interpretation on a map, the range was rescaled to one to four. This rescaled value is the sensitivity class. Hall (1998) suggests that the sensitivity map be combined with other knowledge in order to assess the overall vulnerability if the information is to be used for a state management plan.

2.3.2 DRASTIC

DRASTIC (Aller *et al*., 1985) is an acronym for the seven input parameters in this aquifer sensitivity model: **D**epth to water table, net water **R**echarge, **A**quifer medium, **S**oil medium, land surface **T**opography, **I**mpact of the unsaturated zone, and hydraulic **C**onductivity (U.S. EPA, 1993). In this method, each parameter is given a weight based on its assumed importance. Numerical ratings are subjectively assigned to each parameter for each location in the study area. These ratings are multiplied by the weight of the parameter, and the resulting product for each parameter is added to produce the DRASTIC Index. Higher scores correspond to higher sensitivity to groundwater contamination by pollutants.

The DRASTIC method has been used many times in the field (Kalinski *et al.*, 1994; Rosen, 1994). The index score should only be used to indicate relative sensitivity, not absolute sensitivity. The user defines what values are to be considered high and low sensitivity. The subjective scoring can create problems. Two researchers may assign different parameter weights based on perceived importance, thus resulting in different sensitivity rankings for the same area. The method also neglects pesticide characteristics and land-management practices. These and other limitations are discussed in detail in Meeks and Dean (1990) and Rosen (1994). Meeks and Dean (1990) suggest that the interactions between the pesticide and the physical surroundings are too important to be neglected.

Rupert (1999a) calibrated DRASTIC using three of the seven factors: depth to water table, net recharge, and soil media. Correlations between NO_2+NO_3-N concentrations and the three parameters were made using the Wilcoxon rank-sum nonparametric statistical test (Ott, 1993). A new point scheme was created based on the correlations. This point scheme was used to create a groundwater-contamination probability map. Comparisons of the new and old map against field data showed that the new probability index correlated much better with field data than the old vulnerability map based on nonparametric statistical analysis. Rupert (1999a), however, used a very large number of samples (726). He also had a large variation in land use over his study area (urban to agricultural to forest). With such a large amount of data, calibration is much easier to achieve. While Rupert’s study area contained many pesticides, there was only enough data to calibrate the model for atrazine detections, which limits the ability for the assessment to be extrapolated to other pesticides. The vulnerability assessment methodology for the state of Colorado must cover a wide suite of pesticides.

2.3.3 RAVE (Relative Aquifer Vulnerability Evaluation)

The Environmental Division of the Montana Department of Agriculture developed a vulnerability assessment method to be used for on-site farm vulnerability (DeLuca and Johnson, 1990). The system is scored in a similar fashion to that of DRASTIC, except the parameters are given higher numerical values based on their importance. The parameters included are depth to groundwater, distance to surface water, cropping practice, percent of organic matter, pesticide application frequency, pesticide application method, soil texture, topographic position, and pesticide leachability. The value for each parameter is added to create the vulnerability score, which ranges from 30 to 100. Breaks in the scoring for low, moderate, high, and very high contamination potential are 45, 65, and 80 respectively. If a score of greater than 80 is achieved, a warning against using that specific pesticide is given.

2.3.4 PRZM (Pesticide Root Zone Model)

Carsel *et al.*, (1985) have developed a rigorous one-dimensional pesticide transport model called PRZM or Pesticide Root Zone Model. PRZM calculates a water balance using Richard's equation.

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\right]\frac{\partial h}{\partial t} \tag{2.3}$$

where $K(\theta)$ is hydraulic conductivity as a function of the moisture content [L/T], θ is the moisture content of the soil [unitless], and z soil depth [L] (positive in the downward direction).

Erosion is modeled from the Universal Soil Loss Equation (Williams and Berndt, 1977). Solute transport is modeled using an implicit finite-difference approximation to the one-dimensional ADE. Surface runoff is estimated using the curve number technique designed by the USDA-SCS (1972). PRZM also requires detailed information on rainfall, evapotranspiration, infiltration, and runoff. Most information is available, however, through the relevant U.S. Department of Agriculture (USDA) databases.

Loague *et al.* (1995) used PRZM to assess chemical leaching in Hawaii. Their results showed that PRZM was reasonably accurate, but more research to validate the model was recommended. PRZM has also been adapted for use with Monte-Carlo analysis to add probabilities to the calculated vulnerability. In 1993 PRZM-2 was released. The new model describes pesticide transport from the root zone to the water table, along with the root-zone analysis from PRZM. Volatilization of pesticides has also been incorporated into PRZM-2.

PRZM is widely used because the code is readily available, it is inexpensive, and it has been validated many times in field-size studies. However, because of the site-specific nature of the required input, this model is most appropriate for site-scale evaluations. Model application at the state or county scale is probably too cumbersome to use for regulatory purposes, because of the detailed data-collection requirements.

2.3.5 Root Zone Water Quality Model

Root Zone Water Quality Model (RZWQM) (Ahuja *et al.*,1999) is a one-dimensional water-quality model that integrates physical, biological, and chemical processes to simulate plant growth and nutrient and pesticide distribution through the root zone over an agricultural area. Hydrologic properties are modeled in a soil matrix system that features chemical equilibrium within the soil. Chemical transport is modeled using a numerical solution to the Richard's equation. Biological activity is also incorporated into RZWQM. The model contains a crop growth component that allows the effects of canopy cover on evaporation from the soil surface and transpiration through roots to impact the transport of chemicals through the root zone. The model allows the user to specify many land-management practices including irrigation, tillage, and pesticide and nutrient application. The influence that each management factor has on the soil conditions is represented mathematically in the model and is allowed to change over the time of the simulation, which can range from months to 100 years.

To achieve an accurate simulation, detailed meteorology data, detailed soil profile information, and initial soil chemical conditions are required. This information may not be available for an assessment that is on the scale of a state, however. This model is more applicable for site-specific analyses.

2.3.6 LEACHM (Leaching Estimation and Chemistry Model)

Leaching Estimation and Chemistry Model (LEACHM) is a finite difference chemical transport model (Wagenet and Hutson, 1986) that calculates a water mass balance using Richard's equation (Equation 2.3) for the fate and transport of nonvolatile pesticides in the unsaturated zone. Fate of these chemicals is handled by coupling Richard's equation with a form of the ADE (similar to equation 2.1 except it allows spatially and temporally variable velocity) to predict chemical movement.

This model was designed for research and is capable of modeling a variety of boundary conditions and transport in layered soils. The model can also be used for pesticide metabolites (U.S. EPA, 1993; Wagenet and Hutson, 1986). Important limitations to LEACHM are that it requires the user to be familiar with sophisticated mathematical transport models. It requires a significant amount of data and hydraulic constitutive relationships to calibrate and does not include land management practices. Thus, this method is probably impractical for state- and county-scale vulnerability assessments.

2.3.7 CMLS (Chemical Movement in Layered Soils)

This one-dimensional simulation model developed by Nofziger and Horsnby (1985) can be used to locate the front of non-polar chemicals as they move through the vadose zone. Chemical Movement in Layered Soils (CMLS) is essentially a solution of a simplified advective transport equation. The model uses infiltration and evaporation data, but does not consider dispersion. Runoff and land management are also not incorporated into the model.

2.3.8 Attenuation Factor (AF)

In 1985, Rao *et al.* described a screening method to assess groundwater vulnerability, which is based on calculating an attenuation factor from the relative travel times and mass emissions to the water table.

$$AF = Exp\left[\frac{-0.693 d R \theta_{FC}}{q t_{1/2}}\right] \tag{2.4}$$

where d is the depth to the water table [L], θ_{FC} is the water content at field capacity [unitless], q is the average annual groundwater recharge [L/T], and $t_{1/2}$ is the pesticide half-life [T]. The attenuation factor is a simple solution to the one-dimensional ADE that assumes steady state conditions, constant water velocities and water contents, and ignores dispersion. The retardation factor (R) is expressed by

$$R = 1 + \frac{\rho_b f_{oc} K_{oc}}{\theta_{FC}} + \frac{n_a K_H}{\theta_{FC}} \tag{2.5}$$

where ρ_b is the soil bulk density [M/L^3], f_{oc} is the organic carbon fraction in the soil [unitless], K_{oc} is the pesticide organic-carbon partitioning coefficient [L^3/M], n_a is the soil air filled porosity ($n_a = n - \theta_{FC}$, where n is the porosity) [unitless], and K_H is the dimensionless Henry's constant for the pesticide of interest [unitless]. As the retardation factor increases, the leachability of the pesticide decreases. The values of AF range from zero to one, where zero corresponds to no threat of applied pesticide leaching to the water table and one corresponds to a threat of all applied pesticide reaching the water table.

It is important to note that the AF is exponential, and thus, results in values that range over many orders of magnitude for typical pesticide-leaching scenarios. This complicates assignment of AF values to vulnerability (Meeks and Dean, 1990). In addition, for most pesticides, the value for AF can become intractably small when the depth to water table is more than several feet. Thus, it is perhaps more appropriate for predicting the likelihood of transport below the root zone. The retardation factor is often used as a simplified model when all information needed to calculate *AF* is not available (Rao *et al.*, 1985).

The attenuation factor model was designed to be used for site-specific characterization of vulnerability based on both soil and pesticide characteristics. However, it has also been used for county-level assessments (Shukla *et al.*, 2000). Some of the assumptions of the model include spatially uniform parameters in the vadose zone; that recharge can be calculated from precipitation, irrigation, and evaporation data; and K_{oc} and half-life values for each pesticide can be estimated. The attenuation factor can be easily modified to account for multiple layered soils. Many researchers have used variations of the AF model in their vulnerability assessment methods (Khan and Liang, 1989; Soutter and Pannatier, 1996; Soutter and Musy, 1998).

The AF has recently been modified by Rao *et al.* in a post-publication addendum to allow for multiple layers. The modified equation is

$$AF = \prod \exp\left(B_i\right) \text{ ; i = 1,…,n} \tag{2.6}$$

where *B* is the exponent from equation 2.4, *i* designates the layer, and n is the number of layers. Each layer will have a unique *B*.

Jury *et al.* (1987) also developed a similar method. Jury's model, however, included changes in the magnitude of biodegradation with depth. Jury divided the vadose zone into three intervals: a surface zone, a transition zone, and a residual zone. The calculated attenuation factor for each zone is then different due to the different reactions.

In particular, organic matter content and potential biodegradation are assumed to decrease with depth.

Kleveno *et al*. (1992) attempted to compare the AF model with PRZM. PRZM is thought to be a more rigorous model because, unlike the attenuation factor model, it can account for dispersion, variable recharge, detailed heterogeneities in the soil profile, and is a transient model. These results showed that different layers could be successfully accounted for by using different AF values for each layer. Assuming that travel times calculated by PRZM are accurate and using Darcy's Law to calculate an "AF travel time" from the input factors in the AF, the "AF travel time" was found to overestimate the time to reach the water table. This overestimation was attributed to neglecting dispersion in the AF model. For practical purposes, however, Kleveno *et al*. (1992) found that the results from the AF model to compare well to those from PRZM. Therefore, pesticide leachability indexes such as the AF are fundamentally appropriate for use in vulnerability assessments. This is fortunate, because such models are much more practical for use in county, state, or regional-scale assessments.

2.3.9 Leaching Potential Index (LPI)

Meeks and Dean (1990) developed a method for pesticide vulnerability assessments that used a Leaching Potential Index (LPI). The LPI Model is also derived from a steady-state solution of the ADE (Equation 2.1). The model assumes constant vertical seepage velocity, first-order biochemical decay and linear adsorption isotherms in the soil. By assuming steady-state conditions and no dispersion, Meeks and Dean (1990) simplified the ADE to

$$\frac{dC}{C} = -\lambda z\left(\frac{V}{R}\right)^{-1} \tag{2.7}$$

where *V* is the vertical soil water [L/T] and *R* is the retardation factor. Solving this equation for *C* with the appropriate boundary conditions gives

$$C = C_0 e^{-\lambda z (V/R)^{-1}} \tag{2.8}$$

where C_0 is the concentration of the chemical at the surface (z = 0) [M/L^3]. Also note that the term C/C_0 is equal to the attenuation factor from Rao *et al.* (1985). From this equation, Meeks and Dean (1990) derived the LPI.

$$C = C_0^{\frac{-1000}{LPI}} \tag{2.9}$$

$$LPI = \frac{1{,}000V}{R\,\lambda z} \tag{2.10}$$

The factor of 1000 was arbitrarily included to increase the numerical values of the LPI to yield a range deemed more reasonable by the authors for their field area. The LPI values increase as susceptibility to contamination increases. Similar to the AF, the LPI approach is very useful because it is a simple method, yet is based on soil and chemical characteristics and is not simply a subjective score. It also does not result in infinitesimally small values for depths below the root zone, as does the AF. The resulting scores can also be transferred from one study area to another. However, there are some limitations to the model. The limitations also apply to the widely used AF model and more complex numerical models. The major limitation is the validity of using the ADE to describe flow in the vadose zone. Lately, the ADE has come under scrutiny as to whether it can sufficiently model facilitated transport, nonequilibrium sorption, and preferential flow (Meeks and Dean, 1990). While the ADE has been modified to account for such factors (for a review see Tindall and Kunkel, 1999), using such a modified equation would be impractical for county-level studies because of the unwieldy data requirements. The other limitation is the inability of the model to account for the vapor-phase transport of very volatile chemicals. According to Meeks and Dean, other methods such as those used by Jury *et al.* (1983) might be better suited to model flow under these conditions. In this method, transport of volatile chemicals is modeled assuming linear, equilibrium partitioning between soil, water, and vapor phases. First order degradation and loss through a stagnant surface-air layer is also considered. Assuming steady-state upward and downward flow, an analytical solution is derived for pesticide concentration and volatilization flux. However, our analysis, which will be explained in detail in a subsequent chapter, indicates that for pesticides of concern in Colorado, air-water partitioning is negligible.

The most difficult aspect of using the LPI model is the estimation of the soil-water velocity. This variable is of considerable importance, yet has a wide range of values and is extremely difficult to determine accurately. Velocity depends on hydraulic conductivity of the soil, precipitation and evaporation data, and irrigation recharge. The soil water velocity is divided by the retardation coefficient to obtain a solute velocity. The retardation coefficient can be estimated by

$$R = 1 + \frac{K_d\, \boldsymbol{r}_b}{\boldsymbol{q}} \tag{2.11}$$

where K_d is the soil-water partition coefficient defined previously. There is also a volatilization term in the retardation factor that has been omitted based on a modeling analysis, which is discussed in a subsequent chapter.

The model has been tested using data collected from a 381 sq. mile study area in the San Joaquin Valley of California (Meeks and Dean, 1990). The area was evaluated using the LPI index followed by sampling for DBCP (1,2-dibromo-3-chloropropane) to validate the results of the assessment. The number of pesticide detections was compared to the calculated vulnerabilities for the sampling locations. Pesticide detections correlated well with the calculated vulnerabilities, illustrating the usefulness of the LPI model.

2.3.10 Matrix for Florida Department of Agriculture and Consumer Services

Britt *et al.* (1992) constructed a decision matrix for new pesticides that included leaching potential and chronic toxicity. This matrix has been adopted by the Florida

Department of Agriculture and Consumer Services (FDACS) for use by the state of Florida.

