Atrazine Runoff in the Blue River Basin: Geomorphology, Rainfall, and Agronomic Practices

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ATRAZINE RUNOFF IN THE BLUE RIVER BASIN:
GEOMORPHOLOGY, RAINFALL, AND AGRONOMIC PRACTICES

by

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ATRAZINE RUNOFF IN THE BLUE RIVER BASIN:
GEOMORPHOLOGY, RAINFALL, AND AGRONOMIC PRACTICES

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Atrazine concentrations in the Big Blue River Basin (BRB) in Nebraska and Kansas periodically exceed the U.S. EPA Maximum Contaminant Level (MCL) of 3 µg L⁻¹. The present study is focused on watershed variables influencing surface runoff of atrazine. The assessment includes the impact of corn and sorghum planting progress (indicating atrazine application), rainfall, antecedent soil water content, and soil restrictive layer on stream-measured weekly atrazine load in independent BRB subwatersheds for 1997 - 2004. Maximum atrazine loading occurred after most of the corn had been planted but during sorghum planting from mid-May to early June, immediately following multiple rainfall events that saturated the soil profile and caused runoff from fields. Analysis of covariance was conducted from day 110 when about 10% of the corn was planted to day 170 when 90% of the sorghum was planted. Results from the independent subwatersheds imply that atrazine load weighted by area is related to cumulative weekly rainfall across all years. Statistical analysis showed rainfall was the most significant factor associated with atrazine loading, but soil water content, corn and sorghum planting progress, and the presence of a restrictive layer at the soil surface were also important.

Keywords: atrazine, surface runoff, subwatershed
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<tbody>
<tr>
<td>AWDN</td>
<td>Automated Weather Data Network</td>
</tr>
<tr>
<td>BMPs</td>
<td>Best Management Practices</td>
</tr>
<tr>
<td>BRB</td>
<td>Blue River Basin</td>
</tr>
<tr>
<td>COOP</td>
<td>Cooperative Observer Program</td>
</tr>
<tr>
<td>CDL</td>
<td>Cropland Data Layer (USDA-NASS)</td>
</tr>
<tr>
<td>DEM</td>
<td>Digital Elevation Model</td>
</tr>
<tr>
<td>HPRCC</td>
<td>High Plains Regional Climate Center</td>
</tr>
<tr>
<td>ISW</td>
<td>Independent Subwatershed</td>
</tr>
<tr>
<td>GIS</td>
<td>Geographic Information System</td>
</tr>
<tr>
<td>GPS</td>
<td>Global Positioning System</td>
</tr>
<tr>
<td>MCL</td>
<td>Maximum Contamination Level</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NASS</td>
<td>National Agricultural Statistics Service (USDA)</td>
</tr>
<tr>
<td>NMSS</td>
<td>National Map Seamless Server</td>
</tr>
<tr>
<td>NPS pollution</td>
<td>Nonpoint Source pollution</td>
</tr>
<tr>
<td>NRCS</td>
<td>Natural Resources Conservation Service (USDA)</td>
</tr>
<tr>
<td>RUSLE</td>
<td>Revised Universal Soil Loss Equation</td>
</tr>
<tr>
<td>SOM</td>
<td>Soil Organic Matter</td>
</tr>
<tr>
<td>TMDL</td>
<td>Total Maximum Daily Load</td>
</tr>
<tr>
<td>US</td>
<td>United States</td>
</tr>
<tr>
<td>USDA</td>
<td>United States Department of Agriculture</td>
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<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
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<td>USGS</td>
<td>United States Geological Survey</td>
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CHAPTER 1

1. INTRODUCTION

1.1. Water and Water Quality

Water is a serious challenge for humanity in the 21st century. The quality and quantity of water available for drinking and domestic purposes is diminishing. Nonpoint pollution of surface water through anthropogenic causes is a growing concern. Row crop production systems [corn (Zea mays L.), soybean (Glycine max L.), and sorghum (Sorghum bicolor L. Moench)], which rely heavily on agrichemicals to control weeds, insect pests and pathogens and maximize yields to meet current global food demand, is a leading source of water pollution. Issues arising from farming practices include water contamination and eutrophication. Rivers draining agricultural landscapes are often unable to provide the same level of viable habitat for aquatic species as rivers flowing through forest landscapes (Allan 2004). In the U.S., agriculture affected 18% of the assessed rivers and streams and contributed to 48% of the reported water quality problems in impaired rivers and streams (USEPA 2000). Of 700,000 miles of assessed rivers and streams in the U.S., 39% did not meet water quality requirements in 2000.

Herbicides account for the largest fraction of agrichemicals used in crop production. The U.S. EPA (Environmental Protection Agency) reported glyphosate as the most widely used herbicide in 2007, followed by atrazine. An estimated 75 million pounds of atrazine active ingredient were used in 2007, based on USDA, EPA, and
proprietary data sources. In the U.S., atrazine has been frequently detected in surface and ground waters and even in raindrops during precipitation events.

Pesticide application has saved humankind from starvation and has played an important role in securing food for growing world populations. To some extent, herbicides have also protected the agricultural environment from loss of soil water and erosion, which are exacerbated by mechanical weed removal techniques. The unfortunate aftermath of pesticide applications is their occurrence in surface water and to a lesser extent in ground water, which compromises the quality of major sources of drinking water. Conventional water treatment methods do not remove these contaminants and specialized removal processes are costly.

Large applications of agrichemicals in the Midwest have led to impaired ground and surface water from surface runoff, leaching, and alluvial groundwater contamination. Rainfall and storm events during spring and summer storms flush pesticides, primarily herbicides, from application areas. Peak herbicide concentration occurs approximately concurrent to or in proximity with that of hydrograph peak (Williams et al. 1995). Herbicide losses from surface runoff and leaching are typically very small compared to loss from chemical degradation but impairment of rivers and stream remains a concern. Although pesticide loss by runoff is usually less than five percent of the total amount applied, it is greater than the estimated 0.01-0.05% lost via leaching (Comfort et al. 1996). Although the physicochemical properties of a pesticide are important, Williams et al. (1995) argued that soil properties generally have the greatest effect on offsite movement.
Thurman et al. (1991) reported that median herbicide concentrations in surface water were an order of magnitude greater between the post-planting and harvesting period than for the rest of the season. Atrazine and its transformation product, deethylatrazine (DEA), were found in pre-plant and postharvest samples of Midwest surface waters. The ratio of DEA to atrazine, an indicator of nonpoint source pollution of groundwater, was greater than 1 in groundwater, while the ratio was less than 1 in surface runoff from the fields. The ratio was higher in stream water samples taken at harvest time than in pre- and post-planting samples. The relatively persistent nature of atrazine and its degradation to DEA is the likely reason for the high ratio of DEA to atrazine water samples collected during harvest time. Hydroxyatrazine, another atrazine transformation product, was confirmed in weekly sampled runoff water in a stream of the Missouri claypan region (Lerch et al. 1995). Agricultural landscapes with alluvial aquifers are also likely to contribute atrazine and DEA to rivers during base flow conditions (Thurman and Fallon 1996).

Various studies cite the long-range transport of atrazine, detection in rainfall, and deposition in pristine areas (e.g., Thurman et al. 1995; Thurman and Cromwell 2000). In the Midwest, about 2% loss of the atrazine applied to fields can be expected through volatization, particle transport, and drift, of which about 0.6% will be deposited by precipitation. Loss to the atmosphere is favored by elevated temperature, wind, and high soil water content. Ninety-five percent of the 5.5 ng L$^{-1}$ average atrazine concentration measured in Lake Superior is believed due to atmospheric deposition (Kurt-Karakus et al. 2010). Atrazine in the Great Lakes, however, was said to be below levels of toxicological risk to human and aquatic organisms (Tierney et al. 1999).
Models have been developed based on studies of nonpoint source water pollution. In 1991, the U.S. Geological Survey (USGS) initiated the National Water-Quality Assessment (NAWQA) Program with an objective of identifying factors that impair water quality. The NAWQA is responsible for assessing the nation’s surface and ground water resources and documenting any changes or trends in the water quality (Nakagaki et al. 2005). Environmental processes, such as surface and subsurface water flow and offsite movement of nutrients and agrichemicals, are now more commonly conducted at the watershed scale. Investigating relationships between human actions and biology, chemistry, and hydrology is most appropriate at a watershed level (Carlsen 2004). Geographic Information System (GIS) can be effectively used to assess nonpoint source pollution as it can accommodate spatial scales requiring integration and display of variables from multiple sources (Tsihrintzis et al. 1996). The U.S. EPA has also been reinforcing the watershed as a geographic unit because managing the required coordination is easier using an entire watershed. The abundance of spatial data through several data clearinghouses, coupled with advancing GIS technologies, facilitates nonpoint source pollution study.

1.2. Atrazine

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine; Figure 1), classified as a symmetrical (s) triazine, subclass chloro-s-triazine, is a selective herbicide that is applied preplant, preemergence, and/or postemergence to control broadleaf and some grassy weeds. Triazine herbicides were first discovered by J.R. Geigy, Ltd., in 1952. Atrazine has a heterocyclic ring with nitrogen atoms at positions 1, 3, and 5, a chlorine in position 2, and ethylamine and isopropylamine at positions 4, and 6,
respectively. Atrazine is widely used in the U.S. on corn, sorghum, and sugarcane (*Sachcharum officinarum* L.). Atrazine use is greatest in producing corn, followed by sorghum, throughout the conterminous U.S. Eighty-four percent of the total atrazine application in the U.S. is in corn (Gianessi and Marcelli 2008) and for sorghum it is about 10 percent (Thelin and Stone 2010). Recent data show 34 million kg of active ingredient of atrazine being applied annually in the U.S., with greatest use in the Midwest (USEPA 2009). Alternatives to atrazine that surpass its low price and effective control of broad-leaves and grasses are not currently available.

![Chemical structure of atrazine](image)

**Figure 1**: Chemical structure of atrazine (Ahrens 1994).

The half-life of atrazine is often reported as 60 days (Ahrens 1994); however, persistence can vary considerably with field conditions and may be much shorter after multiple applications. This provides effective long-term weed control, but also can result in water quality problems when it enters surface waters through runoff or groundwater via leaching. Because of its water solubility (about 33 mg L$^{-1}$; Ahrens, 1994), limited adsorption to soil [$K_{oc}$=100 (Ahrens, 1994)], and its potentially longer persistence,
Atrazine may be detected in surface waters where it is used. The U.S. Environmental Protection Agency (1992) established a Maximum Contaminant Level (MCL) of 3.0 µg L\(^{-1}\) for atrazine in finished public drinking water supplies. The EPA is currently reviewing atrazine for its environmental toxicity. While atrazine application has been banned in the European Union because of the potential to contaminate surface and ground water, along with its environmental and health hazard, the U.S. has permitted atrazine registration renewal (Ackerman 2007). Atrazine is now a restricted use herbicide, meaning that only certified applicators can use it and only for agricultural purposes. Over years atrazine manufacturers, agricultural advisors, as well as the EPA have reviewed and lowered the recommended application rate. The label for atrazine strictly restricts application within 15.2 m (50 ft) of surface water bodies or within 60.9 m (200 ft) around lakes and reservoirs. Areas which are highly erodible should have a minimum of 30% soil covered with plant residues and a maximum of 2.24 kg a.i. ha\(^{-1}\) (2 lb ai acre\(^{-1}\)) of atrazine can be applied as a broadcast spray. A buffer setback of 20.2 m (66 ft) from any point where field surface runoff water enters a stream or river is required.

