ENVIRONMENTAL IMPACT ANALYSIS OF BIOFUEL CROPS EXPANSION IN MICHIGAN

By

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A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Biosystems Engineering

2011

ABSTRACT

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The environmental implications of large-scale bioenergy cropping systems are not well understood, making conservation efforts difficult and inefficient. To address these issues, the following research objectives were developed: 1) determine if pesticides are suitable for lignocellulosic ethanol feedstocks, 2) provide critical information to determine the suitability of bioenergy crops on a variety of types of agricultural land in Michigan, 3) determine the possible environmental impacts of bioenergy cropping systems on sediment, nitrogen, and phosphorus yield to surface waters, 4) determine the implications of bioenergy-associated pesticides on aquatic ecosystems and human consumption and 5) obtain information to aid in watershed-scale decision making regarding landuse management. The Soil and Water Assessment Tool (SWAT) was used to understand the impacts of large-scale bioenergy crop expansions on pollutant loads and concentrations. Results indicate that intensive bioenergy crops tend to increase pollutant loads to surface waters, whereas perennial grass species generally mitigate pollutants. Although herbicide treatments mainly positively influenced biomass accumulation in corn during field studies, the application of herbicides at a large-scale was found to increase the impairments of streams in Michigan on the basis of fish ecotoxicity and human consumption thresholds. In general, this study reinforces the importance of maintaining a sustainable bioenergy cropping system implementation strategy to avoid environmental and human health risks.

Copyright by BRADLEY J. LOVE 2011 This thesis is dedicated to my family, friends, and colleagues for their generous love and support.

ACKNOWLEDGMENTS

I would first like to thank my family, my mom and dad, Jon and Gail, my sister and brother-in-law, Katie and Chad for their love and support. Katie and Chad, thank you for going through college first and leading the way and being an ear for phone conversations wondering why we do this to ourselves, dad, for being my best friend and best hunting buddy, and mom for your love, kindness, and for feeding my dog when my research kept me from being home.

I would also like to thank Dr. Amir Pouyan Nejadhashemi for being an extraordinary advisor, mentor, and friend. Without your invaluable research advice, our random conversations, and your persistent encouragement to complete the work in a timely manner, this work and my personal and professional growth would not have been possible. I would also like to thank my committee members Dr. Kurt Thelen, Dr. Yan (Susie) Liu, and Dr. Lizhu Wang for their support, guidance, and knowledge each has provided throughout my research.

I would like to thank my labmates Sean, Matt, Edwin, Yaseen, Subhasis, and Mike, for not only their help, but also for the great memories. Sean for being a great friend throughout our time since BE 130, Matt for being the only fellow hunter and for all of the hysterical laughs, Edwin for bringing out your Air Jordans, Yaseen and Subhasis for changing my perspective of your great cultures, and Mike for... well thanks Mike. Also to my instructor and friend, Dr. Fred Arkema-Bakker for his commitment to provide us with global current events and our great conversations. Finally I would like to give thanks to the greatest university on the planet, Go Green!

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LIST OF ABBREVIATIONS

Parameter	Description
Ae	Acid equivalent
Ai	Active ingredient
Alpha_Bf	Baseflow alpha factor (days)
AnnAGNPS	Annualized Agricultural Non-Point Source Model
Biomix	Biological mixing efficiency
Blai	Maximum potential leaf area index
Canmx	Maximum canopy storage (mm)
CDL	Crop Data Layer
Ch_K2	Channel effective hydraulic conductivity (mm/hr)
Ch_N2	Manning's nvalue for main channel
Ch_Cov	Channel cover factor
Ch_Erod	Channel erodibility factor
Cn2	Initial SCS CN II value
DEM	Digital Elevation Model
Epco	Plant uptake compensation factor
Esco	Soil evaporation compensation factor
GIS	Geographic Information Systems
Gw_Delay	Groundwater delay (days)
Gwgmn	Threshold water depth in the shallow aquifer for flow (mm)
HRU	Hydrologic Response Unit
HSPF	Hydrologic Simulation Program-FORTRAN

HUC	Hydrologic Unit Code
MUSLE	Modified Universal Soil Loss Equation
Nperco	Nitrogen percolation coefficient
NSE	Nash-Sutcliffe Efficiency
N_Updis	Nitrogen uptake distribution parameter
Phoskd	Phosphorus soil portioning coefficient
Pperco	Phosphorus percolation coefficient
Ppm	Parts per million
Ppb	Parts per billion
R ²	Coefficient of determination
Rchrg_Dp	Deep aquifer percolation fraction
RMSE	Root mean square error
RUSLE	Revised Universal Soil Loss Equation
Smtmp	Snowmelt base temperature (⁰ C)
Sol_Awc	Available water capacity (mm H ₂ O/mm soil)
Sol_Z	Soil depth (mm)
Sol_No3	Initial NO ₃ concentration (mg/kg)
Sol_Orgn	Initial Organic N concentration (mg/kg)
Sol_Orgp	Initial Organic P concentration (mg/kg)
Spcon	Linear re-entrainment parameter for channel sediment routing
Spexp	Exponential re-entrainment parameter for channel sediment routing

STATSGO	State Soil Geographic Database
Surlag	Surface runoff lag time (days)
SWAT	Soil and Water Assessment Tool
Timp	Snow pack temperature lag factor
TKN	Total Kjeldahl Nitrogen
TN	Total nitrogen
ТР	Total phosphorus
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

Usle_P USLE support practice factor

1. INTRODUCTION

It is an accepted fact that the availability of fossil fuels is finite and that there will be a peak of oil production. It is suggested that fossil fuel availability is likely currently in decline. In fact, there has been more oil consumed than found for longer than the past two decades (Hanlon and McCartney, 2008). Affordable and accessible oil is therefore beginning to become less obtainable. As domestic crude oil production has decreased over the past decades, imports have filled the gap. For example, Canada nearly doubled their oil production between 2001 and 2007, mainly from oil sands requiring large amounts of water for extraction, to accommodate the immense oil demands of the United States (Wu et al., 2009). Fossil fuels account for about 80 percent of global energy supply, and will be exhausted in a matter of decades at current consumption rates (Goldemberg, 2007). The instability of the global energy sector has led to recent increases in the demand for alternatives, especially in developed countries with a dependence on fossil fuels. Prior to the mid-1990s, Brazil was the only country employing large-scale production of energy through biological means, whereas today the spread of bioenergy production has swept the entire globe (Mol, 2007). Public awareness of United States dependence on oil and the insecurity of the energy sector, climate change, and the current economic downswing has led to great support of renewable energy sources (Wu et al., 2009). In order to meet the demands of a growing global energy budget in a sustainable approach, increased energy use efficiency of existing carbon-based fuels and an unfathomable supply of carbon-neutral energy sources will be required (Lewis and Nocera, 2006). Model-based assessments examining bioenergy expansion rarely account for the competition of land for production of food and animal

feed (Schaldach *et al.* 2010). The implications resulting from a large-scale shift to bioenergy cropping systems to fulfill these needs are not well-known, in which unintended consequences to water resources and ecosystem services such as biodiversity may result (Groom *et al.*, 2008; Stone *et al.*, 2010).

One of the major challenges facing scientists is to determine the associated environmental risks that energy production from agricultural biomass may provoke (Carroll and Somerville, 2009). In addition, determining the vulnerabilities of production spatially is necessary prior to implementing bioenergy crops into systems currently used mainly for food production (Mol, 2007). Understanding the environmental consequences of a production system based on bioenergy crops is needed to develop cost-effective and sustainable management strategies to negate irreversible water quality impacts (Thomas *et al.*, 2009). However, the impact of large-scale production of bioenergy crops on water resources is not well-known (Wu *et al.*, 2009), which is one of the goals of the research presented in this manuscript.

The research in this paper evaluates the long-term environmental implications, specifically water quality, of large-scale bioenergy cropping system expansion using the Soil and Water Assessment Tool (SWAT) for four watersheds in Michigan over a variety of hypothetical landuse and crop rotation scenarios.

The specific objectives of this study are:

- Determine the suitability of pesticides for application on lignocellulosic ethanol feedstocks to avoid yield loss
- Provide critical information to aid in determining the suitability of bioenergy crops on a variety of types of agricultural land in Michigan

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- Determine the possible environmental impacts of bioenergy cropping systems on sediment, nitrogen, and phosphorus yield to surface waters
- Determine the implications of bioenergy-associated pesticides on aquatic ecosystems and human consumption
- Obtain information to aid in watershed-scale decision making regarding landuse management

2. LITERATURE REVIEW

2.1 OVERVIEW

This literature review is divided into sections describing recent global energy demand issues and potential alternatives, bioenergy and the associated water quality and quantity implications, pesticide use repercussions of bioenergy cropping systems, ecosystem services and their role in the valuation of environmental benefits, watershed models useful in determining the potential alterations in the availability of ecosystem services, modeling bioenergy cropping system expansion, and the gaps in knowledge to be addressed by the research presented in the subsequent chapters.

2.2 BIOENERGY

The increased demand of global and domestic energy has led to the start of a transition to alternative sources. Renewable fuel sources originating in the agricultural sector have become a very important means for the replacement, or at least partial substitution, of fossil fuels. Domestic renewable energy sources have the potential to reduce dependence on foreign resources, mitigate climate change, diversify domestic energy sources, and allow for economic growth and rural development (Scheffran and BenDor, 2009). Bioenergy, or energy obtained through biological sources, is the focus of much political debate and research efforts in recent times. Energy from biomass could potentially provide a large portion of the sustainable global energy demands, yet currently only accounts for 7 percent of total global energy supplies (Berndes *et al.*, 2003; de Fraiture *et al.*, 2008). Policy that has been introduced as targets to increase the production of alternative fuels include:

- Biomass Research and Development Act of 2000 (Chum and Overend, 2001)
- Energy Policy Act of 2005 (domestic use of renewable fuels to 28.4 billion liters by 2012) (Balat and Balat, 2009)
- Energy Independence and Security Act (EISA) of 2007 (136 billion liters of biofuels by 2022) (Balat and Balat, 2009)
- Farm Bill (2002 and 2008) (Johnson 2010)

The United States Department of Energy (USDOE) has enacted the Biofuels Initiative (BFI) that sets a target goal of making fuels derived from cellulosic biomass cost competitive by 2012 and replacing 30 percent of current petroleum-based transportation fuels with biofuels by 2030 (USDOE 2007). By the year 2025, global energy consumption is expected to increase by over 57 percent from 2002 values (Rooney *et al.*, 2007). Meanwhile, renewable energy accounts for only about 7 of the nation's 99.3 Quadrillion Btu consumption (USEIA 2009).

To hastily meet demands for biomass and the commitment guidelines set forth by policymakers, significant alterations to current landuse leading to increases in cultivated acreage will result (Rowe *et al.*, 2009). However, large-scale production of bioenergy feedstocks are limited due to landuse competition with traditional food crops (Scheffran and BenDor, 2009). In addition, global population continues to grow, which relies on agriculture to produce more amounts of food on less land (Carroll and Somerville, 2009). In order to avoid sharp inclines in food prices, biofuel crops must also be considered to be grown on agriculturally marginal land or surplus lands with degraded production capabilities (Lal and Pimentel, 2007). Marginal or degraded lands account for 1460 Mha of the 5700 Mha used for agricultural purposes worldwide, in which the production of

biofuels may retard the rate of further degradation through conventional, intensive agricultural practices (Carroll and Somerville, 2009). However, the implications of expanding cropland to accommodate demands (both energy and food) are not adequately understood at a large-scale (Rowe *et al.*, 2009).

2.2.1 Feedstock Sources

Biofuels are liquid fuels, such as ethanol and biodiesel, produced from biological feedstocks and mainly used for transportation and heating (de Fraiture *et al.*, 2008). Lynd *et al.* (2009) specifies four main categories of feedstocks that have potential in a bioenergy-based markets including:

- Lignocellulosic materials (e.g. perennial grasses, woody biomass, agricultural residues)
- Starch-rich crops (e.g. corn and wheat)
- Sucrose-rich crops (e.g. sugarcane and sugarbeets)
- Oilseed crops (e.g. soybeans, palm, and canola)

The feedstocks that are considered a realistic source for biofuels in the United States include native prairie grasses, corn, corn stover, wheat straw, sugar cane, switchgrass, soybeans, rapeseed, oil palm, poplar, willow, wood and crop residues, and algae (Groom *et al.*, 2008). Meanwhile, one of the major goals of the USDOE is to increase the economic stability and improve competiveness of cellulosic feedstocks (primarily switchgrass and agricultural/woody residues) for liquid transportation fuels (Lorenz *et al.*, 2009). Crop residues, unlike biomass from grains that compete with food and feed markets, have great potential as a bioenergy feedstock for both direct combustion and for the synthesis of ethanol from refineries capable of converting lignocellulose (Moebius-

Clune *et al.*, 2008). The removal of large-quantities of crop residue from farmland oftentimes reduces soil health and depletes organic matter, reduces the carbon sequestering abilities of the soil, and increases soil erosion potential (Lal and Pimentel, 2007). However, by removing excess residue from the soil surface, soils warm faster in the spring, have better seed germination, and provides less available habitat for unwanted diseases or parasites (Moebius-Clune *et al.*, 2008).

2.2.2 Benefits of Bioenergy

The benefits associated with the production of biofuels are commonly referenced. Biofuels are looked to as an answer to reducing greenhouse gases responsible for climate change and the nation's vast addiction with fossil fuels, which are politically risky and environmentally harmful (Solomon, 2010). Reducing fossil fuel dependency has the potential to cut consumer costs, mitigate climate change, create new jobs, promote the supply of domestic energy, and diversify energy sources ensuring domestic energy security (Goldemberg, 2007). Climate change is arguably one of the most important issues of the planet and to the sustainability of human practices. Over the long-term past, the mean concentration of atmospheric CO₂ increased from 280 ppm to 380 ppm between the 1700s and 2005, respectively (Raupach et al., 2007). Abrupt climate change resulting from this enormous increase of greenhouse gases will likely be responsible for altering both frequency and magnitude of natural phenomena such as drought, floods, and extreme wind and temperature (Gregory et al., 1997; Alley, 2004). Bioenergy crops show promise in providing carbon sequestering benefits and being a carbon neutral energy source or a net carbon sink (Adler et al., 2007).

In addition, long-rotation perennial bioenergy crops such as C4 grasses (e.g. switchgrass and miscanthus) and woody biomass (hybrid poplar) have higher water use efficiencies (WUE), which is crucial not only to freshwater resources but also to be able to provide sustainable cropping systems under future conditions predicted to have less available water for cultivation (Oliver *et al.*, 2009). Liebig (2008) has shown that grass species such as switchgrass have potential to reduce soil erosion and maintain or enhance soil organic carbon levels.

2.2.3 Problems of Bioenergy

Unfortunately, the negative aspects of bioenergy production are ever-present and must be considered prior to any significant implementation of such practices. In order for biofuels to be a sustainable solution to fossil fuels, their cultivation must avoid additional negative environmental impacts. The expansion of bioenergy systems to meet future demands will require tremendous land requirements, making it essential to examine the large-scale environmental impacts these practices may generate (Nyakatawa *et al.*, 2006). It is likely that the increased demand for bioenergy feedstocks may ultimately transform current agricultural landscapes as production systems evolve and new species of crops become commercially available. When landuse change is considered, the benefits of biofuels become difficult to quantify and may be negated due to possible environmental impacts (McLaughlin and Walsh, 1998). For example, greenhouse gas emissions associated with landuse change from current landcover to large-scale corn production for ethanol are estimated to double (Searchinger *et al.*, 2008).

Climate change will undoubtedly affect water resources. Higher temperatures and less precipitation associated with climate change will ultimately force agriculture utilize

more freshwater for irrigation, even though this sector already accounts for 80 percent of all water consumed in the United States (Stone et al., 2010). In order to meet the Billion-Ton Vision of the USDOE, 8.64 x 10^9 and 5.01 x 10^{10} m³ of water for current and future (2030) goals is required, a 6-fold increase (Stone et al., 2010). The increased water use for both cultivation of feedstock sources and the refining processes associated with biofuels may negatively impact biodiversity and other ecosystem services (Groom et al., 2008). Increasing the yields of bioenergy crops to meet demands will require increased amounts of agricultural inputs (Searchinger et al., 2008). Corn, the current crop supplying majority of biofuels in the United States, requires more fertilizer and pesticides than any other crop grown in the nation (Pimentel and Patzek 2005). However agriculture is already responsible for the largest contribution of non-point source pollution to freshwater in the United States (Foley *et al.*, 2005). The increased inputs associated with many bioenergy crops may lead to a higher number of impaired waterbodies, resulting in risk of human and aquatic ecosystem health hazards (Nyakatawa et al., 2006). Row crop production is the largest contributor of nitrogen and phosphorus fluxes to the Mississippi River basin resulting in eutrophication, reduced dissolved oxygen, algal blooms, and impaired aquatic habitat of surface waterbodies, and hypoxic zones in the Gulf of Mexico (Carpenter et al., 1998; Powers, 2007). Eutrophication is commonly responsible for impaired waterbodies and contaminated drinking water supplies, which increases the cost of treatment for human consumption (Carpenter et al., 1998; Nyakatawa et al., 2006). The supply of adequate and clean freshwater is vital to human existence and is a fundamental requirement for sustainable agricultural production of bioenergy feedstocks (Gleick, 1998).

Agricultural expansion, most likely as input-intense monoculture cropping systems, decreases available habitat for many species, which may inhibit population dynamics and healthy reproduction (Groom *et al.*, 2008). This could be avoided in part by considering the cultivation of cellulosic feedstocks including perennial, polycultured species such as native grasses. However, crops such as these must be economically competitive with traditional crops currently grown for food and fuels and with other fossil fuel sources, which is unlikely without large incentives and subsidies (Khanna *et al.*, 2008). Even with economic incentives, the cost of losing ecosystem services such as biodiversity, carbon sequestration, crop pollination, erosion control, water quality enhancements, flood mitigation, and food production must be considered, which is an extremely daunting task (Groom *et al.*, 2008).

2.2.4 Pesticide Use with Bioenergy

As previously mentioned, an increase in land under agricultural production is expected with an increased demand for biomass for renewable energy. This causes conflicts in multiple ways. For example, competition for land used to produce food and animal feed is likely to inflate food prices and the amount of arable land under production will increase to accommodate demands. In addition, water resources are expected to experience negative consequences due to increased water consumption and pollution resulting from an increased amount of commercial fertilizers and pesticides used as a means to increase yields (Siber *et al.*, 2009). Most pesticides can be harmful to humans, animals, insects, aquatic life, and other organisms due to their hormone disrupting behavior and ability to bioaccumulate in organisms as the predator progresses down the food chain, making consumption toxic and oftentimes leading to chronic illness or reproductive harm (Holvoet *et al.*, 2008). Therefore, there has been a growing concern over the damage to ecosystems and to human health when using surface waters as a drinking water source in agricultural watersheds (Huber *et al.*, 2000; Vazquez-Amabile *et al.*, 2006). Pesticides can be released into rivers and aquifers during and shortly after precipitation events that occur after chemical application (Siber *et al.*, 2009). The most significant pathway for agricultural chemicals to enter streams is through transportation in surface runoff, in which dissolved pesticide losses in runoff generally exceed that of sediment-bound chemicals (Huber *et al.*, 1998; Luo *et al.*, 2008). Aquatic species are especially vulnerable to high levels of soluble pesticide in surface waters (Holden, 1972; Serrano *et al.*, 1995).

Due to the possible detrimental unintended consequences of extensive agricultural chemical use, it is vital to investigate pesticide transport and loss on a large scale. However, decisions regarding landuse management have traditionally been based on rough estimates of pollutant loading, which fails to incorporate the complex relationships between climate, soil and hydrologic characteristics (Kannan *et al.*, 2006). By modeling the fate and transport of pesticides in a watershed with a hydrological model, an evaluation of environmental impacts resulting from various management practices and landuse scenarios is more effective and representative of the true physical and chemical interactions (Du *et al.*, 2006). By having a better understanding of pesticide fate and transportation throughout a watershed, decisions regarding priority areas to target conservation efforts are made more effectively and efficiently, providing greater care of protecting fragile and valuable ecosystems. Several models exist that are useful in

determining the effects of agricultural practices on watershed health, which are discussed in detail below.

2.3 ECOSYSTEM SERVICES

2.3.1 Definition

Ecosystem services are the resources, products, and processes the environment provides that promote sustainable and comfortable human life. By identifying and quantifying these services, the measurement of these contributions and worth of their loss is possible (Ruffo and Kareiva, 2009). Many processes, such as crop pollination and carbon sequestration, go unnoticed on a day-to-day basis. Resources such as clean water, energy, and pharmaceuticals are often taken for granted. It is relatively easy to place value on tangible items. Valuing the loss of an intangible service that is assumed as finite becomes considerably difficult.

Services can be classified into public and private services. Public services are considered nonrivalry (the use/consumption of a service by one person does not reduce the opportunity for others to receive the same benefits) and nonexcludability (no one is excluded from the use/consumption of any given service) (Maler *et al.*, 2009). Climate change is an example that satisfies each; if climate changes for one, it will change for all utilizing the same service, and climate change excludes no one from its use (Maler *et al.*, 2009). Services that do not fall into these typologies are termed private services (Maler *et al.*, 2009). Determining services as public or private influences the value given and the method of valuation techniques, as public services are much more difficult to value than private services that are commonly traded or sold (Maler *et al.*, 2009).

2.3.2 Types

2.3.2.1 Biodiversity

Traditional views of conservation have focused on biodiversity, or the variety of life ranging from plants and animals to genes and biomes (Naidoo *et al.*, 2008). Understanding the overlap of biodiversity and ecosystem services is a fairly new concept. Ecosystem services are provided from biodiversity itself. The intermediate-disturbance hypothesis is a common means of explaining the maintenance of biodiversity in ecosystems (Roxburgh *et al.*, 2004). When disturbance is between extreme levels, the biodiversity in the affected region should be at its highest. However, negative biological impacts have been an increasing concern of anthropogenic activity. Land-use changes and poor land management practices have altered ecosystems in ways consequently resulting in harmful effects to the well-being of humans and natural systems (Nelson *et al.*, 2008).

Biodiversity as a term is ubiquitous in environmental literature and policy. However, ecological, social, and economic sustainability, in which biodiversity provides the very underpinnings, is relatively unknown among the general public (Cork, 2001). In recent years, after the American National Forum on Biodiversity held in 1986, a spike in global awareness of the effects of loss of organisms, communities, and ecosystems has increased the usage and understanding of biodiversity (Thompson and Starzomski, 2007). In science, biodiversity is commonly measured with methods of species richness. By linking species richness and ecosystem function, developing an argument for the conservation of biodiversity is further strengthened (Schwartz *et al.*, 2000). However, the effects of biodiversity on the functioning of ecosystem services are explained more thoroughly with the attributes of species rather than only species richness (Giller *et al.*, 2004). These methods, in a sense, determine the sensitivity of an eco-region to disturbance. Biological indicators, such as macroinvertebrates, are also good sources in assessing the health and level of disturbance in a given ecological area (Walsh, 2006). Indicators are vital in the proper assessment in determining biodiversity protection and maintenance of ecosystem processes (Karr, 1991). Most of the causes of decreased biodiversity, such as forced interactions of native and human-introduced species, can be regulated and reversed with policy and landuse management changes (Chapin et al., 2000). Without careful and adequate preservation efforts, the very "nature" we take for granted will continue to be at risk of great harm. As a result of global environmental change, biodiversity is decreasing a thousand times faster than that indicated by fossil records (Balvanera et al., 2006). Bioenergy cropping systems, with an expected increase in monocropping of a single crop type being cultivated consecutive years without proper rotation, reduces biodiversity in the plant, herbivore, and decomposer ecosystems (Swift and Anderson, 1993). However, coupled with increased global energy-use efficiency and careful environmental considerations, renewable energy sources can potentially expand the diversity of non-fossil, sustainable energy sources (Koh and Ghazoul, 2008). Crops with relatively low agricultural input, such as mixtures of perennial native grasses, cultivated on degraded lands avert habitat destruction and enhance biodiversity over traditional monocultures such as corn and soybeans (Tilman et al., 2006).

2.3.2.2 Carbon Storage

Carbon dioxide is a main contributing greenhouse gas (GHG) to suspected global climate change. Reducing carbon dioxide emissions has become an extremely central topic in governments worldwide (Guthrie and Kumareswaran, 2009). The Kyoto Protocol

is one of the largest attempts at promoting sustainable carbon-related processes worldwide, setting GHG emission limits on participating countries (Laurijssen and Faaij, 2009). Three main Kyoto mechanisms were developed – emissions trading, clean development mechanism, and joint implementation (Garcia-Quijano *et al.*, 2007). From these provisions, the trading of "carbon credits" has emerged as an additional means to stimulate cooperation. Projects that sequester carbon are eligible to earn credits that are sold to entities that require additional credits to compensate for their carbon emissions. The Chicago Climate Exchange and the European Climate Exchange recognize carbon sequestration as a market and actively trade GHG credits. Furthermore, terrestrial-based carbon sequestration has become an extremely valuable ecosystem service (Lippke and Perez-Garcia, 2008). The economy, environment, and society benefit from the market value given to the continued sequestering and long-term storage of carbon.

When there is a landuse change from natural vegetation to farmland or urban land, carbon sequestered in the soil and tied-up in above ground biomass is released to the atmosphere, contributing to climate change (Chan *et al.*, 2006). More than a third of carbon dioxide emission since 1850 has been a result of land conversion, thus natural ecosystems provide a valuable service of storing carbon (Chan *et al.*, 2006).

According to the Intergovernmental Panel on Climate Change (IPCC), trees sequester significant amounts of carbon for the atmosphere as stored carbon-based biomass (Guthrie and Kumareswaran, 2009). Emission trading programs provide an incentive for lowering the cost of emission mitigation programs and technology, and promote environmentally-friendly land use changes that support economic sustainability (Ruddell 2006).

In order to avoid unintended negative consequences that may be counterproductive in promoting participation in reduced-carbon footprint developments and production practices, cap and trade programs need to include all markets that impact carbon emission or storage and sequestration (Lippke and Perez-Garcia, 2008). Carbon sequestration is regulated via plant growth, plant death, and plant oxidation (Huston and Marland, 2003). These factors determine the biomass produced, the size and thus amount of carbon available to be stored in the plant, and the amount of carbon reintroduced into the land (Huston and Marland, 2003). Converting lands, especially native vegetation and forestland, to bioenergy crops could potentially create a carbon debt by releasing stored carbon to the atmosphere (Fargione et al., 2008). On the contrary, implementing these crops on degraded lands can provide GHG mitigation and simultaneous economic advantage (Fargione *et al.*, 2008). The greenhouse gas impact of renewable energy is one of its most attractive qualities. When bioenergy crops, especially low-input grasses, are placed on suitable lands and properly managed, they are capable of sequestering carbon while avoiding competition for land for food production (Tilman et al., 2006).

2.3.2.3 Crop Pollination

Pollination is the natural transfer of pollen to the ovaries of a flowering plant in order for fertilization to occur. Pollination by animal means is required for 15-30 percent of the US food supply and many other insects other than honeybees contribute to pollination of numerous crops (Chan *et al.*, 2006). The stability and amount of crop pollination services that native bee species provide depends on the proportion of natural upland habitat and vegetation surrounding the site, rather than farm management practices (Kremen, 2005). Many farmers temporarily import colonies of European

honeybees during bloom of crops to ensure adequate pollination occurs (Kremen, 2005). However, native, unmanaged bee populations near natural habitat are generally more diverse and abundant, which provides enhanced stability, quality, and quantity of pollination services (Kremen, 2005). Conserving wild, native pollinators near agricultural habitats improves pollination, which increases crop yield (Zhang *et al.*, 2007). It is also important to note that competition for pollinators from flowering weeds and other non-crop plants may decrease yields in some instances (Zhang *et al.*, 2007). The success of crop cultivation directly relates to the caloric and micronutrient availability for human consumption (Klein *et al.*, 2007). Furthermore, the success of pollinators completing their tasks effects the production of food, promotes increased biodiversity, provides the necessary reproduction for plants to continue the food chain, allows for the growth of vegetation for carbon sequestration, amends soil organic material, acts as a source of water treatment, and provides many other ecosystem services.

Not all plants require pollinators, such as wind pollinated or self-pollinating flowering plants. However, 87 of 115 globally important crops require pollination from some animal source (Klein *et al.*, 2007). With habitat conservation considered, maintaining pollination is a valuable ecosystem service. The delivery of this service depends on habitat conservation and is influenced by changing landuse (Lonsdorf *et al.*, 2009). Just as landuse change could potentially negate or worsen GHG emissions of bioenergy production, crop pollination could experience negative impacts resulting from loss of insect habitat and diversity (Norris, 2008). In addition, large-scale landuse change into wind-pollinated transgenic species could potentially provide a means of transgene leaking into native species (Moon *et al.*, 2010). Therefore it is imperative to understand

the environmental consequences of such a shift and to have the appropriate biotechnology policy in place to maintain sustainable genetic containment (Moon *et al.*, 2010). Therefore, mixtures of native grass species remain the most suitable bioenergy crop to maintain suitable pollinator habitat and diversity. Research has shown positive correlation with the diversity of pollinating insects and birds with plant diversity in grasslands in Wisconsin, further solidifying the benefits of perennial polycultures and native species over traditional intensive crops for insect and animal diversity (Fargione *et al.*, 2009). Landuse intensification may ironically result in reduced productivity due to a loss of important insect species, thus a reduction in vital pollination services (Bos *et al.*, 2007).

2.3.2.4 Water Quality

Maintaining the supply of freshwater to agricultural, industrial, and residential lands requires both limiting the degradation of water quality and maintaining active water purification through natural means such as wetlands (Chan *et al.*, 2006). Sediment is the largest pollutant of waterways in the United States (Baker, 1992). Furthermore, agriculture is the largest contributor to excess nutrients, mainly nitrogen and phosphorus, in freshwater in the United States (Foley *et al.*, 2005). Soil erosion and the deposition of soil, or sedimentation, occur naturally. However, through the use of modern agricultural techniques and development with dramatic soil disturbance, soil erosion has accelerated, leading to soil fertility and crop production issues. Sediment that accumulates in wetlands can affect the functioning of the wetland and the ecosystem services provided, such as floodwater storage and habitat, resulting in lower wetland productivity and decreased biodiversity (Gleason, 2008). Excessive sedimentation can also sacrifice the integrity and

operation of infrastructure such as dams, treatment basins, wetlands, and flood mitigating reservoirs. The added maintenance to avoid such issues is costly and increases where sediment removal is difficult, which can lead to ecosystem degradation. The use of best management practices (BMPs) has reduced wind and water soil erosion on sensitive cropland and grasslands. Conservation practices through land use and management practices can significantly reduce soil erosion and nutrient loss from soils, thus improving the ability for the delivery of ecosystem services (Gleason, 2008). Natural landscape acts as a sediment retention service by retaining soil and decreasing the velocity of overland flow. Increased sediment transport associated with intensifying agricultural production for bioenergy feedstocks can potentially cause nutrient loading issues as bound nutrientsoil particles are carried in overland flow during rain events (Nyakatawa et al., 2006). Nutrient loading of nitrogen and phosphorus in surface waters results in algal blooms, reduced dissolved oxygen levels, loss of biodiversity, and impaired aquatic habitat and reproduction (Carpenter et al., 1998). In addition, excessive loading of these pollutants oftentimes result in eutrophic conditions, leading to impaired waterbodies and drinking water contamination, jeopardizing human safety and the health of aquatic ecosystems, and reducing the overall aesthetics of the waterbody (Carpenter *et al.*, 1998; Nyakatawa et al., 2006). Therefore, the sustainability of bioenergy systems is immensely reliant on the decisions made for landscape management to provide economic benefits while maintaining environmentally-friendly landuse practices. As a result of the tremendous uncertainty in water resource allocation during a time of great agricultural expansion, this topic is the defining focus of the presented research.