The ranking index (RI) for leaching potential is calculated from:

$$RI = \left[\frac{0.693 R_f L_g}{\frac{Q_n}{q} T_{1/2}} \right] \tag{2.12}$$

This expression is similar to the exponent in the AF model by Rao *et al.* (1985). If the RI is greater than 500, full registration of the chemical is allowed. If the RI is less than 500, full reports on transport characteristics and all chemical properties are required. This information is then used in a groundwater model, e.g. PRZM, LEACHM, CMLS, or GLEAMS. The model is compared to reference pesticides to decide a relative leaching potential for specific pesticides. This relative leaching potential is used as one variable in a two-variable vulnerability matrix, which is represented on a two-variable (two-axis) plot.

The other matrix variable is chronic toxicity. This factor was included because the pesticide could be found in drinking water. Based on toxicity characteristics including carcinogeneity, mutageneity, neurogeneity, reproductivity problems, and teragenicity, the chemical is assigned a relative toxicity. The pesticide's location in the matrix dictates how or if the pesticide will be allowed for registration. Britt *et al.* (1992) included ranges of values of K_{oc} and half-life, but only central tendencies of these variables were identified and used in the matrix.

2.3.11 Probability Assessments

Rupert (1998) conducted a probability assessment for atrazine/desethylatrazine (DEA) and nitrate (NO_2+NO_3-N) in the upper Snake River Basin of Idaho. His method is termed a probability assessment because it is based on empirical statistical correlations with actual groundwater monitoring data.

Multiple steps were taken in creating the probability maps. Groundwater monitoring data was overlaid with hydrogeologic and land-use data in GIS so each well location included data on atrazine use, depth to water table, geology, soils, land use, precipitation, and well depth. Using logistic regression, univariate relationships between atrazine/DEA detections and type of input data were determined to identify which independent variables were significantly related to detections. Multivariate models were constructed using various combinations of independent variables. The two best models, one that included atrazine use and one without pesticide use (e.g., sensitivity), were chosen for GIS analysis and construction of probability maps. The most significant variables for atrazine/DEA were land use, precipitation, soil hydrologic group, and well depth.

There are some limitations to this assessment method. Large numbers of wells and groundwater contaminant detections are required for the statistical analysis to be valid. A wide range of values is also necessary to develop reliable correlations (Rupert, personal communication, 1999b). This is evident in Rupert's study by the fact that a reliable model could only be developed for atrazine, even though other pesticides were detected in groundwater.

2.3.12 CALVUL (California Vulnerability Modeling Approach)

Troiano *et al.* (1999) developed the California Vulnerability Modeling Approach (CALVUL). The objective of this work was to evaluate similar climatic and geographic features of various sections of land where residues of currently registered pesticides had been found in groundwater. Known contaminated areas were clustered based on climatic and soil variables. An algorithm was then created so that areas where the extent of contamination was unknown could be classified into either high- or low-vulnerability categories. CALVUL was validated in Fresno County, California over an area for which data were available. Areas that had not previously contained detections of norflurazon were assigned vulnerabilities based on the fore-mentioned algorithm. Groundwater was then sampled for pesticides in the areas that were assigned high vulnerability. Pesticides were detected in 8 of the 43 wells sampled. These results indicated that CALVUL was able to successfully aid in locating highly vulnerable areas of land. CALVUL was designed so that other variables (e.g. depth to groundwater) could be incorporated.

2.3.13 GIS Models

Numerous researchers have combined various assessment methods with Geographic Information Systems (GIS) to create maps of vulnerable areas. These maps allow for more selective groundwater monitoring efforts. Khan and Liang (1989) used the Rao *et al.* (1985) attenuation factor method combined with a GIS to create a map of vulnerability of the island of Oahu, Hawaii. Analysis of wells on the island showed that with the appropriate GIS method, the relative vulnerability could be calculated for a large area.

Tim *et al.* (1996) also used a GIS along with three assessment methods: the Rao *et al.* (1985) attenuation factor, the Meeks and Dean (1990) LPI method, and the leaching potential from the Britt *et al.* (1992) model. The GIS model uses a Windows interface to input the necessary data as well as produce output. The interface allows the user to choose which vulnerability method is to be used, and then directs the user as to the information required for the model. The input screens are very straightforward and allow the model to be used by a large number of researchers. The paper illustrated the similarities and differences in vulnerabilities predicted using the three methods. This research did not attempt to compare the accuracy or calibrate the various models using field data.

Shukla *et al.*, (2000) completed a county-level vulnerability assessment using the attenuation factor method combined with GIS. They considered three leaching scenarios, minimum, maximum, and average leaching. The maximum leaching scenario is the only scenario that yielded a contamination potential for a significant portion of the area. An attempted field validation included 19 wells in the county, and resulted in detections in areas of low- and high-predicted contamination potential. Comprehensive monitoring was suggested to improve the study.

2.3.14 Other Models

There have been many other types of models or combinations of models proposed in the literature. Behrendt *et al.* (1999) designed a computer model to assess pesticide contamination potential that was based purely on pesticide chemical structure. Chemical properties for each type of chemical structure were displayed on sunray plots for the seven triazine herbicides and their 35 degradation products. The sunray plots were used to compare the herbicides on a Hasse diagram. Chemicals with higher contamination potentials were placed at the top of the diagram. This model is simply a ranking of pesticides by their hazard potential, and it appears that no field validation has been completed. Gramatica *et al.*, (2000) designed a similar model. They used molecular descriptors to calculate values of K_{oc} for 185 non-ionic organic pesticides. Comparison between calculated K_{oc}'s and observed K_{oc}'s showed that this model was successful at predicting K_{oc} values for various chemicals.

Maxe and Johansson (1998) used travel times and specific surface area to assess the groundwater vulnerability in an area south of Stockholm, Sweden. Factors considered in the assessment included hydrogeologic setting, retention capacity, and travel time. The hydrogeologic settings were used as primary mapping units to which the vulnerabilities were overlain. Vulnerability was assessed for two situations, a spill of liquid that would create a hydraulic surplus or transport of a contaminant by natural groundwater recharge. For the case of a hydraulic surplus, the vulnerability classification was based on the travel time to a specific depth. For the case of groundwater recharge flow, the classification is based on the specific surface area of the soil, which would dictate the retention capacity of the soil.

Assessment methods have also been developed for other contaminants, such as microbes (Wireman and Job, 1997; Jorgenson 1998). Wireman and Job (1997) developed a sensitivity assessment that resembles the sensitivity assessments that have been designed for pesticides and nitrates. The assessment considered only the properties of the hydrologic setting. Jorgenson (1998) later created a vulnerability assessment that incorporated past sampling results, a source risk factor, and condition and construction of the well. This method is still being revised, but it appears to be a strong method for assessing vulnerability to microbes.

Le Seur *et al.* (1987) used a variation of a scoring method combined with a map to assess which areas of Indiana should be a priority for statewide groundwater monitoring for hazardous wastes. The four criteria they used in their method were current groundwater withdrawals, potential groundwater withdrawals, potential hazardous substance sources, and aquifers highly susceptible to contamination. An area was given a value of 1 for each criterion it met, with each area having a maximum score of 4. This information was used to create a map of the state showing the relative vulnerability to hazardous substances contamination. Agricultural non-point sources were not included in this study, due to insufficient information on specific use.

Similar methods have also been used to determine the suitability of certain areas for soil-based wastewater treatment systems. Methods include use of index models (such as DRASTIC), GIS methods, and more complex models. For reviews, the reader is referred to Siegrist *et al.* (2000).

CHAPTER 3 MODEL-SENSITIVITY ANALYSIS

3.1 Introduction to Sensitivity Analysis

One objective of this research was to complete a model-sensitivity analysis to assess the importance of the variations in the input parameters on the calculated vulnerability. The model used for the model-sensitivity analysis was the Leaching Potential Index (LPI) (Meeks and Dean, 1990). Complex methods often require large amounts of data that are unavailable, and therefore, must be estimated. The main purpose of this analysis is to determine which parameters must be estimated and which parameters could be omitted from a vulnerability assessment model. Model-sensitivity analyses have been previously completed during the process of creating a vulnerability assessment method (Britt *et al.*, 1992, Jury *et al.*, 1987, Kleveno *et al.*, 1992, Li *et al.*, 1998, Loague, 1991, Loague *et al.*, 1996, Meeks and Dean, 1990, and Shukla *et al.*, 2000). However, these analyses did not evaluate the impact of all input parameters on the results of the models. The analysis for this research includes all the individual parameters that comprise the LPI. Britt *et al*. (1992) and Jury *et al*. (1987) conducted sensitivity analyses in which they varied only organic-carbon partition coefficient and half-life. Britt *et al.* (1992) reported that even with all variation included, central tendencies were still observed. Jury *et al.* (1987), however, reported that the uncertainties in reported values for chemical properties must be considered in the decision making process. Thus, the issue remains unresolved.

Li *et al*. (1998) also examined the sensitivity of the attenuation factor to perturbations in input parameters. Variations in some chemical properties were considered, but no detailed consideration of physical soil parameters was reported. Loague *et al.* (1990), Loague (1991), and Loague *et al.* (1996) considered land-use variations. First-order uncertainty analysis was used to assess uncertainty in the attenuation factor. Soils were categorized by taxonomy, with uncertainty incorporated when sparse data was extrapolated over large areas. The analysis reported that organic-carbon content was a large contributor to the variation between various soil taxa, and data uncertainty must be accounted for when conducting a pesticide leaching assessment. Hydrologic and chemical properties were not investigated in this analysis.

Shukla *et al.* (2000) conducted a comprehensive model-sensitivity analysis of the AF. These authors combined the factors into groups instead of testing each parameter individually to determine the overall impact on the AF model. Meeks and Dean (1990) state that the sensitivity of one parameter may be influenced by another parameter. This means that consideration of the individual impacts of all chemical properties should be completed before assigning weights to the other hydrogeologic parameters.

This model-sensitivity analysis assesses all input parameters individually. The influence of each input variable is calculated separately. In addition, as will be illustrated, it is useful to evaluate the influence of varying certain parameters on model results over a range of values for other input factors. Variations in the input parameters are based either on values reported in the literature (e.g. for pesticide properties) or upon a reasonable range that one would expect to measure in the field (e.g. for physical properties).

3.2 Soil, land use, and pesticide characteristics

Hydrologic conditions representative of the San Luis Valley, Colorado were chosen for the base-case scenario of the analysis due to data availability at the time this paper was written and the agricultural importance of the region. Soil characteristics and land-use information required for the analysis are listed in Table 3.1. For the base-case, potatoes were chosen as a typical crop for the San Luis Valley. The recharge rate is based on the minimum irrigation needed for successful potato production (Waskom, personal communication, 2000). The soil water velocity is calculated by dividing the irrigation rate by the field capacity of the soil. Various crops would have different irrigation rates, which would result in differing water velocities. When field specific data was not available representative base-case values were used, for example hydraulic conductivity, field capacity, and water-content were obtained from Fetter (1994).

Table 3.1. Soil characteristics and land-use information used in model-sensitivity.

Soil characteristics and land-use information*	
Depth to Groundwater	6 m
Temperature of Soil	15^{o}C
Fraction of Organic-carbon	0.01
Bulk Density	1.6 g/cm^3
Porosity	0.35
Water Content	0.15
Field Capacity	0.1
Hydraulic Conductivity	0.864 m/day
Crop	Potatoes
Recharge Source	Irrigation
Recharge Rate	0.001148 m/day
Soil Water Velocity	0.01148 m/day

Pesticides to be used in the model-sensitivity study include atrazine, cyanazine, simazine, metolachlor, and alachlor. These five pesticides are expected to be included in the state pesticide management plan (Austin, personal communication, 1999). Three other pesticides, 2,4-D, Metribuzin, and Dicamba, were also chosen due to their extensive use in Colorado. These pesticides and their relevant physicochemical properties are listed in Table 3.2. Aqueous solubility is often thought of as an important vulnerability indicator. This parameter is not explicitly considered in the LPI model because it is not a variable in the ADE solution upon which the LPI is based. However, pesticides with high solubilities usually have low K_{oc} values. Thus, the LPI would generally predict a higher vulnerability for a more soluble compound.

Table 3.2. Pesticide properties for selected pesticides (Hornsby *et al.*, 1995).

Pesticide	Mol. Weight (g/mole)	Water Solubility (mg/L)	Sorption Coefficient (Koc) (ml/g)	Vapor Pressure (mm Hg)	Half-life (days)
Atrazine	215.7	33	100	2.89E-07	60
Cyanazine	340.7	170	190	1.60E-09	14
Simazine	201.7	6.2	130	2.21E-08	60
Metolachlor	283.8	530	200	3.14E-05	90
Alachlor	269.8	240	20	1.40E-05	15
2,4-D	221.4	890	20	8.00E-06	10
Metribuzin	214.3	1220	60	1.00E-05	40
Dicamba	211.0	400000	2	0.00E+00	14

3.3 Model Sensitivity Results

To conduct the model-sensitivity analysis, values for selected hydrologic and chemical input parameters for the model are perturbed within a realistic range of values to determine the impact of each parameter on the model-predicted vulnerability. These parameters include organic-carbon content, depth to groundwater, groundwater velocity, soil bulk density, water content, organic-carbon partition coefficient, and pesticide half-life. Partitioning to soil-gas is also included in the retardation factor. However, for the range of conditions used in this study air-phase partitioning was found to be negligible (model predictions varied by less than 0.01% in all cases when air-phase partitioning was omitted), and was therefore excluded from this study.

Initially, f_{oc} was chosen as the primary independent sensitivity parameter, because it was expected to be of importance in any vulnerability model. The presence or lack of organic-carbon in the soil has a large impact on the mass of pesticide that can be absorbed to the soil, and therefore on pesticide leaching velocities and biochemical degradation.

Figure 3.1 shows the calculated LPI vs. f_{oc} using the eight pesticides. Figure 3.1 illustrates that the LPI score is strongly dependent upon organic-carbon content. Small variations in the organic-carbon content have a large effect on the calculated vulnerability (e.g. two orders of magnitude). Thus, the organic-carbon content is a very important input parameter for a vulnerability assessment, and a reliable estimate of organic-carbon is crucial. This analysis assumes a constant f_{oc} throughout the soil profile. However, the organic-carbon content actually varies with depth. The range of f_{oc} values chosen includes values typical of topsoil and deep soil zones. Thus, "best-case" and "worst-case" vulnerabilities are considered even though uniform soil profile is assumed. Even in typical topsoil values, the effect of varying amounts of organic carbon is more than an order of magnitude.

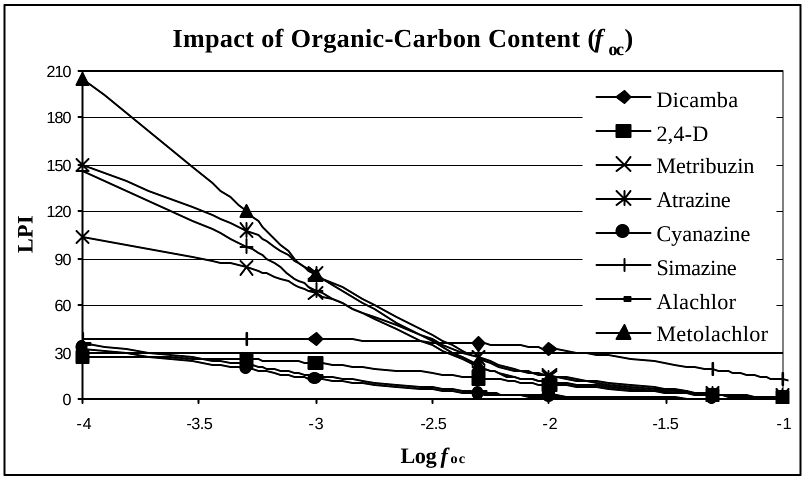

Figure 3.1. Leaching Potential Index for eight pesticides of interest over a range of organic-carbon contents. ($0.0001 < f_{oc} < 0.1$)

The next parameter to be evaluated is the organic-carbon partition coefficient (K_{oc}) (Figure 3.2). The range chosen was based on the range presented in Hornsby *et al.* (1995) for each pesticide. The vulnerability is higher for lower values of K_{oc} because pesticides with higher K_{oc} values are more likely to be strongly sorbed to the soil, inhibiting their transport to the water table. Figure 3.2 essentially illustrates the effect of K_{oc} measurement variability on the LPI. The wide range of K_{oc} values reported in the literature can be attributed to varying laboratory methods or measurement difficulties. The difference in the calculated vulnerability can be minimal, as in the case of cyanazine, or it can be significant, as in the case of simazine. Thus, care should be taken to choose a representative value i.e., one that is not an outlier among the majority of reported values.

