Modeling Field-Scale Vulnerability to Pesticide Runoff

by

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Identifying areas vulnerable to off-site agrichemical movement and surface and ground water contamination through conventional data collection is labor-intensive, costly and time-consuming. To promote efficient pesticide use and protect water resources, a process-based index model was previously developed to estimate landscape vulnerability to pesticide runoff and leaching at a watershed or regional scale using Soil Survey Geographic (SSURGO) data. Because mitigation of contamination requires implementation of best management practices, the model was adapted to the field scale. The field-scale model was developed based on a Digital Elevation Model (DEM) with 5 × 5 m resolution for a research site in Boone County, Missouri. The model uses inputs and functions associated with hydrologic and pesticide dissipation processes. These include saturated hydraulic conductivity of the soil, pH, organic matter, clay content, clay mineralogy, slope, unfilled pore volume above a restrictive layer, and soil moisture content along with pesticide adsorption intensity, relative persistence, and susceptibility to abiotic hydrolysis. Input data were obtained from field measurements, Agricultural Policy/Environmental eXtender (APEX) model soil moisture output, the Soil Survey Geographic (SSURGO) database (flooding frequency class), and pesticide property references. The hydrologic component of the model was converted to a dynamic function using APEX estimates of soil moisture and the model was coded into the ESRI™
ArcGIS (10.0) Model Builder. Sensitivity analyses were performed to assess the weighting of the restrictive layer modifier of the Index Surface Runoff (ISRO) function and to evaluate the hydrolysis time frame. Model estimates of atrazine remaining in the field (assuming no previous runoff or leaching losses) were significantly related to measurements of atrazine in runoff made at the field outlet for odd (corn) years from 1993 to 2001. However, estimates of remaining pesticide exceeded field measurements. The model can be used to identify vulnerable areas within agricultural fields and target sites for implementation of best management practices (BMPs) and regulatory strategies to effectively address water quality issues.
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CHAPTER 1
INTRODUCTION

Background
The quality of water leaving agricultural areas has become a pervasive and global problem over the past decades. Off-site movements of agricultural chemicals to streams and aquifers through surface runoff and leaching make them the major source of surface and groundwater non-point pollution across the United States (Yu et al. 2004). In the U.S., approximately 2.3 billion kg (5.1 billion lb) of pesticides are used each year to control weeds, insects, and other pests in a wide variety of agricultural and non-agricultural settings (figure 1) (Aspelin 1994; USEPA 2012). Herbicides account for more than 70 percent of all agricultural pesticides used in the U.S (Kellogg et al. 2000). Although seven European Union (EU) countries have banned atrazine use, atrazine remains widely used in the U.S. Monitoring of herbicide residues in U.S. surface and ground waters over the past several decades showed increasing concentrations, especially in the 12-state area comprising the major part of the "corn and soybean belt" of the Midwest (Gianessi and Puffer 1986). Crop and soil management practices, soil properties and landscape characteristics, herbicide selection, and the timing of herbicide application in relation to intense rainfall events determine the extent of herbicide loss. Losses are usually greatest from early spring to mid-summer when precipitation is most intense. Herbicides can be transported in surface runoff from agricultural fields, and streams show the highest loads in cultivated areas (Richards et al. 1996).
Intense spring rainfall events occurring shortly after pesticide application generally cause loss of mobile pesticides from agricultural fields, especially between the pre- and post-plant period. Surface runoff is the main pathway for herbicide losses in areas with restrictive claypans or pronounced argillic horizons, which inhibit water infiltration (Saxton and Whitaker 1970; Blanchard and Lerch 2000). Under saturated conditions, surface runoff could approximate precipitation. Conversely, leaching and contamination
of ground waters can be a problem in locations with permeable soils and shallow or perched water tables. The amount of clay and the thickness of the clay layer are both important factors influencing the impact of a restrictive clay layer on water movement and off-site transport of agrichemicals (Willett 2010).

Identifying the most vulnerable areas within a field and applying best management practices (BMPs) can minimize off-site transport and non-point source pollution from agrichemicals. However, variations in landscape, soil properties and management practices across a field can make this process expensive and time-consuming. Most models based on mathematical constructs of complex natural processes are too complex for use as risk indicators by farmers (Hatfield 2000). In addition, direct measurements of pesticide residues at the field scale are time-intensive and costly. A process-based index model based on SSURGO data was previously developed to distinguish the most vulnerable areas within a watershed and estimate the relative potential for pesticide contamination via runoff or leaching (Willett 2010). The model is based on the physicochemical properties of the pesticide, including adsorption (organic carbon partition coefficient, Koc), relative persistence (half-life), and susceptibility to abiotic hydrolysis, along with soil characteristics, including saturated hydraulic conductivity ($K_{sat}$), soil layers restrictive to flow (claypans and fragipans), pH, organic matter (OM), clay content, clay mineralogy and erodibility, and landscape characteristics such as slope, depressions and flood plains. The model evaluates landscape vulnerability to pesticide transport through three hydrologic pathways: runoff, leaching and particle-adsorbed runoff (Willett 2010).
Field-scale data are needed to delineate areas contributing most to off-site movement of agricultural chemicals, but such data are not always available. When available data are combined with Geographic Information System (GIS) modeling software that evaluates complicated hydrologic processes, output can be generated that helps producers avoid pesticide application in the most vulnerable areas and establishes a basis for developing and implementing management strategies that effectively address water quality issues.

**Research Objectives**
In this research, a processed-based index model previously developed to assess watershed vulnerability to pesticide leaching and runoff at the county scale using SSURGO data was adapted to the field scale and used to estimate surface runoff of atrazine in an agricultural field. The resulting model integrates hydrologic and chemistry components and output includes vulnerability assessments and estimates of remaining pesticides, assuming no previous losses. Specific objectives follow.

**Objective 1.** Adapt the regional model to the field-scale and code the model into ESRI™ ArcGIS (v 10.0) Model Builder (Environmental Systems Research Institute, Inc., Redlands, CA) using map algebra and determine the spatial and temporal distribution of areas vulnerable to atrazine loss though surface runoff within a field.

**Objective 2.** Perform sensitivity analysis for hydrolysis time frame and the clay restrictive layer (claypan) modifier.

**Objective 3.** Validate the model by comparison with previously measured atrazine losses from a field.
Organization of the Thesis
This thesis is organized into five chapters. Chapter 1 begins with an introduction to the importance of water quality and assessing contamination of surface water resources. Chapter 2 is a literature review of studies conducted in this area and a discussion of the processes included in the model and the selected herbicide (atrazine). Chapter 3 describes background studies include USDA-Agricultural Research Service (ARS) field work, ARS-APEX work and regional process-based index model descriptions, details steps taken to adapt the model to a field scale, and explains the statistical analysis of model outputs. Chapter 4 presents and discusses model outputs. Chapter 5 includes conclusions drawn from the study and suggests directions for future research.
CHAPTER 2

LITERATURE REVIEW

Pesticides in the Environment

The widespread and long-term agricultural use of pesticides has provoked public concern about their potential adverse effects on public health and the environment. Specific issues include impacts on ecosystems and non-target organisms, including humans and degradation of surface and groundwater resources through erosion and chemical runoff. Pimentel (1995) estimated that less than 0.1% of the pesticide applied to crops reaches target pests. Thus most of the applied pesticide enters the environment where it may have detrimental impacts on non-target organisms, soil, water, and ecosystems (Arias-Estéveza et al. 2008). Some pesticides can persist in an ecosystem for a long time period and may be detected in surface waters years or even decades after application. Some residues may bioaccumulate in the tissues of organisms where they may reach much greater concentrations than in the water or surrounding environment (Brewer 1979). For some compounds biomagnification in the food chain is also possible. Although the processes governing pesticide movement from sites of application to non-target locations are complex, models can be used to estimate pesticide fate. The capability of these models to simulate pesticide movement depends on the availability and accuracy of relevant data, the reliability of mathematical functions used to described each process as well as entire process relationship, and the ability of the model to account for agricultural management practices and changing filed dynamics like soil moisture, surface condition, crop stage and weed growth.
Understanding the processes controlling pesticide movement and fate in the environment (soil, atmosphere, and water bodies) is critical for developing transport models and approaches for sampling and mitigation (Moorman et al. 2001; Arias-Estévez 2008). Major processes affecting transport include soil infiltration and runoff of water and the adsorption, volatilization, abiotic and biotic degradation of the pesticide (figure 2). Under field conditions, natural heterogeneities in the soil horizons control lateral or vertical transport of water and solutes (Beven and Germann 1982).

Figure 2
Representation of routes of pesticide movement in an agricultural field (Leonard et al. 1987).
**Volatileization.** Volatilization is the change from a solid or liquid to the vapor phase, resulting in subsequent movement from soil, plant and water surfaces to the atmosphere. Vapor pressure is a numerical unit characterizing the escaping tendency of a compound to the gaseous state and it can be used to estimate the lifetime of foliar and soil applications. Higher vapor pressures indicate greater pesticide volatility. An important parameter affecting vapor loss is the Henry's law constant ($K_h$, defined as the concentration of pesticide in air divided by the concentration in aqueous phase; larger $K_h$ values indicate a higher potential of a pesticide to volatilize from moist soil (Tiryaki and Temure 2010). In general, the potential vapor loss of a pesticide is inversely related to its water solubility; it will be greater at lower relative humidity and increases with temperature, air movement, and longevity on soil or on plant surfaces.

**Runoff.** Surface runoff depends upon rainfall intensity, antecedent moisture, water storage capacity, surface conditions (i.e. soil roughness, vegetation, and compaction) infiltration rate and slope. There are two major types of surface runoff: *Infiltration excess* or “*Hortonian*” runoff and *saturation excess* runoff. Hortonian runoff occurs when the rate of precipitation exceeds both the infiltration capacity and surface storage capacity of the soil, but the underlying soil is unsaturated. Soils high in silt and clay tend to be dominated by fine pores which produce lower saturated hydraulic conductivity and higher field capacity values than sandy soils and/or soils with relatively stable macropores like earthworm channels (Jarvis and Messing 1995). Soils containing large amounts of silt (loess soils) are easily affected by compaction (wheel tracks or raindrop impact), are more prone to Hortonian runoff and erosion (Garen and Moore 2005; Reichenberger et al. 2007). The second type of surface runoff, *saturation excess runoff,*
occurs when soil is saturated and the water table rises to the soil surface. In this case the soil cannot hold any more water and a small amount of rainfall immediately causes runoff (Garen and Moore 2005). Soil water tends to flow laterally with slope and can saturate downslope areas when impermeable horizons are present, where a perched water table develops, and in areas with shallow groundwater (Hillel 1980). Pesticides can be transported in surface runoff in the dissolved phase (solution runoff) or associated with soil particles or colloids (particle-adsorbed runoff) (Poinke and Chesters 1973). Water flow directly governs the mobility of pesticide in the dissolved phase and indirectly in the particle-associated phase. Except for compounds with $K_{oc}$ (soil organic carbon partition coefficient, which is the linear adsorption distribution coefficient (Kd) normalized to soil organic carbon content) greater than $1000 \text{ L kg}^{-1}$, pesticide loss via solution runoff is considered more important than particle-adsorbed runoff at the field scale (Leonard 1990). Pesticides with a low affinity for soil particles and relatively high water solubility can move with stream flow at a rate approaching river velocity (Chen 2005).