The primary mode of action for atrazine is through inhibition of Photosystem II. Atrazine blocks electron flow to the plastoquinones and cytochrome by competing with plastoquinone II and thereby suppressing the photosystem II pathway (Stephenson and Solomon 2007). Syngenta (Basel, Switzerland) has funded projects to assess the biological impact of atrazine. In one recent Syngenta-funded review, Solomon et al. (2008) observed inconsistencies in the effects of atrazine on lentic and lotic biota in microcosm studies. Abiding by Bradford-Hill guidelines and Koch’s postulate, they...
pooled all previous work done in assessing atrazine effects on aquatic vertebrates. The authors also reviewed the effects of atrazine on endocrine pathways regulated by hormones. The study included gonadal development and the impact of atrazine exposure on amphibians and the authors concluded that ecologically relevant concentrations of atrazine do not affect physical and reproductive growth or the reproductive ability of amphibians, fish, and reptiles. Rohr and McCoy (2010) conducted a meta-analysis of the biological effects of atrazine on fresh water vertebrates, funded by National Science Foundation, U.S. Department of Agriculture, and the U.S. Environmental Protection Agency. They encountered inconsistent results and opined the need of additional studies to measure the effects of atrazine on aquatic biota. Contrary to Solomon et al., Rohr and McCoy declared that ecologically relevant concentrations of atrazine reduce growth rate, alter metamorphosis period, increase infections, promote gonadal abnormalities, and act as an endocrine disruptor, modifying sex hormone production. The authors recommended rigorous studies to assess atrazine effects on aquatic health and the environment and to compare benefits of atrazine against its negative impacts.

Rusiecki et al. (2004) conducted an independent epidemiological study of all cancers among atrazine agricultural workers. No relationship was found between atrazine exposure and cancer among the pesticide applicators. However, atrazine is a secondary amine and at low pH (~ 3 to 3.5) it can form N-nitrosoatrazine. Nitrosoatrazine is hypothesized to form in vivo (in the human stomach) and exposure to drinking water containing both atrazine and nitrate has been associated with an increased risk of developing non-Hodgkin lymphoma (Rhoades 2011). In an agricultural environment, using large amounts of nitrate fertilizer can facilitate nitrosoatrazine formation (Kearney
et al. 1977). Bioconcentration of nitrosoatrazine was observed in a chicken egg and embryo model (Joshi 2011). Nitrosoatrazine was transferred between the egg white and yolk and chicken embryos exposed to nitrosoatrazine exhibited developmental defects (Joshi 2011).

In the Midwest, atrazine is frequently detected in surface waters and in agricultural soils. The EPA is currently conducting an intensive monitoring program for atrazine and its metabolite residues in public drinking water. In a field-scale study on atrazine runoff in Nebraska, Adelman and Stansbury (2007) reported that freshwater life are exposed to unacceptable atrazine concentrations in 20-50% of runoff events. The EPA is currently implementing intensive monitoring in community water systems in the Midwest. Recent drinking water samples did not exceed the 90-day average of 37.5 parts per billion (ppb) of atrazine and its metabolites (U.S. EPA 2011). With advancements in pesticide detection technology, atrazine and its metabolites are being detected at very low (ng per L) concentrations.

Nebraska, one of the many agricultural states in the U.S., has a history of extensive agrichemical use for crop production. Heavy use of herbicides such as atrazine has led to its occurrence in ground water (Spalding et al. 2003). Leaching of atrazine from application in cropland areas with shallow water tables increases susceptibility to groundwater contamination. In another study, approximately 4%, (about 70 sampled Nebraska wells) had detectable atrazine levels, of which 20 wells exceeded the MCL (Gosselin et al. 1997). However, with better water management practices and improvements in center pivot and sprinkler irrigation systems, atrazine concentrations
measured in groundwater samples using multilevel samplers were below the EPA-established MCL (Spalding et al. 2003).

Economic analyses of the consequences of banning atrazine in the U.S. report yield loss, a decrease in corn acres, an increase in corn price, and increased herbicide cost. For safeguarding aquatic biota, respective acute and chronic criteria have been established for atrazine at 330 µg L\(^{-1}\) (1-hour average concentration, which is an average of at least two appropriately spaced measurements, calculated over a period of one hour) and 12 µg L\(^{-1}\) (4-day average concentration, which is an average of the daily mean values calculated over a period of four consecutive days) (NDEQ 2000).

1.3. Objectives

The primary objective of this study was to analyze spatial and temporal patterns in water quality in streams of the Blue River Basin, focusing on atrazine load and the processes and conditions that impair water quality. This assessment included the impacts of rainfall, planting dates, antecedent soil water content, and the presence of a restrictive layer to flow at the soil surface on stream-measured weekly atrazine samples in independent subwatersheds.
1.4. Hypotheses

The hypotheses tested in this study are:

H₁: Area-weighted atrazine loads differ among the independent subwatersheds of the Blue River Basin.

H₂: Area-weighted atrazine load is associated with rainfall between atrazine sampling events.

H₃: Area-weighted atrazine load is associated with soil water content.

H₄: Area-weighted atrazine load is associated with corn planting progress.

H₅: Area-weighted atrazine load is associated with sorghum planting progress.

H₆: Area-weighted atrazine load is associated with the presence of a surface restrictive layer.
2. LITERATURE REVIEW

2.1. Surface Runoff

Pollution from nonpoint sources such as agricultural production and animal operations is the leading cause of impaired water bodies (USEPA 2009). Surface runoff is one of the predominant pathways for pesticide loss from the agricultural environment (Capel and Larson 2001) and is affected by meteorological, landscape, and anthropogenic variables. Among them are rainfall intensity and duration, direction of storm movement, antecedent soil moisture, evapotranspiration, wind, relative humidity, elevation, slope, slope length, catchment size, and soil type (USGS 2011). Surface runoff is of two types, hortonian and saturation excess. Hortonian flow occurs when precipitation rate exceeds infiltration capacity and the saturated soil is not able to hold additional water. Saturation excess runoff is caused by a restrictive layer to flow near the soil surface (Reichenberger et al. 2007). Ng and Clegg (1997) reported atrazine loss associated with surface runoff, interflow (or lateral flow along the top of a restrictive layer), and baseflow (i.e. groundwater flow). In the Midwestern U.S., herbicides flushed from cropland and transported through the surface water system show rapid, large pulses corresponding to late spring and early summer rainfall (Thurman et al. 1991). In highly permeable soils, heavy rainfall immediately after herbicide application causes leaching beyond the root zone where limited biological activity inhibits degradation and promotes further movement to ground water (Eckhardt and Wagenet 1996).

Pesticide loss from runoff is via solution runoff or adsorbed particle runoff. Most of the surface runoff arises from the top 2-3 mm of the soil horizon known as the mixing
zone or effective depth of interaction (Ahuja et al. 1981). Water soluble or hydrophilic pesticides are more likely to be carried away with runoff water than lipophilic pesticides that become adsorbed to soil particles, which can be transported with sediments during runoff. The soil organic carbon partition coefficient ($K_{oc}$) is the ratio of the chemical concentration in the organic carbon phase in soil particles to its concentration in the aqueous phase in soil solution at equilibrium. Pesticides with high $K_{oc}$ values become strongly adsorbed to soil particles and are less likely to leach through the soil profile but more likely lost with sediment in runoff.

The quantity of pesticide runoff depends on rainfall timing and amount, plant growth stage, residue cover, soil water content, pesticide physicochemical properties, application rate, and placement (Gorneau et al. 2001), but Smith et al. (2002) argued that it is primarily a function of soil water content. In a 50-year simulation study using Groundwater Loading Effect of Agricultural Management Systems (GLEAMS), 72 percent of the atrazine lost through runoff occurred within 30 days of application and atrazine loss in 10 years contributed >50% of the cumulative loss for the entire period (Gorneau et al. 2001).

The present study is limited to atrazine, because it is the most extensively used soil active pesticide in Nebraska agriculture (Franti et al. 1997). Atrazine transport in a drainage basin is generally related to basin size, the quantity applied, land use practices, and the volume of runoff into streams (Stamer et al. 1994).
2.2. Rainfall

Studies on hydrologic systems and water quality modeling depend on rainfall data because rainfall controls runoff sediment transport (Chaubey et al. 1999). The Automated Weather Data Network (AWDN), National Oceanographic and Atmospheric Administration’s National Weather Service (NWS), and the NWS Surface Cooperative Observer Program are the main sources of rainfall data, although other agencies, farmers, and individuals may also collect data.

Rainfall varies over space and time. Representative rainfall estimates require data from multiple weather stations. Within a watershed, the gage network should be of sufficient density to capture the true rainfall gradient. Hubbard (1994) suggested the distance between two weather stations should be less than 5 km in order to explain 90% of the variation in rainfall. He also mentioned that for variables such as temperature, relative humidity, solar radiation, and evapotranspiration, the distance must be about 30 km to achieve the same level of accuracy. Church et al. (1999) identified wind velocity as the greatest source of error in rainfall measurement, suggesting the importance of proper siting of rain gauges. High velocity winds cause raindrops to fall obliquely and change trajectory with respect to a rain gauge. Proper positioning of rain gages above the land surface, away from any obstructions and elevated constructions, ensures good rainfall measurements and should produce accurate estimates at a given location (Church et al. 1999).

Hydrographs show temporal fluctuation in discharge of water in rivers and streams over time. Runoff after precipitation is directly reflected in hydrographs. Factors such as watershed characteristics, duration and intensity of precipitation, antecedent soil
water content, and infiltration rate, are major variables influencing stream hydrograph response (Singh 1997). Singh concluded that high peaked and steep hydrographs occur when the storm path and river flow are in the same direction and reported no significant difference in hydrograph peak generated from a long duration storm with spatial and temporal variability.

Most previous water quality research fails to acknowledge the temporal and spatial variability of rainfall within a watershed (Chaubey et al. 1999). Ideally, rainfall is measured throughout and surrounding the entire study area but the distribution density of the weather network and sampling stations is usually sparse. Measurements are needed outside of a study area because interpolators tend to perform poorly at and beyond the geographic extent of the network area. In a large watershed, accurate representative rainfall measurements are difficult to obtain because of the ephemeral nature of storms and their distribution.

The timing of precipitation in relation to pesticide application determines the quantity and phase of remaining pesticide available for transport. Blum et al. (1993) showed a relationship between the amount of precipitation and the amount of atrazine found in rivers. The availability of atrazine on surface soil just after application was the prime reason for its mobility during precipitation runoff. A series of small runoff events, usually shortly after herbicide application, dominate herbicide transport (Shipitalo and Owens 2006). Information on rainfall intensity and distribution as well as transient infiltration rate increases the predictability of instantaneous and total herbicide losses during a precipitation event (Zhang et al. 1997).
A study of the effect of rainfall pattern and soil water content on atrazine and metolachlor losses in runoff revealed that rainfall pattern influenced dissolved herbicide losses from soils (Zhang et al. 1997). Rainfall simulation at 125 mm h\(^{-1}\) for 10 min produced the largest herbicide loss in a Cecil sandy loam, compared to less intense rainfall patterns. Herbicide losses were positively related to runoff volumes and partition coefficients, implying greater losses in wet and clayey soils (Zhang et al. 1997). A 1978 review on pesticide losses in runoff waters from agricultural fields indicated that total pesticide loss is typically not more than 0.5% of the amount applied, unless severe rainfall conditions occur within 1-2 weeks after application (Wauchope 1978).

### 2.3. Stream Order

Fluxes in streams vary in magnitude over time and therefore pesticide loading is likely to have temporal variability and skewed loading distributions. Watershed size and stream order (classification of the relative location of a reach within a larger river system) influence pesticide concentration. Ephemeral pesticide peak concentrations in low-order streams (typically intermittent streams and wetlands) act in concert with hydrologic response. High-order (larger) streams have higher hydrograph with several streams. These streams are less likely to have peak pesticide concentrations at the same time and therefore have slow chemograph fluctuation with extended mid-range chemical concentration (Solomon et al. 1996). Pesticide concentrations in higher-order streams can also decrease because of presence of pre-storm water in downstream channels (Baker and Richards 2000).
2.4. Soil Characteristics

Off-site movement of pesticides is largely determined by soil characteristics such as texture, organic matter (SOM) content, pH, and soil microbial populations (Devlin et al. 2008). Soil texture is a measure of the proportion of sand, silt, and clay particles making up the <2.0 mm soil fraction (Soil Survey Staff 1993). Coarse-textured soils have a limited capacity to adsorb pesticides compared to fine-textured (clayey) soils. Expanding clays, such as montmorillonite, provide greater surface area for pesticide adsorption than non-expanding clays, such as kaolinite. As a result, more pesticide is available for transport via particles carried with runoff water. Compared to sand and silt, SOM and clay have greater surface areas and more sites for pesticide adsorption. In many soils, pesticide retention is primarily controlled by SOM but clay mineralogy and content are very important, especially when SOM content is low. Organic matter content also influences the rate of biotic degradation because it supports microbial communities.