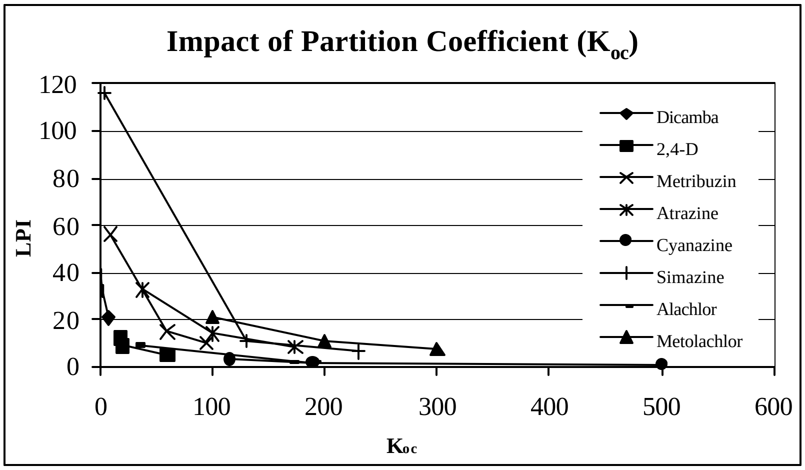

Figure 3.2. Leaching Potential Index for eight pesticides of interest over literature-cited values for K_{oc}.

Figure 3.3 shows the impact of biochemical half-life on the calculated LPI. As expected, the vulnerability increases as the biochemical half-life increases. This occurs because a longer half-life reduces the amount of the chemical lost to biochemical destruction, thus increasing the chance of the chemical reaching the water table. It is useful to note that the half-life probably varies with depth (Jury *et al.*, 1987). In addition, field-soil half-lives are often smaller than laboratory measured values (Beulke *et al.*, 2000). The uncertainty in choosing the correct value for the half-life must once again be considered when selecting the half-life value in an assessment method.

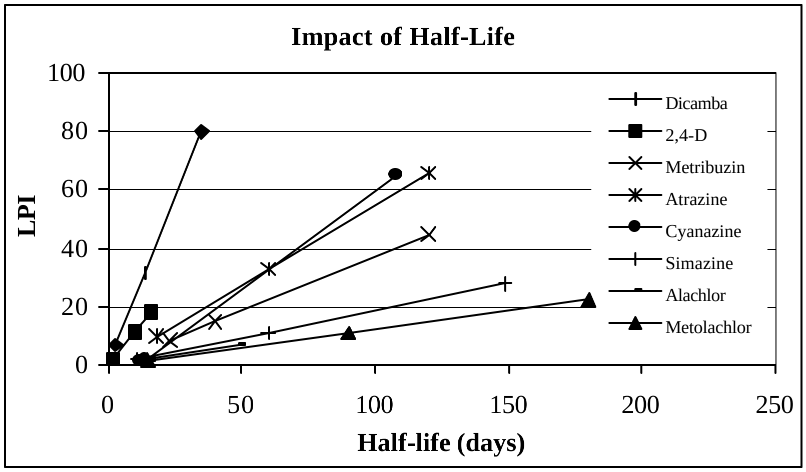

Figure 3.3. Leaching Potential Index for eight pesticides of interest for a range of literature-cited values for biochemical half-life.

The remaining parameters were evaluated separately for each pesticide to estimate the impact of varying field-scale parameters such as depth to groundwater, groundwater velocity, water content, and bulk density on the calculated LPI. Parameters were plotted against values of organic-carbon content since this parameter was previously shown to be of great importance and can vary greatly among different soils or locations. Metolachlor is the only pesticide that is presented because of its high leachability and for brevity. Similar trends were seen for all pesticides, including the low-leachability pesticides.

Figure 3.4 illustrates that an accurate estimation of the depth to groundwater should be very important for vulnerability estimations. In particular, the variability in the calculated vulnerability index is especially large at lower organic-carbon contents and for depths less than 10 meters.

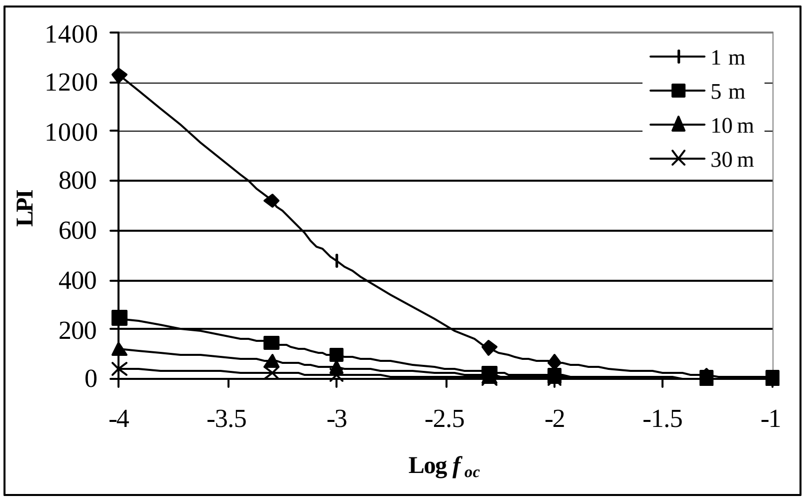

Figure 3.4. Leaching Potential Index for Metolachlor over a range of groundwater depths.

Figure 3.5 depicts the impact of soil-water velocity on the LPI. When comparing velocities for various sediment classes, the LPI can vary by seven orders of magnitude. Soil-water velocity is, therefore, probably the most important parameter in this vulnerability method. Unfortunately, it is also the most difficult parameter to estimate. Soil-water velocity is dependent on recharge rate, soil hydraulic conductivity, surface slope, and soil moisture content. For this study recharge was assumed to be due solely to irrigation because of the dry climate of the San Luis Valley. This is generally true for most agricultural areas in Colorado (Hall, 1998). The values for velocity are assumed to be equal to typical saturated hydraulic conductivity values for the sediment types listed (Fetter, 1994). This would be consistent with unsaturated-zone flow under conditions for a unit hydraulic gradient (e.g. gravity driven flow), which is appropriate for irrigation-based recharge. Table 3.3 lists the velocity values that were used in the model-sensitivity study. The average of each sediment class reported by Fetter (1994) was chosen as the value for that class.

Table 3.3. Assumed hydraulic conductivity values used in model-sensitivity study for various sediment classes.

Sediment Class	Velocity (cm/s)
Clay	$10^{-7.5}$
Silt	10^{-5}
Loam	10^{-4}
Sand	10^{-2}
Gravel	10^{-1}

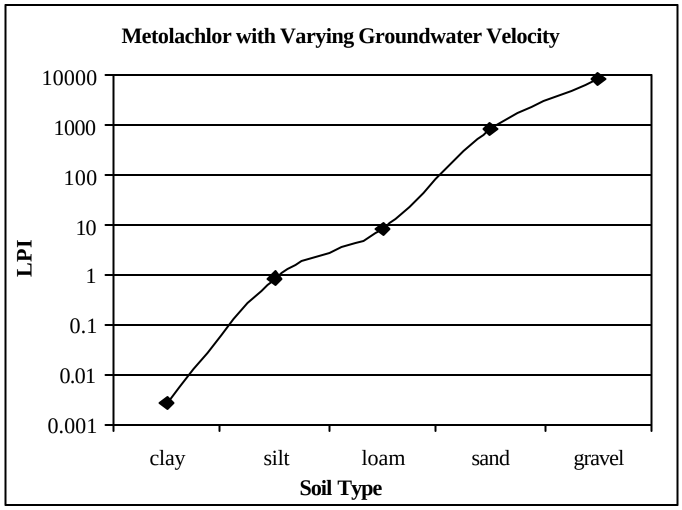

Figure 3.5. Leaching Potential Index for Metolachlor over a range of groundwater velocities and soil types.

Variations in water content and soil bulk density had relatively little influence on calculated vulnerability indexes (Figures 3.6 and 3.7). Over a typical range of values for bulk density, the variability in calculated LPI is minimal compared to the variability induced by variations in f_{oc}, depth to groundwater, etc. The impact of water content on LPI is somewhat more important, but is still likely to be insignificant compared to the influence of other parameters. Thus, for practical purposes a single representative value for an entire geographic region could be used or the parameter could be eliminated altogether from certain models to reduce the data-gathering requirements.

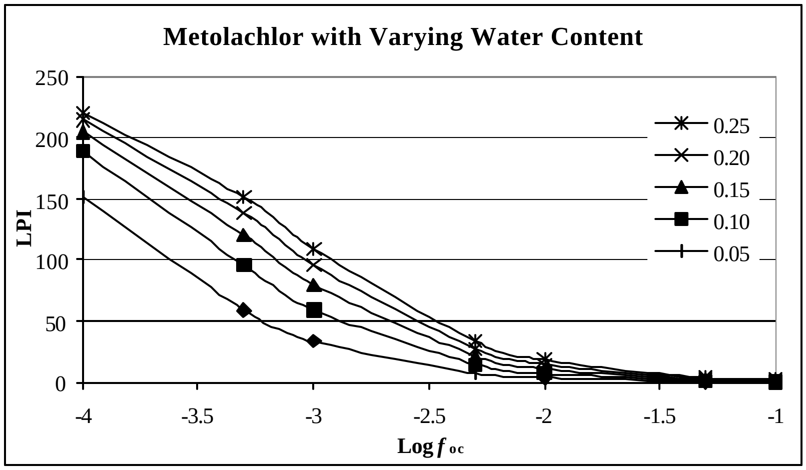

Figure 3.6. Leaching Potential Index for Metolachlor over a range of water content.

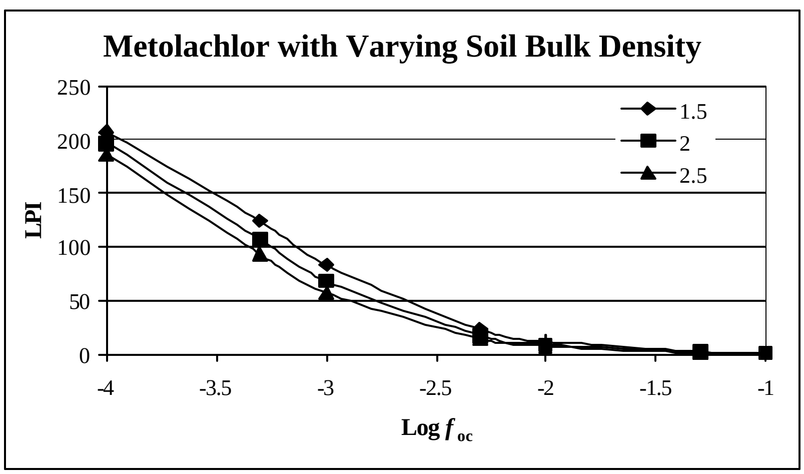

Figure 3.7. Leaching Potential Index for Metolachlor over a range of soil bulk densities (g/cm^3).

3.4 Model-Sensitivity Analysis Conclusions

This model-sensitivity analysis indicates that calculated LPI values are most sensitive to organic-carbon content, depth to groundwater, and recharge velocity, while not particularly sensitive to bulk density or soil moisture content. Organic-carbon partition coefficient and pesticide half-life are also shown to be important; however, the question arises as to which pesticide property value cited in the literature should be used. Perhaps, careful measurements that are relevant to site-specific conditions should be made, although this is not practical for regulatory purposes. Simpler methods to estimate velocity also need to be derived. Knowledge of the importance of various input parameters will allow for more accurate decision-making when developing vulnerability assessment methods.

CHAPTER 4 BASE VULNERABILITY INDEX

4.1 Vulnerability Assessment Method Selection

Many factors were considered in selecting a vulnerability assessment method for the state of Colorado. One of those factors was the degree of accuracy in the predicted results calculated by the potential method. The method must be able to accurately predict the vulnerability of a particular area to be useful. Comparison of calculated vulnerabilities to concentrations and frequency of detections of pesticides in groundwater was used to measure this factor. Another consideration was the data required for the method. The final method should allow for implementation without extensive additional testing. A final consideration is the ease of implementation of the method. The producer should ideally be able to complete his or her own assessment with readily available input data. This requires that the assessment method be relatively simple and very straightforward. All of the above factors were considered for the selection of an assessment method for Colorado.

The assessment method selected is a modification of the leaching potential index (LPI) (Meeks and Dean, 1990). The LPI method is a modification of the attenuation factor (AF) model (Rao *et al.*, 1985). The AF is a simple solution to the one-dimensional advection-dispersion equation that assumes steady state conditions, constant water velocities and water contents, and ignores dispersion. The AF is expressed by

$$AF = Exp\left[\frac{-0.693ZR\theta_{FC}}{qt_{1/2}}\right] \tag{4.1}$$

where Z is the depth to the water table [L], θ_{FC} is the water content at field capacity [unitless], q is the average annual groundwater recharge [L/T], and $t_{1/2}$ is the pesticide degradation half-life [T]. The retardation factor (R) is expressed by

$$R = 1 + \frac{\rho_b f_{oc} K_{oc}}{\theta_{FC}} + \frac{\theta_g K_H}{\theta_{FC}} \tag{4.2}$$

where ρ_b is the soil bulk density [M/L^3], f_{oc} is the organic-carbon fraction in the soil [unitless], K_{oc} is the pesticide organic-carbon partitioning coefficient [L^3/M], θ_g is the gas content [unitless], and K_H is the dimensionless Henry's constant for the pesticide of interest [unitless] (Rao *et al.*, 1985).

Meeks and Dean (1990) inverted the exponential argument of the AF and multiplied it by a factor of 1000 to create an index that increases with increasing vulnerability and that varies over a more practical numerical range. The resulting equation is

$$LPI = \frac{1000t_{1/2}V}{0.693Rz} \tag{4.3}$$

where V is the soil water velocity (L/T). As the LPI increases so does the vulnerability of an area. Meeks and Dean (1990) proposed five categories for leaching potential: very low, low, moderate, high, and very high. The LPI ranges corresponding to each class were zero to 24, 25 to 49, 50 to 74, 75 to 89, and greater than 90, respectively. This is just an example of how the categories could be divided. Designations of low, medium, and high vulnerability should be based on a validation with pesticide soil and groundwater concentrations in an applicable area. This process, as completed for the state of Colorado, is explained in detail below.

Meeks and Dean (1990) validated the LPI model in a 381 sq mile area in the San Joaquin Valley of California. The data set included 272 wells in which there were 70 wells with detections of 1,2-dibromo-3-chloropropane (DBCP). The model was shown to be successful at predicting vulnerability at this scale.