2.3.3 Valuation

Valuation is the last of three steps in decision making (Daily *et al.*, 2000). The first step, identifying any alternatives, is an extremely important part of decision making, as well as the second step of identifying and measuring all possible impacts for each scenario (Daily et al., 2000). However, valuation aids in determining the extent of any and all consequences a decision has on current and future well-being (Daily *et al.*, 2000). Placing a quantifiable value on a system provided by an intangible being is difficult at best, and involves human judgment, which is in no way the absolute answer to the worth of losing or changing such a service (Daily et al., 2000). The economic value of the environment and the associated reasons for its conservation are complex and unclear. Current estimations for the value of ecosystem services \$33 trillion per year compared to a global GNP of \$18 trillion per year (Costanza et al., 1998). However, ecosystem services are often given little weight in terms of policy making, which may ultimately perturb the sustainability of human life (Costanza et al., 1998). The concept of placing value on intangible pieces of human life and the environment is difficult to fathom. Changes in the quality or quantity of services influence the benefits delivered to humans or the costs humans face with the removal of such services (Costanza et al., 1998). A large portion of positive contributions that the environment makes on human well-being benefits people directly, rather than using the market as a vector for translocation of benefits (Costanza et al., 1998). Clean air and water, climate regulation, and recreation are examples of services that are oftentimes overlooked and undervalued. In recent years, with a decline in the honey bee population, the value of ecosystem services such as these has become a topic of substantial interest. It is estimated that pollination and pest control from native insect species was worth in excess of \$240 billion at 1994 prices (Norris,

2008). It is becoming increasingly apparent that maintaining a sustainable ecosystem is crucial both economically and environmentally. Although bioenergy cropping systems have the potential to provide cost-effective, domestic energy, it is clear that without the conservation of ecosystem services, the long-term outlook for the agroeconomy could become disastrously bleak. By taking ecologically-informed approaches to landscape management that include ecosystem service provision, agriculture provides a means of effectively increasing ecosystem services (Porter *et al.*, 2009).

2.4 WATERSHED MODELS AND THEIR APPLICATIONS IN ECOLOGY

Due to the complex physical and chemical relationships present in ecosystems, computer simulation models are useful in determining long-term impacts of altering agricultural land management (Thomas *et al.*, 2009). Evaluating hypothetical situations that may be present in the future and predicting the impacts on ecosystem services at a large-scale requires sophisticated computer models. Proper model selection depends on many factors including the availability data, quality of data, desired model capabilities and the scope of research objectives. Three main types of watershed models exist: empirical, conceptual, and physically based. Physically based models account for physical characteristics of the region such as landcover, soil type, topography and climatic data. Empirical and conceptual models usually do not include these factors. Complex physically based models are useful in describing processes as a result of natural phenomena, but oftentimes require much more data and input parameters. Multiple computer models exist that are suitable for watershed modeling and that have been used in previous studies for both water quantity and quality predictions.
2.4.1 Annualized Agricultural Non-Point Source Model (AnnAGNPS)

The AnnAGNPS model is a single event, continuous version, watershed-scale model designed to estimate the NPS pollution generation watersheds that are devoted mainly to agricultural production (Bingner *et al.*, 2007). AnnAGNPS was developed by the United States Department of Agriculture (USDA) Agricultural Research Service (ARS) and the USDA Natural Resources Conservation Service (NRCS) (Wang *et al.*, 2009). The model performs distributed modeling by dividing a watershed into homogenous units in order to predict surface water loadings of pollutants such as sediment, nitrogen, phosphorus, and agricultural chemicals. Each unit has relatively uniform physical and hydrologic characteristics (i.e. soil type, landuse, and topography).

2.4.1.1 AnnAGNPS Components

AnnAGNPS uses the Soil Conservation Service (SCS) curve number method and the Revised Universal Soil Loss Equation (RUSLE) to generate the daily runoff and daily sheet and rill erosion from fields, respectively (Bingner *et al.*, 2007). In-stream routing simulates the transport of sediment downstream. The Hydro-geomorphic Universal Soil Loss Equation (HUSLE) is used to provide a delivery ratio of sediment yield from erosion to the reach (Wang *et al.*, 2009). Channel runoff uses Manning's equation and lateral, subsurface flow is calculated using Darcy's equation (Borah and Bera, 2003). A modfified Einstein equation and the Bagnold equation are used to calculate the sediment transport capabilities of the reach (Bingner *et al.*, 2007). Precipitation can be in the form of irrigation, snowmelt, or rainfall.

2.4.1.2 Previous AnnAGNPS Research

AnnAGNPS has been used by Parker *et al.* (2008), Yuan *et al.* (2007), Wang *et al.* (2009) and Mankin *et al.* (2003) to evaluate the effects on water quality as a result of

agricultural practices, conservation practices, landuse change, and Best Management Practice (BMP) effectiveness.

2.4.2 Hydrologic Simulation Program-FORTRAN (HSPF)

HSPF is a continuous, lumped-parameter watershed model that produces a time history of water quality and quantity data for mixed agricultural and urban watersheds (Borah and Bera, 2003; Holvoet *et al.*, 2007). The model is commonly used to evaluate the impacts on these processes due to landuse change, point and non-point source pollution, and other physical phenomena and was developed by the Environmental Protection Agency (EPA) National Exposure Research Laboratory (Bicknell *et al.*, 1997). An advantage of HSPF over other models is its hourly temporal scale capable of making long-term predictions during periods of available continuous precipitation data. However, due to its theoretical nature and the empirical equations used for model calculation, HSPF requires a number of parameters, adding to the complexity of the underlying model complexity.

2.4.2.1 HSPF Components

The HSPF model predicts both runoff and constituent transport processes on pervious and impervious land areas and in-stream processes in the main channel as well as mixed reservoirs (Borah and Bera, 2003). Runoff is calculated using the Chezy-Manning equation and subsurface flow is calculated using empirical relationships of interflow, percolation, and groundwater outflow. Overland sediment is calculated using rainfall splash detachment, in which the wash-off of detached sediment particles is based on transport capacity of overland flow.

2.4.2.2 Previous HSPF Research

The HSPF model has been used by Diaz-Ramirez *et al.* (2005), Al-Abed and Al-Shariff (2008), Choi and Deal (2008), and Nasr *et al.* (2007) to evaluate landuse change and management practices on watershed hydrological characteristics and nutrient transport.

2.4.3 Soil and Water Assessment Tool (SWAT)

SWAT is a physically based model developed to estimate streamflow and stream reach loadings of nutrients, pesticides, and sediments on a watershed-scale on a continuous daily time-step in predominantly agricultural watersheds (Spruill *et al.*, 2000). The SWAT model was developed by the USDA-ARS. The SWAT model is used to predict the long-term impact of management practices on constituent yields in complex watersheds with varying soils, landuse, weather conditions, and management operations (Arnold et al., 1998). The model bases its predictions on a complex structure of routing runoff and constituents throughout a defined watershed and is one of the most comprehensive models of its kind (Saleh and Du, 2004; Powers, 2007). The watershed delineation tool in SWAT allows a watershed to be divided into subwatersheds based on topography, which are further divided into HRUs (hydrologic response unit) based on land use, soil type, and slope. By defining HRUs, the location of constituent load origination can be identified based on site-specific (field-scale) characteristics. This is useful for determining the best location for implementing conservation practices and for identifying high-priority areas in need of further evaluation.

2.4.3.1 SWAT Components

The major components of the model include weather data, soils data, slope classifications, landuse data, nutrient and pesticide applications, and management

practices such as tillage, fertilization, and planting/harvesting dates. The hydrologic component of the SWAT model uses the modified SCS curve number method to determine surface runoff during precipitation events (Saleh and Du, 2004). Soil erosion and sediment yields for each HRU are determined by the Modified Universal Soil Loss Equation (MUSLE) (Neitsch, 2005). Lateral subsurface and groundwater flow is calculated based on a kinematic storage model and empirical equations. Channel routing and flow are based on the variable storage coefficient method Manning's equation, respectively (Borah and Bera, 2003). Channel bed degradation and deposition, nitrogen and phosphorus cycles, and pesticide fates are also simulated in SWAT.

2.4.3.2 Previous SWAT Research

A substantial number of studies have used SWAT to evaluate a wide variety of environmental applications. As of 2007, 250 peer-reviewed published articles had been identified that either used SWAT or reviewed SWAT components (Gassman *et al.*, 2007). For example, Kannan *et al.* (2006), Vazquez-Amabile *et al.* (2006), Du *et al.* (2006), Ng *et al.* (2010), Ullrich and Volk (2009), Maski *et al.* (2008), Kamble *et al.* (2005), Arnold *et al.* (1998), Saleh *et al.* (2000), Saleh and Du (2004), Galvan *et al.* (2009), and Santhi *et al.* (2006), Luo *et al.* (2008), Tong and Naramngam (2007), and many others, have used SWAT to evaluate landuse change, BMPs, agricultural practices, spatial scaling effects, and bioenergy production on hydrology, sediment, nutrient, and pesticide yields.

2.4.4 Integrated Valuation of Ecosystem Services and Tradeoffs (InVEST)

InVEST is a model developed by the Natural Capital Project, among others, to support environmental decision-making regarding the change in ecosystem services provided by the environment due to landuse change (Daily *et al.*, 2009). The InVEST model is spatially explicit GIS interfaced program that is based on ecological production functions and methods for assessing the economic value of services, conservation of biodiversity, and value of commodities provided by the landscape, as reported in either biophysical or monetary terms (Nelson *et al.*, 2009). The model operates at different levels of complexity, or tiers, to ensure model adaptability across a variety of applications (Daily *et al.*, 2009). However, the variation in data availability, data quality, and understanding of the underlying model processes results in model uncertainty (Nelson *et al.*, 2009).

2.4.4.1 InVEST Components

The InVEST model relies heavily upon user-defined input parameters such as threats to biodiversity, carbon pools, landcover harvest rates, and market prices of commodities. Due to the subjectivity of this data, the model has an inherent uncertainty associated with the results. However the model does require data layers that are readily accessible and accepted such as landcover, soil depth, precipitation, and the digital elevation model. The model operates on an annual average time step, although future versions are expected to include daily to monthly time steps (Tallis *et al.*, 2010).

2.4.4.2 Previous InVEST Research

The InVEST model has been used by Nelson *et al.* (2009) to predict changes in ecosystem services based on stakeholder-defined scenarios of landuse change.

3. INTRODUCTION TO METHODOLOGY AND RESULTS

This thesis is in the form of four research papers that have been submitted to scientific journals. The first paper entitled "The Effects of Postemergence Herbicides on Biomass Accumulation and Bioenergy Quality of Field and Silage Corn (*Zea mays*)" aims to determine the suitability of pesticide applications in the case that large-scale implementation of lignocellulosic biomass production becomes widespread. This research is the result of field studies conducted at the Michigan State University Agronomy Farm in East Lansing, MI in 2008 and 2009 to evaluate the effects of postemergence herbicide treatments on a) field and silage corn above-ground biomass and b) cell wall digestibility (translated into ethanol yield). The herbicides that were evaluated were 2,4-D amine, atrazine, bromoxynil, dicamba +diflufenzopyr, mesotrione, and nicosulfuron with silage and field corn treated with the same application rates.

The second paper titled "Environmental Impact Analysis of Biofuel Crops Expansion in the Saginaw River Watershed" aims to examine the long-term environmental implications, specifically water quality, of bioenergy cropping system expansion, to determine the environmental suitability of bioenergy crops, and to obtain information to aid in the decision making process regarding landuse management in the Saginaw River watershed. The Soil and Water Assessment Tool (SWAT) model was used to model the effects of four landuse scenarios, 17 different bioenergy crops under 42 rotations on sediment load, total nitrogen load, and phosphorus load during a 19 year (1990 to 2008) period on a daily basis. The SWAT model was calibrated and validated for daily streamflow, sediment load, total Kjeldahl nitrogen load, and total phosphorus load using observed water quality and climate data. Management operations, including crop rotation schedules, fertilizer and pesticide applications, and tillage regimes were applied to provide the most practical and accurate representation of actual agricultural practices in the region. The research presented in this paper was performed at a watershed scale and includes the implications of converting marginal land to bioenergy crops, the importance of using local agricultural management practices in model setup, the temporal variation of pollutant loads as compared to the base scenario (current landcover), and the suitability of bioenergy crops grown on four landuse scenarios.

The third paper titled "Water Quality Impact Assessment of Large Scale Biofuel Crops Expansion" aims to evaluate the environmental impacts of bioenergy cropping systems on a larger scale with extensive spatial variability of landuse and climatic, physiographic, and geographic conditions. The same procedure was followed as the previous paper, with the only difference being a monthly time step and a more expansive study area. The Soil and Water Assessment Tool (SWAT) model was again used to model the effects of four landuse scenarios and 17 different bioenergy crops have on sediment load, total nitrogen load, and phosphorus load during a 19 year (1990 to 2008) period on a monthly basis. The SWAT model was calibrated and validated for monthly streamflow, sediment load, nitrogen load (various nitrogen formulations depending on watershed), and total phosphorus load using observed water quality and climate data. The research presented in this paper assists in land management decision making at a largescale by showing the spatial variability of pollutant loads for each bioenergy rotation, by identifying high priority areas for the implementation of conservation practices to reduce sediment, nitrogen, and phosphorus contribution to surface waters, determining the suitability of bioenergy crops on various landuse scenarios, and determining the statistical significance of the differences of each rotation from the base scenario.

The fourth and final paper titled "Effects on Aquatic and Human Health due to Large Scale Bioenergy Crop Expansion" aims to determine the impacts of agricultural practices (specifically herbicide application in bioenergy cropping systems) on aquatic ecotoxicity and human health. The Soil and Water Assessment Tool (SWAT) model was used to predict pesticide concentration in each stream reach during a six year (2000-2005) study period on a daily basis. The herbicides atrazine, bromoxynil, glyphosate, metolachlor, pendimethalin, sethoxydim, triflualin, and 2,4-D amine were incorporated into the bioenergy crop rotation management practices in SWAT. Threshold toxicity levels were obtained for the bluegill and for human consumption for all pesticides being evaluated through an extensive literature review. The resulting data collection was used to demonstrate the enormous amount of basin-wide pesticide concentration variability and determine the length of stream impairments due to the application of each herbicide. With this data, policy makers and land managers will be able to identify areas where pesticide application will have negative impacts, and therefore, where conservation efforts should be focused.

4. THE EFFECTS OF POSTEMERGENCE HERBICIDES ON BIOMASS ACCUMULATION AND BIOENERGY QUALITY OF FIELD AND SILAGE CORN (ZEA MAYS)

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Abstract. Energy derived from renewable, biological sources is crucial in mitigating negative environmental impacts and ensuring future energy needs. However, despite innumerable advancements in bioenergy research, an improved understanding of the agronomic effects of herbicide treatments on both corn development and ethanol feedstock quality is necessary for the development of successful full-scale feedstock production. Field studies were conducted at the Michigan State University Agronomy Farm in East Lansing, MI in 2008 and 2009 to evaluate the effects of postemergence herbicide treatments on a) grain and silage corn above-ground biomass and b) cell wall digestibility (translated into ethanol yield). Biomass samples were analyzed for glucose release by enzymatic cell wall digestion and potential cellulosic ethanol production was calculated. Injury was observed two weeks after treatment with 2,4-D and bromoxynil in 2008, this resulted in a $1.8 \text{ t} \text{ ha}^{-1}$ decrease of grain corn biomass for bromoxynil

treatments only. In contrast, herbicide treatments had no significant effects on the biomass accumulation of silage corn. Bromoxynil, when sprayed on silage corn, yielded greater biomass than the non-treated. The greatest biomass and glucose release by enzymatic cell wall digestion was observed for the 2008 silage corn at 20 t ha⁻¹ and 17.6 percent glucose release, respectively. Cool weather resulted in poor growing conditions for the 2009 season. The 187 fewer growing degree days in turn exaggerated the effects of herbicide treatment on plant growth and glucose percentages. Silage corn produced significantly greater biomass, glucose release by enzymatic cell wall digestion and ethanol yield than the field variety with the same nutrient inputs. The results suggest that the selection of both corn type and herbicide treatment significantly influences the biomass accumulation as well as the bioenergy feedstock quality.

4.1 INTRODUCTION

Increasing demand for renewable, carbon-neutral energy sources to replace current fossil fuels has led to an increase in the production of fuels derived from biological sources (Pimentel *et al.*, 2009). Biofuels in the United States are currently produced primarily from agricultural feedstocks, specifically from starch-rich corn grain (Mol, 2007). Although corn grain provides a basis for transition from fossil fuels to renewable sources, the current fermentation process excludes much of the sugars located in structural fibers, known as lignocellulose (Himmel *et al.*, 2007). Cellulosic biomass can potentially provide a sustainable source of energy, liquid transportation fuels, and biomaterials, while minimizing competition for food production (Himmel *et al.*, 2007; Antizar-Ladislao and Turrion-Gomez, 2008). As the biofuel industry evolves, the

scientific knowledge base supporting agricultural feedstock production must follow suit. However, many aspects of large-scale bioenergy crop production are adapted from current agronomic practices emphasized on improved grain yields, not cellulosic ethanol yield (Carroll and Sommerville, 2009). In order to allow growers to maximize productivity and further support the need for biofuel production, information regarding the agronomic aspects of bioenergy crop production must be more available, especially relating to herbicides (McLaughlin and Walsh, 1998). It has been shown that herbicides have the potential to affect secondary metabolism and other physiological processes, resulting in altered plant growth, especially during early growth stages (Alla and Younis, 1995; Vencill et al., 1989). In addition, reports have documented injury resulting from herbicide applications of bromoxynil, nicosulfuron, and dicamba on corn, which often leads to only minor grain yield loss (Kunkel et al., 1996; Krausz et al., 1999; Green and Ulrich, 1993). A number of studies have been conducted to evaluate the affect herbicides have on crop yield, based on their effectiveness at suppressing weeds that compete for moisture, sunlight, and nutrients (Vanheemst, 1985; Harvey and Wagner, 1994; Lybecker et al., 1991; Askew and Wilcut, 1999; Hall et al., 1992). However, after an extensive literature review, the authors are unaware of any studies that examine the interaction between herbicides, corn biomass and ethanol yield, based solely on the chemical's influence on cellular and physiological behavior that control plant growth factors. Therefore a study was conducted to evaluate the effect postemergence (POST) herbicides labeled for use in corn have on biomass yield and potential cellulosic ethanol yield. Grain and silage corn hybrids were harvested and dried in the same manner as forage maize, mimicking conditions for treating feedstock that would be used in large-scale cellulosic

ethanol production. The results presented in this study are compared over a two year period and are derived from measurements of above-ground biomass, glucose release by enzymatic cell wall digestion, and theoretical ethanol yield.

4.2 MATERIALS AND METHODS

Experiments were conducted in 2008 and 2009 at two separate field locations at the Michigan State University Agronomy Farm in East Lansing, MI on a sandy-loam (fine-loamy, mixed, mesic, Aeric Ochraqualfs) soil with 2.3 percent soil organic matter (SOM) and pH of 7.1 and 3.3 percent SOM and pH of 6.2 in 2008 and 2009, respectively. Tillage at the site included fall chisel-plowing and spring field cultivation. Two corn hybrids were examined; Dekalb® DKC 46-60 (grain corn hybrid) and NK® N49E3 (silage corn hybrid) were planted at seed populations of 79,074 and 76,603 seeds ha⁻¹, respectively, on May 15, 2008 and May 12, 2009. The entire study received soil-applied S-metolachlor {2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl] acetamide} at 1400 g ai ha⁻¹ and atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5triazine-2,4-diamine] at 1400 g ai ha⁻¹ prior to planting to reduce weed pressure and aid in hand-weeding. Plots were maintained weed-free by hand hoeing throughout the growing season. Each plot (3.05 m x 10.67 m) was planted with four rows of seed spaced 76 cm apart. The experimental design was a split-plot, randomized complete block with four replications of each treatment. Main plot factors were corn type of either grain or silage corn with sub-plot factors consisting of seven herbicides (Table 4). Herbicide

treatments were applied at the V4 growth stage with a tractor-mounted sprayer calibrated to deliver 187 L/ha at 207 kPa using TeeJet® 8003 flat-fan nozzles.

Crop injury was assessed visually 2 weeks after treatment (WAT). Growth stage, corn height, and leaf number were recorded from four representative plants within the two innermost corn rows every two weeks following application until silking. A self-propelled harvester was used to harvest and measure the biomass from the inner two rows of each plot in a manner likely to be used for large-scale bioenergy feedstock production. Forage samples were collected from each plot, weighed, and oven-dried to determine the total dry matter. Samples from each plot were then ground (1-2 mm particle size) and analyzed for percent dry matter, forage quality, and percent glucose.

Glucose release by enzymatic digestion of cell walls for ethanol production was determined using the method described by the Department of Energy Great Lakes Bioenergy Research Center (GLBRC) at Michigan State University (Santoro *et al.* 2010). Microtubes were loaded with 2 mg of thoroughly mixed, dried and ground plant material for each sample of corn biomass. Samples were analyzed in triplicate with biological replicates included (Santoro *et al.* 2010). A dilute NaOH (6.25 mM) pretreatment solution was added to each tube and incubated at 90^oC for 3 hours. After cooling, 50mM citrate buffer (pH 4.5) and 0.01 percent sodium azide were added to the solutions. Digestions were initiated using Accellerase 1000 (a gift from Genencor) at a concentration of 30 mg protein g glucan⁻¹. Samples were incubated at 50 C for 20 hours. The microtubes were centrifuged at 1,500 x g for 3 minutes, separating the solid residue from the digested biomass. Glucose was determined by the glucose oxidase-peroxidase method as described (Santoro *et al.* 2010). In this paper "glucose release" will refer to

the amount of glucose released from cell walls resulting from the enzymatic action of Accellerase 1000. The amount of glucose released is expressed as a percent; w is derived from the mass of glucose detected per total starting dry weight of plant biomass.

All data were subjected to analysis of variance using the MIXED procedure in the SAS Statistical Software Package (SAS, 2009).

4.3 RESULTS AND DISCUSSION

4.3.1 Crop Injury

Bromoxynil and 2,4-D showed significant injury in early growth stages two weeks after treatment. Injury was characterized by twisting and leaning of the stem, fused brace roots, and poor development of brace roots in plots treated with 2,4-D and necrotic tissue in plots treated with bromoxynil. However, no late season corn injury was observed with any of the POST treatments in either year. Significant biomass yield reduction was not observed in silage corn as a result of this injury. However, biomass of grain corn was reduced when treated with bromoxynil, which may be a result of the injury observed in early growth stages.

4.3.2 Variation by Corn Type

A year by corn type interaction was observed for corn maturity (measured in vstage) (Table 1). Silage corn in 2009 was less mature than grain corn in 2008 and 2009 and silage corn in 2008. This is likely due to the N49E3 silage corn variety being longer maturity (106 day) than the DKC 46-60 grain corn variety (96 day), and to adverse growing conditions in 2009. In addition, a year by corn type interaction was observed for biomass yield. Both silage and grain corn yielded significantly less biomass in 2009, likely due to the 187 fewer growing degree days relative to 2008 (Table 2), resulting in delayed maturity for both hybrids. Silage corn in 2008 had the greatest biomass, and biomass within varieties was greater in 2008 than in 2009 (Table 1). Percent glucose released and ethanol yield values followed similar trends as observed for maturity; both values were greater for silage corn in 2008 than in 2009 and also both values were greater for silage corn than grain corn in the two years. The 2009 growing season accumulated fewer heat units, leading to a decrease in vegetative growth and poorly developed plant tissue prior to physiological maturity (Nielsen and Hinkle, 1996). As a result, the 2008 growing season provided sufficient heat units for the silage variety to maximize its yield potential and digestibility for ethanol fermentation. Silage corn, generally used for ruminant dairy feed, is assessed for forage quality using multiple techniques, one of which being neutral detergent fiber digestibility (NDFD). NDFD relates the convertibility of cell wall structures in plant tissue to ethanol and may be an efficient method for determining bioenergy feedstock quality (Lorenz et al., 2009). Silage corn hybrids generally accumulate more biomass than grain corn hybrids (Figure 1). Silage corn surpasses the vegetative growth of grain corn during early growth stages in typical production years like 2008; however, in 2009 no biomass advantage was observed.

Corn Type	Year	Maturity	Yield	Glucose	Ethanol Yield ^b
			-1 t ha	%	L ha ⁻¹
Grain	2008	9.0 a	17 b	15.3 b	1599 b
Silage	2008	9.0 a	20 a	17.6 a	2160 a
Grain	2009	8.6 a	15.6 c	15.3 b	1467 b
Silage	2009	7.9 b	15.9 bc	15.5 b	1507 b
LSD		0.5	1.1	1	170

Table 1. Corn maturity 28 days after postemergence treatment, dry biomass yield, percent glucose, and ethanol yield in 2008 and 2009 by corn type averaged by herbicide treatment.

 a Means within columns followed by the same letter are not significantly different p $\leq 0.05.$

^b Represents 95 percent of the theoretical ethanol yield (0.647 mL ethanol g glucose⁻¹) (Thomas *et al.*, 1996).

Table 2. Growing degree days (GDD) accumulated in East Lansing, MI from 4/1-10/31.

Year	GDD
2008	2467
2009	2654
Normal	2726

^a Source: (MSUEP, 2010)



Days After Treatment (d)

Figure 1. Corn height 28, 42, and 56 days after treatment with error bars representing one standard deviation.

	Intercept	Slope	r ²
Grain Corn 2008	-0.174	0.051	0.990
Silage Corn 2008	-0.737	0.069	0.979
Grain Corn 2009	0.066	0.030	0.822
Silage Corn 2009	-0.454	0.043	0.898

Table 3. Regression values for Figure 1.

4.3.3 Variation by Herbicide Treatment

An herbicide by corn type interaction was observed for grain and silage corn biomass yields as affected by herbicide treatment. No year effect was observed; therefore data are over averaged years (Table 4). In addition, bromoxynil and mesotrione treatments on silage corn resulted in the greatest yields. Atrazine and dicamba + diflufenzopyr treated silage corn produced significantly less yield than the bromoxynil and mesotrione treated silage corn. However the yield of Atrazine and dicamba + diflufenzopyr treated silage corn was not significantly different than the remaining silage corn treatments. Silage corn had a greater biomass yield overall than grain corn regardless of herbicide application. The treatments in grain corn that produced the greatest biomass were the non-treated, atrazine, and mesotrione. The greatest biomass reduction was observed when bromoxynil was applied to grain corn, yielding less than the non-treated grain corn, this is the direct opposite of what was observed for silage corn. Bromoxynil treatments in silage corn resulted in the largest yield increase. It is suggested that many herbicides can actually alter the activity of enzymes that control the secondary metabolism, possibly explaining the increase in yield compared to the nontreated corn (Alla and Younis, 1995; Cottingham and Hatzios, 1992)). As previously discussed Table 1 shows a year by corn type interaction in ethanol yield. Although there appeared to be slight interactions with herbicide treatments, the differences are not statistically significant. This is likely due to the noise in the collected data. However, the interaction between corn type and herbicide treatment is compelling to support careful selection of herbicide treatment for corn to be grown for bioenergy feedstock. It is important to note that this study was conducted on only one variety for each corn type; further research on the differential response to herbicides by hybrid variety may provide additional useful information for future bioenergy feedstock production. Many studies have evaluated the tolerance of various corn hybrids to herbicide treatments and observed a general large span of differing tolerances (Green, 1998; Rowe et al., 1990). Although those comparisons were not performed in this study, the gathered data and evidence of possible herbicidal effects on biomass yield and glucose release from lignocellulose suggest this information is vital for producers considering an herbicide regime for corn

production when optimizing total above-ground biomass while maintaining essential weed control.

Corn	Herbicide ^a	Rate ^b	Biomass		
Туре	Therefore a		Yield ^c		
~ .		g ai (ae) ha ⁻¹		t ha ⁻¹	
Grain		500	150		
	2,4-D amine	530	15.8	de	
	atrazine + COC	1120 + 1.25 % v/v	16.9	bcd	
	bromoxynil	420	14.9	e	
	dicamba + diflufenzopyr + NIS	200 + 0.25 % v/v +	16.1	cde	
	+ AMS	1070			
	mesotrione + COC + AMS	110 + 1 % v/v + 540	17.1	bcd	
	nicosulfuron + COC	30 + 1 % v/v	16.5	cde	
	non-treated		16.7	bcd	
Silage					
Shage	2.4-D amine	530	17.5	abc	
	atrazine + COC	1120 + 1.25 % v/v	17.1	bcd	
	bromoxynil	420	18.9	а	
	dicamba + diflufenzopyr + NIS	200 + 0.25 % v/v +	17.2	bcd	
	+ AMS	1070			
	mesotrione + COC + AMS	110 + 1 % v/v + 540	19.0	а	
	nicosulfuron + COC	30 + 1 % v/v	18.2	ab	
	non-treated		17.4	abc	
LSD			1.6		

Table 4. Dry biomass yield by herbicide treatment and corn type averaged over years.

^a Abbreviations: AMS, ammonium sulfate; COC, crop oil concentrate; NIS, non-ionic surfactant. b Treatment rates for dicamba are expressed in g ae ha⁻¹.

 c Means within columns followed by the same letter are not significantly different $p \leq 0.05.$

4.4 CONCLUSION

The goal of the research done in this study was to determine the impact that postemergence herbicide treatments applied to grain and silage corn varieties has on aboveground biomass accumulation, glucose release from lignocellulose, and ethanol yield. Cellulosic biomass has the potential to be a viable feedstock for liquid fuel production, namely ethanol. However, it is essential to investigate any negative consequences the use of herbicides may have on the biomass yield of corn stover for commercial feedstock production practices. According to observations and data acquired in this study, silage corn hybrids yield more biomass and release greater amounts of glucose per dry weight (resulting in greater ethanol yield) when favorable growing conditions are present. In addition, although visible physiological plant injury was observed in early growth stages, herbicide treatment resulted in increased biomass yield and glucose release compared to non-treated silage corn. Although there was a significant corn type by year interaction, there were no statistically significant interactions with herbicide treatments. In summary, we conclude that postemergence herbicides can have potentially beneficial effects when applied to corn that will be used as a feedstock for cellulosic ethanol production.

Acknowledgments

The authors would like to thank Andrew Chomas, Keith Dysinger, Jacob Gebhardt, Bryce Conklin, and Dan Tratt for their assistance.

5. ENVIRONMENTAL IMPACT ANALYSIS OF BIOFUEL CROPS EXPANSION IN THE SAGINAW RIVER WATERSHED

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Abstract. The Saginaw River watershed (15.262 km^2) located in the east central portion of Michigan's Lower Peninsula is the State's largest and is largely used for agricultural production. Non-point source pollutant loadings in the form of sediment, nitrogen, and phosphorus are a major issue in this watershed and have led to 22 303(d) listed waterbodies and multiple Total Maximum Daily Loads (TMDL). The environmental implications of expanding agricultural land into bioenergy crop production are not wellknown. This study implements the Soil and Water Assessment Tool (SWAT) to predict the effects landuse conversion will have at a large watershed-scale. The model generally performed satisfactory on a daily basis during the calibration and validation periods for flow (2001-2008) and sediment and nutrients (2000-2005). Management operations, including crop rotation schedules, fertilizer and pesticide applications, and tillage regimes were applied to provide the most practical and accurate representation of actual agricultural practices in the region. Four scenarios including 15 crop rotations were developed to reflect current and future trends of producing first and second generation bioenergy crops, respectively. The results from SWAT showed that environmental effects varied greatly between crops based on the landscape being converted. Continuous corn with stover removal, when implemented on all land that can be tilled, has the potential to increase total nitrogen, total phosphorus and sediment loads by up to 1375, 792, and 493

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percent, respectively. However, when applied on land classified as "other" crops, the same rotation experiences reductions in both sediment and phosphorus. Perennial grasses (miscanthus, switchgrass, native grasses) experience similar behavior of varied pollutant loading dependent on landscape.