**Leaching.** Leaching of dissolved compounds can move through the soil matrix or through macropores and channels as preferential flow (Hendrickx and Flury 2001). Preferential gravitational flow may be observed in heavy loam and clay soils, which tend to have large macropores. Through preferential pathways a pesticide can rapidly move through soil to groundwater but movement via the soil matrix is typically a slow process that can take years or decades depending upon soil physical characteristics (texture, organic matter (OM), hydraulic conductivity, and structure) and the physiochemical properties of the pesticide. Pesticide leaching may be very high for compounds with moderate to long half-lives (Ritter 2001). Highly permeable soils are prone to leaching
while runoff is the main route of off-site movement in low permeable soils (McCauley and Jones 2005).

Leaching is prominent in soils with a sandy texture or low in organic matter and in climates with relatively high rainfall and low temperatures (which contributes to high groundwater recharge). Leaching and runoff are mutually exclusive processes, but infiltrated chemicals can resurface and chemicals in runoff can infiltrate from pools, streams or bodies of water. An increase in runoff can decrease leaching of chemicals through the bulk soil matrix but this may not be true for transport via preferential flow.

**Degradation.** Degradation, or the breakdown of pesticides, mitigates residue levels in soil (Guo et al. 2000). Parent compounds are usually transformed to daughter products that are less toxic and eventually decompose to inorganic products (CO₂, H₂O and N, P and/or S salts) (Cheng and Lehman 1985). However intermediate degradation products can have different chemical and physical properties than the parent components. For example, most of the degraded atrazine loses its herbicidal activity; more rapid atrazine degradation led to poorer weed control implying that metabolites have lower herbicidal activity (Zablotowicz et al. 2006). Degradation is controlled by both abiotic and biotic factors and can be divided into three major processes: microbial, chemical and photochemical degradation.

**Microbial degradation** is the predominant mechanism of pesticide loss in soil and water. Biodegradation usually results in products that are more polar and consequently more hydrophilic than the parent pesticide (Steinheimer and Scoggin 2001). The rate (kinetics) of microbial degradation is influenced by soil water content, temperature,
aeration, pH, organic matter content and depth. Pesticide concentration and frequency of application can affect microbial degradation by. Repeated applications can stimulate the development of microorganisms capable of more rapidly degrading the pesticide (Comfort et al. 1994; Tafazoli 2003).

*Chemical or abiotic degradation* Hydrolysis is the most common chemical transformation mechanism though most pesticides are not pH sensitive. Hydrolysis is a reaction with water, usually resulting in replacement of a halide with a hydroxyl group. The presence of protons and inorganic ions such as phosphate can catalyze hydrolysis in an aquatic environment. Adsorption-catalyzed hydrolysis is considered a dominant degradation mechanism for atrazine and certain other s-triazine herbicides (Armstrong and Chesters 1968; Russell et al. 1968), and for the insecticide *O,O*-Diethyl *O*-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate (diazinon) (Konrad et al. 1967). Hydrolysis of atrazine is catalyzed by its protonation (pKa = 1.7; Vencill 2002) and by hydrogen bonds between carboxyl groups in organic matter and nitrogen atoms in the triazine ring (Armstrong and Chesters 1967). The rate of hydrolysis is controlled by adsorption and relates directly to the extent of carboxyl protonation (Armstrong et al. 1967; Armstrong and Chesters 1968). Microbial activity usually decreases as pH deviates from neutrality, but such conditions can accelerate the abiotic degradation of some pesticides (Kerle et al. 1994). Transformation of atrazine to hydroxyatrazine (HA) is a significant process in most surface soils and occurs through chemical hydrolysis but may also result from biological reactions. Sorption of atrazine to soil colloids or dissolved OM accelerates its hydrolysis at pH extremes (Lerch et al. 1999). Soil temperature and water content, microbial population, along with the adsorption and physiochemical properties
of the pesticide, determine which chemical reactions occur along with the associated kinetics.

*Photodegradation* is the breakdown of a pesticide by sunlight. This abiotic process is mitigated by integrating light sensitive pesticides directly into the soil. However, photodegradation may impact pesticide degradation in air and water or plant and soil surfaces. The intensity of radiant energy, characteristics of the application sites, application method, and pesticide properties all influence photodegradation (Comfort et al. 1994; Fishel 2010). Most UV radiation is absorbed in the upper 2 m of water but may penetrate deeper, depending on turbidity (Dbrowska et al. 2004). The reported half-life of atrazine in distilled water irradiated with natural solar light is 34.5 d (Konstantinou et al. 2001).

**Adsorption.** Pesticide retention on the surface of soil particles is known as adsorption. Binding of a pesticide to soil constituents reduces loss through volatilization and leaching, and can affect rates of biological and chemical degradation. Many factors influence the adsorption of pesticides in soil. In general, soils high in organic matter and clay have a large surface area with multiple binding sites, and, therefore, exhibit a high capacity for pesticide adsorption. Wet soils tend to adsorb less pesticide than dry soils due to competition with water molecules for binding sites. Research has shown that pesticide sorption from water primarily depends on the organic carbon content and the potential of a pesticide to adsorb to soil as characterized by its Koc (Karickhoff et al. 1979). The Koc is equivalent to the soil distribution coefficient (Kd) divided by the fractional soil organic carbon content (oc) (Koc = Kd/oc where oc is the carbon mass divided by the total soil mass). A problem with exclusive reliance on the Koc to estimate
adsorption is its inherent assumption that adsorption is restricted to soil carbon only, whereas adsorption to clay may be significant and very important, especially in soils low in organic matter with significant amounts of smectitic (2:1 expanding) clay (Shea 1989).

**Atrazine**
The herbicide atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4-diamine), with 29 to 34 million kg applied annually, is the second most frequently applied pesticide in the U.S. (USEPA 2006). The aqueous solubility of atrazine is 33 mg L\(^{-1}\) at 22°C (Vencill 2002) and its half-life varies from (about 60 d) (Ahrens 1994) to 12 days (Ghidey et al. 1997). The average Kd for atrazine in most soils is less than 3 (USEPA 2006). These properties indicate potential mobility of atrazine in a soil-water environment (Wauchope 1978). Because of its low cost and effective control of broadleaf weeds and several grasses, atrazine has been widely used in the U.S., especially in the Midwest “Corn Belt” where atrazine is primarily applied in corn fields (secondarily to sorghum fields). It is applied to the soil surface before or after planting; or incorporated into the soil prior to planting or postemergence. Soil applied atrazine tends to dissolve in water. Corn and weeds adsorb atrazine through roots but corn plants can detoxify atrazine and are seldom affected by root adsorption. Atrazine applied postemergence will enter the plant through the leaves, but much of it reaches the soil surface during application (Johnson et al. 2004). Atrazine moves primarily in the solution phase (dissolved in water) rather than through sorption to soil particles and its degradation is catalyzed by sorption to organic matter and low soil pH (Lerch et al. 1999).

The widespread use of atrazine and its physicochemical properties have resulted in extensive detection in rivers, lakes, ground waters, and reservoirs (Lerch 1999; USEPA
Atrazine may have adverse effects on humans, wildlife and ecosystems. Atrazine loss via surface runoff is likely the dominant source of exposure for freshwater vertebrates, particularly those in static water systems (lakes, ponds, and wetlands) (figure 3).

![Diagram of possible routes of exposure of wildlife to atrazine.](image)

**Figure 3**
Possible routes of exposure of wildlife to atrazine. The width of the arrow indicates the relative importance of pathway (Solomon et al.2008).

Permeable skin and its aquatic habitat during early development makes amphibians most sensitive to atrazine exposure. Recent studies show that frog skin absorbs atrazine at much higher rates than mammalian skin (Quaranta et al. 2009). (Hayesa 2009), decreased breeding gland size, demasculinized/feminized laryngeal development, suppressed mating behavior, reduced spermatogenesis, and decreased fertility. These observations are consistent with the effects of atrazine in other vertebrate classes (Hayes et al. 2002,
In humans, Rusiecki et al. (2004) found no clear evidence of an association between cancer and atrazine exposure among herbicide applicators (Rusiecki et al. 2004). However, atrazine is a secondary amine and under acidic conditions (pH ~ 3 to 5) and in the presence of nitrate can form N-nitrosatrazine.

Exposure to drinking water contaminated with both atrazine and nitrate can increase the risk of non-Hodgkin lymphoma in humans? (De Roos et al. 2003; Rhoades 2011). There is also some evidence of a correlation between exposure to atrazine and poor semen quality in fertile men in the Midwestern U.S. (Swan et al. 2003a, 2003b) and in rodents (Kniewald et al. 2000). Research also suggests that adverse health effects of atrazine may be intensified through simultaneous exposure to multiple agrichemicals (De Roos 2003; Hayes et al. 2006). To minimize atrazine exposure, under the Safe Drinking Water Act, the U.S. Environmental Protection Agency (USEPA) set a maximum contaminant level of 3 µg L\(^{-1}\) (ppb) for drinking water and 12 – 38 µg L\(^{-1}\) for aquatic environments (USEPA 2009). The World Health Organization (WHO) restricted the atrazine concentration limit to 2 µg L\(^{-1}\) for drinking water (WHO 1993) and in 2003 the European Union banned atrazine application because of health concerns (Sass and Colangelo 2006).

**Restrictive Clay Layers (Claypans)**

A claypan is defined by Foth (1984) as a dense, compact layer in the subsoil with much higher clay content compared to the overlying material. In the U.S, central claypan soils occupy about 4 million ha in Missouri and Illinois (Soil Survey Staff 1992). There are also more than 15.5 million hectares of glacial soils in the central part of the U.S., where subsoils contain a large amount of clay (Kelly and Pomes 1998). Embedded restrictive
layers (argillic horizons or bedrock) with high smectite (2:1 expanding clay) content (often >500 g kg\(^{-1}\)) control claypan hydrologic properties (Jamison and Thornton 1961). Doolittle et al. (1994) and Kitchen et al. (1999) reported that depth to the argillic horizon in a typical claypan field varies from 20 cm (8 in) on side slopes to over 110 cm (39 in) on footslopes. The poor drainage of claypan soils decreases percolation of water during wet seasons (winter and spring), and forms preferential flow through cracks in late summer and early fall (Jamison et al. 1968). Despite the high water-holding capacity of the claypan layer, a large fraction of the water is held below the wilting point and cannot be used by plants (Jamison and Kroth 1958). A study of claypan hydrology suggests that under saturated conditions runoff rates in these areas may be equal to precipitation (Saxton et al. 1970). Identifying areas most vulnerable to pesticide movement in these soils is essential for determining what and where best management practices should be implemented.

**Modeling Pesticide Movement**

As a part of the registration process, characterization of environmental fate and transport is required to evaluate the potential of a pesticide to impair surface or ground waters. Ideally, well-designed field experiments will provide a relatively high level of confidence in predicting pesticide fate under particular conditions, but extrapolation of experimental data to other locations or cropping conditions is often not possible. Field studies are usually very costly and resource intensive and it is not practical to conduct studies over the entire range of possible pesticide applications. As a consequence, the use of models to predict pesticide fate has become increasingly popular in the pesticide industry and for regulators (Spurlock 1998; USEPA 2001).
The growing availability of geo-referenced data in combination with simulation models provide estimates of the magnitude as well as the temporal and spatial patterns of non-point source (NSP) pollution in real world scenarios. Models include: GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) (Leonard et al. 1987), the EPA Pesticide Root Zone Model (PRZM) (Carsel et al. 1984), the Soil and Water Assessment Tool (SWAT) (Arnold et al. 1998; Neitsch et al. 2000), the Environmental Policy Integrated Climate (EPIC) Model (Williams 1995; Izaurralde et al. 2006), Watershed Regressions for Pesticides (WARP) models (Larson et al. 2001), and APEX (Agricultural Policy eXtender) (Williams and Izaurralde 2006).