Because of its published success, the LPI was chosen as the basis for the vulnerability assessment used in this study. One would expect similar relative results if the AF model was used.

The next consideration was the amount of input data required to use the method. Soil-water velocity and soil moisture content were the only input parameters that were not available for this study. However, other minor problems required modification of the LPI or certain input parameters. Details of the solutions to these problems follow.

Soil-water velocity is very difficult to estimate because of the large number of factors that influence it. These factors include precipitation, irrigation, evapo-transpiration, and hydraulic conductivity. Obtaining information for each of the factors at every farm site would require extensive testing and would be costly. This is an unrealistic expectation. However, the permeability or hydraulic conductivity was available for the Weld County field-test area at the time of this research in the STATSGO and SSURGO databases (NRCS, 1994; NRCS, 1999; NRCS, 2000). This permeability or hydraulic conductivity was substituted for soil-water velocity as a reasonable estimate of velocity for a unit hydraulic gradient.

The z-term in the LPI method is defined as the depth to groundwater. This term may be difficult to estimate if there is not a well drilled on or near the field of interest. In addition, the soil properties from the STATSGO and SSURGO databases only apply to the surface soils. As described previously, nearly all the sorption and biodegradation will occur in the surface zone. Thus, this thickness is probably most appropriate for use with sorption and biodegradation. In order to include a depth term in the calculation that could be obtained from nearly all existing soil databases, the thickness of the first soil layer in the SSURGO database was used. This thickness is, essentially, the thickness of the root zone. The actual depth to groundwater will be incorporated into the calculated vulnerability index as a multiplying factor. This allows the producer to correct the depth to groundwater without completing an entirely new vulnerability calculation. This will be explained in more detail below.

Soil moisture content was also unavailable at the time of this study. The previous sensitivity analysis, however, showed that the LPI model was not very sensitive to variations in water content. The STATSGO and SSURGO databases include the field capacity for each soil unit. Therefore, this value is substituted for water content.

The fraction of organic carbon (f_{oc}) was also not available at the time of this study. Our databases, however, did include the percent organic matter (%OM). The %OM is the multiplied by 0.58 to convert organic matter to organic carbon. The %OM is also divided by 100 to convert the value back to a fraction.

The new vulnerability, termed the modified LPI (mLPI), is calculated by

$$mLPI = \frac{1{,}000 t_{1/2} Perm}{0.693 Rz} \tag{4.4}$$

where *Perm* is permeability of the top soil layer from the STATSGO or SSURGO database.

The next step was to study whether any of the other parameters could be eliminated to simplify the model but still allow it to calculate accurate vulnerabilities. Recall the retardation factor (*R*) is given by

$$R = 1 + \frac{r_b f_{oc} K_{oc}}{q_{FC}} + \frac{q_g K_H}{q_{FC}} \tag{4.5}$$

where the last term describes vapor-phase partitioning. A brief analysis was completed to assess the effect of neglecting the vapor-phase partition term. Twenty-four pesticides that are known to be used in Colorado were used to calculate the retardation factor with and without the vaporization term. A base case soil condition was chosen randomly from the SSURGO database from Weld County, Colorado. These parameters included a bulk density of 1.5 g/cm^3, 1 %OM, a field capacity of 0.15, and gas content of 0.15, which yields a total porosity of 0.30. It is important to note that this base case is different from

Table 4.1. Sample analysis to evaluate the effect of neglecting vaporization term in retardation factor.

Common name	K_H	R w/o K_H	R w/ K_H	% Difference
2,4-D	9.51E-05	2.01E+02	2.01E+02	2.37E-05
Alachlor	2.03E-04	1.70E+03	1.70E+03	5.97E-06
Aldicarb	3.07E-04	3.01E+02	3.01E+02	5.10E-05
Atrazine	3.35E-06	1.00E+03	1.00E+03	1.67E-07
Bromacil	4.35E-06	3.21E+02	3.21E+02	6.78E-07
Chlorpyrifos	3.21E-04	6.07E+04	6.07E+04	2.64E-07
Cyanazine	2.07E-08	1.90E+03	1.90E+03	5.45E-10
DCPA	4.46E-05	5.00E+04	5.00E+04	4.46E-08
Diazinon	9.82E-04	1.00E+04	1.00E+04	4.91E-06
Dicamba	0	2.10E+01	2.10E+01	0.00E+00
Dieldrin	6.15E-05	1.20E+05	1.20E+05	2.56E-08
Diquat	0	1.00E+07	1.00E+07	0.00E+00
Endosulfan	3.72E-06	1.24E+05	1.24E+05	1.50E-09
Heptachlor	8.03E-03	2.40E+05	2.40E+05	1.67E-06
Hexazinone	2.71E-06	5.41E+02	5.41E+02	2.51E-07
Lindane	5.16E-04	1.10E+04	1.10E+04	2.35E-06
Malathion	1.42E-04	1.80E+04	1.80E+04	3.95E-07
Metolachlor	4.78E-04	2.00E+03	2.00E+03	1.20E-05
Metribuzin	1.15E-04	6.01E+02	6.01E+02	9.59E-06
Paraquat	0	1.00E+07	1.00E+07	0.00E+00
Parathion	7.83E-05	5.00E+04	5.00E+04	7.83E-08
Picloram	0	1.61E+02	1.61E+02	0.00E+00
Prometon	9.37E-05	1.50E+03	1.50E+03	3.12E-06
Simazine	2.40E-07	1.30E+03	1.30E+03	9.21E-09

the base case used in the model-sensitivity analysis. The percent difference in the resulting retardation factors was then calculated to evaluate the importance of the vapor-phase term. Table 4.1 illustrates the results of this analysis. The vaporization term had little effect (less than 0.001%) on the retardation factor relative to the other parameters included. These results justify neglecting vapor-phase partitioning in the vulnerability method for Colorado.

4.2 Pesticide Leachability Classifications

As part of the vulnerability assessment for Colorado, an assessment will need to be completed for at least six pesticides. The list of pesticides to be assessed may also change or expand in the future. One option is to create an assessment for each pesticide individually. This would be time consuming, costly, and impractical. Another option is to group the pesticides based on their leaching potential. The leaching potential for a pesticide is based mainly on the pesticide half-life and organic carbon partition coefficient (i.e. biochemical degradation and sorption). For this study the pesticides were grouped into one of three categories based on their ratio of half-life to organic carbon partition coefficient. This grouping allows the assessment to include three vulnerability maps rather than for every pesticide. This enhances the simplicity of the method. A similar approach was used by North Dakota in their construction of a vulnerability assessment method (Seelig, 1994).

In addition, this procedure fortuitously allows the model to be validated more efficiently. The data that is available for Weld County, Colorado is limited when comparing data for specific pesticides, but the database increases when it is combined into three leachability groups. For example, there are only 19 detects of metolachlor (a high leachability pesticide) in the 104 wells sampled in 1995 and 1996. However, when the pesticides are combined in the three leachability categories there are 96 detects of pesticides that are in the high leachability classification. This additional data in a sample increases the usefulness of the sample and makes the validation more statistically rigorous.

The process of selecting the distribution of the leaching groups began by ranking all 340 pesticides described by Hornsby *et al.* (1995) based on the ratio of half-life to organic carbon partition coefficient. The Hornsby *et al.* database was used because it is very comprehensive and recent. Arthur Hornsby also collaborated with Don Wauchope in creating a similar database for the United States Department of Agriculture, and this data is included in Hornsby *et al*. (1995). Once the pesticides were ranked, they were divided into three groups to create a low, moderate, and high leachability classes. The ratios of each pesticide appear to exhibit a log-normal distribution (Figure 4.1), therefore the groups were divided as follows: lowly leachable pesticides had ratios less than 0.01, moderately leachable pesticides had ratios between 0.01 and 0.1, and highly leachable

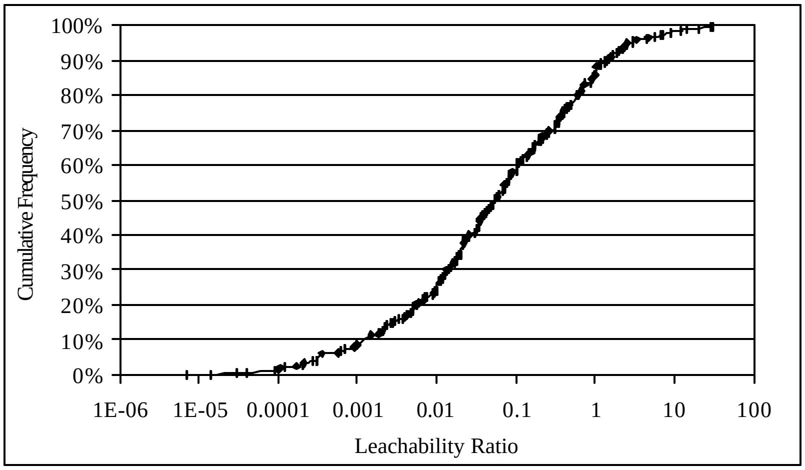

Figure 4.1. Illustration of log-normal distribution of leachability ratios.

pesticides had ratios greater than 0.1. Median values for each leachability class were 0.002 for low, 0.03 for moderate, and 0.5 for highly-leachable pesticides. Please refer to Appendix A for a listing of the pesticides that are in each classification.

The next step was to test the statistical uniqueness of the chosen classification. To classify each pesticide as uniquely low, or moderate, highly leachable the categories must also be unique. That is, we wish to minimize the number of pesticides that would fit into two categories. This would negate the uniqueness of the classifications. There are two statistical measures taken during this process: a measure of the statistical difference in the medians, and a measure of whether the variances of the medians overlap. The Mann-Whitney test (Johnson and Kuby, 2000) was used to evaluate whether the medians were statistically different. The Mann-Whitney test is a nonparametric hypothesis test, which is used to evaluate whether one sample is statistically different from another. A nonparametric test does not require a certain distribution of a sample population. For example, the sample population is not required to have a normal distribution. Nonparametric tests may not be as powerful as parametric tests (e.g. t-test), but they are used when parametric tests are not feasible. The Mann-Whitney test is sensitive to changes in the median and changes in the distribution (e.g. skewness).

The Mann-Whitney test compares statistics associated with two samples. Thus, the low leaching group was compared to the moderate leaching group, and the moderate leaching group was compared to the high leaching group. The Mann-Whitney test results include a confidence interval (CI), chosen by the user, and a p-value, or probability. The p-value is the probability that your null hypothesis is false. For example, my null hypothesis is that the two leachability groups are different. The level of significance (α) is equal to 1 – CI. The confidence interval chosen for this analysis is 95%. This converts to an α of 0.05. If the p-value is less than α, the two groups are statistically different. Table 4.2 shows the results of the analysis using the Mann-Whitney test and a 95% confidence interval. These results indicate that the chosen groups are statistically different because both p-values are much less than 0.05.

Figure 4.2 also shows the results from the statistical analysis. The y-axis is a log scale to better display the separation between the groups.

Table 4.2. Results of Mann-Whitney test to evaluate if the chosen classifications are statistically different (p-values calculated to five significant digits).

Groups being compared	p-value
Low vs. Moderate Leachers	0.0001
Moderate vs. High Leachers	0.0001

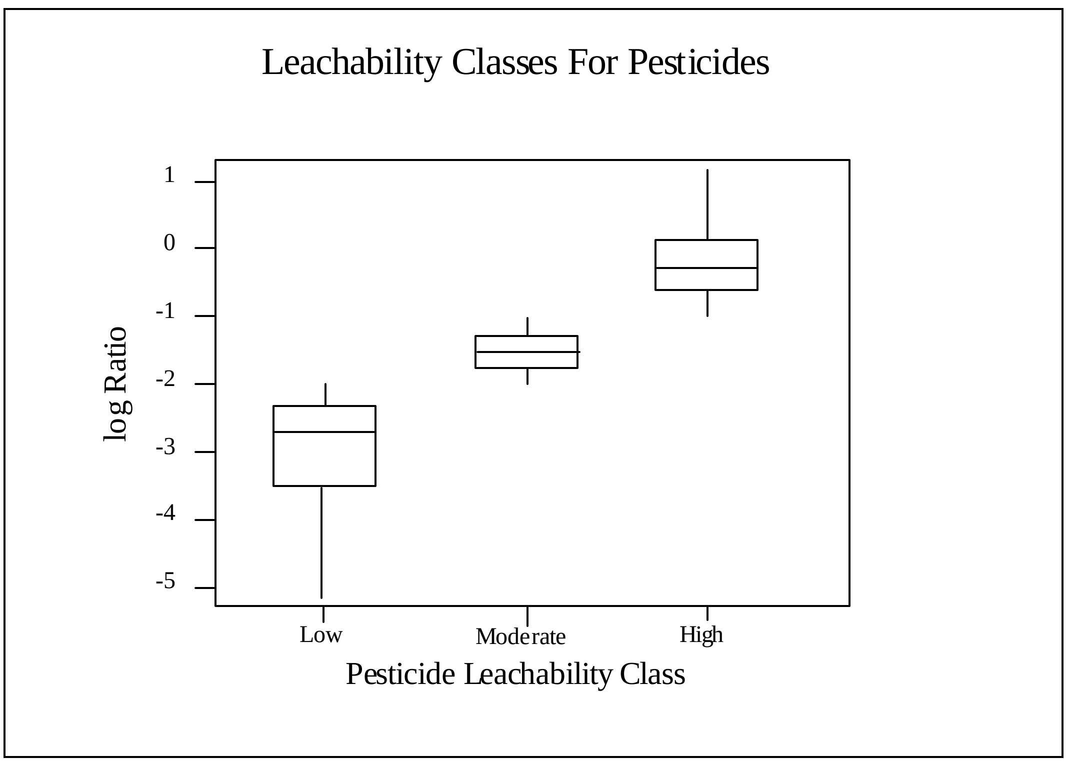

Figure 4.2. Distribution of pesticide leachability classes versus the log of the ratio.

The median of each group was chosen as the representative value for the group. The median was used instead of the mean, because the mean is strongly influenced by extremely low or high values, while the median is not. The median ratio is then incorporated into a base vulnerability index (BVI) as will be explained later. This allows for creation of three statistically unique vulnerability maps for any area based on three leachability groups. The user will choose the map that is appropriate for the pesticide of interest. The appropriate leachability classification for each pesticide listed in the Hornsby *et al.*(1995) database can be found in Appendix B.

4.3 Mathematical Derivation of Leachability Ratio

Modifying the grouping of the pesticides into leachability classes was necessary to allow for a minimum number of vulnerability maps. As will be described, the grouping procedure also facilitated the field test of the method by grouping the sparse pesticide detections in groundwater into three larger data groups.

However, incorporation of this ratio in the vulnerability calculation required another modification to the LPI method. This modification was to isolate the half-life and K_{oc} values from the equation and use the leachability class ratio as a multiplying factor as shown in equation 4.6.

$$BVI = \frac{200 Perm \theta_{FC}}{z \rho_b \%OM}\left(\frac{t_{1/2}}{K_{oc}}\right) \tag{4.6}$$

This modification was necessary to isolate the leachability ratio because the ratio does not naturally occur in the LPI equation (recall equations 4.4 and 4.5). The factor of 200 is an arbitrary multiplying factor that includes the organic matter conversions and converts the range of calculated BVI values to a reasonable range for the regulatory purposes of this research. This will be illustrated in a subsequent section. The conversions are also necessary to accommodate information that is available in the soil unit databases. It is useful to note that soil databases may also have different units for the parameters that are not consistent between databases. However, consistent units must be calculated before the database can be used to calculate the vulnerability. Appropriate units for calculation of the BVI are listed in Table 4.3.