5.1 INTRODUCTION

Increasing global and domestic energy demands have led to an enormous push for a transition to alternative sources. Despite vast increases in traditional energy technology (i.e. petroleum based fuels, nuclear, solar), a viable solution to reliance on fossil fuels has yet to accommodate growing demand. Fossil fuels are available in a finite amount, accounting for about 80 percent of global energy supply, and will be exhausted in a matter of decades at current consumption rates (Goldemberg, 2007). Consequently, renewable fuel sources originating in the agricultural sector have become a very important means for the replacement, or at least partial substitution, of fossil fuels. Reducing fossil fuel dependency potentially cuts consumer costs, mitigates climate change, creates new jobs, promotes the supply of domestic energy, and diversifies energy sources. By the year 2025, global energy consumption is expected to increase by over 57 percent from 2002 values (Rooney *et al.*, 2007). Meanwhile, renewable energy accounts for only 7 percent of the nation's 99.3 Quadrillion Btu consumption (USEIA, 2009).

Biofuels are liquid petroleum replacement fuels, such as ethanol and biodiesel, derived from biomass conversion. Biomass provided 53 percent of the nation's renewable energy in 2008 and is the sole sustainable solution for fuel, chemicals, and materials generally produced from petroleum (USEIA, 2009; Lynd *et al.*, 2009). These "biofuels"

are particular appealing to environmentalists and policymakers for their promise as a solution to foreign oil dependency, increasing greenhouse gases, and rising energy costs (Groom *et al.*, 2008). However, evidence of negative consequences are prevalent, as for example, greenhouse gas emissions from landuse change towards corn-based ethanol are estimated to nearly double (Searchinger *et al.*, 2008). The National Renewable Fuel Standard program (RFS) was created as a provision of the United States Energy Policy Act of 2005 (USEPA, 2009a). Revisions to this program in the 2010 RFS have increased the requirements for renewable fuel volume to 15.2 and 30 billion gallons by 2012 and 2020, respectively (USEPA, 2009a). In order to achieve these milestones, the agricultural production of the nation is going to have to expand and policy must support this sector. Unfortunately, the implications of bioenergy cropping expansion are not adequately understood or accepted especially at large scales.

The aspects of biofuel production, whether positive or negative, are an extremely necessary consideration in the sustainability of such a practice. Biofuel crop production shows promise in reducing the United States' dependency on fossil fuels, adding political and economic stability to the nation, and providing reliable energy sources for future generations (de Friature *et al.*, 2008). However, the long-term environmental repercussions resulting from a shift towards bioenergy cropping systems are of imperious concern. Carbon emissions contributing to global warming through greenhouse gas accumulation are of key significance for the success of biofuels. Energy from bioenergy crops are largely carbon neutral, especially when compared relative to fossil fuels, as the carbon emitted for production is regained during the growth of the replacement crop (Rowe *et al.*, 2009; Gillingham *et al.*, 2008). However, when landuse change is taken into

consideration, many of the benefits associated with biofuels are uncertain, and in some cases offset by the negative environmental implications (McLaughlin and Walsh, 1998). It is possible that the conversion of agricultural land for production of bioenergy feedstock will possibly threaten environmental quality, specifically water quality (Nyakatawa *et al.*, 2006). Therefore, in order for biofuels to be a sustainable solution and to prevent degradation to the natural biodiversity, their existence must avoid intensifying agricultural impacts and the displacement of native habitats or cropland necessary for food production (Groom *et al.*, 2008). Ecosystem services such as biodiversity, carbon sequestration, crop pollination, erosion control, water quality enhancements, flood mitigation, and food production may experience loss (Groom *et al.*, 2008).

Effectively addressing the impacts of bioenergy cropping systems should include water quality and water quantity aspects.

a) Water quality: Increasing the acreage under cultivation to produce bioenergy crops, many of which are input-intensive, may produce negative water quality implications. Agriculture is the largest contributor to excess nutrients, mainly nitrogen and phosphorus, in freshwater in the United States (Foley *et al.*, 2005). The current biofuel crop of choice, corn, is input-intensive, requiring more nitrogen fertilizer, herbicide, and insecticide than any other crop in the United States (Pimentel *et al.*, 2005). Nutrient loading of nitrogen and phosphorus in surface waters results in algal blooms, reduced dissolved oxygen levels, loss of biodiversity, and impaired aquatic habitat and reproduction (Carpenter *et al.*, 1998). During precipitation events, phosphorus binds to the soil particles of sediment carried by overland flow. These pollutants along with nitrogen are responsible for eutrophication, which is a main cause of impaired surface waters, and drinking water

contamination (Nyakatawa *et al.*, 2006). The results are negative effects on human safety and aquatic ecosystems such as death of coral reefs, fish kills, reductions in harvestable fish, and reduced aesthetic value of the water body (Carpenter *et al.*, 1998).

b) Water quantity: With freshwater necessary for human life, the quality of ground and surface water is imperative for survival. However, the quantity of surface waters is an extremely essential topic as well. Agriculture is already responsible for 70 percent of the world's freshwater withdrawals (Stone et al., 2010). Irrigation of agricultural land accounts for 65 percent of total freshwater withdrawals in the U.S. and has increased 60 percent since 1960 (Hutson et al., 2004; Berndes, 2002). A significant amount of water is required for the refining portion of ethanol production (4-6 gallons water per gallon ethanol) as well as for plant growth, especially under irrigation (de Fraiture et al., 2008). This makes it difficult to warrant the expansion and intensification of agricultural production when water use is highly stressed to a point passed sustainable, especially when an increase in irrigation withdrawals by 20 percent are required to meet future global food demand by 2050 (de Fraiture et al., 2008; Berndes, 2002). However, crops such as switchgrass, a C4 perennial crop, have been shown to produce substantial yields without irrigation; and they have a positive effect on water quality and quantity and soil erosion (McLaughlin and Walsh, 1998).

The objectives of this study were to examine the long-term environmental implications, specifically water quality, of bioenergy cropping system expansion, determine the environmental suitability of bioenergy crops, and obtain information to aid in the decision making process regarding landuse management. The Soil and Water Assessment Tool (SWAT) was used to model the effects of four scenarios, 17 different

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bioenergy crops under 42 rotations on sediment load, total nitrogen load, and phosphorus load in the Saginaw River Watershed during a 19 year (1990 to 2008) period on a daily basis. This watershed, which drains into the Saginaw Bay and subsequently Lake Huron, is intensively cultivated with crops.

5.2 MATERIALS AND METHODS

5.2.1 Study Area

The Saginaw River Watershed (hydrologic unit code 040802) is located in the east central portion of Michigan's Lower Peninsula, draining into the Saginaw Bay of Lake Huron. The watershed is the largest in Michigan (22,556 km²) and is home to the nation's largest contiguous freshwater coastal wetland system (USEPA, 2009b). This study focuses on the six watersheds located within HUC 040802 (Figure 2), including the Tittabawassee (04080201), Pine (04080202), Shiawassee (04080203), Flint (04080204), Cass (04080205), and the Saginaw (04080206) watersheds. Consequently, the total watershed area in this study is about 15,262 km² (1,526,200 hectares) with approximately 44.6 percent being used for agricultural purposes, 15 percent developed, 25 percent forest, 14 percent wetlands, and the rest water. The long-term average annual precipitation that was obtained from the National Climatic Data Center (NCDC) precipitation stations selected (Figure 3) is 82.1 centimeters (32.32 inches). The minimum elevation (above the sea level) in the watershed is 177 meters whereas the maximum elevation is 472 meters, resulting in a 245 meter mean elevation.



Figure 2. Location of the Saginaw River Watershed. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis. *5.2.2 General Water Quality Issue*

Non-point source pollution is a major contributor to the deteriorated water quality conditions of the region. The watershed has many threats to water quality, and due to contaminated sediments, degraded fisheries, fish consumption advisories, and impairment to recreational activities, the watershed has been designated as one of the 26 Great Lakes Areas of Concerns (AOCs) listed in the United States (USEPA, 2009c). In order for a waterbody or watershed to qualify as an AOC, it must have at least one beneficial use impairments, such as beach closings or degradation of benthic habitat (GLIN, 2009). The main contributors to these impairments are excessive nutrient loading, soil erosion, and contaminated sediments. There are currently 22 records on the Michigan Section 303(d)

listing, and a number of Total Maximum Daily Loads (TMDLs) have been developed for the Saginaw River Watershed, including sediment (Pine), total suspended solids (Cass), E.Coli (Flint, Cass, Tittabawassee and Shiawassee) and pathogens (Flint) (USEPA, 2010). The 303(d) listed waterbodies are shown in Figure 4 along with the United States Geological Survey (USGS) flow gauging station 04157000 and Michigan Department of Environmental Quality (MDEQ) water quality gauging station 090177.

5.2.3 SWAT Model

The Soil and Water Assessment Tool (SWAT) is a physically based model developed to estimate flow generation and nutrient, pesticide, and sediment loadings on a watershed scale. These estimations are based on landuse practices in complex watersheds with varying soils, landuse, weather conditions, and management operations over long time periods (Arnold et al., 1998). ArcSWAT, the ArcGIS extension of the SWAT 2005 program, is a graphical user interface for the SWAT model used in this study. The major components of the model include weather data, soils data, slope classifications, landuse data, nutrient and pesticide applications, and management practices. The SWAT model uses the modified SCS curve number method to determine surface runoff during precipitation events (Neitsch et al., 2005). Soil erosion and sediment yields are determined by the Modified Universal Soil Loss Equation (MUSLE). If properly calibrated, the SWAT model can efficiently predict the impacts of future land use conditions on flow and water quality. The accuracy of this model depends on complete understanding of the regional processes and of internal model processes. Therefore, setting up the model requires considerable time commitment for both data collection and model familiarization (Gassman et al., 2007).

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Figure 3. Saginaw Weather Stations.



Figure 4. Gauging Stations and 303(d) listed waterbodies.

5.2.4 Crop Rotations and Management Operations

5.2.4.1 Crops

The main focus of this paper is to examine the effects of landuse change into bioenergy crops, therefore the crops had to be identified for their suitability as a potential use in the region for biofuel feedstock. The bioenergy crops considered for conversion from the current landuse were barely, canola, cassava, corn, corn stover, jatropha, miscanthus, native grasses, potato, rice, rye, sorghum, soybean, sugar cane, sugarbeet, switchgrass, and wheat. However, after determining the suitability for growth in the Saginaw Watershed region, the amount of inputs, management practices, climate, and cost of conversion from typical farming practices to the proposed crops, the crops considered were reduced to corn, canola (fall), cereal rye, sorghum, soybean, miscanthus, corn stover (40 percent residue removal), switchgrass, and native grasses.

5.2.4.2 Rotations and Operation Schedules

Crop rotation is a historical cultural practice that effectively controls noxious weeds, pests and disease, increases soil fertility and healthy physical structure, enhances root-zone biological activity, and increases productivity (NCSU, 2005). In this study, possible crop rotations that would be likely implemented were identified. The rotations were assembled using data obtained from the Michigan State University Extension (MSUE) for the bioenergy crops used in the simulations. Based on this information, 15 rotations were developed, including corn-soybean-canola (Crn-Soy-Can), corn-soybeanrye (Crn-Soy-Rye), corn-soybean (Crn-Soy), Corn Stover (40 percent residue removal)soybean (CrnS-Soy), sorghum-soybean (Srg-Soy), continuous canola (CCan), continuous corn (CCrn), continuous corn with stover removal (CCrnS), continuous rye (CRye), continuous sorghum (CSrg), continuous soybean (CSoy), miscanthus (Mis), Switchgrass (Crn-Soy-Swg), and native grasses (NaGr). A summary of the rotations and their associated fertilizer application rates are provided in Table 12. All rotations repeat after the sixth year except miscanthus, switchgrass and native grasses. The miscanthus and native grasses repeat for the entire study period and the switchgrass rotation continues as switchgrass until year ten when the cycle is repeated. Typically, SWAT applies its default

values for crop inputs unless otherwise instructed. Thus, in order to accurately simulate vegetation cover and biomass, cropping systems, and management practices consistent with local standards, management operations were introduced to the model. The operations were based on data obtained from the MSUE and typical farm practice in the Saginaw Watershed region. For example, the corn-soybean-canola (Crn-Soy-Can) operation schedule is provided in Table 13. Each rotation followed the same format with tillage practices, fertilizer and pesticide applications, and planting and harvesting dates developed specifically for each crop.

5.2.4.3 Scenarios

The crop rotations were integrated into the SWAT model and tested under four scenarios. The scenarios were developed for the bioenergy crops, based on suitability and practicality. The scenarios are provided in Figure 15.

- Scenario 1: The first scenario considers all land currently cultivated for row crops and grains, hays, and seeds (i.e. corn, soybeans, wheat, hay, etc.), which represents the majority of current agricultural land in the watershed.
- Scenario 2: The second scenario considers only the other crops (i.e. sugarbeets, potatoes, dry beans, fruit crops, etc.) for conversion to bioenergy crops.
- Scenario 3: The third scenario considers farmland uses and other land (i.e. fallow cropland, pasture, wasteland, etc.), which can be considered marginal land.
- Scenario 4: The final scenario is the combination of the previous scenarios, and represents the overall most significant landuse change from current state to the bioenergy cropping rotations.

The scenarios range in amount of landuse change from very little (1.42 percent of watershed area) to the worst case scenario with 63 percent of the watershed area being converted to the bioenergy rotation. The landuse sections (i.e. Row Crops, Farmland Uses) are based on definitions of landuse classification (CDL). Woodland was not considered for landuse change to bioenergy crops. In addition, the rotations that were acceptable for producing bioenergy crops on the land chosen for each scenario are based on the current landuse, typical production value for the land into bioenergy crops, the feasibility of the expected yield, and the difficulty for farmers to acquire the planting and harvesting equipment and the capital required to invest in the operations not already included the farm's practices. For example, marginal land has generally low levels of soil organic matter, poor soil structure and fertility, and tends to produce low yields for traditional crops. Therefore, crops such as wheat and soybeans are not practical for cultivation. Corn stover was not selected as suitable for this landuse due to the already low levels of soil organic matter in marginal soils, which cannot afford to have additional residue removed post-harvest. Each scenario went through the same steps in order to provide the most realistic rotations that can be grown on each landuse.

5.2.5 Model Setup

5.2.5.1 Input Data Sources

Successful use of the ArcSWAT model relies on acquiring suitable and reliable data The State Soil Geographic Database (STATSGO) developed by the Natural Resources Conservation Service (NRCS) National Cartography and Geospatial Center (NCGC) was used to define the soil characteristics in the basin. The slope classification was performed using two slope classes (0-5 percent and >5 percent). The topography was based on the USGS Digital Elevation Model (DEM 90 meter resolution), which was used in delineation of the watershed boundaries. Subsequently, the watershed was divided into 254 subwatersheds, which allowed the model user to spatially characterize areas of the watershed regarding spatial impacts of land use change.

The watershed was further divided into individual hydrologic response units (HRUs) based on threshold land percentage values in the SWAT HRU definition. The threshold values were the percentage of landuse over the subbasin area, soil class percentage over the landuse area, and slope class percentage over the landuse area. For the purpose of this project, these thresholds were set to 20, 10 and 20 percent, respectively.

The USGS National Hydrography Dataset (NHD) was used to define the stream network. The latest Cropland Data Layer (2008 CDL 56 meter resolution) developed by the USDA National Agricultural Statistics Service (NASS) was used as the landuse representation. This is useful for this study having the agricultural land split into individual crop classes. The landuse values in the CDL were converted to the closest alternative landuse definition in SWAT, resulting in an input table redefining the CDL table grid values in SWAT. As discussed previously, the precipitation and temperature data were collected from the NCDC database at the locations described in Figure 4. Other meteorological data (wind speed, relative humidity, and solar radiation) required by the model was estimated using the SWAT weather generator.

5.2.5.2 Operation of SWAT Model

The period of study for analysis was January 1, 1990 to December 31, 2008. For this time period, daily flow data was available from the USGS without breaks in data.

Model output from a period of this length accurately represents the long-term effects of watershed behavior, especially changes resulting from bioenergy crop production. The model was run 41 times, based on the different scenarios and rotations. The SWAT model output that was compared for this study was total nitrogen ($NH_4 + NO_2 + NO_3 + Organic N$) in kilograms, total phosphorus (Mineral P + Organic P) in kilograms, and Sediment in metric tons. The output data was obtained at the watershed outlet, and on a subbasin level.

5.2.5.3 Sensitivity Analysis

Model performance is dependent on the sensitivities of parameters' influence on the processes inherent in SWAT. A sensitivity analysis identifies the parameters that are most influential on flow, sediment, and nutrients in the model. The result from the sensitivity analysis is useful in determining the parameters to be used for model calibration. A sensitivity analysis was performed for the Saginaw watershed using four different landuse and management combinations: National Land Cover Data (NLCD 2001) without local management practices applied (NLCDN), CDL landuse without management operations applied (CDL_NoMgmt), CDL landuse with management operations applied (CDL_Mgmt), and CDL landuse with management operation applied and observed data (CDL_Mgmt (Obs). The previously developed management operations were applied to the CDL in order to provide a comparison of model output sensitivities based solely on varied practices. It is important to note that the CDL is essentially the NLCD map with higher detail given to agricultural land. For example, the NLCD does not subdivide land used for agricultural purposes into detail, whereas the CDL gives each
landuse a class of its own, such as corn, soybean, sugarbeets, and onions. The 10 most influential parameters for each set of model outputs (out of 41) are presented in Table 5.

The importance of using observed data during the sensitivity analysis procedure is evident in Table 5. The cells highlighted in grey denote parameters that influence the model output differently, based on the landuse, management practice, and observed data combination used. By comparing (CDL_Mgmt) and (CDL_Mgmt (Obs), it is observed that a number of parameters show very different levels of influence on the model predictions. For example, landuse and management combinations have little influence on the outcome of the sensitivity analysis for flow. However, when using observed data, the arrangement and composition of the top ten parameters are significantly different. By omitting the use of observed data, the integrity and quality of further calibrations could be sacrificed.

Similarly, parameters for the sediment sensitivity analysis experienced reorganization. By not using the observed data, the influence Alpha_Bf has on flow is omitted, whereas Blai and Biomix are quite possibly exaggerated in their influence on model predictions. In addition, Rchrg_Dp was ranked 10 for NLCD, yet was ranked 18 and 13 for the CDL_NoMgmt and CDL_Mgmt scenarios, respectively. This could possibly be explained by the inherent differences of the NLCD and CDL landuse classifications. Rchrg_Dp, the deep aquifer percolation fraction, is highly dependent upon land cover, which is in much higher detail in the CDL map. The model sensitivity to nutrient parameters follows a similar trend, in which the variation between landuse, management, and observed data combinations has the potential to produce inconsistent

model predictions, which could in turn adversely affect the confidence in the value of model output.

Sensitivity analysis is merely a tool in helping to identify parameters useful in calibration of the model. A reasonable value of parameters during calibration with reasonable justification for the use of each is imperative to produce results representative of true watershed behavior. Site-specific knowledge and data are helpful in determining which of the most sensitive parameters are practical in application.

		Flo	W			Sedir	nent	
Rank	NLCDN	CDL_NoMgmt	CDL_Mgmt	CDL_Mgmt	NLCDN	CDL_NoMgmt	CDL_Mgmt	CDL_Mgmt
				(Obs)				(Obs)
1	Cn2	Cn2	Cn2	Cn2	Spcon	Spcon	Spcon	Cn2
2	Rchrg_Dp	Alpha_Bf	Alpha_Bf	Alpha_Bf	Ch_N2	Usle_P	Ch_N2	Spcon
3	Esco	Rchrg_Dp	Rchrg_Dp	Surlag	Cn2	Ch_N2	Cn2	Alpha_Bf
4	Sol_Z	Esco	Esco	Rchrg_Dp	Ch_K2	Cn2	Spexp	Ch_K2
5	Sol_Awc	Timp	Timp	Ch_N2	Spexp	Ch_K2	Usle_P	Ch_N2
6	Alpha_Bf	Gwqmn	Gwqmn	Esco	Alpha_Bf	Timp	Alpha_Bf	Surlag
7	Canmx	Canmx	Sol_Awc	Ch_K2	Usle_P	Surlag	Ch_K2	Usle_P
8	Timp	Sol_Awc	Canmx	Sol_Awc	Blai	Blai	Timp	Spexp
9	Gwqmn	Ch_K2	Sol_Z	Timp	Esco	Biomix	Esco	Timp
10	Ch_K2	Sol_Z	Ch_K2	Sol_Z	Rchrg_Dp	Canmx	Surlag	Blai
		Total Ni	itrogen			Total Pho	osphorus	
Rank	NLCDN	CDL_NoMgmt	CDL_Mgmt	CDL_Mgmt	NLCDN	CDL_NoMgmt	CDL_Mgmt	CDL_Mgmt
				(Obs)				(Obs)
1	Cn2	Canmx	Cn2	Canmx	Cn2	Canmx	Cn2	Sol_Awc
2	Surlag	Cn2	Alpha_Bf	Cn2	Sol_Awc	Cn2	Alpha_Bf	Cn2

Table 5. Sensitivity analysis result.

Table 5 (cont'd)

3	Sol_Awc	Alpha_Bf	Canmx	Alpha_Bf	Canmx	Sol_Awc	Ch_K2	Alpha_Bf
4	Rchrg_Dp	Sol_Awc	Timp	Sol_Awc	Surlag	Ch_K2	Timp	Sol_Z
5	Sol_Z	Blai	Sol_Awc	Awc Surlag Gwqmn Blai Usle		Usle_P	Canmx	
6	Alpha_Bf	Sol_Z	Nperco	Sol_Z	Sol_Z	Sol_Z Alpha_Bf		Surlag
7	Ch_K2	Nperco	Blai	Ерсо	Alpha_Bf	Sol_Z	Canmx	Ch_K2
8	Nperco	Ch_K2	Ch_K2	Nperco	Esco	Timp	Surlag	Blai
9	Esco	Esco	Rchrg_Dp	Blai	Blai	Surlag	Blai	Esco
10	Canmx	Timp	Usle_P	Esco	Timp	Esco	Smtmp	Gwqmn

5.2.5.4 Calibration/Validation

Calibration is a necessary component of modeling, especially in hydrologic modeling (Moriasi *et al.*, 2007). This process is the adjustment of input parameter values to best match the observed data, reducing model uncertainty. Calibration is performed either manually or by automatic calibration. Once a period for calibration data has been selected, the model is run with initial values in place, and the agreement between model output and observed data is measured using an objective function, while an optimization procedure finds the parameter values that optimize the objective function (McCuen *et al.*, 2006). Validation follows calibration to establish model credibility. Statistical analysis was performed for the validation period, leading to both qualitative and quantitative verification of the model's degree of accuracy.

Oftentimes, a single evaluation measure may indicate model prediction performance in a biased or exceedingly positive/negative manner. Therefore, model predictions were evaluated using three statistical methods: Nash-Sutcliffe's efficiency (NSE), root mean squared error (RMSE), and the coefficient of determination (\mathbb{R}^2). The Nash-Sutcliffe efficiency determines how well the model output conforms to a 1:1 relationship of observed data, effectively determining goodness-of-fit (McCuen *et al.*, 2006). The NSE is computed with the relationship in Equation 1:

NSE=1-
$$\frac{\Sigma(Y_{obs}-Y_{pred})^2}{\Sigma(Y_{obs}-Y_{mean})^2}$$
 (1)

where Y_{obs} is the observed value for the evaluated component, Y_{pred} is the model predicted value for the evaluated component, Y_{mean} is the mean of observed data for the evaluated component, and n is the total number of data points. NSE ranges from $-\infty$ to 1. If the value for NSE is 1, the model exactly predicts the observed values for the evaluated component. If the value for NSE is 0, the sum of squares of the difference between the observed and model predicted is equal to the difference between the observed and the mean of the observed values. Typically, NSE values greater than 0.65 are very good, greater than 0.50 are satisfactory, and values less than 0.5 are considered unsatisfactory on monthly basis.28

The root mean squared error (see Equation 2) is the vertical deviation of a data point from a fitted line, providing a value in measureable units. The RMSE has important advantages over traditional correlation methods, such as indicating error in the measured units (Moriasi *et al.*, 2007).

$$RMSE = \sqrt{\frac{\Sigma(Y_{obs} - Y_{pred})^2}{n}}$$
(2)

where n is the total sample size. Values of RMSE are that of the predicted variable, such as cubic meters per second for flow. This gives an indication of quantitative differences in the regression prediction from the observed (fitted) line.

The coefficient of determination, R^2 , is a statistical measure for goodness-of-fit. In this case, it is the percent of total variation in the y variable explained by the regression equation (Menard, 2000). R^2 values range from 0 to 1, where values close to one indicate that the regression equation (model) is predicting the y variable with confidence and that the dispersion of the predicted value is equal to the observed value. One of the main drawbacks in using only this method for analysis of statistical fit is that the R^2 relationship fails to address under- or overpredictions (Krause *et al.*, 2005). Values greater than 0.5 are generally considered acceptable in monthly basis (Santhi *et al.*, 2001). The R^2 is calculated with Equation 3:

$$R^{2} = \left(\frac{\sum(O_{i} - O_{mean})(P_{i} - P_{mean})}{\sqrt{\sum(O_{i} - O_{mean})^{2}}\sqrt{(P_{i} - P_{mean})^{2}}}\right)^{2}$$
(3)

where O are the observed values and P are the predicted values.

In order to adjust the model outputs for flow, sediment, and nutrients, a combination of manual calibration and the autocalibration feature imbedded in SWAT were used to enhance the overall effectiveness of parameter estimation. The simulation period for flow calibration was chosen for having periods of high, low, and moderate precipitation years compared to the mean rainfall for the previous 19 years (Figure 5). Flow was calibrated for an 8 year period (2001-2008), and sediment and nutrients for a 6 year period (2000-2005). The first year for each of the simulation periods were treated as a warm-up year, and was not included in the statistical comparisons. Calibration was performed on the first half of the available data periods and validation was performed on the second half.

Calibration and validation was performed once with SWAT default crop values and once with management operations derived from local data. Calibration for each of the model outputs (flow, sediment, nutrients) was performed sequentially, ensuring unbiased and autonomous results. The first calibration was for flow, with the parameters chosen based on the sensitivity analysis and the specific knowledge of the parameters' effect on flow. Sediment calibration followed, again with parameters chosen in a similar fashion while omitting any that influence flow. Nutrient calibration was the final series of simulations, omitting parameters which influence sediment and/or flow. The parameters for each calibration were chosen based on the sensitivity analysis results and on the influence each has on the model output.

Calibration and validation were performed for the watershed twice on a daily basis, once without management operations applied prior to calibration (Tables 6 and 7) and once with them applied (Tables 8 and 9). The goal is to compare the results obtained from these scenarios and emphasis the importance of using local management practice information while setting-up the model.

The model performed poorly with the default values, estimating flow NSE of -1.566 (Table 7). However, the calibrated flow NSE for the calibration and validation periods was 0.647 and 0.726, respectively. For the first set-up calibration (without considering management operations), the default parameter values in the SWAT model resulted in low model efficiency for flow. Kjeldahl nitrogen and sediment performed better with the default values (Table 7) and these results are acceptable for model performance and support the use of calibrated parameter values for predictions. Similarly, evaluations of the sediment and nutrient calibrations were completed. Sediment calibration considerably increased the model performance. However, efforts to calibrate nutrients yielded poor NSE results compared to uncalibrated, even though RMSE and R² were improved. Since nitrogen and phosphorus performed best under default values, further calibration was not necessary and these values were applied in subsequent model simulations. The poor nutrient calibration can likely be attributed to the low availability of monitoring data in the watershed (less than 60 points during 6 years of model simulation). It should be noted that the analyses were performed on a daily basis. In general, monthly or annual evaluations improve statistical values considerably when used in place of daily evaluations (Spruill *et al.*, 2000; Gassman *et al.*, 2007).

Parameter	Change By Method	Parameter input to Swat				
Flow Calibration						
Alpha_Bf	Replace Value	0.999				
Ch_K2	Replace Value	38.937				
Ch_N2	Replace Value	0.845				
Cn2	Multiply By	1.001				
Ерсо	Replace Value	0.840				
Esco	Replace Value	0.457				
Gw_Delay	Add	-9.797				
Rchrg_Dp	Replace Value	0.006				
Sol_Awc	Multiply By	0.875				
Surlag	Replace Value	2.204				
Sediment Calibration						
Biomix	Multiply by (-50 to 50)	0.554				
Ch_Cov	Replace Value	0.696				
Ch_Erod	Replace Value	0.467				
Spcon	Replace Value	0.010				
Spexp	Replace Value	1.156				
Nutrient Calibration						
Nperco	Replace Value	0.200				
Phoskd	Replace Value	175.000				
Pperco	Replace Value	10.000				
Sol_No3	Multiply by (-50 to 50)	Default *				
Sol_Orgn	Multiply by (-50 to 50)	Default *				
Sol_Orgp	Multiply by (-50 to 50)	Default *				

Table 6. Final parameter values (CDL landuse without management operations applied).

* When initial values not user defined (default), SWAT initializes levels based on relationship as function of depth

Parameter		Uncalibrated	Calibration	Validation	Combined
Flow	NSE	-1.545	0.647	0.726	0.692
	RMSE	297.5	77.27	67.80	102.8
	R^2	0.086	0.660	0.735	0.699
Sediment	NSE	0.613	0.462	0.933	0.548
	RMSE	2066	2226	177.3	3111
	R^2	0.589	0.873	0.297	0.861
Kjeldahl	NSE	0.428	0.382	0.209	0.329
Nitrogen	RMSE	5552	3683	3241	4906
Nillogen	R^2	0.366	0.786	0.526	0.692
Total	NSE	0.619	0.657	0.813	0.619
Phosphorus	RMSE	769.1	707.3	302.2	769.1
rnosphorus	R^2	0.671	0.600	0.812	0.671

Table 7. Results of statistical analysis for calibration and validation periods.

As mentioned previously, the calibration process was performed for the watershed by applying the management operations/schedules that were developed based on local data. The parameters that were used in calibration and their associated final values are provided in Table 8. The uncalibrated hydrograph is provided in Figure 6, showing the extent of discontinuity to the observed data. The hydrograph based on model output after calibration was completed is provided in Figure 7. This figure represents both the calibration and validation periods. As observed in Figure 8, showing a 1:1 comparison between predicted and observed flow, the calibrated model tends to predict flows well at low –flow periods (less than 350 cms), yet tends to have a larger span of prediction with flows greater than this point. The calibration statistics for this method are provided in Table 9. The calibrated model performed well for flow, sediment, and phosphorus. However, nitrogen performed poorly after model calibration. This is likely due to the lack of available data and the interrelationship between the parameters affecting both nitrogen and phosphorus. Since both nutrients were calibrated simultaneously, the model found the best prediction for both, which in turn reduced the nitrogen prediction efficiency.

Parameter	Change Method	Parameter input to Swat
Alpha_Bf	Replace Value	0.937
Canmx	Replace Value	6.336
Ch_K2	Replace Value	41.194
Ch_N2	Replace Value	0.312
Cn2	Multiply By	1.068
Esco	Replace Value	0.523
Rchrg_Dp	Replace Value	0.159
Sol_Awc	Multiply By	0.646
Spcon	Replace Value	0.006
Timp	Replace Value	0.068
Usle_P	Replace Value	0.093

Table 8. Final parameter values (CDL landuse with management operations applied).



Figure 5. Precipitation deviation from 19-year mean for study period.



Figure 6. Uncalibrated Flow vs. Observed Flow at USGS Station 04157000.



Figure 7. Calibrated Flow vs. Observed Flow at USGS Station 04157000.



Figure 8. Calibrated Flow vs. Observed Flow at USGS Station 04157000.

Parameter		Uncalibrated	Calibration	Validation	Combined
Flow	NSE	-1.633	0.766	0.666	0.723
	RMSE	297.1	62.94	74.88	69.43
	R ²	0.031	0.771	0.733	0.744
Sediment	NSE	0.474	0.422	0.500	0.467
	RMSE	2902	1977	2152	2922
	R ²	0.496	0.842	0.693	0.712
Kjeldahl	NSE	0.126	-0.293	-0.068	-0.207
Nitrogon	RMSE	5599	5367	3808	6581
Nittogen	R ²	0.370	0.108	0.649	0.193
Total	NSE	-4.852	0.326	0.815	0.452
Dhosphorus	RMSE	3016	882.3	271.7	923.2
rilospilorus	R^2	0.305	0.475	0.839	0.541

Table 9. Results of statistical analysis for calibration and validation periods (CDL landuse with management operations applied).