Soil pH can have a major influence on the activity of microbial populations, the fate of pesticides sensitive to acid or alkaline hydrolysis, and the potential for acidic pesticides to form anions at a pH above their pKa values or for basic pesticides to form cations below their pKa values (Devlin et al. 2008). At typical agronomic pH levels, the surfaces of most soil colloids and soil organic matter are negatively charged. As pH decreases, atrazine becomes protonated (pKa = 1.7; Ahrens 1994) and its adsorption increases as it binds to negatively charged soil particles and organic matter.

The saturated hydraulic conductivity (K_{sat}) of a soil is a measure of water movement when the soil is saturated. It depends on the intrinsic permeability of the soil, which is a function of soil texture and structure. Soils with smaller K_{sat} values are less
permeable and more prone to pesticide runoff, especially if rainfall occurs shortly after application (Devlin et al. 2008).

In the Midwestern U.S., approximately 4 million ha of claypan soils (soils having a dense and fine-textured subsoil horizon with high clay content) are found (Doolittle et al. 1994). Claypan soils have low saturated hydraulic conductivity, significant runoff potential (Ghidey et al. 2010), and also have a tendency to seal when saturated. The amount of clay and thickness of the clay layer have a large influence on pesticide movement via surface runoff or leaching. Herbicide concentrations were significantly lower in samples from wells in areas with a thick clay layer than those from wells in areas with thin overlying clay layers (Kalkhoff et al. 2000). Herbicide concentrations also decreased with increasing depth in the alluvial aquifers.

Sorption and desorption play a key role in the fate and transport of pesticides. Sorption is a broad term which may include adsorption, desorption, and absorption. The phenomenon is termed adsorption if an adsorbate solute clings to a solid surface and absorption if molecules dissolve within a phase. Organic matter and clay minerals can adsorb atrazine via Van der Waal attractions, ligand exchange, and hydrogen bonds (Shea 1989; Davies and Jabeen 2003). At a low pH atrazine protonates, thereby increasing its potential to adsorb to negatively charged clay minerals and organic surfaces, and ionic bonds may form. Atrazine sorption is strongly correlated with soil organic carbon (Novak 1999) and varies with surface area, surface charge density, and clay particle size. Laird et al. (1994) suggested that atrazine retention by silicate clays is mainly due to physical sorption while sorption by soil organic matter is both physical and chemical. The organic matter present in soil clay (11% organic matter) provided 68% of the affinity for atrazine.
Therefore depressions in fields, floodplains with poor drainage are likely to retain more atrazine because of high deposition of organic matter in them. In a study on Iowa glacial till soils, Novak (1999) found that the high amount of soil organic carbon present in potholes increases atrazine adsorption, significantly reducing loss.

Mathematical equations have been developed to quantify pesticide sorption on soils. The most widely used sorption isotherm is Freundlich equation:

\[ S = K_f C^{1/n} \]  

(1)

where \( S \) is the sorbed concentration; \( C \) is the solution concentration at equilibrium; and \( K_f \) and \( 1/n \) are equilibrium constants for a given soil-water matrix.

Desorption is the process by which the adsorbed chemical leaves the adsorbent surface and becomes available for off-site movement. Although herbicide adsorption and desorption isotherms are both often well-described by the Freundlich model, deviations can occur between the rate of adsorption and desorption because some of the compound is strongly and sometimes irreversibly bound to the surface. The compound may also be physically trapped within interlayer matrices. This phenomenon is known as hysteresis. Hysteresis is affected by factors such as soil type, properties of organic matter, clay mineralogy and content, and incubation time (Ma et al. 1993). Most herbicide sorption studies are focused on adsorption kinetics and more research is needed to fully understand desorption processes, which are critical to the availability and fate of pesticides in soil.
2.5. Tillage

Tillage practices modify the environment of the upper soil profile. Although tillage aerates soil, it disrupts soil cover and the aggregate stability of soil particles. Alterations in water potential also occur due to changes in the porous network of macropores within the soil profile. Under conventional tillage, a sealed surface may form in high clay soils when the soil becomes saturated. This impedes infiltration and contributes to increased runoff.

In contrast, conservation tillage practices such as zero tillage (no-till) and minimum tillage do not disrupt or only minimally disrupt the soil cover, thereby leaving crop residue on the soil surface which acts as a mulch. The protective layer helps to reduce soil erosion from wind and water, conserve soil moisture, increase water infiltration, and reduce surface runoff, which generally reduces the loss of agrochemicals through surface runoff.

Although rainfed studies, such as that of Solomon et al. (1996), suggest reduction in atrazine load in surface runoff from fields under conservation tillage, the literature concerning herbicide loss in conservation tillage is mixed. Sauer (1987) found that runoff losses of surface-applied pesticides under conservation tillage seldom exceeded those from conventional tillage. In a small-scale simulated rainfall experiment, Myers et al. (1995) reported a higher percentage of atrazine loss in no-till than from conventional tillage, although the atrazine concentration was higher under conventional tillage. Multiple factors contribute to the impact of tillage on pesticide loss from fields and rainfall may override the influence of other variables. Shipitalo and Owens (2003)
concluded that the timing of runoff-producing rainfall relative to atrazine application has a greater influence on loss of atrazine, DEA, and deisopropylatrazine (DIA) than does tillage practice.

2.6. Seasonality and Temporal Patterns

Pesticide concentration in waterways varies with time and cropping season. During the cropping season, a covariant relation is observed between stream flow and atrazine concentration (Stueber et al. 2003). High pesticide concentrations may persist during the cropping season and exceed the health-based limits. Ephemeral peak pesticide concentrations are primarily observed in small streams, whereas elevated pesticide concentrations are often more sustained in large rivers. During the non-runoff season pesticide concentrations usually dissipate to low concentration. Temporal trends in pesticide concentrations are affected by factors such as pesticide type, tillage, application timing, precipitation-runoff events, hydrology, and crop management (Frey 2000). Multiple temporal scales for pesticide concentrations can be attributed to corresponding storm event signatures and rainfall patterns. Most field scale studies related to pesticide runoff report the first runoff event after pesticide application as critical because that event produces the maximum chemical concentration. Heavily used pesticides such atrazine and metolachlor were detected in low concentrations (< 0.5 µg L⁻¹) in 76% of sampled waters in low streamflow conditions during fall measurements (Goolsby and Battaglin 1995). Field studies in the Loess Hills of southwestern Iowa revealed a complex mechanism in which melting snow during the early cropping season displaces highly
persistent herbicides from agricultural fields and generates runoff (Steinheimer and Scoggin 2000).

2.7. Atrazine Fate and Transport

Atrazine retention in soil is controlled by soil pH (generally increasing as pH decreases), soil organic matter and clay content, atrazine concentration, available soil water, soil temperature, and atrazine concentration (Laird and Koskinen 2008). Atrazine persistence increases in soils with a higher pH and increases the potential for herbicide movement with surface runoff. Hiltbold and Buchanan (1977) reported that with each unit increase in pH, atrazine persistence increased up to 29 days in a Decatur silt loam. Similarly, Kells et al. (1980) examined the relationship between surface pH and atrazine dissipation and found a slower atrazine degradation rate in surface soils with pH greater than 6.5. However, Mueller et al. (2010) found accelerated atrazine degradation as pH increased (at pH 5.2 half-life was 7.1 d in the field and 11.2 d in the laboratory; at pH 7.0 half-life was 4.5 d in the field and 2.7 d in the laboratory). This was likely due to an increase in microbial degradation. From an environmental standpoint accelerated degradation of atrazine means less availability of atrazine and reduced atrazine loading into surface waters.

Landscape position also influences atrazine transport. The aspect of the terrain determines the direction of gravitational flow. Subsurface flow is common in landscapes with flat to gentle slopes, whereas overland flow may be more prevalent in areas with steep slopes, as in hills and valleys (Devin et al. 2008).
CHAPTER 2

3. MATERIALS AND METHODS

This study uses available information to discern the interactions of physical, hydrologic, and land use characteristics of the Blue River Basin (BRB) and their associations with atrazine concentrations measured at stream sampling stations. GIS tools were used in the analysis because of the spatial nature of the data. Data were obtained from various sources with multiple temporal and spatial scales.

Specific atrazine use data were not available but information based on general use statistics suggests that the application rate was relatively constant for the study period (Franti et al. 2009). The expected application rate for atrazine in corn and sorghum is approximately 1.0 kg a.i. ha\(^{-1}\) and 1.49 kg a.i. ha\(^{-1}\) (Franti et al. 2009).

3.1. Study Area

The Big Blue River is the subject of an interstate water quality conflict. The Kansas-Nebraska Big Blue River Commission was created in 1971 to administer the Big Blue River Interstate Compact. The purpose of this commission is to “promote interstate comity and equitable apportionment of waters in the river basin, to promote orderly development of water resources, and to continue active water pollution abatement programs in the party states.”

The BRB is a 2,509,700 hectare agricultural watershed in southeastern Nebraska (Figure 1). Tuttle Creek Reservoir, which drains the entire watershed, has an area of
5,666 ha. It is a primary source of drinking water for Lawrence, Topeka, and Kansas City, (KS and MO). Mean annual rainfall for the watershed is approximately 68 cm (26.8 in; http://hprcc.unl.edu). As of 2009 there were 25,568 wells registered within the BRB, of which 83% are used for irrigation (NDNR, 2010).

The Tuttle Creek Lake Interstate Watersheds Grants Project lists water quality in Tuttle Creek Lake as impaired [Kansas Section 303(d) listing] and has set total maximum daily loads (TMDLs) for sedimentation, eutrophication, atrazine, and alachlor because of incoming runoff from cultivated cropland in Nebraska and Kansas. There is a need to properly target management practices in the BRB that will mitigate pesticide and sediment loss in surface runoff.
Figure 2: Geomorphology of the Blue River Basin.
The main rivers in the study area include the Big Blue (1,481,000 ha), the Little Blue (106,400 ha), and the Black Vermillion River (860,000 ha), and their tributaries. The study area comprises seven 8-digit Hydrologic Unit Codes and three Natural Resource Districts: the Little Blue, Upper Big Blue, and Lower Big Blue (Table 1).

**Table 1:** USGS Hydrologic Unit Codes (HUC) of the major rivers in the Blue River Basin ([http://water.usgs.gov/GIS/huc.html](http://water.usgs.gov/GIS/huc.html)).

<table>
<thead>
<tr>
<th>HUC Code</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>10270201</td>
<td>Upper Big Blue, Nebraska</td>
</tr>
<tr>
<td>10270202</td>
<td>Middle Big Blue, Nebraska</td>
</tr>
<tr>
<td>10270203</td>
<td>West Fork Big Blue, Nebraska</td>
</tr>
<tr>
<td>10270204</td>
<td>Turkey, Nebraska</td>
</tr>
<tr>
<td>10270205</td>
<td>Lower Big Blue, Kansas/ Nebraska</td>
</tr>
<tr>
<td>10270206</td>
<td>Upper Little Blue, Kansas</td>
</tr>
<tr>
<td>10270207</td>
<td>Lower Little Blue, Kansas</td>
</tr>
</tbody>
</table>

Agriculture is the predominant land usage in the BRB. More than 70% of the Nebraska watershed area is used for growing corn, soybean, wheat, and grain sorghum. The watershed area in Kansas is mostly under the Conservation Reserve Program (CRP), wheat, and sorghum. During the study period an estimated 90% of sorghum and 85% of corn acres were treated with atrazine, most frequently as a preplant or preemergence application. The average annual use rate was about 1.1 kg a.i. ha⁻¹. During the study period there was a transition of cropland from conventional to conservation tillage.
Terrain in the BRB is relatively flat in the north and north-west with slopes typically less than 3% while slopes occasionally exceed 10% in the southern and south eastern areas of the basin. The Pre-Wisconsinan Glacial Limit (Aber and Apolzer 2004) divides the BRB (Figure 2). In the southern portion of the BRB clay till appears at the surface east of the glacial moraine while bedrock outcrops appear west of moraine.