Table 4.3. Appropriate units for calculation of BVI.

Parameter	**Units**
Permeability (Perm)	cm/day
Field capacity (θ_{FC})	unitless
Thickness of top soil layer (z)	cm
Bulk density (ρ_b)	g/cm^3
Percent organic matter (%OM)	%

The modifications that have been made alter the original LPI and give it a much different form than the original LPI. The equation still, however, calculates a relative vulnerability, termed base vulnerability index (BVI) for this study. The term “base” is used because it will be corrected to account for various land-management practices to produce a final vulnerability index (VI).

A simple analysis was performed to evaluate the validity of modifying the original LPI equation, which is based on a solid theoretical foundation. The vulnerability was calculated two ways for each pesticide. The first method was to use equation 4.4 to calculate the vulnerability index. The second method used equation 4.6. The site-specific soil conditions were the same conditions as used for the vaporization term analysis. Additional site-specific data included a permeability of 200 cm/day and 20 cm as the thickness of the first soil layer. Two pesticides were randomly chosen from each of the leachability classifications. The percent difference was calculated to evaluate the effect of modifying the calculation. Table 4.4 shows the results of this analysis. The percent difference for each pesticide was less than 0.05%. This analysis illustrates that this modification can be completed without significantly altering the vulnerability calculated from the original LPI.

Table 4.4. Sample analysis to valuate the effect of using equation 4.6 instead of the original LPI.

Leaching Group	Chemical Name	mLPI with R	BVI	% Difference
Low	Chlorpyrifos	5.348786	5.348852	0.0006
	Diquat	1.082251	1.082251	0.0000
Moderate	Alachlor	95.45063	95.49274	0.0220
	Cyanazine	79.71335	79.74481	0.0197
High	Atrazine	648.8640	649.3506	0.0375
	Metolachlor	486.8304	487.0130	0.0187

4.4 Incorporation of Depth to Groundwater in the BVI

The depth to groundwater is also known to be an important factor in predicting aquifer vulnerability. Thicker vadose zones intuitively should provide more protection against groundwater contamination. However, recall that the z term in the BVI equation is the thickness of the first layer of soil in the STATSGO or SSURGO database, and thus the depth to groundwater is not an input parameter in the BVI. The depth to groundwater is thus incorporated as a multiplying factor that alters the BVI based on the vadose-zone depth in the area of interest. Larger multiplying factors are assigned to shallow vadose-zone areas because vulnerability is presumably higher in these areas. Vadose-zone depths (or depth to groundwater) were grouped into classes based on statistical analysis. The 104 wells that were sampled in Weld County in 1995 and 1996 were used to calibrate the groundwater classifications and the multiplying factors by a trial-and-error procedure. The vulnerability of each well was calculated three times, for low, moderate, and highly leachable pesticide classes. Hence, the dataset included 312 data points. The concentration of pesticide in each well was plotted against the BVI score. 15-foot intervals for the groundwater classifications were chosen as a first attempt (e.g. 0-15, 16-30, 31-45, >45), with multiplying factors of 3, 2, 1, and 0.5, respectively. These initial values were chosen arbitrarily. We wanted the multiplying factors to be small so as to keep the range of vulnerability scores reasonable. The correlation coefficient (R^2) was calculated for each set of groundwater classification and multiplying factors as a measure of the fit to a linear trend line. The best fit occurred with multiplying factors of 3, 2.5, 2, and 1, respectively, for the depth classes described earlier. The R^2 for this best-fit case was 0.2073 and indicates that depth to groundwater alone would not provide a good indicator for vulnerability in Weld County. The BVI is then multiplied by the appropriate multiplying factor for the depth to groundwater class to produce a final base vulnerability index value (BVI_f).

4.5 Vulnerability Maps

GIS provides a convenient method to display the vulnerability calculations for a geographic area, given the heavily computational nature of the vulnerability assessment. A map was created for each pesticide leachability class. SSURGO data was used to construct these maps (NRCS, 1999; NRCS, 2000) (Appendix B). Only Weld County is shown due to the detail that is required in the map. The vulnerability assessment has been completed for the entire state; however, the user will need to be able to locate the area of interest from the map. This will be easier if the map is on a county scale.

The SSURGO database for Weld County has also been displayed in a GIS (Appendix B). This map designates which soil unit corresponds to the location of interest. The soil properties that are associated with that soil unit are then used in the calculation of the BVI for the area of interest. The SSURGO database will be available to the user in the event that they dispute the calculated vulnerability.

The depth to groundwater classes will also be displayed with GIS (Appendix C). See Appendix C for the depth to groundwater map. This depth to groundwater map shows the user the depth that was used for their area to calculate the depth-to-groundwater-corrected BVI.

The depth to groundwater map is overlain with the BVI map. The maps are multiplied together to give the final BVI value (BVI_f). See Figure 4.3 for BVI_f maps for the low, moderate, and highly leachability classes for Weld County. The maps are also in jpeg format in Appendix D. Maps for the entire state of Colorado using STATSGO data are also being constructed, but were not available at the time of publication. The BVI_f maps will be the maps that users will consult to evaluate the vulnerability. Work to make the map system more user-friendly is a subject of future research.

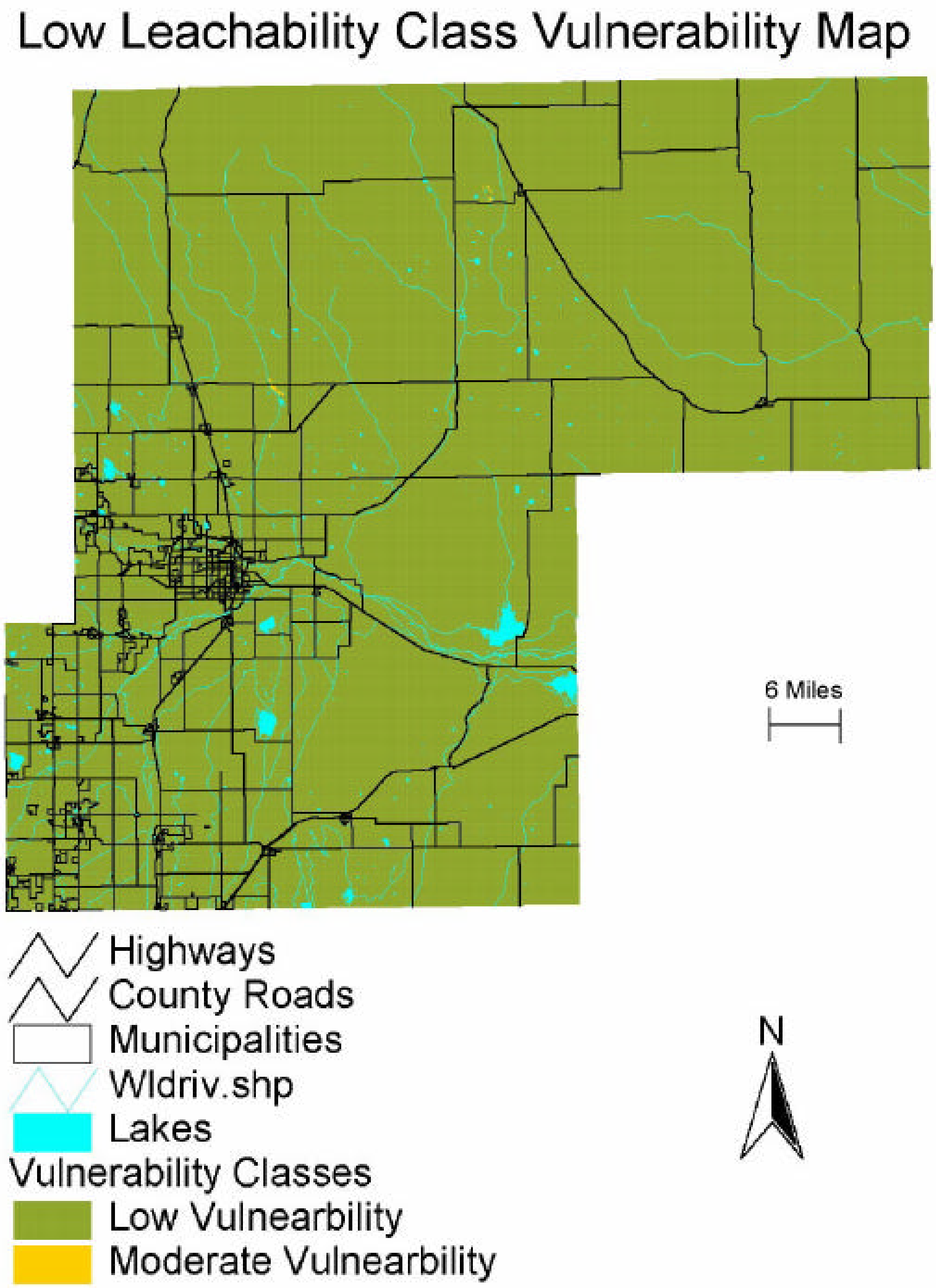

Figure 4.3(a). BVI_f map of Weld County for low leachability pesticides.

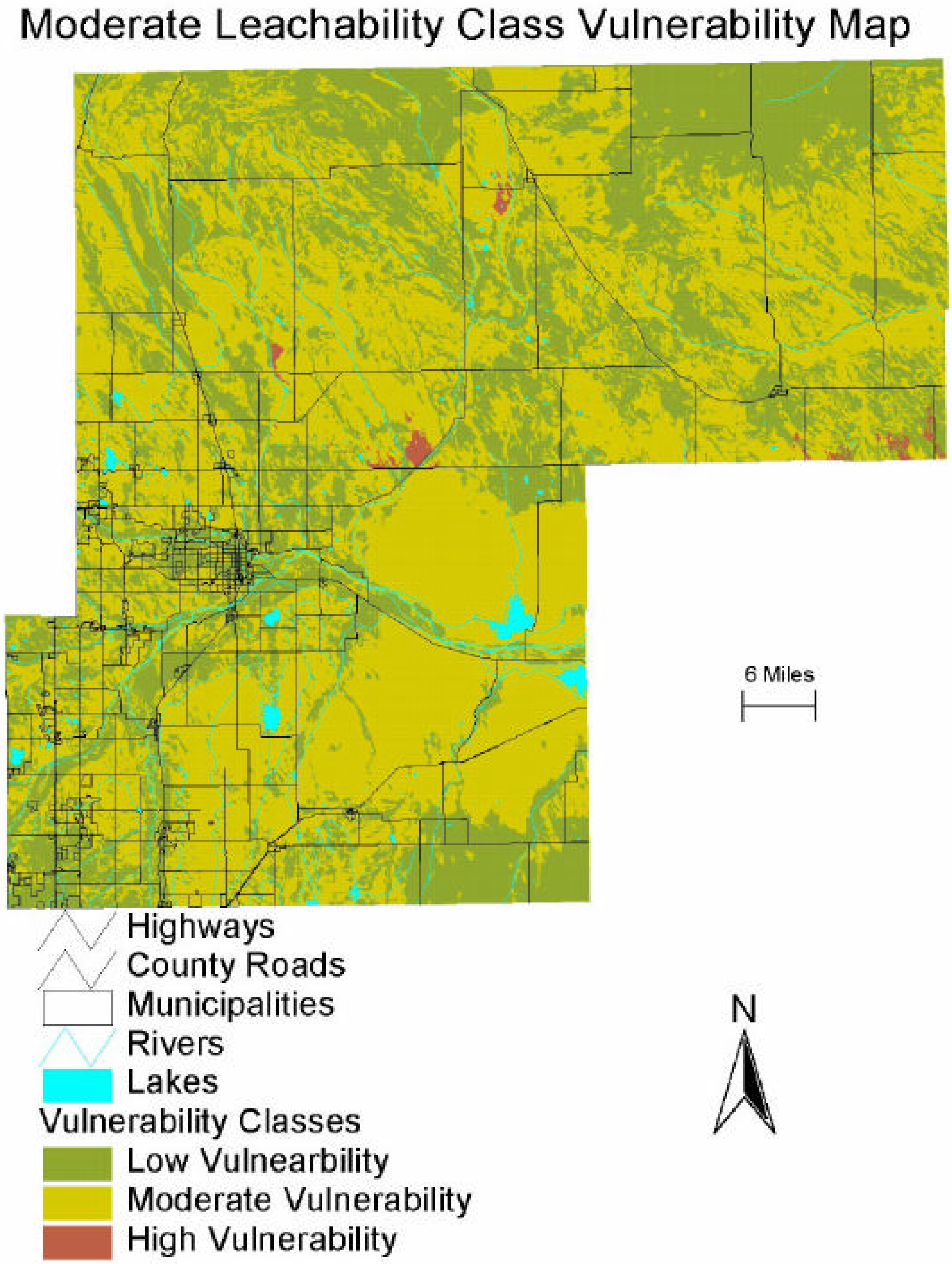

Figure 4.3(b). BVI_f map of Weld County for moderate leachability pesticides.

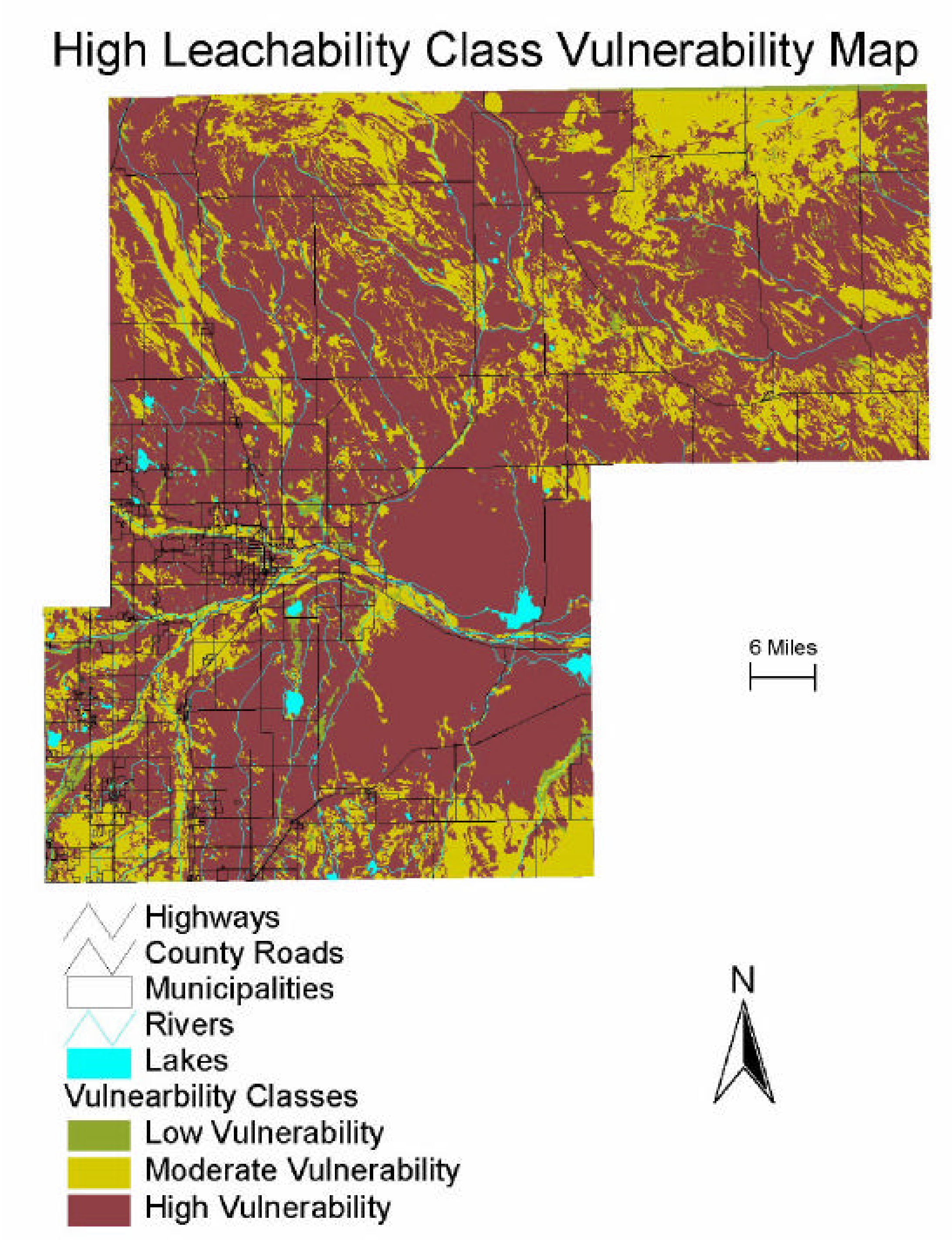

Figure 4.3(c). BVI_f map of Weld County for high leachability pesticides.