5.3 RESULTS AND DISCUSSION

5.3.1 Watershed-level Environmental Impacts of Bioenergy Crop Expansion

The effect of landuse change from current cropland practices to a significant increase in land cover to a bioenergy cropping system is expected to alter the physical and chemical processes in the watershed, leading to variations in pollution load. This is due to increased tillage and wide row spacing with crops such as corn, sorghum, and canola, increased fertilizer use, and variations in seasonal soil cover.

Average annual sediment, total nitrogen, and total phosphorus load for the study period was estimated at a watershed level, reflecting the overall load at the basin main channel outlet into the Saginaw Bay. The results for Scenario 4 are presented in Figure 9. It is important to note that this figure is based on average annual loads, which tend to smooth any radical spikes in constituent loading. The total pollution loads for each constituent were used as a baseline for comparison from the current landuse (2007 CDL-Base scenario). Nearly all crops except miscanthus, native grasses, rye, and switchgrass experience increased pollution to the waterbody outlet. Among the remainder of the studied crops, corn stover removal (40 percent residue removal) scenario experiences the worst overall environmental impact. The predicted sediment load ranged from 93 percent reduction for the miscanthus rotation to a 233 percent increase for the continuous sorghum rotation. Similarly, nitrogen loads varied significantly from a 228 percent increase with introduction of the continuous corn stover rotation to a 14 percent reduction for the switchgrass rotation. The variation of phosphorus load is less significant for the evaluated crop rotations. However the values range from 62 percent increase to 27 percent reduction for continuous corn stover and continuous rye, respectively. Based on the given information, removal of corn stover for bioenergy production has the potential to significantly impact the environment, due to a lower amount of ground cover in the event of a rainstorm. Conversely, the expansion of land to native grasses and switchgrass bioenergy for production can have positive environmental consequences.



Figure 9. 19 Year Annual Sediment/Nutrient Load at Main Channel Outlet (Scenario 4).

5.3.2 Assessment of Marginal Land Conversion Impact on Water Quality

A similar display of pollutant loads for Scenario 3 (Marginal Land) is provided in Figure 10. There is a clear trend as the amount of sediment load decreases with closergrown crops, with less tillage practices, longer growing seasons, and perennial growth cycles. When native grasses are considered for marginal land conversion, nitrogen load increases. This is likely due to the nitrogen cycling methods used in SWAT at the field and in-stream. Marginal land at its current state (prior to landuse change to native grasses) is fallow or under conservation programs to a large extent. The native grass rotation for bioenergy production considers harvesting the above-ground biomass at the end of the growing season. This leaves little ground cover, which allows for the loss of nitrogen in overland flow to a much greater extent than under natural conditions. Without the removal of crop biomass and residue, the carbon:nitrogen ratio results in nitrogen immobilization, decreasing the soil ammonium and nitrate (Knops and Tilman, 2000). By interrupting this natural cycle of nitrogen accumulation as bound particles in the shallow soil layers, it is possible for nitrogen mobilization.



Figure 10. 19 Year Annual Sediment/Nutrient Load at Main Channel Outlet (Scenario 3).

5.3.3 Importance of Using Local Information on Model Predictions

As discussed previously, a sensitivity analysis and model calibration was performed under four different landuse and management combinations: NLCD without local management practices applied, CDL landuse without management operations applied, CDL landuse with management operations applied, and CDL landuse with management operation applied and observed data used. The goal in this discussion is to evaluate the importance of incorporating data of local agricultural practices and observed data on model predictions.

In this study, the results from model calibration for each of the three CDL landuse and management combinations were evaluated and the model results for each of the 42 bioenergy crop rotations were compared. As an example, Figure 11 shows the variation of sediment, nitrogen, and phosphorus loads at watershed scale under three combinations: (MCM) that was calibrated while considering local management information, (MC) that was calibrated without the use of local management operations, but this information was incorporated during model examination of different crop scenarios (sub-scenarios), and (DC) that used the SWAT default crop information for both model calibration and crop sub-scenarios. Since MCM uses the local cropping information, it is expected to generate the most realistic result for comparison with the two other combinations, because it is representative of actual crop production practices in the study area. Based on this analysis, the results of model predictions may be misleading if the practices best suited for the study area aren't addressed. In this case, sediment could be over-predicted by a factor of 11, nitrogen by a factor of 1.2-1.9, and phosphorus by a factor of 2.1-2.4 resulting in possible misinformed decisions of landuse policy.



Figure 11. Annual Average Sediment Load for Three Corn Simulations.

5.3.4 Monthly Pollution Load Variation

Analysis of constituent loads and their resulting change from the base values were also performed on a monthly time-step. This allows for the direct visualization of variation between wet, dry, and average climatological periods. In addition, this can assist in watershed management efforts to mitigate pollution under extreme pollution load discharge to waterbodies. For example, for large-scale bioenergy crop expansion, it is extremely important to determine the optimal landuse combinations and rotations that allow sustainable production of biomass while maximizing economic return. Figure 12 represents the comparison of two severe cases: Continuous Corn Stover (top) and Switchgrass (bottom) and their respective change from the base scenario for sediment load to the main channel outlet. Here it is observed that continuous corn with 40 percent stover removal results in substantial increases in sediment generation at watershed scale, with up to a 493 percent increase over current landuse scenario. The switchgrass rotation also resulted in large increases in sediment loads, with up to a 381 percent increase. However, with the exception of 4 smaller spikes, these increases can be attributed to the corn and soybean years of each rotation cycle (years 1 and 2 of each schedule, as discussed previously and shown in Table 12), and the establishment year of switchgrass in which the crop experiences lower productivity and fraction of soil cover than subsequent growing seasons. Corn and soybeans were used prior to the 8 years of switchgrass for sustainability purposes, as it is generally recommended to incorporate such practices to reduce the chances of disease and poor stands of switchgrass cultivation. The remainder of the years in this rotation experience significant sediment load reductions with up to a 95 percent monthly reduction.

Monthly load changes from base were also calculated for total nitrogen and total phosphorus represented in Figures 13 and 14, respectively. A similar trend is present for total nitrogen as there was in sediment, continuous corn stover experiences overall large spikes in nitrogen loads with up to a 1375 percent increase of nitrogen to the main channel outlet, whereas switchgrass experienced reductions throughout the majority of the study period. Nitrogen load increases during the first few years of each cycle is the result of corn and soybean cultivation, however additional sharp increases outside of these years may be caused by extreme climatological events. Therefore, we can conclude that switchgrass production at large-scale can help in reducing sediment and nitrogen loads within the study area.

Phosphorus loadings consistently increased (up to 792 percent) in the continuous corn stover rotation, while the switchgrass rotation experienced reductions (up to 91 percent) in the periods outside of corn, soybean and establishment years. However, the number and magnitude of significant phosphorus load increases during years under switchgrass cultivation (up to 134 percent increase) are more frequent than both sediment and nitrogen of the same periods. This may be due to the time of fertilizer application (early spring), which usually occurs during the wet months. Another factor possibly contributing to the increases is the collection and storage of nutrients in the soil after application during corn and soybean years. Consequently, the nitrogen and phosphorus is transported when the soil has minimal cover from switchgrass early in the growing season during its recovery from the fall biomass harvest. In regards to corn, the extreme increases in nutrient loads may be due to the increase in intensive practices such as primary and secondary tillage, and increase in fertilizer requirements.



Figure 12. Corn Stover vs. Switchgrass Scenario 4 Monthly Sediment Load Change from Base.



Figure 13. Corn Stover vs. Switchgrass Scenario 4 Monthly Nitrogen Load Change from Base.



Figure 14. Corn Stover vs. Switchgrass Scenario 4 Monthly Phosphorus Load Change from Base.

Long-term monthly average sediment is provided in Table 10. Similar tables were constructed for nitrogen and phosphorus and are available upon request. This information is important because large magnitude increases of pollutant loading to waterbodies during short periods of time may result in severe and detrimental effects on aquatic ecosystems, violate total maximum daily load (TMDL) requirements, and threaten the sustainability of bioenergy cropping systems in agricultural watersheds.

Based on the entire 19-year study period, the highest sediment and phosphorus loads are consistently produced during March. However, the largest amount of nitrogen load is produced in April. The months of December through June have the highest sediment and phosphorus load, while March through May have the highest nitrogen load. The correlation between sediment and phosphorus is expected due to their physical properties of particle binding. However, nitrogen is mainly transported to stream networks through groundwater systems from infiltration. Both extreme precipitation and common time of nitrogen fertilizer application during the months of April and May can explain this phenomenon. The period of second largest contribution of nitrogen is December and January, where fall-applied nitrogen through either fertilizer or manure applications is conveyed to the stream-network via lateral flow. By observing the column providing the ratio of outlet sediment load to subbasin sediment load in Table 10, the outlet produces 15.2-53.7 percent more sediment than at subbasin level. This is likely attributed to bank and streambed erosion or in-stream processes. However, this is important when evaluating the mitigation effects of land management practices. If the pollutant loads are evaluated on subbasin level, the total contribution of load to the watershed may be underestimated.

	Outlet load/	Monthly Sediment Load (metric tons)											
Sub- scenario	subbasin load (Percent)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Base	53.7	4679	5076	12265	5164	7438	4790	1833	1014	1593	1338	2148	3215
Scen1 CCan	48.1	6794	5876	15126	5580	5328	2871	1332	1913	2633	1803	3146	4012
Scen1 CCrn	51.0	7327	7783	17200	7052	9566	5145	1794	1212	2563	2015	3183	4875
Scen1 CCrnS	51.0	6863	7452	16198	6570	8469	5006	1802	1221	2594	2063	3270	4752
Scen1 CRye	43.9	2944	2288	4615	2251	2716	6139	1562	770	1414	635	918	1310
Scen1 CSrg	47.7	13591	13742	32062	11520	13329	8156	2240	1341	2527	1934	4635	8987
Scen1 CSoy	50.1	8205	9476	21822	8291	11473	8981	3367	1403	1939	1760	3052	5543
Scen1 Crn Soy	50.4	7897	8663	19822	7488	10831	6173	2447	1177	2285	1776	3193	5211
Scen1 Crn Soy Can	50.7	9278	8856	20560	8309	9375	6594	2924	1708	2584	2106	3594	5602
Scen1 CrnSoy Rve	47.8	4325	4858	8580	4231	5919	6148	2658	1010	2071	1280	1477	2776
Scen1 CrnSSoy	50.5	7467	8415	19139	7107	10375	5762	2435	1179	2284	1777	3175	5119

Table 10. Long-term average monthly sediment load (Saginaw Bay watershed).

Table 10 (cont'd)

Scen1 Misc	18.9	244	269	504	310	347	325	332	291	297	225	212	184
Scen1 NaGr	19.8	264	292	542	340	404	353	341	295	309	239	226	203
Scen1 SorSoy	49.1	10509	10980	25325	9578	12403	8504	2753	1268	2331	1847	3590	6710
Scen1 Swch	42.7	1421	3258	5874	3515	5413	1734	755	498	721	800	496	944
Scen2 CCrnS	52.7	3799	3828	9080	3827	4468	3331	1404	937	1566	1155	1601	2450
Scen2 CrnSSoy	52.9	3830	3864	9235	3868	4595	3366	1435	932	1546	1144	1596	2472
Scen2 Misc	52.0	3518	3532	8409	3535	4110	3124	1351	882	1461	1068	1455	2265
Scen2 NaGr	52.0	3518	3533	8409	3536	4113	3123	1351	880	1461	1065	1455	2267
Scen2 Swch	52.2	3568	3651	8630	3705	4340	3187	1364	893	1475	1088	1469	2298
Scen3 CCan	41.9	8003	7711	18986	7299	7616	5078	2410	2388	3390	2637	3598	5037
Scen3 CCrn	42.5	8668	8954	20266	8310	10110	6571	2552	1721	3176	2613	3647	5667

· · · · · · · · · · · · · · · · · · ·	/												
Scen3 CRye	45.2	5437	5197	11718	4934	5727	6886	2586	1430	2327	1499	2064	3113
Scen3 CrnSoy	40.9	9847	9566	22388	9037	10202	7471	3301	2282	3208	2693	3888	6054
Scen3 CrnSoy	43.5	6642	6850	14191	6242	7897	7025	3046	1679	2749	1843	2427	4089
Scen3 Misc	49.5	3510	3536	8318	3557	4163	3124	1352	912	1460	1080	1477	2277
Scen3 NaGr	49.5	3537	3546	8344	3579	4231	3166	1359	911	1463	1075	1477	2284
Scen3 Swch	45.0	4296	5731	12078	5560	7462	4164	1678	1116	1794	1639	1740	2879
Scen4 CCan	40.8	10879	9873	24791	9021	8454	4850	2370	3242	4451	3423	5195	6728
Scen4 CCrn	43.4	12139	13064	28443	11574	14892	8347	3022	2042	4196	3528	5286	8223
Scen4 CCrnS	43.9	11573	12562	27091	10993	13454	8222	3044	2066	4202	3618	5457	8026
Scen4 CRye	39.7	4862	4094	8004	3648	4082	9306	2678	1273	2242	1083	1546	2274
Scen4 CSor	37.4	19687	20581	45920	17037	19628	12607	3799	2351	4183	3391	6646	12451

10010 10 (Tuble To (cont d)												
Scen4 CSoy	41.0	13263	15615	34572	12831	17333	13810	5616	2533	3146	3185	4965	9051
Scen4 CrnSoy	42.0	12847	14420	31744	12093	16555	9863	4039	2049	3692	3148	5220	8619
Scen4 CrnSoy	41.8	7369	8217	14409	6904	9152	9669	4276	1812	3323	2002	2426	4602
Scen4 CrnSSoy	42.3	12343	14068	30802	11612	15791	9332	4006	2052	3699	3158	5216	8461
Scen4 Misc	15.2	255	292	552	322	363	313	292	244	254	192	195	191
Scen4 NaGr	17.0	297	332	624	382	475	375	312	260	286	227	223	221
Scen4 SorSoy	39.2	16071	17722	39238	14568	18639	13214	4549	2238	3790	3193	5600	10500
Scen4 Swch	38.4	2170	5391	9431	5432	8374	2702	979	694	1045	1338	774	1546

Table 10 (cont'd)

5.3.5 Determining Practicality of Scenarios for Landuse Change

Table 11 provides a comparison of all rotations based on contribution to annual average sediment, nitrogen, and phosphorus load. This orientation allows for a direct evaluation of the potential environmental impacts for each of the four scenarios, and thus different amounts of landuse change on different landscape classes. This is important for policy making and decisions for landuse change in agricultural region. In order to accommodate the growing demand for available land to produce bioenergy crops, the assessment of environmental implications is imperative.

The scenarios, as presented previously, are as follows: Scenario 1 considers all land currently cultivated for row crops and grains, hays, and seeds (i.e. corn, soybeans, wheat, hay, etc.) for conversion to bioenergy crops, Scenario 2 considers only the other crops (i.e. sugarbeets, potatoes, dry beans, fruit crops, etc.), Scenario 3 considers farmland uses and other land (i.e. fallow cropland, pasture, wasteland, etc.), which in all practical purposes may be deemed as marginal land, and Scenario 4 is the combination of all previous scenarios, and represents the overall most significant landuse change from current state to the chosen bioenergy cropping rotations.

By examining the list based on sediment, a number of rotation placements are of particular interest. As expected, the majority of sediment mitigating crops includes the perennial grasses such as miscanthus, native grasses, and switchgrass. However, continuous rye (Scen1_ContinuousRye) when applied to land currently being cultivated for row crops results in a surprising 45.5 percent reduction in sediment load. Continuous rye under Scenario 4 shows similar results with a 10.8 percent reduction. As rye is most commonly planted in the fall, acting as a cover crop for winter months and begins

growing extensively as soon as the soil warms in the spring. Consequently, this period is during times of heavy rainfall, acting as a cover to what would otherwise be bare soil. When coupled with corn and soybeans, rye fails to mitigate the sediment pollution these two crops produce as efficiently as the continuous rye rotation. Interestingly enough, when land currently under the classification of other crops (Scenario 2) is converted to a corn rotation with stover removal, there is a significant reduction (25.1-25.9 percent) in sediment load. This is extremely important when determining the sustainability of corn stover as a potential bioenergy crop. In most cases, rotations with corn stover removal are considered a risky practice, but when applied to land in this scenario the effects are beneficial. In addition, conservation programs such as the Conservation Reserve Program (CRP) encourage land owners to allow the land currently under cultivation to return to a native vegetation state (USDA-NRCS, 2009). The goal of this is to reduce pollutants in agricultural runoff. However, in this study miscanthus mitigates a higher percentage of sediment than native grasses in every scenario that was evaluated. This suggests that the miscanthus may be a suitable and more economically sustainable practice than would be a native grass landscape. As the data suggests, these long-rotation perennial grasses extend the growing season, require soil disturbance for planting only on the establishment year, and have dense root spacing and canopy cover. The result is consistent and ample ground cover year-round, decreasing erosion potential. Sediment reduction is expected for perennial crops or crops traditionally grown with low-input intensive practices, but not for crops such as continuous corn. Crops such as this are input-intensive and require substantial tillage. Close grown crops and rotations including these, such as continuous rye, also experience reduced sediment yield for similar reasons to the perennial grasses.

Corn stover removal substantially increases the amount of soil loss, accompanying the loss of crop residue, which is valuable in maintaining adequate soil cover until the following growing season.

The organization of the rotations in respect to their nitrogen values compared to base presents yet more unexpected results. Continuous sorghum on Scenarios 1 and 4 result in 20.6 and 2.8 percent reductions in nitrogen, respectively. However sorghum when accompanied with soybeans on Scenario 4 results in a 32.4 percent increase in nitrogen load. Continuous soybean on Scenario 4 has an 86.6 percent increase as well, which helps to explain the increase from continuous sorghum to sorghum soybean. When sorghum is cultivated for five years followed by a year of soybeans, the adverse effect of soybeans is negated to a large extent, unlike the short two year rotation of sorghumsoybean. In either case of continuous sorghum or the sorghum-soybean rotations, nitrogen load is increased when these rotations are implemented on scenario 4. Here, the only difference is more land in production of these rotations (other crops and marginal land). Thus it can be concluded that these lands should not be used for sorghum cultivation at a large extent. The perennial grass species reverse their standings from sediment when considered on a nitrogen basis. Except for native grass and switchgrass on Scenarios 1 and 4, these species exhibit increases in nitrogen load. Miscanthus, the crop with the most positive influence on sediment mitigation, experiences 12.7-72.2 percent increases of nitrogen load. This result makes it difficult to justify converting large amounts of land to miscanthus. However, based on watershed health, miscanthus may be suitable in certain applications. For example, if sediment is of utmost importance,
miscanthus is an excellent mitigation tool, but if nitrogen levels are important, miscanthus may not be the most suitable crop.

Phosphorus loads are closely related to sediment load results. Nearly all of the crops that experience sediment mitigation also show decreases in phosphorus loadings. The exception to this rule is miscanthus on Scenarios 3 and 4. Again, as observed with nitrogen loadings, when miscanthus is considered for marginal land conversion there is an adverse effect on phosphorus load. This further suggests miscanthus is poorly suited for cultivation on marginal lands, as both nitrogen and phosphorus pollutant loads increase. Canola, a crop not yet discussed here, experiences sediment, nitrogen, and phosphorus load increases on every scenario when considered for conversion. This also suggests that canola has poor suitability for extensive cultivation in this watershed.

Sub-scenario	Sediment % Change from Base	Sub-scenario	Total N % Change from Base	Sub-scenario	Total P % Change from Base
Scen4_Miscanthus	-93.1	Scen1_Switchgrass	-26.2	Scen1_Continuous Rye	-33.1
Scen1_Miscanthus	-93	Scen1_Continuous Sorghum	Scen1_Continuous Sorghum -20.6 Scen4_Continuous Rye		-27.2
Scen1_NativeGrass	-92.5	Scen1_Continuous Rye	-17.8	Scen1_NativeGrass	-27.1
Scen4_NativeGrass	-92.1	Scen1_NativeGrass	-16.2	Scen1_Switchgrass	-21.5
Scen1_Switchgrass	-49.7	Scen4_Switchgrass	-14.2	Scen4_NativeGrass	-21
Scen1_Continuous Rye	-45.5	Scen1_SorghumSoy	-6.4	Scen2_Switchgrass	-12.9
Scen2_Miscanthus	-31.3	Scen4_Continuous Sorghum	-2.8	Scen2_Miscanthus	-12.8
Scen2_NativeGrass	-31.3	Scen4_NativeGrass	-1.8	Scen2_NativeGrass	-11.9
Scen3_Miscanthus	-31.2	Scen1_CornSoyRye	-0.6	Scen4_Switchgrass	-11.8
Scen3_NativeGrass	-30.8	Scen1_Continuous Corn	5.3	Scen2_Continuous Corn Stover	-11.4
Scen2_Switchgrass	-29.4	Scen1_CornSoy	9.9	Scen1_CornSoyRye	-11.2
Scen2_Continuous Corn Stover	-25.9	Scen4_Continuous Rye	10.1	Scen2_CornStover Soy	-11.1
Scen2_CornStover Soy	-25.1	Scen1_Miscanthus	12.7	Scen3_Continuous Rye	-7.2

Table 11. Land use scenarios ranking based on environmental benefits.

Table 11 (cont'd)

Scen4_Switchgrass	-21.1	Scen1_Continuous Soybean	23.5 Scen3_NativeGrass		-6.8
Scen4_Continuous Rye	-10.8	Scen1_Continuous	25	Scen1_Miscanthus	-6.2
Scen1_CornSoyRye	-10.3	Scen2_Switchgrass	29.9	Scen3_Switchgrass	-2.7
Scen3_Switchgrass	-0.8	Scen1_CornStover Soy	30.3	Scen3_Miscanthus	2.6
Scen3_Continuous Rye	4.7	Scen2_NativeGrass	30.5	30.5 Scen1_SorghumSoy	
Scen1_Continuous	11.6	Scen2_Miscanthus	31.1	Scen3_CornSoyRye	3.8
Scen3_CornSoyRye	27.9	Scen2_CornStover Soy	32.1	Scen4_CornSoyRye	5.4
Scen1_Continuous Corn	31.1	Scen4_SorghumSoy	32.4	Scen1_Continuous	5.4
Scen1_Continuous Corn	37.9	Scen1_CornSoy Canola	33.2	Scen4_Miscanthus	7.9
Scen3_Continuous Canola	46.7	Scen2_Continuous CornStover	34.8	Scen1_Continuous Sorghum	11.1
Scen4_CornSoyRye	46.7	Scen4_Continuous Corn	43.1	Scen1_Continuous	13.3
Scen1_CornStover Soy	46.8	Scen3_Switchgrass	47.1	Scen1_CornSoy	14.2
Scen1_CornSoy	52.2	Scen4_CornSoyRye	47.9	Scen3_Continuous Canola	15.4

Table 11 (cont'd)

Scen1_CornSoyCanola	61.2	Scen3_NativeGrass 50.4 Scen1_Co		Scen1_Continuous Corn	17.1
Scen3_Continuous Corn	62.7	Scen4_Miscanthus	52.9	Scen1_CornStover Soy	18.3
Scen1_Continuous Soybean	68.8	Scen3_Continuous Rye	60.3	0.3 Scen3_Continuous Corn	
Scen3_CornSoyCanola	77.9	Scen4_CornSoy	60.5	Scen1_Continuous	22
Scen4_Continuous Canola	84.5	Scen3_Continuous Corn	69.3	Scen3_CornSoy Canola	23.9
Scen1_SorghumSoy	89.5	Scen3_Miscanthus	72.2	Scen1_CornSoy Canola	24.1
Scen4_Continuous Corn Stover	118.2	Scen3_CornSoyRye	78.7	Scen4_SorghumSoy	30.9
Scen1_Continuous Sorghum	125.6	Scen4_Continuous Soybean	86.6	Scen4_Continuous Canola	34.5
Scen4_Continuous Corn	127	Scen4_Continuous	95.6	Scen4_Continuous	43
Scen4_CornStover Soy	138.4	Scen3_Continuous Canola	96.8	Scen4_Continuous Soybean	46.3
Scen4_CornSoy	145.9	Scen4_CornStover Soy	98.1	Scen4_CornSoy	53.7
Scen4_Continuous Soybean	168.9	Scen1_Continuous Corn Stover	106.7	Scen4_Continuous Corn	53.9

Table 11 (cont'd)

Scen4_SorghumSoy	195.4	Scen3_CornSoy Canola	111	Scen4_CornStover Soy	58.6
Scen4_Continuous Sorghum	232.9	Scen4_Continuous Corn Stover	227.6	Scen4_Continuous Corn Stover	62.3

5.4 CONCLUSION

The SWAT model is a powerful tool in assessing the environmental implications of the expansion of bioenergy crops, as expressed in the scenarios developed for this project. The objective of this study is to examine the environmental implications, specifically water quality, of bioenergy cropping system expansion. The Soil and Water Assessment Tool (SWAT) was used to model the effects of four scenarios, 17 different bioenergy crops under 42 rotations on sediment load, total nitrogen load, and phosphorus load in the Saginaw River Watershed (hydrologic unit code 040802) during a 19 year (1990 to 2008) period on a daily basis. This watershed, which drains into the Saginaw Bay and subsequently Lake Huron, is intensively cultivated for crops.

The results obtained therein show that there is a direct correlation between landuse change to bioenergy crops and water quality. Significant increases in sediment (up to 233 percent) occurred when converting current landcover to wide-row intensive crops such as a continuous sorghum rotation. Nitrogen and phosphorus loads increased with such crops as well with 228 percent and 62 percent increases of total nitrogen and total phosphorus, respectively, when applied to all currently-available land for cultivation (Scenario 4). However, important second-generation bioenergy grass crops such as miscanthus, native, grasses, and rye experienced admirable pollutant load mitigation, with reductions up to 93 percent, 26 percent, and 33 percent of sediment, nitrogen, and phosphorus respectively. These values reflect average annual reductions, though, which are far less drastic than the fluctuations observed on a monthly time step. For example, continuous corn with stover removal resulted in up to a 493 percent increase of sediment load, up to a 1375 percent increase in total nitrogen load, and up to 792 percent increase

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in total phosphorus load over the current landuse scenario. Increases of pollutant loading to the channel of such large magnitudes may result in direct impairment to aquatic ecosystems, total maximum daily load (TMDL) requirements, and threaten the sustainability of bioenergy cropping systems in agricultural watersheds. The results of this study show that oftentimes bioenergy crops are not suitable for cultivation on certain landscapes. However, multiple crops that were once thought of as detrimental to the environment show promise in certain applications, such as continuous corn with stover removal cultivated in lands previously classified as other crops, which resulted in both sediment and phosphorus mitigation. Equally important is the potential implications that the grass species may have when grown on certain landscapes, especially marginal land, where substantial increases in nitrogen and phosphorus were exhibited.

Acknowledgements

The authors would like to acknowledge Mr. Chaopeng Shen, and Mr. Sean Woznicki and Dr. Fred Bakker-Arkema for their added project support, and Dr. Kurt Thelen, Dr. Wesley Everman, Mr. Dennis Pennington, Dr. Scott Swinton, and Ms. Laura James for their generous contribution of information. APPENDIX

APPENDIX

	Rate			Crop in 1	Rotation		
Rotation	(kg/ha)	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6
		Rye	Canola	Canola	Rye	Canola	Canola
Continuous Canola	Nitrogen	28	140	140	28	140	140
	Phosphorus	39.2	39.2	39.2	39.2	39.2	39.2
		Corn	Corn	Corn	Corn	Corn	Soybean
Continuous	Nitrogen	194	194	194	194	194	-
Corn	Phosphorus	59.5	59.5	59.5	59.5	59.5	45
		Corn	Corn	Corn	Corn	Corn	Soybean
Continuous	Nitrogen	194	194	194	194	194	-
Stover	Phosphorus	59.5	59.5	59.5	59.5	59.5	45
		Soybean	Rye	Rye	Soybean	Rye	Rye
Continuous	Nitrogen	-	28	28	-	28	28
Rye	Phosphorus	45	39.2	39.2	45	39.2	39.2
		Sorghum	Sorghum	Sorghum	Sorghum	Sorghum	Soybean
Continuous	Nitrogen	112	112	112	112	112	-
Sorgnum	Phosphorus	45	45	45	45	45	45

Table 12. Fertilizer application rates for each rotation used in SWAT.

Table 12 (cont'd)

Continuous	Nitrogen	Soybean	Soybean -	Corn 194	Soybean	Soybean	Corn 194				
Soybean	Phosphorus	45	45	59.5	45	45	59.5				
		Miscanthus (Continuous)									
Miscanthus	Nitrogen	-	84	84	84	84	84				
	Phosphorus	-	17	17	17	17	17				
		Corn	Soybean	Switchgrass	Switchgrass	Switchgrass	Switchgrass				
Switchgrass	Nitrogen	194	84	-	84	84	84				
	Phosphorus	59.5	17	-	17	17	17				
		Native Grasses (Continuous)									
Native Grasses	Nitrogen	-	-	-	-	-	-				
	Phosphorus	-	-	-	-	-	-				
Corn		Corn	Soybean	Canola	Corn	Soybean	Canola				
Soybean-	Nitrogen	194	-	140	194	-	140				
Canola	Phosphorus	59.5	45	39.2	59.5	45	39.2				
G		Corn	Soybean	Rye	Corn	Soybean	Rye				
Corn- Soybean-	Nitrogen	194	-	28	194	-	28				
Rye	Phosphorus	59.5	45	39.2	59.5	45	39.2				

Table 12 (co	ont'd)
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Corn- Soybean	Nitrogen	Corn 194	Sovbean -	Corn 194	Sovbean -	Corn 194	Sovbean -
	Phosphorus	59.5	45	59.5	45	59.5	45
Corn		Corn	Soybean	Corn	Soybean	Corn	Soybean
Stover-	Nitrogen	194	-	194	-	194	-
Soybean	Phosphorus	59.5	45	59.5	45	59.5	45
		Sorghum	Soybean	Sorghum	Soybean	Sorghum	Soybean
Sorghum- Soybean	Nitrogen	112	-	112	-	112	-
	Phosphorus	45	45	45	45	45	45

Table 13. Corn-soybean-canola rotation management operations.

Date	Practice	SWAT Practice	Amount/acre	Amount/ha	Year
1-May	Soil Finish	Field Cultivator Ge15ft			
4-May	Nitrogen Application (Urea)	Urea	173 lb	194 kg	
4-May	Soil Finish	Field Cultivator Ge15ft			1
5-May	Phosphorus Application (P ₂ O ₅)	Elemental Phosphorus	53 lb	59.5 kg	1
5-May	Plant Corn Seed	Plant/Begin Growing Season			
5-May	Bicep II Magnum ® (PRE)	Atrazine	0.5 qt	1.39 kg	

Table 13 (cont'd)

1					
5-May	Bicep II Magnum ® (PRE)	Metolachlor	0.39 qt	1 kg	
1-Nov	Combine Harvest Corn Grain	Harvest and Kill			
15-Nov	Fall Chisel	Coulter-chisel Plow			
14-May	Soil Finish	Field Cultivator Ge15ft			
14-May	Phosphorus Application (P ₂ O ₅)	Elemental Phosphorus	40 lb	45 kg	
14-May	Soil Finish	Field Cultivator Ge15ft			
15-May	Plant Soybean Seed	Plant/Begin Growing Season			
7-Jun	Spray Roundup ®	Glyphosate Amine	22 fl oz	0.87 kg	
1-Oct	Combine Harvest Soybean Grain	Harvest and Kill			2
4-Oct	Soil Finish	Field Cultivator Ge15ft			2
7-Oct	Nitrogen Application (Urea)	Urea	125 lb	140 kg	
7-Oct	Phosphorus Application (P ₂ O ₅)	Elemental Phosphorus	35 lb	39.2 kg	
7-Oct	Treflan	Trifluralin	2 pt	1.1 kg	
7-Oct	Plant Canola Seed	Plant/Begin Growing Season			
25-Apr	Post-Emergence Poast ® Herbicide	Sethoxydim	1.5 pt	0.315 kg	
15-Jul	Combine Harvest Canola	Harvest and Kill			3
30-Oct	Fall Chisel	Coulter-chisel Plow			



Figure 15. Scenario 1 (a), 2 (b), 3 (c), and 4 (d) implemented in the SWAT model.