The Nebraska Rainwater Basins (Figure 2) extend into the northern portion of the BRB. The slowly permeable Massie, Fillmore, Scott, or Butler soils are associated with the rainwater basins that provide habitat for several migrating birds, including some endangered species when the basins are not drained for crop production. Rainwater basins, known for their groundwater recharge potential, are shallow, elliptical, southwest to northeast trending depressions believed to have been formed by eroding glacial winds at the end of a Pre-Wisconsinan ice age. Rain and melting snow are the sources of water in these basins.

The upland surrounding the rainwater basins is intensely cropped, mostly to corn and soybean, and is facilitated by center pivot irrigation (Gordon et al. 1993). The rainwater basin can be point sources of pollution because agricultural contaminants from neighboring fields are collected in these depressions. Depth to groundwater in the rainwater basin is shallow (≤ 61 m). Agricultural contaminants have been detected in these wetlands, with atrazine concentrations as high as 10 µg L⁻¹ (Foster 2010).
3.2. Location of Sampling Stations

Precise locations of the sampling stations were necessary to accurately delineate watershed and subwatershed boundaries. The Joint State Atrazine Monitoring Project only reported sampling locations to the nearest second which is not very precise (i.e., plus/minus one second of longitude or latitude in the BRB represents tens of meters). Locations were rectified by hand digitizing using Digital Orthophoto Quadrangles (DOQs) as reference. The DOQs have 1-m ground resolution and meet National Map Accuracy Standards at 1:12,000. Coordinates were imported into ArcGIS (ESRI, Redlands, CA) and the georeferenced coordinates were exported as a point shapefile in ArcGIS.

3.3. Atrazine Loading Data

An EPA-funded Joint State (Kansas and Nebraska) Atrazine Big Blue River Monitoring Project was created to monitor spatiotemporal patterns of pesticides in the Blue River Basin from 1997 to 2004. Fixed weekly sampling was conducted in April through September during the study period and single samples were taken in each winter month. Figure 3 shows the locations of the sampling stations, represented by red and yellow triangles. The red triangles are grab sample locations and the yellow are automatic samplers. Table 2 lists the approximate geographical positions of the sampling stations.

Event sampling was conducted in sites 4, 5, 6, 8, 12, 13, 15, 18, and 19 and grab samples were collected by dipping a sample bottle near the centroid of flow at the remaining monitoring sites. Stream flow readings at the sampling stations were obtained from the web interface of USGS National Water Information System. The data set
includes 3,705 atrazine measurements across all subwatersheds with a mean size of 122,459 ha.

A flow-weighted composite stream water sample is formed by selecting discrete stream water samples. Analysis of composite sample produces mean herbicide concentrations for an entire storm. Using composite sample concentration and recorded flow volume, herbicide mass transport was computed. Herbicide loads were calculated by multiplying the concentration times the discharge estimate for the composite sample:

\[
\text{Herbicide load (g)} = \text{Concentration in composite sample (g L}^{-1}) \times \text{Discharge (m}^3 \text{ s}^{-1})
\] (2)
Figure 3: Locations of sampling stations; blue triangles represent automated sampling stations and red triangles represent grab sampling stations.
Table 2: Coordinates of sampling stations, their drainage areas, and areas as percent of the Blue River Basin.

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Coordinates</th>
<th>Site Location</th>
<th>Drainage Area (ha)</th>
<th>% of Basin</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>39°15'03&quot;N 96°34'55&quot;W</td>
<td>Big Blue River at Tuttle Creek, KS</td>
<td>247,806</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>39°41'03&quot;N 96°26'15&quot;W</td>
<td>Black Vermillion River at Frankfort, KS</td>
<td>106,353</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>39°50'31&quot;N 96°39'39&quot;W</td>
<td>Big Blue River at Marysville, KS</td>
<td>85,974</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>39°46'33&quot;N 96°51'29&quot;W</td>
<td>Little Blue River at Barnes, KS</td>
<td>57,932</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>39°48'50&quot;N 97°02'20&quot;W</td>
<td>Mill Creek at Washington, KS</td>
<td>90,514</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>39°58'48&quot;N 97°00'16&quot;W</td>
<td>Little Blue River at Hollenberg, KS</td>
<td>103,672</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>40°06'54&quot;N 97°10'13&quot;W</td>
<td>Little Blue River at Fairbury, NE</td>
<td>200,477</td>
<td>8</td>
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<tr>
<td>10</td>
<td>40°14'06&quot;N 97°23'20&quot;W</td>
<td>Big Sandy Creek at Alexandria, NE</td>
<td>156,200</td>
<td>6</td>
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<td>11</td>
<td>40°19'58&quot;N 98°04'00&quot;W</td>
<td>Little Blue River near Deweese, NE</td>
<td>253,047</td>
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<td>12</td>
<td>40°02'40&quot;N</td>
<td>Big Blue River at Barneston, NE</td>
<td>90,225</td>
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<tr>
<td></td>
<td>Latitude</td>
<td>Longitude</td>
<td>Location</td>
<td>Value</td>
</tr>
<tr>
<td>---</td>
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<td>----------------</td>
<td>-----------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>13</td>
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<td>Big Indian Creek at Wymore, NE</td>
<td>52,916</td>
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<tr>
<td>14</td>
<td>40°15'22&quot;N</td>
<td>96°44'47&quot;W</td>
<td>Big Blue River at Beatrice, NE</td>
<td>189,066</td>
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<td>15</td>
<td>40°28'48&quot;N</td>
<td>97°00'43&quot;W</td>
<td>Turkey Creek near Wilber, NE</td>
<td>114,952</td>
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<td>16</td>
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<td>96°57'33&quot;W</td>
<td>Big Blue River near Crete, NE</td>
<td>105,835</td>
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<td>17</td>
<td>40°43'52&quot;N</td>
<td>97°10'38&quot;W</td>
<td>West Fork Big Blue River near Dorchester, NE</td>
<td>136,350</td>
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<td>18</td>
<td>40°47'49&quot;N</td>
<td>97°20'56&quot;W</td>
<td>Beaver Creek near Beaver Crossing, NE</td>
<td>72,054</td>
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<td>19</td>
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<td>West Fork Big Blue River near Lushton, NE</td>
<td>102,618</td>
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<td>20</td>
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<td>Big Blue River at Seward, NE</td>
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<td>Lincoln Creek near Seward, NE</td>
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<td>22</td>
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<td>97°18'35&quot;W</td>
<td>Big Blue River at Surprise, NE</td>
<td>88,044</td>
</tr>
</tbody>
</table>
Section 305(b) and 305(d) of the Clean Water Act (CWA) require each state to report the quality of all water resources and identify impaired water bodies. The TMDL guideline is a strategy for allowing the maximum amount of a pollutant that may be present in water to safely meet water quality standards. A TMDL is calculated as:

\[
\text{TMDL} = \text{WLA} + \text{LA} + \text{MOS}
\]

where WLA is the waste load allocations for point sources, LA is the load allocation for nonpoint sources and naturally occurring background sources, and MOS is the margin of safety for uncertainty and any lack of knowledge concerning the relationship between effluent limitations and water quality.

Daily atrazine load at the sampling stations is calculated by multiplying discharge by atrazine concentration in the samples (Equation 2). A load duration curve is widely used in water quality studies to characterize water quality impaired by point and nonpoint sources. The load duration curve provides a visual illustration of the relationship between stream flow and contaminants, showing the frequency and magnitude of water quality standard exceedances. The curve has been adopted because it relates water quality impairments to flow conditions, which provides an understanding of key watershed processes and facilitates TMDL development and best management practices (BMP) implementation (Cleland, 2003). The load duration curve can also help distinguish point and nonpoint pollution. Pesticide loads above the curve represent water quality impairments above environmentally acceptable levels. The pollutant is considered point source if the observed loads in the water flow exceeds the curve more than 85% of the
time and nonpoint source if the observed loads are above the curve for 10-70% of the time (KDHE 2010).

The Barneston and Marysville sampling stations received the highest atrazine loads. Atrazine concentrations at these sampling stations were compared on an event basis and the data were used to calculate TMDL and load curve based on Kansas Department of Health and Environment methodology (Hargrove et al. 2002). Samples not taken on the same day were omitted for generating load duration curve as the atrazine load may vary on a daily basis due to variations in streamflow and rainfall. During June and July, the Barneston and Marysville stations had atrazine loading that frequently exceeded the Kansas TMDL for drinking water. These areas have significantly more sorghum area than other parts of the watershed. Much of the area contains a restrictive layer and bedrock on the surface of cropped land. Over the years farmers have switched from conventional tillage to no-till or minimum tillage. Sorghum is typically planted in marginal lands where corn cannot be grown profitably. Also, sorghum is usually planted later than corn. Compared to tilled fields, atrazine application to no-till sorghum increases the potential for atrazine runoff when rainfall events are intense (P. L. Barnes, personal communication, June 10, 2009).

Figures 4-6 show there is consistent exceedance of the TMDL in atrazine concentrations in the study area. Aside from drinking water concerns, these exceedances coincide with critical development stages of surface water aquatic species (Adelman and Stansbury 2007). Improving water quality in these areas is a challenge because the
headstream area for these drainage points are dominated by irrigated corn farming with prevalent atrazine use.
Figure 4: Atrazine concentration as a function of flow in m\(^3\) sec\(^{-1}\) at Barneston, NE and Marysville, KS from 1997 to 2004.
**Figure 5**: Load duration curve for Barneston, Nebraska.
Figure 6: Load duration curve for Marysville, Kansas.
3.4. Spatial Database

A spatial database for the BRB was assembled from several sources for identifying the most critical factor responsible for surface runoff of atrazine. ArcGIS utilizes Geodatabase, a special data storage and management framework. Geodatabase can accommodate attribute data, geographic features, GPS coordinates, and topology. Advancements in ArcGIS have improved the capability of ArcGIS to store and handle data and manage data framework. A file Geodatabase was created to import all of the tabular data. A File Geodatabase offers advantages over a Personal Geodatabase in ArcGIS, including no file size limitation, raster (grid) storage, and better data management. All data layers were projected in the Universal Transverse Mercator (UTM) Zone 14, North American Datum, 1983.

3.5. Land Use

Information on land use in the BRB was obtained from the USDA-NASS 2006 Cropland Data Layers (CDL) for Kansas and Nebraska (Figure 7). The CDL is available to download from the NRCS Geospatial Data Gateway. The CDL grid is georeferenced imagery from Resourcesat-1 AWiFS and the Landsat 5 TM satellites. The CDL for the study area is based on Resourcesat-1 AWiFS and has a resolution of 56 m pixels in the Universal Transverse Mercator projection. The CDLs are distributed by state but are “seamless” and can be merged for interstate analysis (USDA-NASS 2007). The CDL for Kansas was first available in 2006 which means the cropland characterization does not explicitly match cropland during the pesticide sampling period. For the analysis, Nebraska and Kansas CDL for 2006 were merged into a single raster. A raster is a spatial
data model with group of equal sized cells arranged in rows and columns containing attribute value and spatial information for a geographic feature (Wade and Sommer 2006). An ArcGIS raster calculator was used to clip the grid to the BRB boundary. Clipped grids were reclassified into croplands and non-agricultural lands. Values for non-agricultural lands were set to null so that the final grid only contained the footprint of agricultural land. Only cropped areas were included because most of the atrazine application is associated with cropland. The advantage of using a raster is that each pixel associated with a crop layer can be treated as a unit for atrazine interaction with soil. NASS does not encourage calculating agricultural land from pixel counting of the CDL because not all of the pixels are classified correctly (Table 3). However, to obtain a rough estimate of cropland area, pixel counting was used to calculate $2.39 \times 10^7$ ha of corn and $1.21 \times 10^6$ ha of sorghum in the BRB.