CHAPTER 5 VULNERABILITY METHOD FIELD TEST

The most important step in creating a vulnerability method is evaluating its predictive capability. The standard method to test a model is to compare the predicted vulnerability to some measure of the actual vulnerability. In this case, the concentration of pesticide in the well and frequency of detections are used to represent actual vulnerability. As the predicted vulnerability increases, so should the frequency of detections and the concentration of pesticides that are detected. If the BVI method cannot accurately predict areas that are known to be vulnerable, it would not be a useful method and another method would need to be selected.

Weld County was chosen for the field test because of the abundance of sampling data from multiple years and availability of SSURGO geographic and geologic data. During the 1995 sampling season, 104 wells were sampled, including monitoring, domestic, and irrigation wells. A portion of the irrigation wells that were sampled in 1996 were also included in the field test since they covered areas not previously sampled. The 1995 set contained the most data points, and was therefore used as the main data set to test the method. Other years were also included, but yielded the same trends in the results.

Land-management factors are known to strongly influence the actual movement of various pesticides. However, there was insufficient data on these parameters to attempt a calibration to field data. Thus, a field test on only the BVI_f was attempted. Additional discussion of multiplying factors for land-management factors will be explained in Chapter 6.

Please see Appendix E for the data that were used in this field test. A large portion of the wells are located along the South Platte River, where intensive agricultural activity is located. Figure E-1 shows the distribution of wells throughout Weld County. The well distribution includes monitoring wells, domestic wells, and irrigation wells. The northern part of the county is not dependent upon irrigation, and therefore was not sampled. Since we wanted to evaluate the vulnerability of each well to contamination by all three classes of pesticides, the vulnerability of each well was calculated three times, once for each leachability class. Any detection of a pesticide for a given well was considered a detection of the leachability class that the pesticide belonged to. Land management practices were not included in this field test because they are difficult to assess without visiting all the well locations and because practices in the past were not known.

The calculated vulnerabilities of each well for each leachability class were then compared to the concentrations of pesticide in the wells. Atrazine and its daughter products are combined to give one concentration. For example, if a well sample has 0.2 μg/L atrazine and 0.3 μg/L deethylatrazine and no detections for other daughter products, the atrazine value used for this analysis is 0.5 μg/L. This procedure is performed to estimate the approximate total atrazine in the groundwater. Figure 5.1 shows a plot of concentration versus calculated BVI_f. As predicted, as the vulnerability increases the number of detections and the concentrations associated with those detections also increase. This shows that the BVI_f method is successful in predicting the vulnerability for Weld County. The "zero" values in Figure 5.1 may not be values of zero concentration, are all below the detection limit. They are displayed as zeros for visual purposes.

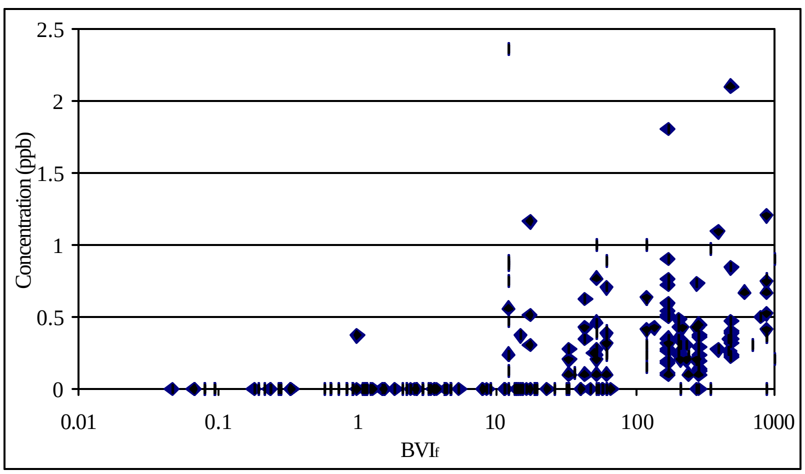

Figure 5.1. Comparison of sampling results from 1995 sampling season versus calculated vulnerabilities.

While concentration data is the most intuitive method to test vulnerability models, the frequency of detects has been used by many researchers in field tests and to determine ranges for low, moderate, and high vulnerability (Meeks and Dean, 1990, Rupert, 1998, Troiano, 1999). From Figure 5.1 one can see that there are natural breaks in the number of detections where the BVI_f could be broken up into low, moderate, and high vulnerabilities. Visual inspection indicates natural breaks at BVI_f values of 10 and 100. Detections appear to start at a vulnerability of 10. Between 10 and 100, the data appears to consist of roughly half detects and half non-detects, while the vulnerabilities above 100 appear to be mostly detects with only a few non-detects. A plot of the percent of the wells with detections versus the vulnerability classifications (Figure 5.2) shows the classifications for a number of potential classification breaks. Figure 5.2a suggests that two breaks are present. The breaks are at 10 and 100. Below 10, there are essentially no detections of pesticides, while between 10 and 100 approximately 40% of the wells have detects. Wells with calculated vulnerabilities above 100 have detections in them at least 90% of the time. Figure 5.2b shows the final three vulnerability classifications plotted against the percent of detections.

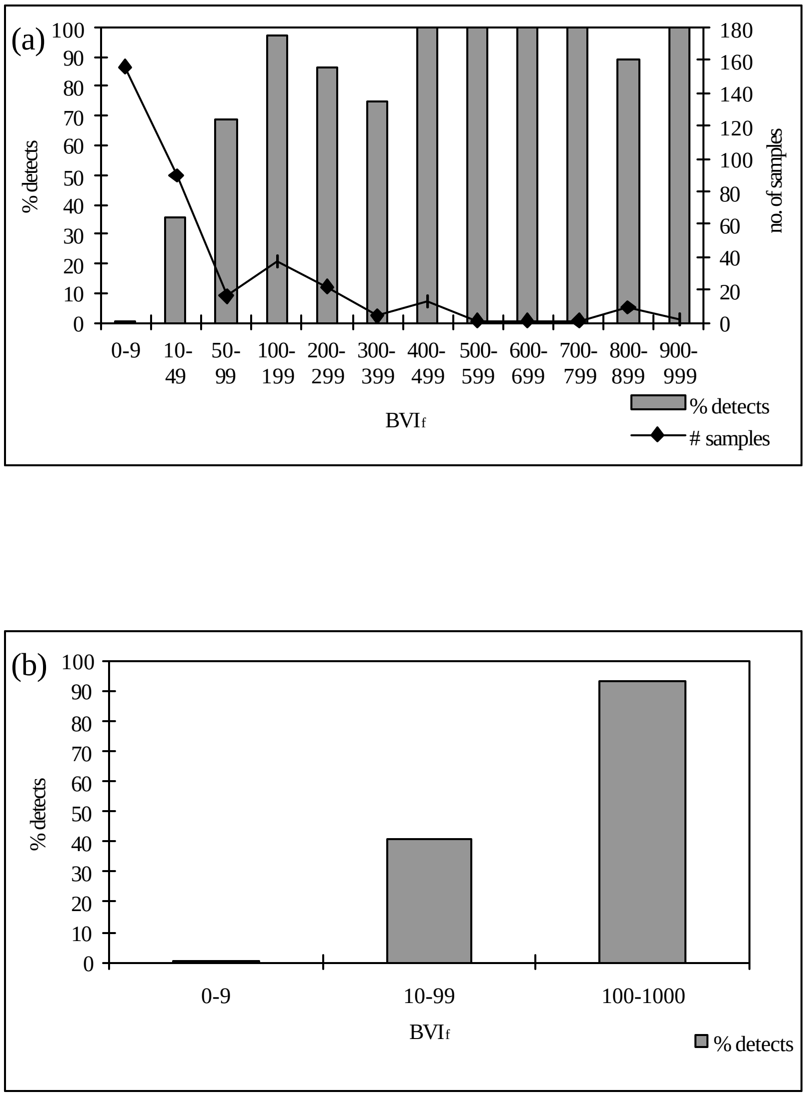

Figure 5.2. Detection frequency plots. (a) Preliminary division of vulnerability classes to evaluate natural breaks. (b) Final vulnerability classification categories.

CHAPTER 6 LAND-MANAGEMENT FACTORS AND USER'S MANUAL

6.1 Land Management Factors

Land management factors have been reported to influence the transport of pesticides to groundwater. Therefore, they were included in this assessment method. Land-management practices are included in the assessment method as multiplying factors to the BVI_f. Unfortunately, insufficient data exists to calibrate the multiplying factors to field data. Thus, to evaluate the relative effects of each factor, and hence the appropriate multiplying factors, Root Zone Water Quality Model (RZWQM) was used.

RZWQM was used to simulate and compare various management practices, such as various methods for irrigation, tillage, and application method. All other input parameters not being assessed as land-management factors were assigned base-case values equal to the default values in the model. See Appendix H for a summary of input parameters used in this analysis. Due to RZWQM's limited choices for crops, corn was chosen for simulations. Loam soil was chosen for the base-case. Atrazine was chosen as the base-case pesticide because it is commonly applied to corn and it is a highly leachable pesticide. Thus, the influence of pesticide transformation processes on the model results is minimized. This is desirable because the purpose of these simulations is to evaluate the influence of land-management factors only. The model was run for a one-year period with a growing season from May 1 to August 31 (last irrigation event). The values for pesticide mass in the soil profile were calculated from December 31.

Irrigation was the first land-management practice to be analyzed. Three practices were chosen: no irrigation, sprinkler irrigation, and furrow irrigation. Flood irrigation is also available in RZWQM, however flood and furrow are similar, and flood irrigation is rarely used on corn. Details of application rates and amounts for each method are listed in Appendix F. Literature research has reported that furrow irrigation increases the amount of pesticide that leaches to the groundwater. This occurs because furrow irrigation typically requires more water applied to the crop at a single event than sprinkler irrigation. The need to apply more water per application is related to the efficiencies of the various irrigation practices. Furrow irrigation typically is approximately 40% efficient, while sprinkler systems are about 70 to 80% efficient (Waskom, 2001, personal communication). Figure 6.1 illustrates the distribution of mass of atrazine in the soil profile after the simulation for the various irrigation practices. As expected, the mass traveled deeper in the profile under furrow as compared to sprinkler, and deeper under sprinkler as compared to no irrigation.

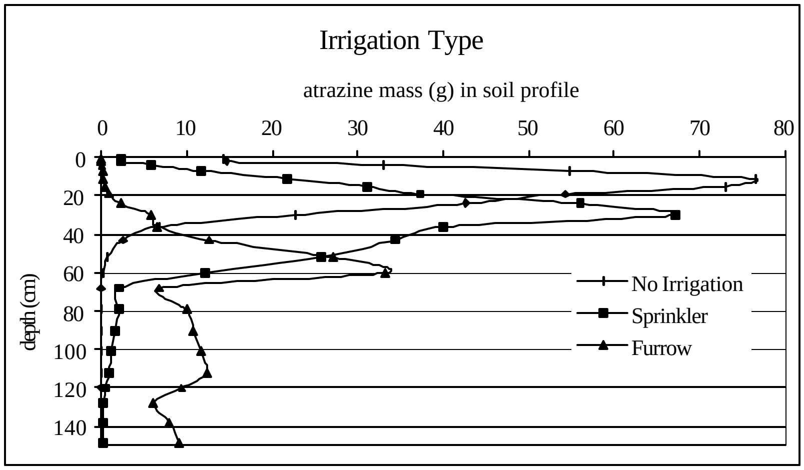

Figure 6.1. Mass of atrazine in the soil profile under various irrigation practices.

For this application, the relative depth of the center of mass of the pesticide under each irrigation practice is correlated to a multiplying factor. The approximate center of mass for each practice is 20 cm for no irrigation, 40 cm for sprinkler irrigation, and 80 cm for furrow irrigation. Recall that the BVI_f calculation will be the worst-case vulnerability, and changing land-management practices can only decrease the vulnerability. Thus, because furrow or flood irrigation is the least efficient practice, it is assigned a multiplying factor of one. Other irrigation practices will decrease the vulnerability score. Considering that under sprinkler irrigation the center of mass reaches a depth half that of furrow, the assigned multiplying factor for sprinkler irrigation is 0.5. These multiplying factors also correlate with average efficiencies of irrigation systems.

Pesticides again reach half the depth under no irrigation as compared to sprinkler irrigation. Thus, the multiplying factor for no irrigation is 0.25.

The next land-management factor analyzed was tillage. Two tillage systems were used: the default tillage system from RZWQM (Appendix F) and a no-till regime. Figure 6.2 shows that RZWQM predicted virtually no difference in the distribution or mass of the pesticide under the two different tillage practices.

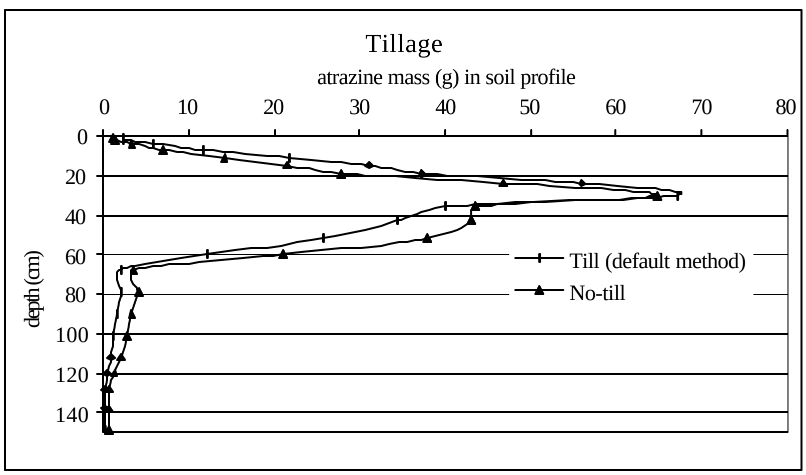

Figure 6.2. Mass of atrazine in the soil profile under various tillage practices.

Due to the possible error in the model, insufficient field data to calibrate a multiplying factor for this land-management practice, and the conflicting description of its importance in the literature, we cannot justify choosing multiplying factors for tillage. Therefore, it is not included in this vulnerability assessment methodology.