Figure 15 (cont'd)



Figure 15 (cont'd)



Figure 15 (cont'd)

* Cells with yellow fill denote crops determined to be unsuitable in the scenario due to the regions physical attributes, climate, and preexisting harvesting equipment. Cells with blue fill denote crops that would further be defined as "poor suitability" based on excessive capital cost for equipment, low productivity on common soil types in the watershed, and the ease of farmers to alter preexisting management practices to accommodate new cropping systems.

6. WATER QUALITY IMPACT ASSESSMENT OF LARGE SCALE BIOFUEL CROPS EXPANSION

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Abstract. The challenges we face in transitioning to global production of biomass as renewable feedstock sources in a way that is both economically feasible and environmentally sustainable are ubiquitous. In this study, the Soil and Water Assessment Tool (SWAT) was used to predict the possible long-term environmental implications, specifically water quality, due to large-scale bioenergy cropping system expansion based on four landuse scenarios and 15 bioenergy crop rotations for four watersheds, totaling 244 model simulations. The study area consists of four large watersheds totaling 53,358 km² located in Michigan's Lower Peninsula used intensively for agricultural production all directly contributing to the Great Lakes. Non-point source pollutant loadings of sediment, nitrogen, and phosphorus are a major issue throughout the study area, contributing to 139 records on the Michigan Section 303(d) list for waterbody impairments. The results from SWAT suggest that in general, perennial grass species are most suitable for large-scale implementation in this study area, whereas traditional intensive row crops should be implemented with caution on such a broad scale. In addition, bioenergy row crops such as continuous sorghum, continuous corn stover, and

continuous canola exhibit dramatic pollution load variation caused by differences in climate and physiographic characteristics throughout the study area. Therefore, additional attention should be made when selecting locations for implementation of these crops. Row crops also had the highest increases of high priority areas for sediment, nitrogen, and phosphorus of 15.82 percent (continuous sorghum), 26.0 percent (continuous corn stover), and 3.35 percent (continuous soybean), respectively. Based on the data from this study, it is not recommended that marginal land be converted to any row crop bioenergy rotation in areas with preexisting high nitrogen levels. Statistical analyses demonstrate that perennial grass species significantly reduce sediment on all lands except marginal lands. Meanwhile, only bioenergy crops grown on row crop land experiences significant decreases in total nitrogen load. With the exception of row crops cultivated on marginal lands and all agricultural land, the majority of bioenergy crops significantly reduce total phosphorus loads.

6.1 INTRODUCTION

Biofuels are liquid fuels, such as ethanol and biodiesel, produced from biological feedstocks and are mainly used for transportation and heating (de Fraiture *et al.*, 2008). The benefits associated with the production of biofuels are commonly referenced. Biofuels are looked to as an answer to reducing greenhouse gases responsible for climate change and the nation's vast addiction with fossil fuels, which are politically risky and environmentally harmful (Solomon, 2010). Renewable energy sources are readily available, ensuring domestic energy security rather than relying on oftentimes politically volatile foreign countries (Goldemberg, 2007). However, negative aspects are equally

important to examine prior to considering large-scale implementation of bioenergy crops as a sustainable practice. When landuse change is considered, the benefits of biofuels become difficult to quantify and may be negated due to possible environmental impacts (McLaughlin and Walsh, 1998). Greenhouse gas emissions associated with landuse change from current landcover to large-scale corn production for ethanol are estimated to double (Searchinger *et al.*, 2008). Bioenergy cropping systems are likely to increase pollution, further impair already damaged soils in consequence of intense agricultural practices, and accumulate harmful greenhouse gases from their production and use (Groom *et al.*, 2008). In addition, the expansion of bioenergy crop production will undoubtedly increase the amount of water use through evapotranspiration and reallocate water resources from available water for human consumption to the atmosphere as water vapor (Berndes, 2002). However, the daunting fact of biofuel production is that landuse change into agricultural production is inevitable.

A revision to the National Renewable Fuel Standard program has mandated 15.2 and 30 billion gallons of renewable fuel by 2012 and 2020, respectively (USEPA 2009a). To hastily meet demands for biomass, significant alterations to current landuse leading to increases in cultivated acreage will result (Rowe *et al.*, 2009). However, large-scale production of bioenergy feedstocks are limited due to landuse competition with traditional food crops (Scheffran and BenDor, 2009). Therefore, biofuel crops must also be considered to be grown on agriculturally marginal land or surplus lands with degraded production capabilities (Lal and Pimentel, 2007). Unfortunately, the implications of expanding cropland to accommodate demands are not adequately understood at a largescale (Rowe *et al.*, 2009).

In order for biofuels to be a sustainable solution to fossil fuels, their cultivation must avoid intensifying any negative environmental impacts. Freshwater is vital to human existence and maintaining its health is a fundamental requirement for sustainable agricultural production (Gleick, 1998). Increased intensive agricultural practices associated with current bioenergy crops such as corn, soybeans, sugarcane, etc. may lead to impairments of waterbodies. Agriculture is responsible for the largest contribution of non-point source pollution to freshwater in the United States (Foley et al., 2005). Corn, the current crop supplying majority of biofuels in the United States, requires more fertilizer and pesticides than any other crop grown in the nation (Pimentel and Patzek 2005). Biofuel production requires increased amounts of fertilizer use and irrigation to increase crop yields to meet demands (Searchinger et al., 2008). However, even under current practice, row crop production is the largest contributor of nitrogen and phosphorus fluxes to the Mississippi River basin resulting in eutrophication, reduced dissolved oxygen, algal blooms, and impaired aquatic habitat of surface waterbodies, and hypoxic zones in the Gulf of Mexico (Carpenter *et al.*, 1998; Powers, 2007). Eutrophication is many times responsible for impaired waterbodies and contaminated drinking water supplies, which increases the cost of treatment for human use (Carpenter et al., 1998; Nyakatawa et al., 2006). As a direct consequence, human safety and aquatic ecosystem health are at risk.

The research in this paper evaluates the long-term environmental implications, specifically water quality, of large-scale bioenergy cropping system expansion. This aids in determining the suitability of bioenergy crops and obtaining information to aid in watershed-scale decision making regarding landuse management. The Soil and Water Assessment Tool (SWAT) was used to predict the effects of four future landuse scenarios and 15 bioenergy crop rotations combined to form 42 total cropping scenarios on sediment, nitrogen, and phosphorus loads in four watersheds in agricultural regions of Michigan during a 19 year (1990 to 2008) period. The model was calibrated and validated on a monthly basis and model output was evaluated on an annual time step.

6.2 MATERIALS AND METHODS

6.2.1 Study Area

The study area is located in the lower portion of Michigan and includes the following four watersheds (Figure 16):

- The Saginaw River basin (hydrologic unit code (HUC) 040802) is located in the east central portion of Michigan's Lower Peninsula and includes six HUC 8-digit watersheds (Tittabawassee, Pine, Shiawassee, Flint, Cass, and Saginaw River). The size of drainage area is 1,526,242 ha in which about 40 percent being used for agricultural productions, 6 percent developed, 42.4 percent forest, and 12 percent wetlands.
- The St. Clair-Detroit basin (HUC 040900) is located in southeast Michigan and includes four HUC 8-digit watersheds (St. Clair, Clinton, Detroit, and Huron River). The size of drainage area is 818,303 ha with approximately 30.3 percent being used for agricultural production, 39.4 percent developed, 28 percent forest, and 2.3 percent wetlands.
- The Southeastern Lake Michigan basin (HUC 040500) is located in southwest Michigan and includes five HUC 8-digit watersheds (Kalamazoo, Upper Grand, Maple, Lower Grand, and Thornapple River). The size of drainage area is

1,889,426 ha with approximately 53.3 percent being used for agricultural production, 10.6 percent developed, 28.8 percent forest, and 7.3 percent wetlands.

The St. Joseph basin (HUC 04050001) is located in the southwest portion of Michigan and the northeast portion of Indiana. The size of drainage area is 1,101,781 ha with approximately 70.9 percent being used for agricultural productions, 6.3 percent developed, 16.4 percent forest, and 6.4 percent wetlands.



Figure 16. Basins included in study area.

6.2.2 General Water Quality Issue

In general, the main source of non-point source pollution in the study region is agricultural production, which is a major contributor to deteriorating water quality conditions. Multiple waterbodies, including the Kalamazoo, Saginaw, Clinton, St. Clair, Detroit, and Rouge Rivers, in the study area have been classified as part of the 26 Great Lakes Areas of Concerns (AOCs) listed in the United States (USEPA, 2009c). In order to be classified as an AOC, the waterbody must have at least one beneficial use impairment such as beach closings, excessive nutrient loading, or contaminated sediment (USEAPA, 2009b). There are currently 139 records listed on the Michigan Section 303(d) of the Federal Clean Water Act for impairments including mercury, nutrient exceedances, endosulphan, total dissolved and total suspended solids, turbidity, polychlorinated biphenyls (PCB), polybrominated biphenyls (PBB), dichlorodiphenyltrichloroethane (DDT), dissolved oxygen, dioxin (TCDD), pathogens, E. coli, poor fish and macroinvertebrate ratings, impaired habitat, nuisance plant and algal growths, and untreated sewage discharge (MSUIWR, 2010).

6.2.3 SWAT Model

Pollution transport estimation requires large amounts of complex datasets in order to accurately represent the chemical, physical, and biological processes, in which highly sophisticated hydrologic models excel (Powers, 2007). Therefore, the Soil and Water Assessment Tool (SWAT) was used in this study. This is a physically based model developed to estimate streamflow and stream reach loadings of nutrients, pesticides, and sediments on a watershed scale (Spruill *et al.*, 2000). The model bases its predictions on a complex structure of routing runoff and constituents throughout a defined watershed and is one of the most comprehensive models of its kind (Saleh and Du, 2004; Powers, 2007). SWAT generates flow and constituent load estimates based on landuse practices in complex watersheds with varying soils, landuse, weather conditions, and management operations over long time periods (Arnold *et al.*, 1998). ArcSWAT version 2005 is an ArcGIS extension and graphical user interface for the SWAT model that was used in this study. The major components of the model include weather data, soils data, slope classifications, landuse data, nutrient and pesticide applications, and management practices including extensive agricultural operations. The hydrologic component of the SWAT model uses the modified SCS curve number method to determine surface runoff during precipitation events (Saleh and Du, 2004). Soil erosion and sediment yields are determined by the Modified Universal Soil Loss Equation (MUSLE) (Neitsch *et al.*, 2005). With successful model calibration, SWAT is an extremely useful tool in predicting the environmental implications of land use change.

6.2.4 Crop Rotations and Management Operations

6.2.4.1 Rotations and Operation Schedules

Crop rotations have traditionally been used throughout the history of modern agriculture as a method to control noxious weeds, pests and disease, and to enhance soil fertility, physical structure, root-zone biological activity, productivity (NCSU, 2005). In this study, crops suitable for bioenergy feedstock and their associated crop rotations that would be likely implemented were identified. The bioenergy crops considered for conversion from the current landuse were barely, canola, cassava, corn, corn stover, jatropha, miscanthus, native grasses, potato, rice, rye, sorghum, soybean, sugar cane, sugarbeet, switchgrass, and wheat. However, after determining the suitability for growth throughout the study region the crops considered were reduced to corn, canola (fall), cereal rye, sorghum, soybean, miscanthus, corn stover, switchgrass, and native grasses. The rotations that were deemed as acceptable for producing bioenergy crops on a specific landuse were based on the current landuse and its typical production capability, the difficulty for farmers to acquire the planting and harvesting equipment, and the capital investment required to invest in the operations not already included the farm's practices. For example, marginal land has generally low levels of soil organic matter, poor soil structure and fertility, and tends to produce low yields for traditional crops. Therefore, crops such as wheat and soybeans are not practical for cultivation. Additionally, due to low soil organic matter in marginal soils, corn stover was not selected as suitable for this landuse. Each scenario was subject to a series of reviews in order to provide the most realistic rotations for the region of study.

The rotations were assembled using data obtained from the Michigan State University Extension (MSUE) for the bioenergy crops used in the simulations. However, it is important to note that the information obtained from MSUE is general for the study area and may vary from field-to-field. Based on this information, 15 rotations were developed, including corn-soybean-canola (Crn-Soy-Can), corn-soybean-rye (Crn-Soy-Rye), corn-soybean (Crn-Soy), Corn Stover (40 percent residue removal)-soybean (CrnS-Soy), sorghum-soybean (Srg-Soy), continuous canola (CCan), continuous corn (CCrn), continuous corn with stover removal (CCrnS), continuous rye (CRye), continuous sorghum (CSrg), continuous soybean (CSoy), miscanthus (Mis), Switchgrass (Crn-Soy-Swg), and native grasses (NaGr). For example, the corn-soybean-canola (Crn-Soy-Can) operation schedule is provided in table (detail information for the rest of agricultural rotations can be found in Love and Nejadhashemi (2010a). Each rotation followed the same format with tillage practices, fertilizer and pesticide applications, and planting and harvesting dates developed specifically for each crop.

6.2.4.2 Scenarios

The crop rotations were integrated into the SWAT model and tested under four scenarios. The scenarios were developed for the bioenergy crops, based on suitability and practicality.

- Scenario 1: The first scenario considers all land currently cultivated for row crops and grains, hays, and seeds (i.e. corn, soybeans, wheat, hay, etc.), which represents the majority of current agricultural land in the watershed. This scenario is the most likely if and only if the commodity prices for bioenergy feedstock are competitive with traditional crops and the equipment needed for their cultivation is similar to preexisting machinery requiring justifiable capital investment.
- Scenario 2: The second scenario considers only the other crops (i.e. sugarbeets, potatoes, dry beans, fruit crops, etc.) for conversion to bioenergy crops. This scenario represents the least amount of land considered for conversion and represents a case in which bioenergy crops may not gain momentum on typical agricultural land.
- Scenario 3: The third scenario considers cultivation in lands that are not currently used for agricultural productions (i.e. fallow cropland, pasture, wasteland, etc.), which can be considered marginal land. This scenario would be typical if bioenergy feedstock prices were not competitive with traditional commodities, but there was still enough demand to drive farmers to turn marginal land into production they would otherwise not use due to low productivity of row crops.
- Scenario 4: The final scenario is the combination of all previous scenarios, and represents the overall most significant landuse change from current state to the bioenergy cropping rotations. This scenario would likely occur if demand for

bioenergy feedstock increased to economically justify the displacement of land for traditional crops for livestock and human consumption.

In the above scenarios, the range converted to the bioenergy rotation varies from 0.2 percent to 54 percent of the watershed area. The data for the above analysis was acquired from the US Department of Agriculture- National Agricultural Statistics Service cropland data layer. In addition, the conversion of woodlands to bioenergy crop productions was not considered as a viable option in this region and therefore was not included in this study.

6.2.5 Model Setup

6.2.5.1 Input Data Sources

Successful use of the ArcSWAT model relies on acquiring suitable and reliable data. The soil characteristics of the four basins were defined by the State Soil Geographic Database (STATSGO) developed by the National Cartography and Geospatial Center (NCGC) of the Natural Resources Conservation Service (NRCS). The topography was based on the USGS Digital Elevation Model (DEM 90 meter resolution), which was used in delineation of the watershed boundaries. The USGS National Hydrography Dataset (NHD) was imposed on the DEM maps to define the stream network. Subsequently, each watershed was divided into subbasins, which allowed characterizing different areas of the watershed regarding potential environmental impacts of land use changes.

Each watershed was further divided into individual hydrologic response units (HRUs) by defining thresholds based on the percentage of landuse, soil class, and slope over the subbasin area. The slope classification was performed using four slope classes (0-2, 2-5, 5-10 and >10 percent). For the purpose of this project, these thresholds were set to 20, 10 and 20 percent, respectively (Winchell *et al.*, 2009).

The Cropland Data Layer (2008 CDL 56 meter resolution) developed by the USDA National Agricultural Statistics Service (NASS) was used as the landuse representation. A table was created to relate CDL landuse values to corresponding SWAT landuse values, which was referenced in the "lookup table" feature in SWAT. In the case when a crop did not exist in the SWAT database, such as miscanthus, a new crop was defined based on agronomic aspects found in literature and consultation with bioenergy crop experts. For basin-wide climatic data, long-term precipitation (74 stations) and temperature (56 stations) data was collected from the National Climatic Data Center (NCDC) for a 19-year period (1990-2008). Other meteorological data (wind speed, relative humidity, and solar radiation) required by the model was estimated using the SWAT weather generator.

6.2.5.2 Operation of SWAT Model

The period of study for analysis was January 1, 1990 to December 31, 2008. Model output from a period of this length accurately represents the long-term effects of watershed behavior. This is vital when considering the effects that bioenergy cropping systems may have on watershed characteristics, which often takes extended time to develop. The SWAT model outputs that were compared for this study were total nitrogen $(NH_4 + NO_2 + NO_3 + Organic N)$ in kilograms, total phosphorus (Mineral P + Organic P) in kilograms, and sediment in metric tons. The output data was obtained at 4

watershed outlets, 879 subbasins, and over 5,970 km of stream networks.

6.2.5.3 Sensitivity Analysis

A sensitivity analysis identifies and ranks the parameters that are most influential on model output (flow, sediment, and nutrients) and is useful for determining the parameters for successful model calibration (Moriasi *et al.*, 2007). In this study, each watershed was subjected to a sensitivity analysis in which observed daily flow rate, sediment, and nutrients load were used. In addition, management operations were applied to provide the most accurate representation of physical and chemical interactions that may influence model output. Although a sensitivity analysis aids in identifing parameters useful in calibration of the model, a reasonable value and reasonable justification (site-specific knowledge and data) for the use of each parameter is imperative to produce results representative of true watershed behavior. The importance of using both observed data and local management operations during the sensitivity analysis procedure was discussed in Love and Nejadhashemi (2010a).

6.2.5.3 Calibration/Validation

Model calibration is a necessary component of hydrologic modeling to increase confidence of model predictions (Moriasi *et al.*, 2007). The calibration process estimates model input parameter values by comparing the generated output for a simulation to an observed dataset. Calibration is performed manually or automatic or combination of manual and auto-calibration. Once a period for calibration data is set, the model is run with the model initial parameter values. The agreement between model output and observed data is measured using a mathematical relationship, or objective function, and an automated optimization procedure finds the values for each parameter that optimize the objective function (Gupta *et al.*, 1999). Validation follows calibration to establish the capability of the calibrated model to make accurate predictions by comparing model output to an observed dataset of a period not used in calibration (Moriasi *et al.*, 2007). The calibration and validation periods are provided in Table 14.

In order to avoid providing biased, exceedingly positive or negative evaluation of model performance, multiple model evaluation statistics should be used (Krause *et al.*, 2005). For this study, the Nash-Sutcliffe efficiency (NSE), root mean squared error (RMSE), and the coefficient of determination (\mathbb{R}^2) were selected to determine model prediction efficiency. The Nash-Sutcliffe efficiency determines conformity of the model output to the observed dataset based on a 1:1 relationship, effectively determining goodness-of-fit (McCuen *et al.*, 2006). The NSE is computed with the relationship in Equation 4:

NSE=1-
$$\frac{\Sigma(Y_{obs}-Y_{pred})^2}{\Sigma(Y_{obs}-Y_{mean})^2}$$
 (4)

where Y_{obs} is the observed value for the evaluated component, Y_{pred} is the model predicted value for the evaluated component, Y_{mean} is the mean of observed data for the evaluated component, and n is the total number of data points. NSE ranges from $-\infty$ to 1. If the value for NSE is 1, the model exactly predicts the observed values. If the value for NSE is 0, the sum of squares of the difference between the observed and model predicted is equal to the difference between the observed and the mean of the observed values. Typically, NSE values greater than 0.75 are very good, greater than 0.65 are good, greater than 0.5 are satisfactory, and values less than 0.5 are considered unsatisfactory on monthly basis (Moriasi *et al.*, 2007). However, statistical ratings such as NSE are projectspecific, and oftentimes are difficult to obtain satisfactory results in situations when a complete time series of data are not available (Moriasi *et al.*, 2007). The NSE is at a disadvantage due to the fact that the differences between predicted and observed values are squared, resulting in overestimation of model performance for large values (i.e. peak flows) and underestimation for lower values (i.e. low flow conditions) (Krause *et al.*, 2005).

The root mean squared error (eq. 5) is the vertical deviation of a data point from a fitted line, providing a value in measureable units. The RMSE has important advantages over traditional correlation methods, such as indicating error in the measured units (Moriasi *et al.*, 2007).

$$RMSE = \sqrt{\frac{\Sigma(Y_{obs} - Y_{pred})^2}{n}}$$
(5)

where n is the total sample size. Values of RMSE are that of the predicted variable, such as cubic meters per second for flow. This gives an indication of quantitative differences in the regression prediction from the observed (fitted) line in the squared units of the constituent being evaluated.

The coefficient of determination, R^2 , is a statistical measure for goodness-of-fit. In this case, it is the percent of total variation in the dependent variable explained by the regression equation (Menard, 2000). R^2 values range from 0 to 1, where values close to 1 indicate that the regression equation (model) is predicting the dependent variable with confidence and that the dispersion of the predicted value is equal to the observed value. One of the main drawbacks of the R^2 method is its failure to address under- or overpredictions (Krause *et al.*, 2005). Values greater than 0.5 are generally considered acceptable when the model operates on a monthly basis (Santhi *et al.*, 2001). The R^2 is calculated with Equation 6:

$$R^{2} = \left(\frac{\sum(O_{i} - O_{mean})(P_{i} - P_{mean})}{\sqrt{\sum(O_{i} - O_{mean})^{2}}\sqrt{(P_{i} - P_{mean})^{2}}}\right)^{2}$$
(6)

where O are the observed values and P are the predicted values.

Combination of manual and autocalibration were used for flow, sediment, and nutrient calibration. Calibration should include data from a 3-5 year period during high, low, and moderate precipitation years to effectively activate all model processes for a diverse range of hydrologic events (Moriasi *et al.*, 2007). Therefore, based on a comparison with the 19-year mean of precipitation for all watersheds, the period of 2000-2005 was used for the calibration and validation (figure 17). However, due to periods lacking observed data, calibration periods varied slightly between watersheds (Table 14). Constituent samples were available only in a limited amount. Therefore LOADEST, a FORTRAN program developed by the USGS, was used in this study to estimate monthly sediment, total phosphorus, and total nitrogen loads for calibration (Runkel *et al.*, 2004).

One year prior to each period listed in Table 14 was treated as a warm-up period and was not included in the statistical comparisons. Calibration was performed on the first half of the period with available data and validation was performed using data from the second half of the available data period.



Figure 17. Precipitation deviation from 19-year mean for study period.

Table 14. Calibration and validation periods for each basin.

			Basi	n	
		040500	04050001	040802	040900
Flow	Calibration	1/2000- 6/2002	6/2001-9/2003	1/2002- 12/2003	1/2000- 12/2002
	Validation	7/2002- 12/2004	10/2003- 12/2005	1/2004- 12/2005	1/2003- 12/2005
Sediment	Calibration	1/2000- 6/2002	6/2001-9/2003	1/2002- 12/2003	1/2001- 6/2003
	Validation	7/2002- 12/2004	10/2003- 12/2005	1/2004- 12/2005	7/2003- 12/2005
Nitrogen ^[a]	Calibration	1/2000- 6/2002	6/2001-3/2003	6/2003- 9/2004	1/2002- 12/2003
	Validation	7/2002- 12/2004	4/2003- 12/2005	10/2004- 12/2005	1/2004- 12/2005
Phosphorus	Calibration	1/2000- 6/2002	6/2001-9/2003	1/2002- 12/2003	1/2001- 6/2003
	Validation	7/2002- 12/2004	10/2003- 12/2005	1/2004- 12/2005	7/2003- 12/2005

[a] Nitrogen was evaluated with Total Nitrogen (040500), Nitrate (04050001), Total Kjeldahl Nitrogen (040802), and Total Nitrogen (040900).

According to the evaluation criteria discussed before, the uncalibrated model performed poorly using the model default values for all watersheds (table 15). However, the combined NSE for the calibrated model performed well above satisfactory for flow, sediment, and phosphorus, yet failed to meet the NSE of 0.5 requirement for nitrogen. However, due to the very low availability of sampling data in each watershed and the difficulty in obtaining suitable nitrogen calibration, these statistical values were deemed as satisfactory for the purposes of this project. The intended use of the model is to evaluate changes of constituent loads on a large-scale for a variety of scenarios requiring high flexibility. Overall, calibration resulted in satisfactory statistical analysis indicating the more than adequate prediction capabilities of the model, allowing for confidence in model output for comparison. NSE values for flow, sediment, nitrogen, and phosphorus ranged from 0.628 to 0.803, 0.589 to 0.843, 0.232 to 0.398, and 0.628 to 0.900, respectively. Values for R² followed a parallel trend, with adequate levels of correlation with values for flow, sediment, nitrogen, and phosphorus ranging from 0.676 to 0.809, 0.590 to 0.867, 0.508 to 0.680, and 0.656 to 0.904, respectively. The values obtained for the RMSE statistic are well within acceptable limits for the given scope of this project. The final parameter values that were obtained during calibration are provided in table 16 and were applied prior to each subsequent model simulation. As a result of the calibration and validation process, the model is able to effectively capture the complex physical and chemical interactions taking place to provide confident, representative predictions of future pollution generation due to the large-scale application of bioenergy cropping systems.

Parameter	Period	Statistic	Basin			
			040500	04050001	040802	040900
Flow	Uncalibrated	NSE	0.229	0.098	0.472	-0.136
		R^2	0.571	0.579	0.544	0.655
		RMSE ^[b]	61.88	51.22	52.98	11.82
	Calibrated	NSE	0.718	0.652	0.628	0.541
		R^2	0.753	0.629	0.730	0.674
		RMSE ^[b]	35.20	45.63	47.53	7.381
	Validated	NSE	0.843	0.603	0.714	0.695
		R^2	0.838	0.769	0.716	0.702
		RMSE ^[b]	30.24	31.24	60.38	6.205
	Combined	NSE	0.803	0.628	0.698	0.689
		R^2	0.809	0.692	0.713	0.676
		RMSE ^[b]	35.85	39.11	54.34	5.950
Sediment	Uncalibrated	NSE	-0.717	-18.763	0.388	0.046
		R^2	0.367	0.430	0.407	0.475
		RMSE ^[c]	563.3	1003	510.7	266.9
	Calibrated	NSE	0.782	0.621	0.544	0.332
		R^2	0.809	0.601	0.668	0.488
		RMSE ^[c]	201.7	149.6	245.9	121.1
	Validated	NSE	0.878	0.560	0.702	0.785
		R^2	0.904	0.565	0.766	0.955
		RMSE ^[c]	183.6	140.5	629.9	175.0
	Combined	NSE	0.843	0.589	0.693	0.763
		R^2	0.867	0.590	0.743	0.755
		RMSE ^[c]	193.0	145.1	478.2	150.5
Nitrogen ^[a]	Uncalibrated	NSE	-1.157	-15.91	-0.159	-174.5

Table 15. Results of statistical analysis for calibration and validation periods.

Table 15 (cont'd)

		R^2	0.238	0.391	0.273	0.309
	Calibrated	RMSE ^[d]	39986	469.9	6615.5	34929
		NSE	0.121	0.278	0.445	-0.044
		R^2	0.331	0.634	0.552	0.534
	Validated	RMSE ^[d]	25608	14356	7917	2066
		NSE	0.596	0.189	-0.603	0.318
		R^2	0.740	0.627	0.750	0.654
	Combined	DMCE [d]	18199	7730	5281	2633
		NSE	0.398	0.320	0.315	0.232
		R ²	0.508	0.549	0.680	0.619
Phosphorus	Uncalibrated	DMCE [d]	22277	11530	6729	2367
		NSE	-5.047	-3.960	0.146	-0.054
		R^2	0.553	0.114	0.346	0.222
	Calibrated	DMCE [d]	2994	31711	1089	402.4
		NSE	0.793	0.624	0.581	0.450
		R^2	0.853	0.659	0.635	0.471
	Validated	DMCE [d]	487.9	502.5	558.3	184.3
		NSE	0.947	0.632	0.712	0.964
		R ²	0.959	0.643	0.746	0.948
	Combined	DMCE [d]	368.7	384.1	1073	90.6
		NSE	0.900	0.628	0.699	0.839
		R ²	0.904	0.656	0.734	0.813
		RMSE ^[d]	433.5	447.3	855.6	145.2

- [a] Nitrogen was evaluated with Total Nitrogen (040500), Nitrate (04050001), Total Kjeldahl Nitrogen (040802), and Total Nitrogen (040900).
- [b] The units for flow RMSE are meters 3 s $^{-1}$.
- [c] The units for sediment RMSE are tons day⁻¹.
- [d] The units for nutrients RMSE are kilograms day⁻¹.

Table 16. Final parameter values from calibration.

		Basin					
Parameter	Change Method	040500	04050001	040802	040900		
Alpha Bf	Replace Value	0.32509	0.58501	0.69280	0.071630		
Biomix	Replace Value	-	-	-	0.1		
Canmx	Replace Value	-	-	-	0.27201		
Ch K2	Replace Value	115.94	44.735	87.931	25.828		
Ch N2	Replace Value	0.075737	0.44107	0.58573	0.081347		
Cn2	Multiply By	1.20925	1.20038	1.13267	1.15602		
Esco	Replace Value	0.42962	0.33532	0.34490	0.37760		
Nperco	Replace Value	1.0	-	-	0.5		
N Updis	Replace Value	-	-	-	10		
Rchrg Dp	Replace Value	0.31961	0.33342	0.19753	0.87389		
Smtmp	Multiply By	-	-	1.0079364	-		
Sol Awc	Multiply By	1.29317	1.079115	0.8747	-		
Spcon	Replace Value	0.00055413	0.0044107	0.0074351	0.0091561		
Surlag	Replace Value	8.7156	9.7813	6.1303	9.7684		
Timp	Replace Value	0.37496	0.58155	0.16357	0.39598		
Usle P	Replace Value	0.35780	0.23878	0.63399	0.95221		

6.3 RESULTS AND DISCUSSION

6.3.1 Basin-wide Impact of Bioenergy Cropping Rotations

Altering the landscape with the introduction of agriculturally-intensive bioenergy crops is expected to result in changed pollutant loadings to waterbodies. In this study, average annual sediment, total nitrogen, and total phosphorus loads were obtained for each watershed at the outlet for the study period (1990-2008). In order to examine the impacts of landuse conversion on water quality, the model results obtained from the four

cropping scenarios (Scenario 1 to 4) and throughout the study area were evaluated (Figure 18, Figure 19, and Figure 20). The statistical analysis provided in this section was performed in STATISTICA data analysis software (StatSoft, Inc., 2010). This allowed for a large-scale assessment encompassing all watersheds and all possible landuse scenarios, providing insight to the potential extreme pollutant load variation. Traditional, intensive crops such as corn, sorghum, canola and soybean experience increases in sediment and nitrogen load, yet in certain cases have the potential to reduce phosphorus loads. In general, sorghum is not a viable option for cultivation in regions with concerns of sedimentation and phosphorus loadings, yet this crop has nearly zero median impact on nitrogen loads. In addition, the perennial grass species (miscanthus, native grasses, and switchgrass) extensively mitigate sediment and phosphorus, yet have the potential to increase nitrogen slightly. By adding rye, a close-grown annual grass, to a rotation (i.e. into a corn-soybean rotation) pollutant loadings experience an overall decrease. When rye is grown in a continuous rotation, nitrogen and phosphorus loads experience a decrease, while sediment is nearly zero impact. It is important to note that in general, all cropping rotations have both maximum and minimum values of increased and decreased pollutant loadings, respectively. This is expected due to evaluating an extremely large region with diverse climatological, geological, and agricultural characteristics. However, some rotations exhibit the magnitude of this behavior in different amounts. For example, miscanthus and switchgrass have the least sediment load variability (141 and 142 percent range, respectively), whereas continuous sorghum has the highest variability (321 percent range) as well as the highest maximum change from the base scenario (312 percent). Ironically, continuous sorghum has the smallest range of total nitrogen load, with

continuous corn stover having the largest span of values. The perennial grass species have low variability of sediment and phosphorus load, further supporting their use in watersheds with loading issues regarding these pollutants. In general, perennial grass species are most suitable for large-scale implementation in this study area, whereas traditional intensive row crops should be implemented with caution on such a broad scale. The highest ranges for sediment, total nitrogen, and total phosphorus, as expected, were the result of the row crop rotations continuous sorghum, continuous corn stover, and continuous canola, respectively. The large ranges observed show the variability that bioenergy crop rotations are likely to exhibit. This is largely in part to their unsuitability in various locations in such a large study area, which also has large variation in climatological factors. Small ranges show how certain crops are less dependent on these drivers.