**Table 3:** Attribute accuracy report (USDA-NASS 2007).

<table>
<thead>
<tr>
<th>State</th>
<th>Crop</th>
<th>Producer Accuracy (%)</th>
<th>Commission Accuracy (%)</th>
<th>Conditional Kappa $^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nebraska</td>
<td>Corn</td>
<td>97.75</td>
<td>4.55</td>
<td>95.12</td>
</tr>
<tr>
<td></td>
<td>Sorghum</td>
<td>51.59</td>
<td>21.44</td>
<td>51.03</td>
</tr>
<tr>
<td>Kansas</td>
<td>Corn</td>
<td>88.85</td>
<td>7.81</td>
<td>91.57</td>
</tr>
<tr>
<td></td>
<td>Sorghum</td>
<td>77.84</td>
<td>18.67</td>
<td>80.17</td>
</tr>
</tbody>
</table>

$^1$Conditional Kappa Coefficient is the maximum likelihood estimate of Kappa coefficient (probability of better classification than that expected by random assignment of classes) for conditional agreement for the $i^{th}$ category.
Figure 7: Land use within the Blue River Basin, USDA-NASS (USDA- National Agricultural Statistical Service) Cropland Data Layer, 2006 (USDA-NASS 2007).
3.6. Soils

Soil Survey Geographic (SSURGO) data (Soil Survey Staff 2009) were obtained from the USDA-NRCS Soil Data Mart (http://soildatamart.nrcs.usda.gov). U.S. soils are generally mapped by county at a 1:12,000 or 1:240,000 map scale. SSURGO provides an estimate of what one might expect to find at the field scale and it is very useful for modeling regional processes related to climate and vegetation. The accuracy of SSURGO data is based on compilation to base maps that meet National Map Accuracy Standards at a scale of 1 cm equals 120 m. A small number of representative samples are analyzed for each soil map unit within a county. A range of soil property values are reported in the SSURGO data tables. Only representative values are reported because soil properties are not necessarily normally distributed.

Each county soil mapping model is based on local dominant soil development factors. Discontinuities of soil properties at county borders were observed in SSURGO data within the study area. Discontinuities are believed to arise because soil mapping and classification were conducted by different soil mapping teams with disparate mapping models over time. This disparity in mapping model can be more pronounced when the local geomorphology is not well understood and significant discontinuities in soil property estimates are observed.

The dominant soils are soil types with the largest percent area within a given county. Predominant soils within the watershed included silt loams, silty clay loams, and clay loams, primarily Wymore silty clay, Pawnee clay, Hastings silt loam, Crete silty loam, and Holdrege silt loam, with slopes ranging from 0 to 30%.
3.7. Elevation (Slope)

Elevation data are needed to compute slopes and delineate boundaries of the BRB subwatersheds. USGS and USGS contractors digitized elevation contour maps into digital line graphs (DLGs), which were then converted into digital elevation models (DEMs). Using DEM, slope can be calculated from uniform grids of cells associated with elevation values in those cells. The elevation data are continually updated as new data becomes available and it is now referred to as National Elevation Data (NED). The original intent was to calculate DEMs from the digital contour files, but USGS lost some of the Kanas DLG files. Ten m resolution NED files were downloaded by county from the USGS Seamless Data Warehouse (http://seamless.usgs.gov) in 2008 and were merged.

DEMs must abide by National Map Accuracy Standards (NMAS). NMAS requires 90% of all points tested to be accurate within 1/50th of an inch (0.05 cm) on the map. At 1:24,000 scales, 1/50th of an inch is 40 feet (12.2 m). The vertical accuracy standard requires that the elevation of 90% of all points tested must be correct within half of the contour interval. The main purpose of including DEM in this study is to delineate subwatershed areas within the study area. The DEM captures terrain detail from which delineation of watersheds can be automated in the GIS platform.

3.8. Watershed and Subwatershed Delineation

As mentioned previously, the BRB consists of 8 HUCs, but in order to analyze the processes associated with each sampling site, a new delineation was developed. Watershed and subwatershed are spatial reference units that facilitate study of processes
involving water quality, sediment transport, and soil erosion. DEMs are now being extensively used in automated catchment delineation in a GIS platform because of their capacity to model terrain and capture details spatially. The availability and affordability of powerful computer processors and the wide availability of high resolution DEMs has been an added advantage. Most GIS systems have the capacity to automate watershed delineation using DEMs. Areas contributing to runoff and pesticide load can be easily identified based on terrain. With this information, sediment load can be calculated per unit land. This helps in prioritizing the watershed in terms of vulnerability and for targeting best management practices to the vulnerable areas.

Characterizing upstream contributing areas for downstream water quality assessment is very common and watersheds can provide a good framework for many environmental studies (Kolok et al. 2009). Boundaries of contributing drainage area for each sampling station were delineated from a 10-m DEM using an interactive batch delineation method in Arc Hydro Tools version 1.3 Beta in ArcGIS 9.2 (ESRI, Redlands, CA). Interactive batch delineation method was very sensitive to the location of the sampling site. Sampling stations were specified as drainage points and their corresponding contributing runoff areas were identified. The delineated areas contribute to the water quality of the corresponding sampling station. The time required for watershed delineation is grid size dependent. A grid size of 10 m was used for the delineation process.
3.9. Rainfall

Estimates of rainfall by event and subwatershed were made from serially complete rainfall data (You forthcoming) were obtained from the University of Nebraska-Lincoln High Plains Regional Climate Center (HPRCC). Rainfall is measured using the tipping bucket method.

Runoff from landscapes is determined by soil type, its saturated hydraulic conductivity, the presence and depth of a restrictive layer, soil water content, and the intensity and duration of rainfall. The purpose of estimating rainfall is to obtain an understanding of the amount of rainfall received in the watershed and to extract daily mean rainfall values on a subwatershed level. Thirty-nine National Weather Service Cooperative Observer Network (COOP) weather stations distributed throughout and surrounding the study area were selected for the analysis (Figure 8). Using a python script in ArcGIS 9.3, seasonal events that exceeded 0.64 cm at any station between April 1 and September 30 were interpolated by inverse-distance weighting and the average rainfall received in each subwatershed was computed and saved. The presence of too many low magnitude rainfall events were deemed insignificant and eliminated from the analysis.
Figure 8: Locations of National Weather Service Cooperative weather stations.

Irmak et al. (2010) found no significant difference between interpolation techniques (inverse distance weighted, spline, and kriging) in predicting the 30-year climate data in Nebraska. Interpolated precipitation values were compared with measured precipitation values at three AWDN stations for validation (Figure 9).
Figure 9: Locations of the Automated Weather Data Network (AWDN) stations within the Basin.

Rainfall values for three AWDN stations within the study area at York, Red Cloud, and Beatrice, Nebraska for April 15, 2004 to September 30, 2004 were plotted against their associated subwatershed values (Figures 10-12). Estimated subwatershed rainfall cumulative values correlated well with those of cumulative rainfall measured at the nearest AWDN stations ($R^2 = 0.95$, $p < 0.0001$).
**Figure 10:** Trend analysis of AWDN point measured rainfall and the corresponding estimated subwatershed rainfall at York, Nebraska.

**Figure 11:** Trend analysis of AWDN point measured rainfall and the corresponding estimated subwatershed rainfall at Beatrice, Nebraska.
Figure 12: Trend analysis of AWDN point measured rainfall and the corresponding estimated subwatershed rainfall Red Cloud, Nebraska.

3.10. Soil Water Content Interpolation

Because antecedent soil water content can determine whether a rainfall event will induce runoff, daily volumetric water content was estimated from the NWS cooperative stations using Hybrid-Maize (Yang et al. 2004), a corn growth simulation program. The program is mainly intended for use in rainfed and irrigated corn fields of the U.S. Corn Belt. An unpublished version of Hybrid-Maize was used to calculate daily soil water content because it includes more soil texture classifications. Hybrid-Maize inputs include precipitation, temperature, soil texture (surface and subsurface), bulk density, initial soil moisture, seed variety, planting and maturity dates, rooting depth and population. A dominant soil from the county in which each NWS cooperative station is located was identified and surface soil texture and bulk density of that soil were inputted into Hybrid-
Maize. Hybrid-Maize assumes that germination only initiates when soil temperature reaches 10 °C. So temperature values obtained from HPRCC were adjusted to fit the temperature requirement to run Hybrid Maize, i.e. minimum and maximum temperatures of 7 and 10 °C. Soil water content estimation was initiated from the 85th day of each calendar year. To run Hybrid-Maize, corn hybrid Pioneer was chosen as the seed variety, 4 cm as the planting depth, 1,389 as the number of growing degree days, and 74,100 as the plant population per ha (personal communication, Mark L. Bernards, March 18, 2011). Soil texture and corresponding bulk density were assigned based on predominant values in the SSURGO data for each cooperative station location.

The python script used to estimate average precipitation by subwatershed was also used to estimate soil water content, but for this variable ordinary kriging was used because it produced the lowest root-mean-square and average standard error for the interpolators examined. Ordinary Kriging is a geostatistical approach for estimating values based on the spatial correlation structure of the data.

Among several spatial analyst tools in ArcGIS, Zonal Statistics and Zonal Statistics as Table summarize the value of raster within the zones of another dataset such as subwatershed boundaries in raster and tabular format. The shapefile for each subwatershed was provided as the input feature with subwatershed name as the field name in Zone field input for Zonal Statistics and Zonal Statistics as Table. Daily mean soil water content was generated for each subwatershed. Zonal Statistics as Table was used in a similar format to generate the daily soil water content mean of the subwatershed in a tabular format so that it could be readily imported for statistical analysis.
3.11. **Crop Planting Progress Data**

Although postemergence applications may be made, most of the atrazine is typically applied to corn and sorghum preplant or at planting time. Information on crop planting progress within a region allows a rough estimate of the extent of atrazine application with time. Information on crop planting dates and area planted was acquired from the USDA Risk Management Agency (USDA-RMA). The USDA-RMA reports area planted with crops (corn, sorghum, soybean, and wheat) on a county scale.

With the acquired data, dates for 10, 50 and 90% completion of crop planting were identified. This provides insight into field conditions and ease of operating farm equipment in the fields during a planting season. The 50% planted point provides a general characterization of planting date.

County-based information needed to be incorporated into subwatershed level data. In ArcGIS the percentage of corn and sorghum planted (10, 50, and 90%) in each county and corresponding dates (DOY) was assigned to each county’s centroid location. From the centroid locations, dates for crop planting progress (10, 50, and 90%) for subwatersheds were calculated by ordinary kriging interpolation. Reported planting dates were not continuous and curve-fitting was used to estimate area planted for specific time intervals. In SigmaPlot (Systat Software, Inc., Chicago, IL), planting dates in day of year were plotted on the x axis and percent of each crop planted in y axis. A sigmoidal curve was fitted to the data and used to estimate crop planting progress and its corresponding planting dates for each cropping season.
3.11.1. Crop planted area

County-level crop planting (corn, soybean, and sorghum) was obtained from NASS annual county report. Crop planted area in each subwatershed was estimated using the ordinary kriging interpolation in ArcGIS. Centroids for each county were first generated in ArcGIS using the “Feature to Point” command.