The final land-management factor considered was application method. Bare soil, foliar, and band applications were considered for this vulnerability assessment method. Bare soil is taken for the worst-case practice, because essentially all of the pesticide applied reaches the soil surface. Under band or foliar applications only a fraction of the pesticide will reach the ground surface (Waskom, 2001, personal communication). This is because under foliar applications the presence of the canopy limits the soil area available to pesticides. Under band application, the pesticide is applied in a band along the crop rows. The width of the band and the amount of canopy closure dictates the amount of pesticide available to reach the soil surface. Thus, only a fraction of the pesticide applied has a potential of reaching groundwater. Therefore, the multiplying factor for bare soil is one, and the multiplying factor for foliar or band application is 0.5.

Once the land-management multiplying factors have been used, the final value is termed the Vulnerability Index (VI). This value will determine the vulnerability of an area. Land-management practices may be changed to decrease the VI score from the high-vulnerability class to the moderate-vulnerability class. If the vulnerability cannot be decreased by changing land-management practices, a change in pesticide may be required.

6.2 Vulnerability Assessment User's Manual

Since this vulnerability assessment may be used for regulatory purposes, a User's Manual was developed. See Appendix G. This User's Manual will be used either solely by farmers or, more likely, with the aid of their local extension agent. The manual explains the parameters that are incorporated into the BVI calculation and the land-management factors used to correct the BVI to obtain the final vulnerability index (VI). All the maps necessary to complete an assessment are also included in the manual. The maps for the manual in Appendix G show only Weld County for purposes of scale.

The first section of the manual contains background information and a table of all the input parameters. The purpose of this section is to explain why the assessment is important and to describe the parameters that are included. The next section contains detailed instructions on use of the assessment method. Example modifications are given throughout the manual. The relevant maps and tables are then listed as appendices. The last section of the manual is a set of worksheets. These worksheets allow direct input of relevant information. The calculations are also repeated in this section. The hope is that the manual explains the material adequately and is simple enough that someone with a limited technical background will be able to complete the vulnerability assessment, given site-specific measurements for model parameters. It is likely that a professional soil scientist would need to be employed to obtain these values.

CHAPTER 7 SUMMARY AND DISCUSSION

7.1 Summary of Research

The objective of this research was to create a vulnerability assessment method for Colorado that can be used as a screening tool for the entire state. The first step to accomplish this objective was to complete an extensive literature review. The literature review presented an in-depth background on vulnerability assessments, what information is necessary to develop an assessment, their limitations, and their applicability for regulatory purposes.

The LPI method (Meeks and Dean, 1990) was chosen as the basis for the assessment method for Colorado, because it is based on a solution to the ADE and is simple with regard to the amount and type of input parameters required. This method was then used to conduct a model-sensitivity study. The model-sensitivity study evaluated the effect of variability of physical-chemical input parameters on the calculated vulnerability. The model-sensitivity analysis showed that the LPI method was highly sensitive to changes in organic-carbon content, soil-water velocity, and depth to groundwater. The results indicate that accurate estimation of these parameters is required for a successful vulnerability assessment. The LPI method was not sensitive to other parameters including bulk density and water content, which implies that these parameters can be roughly estimated or set constant.

The LPI equation was then modified to allow for input parameters that were readily available for this assessment. Modifications included substituting permeability for the velocity term and incorporating conversion factors for obtaining the fraction of organic carbon from the percent of organic matter. Pesticide leachability classifications were also created in an effort to simplify number of maps needed to assess the vulnerability and increase the size of the data set for the field test.

The depth to groundwater was incorporated as a multiplying factor as were the land-management practices. The depth-to-groundwater classifications and the corresponding multiplying factors were chosen by fitting the field data to a linear trend line. The vulnerability value is then termed the BVI_f, as it is the final base vulnerability that is used to create the vulnerability maps.

A test of the BVI_f method's predictive capability was completed by comparing calculated vulnerabilities to actual water-quality data. A data set of 104 wells in agricultural regions of Weld County, Colorado was used because of the large amount of data available and the numerous pesticide detections. The field test showed that the BVI_f successfully predicted vulnerability across the county.

The field test data set was also used to choose the vulnerability classifications. Natural breaks were visible in the comparison of BVI_f values versus concentrations. These natural breaks were verified when comparing the percent of samples that had pesticide detections against the BVI_f values. These natural breaks were chosen as the breaks for the vulnerability classes.

RZWQM (Ahuja *et al.*, 1999) was used to evaluate the impact of various land-management practices on the contamination potential for pesticides. The RZWQM simulations indicated that varying tillage practices has little impact on the depth or amount of pesticide in the soil profile. Multiplying factors were then calculated based on the relative percent of applied pesticide that reaches a specified depth for the remaining land-management practices (irrigation and application method).

The land-management factors were not included in the previous field test due to lack of field data on land-management factors. Land-management multiplying factors were calculated by running RZWQM and using the resulting pesticide distributions through the soil profile to assign multiplying factors. At the request of the CDPHE and CDA, a User's Manual was proposed for implementation of land-management factors into the BVI_f method. The manual gives detailed instructions and worksheets along with all maps that are required to complete an assessment of a site-specific area, such as a farm field. The vulnerability that the user calculates will be considered the maximum vulnerability for that area. The user may decrease the vulnerability (VI) for their site by choosing different land-management practices, by implementing a new crop system, or choosing a different pesticides.

7.2 Discussion

Once an appropriate vulnerability method has been chosen and field-tested, an explanation of when and where the method is appropriate must be completed. The VI method that has been created for this research will be used throughout the state of Colorado. It will be used to delineate agricultural areas that are highly vulnerable to pesticide contamination, which will aid in designing future monitoring efforts. The assessment methodology will allow farmers to determine the predicted site-specific vulnerability for their farm, allowing for changes in management practices if the vulnerability is too high.

The vulnerability assessment method has focused on Weld County for this research primarily for practicality and because of data availability in this county. A vulnerability map for the entire state has also been created, however at this scale it is difficult to locate a single farm to evaluate its vulnerability. Research to improve the user friendliness of a statewide assessment method is recommended.

The computational complexity of a vulnerability assessment is an important factor to consider when selecting an assessment method. Vulnerability assessment methods that are thought to be more rigorous are sometimes preferred to methods that use simple ranking indices. However, vulnerability calculations may not improve with the additional data required from a more rigorous method. In addition, data are often not available for these methods. When data are not available they must be estimated, introducing error into the vulnerability calculation (Li *et al.*, 1997).

The suggested BVI_f method may appear less rigorous than PRZM, for example, but it has been shown to successfully assess the vulnerability in areas throughout Weld County. PRZM requires a large amount of detailed input parameters and expertise in mathematical modeling. This makes this model impractical for many regulatory purposes. DRASTIC is a simple subjective assessment method. However, it does not include pesticide characteristics or land-management practices. The U.S. EPA has stated that pesticide properties and land-management practices should be included in a vulnerability assessment method (U.S. EPA, 1993). DRASTIC would fit into the U.S. EPA's classification as a sensitivity assessment, since sensitivity only includes soil and hydrogeologic properties. It has been shown to accurately model nitrate contamination because nitrate is often considered a conservative tracer, and interactions between the nitrate and the soil or groundwater are minimal.

A more rigorous vulnerability assessment method may be desired for other purposes (e.g. detailed site-specific assessments), but a simpler screening tool is generally preferred for regulatory purposes. This allows for quick, accurate assessment of the vulnerability of an area without intense calculations and large amounts of input data.

There are also limitations to this method. The first limitation is associated with volatile pesticides (large Henry's constant). Recall that the volatilization term in the retardation factor has been neglected, and hence not considered in the BVI_f equation.

This means that the BVI_f equation does not account for volatilization of pesticides into the soil-vapor phase. This will cause the BVI_f to overestimate the vulnerability with respect to volatile pesticides. If a more specific vulnerability calculation is required for volatile pesticides, perhaps Jury *et al.* (1983) may be more suited for this purpose. The Jury *et al.* method is specifically designed for volatile pesticides. However, the analysis in Chapter 4 suggested that volatilization would be negligible for all but a few pesticides.

The VI method also assumes that irrigation is the sole source of recharge. This is a valid assumption for most agricultural areas of the state of Colorado because of the dry climate. If this method is to be implemented in other states where precipitation is a significant portion of the recharge, the velocity term may have to be calculated more rigorously using meteorologic and soil property data. As part of neglecting recharge from precipitation, preferential flow caused by large rainfall events is also neglected. Pesticide transport through preferential pathways has been shown to be an effective method of moving pesticides to groundwater.

The effect of slope variations, which would in turn affect the amount of runoff, is also neglected. As the slope increases, the loss of pesticides due to runoff would also increase. This may be important if the vulnerability assessment method is to be used in areas with significantly varying slopes.

This vulnerability assessment method should also not be used to predict concentrations of pesticides in the soil profile or groundwater. The BVI_f method is designed to calculate relative groundwater vulnerabilities at specific locations from large-scale data. Other models, such as PRZM (Carsel *et al*., 1985) and RZWQM (Ahuja *et al*., 1999) should be used if concentration data is desired.

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Many conclusions have been reached upon completion of this research.

- A transport-based vulnerability assessment (BVI_f) can be used to identify the site-specific groundwater vulnerability for the state of Colorado.

- The results of a model-sensitivity study indicate that the LPI is sensitive to the fraction of organic-carbon, the depth to groundwater, and the groundwater velocity. The study also showed that the LPI was not sensitive to bulk density or soil moisture content.

- The BVI_f method incorporates depth-to-groundwater as multiplying factors, which have been calibrated using field data from Weld County, Colorado.

- A field test of predicted vulnerabilities to water-quality data in Weld County, Colorado has shown the BVI_f method successfully assessed the vulnerability throughout the county.

- Due to lack of field data for land-management factor calibration, RZWQM was used to assess relative distribution of pesticides in the soil profile. The results indicate that the style of irrigation is very important when assessing sit-specific vulnerability to pesticides. The method of tillage used yielded ambiguous results. Tillage has, therefore, not been included in this assessment methodology. The method of pesticide application could not be assessed clearly with RZWQM. Thus, multiplying factors were assigned based on the amount of applied pesticide that reaches the soil surface.

8.2 Recommendations for Future Work

There are several areas where the research initiated in this study could be expanded upon.

- Additional data would be helpful in a more accurate calibration of the land-management factors along with the groundwater classifications and the vulnerability classes.

- A detailed assessment of land-management factors is needed to accurately calibrate the multiplying factors for the VI method.

- Statewide field-testing of the BVI assessment method is needed for delineating areas that are highly vulnerable to pesticide contamination. A statewide field test would also identify areas where monitoring efforts need to be improved.

- The current format of paper maps and worksheets is sufficient for an initial test of the appropriateness of the BVI method for regulatory purposes. The ideal format for this vulnerability assessment, however, would be an interactive web-based GIS format. This would allow user's to quickly focus on their area from a larger map with a simple mouse-click on a map, and locate their specific farm. All soil unit parameters would be attached to the vulnerability value that is taken from the map. All the land-management calculations would also be included in a GIS format.

- For site-specific assessments where detailed transport information (or risk) is required, use a more rigorous numerical model (e.g. PRZM, RZWQM, etc.)

REFERENCES

Ahuja, L.R., Rojas, K.W., Hanson, J.D., Shaffer, M.J., and Ma, L. eds., 1999. Root Zone Water Quality Model: Modeling Management Effects on Water Quality and Crop Production, Water Resources Publications, LLC, Highlands Ranch, CO, 360 pp.

Aller, L.T., Lehr, J.H., and Petty, R.J., 1985. DRASTIC: A Standardized System for Evaluating Ground Water Pollution Potential Using Hydrogeologic Settings, EPA-600/2-85/018, U.S. Environmental Protection Agency, Ada, Okla.

Andreini, M.S. and Steenhuis, T.S., 1990. Preferential paths of flow under conventional and conservation tillage, Geoderma, 46, 85-102.

Austin, B., 1999. Personal communication, Colorado Department of Public Health and Environment.

Behrendt, H., Altschuh, J., Sixt, S., Gasteiger, J., Hollering, R., and Kostka, T., 1999. A unified approach to exposure assessment by computer models for degradation reactions and soil accumulation: the triazine herbicide example, Chemosphere, 38(8), 1811-1823.

Beulke, S., Dubus, I.G., Brown, C.D., and Gottesbüren, B., 2000. Simulation of pesticide persistence in the field on the basis of laboratory data – A Review, J. Environ. Qual., 29(5), 1371-1379.

Beltman, W.H.J., Boesten, J.J.T.I., van der Zee, S.E.A.T.M., and Quist, J.J., 1996. Analytical modeling of effects of application frequency on pesticide concentrations in wells, Ground Water, 34(3), 470-499.

Britt, J.K., Swinell, S.E., and McDowell, T.C., 1992. Matrix decision procedure to assess new pesticides based on relative groundwater leaching potential and chronic toxicity, Environ. Toxicol. Chem., 11, 721-728.

Buhler, D.D., Koskinen, W.C., Schreiber, M.M., and Gan, J.Y., 1994. Dissipation of alachlor, metolachlor, and atrazine from starch-encapsulated formulations in a sandy loam soil, Weed Sci., 42, 411-417.

Carsel, R.F., Mulkey, L.A., Lorber, M.N., and Baskin, L.B., 1985. The Pesticide Root Zone Model (PRZM): A Procedure for Evaluating Pesticide Leaching Threats to Groundwater. Ecological Modeling, 30, 49-69.

Charizopoulos, E. and Papadopoulou-Mourkidou, E., 1999. Occurrence of pesticides in rain of the Axios River basin, Greece, Environ. Sci. Technol., 33(14), 2362-2368.

Colorado Agricultural Statistics, 2000. Personal communication with Reagan Waskom, Dept. of Soil and Crop Sciences, Colorado State University.

Colorado Department of Agriculture (CDA), 1996. A method for assessing sensitivity of Colorado Aquifers to pesticide contamination: A pilot evaluation of the lower South Platte Basin, prepared by Maurice D. Hall in cooperation with Colorado State University Cooperative Extension and USDA/ARS Great Plains Systems Research.

Corwin, D.L., Loague, K., and Ellsworth, T.R., eds., 1999. Assessment of Non-Point Source Pollution in the Vadose Zone. Geophysical Monograph Series 108, American Geophysical Union, Washington D.C., 369 pp.

DeLuca, T. and Johnson, P., 1990. Rave: Relative Aquifer Vulnerability Evaluation. An On-Farm Scoring System to Evaluate Aquifer Vulnerability to Pesticide Contamination, Montana Department of Agriculture – Environmental Management Division, Helena, MT, MDA Technical Bulletin 90-01.

Dick, W.A., Rosenberg, R.J., McCoy, E.L., Edwards, W.M., and Haghiri, F., 1989. Surface Hydrologic Response of Soils to No-Tillage, Soil Sci. Soc. Am. J., 53, 1520-1526.

Dubois, D., 1993. Study of Pesticides in Groundwater Weld County, Colorado 1992-1993. North Front Range Water Quality Planning Association, Loveland Colorado.

Fetter, C.W., 1994. Applied Hydrogeology, Third Edition, Macmillan College Publishing Company, Inc., New York, New York, 691 pp.

Fetter, C.W., 1999. Contaminant Hydrogeology: Second Edition, Prentice-Hall, Inc., Upper Saddle River, NJ., 500 pp.

Fleming, G.F., Wax, L.M., Simmons, F.W., and Felsot, A.S., 1992. Movement of alachlor and metribuzin from controlled release formulations in a sandy soil, Weed Sci., 40, 606-613.