**GLEAMS** is a modified version of the extensively tested Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS) model created by the U.S. Department of Agriculture (USDA) (Knisel 1980, 1993). The model is one-dimensional (soil depth is the only spatial dimension) and classified as a field-scale model that emphasizes the effects of agricultural management systems on agrichemical movement within and through the plant root zone (Leonard et al. 1987). GLEAMS has four major components: hydrology, erosion/sediment, pesticide transport, and nutrient (Reyes et al. 2001). A study by Zacharias and Heatwole (1994) showed that GLEAMS can provide a better representation of pesticide movement and fate at a field level than PRZM. However other studies demonstrated that GLEAMS has no advantage over PRZM for modeling chemical leaching (Pennell et al. 1990; Smith et al., 1991; Persicani 1996).

**PRZM** was developed by USEPA scientists to simulate agrichemical movement in unsaturated soil systems within and immediately below the plant root zone for site-specific leaching estimation (Carsel et al. 1984). This one-dimensional-model predicts
hydrologic and chemical movement of pesticides in soil. Major deficiencies of GLEAMS and PRZM include omission of preferential flow, overestimation of downward movement through soils (particularly at late sampling intervals), and underestimation of surface runoff (Jones and Russell 2001).

The WARP model was developed by the U.S. Geological Survey (USGS) to predict pesticide (percent) concentration in runoff using watershed characteristics as explanatory variables and multiple regression equations (Larson and Gilliom 2001). The mass of applied pesticide divided by watershed area is the most effective parameter in WARP-CB models to estimate atrazine-use intensity (Stone and Gilliom 2012). WARP-BC model was used to predict atrazine concentration in corn belt streams in presence of a restrictive layer within 25 cm of the surface (Stone and Gilliom 2012).

The EPIC model was created by a USDA modeling team to address soil erosion impacts for 135 USDA Land Resource Regions (Williams 1995; Putnam et al. 1988). Over time additional functions related to water quality and atmospheric CO₂ levels were integrated into the model and eventually Erosion Productivity Impact Calculator (EPIC) was changed to Environmental Policy Impact Climate model (Williams et al. 1996).

SWAT is a continuous (daily time-step), watershed-scale, and physically based model developed by the USDA Agricultural Research Services (USDA-ARS) (Arnold et al. 1998; Neitsch et al. 2000). SWAT simulates the hydrologic processes, sediment yield, nutrient loss, and pesticide losses into surface and groundwater. Model inputs include weather, soil properties, topography, vegetation and crop growth, and agricultural management practices.
The APEX model is an extension of EPIC developed in the late 1990s to address environmental issues associated with livestock and other agricultural production systems on a whole-farm or small watershed basis (Gassman et al. 2005; Shukla 2011). APEX operates on a daily time-step and performs long-term continuous simulations of the impacts of various nutrient management practices, tillage operations, conservation practices, alternative cropping systems, and other management practices on surface runoff and losses of sediment, nutrients, and other pollutants (Gassman et al. 2009; Shukla 2011). This model is one of the few that can simulate water, sediment, nutrient, and pesticide transport routing across complex landscapes and channel systems to the outlet of small watersheds (Srivastava et al. 2007). There are two major APEX platforms, the standalone, windows-based WinAPEX (Magre et al. 2006) and ArcAPEX, an ESRI ArcGIS 9.2 and 9.3 extension for MS-windows (Tuppad et al. 2010). Gassman et al. (2010) evaluated APEX’s ability to simulate runoff and herbicide and nutrient losses inside and at the outlet of watersheds under various environmental conditions and agricultural management practices. The results of these studies showed the satisfactory capacity of APEX to simulate different agrichemical loss under complex farming systems (Wang et al. 2006).

SWAT and APEX are increasingly being used to predict pesticide movement in the environment. Both models have been tested at watershed and field scales. Major limitations of these models are their dependency on specific American data sets (especially soil and climate) and curve number calculation (Krysanova et al. 2000; Holvoeta et al. 2007).
The discussed models simulate sophisticated processes for tracing pesticide fate in the environment. Modeling is a balance between representing all possible processes in a realistic fashion and generalizing the most significant processes while recognizing limitations of data availability and our understanding of complex interactions. The spatial variability of soil, land use, and weather conditions affect pesticide behavior in soil and water. Development of a model that links pesticide transport to the spatial characteristics of a field using a simplified process is desirable. The process-based index model developed in this research uses readily available soil, topographic, and hydrologic data to produce graphical representations of vulnerability to off-site movement of pesticides from a field. The model is a useful tool for land management agencies tasked with implementing management practices.
CHAPTER 3

BACKGROUND STUDIES AND MODEL ADAPTATION

USDA-Agricultural Research Service (ARS) Field Work

Field Site for Model Adaptation and Assessment. A 36-ha (89-acre) agricultural field in Boone County, north central Missouri (Latitude 39.2297, Longitude - 92.1169) was used to develop the field-scale model. The field is situated within the Goodwater Creek Experimental Watershed (GCEW), a 7,250-ha (17,920 acre) agricultural area heavily dominated by claypan soil (USDA-NRCS 2000). A first order soil survey (1:5,000 scale) was conducted in the field during 1993 and 1997, which categorized the field into 7 different soil series (Ghidey et al. 1997; Fraisse 2001) (figure 4). Average annual precipitation at the field location is 968 mm (38.1 in) and average annual minimum and maximum daily temperatures are 6.3 and 16.9°C (43.3 and 62.5°F), based on 30 years from 1978 to 2007 (Mugdal et al. 2011). The field was under uniform management with a corn-soybean (Zea mays L. – Glycine max (L.) Merr.) rotation with mulch tillage between 1991 and 2003 (Lerch et al. 2005).
Figure 4
Location of the study area in Boone County, MO, showing first order soil survey and locations of soil sampling for OM and pH.
**Surface Runoff Measurement and Analysis.** For surface water assessment, a 3:1 broad-crested, pre-calibrated v-notch weir was constructed at the field outlet in 1991 and was equipped with a runoff water stage recorder and a refrigerated automated pumping sampler (ISCO 3230, Teledyne Isco, Inc., Lincoln, NE) (Lerch et al. 2005; Ghidey et al. 2010). Based on APEX output, the actual drainage area at the weir was 32 ha (80 ac). Ninety-seven percent of the runoff from the total field area drains to the sampling location, and there was no runoff from adjacent fields onto this field. During runoff events an automated sampler collected flow-weighted samples at a threshold value of 0.8 mm (0.03 in), and continued to sample for the duration of the event. Samples were refrigerated and transported to the laboratory, where they were filtered through 0.45-lm nylon filters within 48 h of receipt and analyzed for atrazine concentration. Details on sampling and analysis are available in Ghidey et al. (1997), Lerch et al. (2005), Sadler et al. (2006), and Ghidey et al. (2010). Between 1993 and 2001, 815 surface runoff samples were collected and analyzed. Daily runoff volume and atrazine concentration data were used for the present study. Hourly and daily precipitations were collected between 1991 and 2002 by an automated weather station installed on the west side of the field in 1991. Hourly rainfall (mm) data were collected, recorded and maintained in a server database managed by USDA-ARS-CSWQRU at the University of Missouri-Columbia (Sadler et al. 2006; Mugdal et al. 2011).

**Soils.** The field represents a typical upland claypan catena sequence of the ADCO-Mexico-Putnam soil association (USDA-NRCS 2001). The summit landscape position was mapped as Adco (fine, smectitic, mesic Vertic Albaqualf) silt loam with 0 to 1% slope and is the dominant soil in the field; the backslope position was mapped as Mexico
(fine, smectitic, mesic Vertic Epiaqualf) silty clay loam with 1 to 3% slope; and the footslope position was mapped as Mexico silt loam with 1 to 2% slope and somewhat poorly drained (Jung et al. 2010) (figure 4). The landscape is linear to slightly convex at the summit position and linear to slightly concave at the backslope and footslope landscape positions. The elevation difference between summit and footslope positions is 2 to 3 m. The claypan soils are characterized by argillic horizon containing 40-60% clay of smectetic mineralogy. Surface soils are typically silt loams with an abrupt occurrence of silty clay loam, silty clay, or clay loams in the subsoil horizons (Chaudhary et al. 2012).

**Depth to Claypan.** Spatial measurement of apparent electrical conductivity (ECa) is a relatively inexpensive and accurate way to predict subsurface variations in soil properties such as depth to the claypan. The claypan soils of the Missouri field have high clay contents and cation exchange capacities (CEC), soil properties highly correlated with ECa (Sudduth et al., 2003). ECa measurements were used as a surrogate to estimate depth to claypan (Kitchen et al. 1999; Sudduth et al. 2005; Sudduth et al. 2010). A Veris™ model 3100 sensor (Veris Technologies®, Kansas; Lund et al. 1999) and an EM38 (Geonics Limited, Mississauga, Ont., Canada; Sudduth et al. 2003) were used to measure ECa. The Veris electrodes were pulled through the field to directly sense soil electrical conductivity at one second intervals and the locations were geo-referenced with a differentially–corrected global positioning system (DGPS) vertical accuracy of 3-5 cm (Kitchen et al. 2003). Measurement sensors are configured to provide both shallow (0-30 cm) and deep (0-90 cm) readings of ECa (designated as ECa-sh and ECa-dp,
respectively). EM38 and the Veris measurements show that soil conductivity varies as a nonlinear function of depth (Kitchen et al. 2003, 2005; Sudduth et al. 2005) (figure 6B).

**Elevation and Slope.** Elevation data were obtained using a real-time kinematic global positioning system (RTK-GPS) survey on 10 m (32.8 ft) transects with a vertical accuracy 3 to 5 cm (1.2 to 2 in) (Fraisse et al. 2001; Kitchen et al. 2005; Mugdal et al. 2011). The data were interpolated into a 5 m resolution digital elevation model DEM that contains horizontal artifacts which are evident in the model output (figure 5A). Percent slope was calculated from the DEM using ArcGIS 10 (figure 5B). Most cultivation occurs on slopes with a gradient less than 10%. Slope is one of the components used to calculate the functionalized Index Surface Runoff (ISRO) (Schoeneberger et al. 1998).

**Soil Organic Matter (SOM).** SOM is the primary substrate for pesticide sorption in soils containing significant amounts of well-decomposed (humified) organic material (Bailey and White 1970; Shea 1989). SOM is also associated with microbial activity so influences pesticide biodegradation. The relative affinity of a pesticide for SOM depends on its physiochemical properties and is characterized by the organic carbon sorption coefficient (Koc). SOM is used to determine weights associated with the soil adsorption and biodegradation functions.