In ArcGIS the percentage of corn, sorghum, and soybean planted for each county was assigned to their centroid locations. The crop percent value for the centroid was interpolated using ordinary kriging. Before executing the interpolation, the working environment was set up in Spatial Analyst to limit the extent of the interpolated grid to the extent of the basin boundary. Separate rasters were generated for corn, soybean, and sorghum. A shapefile for each subwatershed was provided as the input feature with the name of the subwatershed as field name in Zone field input for Zonal statistics. The mean of the percentage of each crop planted for each subwatershed was generated. Zonal Statistics as Table was used in a similar format to generate mean of percent crop planted for the subwatersheds in a tabular format so that it could be readily imported for statistical analysis.

A second way to estimate crop areas within each subwatershed is using the NASS Cropland Data layer (CDL). A CDL is not available for Kansas prior to 2006. Therefore, the CDL for 2006 was used for both Nebraska and Kansas to estimate area of cropped hectares within each subwatershed. Cropland area refers to the area used for cultivation of corn, soybean, and sorghum. In ArcGIS subwatershed boundaries were used to calculate cropland area within each subwatershed. Although NASS does not encourage
pixel counting because counting pixels and multiplying by the area of each pixel will result in biased area estimates, it provided an estimation of cropland area (each pixel was $56 \times 56$ m). The estimated cropland area was compared with interpolated cropland area from NASS county reports. The mean of cropland area for each subwatershed for the eight years of the study was plotted against pixel counted cropped area for each subwatershed for year 2006 ($R^2 = 0.73$) (Figure 13). Correlation suggests both methods estimate a similar cropland area in each subwatershed.

**Figure 13:** Comparison of interpolated crop area from NASS County with NASS CDL crop area.
3.12. **Restrictive Layer**

Criteria were developed to identify common properties associated with the Rainwater Basin soils in Nebraska and claypans of Missouri, using several variables within the SSURGO horizon data. Criteria used to categorize a restrictive layer include smectitic clay mineralogy, the presence of free water, soil drainage, $K_{sat} \leq 1 \, \mu\text{msec}^{-1}$, clay $\geq 35\%$, and horizon thickness $\geq 20 \, \text{cm}$. These criteria were applied to both Missouri claypans and rainwater basins in Nebraska, which successfully identified fragipans, pre-Illinoisan till restrictive layers known to seep when exposed to side slopes.

3.13. **Statistical Analysis**

As water flows downstream, addition, dilution, adsorption, degradation and other losses of atrazine can occur. Modeling those processes was beyond the scope of this project. Therefore statistical analysis was limited to independent subwatersheds to avoid a headstream effect. Data from five independent subwatersheds from the Big Blue, four from the Little Blue and one from the Black Vermillion, were included in the analysis (Figure 14).
Figure 14: Independent subwatersheds included in the statistical analysis.

Linearity of data and normality of residuals were improved by taking the log of the atrazine weighted by corn and sorghum planted area (log atrazine ha\(^{-1}\)) (Figure 15). The variables associated with atrazine loading were checked for multicollinearity. Cumulative rainfall between atrazine sampling events, soil water content, corn planting progress, sorghum planting progress at each atrazine sampling event, and surface restrictive layer as a function of independent subwatershed were used as explanatory variables.
Figure 15: Residual plots were constructed to check normality and homogeneity of the data.

An analysis of covariance (ANCOVA) was conducted using the PROC GLM procedure (SAS, Cary, NC), in which rainfall between atrazine sampling events, soil water content, corn and sorghum planting progress, and percent area with a surface restrictive layer serve as a reference to account for variation in atrazine loads in the subwatersheds. Year and independent subwatersheds (ISW) were defined as class variables (Table 4).
Table 4: Variables included in the PROC GLM procedure for ANCOVA analysis (SAS, 1999).

<table>
<thead>
<tr>
<th>Class</th>
<th>Levels</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year</td>
<td>8</td>
<td>1997 1998 1999 2000 2001 2002 2003 2004</td>
</tr>
<tr>
<td>ISW</td>
<td>10</td>
<td>4 7 10 11 13 15 18 19 21 22</td>
</tr>
</tbody>
</table>

Number of Observations Read 614
Number of Observations Used 610

ANCOVA was used for this statistical analysis to account for differences in the covariates in the subwatersheds. ANCOVA is conducted to assess how much variance is accounted for in the dependent variable after partialling out the effects of one or more continuous covariates. The following ANCOVA model was constructed to evaluate the associations of the selected variables on area-weighted atrazine load:

\[
\log \text{atrazine ha}^{-1} = \mu + \text{year} + \beta_{RL} + \text{error (a)} + \beta_{1}\text{RNBTE} \\
+ \beta_{2}\text{SM} + \beta_{3i}\text{CPP} + \beta_{4i}\text{SPP} + \text{error (b)}
\]  

where \(\log \text{atrazine ha}^{-1}\) is the log of atrazine load (g ha\(^{-1}\)), \(\mu\) is the mean, ISW is the independent subwatershed, RL is the percent area with surface restrictive layer, RNBTE is the rainfall between sampling events, SM is the soil water content, CPP is the corn planting progress, SPP is the sorghum planting progress, \(\beta\) is the slope coefficient, and error (a) and error (b) are the errors associated with independent subwatersheds and covariates. Year and subwatershed by year were considered random effects. Cumulative rainfall between
sampling events, soil water content, corn planting progress, sorghum planting progress, and percent of cropped area with a restrictive soil layer were treated as covariates.

Type I sums of squares (SS) were used for tests of significance and the slope for restrictive layer was estimated from the model only including terms up to restrictive layer in the model. Type I SS were used because restrictive layer was used as the covariate to explain a portion of the variation across the subwatersheds. The ANCOVA model was fitted to each variable using log of atrazine as the dependent variable, with rainfall between atrazine sampling events, soil water content, corn and sorghum planting progress, year, and surface area restrictive layer as independent variables. Interactions between subwatershed and covariates were also tested.
CHAPTER 3

4. RESULTS AND DISCUSSION

4.1. Scope and Limitations

The objective of the study was to evaluate processes contributing to water quality impairment in a watershed due to surface runoff of atrazine from agricultural fields. Variables included rainfall, soil water content, crop planting progress (indicating atrazine application), and the presence of restrictive layers at the surface. Interrelationships among the variables are complex. We were not able to include the impacts of best management practices, irrigation, tillage type, and specific atrazine application rates and timing. Such factors also contribute to the extent and amount of atrazine in surface runoff. There was no information on surface runoff, interflow, and baseflow of atrazine from the fields. Data for well water quality were not available. Data for DEA, DIA and other atrazine metabolites and transformation products were not available. Inclusion of these variables would strengthen the study and provide a more complete understanding of catchment-scale dynamics and manage agricultural watersheds.

4.2. Atrazine Loading

There are 19 automated and manual stream sampling stations within the BRB (Barnes 2007). If data are segregated by average seasonal atrazine concentrations, the Black Vermillion tributary of the Blue River Basin has an average seasonal atrazine concentration below the $3 \, \mu g \, L^{-1}$ EPA MCL whereas annual seasonal atrazine concentration at Big Blue and Little Blue (Figure 16) exceed $3 \, \mu g \, L^{-1}$. However, the
Black Vermillion frequently had elevated weekly atrazine levels, mostly below 10 µg L⁻¹ unless very high flow conditions occurred (USEPA 2007). In the Little Blue, the MCL was exceeded in 1999, 2002, and 2004, while the Big Blue had annual average atrazine concentrations above the MCL in most years. Streamflow per unit area is greatest in the Big Blue, followed by the Little Blue, and the Big Blue River has the dominant inflow and outflow of water (USEPA 2007).

**Figure 16:** Average seasonal atrazine concentration in the tributaries of the Blue River Basin. The broken black line indicates the EPA MCL for atrazine (3 µg L⁻¹).

The Beatrice, NE station often showed greater atrazine loading compared to the other sampling stations during the study period. As shown in Figure 17, by the time 50% of the
corn was planted, a series of rainfall events increased soil water content and a spring flush followed by a large amount of rainfall washed atrazine from the fields.

*Figure 17:* Weekly atrazine load, cumulative interpolated precipitation, estimated volumetric soil water content, and crop planting trends for the subwatersheds draining the Big Blue River at Beatrice, Nebraska.

The atrazine concentration is highest during spring runoff events (DOY 110 – 170) and steadily decreases with time. Larger atrazine loads also coincide with sorghum planting time. These observations suggest that atrazine found in the streams is coming from both corn and sorghum fields. Monthly average atrazine concentrations were
highest at Beatrice and Barneston, NE, and Marysville, KS (subwatersheds 14, 12, and 5, respectively). The subwatersheds at Beatrice, Barneston, and Marysville are of concern and require careful evaluation because the average measured atrazine concentrations exceeded the MCL by tenfold during each cropping season. This part of the watershed is characterized by marginal land with greater slopes. Sorghum is usually planted in these highly erodible lands and atrazine application in sorghum poses significant risk of surface runoff during precipitation events. In most years, monthly average atrazine concentrations start increasing in early May and by July concentrations decline. However, low atrazine concentrations tend to remain throughout the year. Although the decrease in atrazine in runoff after 2002 may be due in part to increased use of glyphosate-ready corn (personal communication, P.L. Barnes, December 1, 2011), Nebraska Department of Agriculture data (http://www.agr.ne.gov/pesticide/pesticide use trends.pdf) shows atrazine use as relatively constant during the period.

Spring applications of atrazine include preplant, preemergence, and early postemergence in corn and sorghum during April and May. Rainfall during this period can be heavy and produce runoff events. Such continuous precipitation saturates soils and removes some of the surface-applied atrazine. Offsite atrazine transport from crop fields to nearby water bodies has been primarily associated with direct surface runoff from rainwater (Isensee and Sadeghi 1994; Southwick et al. 2003; Warnemuende et al. 2007). Herbicide application rates may not be uniform across cropland within the watershed, as they are determined by soil type, soil texture, and organic matter content. Information on the amount, rate and timing of herbicide applications for each field is needed to better
understand the effects of the variables included in the present study. Unfortunately such data were not readily available due to privacy constraints.

Concentration and stream flow rate vary among the sampling stations. Atrazine loading was used as a response variable for comparisons. (Atrazine loading data were not available for minor tributaries.) Logarithmic transformation of atrazine loading data implies significant differences in measurements from one event to another. There is temporal variation in atrazine found at the sampling stations in the Blue River Basin (subwatersheds 19, 20, and 21). Within a short period after application, some of the atrazine can be washed from cropland into streams in response to precipitation events. Observations from April through September of each cropping season indicate that atrazine loading was higher during late April through early July (DOY 120 – 190) (Figure 18). By the end of July less atrazine is available for transport and there are fewer major precipitation and runoff events. Although concentrations decrease with time, atrazine was frequently detected after the peak measurement. Results from this study are consistent with previous studies showing higher atrazine loading during the first spring storm events with increased stream flow due to rainfall events on the hydrograph (Thurman et al. 1991, 1992; Goolsby and Battaglin 1995). The occurrence of atrazine in stream samples at low concentrations during the late cropping season is due to its heavy use and relative persistence (Goolsby and Battaglin 1995).
Figure 18: Monthly average atrazine concentrations at (a) Beatrice, NE (b) Barneston, NE, and (c) Marysville, KS.
Atrazine loading varied across years (Figure 19), likely due in part to factors such as rainfall, cumulative rainfall before a major rainfall, and soil water content (Capel and Larson 2001). Discussion of relationships between atrazine loading and these variables follows.

**Figure 19:** Seasonal (April 1 – September 30) atrazine load (kg) from 1997-2004 (not area weighted). The blue dotted lines represent mean atrazine loading for each year. The horizontal lines in each boxplot represent the 10th, 25th, 50th, 75th, and 90th percentiles of seasonal atrazine loading, bottom to top.

Examination of atrazine loading across all sampling stations and all years (Figure 20) confirms seasonal trends in atrazine levels, with greatest loading during mid-June
before maximum stream flows are observed. Decreases in load at the sampling stations suggest less available atrazine for transport in the subwatersheds due to its biotic and abiotic degradation and conversion to metabolites and other transformation products.