Figure 18. 19-year annual average basin-wide sediment load at the watershed outlet.



Figure 19. 19-year annual average basin-wide total nitrogen load at the watershed outlet.



Figure 20. 19-year annual average basin-wide total phosphorus load at the watershed.

6.3.2 Basin-level Priority Areas for Targeting Conservation Efforts

In order to effectively target agricultural areas for the implementation of conservation efforts and Best Management Practices (BMPs), and to determine the areas in greatest need for further research and investigation, priority maps were created for the entire basin. Three classes (low, medium, and high) of priority concerns were formed by dividing the study area based on what was essentially a quantile classification for each constituent. As it was discussed earlier, Scenario 4 of the landuse conversion represents the most extreme landuse conversion scenario among the studied scenarios. Therefore, in this section of study, the impacts of landuse conversion on both priority concerns areas and streams were evaluated by comparing Base Scenario and Scenario 4. The overall changes in the length of river network priority streams, based on stream concentration, at different locations of the study area are provided in Table 17 with the corresponding percentages change from low, medium, and high compared to the base scenario. Identifying, these streams is important since changes in stream concentration can directly or indirectly endanger aquatic organisms living in those streams. Figure 21 provides a visualization on priority concerns streams and the impacts of intensive bioenergy crop expansion. In this figure, the stream concentration under Base scenario is compared with continuous corn (Scenario 4), and switchgrass (Scenario 4) rotations. This indicates that converting all agricultural land to a continuous corn rotation will result in a substantial increase in stream reaches classified as high priority as well as nearly all low priority streams shifting to medium priority for all constituents. These findings support those discussed in the previous section (3.1) for pollutant loads found at the main channel outlet under a continuous corn rotation (for all four scenarios). Switchgrass experiences a mixed change of sediment concentration, with some streams being reduced to low or

medium priorities, whereas others experience a jump to the high priority. Also with switchgrass, a substantial amount of stream reaches (34 percent) change to medium or high priorities for total nitrogen concentration. However, when total phosphorus concentration is considered, there is a general reduction in high priority streams. In general, the perennial grasses, although mixed benefits are present, are more suitable for implementation than intensive annual bioenergy crops. Miscanthus had the least amount of high priority streams of 7.1 and -23.1 percent change from the base scenario for nitrogen and phosphorus, respectively (Table 17). By adding rye into a corn-soybean rotation, the amount of high priority streams is decreased by 10.8, 6.4, and 20.9 percent for sediment, total nitrogen, and total phosphorus, respectively. The sorghum-soy rotation is suitable for implementation in regions where stream concentration of sediment and phosphorus are of concern, as it reduced the most high priority streams by 21.8 percent over base, but not in regions with high preexisting levels of nitrogen. The agriculturally intensive row crops had the highest increases of high priority streams for sediment, nitrogen, and phosphorus of 39.1 percent (continuous sorghum), 67.9 percent (continuous corn stover), and 25.5 percent (continuous corn stover), respectively.

As it was discussed earlier, identifying the area of concerns in a watershed is the first step in developing the control strategy to mitigate negative impacts of agricultural expansions. The changes in priority areas at subbasin level are provided in Figure 22 with the corresponding percentages provided in Table 18. The results for this analysis are comparable to the stream, yet have some subtle differences. In general, when a continuous corn rotation is applied to all agricultural land, there is a considerable increase of medium and high priority areas by 44.7, 45.7, and 42.1 percent for sediment, total

nitrogen, and total phosphorus load, respectively. However, some subbasins that were originally high priority were reduced to medium priority, resulting in a shift of priority area focus to other sensitive regions. Switchgrass appears to have a mitigation effect on sediment and total phosphorus loads (Figure 22). Again, a small number of previously low priority subbasins have been shifted to medium or high priority for sediment load. Meanwhile, high priority areas were reduced by 8.9 percent due to large-scale switchgrass production implementation, although the amount of high priority areas is reduced for total nitrogen (5.1 percent), the number of medium priority areas is increased by 29.2 percent over the base scenario. Corn stover removal has the potential to increase the amount of high priority streams and subbasins, both over the base scenario and over continuous corn and corn soybean rotations. As was observed in the priority streams previously mentioned, the agriculturally intensive row crops had the highest increases of high priority areas for sediment, nitrogen, and phosphorus of 15.8 percent (continuous sorghum), 26.0 percent (continuous corn stover), and 3.35 percent (continuous soybean), respectively. However, adding a close-grown grass specie (i.e. rye) into the rotation is advantageous. Continuous rye decreases the amount of high priority areas by 9.0, 6.0 and 8.2 percent for sediment, total nitrogen, and total phosphorus, respectively. The sorghumsoybean rotation is in general highly suitable for large-scale implementation based on this analysis. The perennial grass species are overall very suitable for large-scale implementation. Miscanthus reduced high priority areas for total nitrogen and total phosphorus by 7.7 and 8.4 percent, respectively. This analysis is merely a tool to help decision makers identify the possible locations that may be of high concern to monitor in

the event of large-scale expansion of bioenergy cropping rotations as discussed in this paper.



Figure 21. Priority streams for base scenario sediment, nitrogen and phosphorus (a,b,c), continuous corn sediment, nitrogen and phosphorus (d,e,f), and switchgrass sediment, nitrogen and phosphorus (g,h,i) (in μ g L⁻¹)



Figure 22. Priority areas for base scenario sediment, nitrogen and phosphorus (a,b,c), continuous corn sediment, nitrogen and phosphorus (d,e,f), and switchgrass sediment, nitrogen and phosphorus (g,h,i) (in kg ha⁻¹)

	Sediment		Nitrogen			Phosphorus			
	Low	Medium	High	Low	Medium	High	Low	Medium	High
	-1944	998	946	-2437	-810	3247	-1638	981	658
Continuous Canola	-32.56	16.72	15.84	-40.82	-13.56	54.38	-27.44	16.43	11.02
Continuous Corn	-2438	836	1602	-2321	-263	2584	-1820	894	926
Continuous Com	-40.83	14.00	26.83	-38.88	-4.40	43.28	-30.48	14.97	15.52
Continuous Corn stover	-2571	749	1822	-2472	-1584	4055	-2323	801	1521
Continuous Com stover	-43.06	12.54	30.53	-41.40	-26.52	67.93	-38.90	13.42	25.48
Continuous Rye	-2281	1218	1062	-2120	259	1861	111	333	-443
Continuous Ryc	-38.20	20.41	17.79	-35.52	4.34	31.18	1.85	5.57	-7.42
Continuous Sorahum	-2628	291	2338	-2242	-102	2343	-2199	706	1493
Continuous Sorghum	-44.02	4.87	39.15	-37.55	-1.70	39.25	-36.83	11.82	25.00
Continuous Souhean	-2588	425	2162	-2418	-936	3354	-2209	780	1429
Continuous Soybean	-43.34	7.13	36.22	-40.50	-15.67	56.17	-37.00	13.06	23.94
Corn Sov	-2588	556	2031	-2389	-732	3121	-2155	755	1400
Com Soy	-43.34	9.32	34.03	-40.01	-12.26	52.28	-36.09	12.65	23.44
Corn Sov Rye	-2399	1010	1389	-2373	-366	2738	-1116	964	152
Com Soy Rye	-40.18	16.92	23.26	-39.74	-6.12	45.87	-18.69	16.15	2.55
Corn stover Sov	-2588	602	1985	-2457	-966	3422	-2266	774	1492
Com stover Soy	-43.34	10.08	33.26	-41.15	-16.18	57.33	-37.95	12.96	25.00
Sorghum Soy	-2623	318	2306	-2343	-525	2868	-2080	852	1227
Sorghum Soy	32.40	-10.58	-21.82	-38.11	-5.74	43.85	11.13	3.75	-14.88
Miscanthus	1934	-632	-1303	-2275	-342	2618	665	224	-889
wiiseantiius	30.93	-10.40	-20.53	-22.20	15.10	7.10	32.09	-9.00	-23.09
Native Grass	1846	-621	-1226	-1326	901	424	1916	-537	-1379
	-43.94	5.32	38.62	-39.25	-8.79	48.04	-34.84	14.28	20.56
Switchgrass	-1034	915	118	-2030	264	1766	724	-138	-586
5 witchgrass	-17.31	15.33	1.98	-34.00	4.43	29.57	12.12	-2.31	-9.81

Table 17. Length of priority stream change from base (km) for Scenario 4 (the values with gray background represent the percent changes from the Base or current landcover scenario).

	Sediment		Nitrogen			Phosphorus			
	Low	Medium	High	Low	Medium	High	Low	Medium	High
Continuous Conolo	-16529	16375	154	-24645	22346	2299	-18995	20906	-1911
Continuous Canola	-30.97	30.69	0.29	-46.18	41.87	4.31	-35.60	39.18	-3.58
Continuous Corn	-23877	21025	2852	-24371	21041	3330	-22485	22062	423
Continuous Com	-44.74	39.40	5.34	-45.67	39.43	6.24	-42.14	41.34	0.79
Continuous Corn stover	-18135	15976	2159	-29693	15821	13872	-24788	23815	974
Continuous Com stover	-33.98	29.94	4.05	-55.64	29.65	26.00	-46.45	44.63	1.82
Continuous Rya	-13255	14515	-1260	-14262	16986	-2724	4511	0	-4511
Continuous Ryc	-24.84	27.20	-2.36	-26.73	31.83	-5.10	8.45	0.00	-8.45
Continuous Sorghum	-22896	14455	8441	-22340	21553	787	-23627	21887	1741
Continuous Sorghum	-42.91	27.09	15.82	-41.86	40.39	1.47	-44.28	41.01	3.26
Continuous Souhean	-21179	15560	5619	-27775	22371	5404	-23447	21657	1790
Continuous Soybean	-39.69	29.16	10.53	-52.05	41.92	10.13	-43.94	40.58	3.35
Corn Sov	-19561	15479	4082	-26973	23153	3820	-22577	21765	812
Colli Soy	-36.66	29.01	7.65	-50.55	43.39	7.16	-42.31	40.79	1.52
Corn Sov Rye	-15036	15780	-744	-22675	21616	1059	-9455	13014	-3559
Com Soy Rye	-28.18	29.57	-1.39	-42.49	40.51	1.98	-17.72	24.39	-6.67
Corn stover Sov	-19108	15571	3537	-28523	20169	8354	-23593	22120	1473
Com stover boy	-35.81	29.18	6.63	-53.45	37.80	15.65	-44.21	41.45	2.76
Sorghum Soy	-22257	14566	7691	-24734	23007	1727	-21842	21177	665
Sorghum Soy	22.21	-12.44	-9.78	-35.94	35.88	0.05	25.38	-16.93	-8.45
Miscanthus	11854	-6636	-5218	-19177	19149	28	13543	-9032	-4511
wiiseantiius	20.86	-11.08	-9.78	-7.50	15.16	-7.66	29.19	-20.74	-8.45
Native Grass	11133	-5915	-5218	-4001	8089	-4088	15579	-11068	-4511
Native Glass	-41.71	27.30	14.41	-46.35	43.11	3.24	-40.93	39.68	1.25
Switchorass	-369	5121	-4752	-12866	15590	-2724	7672	-3161	-4511
5 witchgrass	-0.69	9.60	-8.90	-24.11	29.21	-5.10	14.38	-5.92	-8.45

Table 18. Area of priority subbasins change from base (km^2) for Scenario 4 (the values with gray background represent the percent changes from the Base or current landcover scenario).

6.3.3 Suitability of Bioenergy Cropping Rotations on Different Scenarios

A major intent of this paper is to provide decision makers insight as to the changes of pollutant loadings that could be expected from changes to bioenergy crops. In order to accommodate the growing demand for available land to produce bioenergy crops sustainably, the assessment of environmental implications is imperative. As previously mentioned, a total of 4 landuse scenarios were developed in this study, resulting in a broad range of land conversion amounts. The scenarios are as follows: Scenario 1 considers all land currently cultivated for row crops and grains, hays, and seeds (i.e. corn, soybeans, wheat, hay, etc.) for conversion to bioenergy crops, Scenario 2 considers only the "other crops" land (i.e. sugarbeets, potatoes, dry beans, fruit crops, etc.), Scenario 3 considers farmland uses and other land (i.e. fallow cropland, pasture, wasteland, etc.), which in all practical purposes may be deemed as marginal land, and Scenario 4 is the combination of all previous scenarios, and represents the overall most significant landuse change. Table 19 provides a comparison of all rotations based on their contribution to annual average sediment, nitrogen, and phosphorus loads at the study area. By arranging the data in this manner, direct evaluation of the potential environmental impacts for each of the four scenarios is made apparent.

By examining Table 19, there are a number of points that need further discussion. As expected the perennial grass species reduced sediment, nitrogen, and phosphorus loadings in Scenario 1 with the exception of miscanthus, which slightly increased total nitrogen by 4.62 percent. Adding canola to the corn-soybean rotation in Scenario 1 increased all constituents, whereas adding rye has the opposite effect, which is also true of Scenario 4. This is expected as adding rye, a close-grown annual cereal grass, into the rotation postpones the cultivation of corn by a year every 3 years. This provides vegetative cover during vulnerable winter and early spring months with extensive growth occurring during late spring and early summer, a period usually experiencing large amounts of rainfall.

Based on the data from this study, it is not recommended to convert land previously cultivated with "other crops" (Scenario 2) to any bioenergy rotation in areas with preexisting high nitrogen levels. The same argument can be made for converting marginal land (Scenario 3) as all rotations on this landuse increases nitrogen levels and are not suitable replacements for the current landcover here, though miscanthus and native grasses are suitable when nitrogen levels are of less concern. Only land that is currently cultivated for row crops (Scenario 1) experiences any form of nitrogen mitigation, in which continuous rye, sorghum-soybean, native grass, and switchgrass decrease total nitrogen from the base scenario. The removal of corn stover is also not recommended as it increases the levels of total nitrogen and total phosphorus loadings at the watershed outlets when compared to the base scenario and the continuous corn rotation.

The perennial grass rotations (switchgrass, miscanthus, native grasses) are the saviors of bioenergy cropping rotations in general. They reduce sediment up to 86.76 percent except when grown on marginal land, which experiences a 17.87 percent increase of sediment when switchgrass is applied. This is most likely due to this rotation having corn and soybeans during the first two years of each rotation cycle. Love and Nejadhashemi (2010a) observed drastic increases of pollutants during these years when evaluated on a monthly time step. However, during periods the following years of switchgrass as the landcover, a 93 percent reduction in sediment occurred. Therefore, it is

suggested that switchgrass be considered as a suitable bioenergy crop in this case, as long as conservation tillage or no-till management operations be considered for corn and soybeans in this rotation. In general, the perennial grasses and rye decrease phosphorus and the intensive crops such as corn and sorghum increase phosphorus loads.

Sub-scenario	Sediment		Total N	litrogen	Total Phosphorus	
	Load	% Change		% Change		% Change
	(tons)	from Base	Load (kg)	from Base	Load (kg)	from Base
Base	473470	-	20062390	-	1606130	-
Scen1_Continuous Canola	474950	0.31	21992080	9.62	1212830	-24.49
Scen1_Continuous Corn	569040	20.19	21163620	5.49	1370890	-14.65
Scen1_Continuous CornStover	552470	16.69	27515330	37.15	1410920	-12.15
Scen1_Continuous Rye	399790	-15.56	17053860	-15.00	853790	-46.84
Scen1_Continuous Sorghum	662380	39.90	18350560	-8.53	1421670	-11.48
Scen1_Continuous Soybean	616680	30.25	22616070	12.73	1402420	-12.68
Scen1_Corn Soy	590170	24.65	21549760	7.41	1374450	-14.42
Scen1_Corn Soy Canola	597820	26.26	23932710	19.29	1460160	-9.09
Scen1_Corn Soy Rye	458230	-3.22	20540200	2.38	1070030	-33.38
Scen1_CornStover Soy	577190	21.91	23786210	18.56	1393350	-13.25
Scen1_Sorghum Soy	654390	38.21	19910470	-0.76	1345990	-16.20
Scen1_Miscanthus	91110	-80.76	20989570	4.62	802720	-50.02
Scen1_Native Grass	119280	-74.81	15993390	-20.28	677780	-57.80
Scen1_Switchgrass	282200	-40.40	17579150	-12.38	852380	-46.93
Scen2_Continuous CornStover	436020	-7.91	28071700	39.92	1175200	-26.83
Scen2_CornStover Soy	438320	-7.42	27960600	39.37	1174410	-26.88
Scen2_Miscanthus	421080	-11.07	27893180	39.03	1157450	-27.94
Scen2_Native Grass	421400	-11.00	27850050	38.82	1158060	-27.90
Scen2_Switchgrass	426690	-9.88	27851420	38.82	1161520	-27.68
Scen3_Continuous Canola	674100	42.37	40197350	100.36	1580440	-1.60
Scen3_Continuous Corn	723000	52.70	38603750	92.42	1668360	3.87
Scen3_Continuous Rye	629560	32.97	36226820	80.57	1382760	-13.91
Scen3_Corn SoyCanola	741700	56.65	41356770	106.14	1710840	6.52
Scen3_Corn Soy Rye	657240	38.81	38558350	92.19	1493810	-6.99
Scen3_Native Grass	475010	0.33	35592530	77.41	1282170	-20.17

Table 19. Total combined pollutant load of all watersheds.

Table 19 (cont'd)

Scen3 Miscanthus	462470	-2.32	39169110	95.24	1344380	-16.30
Scen3_Switchgrass	558090	17.87	36533490	82.10	1376500	-14.30
Scen4_Continuous Canola	649600	37.20	34461140	71.77	1674150	4.24
Scen4_Continuous Corn	772300	63.11	32483590	61.91	1963300	22.24
Scen4_Continuous CornStover	755900	59.65	44351540	121.07	2038100	26.90
Scen4_Continuous Rye	538090	13.65	25395310	26.58	1010140	-37.11
Scen4_Continuous Sorghum	887700	87.49	27805260	38.59	2047510	27.48
Scen4_Continuous Soybean	824700	74.18	35339620	76.15	2016760	25.57
Scen4_Corn Soy Rye	620860	31.13	31481110	56.92	1406110	-12.45
Scen4_Corn Soy	794200	67.74	33302840	66.00	1956950	21.84
Scen4_CornStover Soy	780300	64.80	37242850	85.64	2002750	24.69
Scen4_Sorghum Soy	872500	84.28	30532740	52.19	1896260	18.06
Scen4_Miscanthus	91850	-80.60	32404910	61.52	913240	-43.14
Scen4_Native Grass	135390	-71.40	23694470	18.10	679540	-57.69
Scen4_Switchgrass	366360	-22.62	26310980	31.15	994880	-38.06

6.3.4 Statistical Significance of Bioenergy Cropping Rotations Changes from Base

A key question is whether the changes in pollution load are statistically different from the current landuse scenario. To accomplish this, t-tests were performed to determine the statistical significance levels. A p-value of 0.05 or less rejects the hypothesis, in which there are no significant differences in pollution generation between the bioenergy crop rotation and the current landuse scenario (Base Scenario). The results from the t-tests are provided in Table 20. A cell highlighted in green denotes a significant decrease in pollutant load from the base scenario, where a red cell denotes an increase in pollutant load. Based on the analysis, it is apparent that in general perennial grass species significantly reduce sediment. The exception to this is when these crops are cultivated on marginal lands (Scenario 3). As discussed previously, only bioenergy crops grown on land typically devoted to cultivating row crops (Scenario 1) experiences any significant decrease in total nitrogen load. It is recommended that bioenergy crops be placed sparingly in areas that have preexisting high levels of nitrogen load to streams. With the exception of traditional, intensive row crops cultivated on marginal land (Scenario 3) and all agricultural land (Scenario 4), the majority of bioenergy crops significantly reduce total phosphorus loads.

Sub-scenario	p-value for given constituent ^[a]					
	Sediment (tons)	Total N (kg)	Total P (kg)			
Scen1 Continuous Canola	0.96590	0.00156	0.00009_			
Scen1 Continuous Corn	0.00000	0.02167	0.00000			
Scen1 Continuous CornStover	0.00000	0.00000	0.00000			
Scen1 Continuous Rye	0.09421	0.00029	0.00000			
Scen1 Continuous Sorghum	0.00000	0.00318	0.00001			
Scen1 Continuous Soybean	0.00000	0.00011	0.00000			
Scen1 Corn Soy	0.00000	0.00286	0.00000			

Table 20. Significant difference (p-value) between bioenergy rotation and base scenario. Sub-scenario [a]

Table 20 (cont'd)

Scen1	Corn Soy Canola	0.00000	0.00000	0.00033
Scen1	Corn Soy Rye	0.66593	0.32899	0.00000
Scen1	CornStover Soy	0.00000	0.00000	0.00000
Scen1	Sorghum Soy	0.00000	0.00659	0.00000
Scen1	Miscanthus	0.00000	0.00000	0.00000
Scen1	Native Grass	0.00000	0.73903	0.00000
Scen1	Switchgrass	0.00024	0.00187	0.00000
Scen2	Continuous CornStover	0.00000	0.00000	0.00000
Scen2	CornStover Soy	0.00000	0.00000	0.00000
Scen2	Miscanthus	0.00000	0.00000	0.00000
Scen2	Native Grass	0.00000	0.00000	0.00000
Scen2	Switchgrass	0.00000	0.00000	0.00000
Scen3	Continuous Canola	0.00000	0.00000	0.65024
Scen3	Continuous Corn	0.00000	0.00000	0.05087
Scen3	Continuous Rye	0.00004	0.00000	0.00115
Scen3	Corn SoyCanola	0.00000	0.00000	0.01173
Scen3	Corn Soy Rye	0.00000	0.00000	0.04407
Scen3	Native Grass	0.80892	0.00000	0.00001
Scen3	Miscanthus	0.12460	0.00000	0.00001
Scen3	Switchgrass	0.00163	0.00000	0.00112
Scen4	Continuous Canola	0.00228	0.00000	0.60469
Scen4	Continuous Corn	0.00000	0.00000	0.00000
Scen4	Continuous CornStover	0.00000	0.00000	0.00000
Scen4	Continuous Rye	0.26324	0.00303	0.00007
Scen4	Continuous Sorghum	0.00000	0.00003	0.00000
Scen4	Continuous Soybean	0.00000	0.00000	0.00000
Scen4	Corn Soy Rye	0.00828	0.00000	0.08777
Scen4	Corn Soy	0.00000	0.00000	0.00000
Scen4	CornStover Soy	0.00000	0.00000	0.00000
Scen4	Sorghum Soy	0.00000	0.00000	0.00000
Scen4	Miscanthus	0.00000	0.02608	0.00000
Scen4	Native Grass	0.00000	0.00000	0.00000
Scen4	Switchgrass	0.07133	0.00171	0.00008

[a] P-values less than 0.05 indicate significant difference in change from base

[b] Cells highlighted in Green denote a significant decrease in pollutant load over base [c] Cells highlighted in Red denote a significant increase in pollutant load over base

6.4 CONCLUSION

Instability of the global energy sector has led to recent increases in the demand for alternatives to fossil fuels to meet the energy and transportation needs of the nation. In addition, domestic renewable energy sources have the potential to reduce dependence on foreign resources, mitigate climate change, diversify domestic energy sources, and allow for economic growth and rural development (Scheffran and BenDor, 2009). Biomass is expected to play a key role in developing alternative fuel sources, but only accounts for 7 percent of total global energy supplies (de Fraiture *et al.*, 2008). Therefore, a global shift in biomass production is expected to occur. The challenges we face in transitioning to a system that is both economical feasible and low-impact on the environment are ubiquitous. In order to evaluate the environmental consequences of such expansion of bioenergy crops, specifically on water quality, a large-scale assessment using models is imperative.

The Soil and Water Assessment Tool (SWAT) was used in this study to model the effects of bioenergy cropping expansion on water quality based on four landuse scenarios and 15 bioenergy crop rotations for four large watersheds, totaling 244 model runs. The output data that was evaluated in this study was sediment, total nitrogen, and total phosphorus for a 19 year (1990-2008) period on an annual basis. The watersheds included in this study are intensively cultivated for agricultural production and all flow into the Great Lakes.

The results obtained from this study were arranged in three sections and can be summarized in the following:

- 6.3.1 Basin-wide Impact of Bioenergy Cropping Rotations: Traditional, intensive crops such as corn, sorghum, canola and soybean experience increases in sediment and nitrogen load, yet in certain cases have the potential to reduce phosphorus loads. Miscanthus and switchgrass have the least sediment load variability (141 and 142 percent range, respectively), whereas continuous sorghum has the highest variability (321 percent range) as well as the highest maximum change from the base scenario (312.3 percent). In general, sorghum is not a viable option for cultivation in regions with concerns of sedimentation and phosphorus loadings, yet has nearly zero median impact on nitrogen loads. In addition, the perennial grass species (miscanthus, native grasses, and switchgrass) extensively mitigate phosphorus, yet have the potential to increase nitrogen slightly.
- 6.3.2 Basin-level Priority Areas for Targeting Conservation Efforts: It is evident that converting all agricultural land (Scenario 4) to a continuous corn rotation will result in a considerable increase of medium and high priority areas by 44.74, 45.67, and 42.13 percent for sediment, total nitrogen, and total phosphorus load, respectively. Also with switchgrass, a substantial amount of stream reaches (34 percent) change to medium or high priorities for total nitrogen concentration. The agriculturally intensive row crops had the highest increases of high priority streams for sediment, nitrogen, and phosphorus of 39.15 percent (continuous sorghum), 67.93 percent (continuous corn stover), and 25.48 percent (continuous

corn stover), respectively. As was observed in the priority streamss, the agriculturally intensive row crops had the highest increases of high priority areas for sediment, nitrogen, and phosphorus of 15.82 percent (continuous sorghum), 26.0 percent (continuous corn stover), and 3.35 percent (continuous soybean), respectively. Miscanthus reduced high priority areas for total nitrogen and total phosphorus by 7.66 and 8.45 percent, respectively. In general, the perennial grasses, although mixed benefits are present, are more suitable for implementation than intensive annual bioenergy crops.

6.3.3 Suitability of Bioenergy Cropping Rotations on Different Scenarios: As expected the perennial grass species reduced sediment, nitrogen, and phosphorus loadings when applied on row-crop land (Scenario 1) with the exception of miscanthus, which slightly increased total nitrogen by 4.62 percent. Adding canola to the corn-soybean rotation in Scenario 1 increased all constituents, whereas adding rye has the opposite effect, which is also true of Scenario 4. Based on the data from this study, it is not recommended to convert land previously cultivated with "other crops" (Scenario 2) to any bioenergy rotation in areas with preexisting high nitrogen levels. The same argument can be made for converting marginal land (Scenario 3) in which all rotations increased nitrogen levels and are not suitable replacements for the current landcover here, though miscanthus and native grasses are suitable when nitrogen levels are of less concern. Only land that is currently cultivated for row crops (Scenario 1) experiences any form of nitrogen load reduction, in which continuous rye, sorghum-soybean, native grass, and switchgrass decrease total nitrogen from the

base scenario. The removal of corn stover is also not recommended as it increases the levels of total nitrogen and total phosphorus loadings at the watershed outlets when compared to the base scenario and the continuous corn rotation. The perennial grass rotations reduce sediment up to 86.76 percent except when grown on marginal land, which experiences a 17.87 percent increase of sediment when switchgrass is applied.

 6.3.4 Statistical Significance of Bioenergy Cropping Rotations Changes from Base: Based on a series of t-test analyses, it is apparent that in general perennial grass species significantly reduce sediment. The exception to this is when these crops are cultivated on marginal lands (Scenario 3). As discussed previously, only bioenergy crops grown on land typically devoted to cultivating row crops (Scenario 1) experiences any significant decrease in total nitrogen load. With the exception of traditional, intensive row crops cultivated on marginal land (Scenario 3) and all agricultural land (Scenario 4), the majority of bioenergy crops significantly reduce total phosphorus loads.

Based on the results aforementioned, it is evident that the suitability of bioenergy crops for large-scale implementation is dependent upon the application in question, specifically the landuse it is intended to replace. Additionally, rotations that are deemed unsuitable for cultivation may be tailored to meet the requirements of a specific landuse. For example, corn that is included in the switchgrass rotation may have to include conservation practices such as conservation tillage or no-till and reduced fertilizer application rates in order to reduce sedimentation and nutrient transport to surface waters. In order to expand our understanding of large-scale bioenergy crop expansion, it is suggested that additional studies in different climatological and physiographic regions are performed to validate the findings discussed in this paper.

Acknowledgements

The authors would like to acknowledge Mr. Sean Woznicki and Dr. Fred Bakker-Arkema for their added project support, and Dr. Kurt Thelen, Dr. Wesley Everman, Mr. Dennis Pennington, Dr. Scott Swinton, and Ms. Laura James for their generous contribution of information.

7. EFFECTS ON AQUATIC AND HUMAN HEALTH DUE TO LARGE SCALE BIOENERGY CROP EXPANSION

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Abstract. The environmental consequences of a shifting agricultural production system are not well known, especially in regards to aquatic ecosystem and human health. In this study, the environmental impacts of large scale bioenergy crops were evaluated using the Soil and Water Assessment Tool (SWAT). Daily pesticide concentration data for a study area consisting of four large watersheds located in Michigan (totaling 53,358 km²) was estimated over seven year period (2000-2006). Atrazine, bromoxynil, glyphosate, metolachlor, pendimethalin, sethoxydim, triflualin, and 2,4-D model output was used to predict the possible long-term implications that large-scale bioenergy crop expansion may have on the bluegill (Lepomis macrochirus) and humans. Threshold toxicity levels were obtained for the bluegill and for human consumption for all pesticides being evaluated through an extensive literature review. Model output was compared to each toxicity level for the suggested exposure time (96-hr for bluegill and 24-hr for humans). The results suggest that traditional intensive row crops such as canola, corn and sorghum

drinking water. The continuous corn rotation, the most representative rotation for current

may negatively impact aquatic life, and in most cases do affect the availability of safe

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agricultural practices for a starch-based ethanol economy, delivers the highest concentrations of glyphosate to streams. In addition, continuous canola contributed to a 96-hr concentration of 1.11 ppm of trifluralin, a highly toxic herbicide, which is 8.7 times the ecotoxicity of bluegills and 21 times the safe drinking water level. Continuous corn also resulted in the impairment of over 541,152 kilometers of stream. However, there is promise with second-generation lignocellulosic bioenergy crops such as switchgrass, which resulted in a 171,667 kilometers reduction in total stream length that exceeds the human threshold criteria, as compared to the base scenario. Results of this study may be very useful in determining the suitability of bioenergy crop rotations and aid in decision making regarding the adaption of large-scale bioenergy cropping systems.

7.1 INTRODUCTION

Biofuels are energy sources, mainly liquid petroleum replacement fuels such as ethanol and biodiesel, that are derived from the conversion of biological resources (Hoogeveen *et al.*, 2009). In 2008, biomass provided 53 percent of the nation's renewable energy (USEIA, 2009) while production of ethanol derived from biological sources tripled between 2000 and 2007 (Hoogeveen *et al.*, 2009).

It is expected that global energy consumption will increase by 57 percent in the next 25 years (Rooney *et al.*, 2007). Meanwhile, rising oil prices and increased political pressure to develop carbon-neutral fuels have led to an increase in demand for alternative energy sources. As for the United States, reducing dependency on foreign petroleum imports may provide many benefits such as lower consumer costs, climate change mitigation, job creation, and diversification of domestic energy sources. As a possible

scapegoat for the global petroleum feeding frenzy, the popularity of biofuels has increased as they may provide the means for a shift away from conventional petroleum sources (Solomon, 2010). There is, however, evidence of negative consequences are prevalent, as for example, greenhouse gas emissions from landuse change towards cornbased ethanol are estimated to nearly double (Searchinger *et al.*, 2008). Therefore, all negative and positive aspects of large-scale bioenergy crop production are important to consider in order for this approach to be a sustainable and cost-effective replacement of current production methods (Nyakatawa *et al.*, 2006).