**pH.** The pH of the soil measured using a 1:1 (w/v) soil-water ratio and is a relative expression of the acidity or alkalinity of a soil sample (Soil Survey Staff 1996). The pH is used in the adsorption function for ionizable pesticides such as atrazine, to determine abiotic hydrolysis (for hydrolysis-sensitive pesticides such as atrazine), and to calculate the extent of biotic degradation.
Soil and Crop Management Practices. The study area was in a corn-soybean rotation under uniform management practices from 1991 to 2003, in which corn was planted in odd years and soybean in even years. However, there was an exception in 1995 because persistent spring rains delayed planting date and grain sorghum (*Sorghum bicolor* L.) was grown instead of corn. The field was under mulch tillage to maintain ~30 percent crop residue, usually with one disking and one or two field cultivation passes before spring planting (table 1 and 2; Lerch et al. 2005; Mudgal et al. 2010).
Table 1
Herbicide application and management practices at the Missouri field (Lerch et al. 2005; Ghidey et al. 2010).

<table>
<thead>
<tr>
<th>Year</th>
<th>Crop</th>
<th>Planting Date</th>
<th>Herbicide</th>
<th>Application Rate (g ha⁻¹)</th>
<th>Date of application</th>
<th>Method of Application</th>
<th>Tillage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>Corn</td>
<td>6-May</td>
<td>Atrazine</td>
<td>2,460</td>
<td>6-May</td>
<td>Broadcast, incorporated</td>
<td>Mulch</td>
</tr>
<tr>
<td>1999</td>
<td>Corn</td>
<td>24-May</td>
<td>Atrazine</td>
<td>2,240</td>
<td>23-May</td>
<td>Broadcast, incorporated</td>
<td>Mulch</td>
</tr>
<tr>
<td>2001</td>
<td>Corn</td>
<td>28-Apr</td>
<td>Atrazine</td>
<td>2,240</td>
<td>27-Apr</td>
<td>Broadcast, incorporated</td>
<td>Mulch</td>
</tr>
</tbody>
</table>

Table 2
Annual precipitation, runoff, and atrazine transport in surface runoff at the Missouri field (Lerch et al. 2005).

<table>
<thead>
<tr>
<th>Year</th>
<th>Crop</th>
<th>Precipitation (mm)</th>
<th>Runoff (mm)</th>
<th>Atrazine Losses (g ha⁻¹)</th>
<th>Atrazine Application Rate (g ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993</td>
<td>Corn</td>
<td>1340</td>
<td>540</td>
<td>17.1</td>
<td>2,240</td>
</tr>
<tr>
<td>1995</td>
<td>Sorghum</td>
<td>1150</td>
<td>380</td>
<td>47.3</td>
<td>1,940</td>
</tr>
<tr>
<td>1997</td>
<td>Corn</td>
<td>940</td>
<td>210</td>
<td>35.7</td>
<td>2,460</td>
</tr>
<tr>
<td>1999</td>
<td>Corn</td>
<td>820</td>
<td>240</td>
<td>12.6</td>
<td>2,240</td>
</tr>
<tr>
<td>2001</td>
<td>Corn</td>
<td>1030</td>
<td>340</td>
<td>29.7</td>
<td>2,240</td>
</tr>
</tbody>
</table>
Figure 5
(A) Elevation (m), (B) slope (%), and (C) saturated hydraulic conductivity (Ksat) (mm h\(^{-1}\)) for the Missouri field.
ARS-APEX WORK

APEX Simulation. APEX simulation was performed by Mughal in December 2008 (using version 0604) and updated using the July 2010 version (Gassman et al. 2010; Mugdal et al. 2011). The APEX model divided the field into smaller spatial units (sub-areas) with homogenous soil and topographic properties. Major APEX components include weather, hydrology, soil erosion, nutrients (nitrogen, phosphorus and carbon), pesticide fate, crop growth, soil temperature, tillage, plant environment control (drainage, irrigation and liming) and economics on a subarea basis (Shukla 2011). Depth to the claypan layer estimated from measured EC$_a$ data and a first order soil map of the field were used to delineate polygons with homogenous claypan depth and soil type, resulting in 35 subareas (figure 6A and C; figure 7C; Mugdal et al. 2011). The 5 m DEM was used in ArcGIS™ to create flow paths in the field which were then used to describe the APEX routing scheme from one subarea to another and to the field outlet (Lerch et al. 2005; Mugdal et al. 2011). The model was used to simulate event runoff, sediment, and atrazine loss from 1991 to 2002. APEX outputs for soil hydrologic properties (saturated water content, field capacity, and daily soil moisture) and subsurface clay content (15 cm depth) for each subarea were extracted for the selected events included in the present study.
**Clay Content.** Total clay content is the percent (by weight) of mineral particles less than 0.002 mm in equivalent diameter of the fine earth fraction (particles <2 mm) of a soil (Soil Survey Staff 2005). Clay content is important in defining pesticide sorption, especially when organic matter is low (Shea 1989) and smectitic clay has a greater influence on sorption than other clay minerals (Bailey et al. 1970).

**Saturated hydraulic conductivity (K_{sat}).** Saturated hydraulic conductivity (K_{sat}) is a quantitative measure of the velocity of water moving vertically through a unit area of saturated soil over a unit time under a unit hydraulic gradient, expressed in µm sec^{-1} (Soil Survey Staff 2005). K_{sat} is used in the Index Surface Runoff (ISRO) function. Mudgal et al. (2010) measured at 19 points spread across the field and used these data to run the APEX (Mudgal et al. 2011) (figure 5C).
Figure 6
Representation of 35 APEX subareas with (A) first-order soils and, (B) depth to claypan (cm). (C) Dominant first order soil properties corresponded to each APEX subarea for the Missouri field.
Figure 7
(A) Subsurface clay content (%), (B) effective half-life (days), and (C) pour point and 35 APEX subareas for the Missouri field.
Regional Vulnerability Model

The previously developed regional vulnerability model contains two parts: hydrology and chemistry. The hydrologic component is based upon the functionalized Natural Resources Conservation Service (NRCS) runoff table (ISRO) that in turn is based on slope and $K_{sat}$. ISRO can be adjusted to account for local factors that significantly impact pesticide movement such as layers restrictive to permeability (increases runoff), flooding (increases leaching and runoff), proximity to streams, lakes or karst openings (increases contamination vulnerability) and depressions (increases leaching). The chemistry component consists of adsorption, hydrolysis and biotic degradation functions that are integrated into a relative mass-balance using a unit load of 10.

**Modes of Transport.** Vulnerable areas within a field are identified based on relative weights (relative risk) with respect to ISRO (Index Surface Runoff), LISRO (leaching ISRO), and ISRO-K (particle-adsorbed runoff). These functions, associated with the hydrologic pathway of interest (leaching, solution runoff (SRO), and particle adsorbed runoff (ARO)), along with the modifiers, are used to evaluate overall vulnerability for agrichemical transport within the study area.

**Hydrology Component: Index Surface Runoff.** The hydrologic component of the model includes core functions and modifiers.

**Core Functions.** The hydrologic component of the model contains the following core functions:

**ISRO.** In hydrologic modeling, the influence of topographic features on water movement is expressed as topographic indices. NRCS Index Surface Runoff (ISRO)
Classes (Soil Survey Division Staff 1993) provided a framework for calculating ISRO from slope and $K_{sat}$ for the top 15 cm of soil. The equation follows a first-order curve and shows high sensitivity at low slopes. ISRO is used in all three transport scenarios. Areas with high saturated hydraulic conductivity ($K_{sat}$) and low slope tend to infiltrate surface water while areas with low $K_{sat}$ and high slope tend to produce runoff. Midpoints of each $K_{sat}$ class and the three slope classes associated with agronomic production were uniformly assigned ISRO values from 0 (negligible runoff) to 10 (very high runoff). One NRCS class value was changed from negligible to very low in order to keep the attribution uniform. A log $K_{sat}$ transform produced equal sloped, linear relationships between log $K_{sat}$ and ISRO for each NRCS slope class (equation 1; figure 8).

$$\text{ISRO Weight} = -2 \times \log(K_{sat}) + (2.9661 + 6.2137 \times (1 - \exp(-0.1729 \times \text{Slope}(%)))$$  \hspace{1cm} (1)

**Figure 8**
ISRO iso-$K_{sat}$ lines as a function of ISRO and slope.
**LISRO.** Leaching ISRO vulnerability (LISRO) is calculated by inverting ISRO (i.e. 10 – ISRO) (equation2). Areas with low slope and high $K_{sat}$ reflect the most vulnerable condition for leaching.

\[
\text{LISRO (Leaching)} = 10 - \text{ISRO} \tag{2}
\]

**ISRO-K.** ISRO-K characterizes vulnerability to particle-adsorbed pesticide runoff by multiplying ISRO by the erodibility factor ($K_{wf}$) (equation 3; figure 9). $K_{wf}$ is an empirical factor defining the relative susceptibility of a soil to erode by runoff and raindrop impact and the rate at which it erodes per unit area when all other factors are the same (Renard et al. 1997; Willett 2010). The amount of silt and OM influence soil erodibility. Hence, soils with less OM and silt are more resistant to detachment and have lower erodibility (Wischmeier and Smith 1978).

\[
\text{ISRO} - K = 1.56 * K * \text{RISRO} \tag{3}
\]

**Figure 9**
ISRO-K function.
**Modifiers.** The hydrologic component includes modifiers for restrictive layers, depressions, and flooding.

**Depression Modifier.** A depression is a shallow, convex feature. Runoff captured by depressions potentially increases the vulnerability of leaching and pesticide reaching a subsurface water table depending upon surface $K_{sat}$. In the regional version of the model, soil map units associated with depressions or playas are given a 2-point leaching penalty. A more serious risk to groundwater contamination occurs when pesticides move into a karst opening at the surface (which may or may not be associated with a depression) or when a pesticide is applied near an engineered drainage feature (such as a French drain or tile inlet).

**Flooding Frequency Modifier.** The flooding frequency reflects the annual probability of a flooding event, and is expressed as *None, Very Rare, Rare, Occasional, or Frequent.* The five maximum flooding frequency classes and their assigned modifier values (which were added to ISRO, LISRO and ISRO-K) are none (0), very rare (0.5), rare (1), occasional (2) and frequent (3) (table 3). The dominant flooding frequency class for the map unit is on composition percentage of map unit components (Soil Survey Staff 2005). According to the SSURGO data, the flooding frequency of the field is considered as “None.”
Claypan Modifier. The original model overestimated leaching by a factor of roughly 60% when applied to an ARS claypan study area so a clay restrictive layer modifier was developed to increase ISRO and ISRO-K and decrease LISRO based on the relatively quick draining large pore volume above a restrictive layer or water table. Large pore volume (cm$^3$) was calculated from 0.33 bars and saturated soil moisture and depth (cm). Claypans are not morphometric features so a set of identifying criteria were developed based on the clay restrictive layers of Rainwater Basin soils found in the Blue River Basin and the Missouri claypan soils. Claypans or clay restrictive layers were defined as having smectitic clay mineralogy, $K_s < 1 \, \mu \text{msec}^{-1}$, clay content $> 35\%$, and a horizon thickness $> 20 \, \text{cm}$. Restrictive layer soils have an elevated water table (April to June) and drainage classes ranging from well drained to very poorly drained depending in part upon the depth to the restrictive layer. Upon examining the range of large pore volumes associated with the top meter of Rainwater Basin restrictive layer soils, a linear restrictive layer modifier was derived (equation 4; figure 10)

### Table 3
Flooding frequency weight (based on the flooding frequency maximum parameter (floodfreqmax) from SSURGO).

<table>
<thead>
<tr>
<th>Flooding Frequency Class</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>Very Rare</td>
<td>0.5</td>
</tr>
<tr>
<td>Rare</td>
<td>1</td>
</tr>
<tr>
<td>Occasional</td>
<td>2</td>
</tr>
<tr>
<td>Frequent</td>
<td>3</td>
</tr>
</tbody>
</table>
$\text{Modifier}_{\text{Clay}} = -0.3 \times \text{Larg ePoreVolume} + 6$  

Equations for pesticide degradation, hydrologic properties, and time-dependent adsorption functions developed in the regional-scale model were applied to each hydrologic pathway: leaching, SRO, and ARO (equations 5, 6, and 7).