Flury, M, 1996. Experimental Evidence of transport of Pesticides through Field Soils—A Review. J. Environ. Qual., 25(1), 25-45.

Freissinet, C., Vauclin, M., and Erlich, M., 1999. Comparison of first-order analysis and fuzzy set approach for the evaluation of imprecision in a pesticide groundwater pollution screening model, J. Contam. Hydrol., 37, 21-43.

Furmidge, C.G.L., 1984. Formulation and application factors involved in the performance of soil applied pesticides, *In* R.J. Hance (ed.) Soils and crop protection chemical. Monogr. 27, British Crop Protection Council, Croydon, UK. 49-64.

Gaynor, J.D., MacTavish, D.C., and Findlay, W.I., 1992. Surface and subsurface transport of atrazine and alachlor from a Brookston clay loam under continuous corn production, Arch. Environ. Contam. Toxicol., 23, 240-245.

Gaynor, J.D., MacTavish, D.C., and Findlay, W.I., 1995. Atrazine and metolachlor loss in surface and subsurface runoff from three tillage treatments in corn, J. Environ. Qual., 24, 246-256.

Ghodrati, M. and Jury, W.A., 1992. A field study of the effects of structure and irrigation method on preferential flow of pesticides in unsaturated soil, J. Contam. Hydrol., 11, 101-125.

Gish, T.J, Isensee, A.R., Nash, R.G., and Helling, C.S., 1991. Impact of pesticides on shallow groundwater quality, Trans. ASAE, 34, 1745-1753.

Gish, T.J., Shirmohammadi, A., Vyravippillai, R., and Weinhold, B.J., 1995. Herbicide Leaching under Tilled and No-Tillage Fields, Soil Sci. Soc. Am. J., 59, 895-901.

Gramatica, P., Corradi, M., and Consonni, V., 2000. Modelling and prediction of soil sorption coefficients of non-ionic organic pesticides by molecular descriptors, Chemosphere, 41, 763-777.

Gückel, W., Ritting, F.R., and Synnatschke, G., 1974. A method for determining the volatility of active ingredients used in plant protection II. Applications to formulated products, Pest. Sci., 5, 393-400.

Hall, J. K., Murray, M. R., and Hartwig, N. L., 1989. Herbicide Leaching and Distribution in Tilled and Untilled Soil, J. Environ. Qual., 18, 439-445.

Hall, M.D., 1998. Sensitivity of Colorado Aquifers to Pesticide Contamination: A Regional-Scale Hydrogeologic Analysis, report prepared for Colorado Dept. of Agriculture and Colorado Department of Public Health and the Environment, May, 1998.

Hantush, M.M., Marino, M.A., and Islam, M.R., 2000. Models for leaching of pesticides in soils and groundwater, J. Hydrology, 227, 66-83.

Helling, C.S. and Gish, T.J., 1991. Physical and chemical processes affecting preferential flow. In Preferential Flow. Gish, T.J. and Shirmohammadi, A., Eds., Am. Soc. Agric. Eng., St. Joseph, MI, United States, 77-86.

Hornsby, A.G., Wauchope, R.D., and Herner, A.E., 1995. Pesticide Properties in the Environment. Springer-Verlag, New York, NY. 227 pp.

Isensee, A.R., Nash, R.G., and Helling, C.S., 1990. Effect of Conventional vs. No-Tillage on Pesticide Leaching to Shallow Groundwater, J. Environ. Qual., 19, 434-440.

Isensee, A.R and Sadeghi, A.M., 1995. Long-term effect of tillage and rainfall on herbicide leaching to shallow groundwater, Chemosphere, 30(4), 67-685.

Isensee, A.R. and Sadeghi, A.M., 1996. Effect of Tillage Reversal on Herbicide Leaching to Groundwater, Soil Sci., 161(6), 382-389.

Johnson, R.R. and Kuby, P., 2000. Elementary Statistics. Duxbury, Pacific Grove, CA. 741 pp.

Jorgenson, D., 1998. Assessing the Vulnerability of Public Water Supply Wells to Microbial Contamination, Ground Water Monitoring and Remediation, 18(2), 60-66.

Jury, W.A., Spencer, W.F., and Farmer, W.J., 1983. Behavior assessment model for trace organics in soil: I. Model description, J. Environ. Qual., 12, 558-564.

Jury, W.A., Focht, D.D., Farmer, W.J., 1987. Evaluation of pesticide groundwater pollution potential from standard indices of soil chemical adsorption and biodegradation, J. Environ. Qual., 16, 422-428.

Kalinski, R.J., Kelly, W.E., Bogardi, I., Ehrman, R.L., and Tamamoto, P.D., 1994. Correlation between DRASTIC vulnerabilities and incidents of VOC contamination of municipal wells in Nebraska, Ground Water, 32 (1), 31-34.

Kelly, B.P. and Pomes M.L., 1998. Preferential flow and transport of nitrate and bromide in claypan soil, Ground Water, 36(6), 484-494.

Khan, M.A. and Liang, T., 1989. Mapping pesticide contamination potential, Environmental Management, 13, 233-242.

Kleveno, J.J., Loague, K., and Green, R.E., 1992. Evaluation of a pesticide mobility index: impact of recharge variation and soil profile heterogeneity, J. Contam. Hydrol., 11, 83-99.

Le Seur, L.P., Wehrmann, H.A., Schock, S.C., and Shafer, J.M., 1987. Prioritizing Areas for Statewide Groundwater Monitoring, J. Water Resour. Plng. and Mgmt., 113(2), 204-215.

Li, Z.C., Yost, R.S., and Green, R.E., 1998. Incorporating uncertainty in a chemical leaching assessment, J. Contam. Hydrol., 29, 285-299.

Loague, K., Green, R.E., Giambelluca, T.W., Liang, T.C., and Yost, R.S., 1990. Impact of uncertainty in soil, climatic, and chemical information in a pesticide leaching assessment, J. Contam. Hydrol., 5, 171-194.

Loague, K., 1991. The impact of land use on estimates of pesticide leaching potential: Assessments and uncertainties, J. Contam. Hydrol., 8, 157-175.

Loague, K., Miyahira, R.N., Oki, D.S., Green, R.E., Schneider, R.C., and Giambelluca, T.W., 1995. Chemical Leaching Near the Waiawa Shaft, Oahu, Hawaii: 2. Modeling Results, Ground Water, 33(1), 124-138.

Loague, K., Bernknopf, R.L., Green, R.E., Giambelluca, T.W., 1996. Uncertainty of Groundwater Vulnerability Assessments for Agricultural Regions in Hawaii: Review, J. Environ. Qual., 25, 475-490.

Locke, M.A. and Harper, S.S., 1991. Metribuzin degradation in soil: II-Effect of tillage, Pest. Sci., 31, 239-247.

Loll, P. and Moldrup, P., 2000. Stochastic Analyses of field-scale pesticide leaching risk as influenced by spatial variability in physical and biochemical parameters, Water Resources Research, 36(4), 959-970.

Maxe, L. and Johansson, P., 1998. Assessing groundwater vulnerability using travel time and specific surface area as indicators, J. Hydrogeology, 6, 441-449.

Meeks, Y.J. and Dean, J.D., 1990. Evaluating groundwater vulnerability to pesticides. J. Water Resour. Plng. Mgmt., 116(5), 693-707.

Miller, J.J., Lamond, B.J., Sweetland, N.J., and Larney, F.J., 1999. Preferential leaching in large undisturbed soil blocks from conventional tillage and no-till fields in southern Alberta, Water Quality Research Journal of Canada, 34(2), 249-266.

Myers, J.L., Wagger, M.G., and Leidy, R.B., 1995. Chemical movement in relation to tillage system and simulated rainfall intensity, J. Environ. Qual., 24, 1183-1192.

Nachabe, M.H., Ahuja, L.R., and Butters, G., 1999. Bromide transport under sprinkler and flood irrigation for no-till soil condition, J. Hydrology, 214(1-4), 8-17.

NRCS, 1994. State Soil Survey Geographic (STATSGO) Database: Data Use Information. Miscellaneous Public Rep. No. 1492. U.S. Department of Agriculture, Natural Resources Conservation Service, National Soil Survey Center, Fort Worth, TX.

NRCS, 1999. SSURGO database for Weld County, Colorado, Northern part. U.S. Department of Agriculture-National Resource Conservation Service. certified

NRCS, 2000. SSURGO database for Weld County, Colorado, Southern part. U.S. Department of Agriculture-National Resource Conservation Service. uncertified

Nofziger, D.L. and Hornsby, A.G., 1985. Chemical Movement in Soil. User's Guide. University of Florida, Gainesville.

Ott, R.L., 1993. An introduction to statistical methods and data analysis, Belmont, CA, Duxbury Press, Wadsworth Publishing Co., 1051 pp.

Pivetz, B. and Steenhuis, T.S., 1989. Pesticide, nitrate, and tracer loss in agricultural tile lines and to groundwater under conventional and conservational tillage. ASAE Paper 89-2579. Amer. Soc. Agric. Eng. , St. Joseph, MI.

Rao, P.S.C., Hornsby, A.G., and Jessup R.E., 1985. Indices for ranking the potential for pesticide contamination of groundwater, Soil Crop Science Society of Florida Proceedings 44, 1-8.

Ren, G-L, Izadi, B., King, B., and Dowding, E., 1996. Preferential Transport of Bromide in Undisturbed Cores Under Different Irrigation Methods, Soil Sci., 161(4), 214-225.

Ritter, W.F., Scarborough, R.W., and Chirnside, A.E.M., 1994. Contamination of groundwater by triazines, metolachlor, and alachlor, J. Contam. Hydrol., 15(1-2), 73-92.

Rosen, L., 1994. A study of the DRASTIC methodology with emphasis on Swedish conditions, Ground Water, 32(2), 278-285.

Rupert, M., 1998. Probability of Detecting Atrazine/Desethylatrazine and Elevated Concentrations of Nitrate (NO2+NO3-N) in Groundwater in the Idaho Part of the Upper Snake River Basin. U.S. Geological Survey Water-Resources Investigations Report 98-4203, 32 pp.

Rupert, M., 1999a. Improvements to the DRASTIC Groundwater Vulnerability Mapping Method. U.S. Geological Survey Fact Sheet FS-066-99, 6 pp.

Rupert, M., 1999b. Personal communication, U.S. Geological Survey.

Sadeghi, A.M. and Isensee, A.R., 1994. Spatial distribution of atrazine residues in soil and shallow groundwater: effect of tillage and rainfall timing, Agriculture, Ecosystems and Environment, 48, 67-76.

Sadeghi, A.M., Isensee, A.R., and Shirmohammadi, A., 2000. Influence of soil texture on herbicide transport, Chemosphere, 41, 1327-1332.

Schreiber, M.M., Hickman, M.V., and Vail, G.D., 1993. Starch-encapsulated atrazine: Efficacy and transport, J. Environ. Qual., 22, 443-453.

Schwartz, R. C., McInnes, K. J., Juo, A. S. R., and Cervantes, C.E., 1999. The Vertical Distribution of a Dye Tracer in a Layered Soil, Soil Sci., 164(8), 561-573.

Seelig, B.D. 1994. An assessment system for potential groundwater contamination from agricultural pesticide use in North Dakota, EB-63. North Dakota State University Extension Service, Fargo, ND.

Shang, C. and Arshad, M.A., 1998. Sorption of clopyralid, dicamba and MCPA by two soils with conventional and no-till management, Canadian J. of Soil Science, 78(1), 181-186.

Shukla, S., Mostaghimi, S., Shanholt, V.O., Collins, M.C., and Ross, B.B., 2000. A county-level Assessment of ground water contamination by pesticides, Ground Water Monitoring and Remediation, 20(1), 104-119.

Siegrist, R., J. McCray, D. Huntzinger, S. Kirkland, and S. Van Cuyk, 2000. Use of Mathematical Models to Understand and Predict Wastewater Flow and Pollutant Treatment for Decentralized Systems from the Site Scale to the Watershed Scale, National Onsite Wastewater Recycling Association Annual Conference, Grand Rapids, MI, September 2000.

Soutter, M. and Musy, A., 1998. Coupling 1D Monte-Carlo simulations and geostatistics to assess groundwater vulnerability to pesticide contamination on a regional scale, J. Contam. Hydrol., 32, 25-39.

Soutter, M. and Pannatier, Y., 1996. Groundwater vulnerability to pesticide contamination on a regional scale, J. Environ. Qual., 254(3), 439-443.

Starr, J.L. and Glotfelty, D.E., 1990. Atrazine and bromide movement through a silt loam soil, J. Environ. Qual., 19, 552-558.

Steenhuis, T.S., Staubitz, W., Andreini, M.S., Surface, J., Richard, T.L., Paulsen, R., Pickering, N.B., Hagerman, J.R., and Geohring, L.D., 1990. Preferential movement of pesticides and tracers in agricultural soils, J. Irrig. Drain. Eng., 116, 50-66.

Sun, M., 1986. Groundwater ills: Many diagnoses, few remedies, Science, 232, 1490-1493.

Tim, U.S., Jain, D., and Liao, H., 1996. Interactive Modeling of Ground-Water Vulnerability Within a Geographic Information System Environment, Ground Water, 34, 618-627.

Tindall, J.A. and Kunkel, J.R., 1999. Unsaturated Zone Hydrology for Scientists and Engineers, Upper Saddle River, NJ, Prentice-Hall, Inc., 624 pp.

Troiano, J., Garretson, C., Krauter, C., Brownell, J., and Huston, J., 1993. Influence of Amount and Method of Irrigation Water Application on Leaching of Atrazine, J. Environ. Qual., 22, 290-298.

Troiano, J., Marade, J., and Spurlock, F., 1999. Empirical Modeling of Spatial Vulnerability Applied to a Norflurazon Retrospective Well Study in California, J. Environ. Qual., 28, 397-403.

Turpin, J.E., Bridge, B.J., Orange D., Thompson, J.P., 1999. Water and bromide movement in a Vertosol under four fallow management systems, Australian

J. of Soil Research, 37(1), 75-89.

Tweto, O., 1979. Geologic Map of Colorado, U.S. Geological Survey. Special Geologic Map.

U.S. Department of Agriculture, Soil Conservation Service (USDA-SCS), 1972. National Engineering Handbook: Section 4, Hydrology. Washington, D.C. 548 pp.

U.S. EPA, 1993. A review of Methods for Assessing Aquifer Sensitivity and Groundwater Vulnerability to Pesticide Contamination. (EPA 813/R-93-002) 204 pp.

van den Bosch, H., Ritsema, C.J., Boesten, J.J., Dekker, L.W., and Hamminga, W., 1999. Simulation of water flow and bromide transport in a water repellent sandy soil using a one-dimensional convection-dispersion model, J. Hydrology, 215, 172-187.

Wagenet, R.J. and Hutson, J.L., 1986. Predicting the fate of nonvolatile pesticides in the unsaturated zone. J. Environ. Qual, 15, 315-322.

Waskom, R.M., 2000. Personal Communication, Dept. of Soil and Crop Sciences, Colorado State University.

Weed, D.A.J., Kanwar, R.S., Stoltenberg, D.E., and Pfeiffer, R.L., 1995. Dissipation and distribution of herbicides in the soil profile, J. Environ. Qual., 24(1), 68-79.

Williams, J.R. and Berndt, H.D., 1977. Sediment yield prediction based on watershed hydrology. Transactions of ASAE 20:1100-1104.

Wireman, M. and Job, C., 1997. The use of ground water sensitivity assessments for purposes of the ground water disinfection rule, Ground Water Monitoring and Remediation, 17(4), 63-66.