Agriculture is the largest contributor to excess nutrients, mainly nitrogen and phosphorus, in freshwater in the United States (Foley et al., 2005). In addition, The demand for higher yields and more acreage in production will consequently increase pressure to apply more pesticide likely resulting in more frequent occurrences of pollution of these types in waterbodies (Landis et al., 2008). For example, the current biofuel crop of choice, corn, is agrichemicals input-intensive, requiring more nitrogen fertilizer, insecticide, and herbicide than any other crop in the U.S. (Pimentel, 2005). Many of the other first-generation biofuel feedstocks follow suit requiring large amounts of inputs in order to produce a viable crop. Oftentimes, this results in increased nutrient and chemical loadings in water, leading to negative effects on human safety and aquatic ecosystems such as death of coral reefs, fish kills, reductions in harvestable fish, and reduced aesthetic value of the water body (Carpenter et al., 1998). Therefore, surface waters are at a considerable risk of impairment due to the amount of pesticides that may be present in surface runoff and infiltration to groundwater resources (Hoogeveen et al., 2009). However, second generation bioenergy crops, including switchgrass, miscanthus,

and native grasses, require less intensive practices and less commercial fertilizers and pesticides (Oliver *et al.*, 2009).

Pesticides are applied to agricultural fields in the effort to control and eliminate pests (Pimentel, 2005), often minimizing crop loss and leading to more efficient production (Helfrich *et al.* 2009). There are three main types of pesticides utilized in agriculture, including herbicides, used to control noxious and invasive vegetation; insecticides, used to protect crops against insects; and fungicides, used for protecting crops from diseases (Helfrich *et al.* 2009). Of the three types, herbicides are the most commonly used (Gilliom, 2007; Helfrich *et al.*, 2009) and account for 70 percent of national used pesticides (USGS, 1999). Some commonly applied and detected herbicides include atrazine, metolachlor, alachlor, cyanazine, simazine, and 2,4-D (Gilliom, 2007; USGS, 1999).

Pesticides are most frequently detected within streams in areas of agriculture, as seen in a ten year U.S. Geological Survey's National Water-Quality Assessment program (USGS NAWQA) study who observed that 97 percent of streams samples and 61 percent of shallow groundwater samples taken at agricultural sites had detections of one or more pesticides (Gilliom 2007). However, it is difficult to measure their occurrence since they are often in mixtures with several other compounds (USGS, 1999; Belden *et al.*, 2007; Gilliom, 2007). While, contamination from pesticides is more of a threat to streams and other surface water, groundwater contamination can be more difficult to reverse and can take longer in recovering (USGS, 1999).

Transport of pesticides can occur through numerous modes including, overland runoff, lateral movement, soil erosion, leaching, groundwater, tile drainage, and drift

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during application (Pimentel, 2005; USGS, 1999; Solomon *et al.*, 2008). Meanwhile, there are several factors that have been shown to determine and influence this transportation. Precipitation, storm water runoff, soil drainage, slope, irrigation practices, groundwater connections, and application timing are some of these influences (Domagalski *et al.*, 2008; USGS, 1999; MSU Weeds, 2010). The pesticide itself can also effect transportation through characteristics such as its solubility, stability, and ability to be broken down by climatic conditions and microorganisms within soils (USGS, 1999; Helfrich *et al.*, 2009). Once pesticides reach a channel they can travel to downstream unpolluted waters (Schulz and Liess, 1999) and continue to persist in both the water and bed sediments (Gilliom, 2007), eventually being exposed to biota through respiration, absorption through the skin, or consumption (Helfrich *et al.*, 2009).

The presence of pesticides within a lotic system can have both direct and indirect influences on aquatic biota, leading to lethal and sub-lethal effects (Scott and Sloman, 2004; Fleeger *et al.*, 2003; Cook and Moore, 2008; Relyea, 2009). These effects can be controlled by toxicity and persistence of a pesticide, exposure time, and the quantity that an organism is exposed to (Helfrich *et al.*, 2009). Studies have shown that pesticides can influence and impede on behavioral and physiological characteristics of aquatic organisms (Cook and Moore, 2008; Scott and Sloman, 2004). More specifically, sensory, hormonal, neurological, and metabolic systems can be affected, leading to reductions in reproduction, biomass, and health of individuals and communities (Cook and Moore, 2008; USGS, 1999). With fish in particular, Baldwin *et al.* (2009) observed that threatened salmon species recovery could be constrained due to pesticides, based on reductions in survival and productivity. Goodbred *et al.* (1997) demonstrated that sites

with higher pesticide concentrations showed lower hormone ratios in common carp, which could indicate further potential effects (USGS, 1999). Impacts can even reach to the point of mortality and fish kills have been reported due to pesticides. According to Pimentel *et al.* (1993), between six and fourteen million fish are killed by pesticides each year, which is often an underreported statistic (Pimentel, 2005). Macroinvertebrates also have shown similar direct responses to pesticides, especially insecticides, for which they are very sensitive to (Overmeyer, 2010). Schulz and Liess (1999) observed 11 common macroinvertebrate species disappear and others' populations reduce due to insecticide contamination within a stream. Reductions in relative abundance and number of sensitive species have also been shown to be related to the stress of pesticides (Schafer et al., 2007). Although herbicides are not generally as toxic to aquatic biota as insecticides are, they have still been shown to have similar effects (Helfrich et al., 2009; USGS, 1999). This is especially apparent when it comes to indirect influences. This includes herbicides' tendency to reduce aquatic vegetation, effecting food sources, habitat, and dissolved oxygen conditions for both fish and macroinvertebrates (Pimentel, 2005; Overmeyer, 2010). For example, in a review looking at atrazine and its effects on fish, Solomon et al. (2008) found little consistency on any direct affects from the pesticide, however did recognize a consistency with indirect affects through food supply and habitat loss. Macroinvertebrates have also shown similar indirect relationships with herbicides as well (Overmeyer, 2010). By considering the negative impacts that pesticides can have on aquatic ecosystems, the U.S. Environmental Protection Agency (USEPA, 2008) performed ecological risk assessments to investigate the threats involved with the use of specific pesticides based on scientific measurements and judgment.

Along with aquatic health, human health can also be jeopardized by exceedingly high levels of pesticides within water resources. Several studies have shown that exposure to pesticides can contribute or lead to cancer and other harmful human illnesses (Safe, 2004; Fan *et al.*, 2007). While some pesticides may be carcinogenic, others may affect humans in other ways including risks to the nervous system and hormones, along with less severe risks including skin irritations (Omalley, 1997). These risks are often only seen at high levels of exposure, yet some pesticides have been banned from use due to their extreme toxicity, including DDT (1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane) within the United States and atrazine (2-chloro-4-ethylamine-6-isopropylamino-S-triazine) in Germany (Helfrich *et al.*, 2009; Takacs *et al.*, 2002).

Specific water quality benchmarks or thresholds are also often set to recognize areas where individual pesticides are present at concentrations that can harm aquatic biota or even human health. These benchmarks are commonly presented in LC50 measures that reflect lethal concentrations at which 50 percent of tested animals are killed in a given period of time (USEPA, 2009d; Gilliom, 2007; Helfrich *et al.*, 2009). It is important to note that the LC50 is an extreme case of lethality and does not consider any other biotic factor such as nutrient loading, dissolved oxygen, and turbidity. It is possible that there may be impairments to aquatic health well in advance of reaching these LC50 toxicity levels.

7.1.2 Modeling Pesticide Fate and Transport

Simulation models have been shown to be a valuable tool when looking at pesticide fate and transport and can be useful in executing ecological risk assessments both at a field and watershed scales (Parker *et al.*, 2007; Vazquez-Amabile *et al.*, 2006;

Luo and Zhang, 2009a; Quilbe *et al.*, 2006; Luo and Zhang, 2009a). Several models that were used in the past to study the fate and transport of pesticides including the Hydrological Simulation Program-HSPF (Laroche *et al.*, 1996), Groundwater Loading Effects of Agricultural Management Systems Model-GLEAMS (Vazquez-Amabile *et al.*, 2006; Thomas *et al.*, 2009), Agricultural Policy / Environmental eXtender model-APEX (Harman *et al.*, 2004; Mudgal *et al.*, 2008), Annualized Agricultural Non-Point Source model-AnnAGNPS (Heathman *et al.*, 2008) and Soil and Water Assessment Tool-SWAT (Larose *et al.*, 2007; Luo and Zhang, 2009b; Holvoet *et al.*, 2007). Due to the comprehensive nature and ability to include in-stream processes, SWAT was chosen as the best model for the scope of this project.

SWAT utilizes equations adopted from GLEAMS to simulate pesticide movement on land (Neitsch *et al.*, 2005). The processes involved in the model include plant foliage interaction and wash-off, degradation, leaching, percolation, as well as surface runoff and sediment transport of soluble and sorbed pesticides. SWAT differs from GLEAMS in that it can only model one pesticide at a time; however, its capability to simulate in-stream processes, gives it an advantage (Neitsch *et al.*, 2005; Vazquez-Amabile *et al.*, 2006). SWAT has been evaluated and implemented in multiple studies looking at the fate of pesticides. A Vazquez-Amabile *et al.* (2006) study used SWAT model to estimate atrazine level with varying corn planting season scenarios. The study further applied the results to perform risk analysis by calculating exceedance probabilities and comparing average monthly levels with US Environmental Protection Agency (USEPA) drinking water standards. Some have proposed and implemented some modifications to SWAT code, including enabling the code to account for direct loss of pesticides during application and have observed more accurate simulated results (Holvoet *et al.*, 2008).

Determination of which biofuel crops and management strategies may have the least unfavorable consequences to environments is vital for future decision making (Thomas *et al.*, 2009). In this regard, the use of models including SWAT, have been demonstrated to be valuable in obtaining the information needed to perform risk analysis (Thomas *et al.*, 2009; Vazquez-Amabile *et al.*, 2006), however, based on an extensive literature review the authors are unaware of any study using modeling tools and risk analysis in determining pesticide levels dealing with conversions of lands to biofuel crops in a large-scale. In addition, recent modeling studies have been limited to one to four pesticides at small scales (field to small watershed) (Kannan *et al.*, 2006; Luo *et al.*, 2008; Luo and Zhang, 2009b; Vazquez-Amabile *et al.*, 2006; Larose *et al.*, 2007; Neitsch *et al.*, 2002).

The study conducted here evaluates the long-term environmental implications, specifically on fish and humans from pesticides, of large-scale bioenergy cropping system expansion. This aids in determining the suitability of bioenergy crops and obtaining information to aid in watershed-scale decision making regarding landuse management. The Soil and Water Assessment Tool (SWAT) was used to predict the effects of 14 future landuse/bioenergy crop rotations scenarios in four large watersheds in agricultural regions of Michigan over six years (2000 to 2005). The model was calibrated and validated for flow, sediment, and nutrients and the model outputs on seven pesticides loads and concentrations were estimated on a daily time step.

7.1.3 Pesticides

Based on information obtained from the Michigan State University Extension (MSUE), pesticide application rates for different bioenergy crops were estimated and later used for modeling purposes. In addition, both human consumption and aquatic ecotoxicity thresholds were obtained from literatures. The pesticides included in analysis are presented in the subsequent sections.

7.1.3.1 Atrazine

One of the most commonly and widely applied agricultural herbicides, particularly in corn production, is Atrazine [2-chloro-4-ethylamine-6-isopropylamino-Striazine] (Ribaudo and Bouzaher, 1994; EXTOXNET, 1996). With corn and other crops being able to metabolize and detoxify atrazine (Ribaudo and Bouzaher, 1994), it selectively targets and controls broadleaf weeds by inhibiting photosynthesis (MSU Weeds, 2010). Atrazine is a Chloro-triazine herbicide, whose transport, based on its chemical properties, is often through leaching and runoff. A secondary means of transport can also be through its absorption to sediments. Atrazine can persist in environments with a half-life of 60 to 150 days in soils and exceptionally longer in anaerobic conditions along with in surface and ground water. Because atrazine and its degradates can be moderately toxic at high concentrations and for long periods of time to both aquatic animals and humans, the USEPA has established maximum concentration levels (Ribaudo and Bouzaher, 1994; Vazquez-Amabile et al., 2006). Standards for drinking water for humans have been established at 0.003 mg/L (USEPA, 2010d; Vazquez-Amabile et al., 2006).

7.1.3.2 Bromoxynil

Bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) is a widely used postemergence, contact herbicide selective to broad-leaved weeds (Topp *et al.*, 1992). Bromoxynil enters the environment through many pathways such as to the atmosphere by plant evapo-transpiration and volatilization from soil surface, incorporation with surface runoff, especially during precipitation events immediately following application, and released into soil by treated vegetation (Baxter and Cummings, 2008). Bromoxynil has a low persistence in soil with a half-life of several days, with microbial activity being the primary degradation mechanism (Topp *et al.*, 1992; Baxter and Cummings, 2008). It is also suspected that bromoxynil has teratogenic effects on mammals, inhibiting or altering the reproductive and developmental capabilities (EXTOXNET, 1996).

7.1.3.3 Glyphosate

Glyphosate [N-(phosphonomethyl) glycine] is a nonselective, post emergence herbicide that is one of the most widely used (USEPA, 1993; Duke and Powles, 2008; USDA, 1997). It is taken up by plants rapidly through leaves and then prevents the plant from making amino acids, which restricts the making of protein and eventually leads to death. Glyphosate and surfactants associated with the pesticide are strongly absorbed in soils and degraded by microorganisms leading to a soil half-life, depending on conditions, that can range from 3 to 249 days. This strong absorption also limits its ability to be transported by runoff and its movement into groundwater (USDA, 1997; Duke and Powles, 2008). Glyphosate, once in water, is easily dissolved and has a half-life of 35 to 63 days (USDA, 1997). Although Glyphosate can be toxic to aquatic non-targeted vegetation, which can indirectly can affect biota, it is relatively non-toxic to fish and invertebrates (USEPA, 1993; Duke and Powles, 2008; USDA, 1997; EXTOXNET, 1996). Drinking water standards for Glyphosate have been established by the USEPA at 0.7 mg/L (USEPA, 2010d).

7.1.3.4 Metolachlor

Metolachlor [2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidide] is an herbicide used on corn, soybeans, sorghum and other crop lands in effort to have preemergent control of grasses and broadleaf weeds. Metolachlor, a chloroacetanilide herbicide, controls these unwanted species through the inhibition of protein synthesis. It has a soil half-life of 15 to 70 days and an even higher persistence in water, leading it to be detected, along with its degradates, in groundwater and surface waters. Metolachlor, although not much of a threat in bioaccumulation, is moderately toxic to aquatic biota (CDC, 2010; EXTOXNET, 1996).

7.1.3.5 Pendimethylin

Another selective herbicide is Pendamethlin [N-(1-ethylpropyl)-3,4-dimethyl-2,6dinitrobenzenamine], which is used in controlling both broadleaf weeds and grassy weed species. This dinitroanililine herbicide can be used in both pre-emergence and early postemergence scenarios, when managing crop productions such as corn, soybeans, winterwheat, and several others (Triantafyllidis *et al.*, 2009; USEPA, 1997; EXTOXNET, 1996). Pendimethalin restricts seedling growth by inhibiting cell division and elongation (Triantafyllidis *et al.*, 2009). It's moderately persistent in the environment with a field half-life of 40 days. Due to being highly absorbed by soils and insoluble in water, Pendimethalin has limited risk to groundwater and the transport to surface waters is mainly through soil erosion (EXTOXNET, 1996; Triantafyllidis *et al.*, 2009). Pendimethalin has a low acute toxicity, yet is highly toxic to aquatic species, including fish, and is a possible carcinogen in humans (Megadi *et al.*, 2010).
7.1.3.6 Sethoxydim

Sethoxydim (2-[1-(ethoxyiamino)]butyl-5-[2-ethyl-thio propyl]-3-hydroxy-2cyclohexen-1-one) is a postemergence herbicide selective against annual and perennial grass species in broadleaf crops (Holshouser and Coble, 1990). It acts as an inhibitor of the plastidic enzyme acetylcoenzyme A carboxylase (Tardif *et al.*, 1993). Sethoxydim has low persistence with reported half-lives of 5 to 25 days in soil, in which photodegradation on soil takes only several hours (Wauchope *et al.*, 1992). Sethoxydim has been observed to be slightly toxic to aquatic species and less toxic to humans, with unlikely chronic effects (Tu *et al.*, 2001).

7.1.3.7 Trifluralin

Like Pendamethlin, Trifluralin [a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-ptoluidine] is a dinitroaniline herbicide and is applied pre-emergence for inhibiting growth of grasses and broadleaf weeds in agricultural areas (Grover *et al.*, 1997; EXTOXNET, 1996; USEPA, 1996). Trifluralin is highly absorbed by soil and low solubility in water, leading it to become immobile often and less of a threat to groundwater. The persistence of Trifluralin is dependent on several soil conditions and its half-life can range from 45 days to 8 months. It can be degraded through several processes including microbial activity, volatilization, and photolysis (Grover *et al.*, 1997; EXTOXNET, 1996). Trifluralin is highly toxic to fish, macroinvertebrates, and aquatic vegetation (EXTOXNET, 1996).

7.1.3.8 2,4-D

In continuing efforts to control broadleaf weeds, 2,4-D [(2,4-dichlorophenoxy) acetic acid] is a phenoxyacetic herbicide that is used post emergence and widely applied throughout many land uses, agricultural lands being the dominant application setting

(USEPA 2008). 2,4-D can be in several forms, including salts, acids, amines, or esters (Munro *et al.*, 1992; EXTOXNET, 1996). Controlling weed growth is achieved through the absorption of 2,4-D by roots and leaves, ultimately affecting metabolism, growth patterns, and food transport (Munro *et al.*, 1992). 2,4-D, although lacking persistence in soils and aerobic aquatic systems with a half-life of 6.2 days and 15 days respectively, has been shown to be moderately persistent in anaerobic aquatic conditions with a half-life of up 333 days (USEPA, 2008). 2,4-D has been shown to be detected in both groundwater and surface waters despite its shorter half-life (EXTOXNET, 1996). Its toxicity varies with form, esters being highly toxic to aquatic biota while amines and acids are far less toxic. 2,4-D is also toxic to aquatic vascular plants, which can further their risk to biota. In addition, human health risks are a potential and standards of 0.07 mg/L have been set by the USEPA (USEPA, 2010b).

7.1.3.9 Aquatic and Human Toxicity Thresholds

Threshold levels were used for both humans and fish, in attempt to evaluate the potential harmful impacts of pesticide concentrations within streams. Measures often used to describe levels of concern for humans, are based on USEPA set maximum concentration levels (MCL) for drinking water. MCLs are defined as the "maximum permissible level of a contaminant in water which is delivered to any user of a public water system" (USEPA, 2010a). In the absence of a MCL for specific pesticides, a maximum permissible level goal (MCLG) was calculated based on the reference dose (RfD), which is the amount a human can be exposed to on a daily basis with no harmful effects. The RfD is multiplied by an assumed weight of an adult (70 kg) and then divided by the average amount of daily water consumption (2 Liters). This is then multiplied by a

drinking water contribution which is commonly assumed as 20 percent (Lin and Lee, 2007). This technique has been documented and is used by the USEPA and many other governments (USEPA, 2010a; Massachusetts Department of Environmental Protection, 2010).

For fish a standard measurement commonly used, when dealing with pesticides, is the 96 hour LC50. LC50s are concentrations for a set period of time that are lethal to 50 percent of a test population (Helfrich, 2009). Due to the inherent complexity of pesticide fate in the environment and maintaining overall impact of these agrochemicals applications of aquatic ecosystems, an umbrella specie should be selected. In this study, the Bluegill (Lepomis macrochirus), was selected as a biological indicator acting as representation of aquatic health and habitat needs of other aquatic life (Fargione *et al.*, 2009). In addition, Bluegill is a native fish and historically widely distributed throughout the study area. In the next step, the median LC50 levels for Bluegill and different herbicides were obtained from thousands of studies available on the USEPA's ECOTOX database (USEPA, 2010b). The previously discussed threshold values used in this study are provided in Table 21.

	2,4 - D	Atrazine	Bromoxynil	Glyphosate	Metolachlor	Pendimethalin	Sethoxydim	Trifluralin
Bluegill, 96 hour LC50	263000	24000	13500	5600	10000	980	133300	127.5
Human, MCL	70	3	140*	700	700*	280*	630*	52.5*
* MCLG – based off of	RfD							

Table 21. Bluegill and human toxicity thresholds.

The use of models, including SWAT, have been demonstrated to be valuable in obtaining the information needed to perform risk analysis (Thomas *et al.*, 2009; Vazquez-Amabile *et al.*, 2006). However, based on an extensive literature review the authors are unaware of any studies using SWAT and risk analysis in determining pesticide levels dealing with conversions of lands to biofuel crops. In addition, SWAT simulations within recent studies have been limited to one to four pesticides at small scale (1.42 km² to 14983 km²) (Kannan *et al.*, 2006; Luo *et al.*, 2008; Luo and Zhang, 2009b; Vazquez-Amabile *et al.*, 2006; Larose *et al.*, 2007; Holvoet *et al.*, 2007; Neitsch *et al.*, 2002).

The research in this paper evaluates the long-term environmental implications, specifically on fish and humans from pesticides, of large-scale bioenergy cropping system expansion. This aids in determining the suitability of bioenergy crops and obtaining information to aid in watershed-scale decision making regarding landuse management. SWAT was used to predict the effects of 14 future landuse/bioenergy crop rotations scenarios in four large watersheds in agricultural regions of Michigan over six year (2000 to 2005) period. The model was calibrated and validated for flow, sediment, and nutrients and the model outputs on pesticides loads and concentrations were evaluated on a daily time step.

7.2 MATERIALS AND METHODS

7.2.1 Study Area

The study area consists of four large watersheds totaling $53,358 \text{ km}^2$ located in Michigan's Lower Peninsula used intensively for agricultural production. Meanwhile, these watersheds, described below, directly discharge to the Great Lakes (Figure 23):

- The Saginaw River basin (hydrologic unit code (HUC) 040802) is located in the east central portion of Michigan's Lower Peninsula and includes six HUC 8-digit watersheds (Tittabawassee, Pine, Shiawassee, Flint, Cass, and Saginaw River). The region drains 1,526,242 ha with 40 percent used for agricultural production, 6 percent developed, 42.4 percent forest, and 12 percent wetlands.
- The St. Clair-Detroit basin (HUC 040900) is located in southeast Michigan and includes four HUC 8-digit watersheds (St. Clair, Clinton, Detroit, and Huron River). The region drains 818,303 ha with 30.3 percent used for agricultural production, 39.4 percent developed, 28 percent forest, and 2.3 percent wetlands.
- The Southeastern Lake Michigan basin (HUC 040500) is located in southwest Michigan and includes five HUC 8-digit watersheds (Kalamazoo, Upper Grand, Maple, Lower Grand, and Thornapple River). The region drains 1,889,426 ha with 53.3 percent used for agricultural production, 10.6 percent developed, 28.8 percent forest, and 7.3 percent wetlands.
- The St. Joseph basin (HUC 04050001) is located in the southwest portion of Michigan and the northeast portion of Indiana. The region drains 1,101,781 ha with 70.9 percent used for agricultural production, 6.3 percent developed, 16.4 percent forest, and 6.4 percent wetlands.



Figure 23. Basins included in study area.

7.2.2 SWAT Model

In order to effectively model the dynamic relationships of pesticides at a watershed scale, a reliable hydrodynamic model must be used (Holvoet *et al.*, 2004). SWAT is a hydrodynamic and physically based model developed to predict the impacts of land use scenarios on flow and nutrient, pesticide, and sediment loadings on a watershed scale. The model can be setup based on landuse practices in complex watersheds with varying soils, landuse, weather conditions, and management operations over long time periods (Arnold *et al.*, 1998). ArcSWAT, the ArcGIS extension of the SWAT 2005 program, is a graphical user interface for the SWAT model used in this

study. The major inputs to the model include weather datasets, soils data, elevation map, landuse data, nutrient and pesticide applications, and management practices. The SWAT model uses the modified SCS curve number method to determine surface runoff during precipitation events (Neitsch *et al.*, 2005). Soil erosion and sediment yields are determined by the Modified Universal Soil Loss Equation (MUSLE). The accuracy of this model depends on complete understanding of the regional processes and of internal model processes. Therefore, setting up the model requires considerable time commitment for both data collection and model familiarization (Gassman *et al.*, 2007).

7.2.2.1 Pesticides in SWAT

The fate and transport of pesticides in the SWAT model include, plant foliage interaction and wash-off, degradation, leaching, percolation, as well as surface runoff and sediment transport of soluble and sorbed pesticides.

During a precipitation event, a portion of the pesticide applied onto the foliage may be washed off. The solubility of the applied chemical, the timing of application and precipitation, rainfall intensity, and plant morphology determine the fraction that is lost (Eq. 7).

$$pst_{f,wsh} = fr_{wsh} * pst_f \tag{7}$$

where, $pst_{f,wsh}$ is the amount of pesticide washed from foliage to the soil surface (kg pesticide/ha), fr_{wsh} is the pesticide wash-off fraction, and pst_f is the amount of pesticide on the foliage (kg pesticide/ha).

Pesticides also experience degradation, in which chemical conversion of compounds into simpler forms occurs. The time it takes for a compound concentration to

be reduced by half is termed the *half-life*. The half-life in soil layers (Eq. 8) is a combination of effects caused by volatilization, photolysis, hydrolysis, biodegradation, and chemical reactions.

$$t_{1/2,s} = \frac{0.693}{k_{p,soil}} \tag{8}$$

where, $t_{1/2,s}$ is the half-life of the pesticide in the soil (days) and $k_{p,soil}$ is the soil degradation rate constant (1/day). The corresponding foliar half-life is presented below in Eq. 9:

$$t_{1/2,f} = \frac{0.693}{k_{p,foliar}}$$
(9)

where, $t_{1/2,foliar}$ is the half-life of the pesticide on foliage (days) and $k_{p,foliar}$ is the foliar degradation rate constant (1/day). In SWAT, pesticides that are highly soluble in water have the potential to be transported with percolation throughout the shallow soil layers. Pesticides in the soil are transported as a dissolved solution or attached to sediment particles.

7.2.2.2 Movement of soluble pesticide

Pesticide that is soluble in water is highly mobile in surface runoff, lateral flow, and percolation through shallow surface layers. The amount of pesticide in each type of movement is calculated by a number of equations representing the physical and chemical processes that control the flow or surface and soil layer water, the properties of the soil and pesticide, and the pesticide percolation coefficient.

7.2.2.3 Transport of sorbed pesticide

Sediment that is delivered to the main stream channel due to surface runoff may also be transporting pesticides attached to soil particles. The amount of sorbed pesticides depends on the sediment load delivered from the agricultural fields. Since the sediment load in overland flow delivered to the stream is enriched by colloidal clay particles, the sediment load contains a larger proportion of pesticides than that of the soil layer itself. This relationship is defined by the enrichment ratio, or the ratio of pesticide transported with the sediment to the concentration on the soil surface, developed by Menzel (1980).

7.2.2.4 Pesticide routing

It is important to note that SWAT incorporates routing and reservoir and instream pesticide transformations, leading to a fundamentally superior model (Vazquez-Amabile *et al.*, 2006). A limitation to the capabilities of pesticide routing, though, is that the model can only route a single pesticide through the stream network at a time. The model uses a mass balance approach to determine the pesticide in a stream segment by determining any additions from inflow and resuspension and diffusion of pesticide from the sediment layer. Since SWAT can essentially model only one pesticide during each simulation, 168 model runs were performed to study the impacts of eight herbicides including atrazine, metolachlor, glyphosate, 2,4-D, pendimethylin, trifluralin, bromoxynil, and sethoxydim on water quality and aquatic and human health.

7.2.2.5 SWAT Model Setup

In order to provide the most realistic and accurate representations of flow and water quality, the SWAT model was calibrated for flow, sediment, and nutrients (total nitrogen and phosphorus) on a monthly time step. Calibration should include data from three to five years during both dry and wet periods to effectively activate all model processes for a diverse range of hydrologic events (Moriasi *et al.*, 2007). Therefore, based on a comparison with the 19-year mean of precipitation for all watersheds, the period of 2000-2005 was used for the calibration and validation. Detailed information about model calibrations and validations were presented in Love and Nejadhashemi (2010). Management operation schedules were incorporated into the SWAT model to provide a more realistic representation of the true agricultural practices in the study area. Bioenergy cropping rotations were developed to provide a depiction of the practices that would be likely associated with these crops in Michigan. A schedule was developed for each rotation based on data collected from the Michigan State University Extension. The schedule for the corn-soybean-rye rotation is provided in Table 22 as an example. Table 23 represents the pesticide application rates that were used in all of the rotations in this study. Each rotation was applied on all agricultural land in the study area, providing the most extreme scenario of landuse conversion representing future bioenergy crop expansion in the region.

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Date	Practice	SWAT Practice	Amount/acre	Amount/ha	Year
1-May	Soil Finish	Field Cultivator Ge15ft			
4-May	Nitrogen Application (Urea)	Urea	173 lb	194 kg	
4-May	Soil Finish	Field Cultivator Ge15ft			
5-May	Phosphorus Application (P_2O_5)	Elemental Phosphorus	53 lb	59.5 kg	
5-May	Plant Corn Seed	Plant/Begin Growing Season			1
5-May	Bicep II Magnum (PRE)	Atrazine	0.5 qt	1.39 kg	
5-May	Bicep II Magnum (PRE)	Metolachlor	0.39 qt	1 kg	
1-Nov	Combine Harvest Corn Grain	Harvest and Kill			
15-Nov	Fall Chisel	Coulter-chisel Plow			
14-May	Soil Finish	Field Cultivator Ge15ft			
14-May	Phosphorus Application (P ₂ O ₅)	Elemental Phosphorus	40 lb	45 kg	
14-May	Soil Finish	Field Cultivator Ge15ft			
15-May	Plant Soybean Seed	Plant/Begin Growing Season			2
7-Jun	Spray Roundup Weathermax ®	Glyphosate Amine	22 fl oz	0.87 kg	
1-Oct	Harvest Soybean Grain	Harvest and Kill			
4-Oct	Soil Finish	Field Cultivator Ge15ft			
7-Oct	Nitrogen Application (Urea)	Urea	25 lb	28 kg	

Table 22 (cont'd)

7-Oct	Phosphorus Application (P_2O_5)	18-46-0	35 lb	39.2kg	
 7-Oct	Plant Rye Seed	Plant/Begin Growing Season			
15-Apr	Nitrogen Application (28% N)	Elemental Nitrogen	25 lb	28 kg	-
25-Apr	Spray Frontline 2,4-D	2,4-D Amine	0.5 lb a.i.	0.56 kg	3
15-Jul	Harvest (0.7 Efficiency)	Harvest and Kill			
30-Oct	Fall Chisel	Coulter-chisel Plow			

Table 23. Pesticide application rates for each rotation.