Leaching = \((\text{Flooding penalty} + \text{LISRO} - \text{Restrictive layer penalty} + \text{Depression/Playa penalty}) / 10\)  

SRO = \((\text{Flooding penalty} + \text{RISRO} + \text{Restrictive layer penalty} - \text{Depression/Playa penalty}) / 10\)

**Figure 10**
Claypan (restrictive layer) modifier.

**Vulnerability Indices for Pesticide Loss Pathways.** Equations for pesticide degradation, hydrologic properties, and time-dependent adsorption functions developed in the regional-scale model were applied to each hydrologic pathway: leaching, SRO, and ARO (equations 5, 6, and 7).
ARO = \frac{(Flooding\ penalty + ISRO-K + Restrictive\ layer\ penalty \ - \ Depression/Playa\ penalty)}{10} \tag{7}

where SRO is solution runoff and ARO is particle-adsorbed runoff.

**Chemistry Component of the Model.** Chemistry is calculated using a quasi mass balance approach. For any day after application a unit load is partitioned between adsorbed and solution phases. Losses due to hydrolysis are calculated (if appropriate) then losses due to biotic degradation are calculated. The remaining load is reported as vulnerability in the regional-scaled model. At the field scale, the product of the chemistry component (expressed on a 0 to 1 scale) and atrazine applied per cell is the amount of remaining pesticide on the field, assuming no previous losses.

**Pesticide Adsorption.** The pesticide adsorption function depends on SOM, clay, and time. Pesticides are primarily adsorbed by OM but also by clay, especially when the amount of SOM is low (<2.1% in the model). The SOM and clay parameters in the adsorption component follow a sigmoidal curve. The impact of OM is assumed minimal at low percentages (OM < 1.2%). From 1.2-3% OM the relationship becomes linear with a positive slope (Weed and Weber 1974; Villaverda et al. 2008; Willett 2010). The clay weight for the adsorption function depends on percent clay and OM. The highest clay values were assigned for soil with low OM (<1.2%) and the value decreased with increasing SOM, reflecting the much greater effect of SOM than clay on pesticide sorption (He et al. 2006; Willett 2010).
Assuming limitations to sorption at low and high SOM concentrations, a four parameter sigmoid SOM adsorption function assigns up 10 points which represents a full unit load (equation 8; figure 11).

\[
Adsorption_{SOM} = -0.3033 + \frac{10.6066}{1 + e^{\left(\frac{SOM \%-2.0}{0.5673}\right)}}
\]  \hspace{1cm} (8)

The smectitic clay adsorption function was also assumed to be limited at low and high smectitic clay concentrations and could contribute up to 50% of total soil absorption (equation 9; figure 12).

**Figure 11**
Soil organic matter adsorption function.

The smectitic clay adsorption function was also assumed to be limited at low and high smectitic clay concentrations and could contribute up to 50% of total soil absorption (equation 9; figure 12).
\[
\text{Adsorption}_{\text{Smectite}} = -0.1517 + \frac{5.3033}{1 + e^{\left(\frac{\text{Smectite} \%- 30}{8.5094}\right)}}
\]  
(9)

The generic clay adsorption function could contribute up to 40\% of total soil adsorption for a clayey soil (60\% clay) but only when SOM was < 2.1\% (equation 10; figure 13). The sum of clay and SOM adsorption was not allowed to exceed 10, the maximum unit load.

\[
\text{Adsorption}_{\text{Clay}} = \text{Clay}\% \times \left(0.0667 - 0.147 \times \text{SOM}\% + 0.0074 \times \text{SOM}\%^2 - 0.0074 \times \text{SOM}\%^3\right)
\]  
(10)

**Figure 12**
Smectitic clay adsorption function.
Adsorption was assumed complete in 7 days (equation 11; figure 14). The model is a single time-step model so when the time interval exceeds one week, the 7-day time function is used to calculate load.

\[
\text{Adsorption}_{\text{Time}} = 1 - e^{(-1.6904 \cdot \text{Time (days)})}
\]  

(11)

Figure 13
Non-smectitic clay adsorption iso-clay% lines as a function of soil organic matter.
**Pesticide Input Parameters.** Pesticide parameters include the soil organic carbon partition coefficient (Koc), the impact of which is linked to SOM, and biodegradation half-life ($t_{1/2}$). The Koc value is used in the adsorption functions. The biodegradation half-life ($t_{1/2}$) for each pesticide is given in days and is used in the biotic degradation function.

The Koc adsorption function has a maximum unit load of 10 and equals 0 for Koc values $\leq 5$ (equation 12; figure 15), and controls initial adsorption load. In other words, if soil adsorption exceeds Koc adsorption, the initial adsorption load equals Koc adsorption.
Otherwise, soil adsorption is the initial adsorption load. Initial solution load is the difference between maximum load (10) and initial adsorption load.

\[
\text{Adsorption}_{Koc} = 1.0857 \times \ln(Koc) - 1.7474
\]  

\text{(12)}

**Hydrolysis.** Hydrolysis occurs as a function of pH and time. This function is only applicable for pesticides (such as atrazine) which are susceptible to hydrolysis under acidic or alkaline conditions. Therefore, some knowledge about the properties of the pesticide of interest is required for proper use of this parameter in the model. Hydrolysis can increase with acidity or basicity but the relative increase is not symmetric due to agronomic pH limitations. As a result unique functions were developed for acid- (equation 13) and base-sensitive pesticides (equation 14; figure 16). If the conditions are

![Koc adsorption function](image-url)

**Figure 15**
Koc adsorption function.
not appropriate for hydrolysis (based on the pesticide and soil properties), load is not
dissipated.

\[
Hydrolysis_{\text{Acid}} = -0.1781 + \frac{1.2838}{1 + \left(\frac{pH}{6.0293}\right)^{12.5058}} \\
Hydrolysis_{\text{Basic}} = -0.0593 + \frac{1.0457}{1 + \left(\frac{pH}{7.9496}\right)^{-22.1013}}
\]

Figure 16
Abiotic hydrolysis fraction as a function of pH.

Pesticides can hydrolyze over a relatively short time span. The original process-based
index model assumed that hydrolysis is completed within 7 days (equation 15, figure
17).
\[ \text{Hydrolysis}_{\text{Time}} = 1.004 - e^{(-0.794\text{Time}(\text{days}))} \]  

**Figure 17**  
Abiotic hydrolysis time fraction.

**Biotic Degradation.** Biotic degradation occurs as a function of time, soil pH, and microbial species and populations (the latter is approximated by SOM content). The model assumes the total load (both the adsorbed and solution phases) is subject to biotic degradation. The pH and population dynamics can vary considerably from field to field and replicating these conditions in the laboratory can be difficult, which complicates pesticide half-life measurements. Under optimal pH and microbial populations, the model assumes effective half-life can be as small as half the reported value while under the least optimal agricultural conditions effective half-life can be doubled. Further, the ability of a
microbial population to degrade a given pesticide can increase with time through selection pressure, but the model does not reflect that adaptation.

\[ BD_{\text{Acid}} = -0.1391 + \frac{1.1535}{1 + e^{-\frac{(\text{pH} - 6.0813)}{0.6220}}} \]  
\[ BD_{\text{Alkaline}} = \frac{1.0186}{1 + e^{-\frac{(\text{pH} - 7.9891)}{-0.2985}}} \]

Figure 18
The pH biotic degradation function.

Biotic degradation in response to pH is assumed asymmetric around an optimal pH of 6.8. This pH response is represented by two sigmoidal functions (equations 16 (acid) and 17 (alkaline); figure 18). The biotic degradation function associated with SOM assumes kinetic limitations at low and high SOM values (equation 18; figure 19).
The product of the pH and SOM biodegradation functions was rescaled to produce a range of output from 0.5 to 2.0 which was then multiplied by reported pesticide half-life to estimate effective half-life (equation 19).

\[
Hatf - Lifef\text{ffective} = \left(-1.5*\left(BD_{pH} * BD_{OM\%}\right) + 2\right)*Hatf - Lifef
\]  

(19)

Biotic degradation is calculated on the load remaining after hydrolysis (assuming the pesticide is pH sensitive) on each pesticide phase (bound and unbound) (equation 20).

\[
BD = \frac{1}{2^{\left(\frac{\text{Days}}{\text{EffectiveHalf} - \text{Life}}\right)}} * \text{Load}_{\text{Phase}}
\]  

(20)
**Model Application to the Missouri Field Site**

To adapt the watershed model to the Missouri field site, interpolated data from OM and pH measurements, APEX output for clay content, Ksat and dynamic unfilled pore volume for sub-areas and atrazine properties were used to calculate weights for each component. To show the influence of hydrologic variables and chemistry functions on pesticide loss, vulnerability indices for each component were calculated separately and scaled from 0 to 1. The equations follow. The divisor (10) is used to convert a 10-point to a 1-point scale. At the field-scale geomorphological features such as depressions can be detected from high resolution DEMs. Depression modifiers can be applied at the field scale using a high resolution DEM and field observations. No significant depressions were detected in the field using the SINK function on the 5m DEM and this modifier was assumed to be "0." Clay cmineralogy from first order soil survey and percent of clay for each layer from APEX outputs were used to define a clay-dominated layer that is restrictive to flow. Percent clay for the top 15 cm of soil was calculated from APEX outputs for each subarea (figure 7A). Also saturated hydraulic conductivity was extracted from APEX outputs for each subarea (figure 5C). Model functions were imported into ArcGIS (10.0) Map Algebra and Model Builder™. For atrazine, the Koc is reported as 100 L kg⁻¹ (SCS 1990) and half-life is assumed to be 60 d for topsoil (Christensen and Ziegler 1998); however, Ghidey et al. (1997) reported a dissipation half-life of 12 d at the Missouri field site. Therefore, using the dissipation half-life of 12 d times 1.5 or 2 provides a more realistic half-life range for the model.