**Figure 20:** Monthly atrazine load distribution (not area-weighted) in the BRB (1997-2004). Grey dots and blue lines represent outliers and means of atrazine loading. The horizontal lines in each boxplot represent the 10\(^{th}\), 25\(^{th}\), 50\(^{th}\), 75\(^{th}\), and 90\(^{th}\) percentiles of atrazine loading, bottom to top.

Under similar weather conditions, herbicide losses may vary within landscapes due to intrinsic field properties, variable topography, and runoff potential of the soils (Leu et al. 2005). Atrazine loading was greatest at the Big Blue River at Marysville, Barneston, and Beatrice sampling stations (5, 12, and 14, respectively) (Figures. 21, 24, and 26). The Big Blue River at Marysville, KS had the largest median (50\(^{th}\) percentile)
atrazine loading followed by the Blue River at Beatrice and Barneston, NE. The mean and 90th percentiles of atrazine loading were largest at Marysville, KS, followed by Barneston and Beatrice, NE.

Figure 21: Atrazine monitored at each sampling station (not area-weighted) from 1997-2004. Grey dots and blue lines represent outliers and means of atrazine loading. The horizontal lines in each boxplot represent the 10th, 25th, 50th, 75th, and 90th percentiles of atrazine loading, bottom to top.

Maximum event-based (1-day) atrazine loss was 11.3 g ha$^{-1}$ (Figure 25), similar to a field-scale study on atrazine runoff in response to tillage treatments reported on event-
based (1-day) atrazine losses of 0.02-25.4 g ha\(^{-1}\) (Gorneau et al. 2001). Seasonal mean herbicide loss ranged from 0.03 to 0.44 g ha\(^{-1}\) (Table 5).

**Figure 22:** Seasonal distribution of atrazine load weighted by area (g ha\(^{-1}\)).
Table 5: Descriptive statistics of atrazine load weighted by area (g ha\(^{-1}\)) from 1997 to 2004 for the entire Blue River Basin.

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<tbody>
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<td>Mean</td>
<td>0.10</td>
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<td>0.03</td>
<td>0.16</td>
<td>0.11</td>
<td>0.08</td>
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<tr>
<td>S.E. (^1)</td>
<td>0.01</td>
<td>0.03</td>
<td>0.04</td>
<td>0.00</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.09</td>
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<td>Median</td>
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<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
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<tr>
<td>S.D. (^2)</td>
<td>0.40</td>
<td>0.75</td>
<td>0.99</td>
<td>0.12</td>
<td>0.59</td>
<td>0.43</td>
<td>0.27</td>
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<tr>
<td>Skewness</td>
<td>12.22</td>
<td>7.04</td>
<td>6.56</td>
<td>9.69</td>
<td>6.41</td>
<td>6.78</td>
<td>7.48</td>
<td>4.65</td>
</tr>
<tr>
<td>Range</td>
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<td>8.00</td>
<td>11.32</td>
<td>1.90</td>
<td>5.98</td>
<td>4.45</td>
<td>3.68</td>
<td>9.74</td>
</tr>
</tbody>
</table>

\(^1\) S.E. = standard error  
\(^2\) S.D. = standard deviation

Each year, atrazine load was greatest when soil water content was 34 to 43% (v/v). Table 5 shows that subwatershed 5, comprising 84% of the total cropped area with restrictive soil layers, is vulnerable to atrazine loss in surface runoff. The highest atrazine loading of 11.3 g ha\(^{-1}\) was recorded in 1999 when the soil was relatively saturated, with a weekly and total rainfall of 84 and 344 mm at the subwatershed level. Also, corn planting and sorghum planting were still in progress (97 and 54%, respectively) at that time.
Figure 23: Total seasonal atrazine load (g ha⁻¹) by subwatershed area in the Blue River Basin.
Table 6: Daily maximum atrazine measured in a subwatershed for each year and values of the corresponding associated variables (subwatershed 5 comprised 84% of the total cropped area with restrictive layer).

<table>
<thead>
<tr>
<th>Year</th>
<th>SW</th>
<th>Date</th>
<th>Atrazine load (g ha(^{-1}))</th>
<th>Rainfall (mm)(^1)</th>
<th>WR (mm)(^2)</th>
<th>TR (mm)</th>
<th>SM (%)(^3)</th>
<th>CPP (%)</th>
<th>SPP (%)</th>
<th>CA (%)</th>
<th>RL (%)</th>
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<tr>
<td>1997</td>
<td>5</td>
<td>05/28</td>
<td>2.5</td>
<td>1</td>
<td>32</td>
<td>159</td>
<td>0.43</td>
<td>97</td>
<td>84</td>
<td>57</td>
<td>84</td>
</tr>
<tr>
<td>1998</td>
<td>12</td>
<td>06/14</td>
<td>8.0</td>
<td>45</td>
<td>113</td>
<td>231</td>
<td>0.41</td>
<td>100</td>
<td>97</td>
<td>65</td>
<td>93</td>
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<td><strong>1999</strong></td>
<td><strong>5</strong></td>
<td><strong>06/02</strong></td>
<td><strong>11.3</strong></td>
<td><strong>0</strong></td>
<td><strong>84</strong></td>
<td><strong>344</strong></td>
<td><strong>0.42</strong></td>
<td><strong>97</strong></td>
<td><strong>54</strong></td>
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<td>2000</td>
<td>5</td>
<td>07/05</td>
<td>1.9</td>
<td>11</td>
<td>78</td>
<td>281</td>
<td>0.41</td>
<td>100</td>
<td>100</td>
<td>54</td>
<td>84</td>
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<tr>
<td>2001</td>
<td>14</td>
<td>05/07</td>
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<td>0</td>
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<td>52</td>
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<td>05/31</td>
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<td>0.40</td>
<td>96</td>
<td>84</td>
<td>54</td>
<td>84</td>
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<tr>
<td>2003</td>
<td>8</td>
<td>06/25</td>
<td>3.7</td>
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<td>94</td>
<td>381</td>
<td>0.34</td>
<td>100</td>
<td>100</td>
<td>47</td>
<td>2</td>
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<tr>
<td>2004</td>
<td>12</td>
<td>05/26</td>
<td>9.6</td>
<td>0</td>
<td>14</td>
<td>137</td>
<td>0.36</td>
<td>99</td>
<td>61</td>
<td>50</td>
<td>93</td>
</tr>
</tbody>
</table>

\(^1\)WR = cumulative weekly rainfall prior to atrazine sampling (mm)  
\(^2\)TR = total rainfall (mm) up to the atrazine sampling date  
\(^3\)SM = soil water content (%) for the atrazine sampling date  
CPP = Corn planting progress (%)  
SPP = Sorghum planting progress (%)  
CA = Cropped subwatershed area (%)  
RL = Area with restrictive layer (%)
A declining trend in the sorghum-planted area was observed within the basin during the study period (Figure 24), which may be largely due to the increasing profitability of growing corn and soybean. Similar trends were observed in Nebraska and the U.S. during the study period (Figure 25). Higher atrazine loading observed in 1999, 2001, 2003, and 2004 may be due to the use of atrazine in added corn areas within the more vulnerable subwatersheds over these years (Figure 26). Atrazine loading was relatively low in 2000 and 2002 because those years received comparatively less rainfall than the other years (Figure 27).

**Figure 24:** Corn and sorghum cropped area within the Blue River Basin.
Figure 25: Trend in crop planted area in Nebraska and the U.S. (Quick Statistics, USDA-NASS, 2010).

A comparison of corn-to sorghum-planted area ratios at Beatrice, Barneston, and Marysville (subwatersheds 14, 12, and 5) indicates more sorghum area than in the other subwatersheds. This suggests that atrazine applied to sorghum is contributing to runoff and atrazine loading in the watershed (Figure 26).
**Figure 26:** Corn-to sorghum-planted area ratio for each subwatershed, 1997-2004.

### 4.3. Variables Affecting Atrazine Load

The selected variables were checked for multicollinearity to determine if any two were highly correlated. No independent variables were correlated more than 61% \((p < 0.001; \text{Table 7})\). As expected, the highest correlation was observed between corn planting progress (CPP) and sorghum planting progress (SPP), followed by log of area-weighted atrazine load and cumulative rainfall (RNBTE) between weekly atrazine measurements.
Table 7: Multicollinearity among the variables potentially contributing to atrazine loading.

<table>
<thead>
<tr>
<th></th>
<th>logatrh</th>
<th>RNBTE</th>
<th>SW</th>
<th>CPP</th>
<th>SPP</th>
<th>RL</th>
</tr>
</thead>
<tbody>
<tr>
<td>logatrh</td>
<td>—</td>
<td>0.56674</td>
<td>0.44186</td>
<td>0.37955</td>
<td>0.33517</td>
<td>0.10719</td>
</tr>
<tr>
<td></td>
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<td>&lt;.0001</td>
<td>&lt;.0001</td>
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<td>612</td>
<td>612</td>
<td>614</td>
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</tr>
<tr>
<td>RNBTE</td>
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</tr>
<tr>
<td>SW</td>
<td>0.44186</td>
<td>0.45162</td>
<td>—</td>
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<td>0.33821</td>
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<td>&lt;.0001</td>
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<td>612</td>
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<td>614</td>
<td></td>
</tr>
<tr>
<td>CPP</td>
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<td>612</td>
<td>610</td>
<td>612</td>
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<tr>
<td>SPP</td>
<td>0.33517</td>
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<td>-0.11753</td>
<td>0.61786</td>
<td>—</td>
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<tr>
<td>RL</td>
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<td>0.01203</td>
<td>0.33821</td>
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</table>

Logatrh = log of atrazine load (g ha\(^{-1}\))
RL = percent area with restrictive layer
RNBTE = rainfall between sampling events
SW = soil water content
CPP = corn planting progress
SPP = sorghum planting progress
The overall $R^2$ for the ANCOVA model is 0.68 and the adjusted $R^2$ is 0.60. The adjusted $R^2$ was calculated from $1-(1-R^2)/(n-p-1)$, where $n$ is the number of observations and $p$ is the number of parameters.

Analysis of covariance (Table 8) indicated that year, cumulative rainfall between two atrazine sampling periods, corn planting progress, and sorghum planting progress are most highly significant ($p<0.0001$) relative to atrazine load. In addition there were highly significant associations with restrictive layer ($p=0.0006$), soil water content ($p=0.002$), and subwatershed ($p<0.01$). There also were significant effects of corn planting progress and watershed interaction, subwatershed, year and subwatershed interaction. However, based on the F-ratio, the variation in atrazine load explained by these variables was small compared to that explained by rainfall between two atrazine sampling periods and corn planting progress alone. A discussion of the major variables affecting atrazine load follows.
### Table 8: ANCOVA results. Significance levels (Pr > F) are in bold where P <0.05.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
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<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
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<td>Error</td>
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<td>1120.60</td>
<td>2.22</td>
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<tr>
<td>Corrected Total</td>
<td>609</td>
<td>3456.26</td>
<td>—</td>
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<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Type I SS</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
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<tr>
<td>Rnbte</td>
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<td>686.19</td>
<td>686.12</td>
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<tr>
<td>CPP</td>
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<td>317.98</td>
<td>317.98</td>
<td>143.3</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Year</td>
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<td>883.58</td>
<td>126.23</td>
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<td>60.17</td>
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<tr>
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<td>SM</td>
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<table>
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<td>0.676</td>
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</table>

#### 4.3.1. Rainfall

Average rainfall values obtained after interpolation across the watershed area from 1997 to 2004 showed rainfall was highest in 1999 followed by 1998 and 2003 (Figures 27 and Figure 28). Saturation of the soils facilitated loss of atrazine via surface runoff. Years 2000 and 2002 were driest during the study period and were also the years with relatively less atrazine loading. Although information on duration and intensity of
rainfall relative to pesticide application could not be included, such data would be useful in the analysis. Devlin et al. (2000) reported that the first major storm event following atrazine application is responsible for about two-thirds of total atrazine loss and the increment in duration between atrazine application and runoff events reduces the amount of atrazine loss in runoff. Increases in rainfall duration and intensity increases water runoff rate, thereby increasing the potential for atrazine loss.