**Field Scale Inputs: Interpolation of pH and OM.** Interpolation methods generate a surface that gives the best results when the data are normally distributed. Using SAS
codes, histograms and Q-Q plots were generated for pH and SOM. The closer the histogram to a bell-shaped curve or closer the points are to the straight line in the Q-Q graph, the closer the data follow a normal distribution. SOM and pH were measured at 476 geo-referenced points across the field (figure 20). The interpolation maps for SOM and pH were created using ordinary kriging as an exact interpolator. Previous studies show that ordinary kriging is a good interpolation method for spatially correlated soil properties (Yasrebi et al. 2009; Mabit and Bernard 2010). However, variability and spatial structure of the data, choice of variogram model, search radius, and the number of neighboring points used for the estimation can significantly affect the performance of the Kriging method (Leenaers et al. 1990). Therefore, three common semivariogram models (Spherical, Exponential and Gaussian) were evaluated using PROC 2DKRIG in SAS (SAS 2008) based on Akaike’s information criterion (AIC) and lowest sum of squares error (SSE) and using the geospatial analyst function in ArcGIS version 10.0.

**Parameter Adjustment: Sensitivity Analysis of Hydrolysis Time Frame.** Some pesticides are subject to hydrolysis, an abiotic chemical reaction of the pesticide with water that may be rapid but can vary considerably with matrix and reaction conditions. Hydrolysis of atrazine in a buffered aqueous system and sterilized soil systems typically follows first-order kinetics. However, the rate of atrazine hydrolysis can be influenced by sorption and with deviations in soil pH from neutrality. This means that soils with high OM and clay contents and low pH will exhibit greater atrazine hydrolysis and sorption (Armstrong et al. 1967; Lerch et al. 1999).

The original vulnerability model assumed that hydrolysis is complete within 7 d and equations for acid and alkaline hydrolysis were created as a function of pH and time
based on research on Atrazine (equations 13, 14 and 15). In a study conducted at the same Missouri field, Ghidey et al. (1997) found that atrazine in surface runoff exceeded the drinking water limit (3 µg L\(^{-1}\)). Atrazine loss from the study area, especially after a heavy rainfall in dry years (e.g., 41.27 g atrazine lost per ha on 25 June 1995, 10 days after application), indicated that the proposed time frame of hydrolysis may not reflect what is occurring in the field. To evaluate the impact of the hydrolysis time frame, two approaches were taken using a subset of the data. The first approach considered three 2001 runoff events, with the same amount of the applied atrazine at approximately 7, 14 and 21 d after application. This approach isolated the hydrolysis function from other transformation processes. To normalize the three events, the amount of unabsorbed pesticide (atrazine load in the solution phase) was assigned a value of 1. In absence of any field measurements the first method could not be used to select the best hydrolysis time-frame. Based on results from the 1997 study (Ghidey et al. 1997), a second approach focused on the first runoff events after atrazine application in 1993 and 1995, which respectively occurred at 3 and 10 days after application. The first event in 1995 (25 June) produced the greatest atrazine loss observed in the five years of the study. The amounts of unbound and adsorbed atrazine in the field were calculated for three hydrolysis time frames (7, 14 and 21 d), including both biological and chemical degradation. Adding these two measurements provided the amount of atrazine remaining in the field for each event. Model results were compared to those of Ghidey et al. (1997), who reported 53% loss of atrazine in surface runoff in 1993 (3 d after application) and 60% loss in 1995 (10 d after application) (table 7).
Figure 20
Histogram and normal Q-Q plot for (A) OM and (B) pH.
**Optimzation of the Claypan Modifier.** The original restrictive layer modifier function was linear, based on a range of representative large pore volume values and it could alter ISRO by up to 60%, a number based on previous research of runoff on claypan soils. For the field study the maximum large pore volume for the study area was 226 cm$^3$. The function was fit to 25 cm$^3$ using three modifier thresholds (50, 60 and 70% ISRO) and applied to three events representing high, medium and low unfilled pore volume values. The events were selected by means and standard deviations of unfilled pore volume for each event after pesticide application were calculated by stacking three layers with different modifiers in ArcGIS for 35 sub-areas. Based on the highest and lowest average values, outputs were divided into low, medium, and high categories. From each category a representative event with a moderate standard deviation was selected as a sub-sample to identify the best claypan modifier. Consequently the hydrology component of the model was calculated for the day prior to 15 Oct.1993, 29 Jun.1999, and 14 Aug.1995, representing low to high unfilled pore volumes (and high to low claypan penalties) for each claypan modifier.

**Estimation of Atrazine in Runoff.** Thirty nine atrazine runoff events ($\geq$ 0.8mm) for years in which atrazine had been applied (1993, 1995, 1997 and 2001) were identified for this study (figure 21). The amount of atrazine applied each year (g ha$^{-1}$) was converted into values applied per 5 $\times$ 5 (m$^2$) raster layer cell. Multiplying the amount applied for each cell by composite chemistry component (scaled from 0-1) for that cell provides an estimation of amount of unbound atrazine (g ha$^{-1}$) on the field (equation 21). The amount of unbound atrazine (g ha$^{-1}$) can then be multiplied by the hydrologic component (scaled
from 0-1) to define the amount of unbound atrazine prone to runoff (g ha⁻¹) (equation 22).

For qualitative approach:

Unbound atrazine (g ha⁻¹) = (Chemistry grid (0 to 1 scale))

\[ \times (\text{Atrazine per cell for corresponding year}) \]  \hspace{1cm} (21)

Unbound atrazine prone to runoff (g ha⁻¹) = (Unbound atrazine)

\[ \times (\text{Solution Hydrology grid (0 to 1 scale)}) \]  \hspace{1cm} (22)

**Figure 21**
Table 4
Runoff events for years planted to corn (odd years) from 1993 to 2001.

<table>
<thead>
<tr>
<th>Date</th>
<th>Days after Atrazine Application</th>
<th>Precipitation (mm)</th>
<th>Runoff (mm)</th>
<th>Atrazine (g ha$^{-1}$)</th>
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<tr>
<td>14-May-93</td>
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<td></td>
<td></td>
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<tr>
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<td>23</td>
<td>37.72</td>
<td>12.09</td>
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<tr>
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<td>0.44</td>
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<td>15.91</td>
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<tr>
<td>15-Jun-95</td>
<td>(Date of Application)</td>
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<td></td>
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<tr>
<td>25-Jun-95</td>
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<td>89.67</td>
<td>39.72</td>
<td>41.27</td>
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<td>16-Aug-95</td>
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<td>232</td>
<td>20.37</td>
<td>1.21</td>
<td>0.02</td>
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</table>
Table 4
Runoff events for years planted to corn (odd years) from 1993 to 2001 (continued).

<table>
<thead>
<tr>
<th>Date</th>
<th>Days after Atrazine Application</th>
<th>Precipitation (mm)</th>
<th>Runoff (mm)</th>
<th>Atrazine (g ha(^{-1}))</th>
</tr>
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Statistical Analyses
The watershed-scale model was generated as a qualitative approach to delineate areas vulnerable to pesticide runoff, leaching, and particle-adsorbed runoff. Multiplying the amount of applied atrazine per cell by the solution or adsorbed chemical components and hydrology scaled from 0 to 1 provides a way to evaluate the model quantitatively. Data for 39 events after atrazine application for corn planted in odd years from 1993 to 2001 were included in the model. Logarithmic transformations of the atrazine data were performed prior to analyses to minimize the effects of extreme values and increase the normality of residuals.

Parametric statistical tests such as an Analysis of Variance (ANOVA) can be used if the data are normally distributed with constant variance (Montgomery 2004). To determine an appropriate model for data distribution, density curves on the histograms and the Kolmogorov-Smirnov test as an empirical distribution function (EDF) were used.
to assess whether data were normally distributed (figure 22; table 5). The bell-shaped curve and the Kolmogorov-Smirnov test ($P > 0.15$) in table 4 indicate that the data are normally distributed.

Variance inflation factors (VIF) and PROC CORR from SAS (SAS, SAS/STAT® 9.2 User’s Guide Introduction to Survival Analysis Procedures 2008) were used to check for multicollinearity among the variables. When data (or log-transformed data) were normally distributed and no colinearity was detected among independent variables, ANOVA and GLM procedures from SAS and the F-test were used to detect significant factors ($\alpha = 0.05$) contributing to the variation of atrazine loss from the field. The following regressions were constructed to evaluate the association of the selected variables with the amount of atrazine measured in runoff at the Missouri field site:

Regression 1:

$$\text{Log Atz (g ha}^{-1}) = \beta_0 + \beta_1\text{Prec.} + \beta_2\text{Applied Atz Yr} + \text{Days} + \epsilon$$  \hspace{1cm} (23)

Regression 2:

$$\text{Log Atz (g ha}^{-1}) = \beta_0 + \beta_1\text{Prec.} + \beta_2\text{Applied Atz Yr} + \beta_3\text{logSRO Atz} + \epsilon$$  \hspace{1cm} (24)

Regression 3:

$$\text{Log Atz (g ha}^{-1}) = \beta_0 + \beta_1\text{Prec.} + \beta_2\text{Applied Atz Yr} + \beta_3\text{logSRO_Hydro Atz} + \epsilon$$  \hspace{1cm} (25)

where $\text{logAtz (g ha}^{-1})$ is the log of measured atrazine loss in runoff, $\text{Prec.}$ is precipitation (mm), $\text{Applied Atz Yr}$ is applied atrazine for each year (g ha$^{-1}$), $\text{Days}$ is the number of
days after application, SRO Atz (g ha$^{-1}$) is the model-estimated amount of unbound atrazine, SRO_Hydro Atz (g ha$^{-1}$) is the model-estimated amount of unbound atrazine prone to runoff. $\beta_0$ is the intercept, $\beta$ is the slope coefficient and $\epsilon$ denotes model deviations (error). Type III (Marginal) Sums of Squares was used to define the significant factors. In Type III SS, sums of squares for each independent variable corrected for the other terms in the model and sequential order of fitting the variables in the model do not affect the Sums of Squares (SAS 2008).
Table 5
Goodness of fit represented by (A) Kolmogorov-Smirnov test for measured atrazine and (B) log-transformed atrazine measurements.

<table>
<thead>
<tr>
<th>A</th>
<th>Goodness-of-Fit Tests for Normal Distribution</th>
<th>B</th>
<th>Goodness-of-Fit Tests for Normal Distribution</th>
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<td>Test</td>
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<td>p Value</td>
<td>Test</td>
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<td>A-Sq</td>
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<td>Pr &gt; A-Sq</td>
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</table>

Figure 22
Goodness of fit represented by fitted curves on the histogram for (A) measured atrazine and (B) log-transformed Atrazine measurements.
CHAPTER 4
RESULTS AND DISCUSSION

Interpolated OM and pH Measurements
SAS produces variograms with the highest Akaike’s information criterion (AIC) and lowest SSE defined the best fitted variogram models (Gaussian, empirical, or spherical) for interpolating OM and pH across the field. Maps were created using ordinary kriging with Gaussian empirical semivariogram for OM and spherical for pH (figure 23 A and B). However variograms did not fit any of the models very well (figures 24 and 25). Scatter plots and variogram-estimated parameters (nugget, sill and range) for soil sampled OM and pH are shown in figures 26 and 27 and in tables 5 and 6. The scatter plot shows a regular (normal) distribution of the measurements throughout the area and anisotropy (directional dependency) was assumed negligible. The lowest pH values (highest acidity) occur on the middle to north side of the field (pH ≅ 5.7 to 6). The pH is highest in a large area in the southernmost part of the field. pH map indicates areas where chemical degradation may be significant. According to the kriged estimates, only a few pixels adjacent to the southern border of the field in the interpolated layer have pH > 7. Based on the interpolated OM map, the northwest area and south side of the field have the most OM and the middle of the field has very low OM content. OM does not exceed 2.7%. Because of its weak basicity, atrazine has a considerable affinity for negatively charged surfaces on clay and acidic groups in organic matter (Schnitzer and Khan 1978) and its adsorption is positively correlated with soil organic matter (Barriuso et al. 1992; Park et al. 2004). A low SOM content may limit the number of atrazine-degrading microorganisms and can decrease its biotic degradation (Radosevich et al. 1989). SOM
also reduces the amount of the available atrazine for plant uptake and leaching (Best and Weber 1974). Variations in pH can significantly affect all chemical reactions within the soil matrix. Based on the OM content and pH of the study area, atrazine likely degraded more quickly in the north and near-southern parts of the field than in the middle. Therefore, for the chemistry component of model, the middle of the field is expected to be most vulnerable to atrazine loss though runoff, which was in consistent with the results of Ghidey et. al (1997) (figure 23).
Figure 23
Interpolated maps of (A) soil organic matter (%) and (B) pH for the Missouri study area.
Figure 24
Fitted SAS variograms for organic matter: (A) Gaussian AIC = 9.28, SSE = 14.82, (B) spherical model AIC = 9.16, SSE = 14.66, and (C) exponential model AIC = 8.88, SSE = 14.29.
Figure 25
Fitted SAS variograms for pH: (A) Gaussian AIC = 91.94, SSE = 29.36, (B) spherical model AIC = 26.61, SSE = 71.95 and, (C) exponential model AIC = 26.66, SSE = 71.94.
Table 6
Estimated parameter values (nugget, scale and range) of the selected Gaussian model for OM.

| Parameter | Estimate | Std Error | Lower  | Upper  | DF | t Value | Pr > |t| |
|-----------|----------|-----------|--------|--------|----|---------|------|---|
| **Nugget** | 0.04534  | 0.001293  | 0.04236| 0.0483 | 8  | 35.07   | <.0001|
| **Scale**  | 0.04457  | 0          | 0.04457| 0.0446 | 8  | .       | .    |  |
| **Range**  | 2.2533   | 0.8257    | 0.3493 | 4.1573 | 8  | 2.73    | 0.0259|  |

Figure 26
The observations scatter plot for OM.
Table 7
Estimated parameter values (nugget, scale and range) of the selected Gaussian model for pH.

| Parameter | Estimate | Approx Std Error | Approximate 95% Confidence Limits | DF  | t Value | Approx Pr > |t| |
|-----------|----------|-----------------|-----------------------------------|-----|---------|-------------|---|
| Nugget    | 0.01924  | 0.002884        | 0.01259 0.0259                    | 8   | 6.67    | 0.0002      |
| Scale     | 0.07504  | 0.003252        | 0.06755 0.0825                    | 8   | 23.08   | <.0001      |
| Range     | 14.3624  | 2.2261          | 9.229 19.496                      | 8   | 6.45    | 0.0002      |

Figure 27
The observations scatter plot for pH
**Hydrolysis Sensitivity Analysis and Model Validation**

Hydrolysis of atrazine to the inactive hydroxyl form is a primary mechanism of abiotic atrazine degradation and this process can be catalyzed at soil surfaces. Burkhard and Guth (1981) showed that the hydrolysis half-lives of atrazine and other 1,3,5 chlorinated triazine herbicides are much shorter when soil is present than in buffered aqueous solution. Acidification of soil can promote rapid degradation of atrazine and reduce the amount in the solution phase (Hiltbold and Buchanan 1977). A project objective was to determine the best hydrolysis time frame for the model but the sensitivity analyses did not clearly resolve the issue. Figures 28, 29, and 30 show hydrolysis component maps for three 2001 events, at approximately 7, 14 and 21 d after application of 2240 g ha\(^{-1}\) atrazine. Table 7 compares model-estimated atrazine left in the field with measured values from Ghidey et al. (1997) for the same rainfall events in 1993 and 1995. Results of the hydrolysis time frame sensitivity analysis using either approach may indicate that model output vlaues are insenstivie to differences in hydrolysis time between 7 and 21 d (figures 28, 29, and 30). For the current study, hydrolysis time frame was increased to 21 d based on a discussion with R.N. Lerch, USDA-ARS (personal communication, May 20, 2012). Figure 7B shows that after applying the effective half-life, atrazine half-life increases to the unrealistic range of 70-90 days. This indicates that effective half-life multiplier in the regional-scale model needs to be modified to have closer values to the field measurements. Changing atrazine half-life according to previous study (Ghidey et al.) and microbial adaptation without altering the effective half-life multiplier did not improved the model estimated amount of remaining Atrazine in the field.
Figure 28
Range of atrazine hydrolysis completion for three hydrolysis time functions applied on May 4, 2001, 6 d after pesticide application: (A) hydrolysis completed 7 d, (B) hydrolysis completed 14 d and (C) hydrolysis completed 21 d.
Figure 29
Range of atrazine hydrolysis completion for three hydrolysis time functions applied on May 7, 2001, 9 d after pesticide application: (A) hydrolysis completed 7 d, (B) hydrolysis completed 14 d and (C) hydrolysis completed 21 d.
Figure 30
Range of atrazine hydrolysis completion for three hydrolysis time functions applied on May 18, 2001, 19 d after pesticide application: (A) hydrolysis completed 7 d, (B) hydrolysis completed 14 d and (C) hydrolysis completed 21 d.
Table 8
Model-estimated atrazine remaining on the field (adsorbed atrazine + unbound atrazine) through runoff at 3 d after application in 1993 and 19 d in 1995 using three hydrolysis time frames (7, 14, and 21 d) compared to the finding of Ghidey et al. (1997) for the same site.

<table>
<thead>
<tr>
<th>Hydrolysis Time Frame</th>
<th>Atrazine Application</th>
<th>Model Estimation</th>
<th>Reported (Ghidey et al. 1997)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Atrazine Left in the Field</td>
<td>Atrazine Loss</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unbound Atrazine</td>
<td>Adsorbed Atrazine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Days)</td>
<td>(g ha⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 d after application in May 17, 1993</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1,144</td>
<td>545</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>1,222</td>
<td>582</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>1,275</td>
<td>607</td>
</tr>
<tr>
<td>10 d after application in June 6, 1995</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>905</td>
<td>436</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>1,940</td>
<td>438</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>924</td>
<td>445</td>
</tr>
</tbody>
</table>
Optimization of the Restrictive Layer Modifier
The desired modifier value when added to ISRO would produce values within the range of the ISRO output and optimize variability. When the Restrictive Layer Modifier was assigned 70% of the ISRO value, the result exceeded the range of ISRO values which would exaggerate runoff loss. Standard deviation maps show three events with a 50% ISRO claypan modifier and the same events with a 60% ISRO claypan modifier. Based on the average and range of standard deviations, the 60% IRSO modifier was selected for the field-scale model (figure 31). The selected claypan modifier was in consistent with the proposed modifier for the regional-scale model.
Figure 31
Standard deviation maps for the claypan (clay restrictive layer) penalty based on runoff events occurring on October 15, 1993, June 29, 1999 and August 14, 1995: (A) restrictive layer modifier = 5; (B) restrictive layer modifier = 6.
Qualitative Vulnerability at the Field-Scale
The spatial distribution of areas prone to atrazine runoff across the Missouri field was first characterized for the chemistry and solution runoff hydrology components for two selected events in 1993 (3 and 23 d after application) (figures 32 and 33, A and B). Maps in figures 32C and 33C show vulnerability to atrazine loss in runoff after averaging chemistry and solution runoff hydrologic components. Once atrazine equilibrates between the sorbed and solution phases, vulnerability based on chemistry alone decreases with time due to hydrolysis and biotic degradation. Hydrology vulnerability varies with rainfall and soil drainage. Respective maps show how the sensitivity of the field to atrazine loss in the solution runoff phase decreases significantly between 3 and 23 d after application.
Figure 32
Relative vulnerability across the Missouri field for (A) solution chemistry (0 to 1 scale), (B) solution hydrology (0 to 1 scale), and (C) the product of the two model components for a May 17, 1993 runoff event (3 d after atrazine application).
Figure 33

Relative vulnerability across the Missouri field for (A) solution chemistry (0 to 1 scale), (B) solution hydrology (0 to 1 scale), and (C) the product of the two model components for a June 6, 1993 runoff event (23 d after atrazine application).
Modeling Atrazine Runoff and Model Validation

Knowing the amount and date of atrazine application enables a quantitative estimate of pesticide remaining on the field. Because management practices were constant for the five years of the study, the impact of tillage type, irrigation and atrazine application method were not considered in evaluating the model. No field measurements were available to assess atrazine loss through leaching and particle-adsorbed runoff, so the capacity of the model to project atrazine loss via these hydrologic processes was not evaluated.

The amount of atrazine runoff would likely be related to the amount of atrazine applied and precipitation. A test was constructed to determine whether unbound atrazine remaining in the field or unbound atrazine remaining in the field that was associated with runoff prone areas would produce a better atrazine runoff prediction model than using days after application, a property that could be determined without the model. Each independent variable included in the regression was checked for multicollinearity to determine if any two parameters are highly correlated. For all regressions, correlations between independent variables (precipitation, applied atrazine for each year, and model-estimated amount of unbound atrazine prone to runoff) did not exceeded 25%. The highest correlations were observed between measured atrazine loss from the field and the model-estimated unbound atrazine prone to runoff (0.91), model estimated amount of unbound atrazine (0.87), and days after application (0.85), respectively (tables 8, 9 and 10). The correlation analysis indicates no inter-dependence among independent variables in the regressions and that model-estimated atrazine in runoff and days after application have the largest impact on predicting the amount of atrazine lost through runoff.
### Table 9
Multicollinearity of the variables in Regression 1.

<table>
<thead>
<tr>
<th></th>
<th>logAtz</th>
<th>Prec</th>
<th>AppliedAtzYr</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>logAtz</strong></td>
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<td>0.24598</td>
<td>0.09449</td>
<td>-0.8524</td>
</tr>
<tr>
<td></td>
<td>0.1312</td>
<td>0.5672</td>
<td>&lt;.0001</td>
<td></td>
</tr>
<tr>
<td><strong>Prec</strong></td>
<td>0.246</td>
<td>1</td>
<td>-0.1388</td>
<td>-0.1106</td>
</tr>
<tr>
<td></td>
<td>0.1312</td>
<td>0.3993</td>
<td>0.5025</td>
<td></td>
</tr>
<tr>
<td><strong>AppliedAtzYr</strong></td>
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<td>-0.1388</td>
<td>1</td>
<td>0.14304</td>
</tr>
<tr>
<td></td>
<td>0.5672</td>
<td>0.3993</td>
<td>0.385</td>
<td></td>
</tr>
<tr>
<td><strong>Days</strong></td>
<td>-0.1106</td>
<td>0.14304</td>
<td>1</td>
<td></td>
</tr>
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### Table 10
Multicollinearity of the variables in Regression 2.