![Seasonal average, median and maximum rainfall in the Blue River Basin, April 1 to September 30.](image)

**Figure 27:** Seasonal average, median and maximum rainfall in the Blue River Basin, April 1 to September 30.
Figure 28: Time series of seasonal mean rainfall for each subwatershed. Numbers in parenthesis identify the subwatershed.
Most atrazine runoff studies are conducted on plots using rainfall simulation. Artificial rain may not closely resemble natural rainfall because the falling raindrops have lower kinetic energy. The high cost for installing simulators for large areas also limits use of simulators to small plots. At the watershed level, the amount of rainfall for the entire basin can be obtained using interpolation methods. Three AWDN weather stations not used in rainfall interpolation were left for comparison purposes. Comparison of rainfall values obtained from interpolation for subwatersheds in proximity with those three AWDN stations showed a good correlation. Greater numbers of weather stations are needed for such interpolations and their limited availability in this study was realized.

Plotting atrazine loading, weighted by area, against cumulative rainfall between atrazine sampling events shows that loading is associated with amounts of rainfall throughout the entire study period (Figure 29). Kalkhoff et al. (2003) found that increased rainfall during mid-summer (July) flushed most of the atrazine and atrazine-derived compounds from the watersheds, resulting in lower concentrations in August. Their study also mentions the presence of substantial concentrations of triazine degradation products in streams of the Midwest during late summer.
Figure 29: Scatterplot of atrazine loading vs. cumulative rainfall between atrazine sampling events for the subwatersheds ($R^2 = 0.20$).

4.3.2. Soil Water Content

Examination of soil water content across all sampling stations (Figure 30) showed that soil water content varied across all years and was highest in 1999. Soil water content was associated with area-weighted atrazine load. Wetter soils have a lower water-holding capacity, facilitating runoff. The results are similar to those of Zhang et al. (1997), who reported a greater potential for dissolved and particle-adsorbed runoff of herbicides for soils under wet conditions. In another study, use of controlled drainage with subsurface irrigation increased surface runoff loss of atrazine because it increased subsoil water content, which reduced infiltration (Gaynor et al. 2002). However, greater atrazine
Degradation was reported in soils with 35 and 50% (w/w) water content due to increased soil microbial activity (Jebellie et al. 1996).

**Figure 30**: Volumetric soil water content (%) in the BRB for the study period.
Results from the ANCOVA analysis and scatterplot (Figure 31) suggest greater atrazine loading is associated with saturated or nearly saturated soils.

![Scatterplot of area-weighted atrazine load and volumetric soil water content](image)

**Figure 31:** Scatterplot of area-weighted atrazine load and volumetric soil water content (% v/v) ($R^2 = 0.19$).

### 4.3.3. Corn and Sorghum Planting Progress

The highest atrazine loading was associated with the time when corn planting was nearly completed in the watershed. The significant interaction between corn planting progress and area-weighted atrazine load suggests that most of the atrazine loading is associated with atrazine applied to corn fields. However, the scatterplot (Figure 32) does not show a strong association between corn planting progress and atrazine loading.
Figure 32: Scatterplot of area-weighted atrazine load and corn planting progress (%) ($R^2 = 0.09$).

In the case of sorghum, atrazine loading was high at both the beginning and at the end of the planting period. Higher loading at the start of sorghum planting may be due to the completion of corn planting at that time. Results indicate that compared to corn, sorghum planting progress is less likely associated with atrazine load measured at the sampling stations. No trend was observed in the scatterplot (Figure 33). The decrease in area planted to sorghum may be due to farmer preference, improved and more efficient irrigation systems, and the availability of improved and drought tolerant corn hybrids that can be readily grown on marginal lands.
Figure 33: Scatterplot of area-weighted atrazine load and sorghum planting progress (%) 
($R^2 = 0.03$).
4.3.4. Restrictive Layer

Although the scatterplot (Figure 34) does not indicate a strong association, the greatest atrazine loadings occurred in subwatersheds having croplands with large percentages of soil with near-surface restrictive layers. Statistical analysis also suggested that the presence of a restrictive layer was associated with atrazine loading.

Figure 34: Scatterplot of area-weighted atrazine load and restrictive layer (%) ($R^2 = 0.05$).
CHAPTER 5

5. CONCLUSIONS

Rainfall events, along with high water content in the surface soil during crop planting time, greatly impacted surface runoff of atrazine. Maximum atrazine loading in the BRB occurred after most of the corn had been planted but during sorghum planting between mid-May and early June, immediately following multiple rainfall events that saturated the soil profile and caused runoff from agricultural fields. Results from the independent subwatersheds imply that atrazine load weighted by area is related to cumulative weekly rainfall across all years. Analysis of covariance showed rainfall was the most significant factor associated with atrazine loading, but soil water content, corn and sorghum planting progress, and the presence of a restrictive layer were also important.

Providing decision support to farmers, agencies, extension workers, and scientists can help promote best management practices in the most vulnerable landscapes to mitigate surface runoff of atrazine and other agrichemicals. However, detailed assessments are needed in subwatersheds with the highest atrazine loading. Although the extent of upstream land use for agriculture was included in the ANCOVA model, the proximity of agricultural fields to streams throughout the watershed was not measured. Travel time for storm water both between and within catchments is mostly influenced by rainfall. Travel time, which could be a significant variable in the regression analysis, was not calculated. Flushing time constants for the overland-flow and soil-water reservoirs
can be calculated on a storm-by-storm basis using separate tracers for each time-variable reservoir.

There remains a need to conduct long-term, field-scale runoff studies for water quality monitoring and modeling using pesticide application information. These studies should include other herbicides, as well as phosphorus and sediment. With some approximation of flushing time, storms within catchments can be differentiated. Identification of storm events for each catchment can provide an added advantage in analyzing the gain from each catchment as the river flows downstream.

The present study provides a spatial database of stream-measured atrazine loading, rainfall, soil water content, crop-planted area, crop planting progress, and the occurrence of restrictive layers in cropped land of the Nebraska-Kansas Blue River Basin. Results demonstrate how integration of a finer resolution spatial database in GIS, using surrogates from spatial interpolation, can be an effective approach for assessing complex physicochemical dynamics at a watershed level.
### 6.1. Atrazine Physical and Chemical Properties

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<th>Value</th>
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<td>White crystalline solid</td>
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<td>Molecular Formula</td>
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<td>Water solubility</td>
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<tr>
<td>Appearance</td>
<td>Colorless/white crystalline solid</td>
</tr>
<tr>
<td>Half-life</td>
<td>60 days</td>
</tr>
</tbody>
</table>

Source: (Giddings 2005)
6.2. SAS Codes

/*Import Data from Excel Spreadsheet in SAS */
PROC IMPORT OUT= WORK.msproject
   DATASET = "C:\User\Documents\database.xls"
   DBMS=EXCEL REPLACE;
   RANGE="Sheet1$";
   GETNAMES=YES;
   MIXED=YES;
   SCANTEXT=YES;
   USEDATE=YES;
   SCANTIME=YES;
RUN;
ods rtf; /* Generates output in rich text format*/

proc print; /* Print the whole dataset*/
run;

data msproject; set msproject; if 109< DOY < 172; /*Limit the study window for each year, from DOY 109 to 172*/
   if ISW = 4 or ISW = 7 or ISW = 10 or ISW = 11 or ISW = 13 or ISW = 15 or ISW = 18 or ISW = 19 or ISW = 21 or ISW = 22 ; /*Selection of independent subwatershed*/
   logatrh = log(Atr_gm_ha);
run;

proc print;
run;

proc sort data=msproject; by ISW year;
/* Test for Multicollinearity & Normality*/
ods rtf file = "Multicollinearity.rtf";
proc corr; var Rnbte logatrh sm cpp spp rl;
run;
ods rtf close;

proc corr data=msproject nomiss
   plots=scatter(ellipse=confidence nvar=2 alpha=.10 .05);
   var Rnbte logatrh sm cpp spp rl;
run;

/*Create Residual Plots for the Data*/
proc glm data=msproject; class year ISW;
model logatrh = year rl ISW*year rnbte rnbte*ISW sm cpp cpp*ISW spp spp*ISW;
output out=xx p= plogatrh  r=rlogatrh;
run;
proc gplot data=xx;
   plot rlogatrh*plogatrh;
run;

/* Ancova Model for analyzing the data*/
ods rtf file = "ANCOVA.rtf";
proc glm data=msproject; class year ISW;
model logatrh = year r1 ISW ISW*year rnbte rnbte*ISW sm cpp cpp*ISW spp spp*ISW/solution el;
random year ISW*Year/ test;
output out=xx p= plogatrh r=rlogatrh;

proc plot;
plot plogatrh*logatrh/ vpos=17 hpos=45;
run;
ods rtf close;

proc glm data=msproject; class year ISW;
model logatrh = year r1 ISW / solution;
run;
6.3. Atrazine Load

**Figure 35**: Subwatersheds within the Blue River Basin.
**Figure 36:** Atrazine load for each subwatershed in 1997.

**Figure 37:** Atrazine load for each subwatershed in 1998.
Figure 38: Atrazine load for each subwatershed in 1999.

Figure 39: Atrazine load for each subwatershed in 2000.
Figure 40: Atrazine load for each subwatershed in 2001.

Figure 41: Atrazine load for each subwatershed in 2002.
Figure 42: Atrazine load for each subwatershed in 2003.

Figure 43: Atrazine load for each subwatershed in 2004.
6.4. Time series of interpolated rainfall (>0.6 cm or >.25 in) for the independent subwatersheds (ISWs)

Figure 44: Times series of rainfall for ISWs (1997). Refer to Figure 35 for locations of subwatersheds.

Figure 45: Time series of rainfall for ISWs (1998).
**Figure 46:** Time series of rainfall for ISWs (1999).

**Figure 47:** Time series of rainfall for ISWs (2000).
**Figure 48:** Time series of rainfall for ISWs (2001).

**Figure 49:** Time series of rainfall for ISWs (2002).
Figure 50: Time series of rainfall for ISWs (2003).

Figure 51: Time series of rainfall for ISWs (2004).
6.5. Time series of estimated soil moisture (top 30cm) for subwatersheds, 1997-2004

Figure 52: Soil water content for ISWs (1997). Refer to Figure 35 for ISWs.

Figure 53: Time series of soil water content for ISWs (1998).
Figure 54: Time series of soil water content ISWs (1999).

Figure 55: Time series of soil water content ISWs (2000).
Figure 56: Time series of soil water content ISWs (2001).

Figure 57: Time series of soil water content ISWs (2002).
**Figure 58:** Time series of soil water content ISWs (2003).

**Figure 59:** Time series of soil water content ISWs (2004).
6.6. Details of Tipping Bucket

Range of Indication: Infinite in increments of tip (least count) of rainfall.

Rainfall per Tip: TE525 0.01 in.

Volume per Tip: TE525: 0.16 fl. oz./tip (4.73 ml/tip)

Accuracy

<table>
<thead>
<tr>
<th>Rainfall Rate</th>
<th>TE525</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 1 in./hr</td>
<td>±1%</td>
</tr>
<tr>
<td>1 to 2 in./hr</td>
<td>+0, −3%</td>
</tr>
<tr>
<td>2 to 3 in./hr</td>
<td>+0, −5%</td>
</tr>
</tbody>
</table>

(personal communication, Natalie Umphlett, February 8, 2011)
7. REFERENCES


Nebraska Department of Natural Resources. 2010. 2011 Annual Evaluation of Availability of Hydrologically Connected Water Supplies. Lincoln, NE: Nebraska Department of Natural Resources.