<table>
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<th>Prec</th>
<th>AppliedAtzYr</th>
<th>SRO_Atz</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>logAtz</strong></td>
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<td>0.24598</td>
<td>0.09449</td>
<td>0.87383</td>
</tr>
<tr>
<td></td>
<td>0.1312</td>
<td>0.5672</td>
<td>&lt;.0001</td>
<td></td>
</tr>
<tr>
<td><strong>Prec</strong></td>
<td>0.246</td>
<td>1</td>
<td>-0.1388</td>
<td>0.09576</td>
</tr>
<tr>
<td></td>
<td>0.1312</td>
<td>-0.1388</td>
<td>0.562</td>
<td></td>
</tr>
<tr>
<td><strong>AppliedAtzYr</strong></td>
<td>0.0945</td>
<td>-0.1388</td>
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<td>-0.03058</td>
</tr>
<tr>
<td></td>
<td>0.5672</td>
<td>0.3993</td>
<td>0.8534</td>
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</tr>
<tr>
<td><strong>logSRO_Atz</strong></td>
<td>0.8738</td>
<td>0.09576</td>
<td>-0.0306</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>&lt;.0001</td>
<td>0.562</td>
<td>0.8534</td>
<td></td>
</tr>
</tbody>
</table>
The analysis of variance for the three regressions indicated that days after application, model-estimated amount of unbound atrazine, and the model-estimated amount of unbound atrazine prone to runoff are significant \((p \leq 0.0001)\) in predicting atrazine runoff loss from the study area (tables 11, 12, and 13). There also was a significant association between precipitation and measured atrazine loss in all regressions but the amount of applied atrazine for each year did not have a significant influence on atrazine loss in the regressions 2 and 3 because it has been already integrated to the model estimated of unbound atrazine and unbound atrazine prone to runoff. This factor was only significant \((p = 0.0027)\) in regression 1.

### Table 11
Multicollinearity of the variables in Regression 3.

<p>| Pearson Correlation Coefficients, (N = 39) | Prob &gt; (|r|) under (H_0: \text{Rho}=0) |
|---------------------------------------------|------------------------------------------|</p>
<table>
<thead>
<tr>
<th>logAtz</th>
<th>Prec</th>
<th>AppliedAtzYr</th>
<th>SRO_Hydro_Atz</th>
</tr>
</thead>
<tbody>
<tr>
<td>logAtz</td>
<td>1</td>
<td>0.24598</td>
<td>0.09449</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1312</td>
<td>0.5672</td>
</tr>
<tr>
<td>Prec</td>
<td>0.246</td>
<td>-0.1388</td>
<td>0.09408</td>
</tr>
<tr>
<td></td>
<td>0.1312</td>
<td>1</td>
<td>0.3993</td>
</tr>
<tr>
<td>AppliedAtzYr</td>
<td>0.0945</td>
<td>-0.1388</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.5672</td>
<td>0.3993</td>
<td>0.8633</td>
</tr>
<tr>
<td>logSRO_Hydro_Atz</td>
<td>0.907</td>
<td>0.09408</td>
<td>0.02848</td>
</tr>
<tr>
<td></td>
<td>&lt;.0001</td>
<td>0.5689</td>
<td>0.8633</td>
</tr>
</tbody>
</table>
Table 12

ANOVA results for Regression 1. Significance levels (Pr>F) are in bold where p<0.05.

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<tr>
<th>Source</th>
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<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
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<td>240.3986385</td>
<td>80.1328795</td>
<td>48.87</td>
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</tr>
<tr>
<td>Error</td>
<td>35</td>
<td>57.3863409</td>
<td>1.6396097</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>38</td>
<td>297.7849794</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-Square Coeff Var Root MSE logAtz Mean
0.807289 -77.98837 1.280472 -1.641876

<table>
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<th>Source</th>
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<th>Type III SS</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
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</thead>
<tbody>
<tr>
<td>Prec</td>
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<td>9.7962632</td>
<td>9.7962632</td>
<td>5.97</td>
<td>0.02</td>
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<tr>
<td>AppliedAtzYr</td>
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<td>17.0997105</td>
<td>17.0997105</td>
<td>10.43</td>
<td>0.003</td>
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<tr>
<td>Days</td>
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<td>217.356365</td>
<td>217.356365</td>
<td>132.57</td>
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</tbody>
</table>

Table 13

ANOVA results for Regression 2. Significance levels (Pr>F) are in bold where p<0.05.

<table>
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<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
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<td>241.5515903</td>
<td>80.5171968</td>
<td>50.11</td>
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<tr>
<td>Error</td>
<td>35</td>
<td>56.2333891</td>
<td>1.6066683</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>38</td>
<td>297.7849794</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-Square Coeff Var Root MSE logAtz Mean
0.811161 -77.20096 1.267544 -1.641876

<table>
<thead>
<tr>
<th>Source</th>
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<th>F Value</th>
<th>Pr &gt; F</th>
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<tbody>
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<td>218.5093168</td>
<td>218.5093168</td>
<td>136</td>
<td>&lt;.0001</td>
</tr>
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</table>
Table 14

ANOVA results for Regression 3. Significance levels (Pr>F) are in bold where p<0.05.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
</tr>
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<tbody>
<tr>
<td>Model</td>
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<td>255.2559802</td>
<td>85.0853267</td>
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<td>Error</td>
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<td>42.5289993</td>
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</tr>
<tr>
<td>Corrected Total</td>
<td>38</td>
<td>297.7849794</td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>R-Square</th>
<th>Coeff Var</th>
<th>Root MSE</th>
<th>logAtz Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.857182</td>
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<td>-1.641876</td>
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<table>
<thead>
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</tr>
</thead>
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<td>8.9012097</td>
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<td>logSRO_Hydro_Atz</td>
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<td>232.2137066</td>
<td>232.2137066</td>
<td>191.1</td>
<td>&lt;.0001</td>
</tr>
</tbody>
</table>

logAtz = -9.8656 +0.0186 Prec +0.0048 AppliedAtzYr -0.0346 Days

Figure 34
Scatter plot of predicted values for atrazine loss in runoff versus residuals for Regression 1.
Figure 35
Scatter plot of predicted values for atrazine loss in runoff versus residuals for Regression 2.

\[
\log(Atz) = -34.625 + 0.0186 \text{Prec} + 0.0029 \text{AppliedAtzYr} + 4.1242 \log(SRO\_Atz)
\]

N = 39
Rsq = 0.8112
AdjRsq = 0.7950
RMSE = 1.2675

Figure 36
Scatter plot of predicted values for atrazine loss in runoff versus residuals for Regression 3.

\[
\log(Atz) = -31.192 + 0.0178 \text{Prec} + 0.0018 \text{AppliedAtzYr} + 4.3164 \log(SRO\_Hydro\_Atz)
\]

N = 39
Rsq = 0.8572
AdjRsq = 0.8449
RMSE = 1.1023
Based on the adjusted R², RMSE and residual distribution plots (figures 34, 35 and 36), Models 1 and 2 are nearly identical while Model 3 performed slightly better. Cluster of points in residual distribution plots are related to late season atrazine losses. There was a small difference between Models 2 and 3 R² (≅ 0.04) and Model 3 gave a slightly higher adjusted R² and lower RMSE. A discussion of the impacts of precipitation and model-estimated values on the regression models for predicting atrazine loss through runoff follows.

Precipitation. Lerch et al. (2005) reported that annual precipitation in 1993, 1995, and 2001 was above the long-term average, with 1993 having the highest annual precipitation. These years were considered “wet” years. Annual precipitation in 1997 was almost equal to the long-term mean and in 1999 precipitation was below the long-term average, which represented a dry year. Years with above average precipitation consequently have more runoff than years with less precipitation but the amount of runoff is not directly proportional to precipitation. For example, in 1995, 115 cm (45 in) of precipitation resulted in only 38 cm (15 in) of runoff, but in 1999, 82 cm (32 in) of precipitation resulted in 24 cm (9.4 in) of runoff. This shows that, on an annual basis, the number, intensity, distribution, and duration of precipitation events are more important than total precipitation in determining the magnitude of runoff (Lerch et al. 2005). Devlin et al. (2008) explained that most pesticide loss in runoff occurs when rainfall immediately follows pesticide application. Most of the runoff-producing rainfall in the central U.S. occurs between April and early July; so application of pesticides on sloping land with poorly drained soils should be delayed until there is less chance of a major storm event.
**Model-Estimated Atrazine Loss in Runoff.** The model-estimated amounts of atrazine loss in runoff using both “unbound atrazine” and “unbound atrazine prone to runoff” were much higher than atrazine measured at the field outlet. In a previous study at the same field, Blanchard and Donald (1995) found that only a small amount of applied atrazine was leached to groundwater, due to the prevalence of a clay restrictive layer, which favors runoff over leaching. The estimated average depth to the claypan for this field is 39.6 cm and ranges from 7 cm to 105 cm (Doolittle et al. 1994). Atrazine can be lost through volatilization; however, vapor loss is highly dependent on ambient temperature and soil moisture conditions. Rice et al. (2002) reported that volatilization accounts for 7.5% of atrazine lost from freshly tilled soil and Gish et al. (2010) showed an average loss of <4% of that applied. Although these losses may be comparatively small, the initial amount of atrazine should be adjusted for vapor and leaching losses, based on available field measurements and previous research. Zablotowicz et al. (2006) demonstrated that atrazine half-lives in sampled soils with at least one year of atrazine exposure may be at least 50% shorter than in soils with no history of atrazine application. This suggests that microbial adaptation in soil with extensive exposure to atrazine, such as at the Missouri field site, reduces residual weed control but accelerates atrazine degradation and decreases the amount available for off-site movement. Thus biological degradation of atrazine may be underestimated in the current model and adjusting the half-life and degradation time in soil should bring model-estimated atrazine losses more closely in line with field-measured values.
CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

A process-based index model was developed to delineate areas vulnerable to off-site movement of pesticides at a field scale. Model sensitivity to soil physiochemical properties and topographical position was demonstrated. Model estimates of atrazine remaining in the Missouri study area overpredicted field measurements by a factor of < 2. Days since application, and model-estimated amounts of “unbound atrazine” and “unbound atrazine prone to runoff” were highly correlated to atrazine measured in runoff from the field. Multiple regression showed that precipitation, unbound atrazine and unbound atrazine prone to runoff were highly correlated with measured atrazine in surface runoff. Close results between regressions 1 (days after application) and 2 (unbound atrazine remaining in the field) suggests the chemistry component of the model adds little to estimate atrazine loss in runoff. However, the larger $R^2$ and smaller RMSE of regression 3 show the important contribution of model-estimated unbound atrazine prone to runoff, which is highly dependent on unbound atrazine (from the chemistry component). Because the effective half-life function currently used in the chemistry component inflates atrazine half-life, adjusting that function would likely improve the model.

Because of the large difference between model-estimated values and measured atrazine loss in surface runoff, hydrolysis time frame sensitivity analysis did not reveal any significant differences among the selected time periods (7, 14, and 21 d) and atrazine remaining in the field for the selected events in 1993 and 1995. Microbial adaptation has
been shown to accelerate atrazine degradation in fields receiving multiple years of application and this can dramatically reduce its half-life. Adjustment of biotic degradation half-life should produce closer agreement between model-generated and field-measured herbicide in runoff water. The hydrologic component of the model could also be improved by integrating BMPs and rainfall intensity.

Validation of the model was limited to one Missouri field with soil layers restrictive to water flow (claypans). To ensure the capacity of the model to accurately delineate areas vulnerable to pesticide movement within a field and estimate losses, further testing should be conducted on fields differing from the study area and where the required data are available.
REFERENCES