Rotation				Pesticide Rat	tes (kg ha ⁻¹)			
	Atrazine	Bromoxynil	Glyphosate	Metolachlor	Pendimethalin	Sethoxydim	Trifluralin	2,4-D
Base	1.39	-	0.87	1.00	-	-	-	-
Continuous Canola	-	-	-	-	-	0.315	1.10	0.56
Continuous Corn	1.39	-	0.87	1.00	-	-	-	-
Continuous Corn Stover	1.39	-	0.87	1.00	-	-	-	-
Continuous Rye	-	-	0.87	-	-	-	-	0.56
Continuous Sorghum	1.39	0.42	0.87	1.00	-	-	-	-
Continuous Soy	1.39	-	0.87	1.00	-	-	-	-
Corn Soy	1.39	-	0.87	1.00	-	-	-	0.56

Table 23 (cont'd)

Corn Soy Rye	1.39	-	0.87	1.00	-	-	-	-
Corn stover Soy	1.39	-	0.87	1.00	-	-	-	-
Miscanthus	1.39	0.42	0.87	1.00	-	-	-	-
Native Grass	-	-	-	-	1.12	-	-	0.28
Sorghum Soy	-	-	-	-		-	-	-
Switchgrass	1.39	-	0.87	1.00	1.12	-	-	0.28

7.2.2.6 Pesticide Monitoring Dataset

All pesticide monitoring datasets were obtained from the USEPA STORET (http://www.epa.gov/storet/dbtop.html), and the USGS surface-water data collection (http://water.usgs.gov/osw/data.html) for each watershed. However, the available data was limited to a fraction of both the herbicides and watersheds. Out of the 32 total watershed/herbicide combinations needed for the model calibration, only 12 were found. Furthermore, three of the four watersheds were missing data for six of the eight herbicides. The data at these locations were generally limited to less than a dozen grab samples, making calibration impractical and unreliable. It is important to note that a number of the pesticides are not widely used in Michigan. For example, pendimethalin was included in this study as a possible herbicide to be used in switchgrass and miscanthus, yet is not labeled for their use currently. Therefore, the best alternative is to adjust model parameters using datasets presented in literatures. This is the common practice and others, including Coffey et al. (2010), have used literature values in place to adjust model parameters for calibration when adequate observed data is not available. Based on an extensive literature review, it was determined that the pesticide percolation coefficient (PERCOP) was the most influential parameter in SWAT for pesticide transport (Du et al., 2006; Vazquez-Amabile et al., 2006; Larose et al., 2007; Luo et al., 2008). From Du et al. (2006) and Neitsch et al. (2002), the PERCOP value for atrazine, metolachlor, and trifluralin were obtained to be 0.025, 0.3 and 0.3, respectively. Values for pesticides not included in previous studies were modeled using for the default values included in SWAT (Neitsch et al., 2005). It is also important to note that pesticide transport is influenced most by the surface runoff and sedimentation pathways, which

were successfully calibrated in this study (Pionke and Chesters, 1973; Karickhoff *et al.*, 1979; Weston *et al.*, 2004).

7.3 RESULTS AND DISCUSSION

In the following sections, the results obtained in this study are presented in a manner to highlight the possible implications of landuse change towards bioenergy cropping systems on surface water quality. The concentration fluctuation that is likely to be observed over a large basin with varying geographic and climatic characteristics are highlighted in the first section, followed by a discussion accentuating the possibility of impairing stretches of streams by exceeding the thresholds of toxicity for aquatic biota (represented by the Bluegill fish) and human health as a function of direct consumption from these waterbodies. The final two sections, temporal and spatial variation of stream impairment identify the location in time and space that require consideration prior to implementing bioenergy crops on a large-scale to refrain from damaging aquatic ecosystems and water quality.

7.3.1 Basin-wide Concentration Fluctuation

By altering the landscape into large-scale agricultural production focused on bioenergy feedstocks, an expected change in pollutant concentrations in surface waters may occur. In this study, the daily concentrations of pesticides in stream reaches were collected within the study area for the period (2000-2006). In order to demonstrate the immense variability that occurs over a large scale, a box plot was created for one of the pesticides studied here (Glyphosate) showing the basin wide stream concentration variations based on different crop rotations. Due to large variability in pesticide concentration, log transformations were used (Figure 24). Glyphosate was chosen as it is commonly applied throughout the entire study area and is included in all rotations but the continuous canola, miscanthus, and native grass landuse scenarios. Similar concentration variations were observed in other pesticides, which are presented in Tables 24 through 31. However, only maximum and median values are presented in these tables because they are more important to aquatic and human toxicity. Below these variations will be discussed for each pesticide:

By examining the fluctuation present over the entire basin, it is apparent that many factors play a role in determining the actual stream concentration of pesticides upon application to agricultural areas. Continuous corn, the most representative rotation for current agricultural practices for a starch-based ethanol economy, delivers the highest concentrations of Glyphosate to the stream (Table 26). In essence, this rotation has the greatest possibility of containing the highest levels of glyphosate, well above both the bluegill and human toxicity levels. The base scenario (current landcover and practices) actually did not reach the threshold for bluegill ecotoxicity, which is an indicator that current trends in agricultural production may not endanger aquatic species or human health. Meanwhile, switchgrass has the lowest median values indicating that this rotation is the safest of any of the rotations examined. In general, the close-grown grass species of rye and switchgrass have the lowest negative impacts on water quality, whereas the intensive crops corn and sorghum show the worst cases of glyphosate concentrations. In general, all of the bioenergy cropping scenarios have the possibility of jeopardizing the safety of surface waters for human consumption due to glyphosate contamination but at different levels.

Atrazine, another common herbicide is represented in Table 24 and experiences similar results. Here, the most intensive rotations, continuous corn and continuous corn stover, experience increased maximum and median concentrations over base, whereas the majority of other rotations experience negligible or decreased levels of atrazine in the stream reach.

Metolachlor, another extensively used agricultural pesticide, yields mixed results (Table 27). In general, metolachlor concentrations increase over base with intensive cropping rotations that includes corn and sorghum, indicating the low suitability of these crops to be adopted at a large scale.

The remainder of presented pesticides (bromoxynil, pendimethalin, sethoxydim, triflualin, and 2,4-D) cannot be compared directly to the base scenario since these pesticides are not currently used in crop rotations. However, these pesticides will be introduced in the basin upon implementation of second generations of bioenergy crops. The results from bromoxynil application indicate that continuous sorghum tends to increase pesticide pollution, whereas including soybeans in a two-year rotation reduces the amount of this chemical in surface waters (Table 25). Pendimethalin is applied on switchgrass only and is not currently labeled for this specific crop, yet does suggest that large-scale adoption of a bioenergy system based on switchgrass may have negative water quality effects due to the use of this chemical (Table 28). Sethoxydim and trifluralin (Table 29 and Table 30) are only applied to continuous canola. Again this is useful in simply showing the possibility of introducing two chemicals that may lead to further degradation of waterbodies. In the case that switchgrass is implemented to a large scale, the results in Table 31 suggest that switchgrass has the potential to reduce

concentrations of 2,4-D over continuous rye and corn-soybean-rye rotations. Although the aforementioned pesticides cannot be compared to the base scenario, they can be compared based on the amount of stream length that exceeds toxicity threshold criterion presented in the next section (7.3.2).



Figure 24. Basinwide variability of Glyphosate concentrations in log-scale (Dotted line represents the Bluegill ecotoxicity threshold of 5600 ppb and solid line represents the human toxicity threshold of 700 ppb).

	40500)	405000	1	40802	2	40900)
	Max	Median	Max	Median	Max	Median	Max	Median
Base	1.04E+03	1.18E-02	3.16E+02	4.23E-03	1.58E+02	2.23E-03	5.80E+03	1.20E-03
Continuous	-	-	-	-	-	-	-	-
Canola								
Continuous	1.24E+03	2.23E-02	6.40E+02	4.19E-03	2.28E+02	2.47E-02	2.22E+06	1.64E-02
Corn								
Continuous	1.16E+03	2.34E-02	6.51E+02	4.34E-03	2.27E+02	2.48E-02	7.47E+03	1.02E-02
Corn stover								
Continuous	-	-	-	-	-	-	-	-
Rye								
Continuous	1.38E+03	1.59E-02	6.33E+02	2.79E-03	1.80E+02	1.65E-02	8.44E+03	6.66E-03
Sorghum								
Continuous	1.59E+03	6.99E-04	2.35E+02	2.23E-05	2.02E+02	1.54E-04	4.00E+03	3.29E-04
Soy								
Corn Soy	1.59E+03	9.07E-05	4.03E+02	6.87E-06	2.30E+02	1.40E-04	4.33E+03	4.95E-05
Corn Soy Rye	6.59E+02	1.25E-06	3.40E+02	3.15E-07	1.18E+02	8.60E-07	7.03E+02	1.12E-06
Corn stover	1.59E+03	9.54E-05	4.03E+02	6.80E-06	2.30E+02	1.42E-04	4.32E+03	4.93E-05
Soy								
Miscanthus	-	-	-	-	-	-	-	-
Native Grass	-	-	-	-	-	-	-	-
Sorghum Soy	1.37E+03	3.78E-05	3.25E+02	3.21E-06	1.86E+02	4.58E-05	3.49E+03	1.49E-05
Switchgrass	6.69E+00	2.27E-07	3.93E+00	5.44E-08	4.28E+00	5.96E-08	9.75E+00	2.15E-07

Table 24. Concentrations of Atrazine ($\mu g L^{-1}$)

	40500		4050001		40802		40900	
	Max	Median	Max	Median	Max	Median	Max	Median
Base	-	-	-	-	-	-	-	-
Continuous								
Canola	-	-	-	-	-	-	-	-
Continuous								
Corn	-	-	-	-	-	-	-	-
Continuous								
Corn stover	-	-	-	-	-	-	-	-
Continuous								
Rye	-	-	-	-	-	-	-	-
Continuous								
Sorghum	1.85E+02	6.63E-06	8.03E+01	2.02E-06	4.19E+01	4.74E-06	4.44E+02	1.04E-05
Continuous								
Soy	-	-	-	-	-	-	-	-
Corn Soy	-	-	-	-	-	-	-	-
Corn Soy Rye	-	-	-	-	-	-	-	-
Corn stover								
Soy	-	-	-	-	-	-	-	-
Miscanthus	-	-	-	-	-	-	-	-
Native Grass	-	-	-	-	-	-	-	-
Sorghum Soy	1.26E+02	7.37E-07	3.97E+01	2.35E-07	4.74E+01	1.55E-06	4.48E+02	1.18E-05
Switchgrass	-	-	-	-	-	-	-	-

Table 25. Concentrations of Bromoxynil ($\mu g L^{-1}$)

	40500		4050001		40802		40900	
	Max	Median	Max	Median	Max	Median	Max	Median
Base	6.31E+02	4.51E-03	2.02E+02	7.95E-03	5.11E+02	6.19E-04	4.74E+03	1.67E-02
Continuous								
Canola	-	-	-	-	-	-	-	-
Continuous								
Corn	4.14E+02	2.19E-01	2.66E+02	1.17E-01	5.42E+01	3.32E-03	3.10E+05	3.22E-01
Continuous								
Corn stover	4.15E+02	2.21E-01	2.30E+02	1.17E-01	5.39E+01	3.34E-03	3.71E+03	2.04E-01
Continuous								
Rye	2.46E+03	4.56E-03	4.94E+01	6.94E-04	3.68E+02	8.18E-04	3.14E+03	1.43E-03
Continuous								
Sorghum	4.13E+02	2.17E-01	3.40E+02	1.18E-01	5.74E+01	4.64E-02	4.59E+03	2.00E-01
Continuous								
Soy	1.05E+03	1.18E-02	1.89E+02	7.34E-03	5.76E+02	4.86E-03	1.13E+04	1.26E-02
Corn Soy	9.24E+02	9.09E-03	2.59E+02	5.06E-03	5.52E+02	2.44E-03	9.62E+03	6.27E-03
Corn Soy Rye	9.24E+02	2.41E-03	1.72E+02	1.19E-03	5.52E+02	6.31E-04	9.62E+03	3.15E-03
Corn stover								
Soy	8.71E+02	9.18E-03	2.18E+02	5.10E-03	5.37E+02	2.44E-03	9.16E+03	6.28E-03
Miscanthus	-	-	-	-	-	-	-	-
Native Grass	-	-	-	-	-	-	-	-
Sorghum Soy	1.05E+03	9.17E-03	3.36E+02	5.00E-03	5.73E+02	2.46E-03	1.13E+04	6.58E-03
Switchgrass	9.24E+02	1.34E-03	1.72E+02	1.16E-03	5.52E+02	6.03E-04	9.62E+03	1.30E-03

Table 26. Concentrations of Glyphosate ($\mu g L^{-1}$)

	40500		4050001		40802		40900	
	Max	Median	Max	Median	Max	Median	Max	Median
Base	1.87E+03	3.39E-02	1.08E+03	1.75E-02	9.04E+02	6.97E-03	1.11E+04	1.48E-02
Continuous								
Canola	-	-	-	-	-	-	-	-
Continuous								
Corn	2.19E+03	6.35E-02	1.72E+03	1.79E-02	7.47E+02	6.64E-02	3.75E+06	1.01E-01
Continuous								
Corn stover	2.19E+03	6.45E-02	1.72E+03	1.80E-02	8.81E+02	6.65E-02	1.24E+04	6.03E-02
Continuous								
Rye	-	-	-	-	-	-	-	-
Continuous								
Sorghum	2.34E+03	7.30E-02	1.81E+03	2.13E-02	7.94E+02	7.25E-02	2.06E+04	7.24E-02
Continuous								
Soy	1.75E+03	4.14E-04	8.66E+02	8.44E-05	6.13E+02	7.07E-04	5.86E+03	9.03E-04
Corn Soy	2.06E+03	1.23E-03	1.06E+03	2.20E-04	7.53E+02	2.49E-03	6.20E+03	3.66E-03
Corn Soy Rye	1.38E+03	1.00E-05	8.26E+02	3.49E-06	4.42E+02	8.80E-06	1.58E+03	1.68E-05
Corn stover								
Soy	2.06E+03	1.25E-03	1.06E+03	2.18E-04	7.53E+02	2.51E-03	6.19E+03	3.66E-03
Miscanthus	-	-	-	-	-	-	-	-
Native Grass	-	-	-	-	-	-	-	-
Sorghum Soy	2.21E+03	1.17E-03	1.14E+03	1.98E-04	8.06E+02	2.47E-03	6.64E+03	3.09E-03
Switchgrass	9.34E+00	1.32E-07	4.83E+00	8.17E-08	6.87E+00	6.14E-08	1.20E+01	3.43E-07

Table 27. Concentrations of Metolachlor ($\mu g L^{-1}$)

	40500		4050001		40802		40900	
	Max	Median	Max	Median	Max	Median	Max	Median
Base	-	-	-	-	-	-	-	-
Continuous								
Canola	-	-	-	-	-	-	-	-
Continuous								
Corn	-	-	-	-	-	-	-	-
Continuous								
Corn stover	-	-	-	-	-	-	-	-
Continuous								
Rye	-	-	-	-	-	-	-	-
Continuous								
Sorghum	-	-	-	-	-	-	-	-
Continuous								
Soy	-	-	-	-	-	-	-	-
Corn Soy	-	-	-	-	-	-	-	-
Corn Soy Rye	-	-	-	-	-	-	-	-
Corn stover								
Soy	-	-	-	-	-	-	-	-
Miscanthus	-	-	-	-	-	-	-	-
Native Grass	-	-	-	-	-	-	-	-
Sorghum Soy	-	-	-	-	-	-	-	-
Switchgrass	4.30E+01	3.42E-03	5.33E+01	7.73E-04	2.92E+01	4.79E-04	2.65E+02	2.49E-03

Table 28. Concentrations of Pendimethalin ($\mu g L^{-1}$)
--

	40500		4050001		40802		40900	
	Max	Median	Max	Median	Max	Median	Max	Median
Base	-	-	-	-	-	-	-	-
Continuous								
Canola	6.85E+02	4.82E-05	4.80E+02	7.46E-07	4.17E+02	2.16E-04	0.00E+00	0.00E+00
Continuous								
Corn	-	-	-	-	-	-	-	-
Continuous								
Corn stover	-	-	-	-	-	-	-	-
Continuous								
Rye	-	-	-	-	-	-	-	-
Continuous								
Sorghum	-	-	-	-	-	-	-	-
Continuous								
Soy	-	-	-	-	-	-	-	-
Corn Soy	-	-	-	-	-	-	-	-
Corn Soy Rye	-	-	-	-	-	-	-	-
Corn stover								
Soy	-	-	-	-	-	-	-	-
Miscanthus	-	-	-	-	-	-	-	-
Native Grass	-	-	-	-	-	-	-	-
Sorghum Soy	-	-	-	-	-	-	-	-
Switchgrass	-	-	-	-	-	-	-	-

Table 29. Concentrations of Sethoxydim ($\mu g L^{-1}$)

	40500		4050001		40802		40900		
	Max	Median	Max	Median	Max	Median	Max	Median	
Base	-	-	-	-	-	-	-	-	
Continuous									
Canola	9.59E+02	9.68E-02	1.30E+02	4.58E-02	5.00E+02	2.58E-02	1.11E+03	7.65E-02	
Continuous									
Corn	-	-	-	-	-	-	-	-	
Continuous									
Corn stover	-	-	-	-	-	-	-	-	
Continuous									
Rye	-	-	-	-	-	-	-	-	
Continuous									
Sorghum	-	-	-	-	-	-	-	-	
Continuous									
Soy	-	-	-	-	-	-	-	-	
Corn Soy	-	-	-	-	-	-	-	-	
Corn Soy Rye	-	-	-	-	-	-	-	-	
Corn stover									
Soy	-	-	-	-	-	-	-	-	
Miscanthus	-	-	-	-	-	-	-	-	
Native Grass	-	-	-	-	-	-	-	-	
Sorghum Soy	-	-	-	-	-	-	-	-	
Switchgrass	-	-	-	-	-	-	-	-	

$T_{abla} 20$	Concentrations of Trifluralin (-1	`)
Table 30.	Concentrations of Trifluralin (µ	ıg L)

	40500		4050001		40802		40900	
	Max	Median	Max	Median	Max	Median	Max	Median
Base	-	-	-	-	-	-	-	-
Continuous								
Canola	-	-	-	-	-	-	-	-
Continuous								
Corn	-	-	-	-	-	-	-	-
Continuous								
Corn stover	-	-	-	-	-	-	-	-
Continuous								
Rye	8.68E+04	3.78E-03	6.35E+04	3.82E-04	4.19E+04	6.51E-03	4.31E+04	1.01E-02
Continuous								
Sorghum	-	-	-	-	-	-	-	-
Continuous								
Soy	-	-	-	-	-	-	-	-
Corn Soy	-	-	-	-	-	-	-	-
Corn Soy Rye	8.51E+02	7.07E-04	6.38E+02	6.14E-06	5.66E+02	2.02E-03	5.42E+02	7.98E-04
Corn stover								
Soy	-	-	-	-	-	-	-	-
Miscanthus	-	-	-	-	-	-	-	-
Native Grass	-	-	-	-	-	-	-	-
Sorghum Soy	-	-	-	-	-	-	-	-
Switchgrass	3.02E+02	3.37E-05	3.08E+02	2.42E-06	3.19E+02	8.82E-05	3.05E+02	1.76E-04

Table 31. Concentrations of 2,4-D (μ g L⁻¹)

7.3.2 Basin-wide Impact of Pesticides on Stream Impairment

The concentration of agricultural chemicals in streams is highly variable, making it difficult to predict possible waterbody impairments. This variability is important as it oftentimes leads to excessive chemical concentrations that potentially degrade the quality of the waterbody for human consumption and aquatic health. In order to better understand the impacts of agricultural chemical applications on surface water contaminations, the total length of impaired streams that exceeded the predefined threshold values for aquatic and human health were calculated. Table 32 provides the total basinwide length of impaired waterbodies for each rotation and herbicide. By finding the total length of streams that exceeded the toxicity levels for the exposure limit, each rotation can be compared to one another when they share the same pesticides applied.

By examining Table 32, it is important to note that the base scenario does have a large number of stream reaches that exceeds the human threshold level for atrazine, glyphosate, and metolachlor of 180597, 1033, and 1348 km, respectively, totaling 181,630 km of the 11,438,253 km total stream length (1.6 percent of total streams' lengths). As discussed previously, continuous corn was observed to have the highest basinwide glyphosate concentration. This was again observed in this analysis as continuous corn yielded the most extensive length of streams exceeding the human threshold (8572 km, an increase of 7719 km over base) and the only rotation to exceed the bluegill threshold (1063 km of stream). This rotation also has atrazine and metolachlor exceeding the bluegill threshold criteria. Human thresholds were also exceeded for the continuous corn rotation for atrazine, glyphosate, and metolachlor totaling 541,141 km of stream impairments. The result of such extensive waterbody

impairments, whether bluegill or human, strongly challenges the suitability of continuous corn rotations for large-scale implementation. Continuous sorghum experienced a small amount of streams exceeding the metolachlor threshold criteria for bluegills, resulting in 6.3 km. The continuous canola rotation resulted in 17152 and 110790 km of streams exceeding the bluegill and human thresholds for trifluralin, respectively.

Not all rotations experienced increases of pesticide impairments, though. Perhaps the most significant decreases of threshold exceedances can be credited to the perennial grass species. Switchgrass resulted in a 171,667 km reduction in total stream length hat exceeds the human threshold criteria, and miscanthus and native grasses do not have any impaired stream length. Miscanthus requires only a single application of pendemethalin and 2,4-D during the establishment year only and native grasses do not require herbicide application. Switchgrass, however, is not suggested to be cultivated for indefinite time limits like miscanthus and native grass, and is suggested to incorporate corn and soybean in the first two years of each rotation cycle, which is typically around 10 years. Thus, switchgrass does have atrazine, metolachlor, and glyphosate applied in the first two rotation years, followed by pendimethalin and 2,4-D during the establishment year. However, even with these pesticide applications, switchgrass still manages to mitigate overall pesticide contribution to streams. It is important to note that no herbicides are currently labeled for application on miscanthus and switchgrass, the results presented in this paper are therefore hypothetical scenarios in which are expected to occur if these crops are adapted into a large-scale production scheme.

Scenario	Atrazine	Bromoxynil	Glyphosate	Metolachlor	Pendimethylin	Sethoxydim	Trifluralin	2,4 - D	Total
Base	0	0	0	0	0	0	0	0	0
	180597	0	1033.1	1348.4	0	0	0	0	181630
Continuous	0	0	0	0	0	0	17151.8	0	17152
Canola	0	0	0	0	0	11.1	110790	0	108842
Continuous	656.9	0	1063.4	2906	0	0	0	0	3969.5
Corn	532056	0	8571.9	34121	0	0	0	0	541152
Continuous	0	0	0	0	0	0	0	0	0
Corn stover	399423	0	422.3	4376.7	0	0	0	0	399846
Continuous	0	0	0	0	0	0	0	0	0
куе	0	0	1327.4	0	0	0	0	137677	139004
Continuous	0	0	0	6.3	0	0	0	0	6.3
Sorgnum	339631	104.9	473.1	7769.7	0	0	0	0	340198
Continuous	0	0	0	0	0	0	0	0	0
Soybean	154049	0	4727.4	1900.8	0	0	0	0	158777
Corn	0	0	0	0	0	0	0	0	0
Soydean	173001	0	3536.0	2733.5	0	0	0	0	176537
Corn Sovbean	0	0	0	0	0	0	0	0	0
Rye	81117	0	3690.1	181.9	0	0	0	12972	97779
Corn stover	0	0	0	0	0	0	0	0	0
Soybean	173169	0	3392.5	2737.2	0	0	0	0	176561
Miscanthus	0	0	0	0	0	0	0	0	0

Table 32. Kilometers of stream segments exceeding threshold toxicity levels for the Bluegill and humans (the values with gray background represent Bluegill and white represents human threshold exceedances).

Table 32 ((cont'd)
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	0	0	0	0	0	0	0	0	0
Native	0	0	0	0	0	0	0	0	0
Grass	0	0	0	0	0	0	0	0	0
Sorghum	0	0	0	0	0	0	0	0	0
Soybean	130941	84.4	4082.9	3492.6	0	0	0	0	158033
Switch-	0	0	0	0	0	0	0	0	0
grass	212.1	0	2589.8	0	0	0	0	7161.4	9963.2

Note: Total basinwide stream length is 11,438,253 km

7.3.3 Basin-wide Temporal Variation of Stream Impairment

As previously discussed in Section 7.3.1, the concentration of pesticides in the stream fluctuates depending on many drivers such as application timing and amount, precipitation, etc. This is important in determining the proper management practices to attempt to minimize the amount of agricultural chemicals introduced to surface water bodies. However, temporal variation is needed to adjust agricultural practices and determine proper chemical application timing to minimize losses to streams and to properly allocate conservation resources and perform monitoring to detect possible threats to aquatic ecosystems and humans health. Figures 25 and 26 are provided to give an example of the temporal variability of stream impairments due to pesticide concentrations exceeding thresholds set forth to represent safe levels for aquatic ecosystems (Bluegill) and humans uses, respectively. These analyses are presented only for year 2 of the base, continuous corn, and switchgrass cropping rotations for all pesticides. This year was chosen as pesticides were only applied to switchgrass during the establishment year, which was the second modeled year.

The length of streams in exceedance of the threshold level for the base scenario includes glyphosate, atrazine, and metolachlor, continuous corn includes atrazine, glyphosate, metolachlor, and the switchgrass rotation scenario contains pendimethalin and 2,4-D. Overall, June appears to be the month that the most streams (in length) exceed the threshold limit for the Bluegill, followed by July with 452.4 and 441 kilometers, respectively. Meanwhile, May experiences a considerably less amount (58.6 kilometers) yet this marks the start of the pesticide concentration increase in surface waters. This is expected as this period has substantial precipitation and it follows the planting dates of

corn, which has a pre-emergent application of atrazine and metolachlor on the day of planting. A similar trend was observed for human threshold exceedances (Figure 26) where May, June and July had the most stream segments exceeding the human health thresholds for atrazine, glyphosate, and metolachlor. Again, base and continuous corn have pre-emergent applications of atrazine and metolachlor in May, whereas switchgrass has pendimethalin and 2,4-D applications in June, explaining why switchgrass has the most exceedances in this month. The decreasing length of exceeded streams following the month of application for each rotation reflects the trend of decreasing available chemical concentrations in soil and on foliage. These chemicals have short half-lives (3 to 249 days) and degrade quickly in aerobic conditions present throughout the study area. By determining the most susceptible times of the year, appropriate conservation planning can follow, effectively decreasing the amount of impaired waterbodies. With a proper assessment of spatial variation in compliment with this temporal variation could provide a more comprehensive understanding of the effects bioenergy cropping systems may have on surface water impairments.



Figure 25. Basinwide temporal variation in stream length impairments of three crop rotation scenarios based on fish thresholds



Figure 26. Basinwide temporal variation in stream length impairments of three crop rotation scenarios based on human thresholds
7.3.4 Basin-wide Spatial Variation of Stream Impairment

In order to control and mitigate the negative impacts of bioenergy crop expansion, it is important to first identify the locations within the watershed in which the impairment occur. This will allow us to not only identify the source of impairment, but also, helps in the decision making processes by identifying the most appropriate control practices that can be implemented. Based on the previous section of this study (Section 7.3.3), the months with the largest length of stream impairments were identified. May was observed as the worst month for human threshold exceedances for the base and continuous corn scenarios, whereas June was the worst for the human threshold exceedances in the switchgrass rotation and aquatic exceedances in the continuous corn rotation (only rotation to exceed bluegill thresholds). In the next step, the concentrations for each stream segment for the day in this month with the worst amount of exceedance were collected and mapped (Figure 27). It is important to note that Figure 27 presents the worst case scenario; however, the risk associated with impairment is significant. For example, the continuous corn rotation is the only rotation to exceed bluegill ecotoxicity levels while both base and switchgrass scenarios did not cause impairment concerning bluegill health. When comparing these rotations based on human health thresholds, it is observed that all have the potential to drastically impair surface waters for human consumption. Continuous corn has an extensive amount of impairment (77.8 percent of total stream length impaired), due to the increased pesticide use associated with the large-scale implementation of this intensive row crop. However, impairment on the given day for switchgrass results in only 38 percent of total stream length exceeding the human toxicity threshold.

It is important to note here that base does have a fair amount of impairment itself (34.5 percent of stream lengths), indicating that the current practices in this study area are inadequate at mitigating pollutants and have the potential to continue to create hazardous conditions for drinking water. This is, of course, in the absence of water treatment, which is costly and not available throughout the entirety of the study area. These findings suggest the great importance of taking caution when implementing agricultural practices or altering landscapes on a large-scale. Shifts of landuse towards bioenergy cropping rotations have the potential to alter the safety of surface waters in regards to pesticide concentration, which could potentially increase with intensive row crops or decrease with second generation crops such as switchgrass.



Figure 27. Streams exceeding Bluegill toxicity threshold (top) and human threshold (bottom) for base, continuous corn, and switchgrass (in order left-to-right)

7.4 CONCLUSIONS

Recent shifts in the global energy sector have led to an increased demand for bioenergy feedstock production for renewable energy. However, the environmental consequences of this shift in agricultural production system are not well known, especially in regards to aquatic and human health. Therefore, determination of which biofuel crops and management strategies may have the least unfavorable consequences to environments is vital for future decision making (Thomas *et al.*, 2009). In order to evaluate these consequences, a large-scale assessment using models is imperative.

The Soil and Water Assessment Tool (SWAT) was used in this study to evaluate the effects that large-scale bioenergy crop production may have on pesticide fate and transport and subsequently on aquatic and human health. The evaluation included four large watersheds (totaling 53,358 km²), 14 bioenergy cropping rotations, and 8 pesticides including atrazine, bromoxynil, glyphosate, metolachlor, pendimethalin, sethoxydim, trifluralin, and 2,4-D. The watersheds included in this study are intensively cultivated for agricultural production and all flow into the Great Lakes. Due to the manner in which SWAT simulate pesticide, each pesticide had to be individually evaluated. Therefore, 168 model runs were performed and the model output was evaluated for a six year period (2000-2005) on a daily time step.

The results obtained from this study were arranged in three sections and can be summarized in the following:

• 7.3.1 Basin-wide Concentration Fluctuation: Among all studied crop rotations, continuous corn caused the highest concentrations of Glyphosate to the stream. In

essence, this rotation has the greatest possibility of containing the highest levels of glyphosate, well above both the bluegill and human toxicity levels. The result of such extensive waterbody impairments strongly challenges the suitability of continuous corn rotations for large-scale implementation. However, the base scenario (current landcover and practices) actually did not reach the threshold for bluegill ecotoxicity, which is an indicator that current trends in agricultural production may be tolerable for aquatic ecosystems. In general, all of the bioenergy cropping scenarios have the possibility of jeopardizing the safety of surface waters for human consumption due to glyphosate contamination. In addition, atrazine and metolachlor, which are both very commonly applied in the study area, experience similar results with increased maximum and median concentration over the base scenario, indicating the low suitability of these crops to be adopted at a large scale. Crop rotations that incorporate close-grown grass species, especially switchgrass and native grasses, are the most suitable for largescale implementation.

7.3.2 Basin-wide Impact of landuse conversion on Stream Impairment: By finding the total length of streams that exceeded the toxicity levels for the exposure limit, each rotation can be compared to one another when the same pesticides are applied. The base scenario does result in a large amount of stream impairments for either human or aquatic bluegills for atrazine, glyphosate, and metolachlor. Meanwhile, continuous corn rotation caused water body impairment (exceeding the human consumption threshold) from 181629.9 km (under current landuse scenario) to 541151.5 km. In addition, this rotation also degraded water quality

for aquatic ecosystems in 3969.5 km of stream in which atrazine, glyphosate, and metolachlor concentration exceeded the bluegill threshold of LC50. Meanwhile, in many cases the results were positive. Meanwhile, the pollution mitigation exhibited by the perennial grass species. For example, switchgrass resulted in a 171,667 km reduction in total impaired stream that exceeds the human threshold criteria, and miscanthus and native grasses rotation did not cause any water quality impairment.

- 7.3.3 Basin-wide Temporal Variation of Stream Impairment: Temporal variation in water quality is important to identify threats to aquatic ecosystems and humans health during various time periods to focus conservation efforts. Overall, June appears to be the month that the most streams (in length) exceed the threshold limit for the Bluegill. A similar trend was observed for human threshold exceedances where May, June and July had the most stream segments exceeding the human health thresholds for atrazine, glyphosate, and metolachlor. By determining the most susceptible times of the year, appropriate conservation planning can follow, effectively decreasing the amount of impaired waterbodies.
- 7.3.4 Basin-wide Spatial Variation of Stream Impairment: Identifying locations
 that are at high risk for exceeding aquatic and human toxicity levels aids in
 watershed management to avoid waterbody impairment. Applying agricultural
 chemicals in a region where surface runoff and sedimentation are common leads
 to the possibility of waterbody impairment. For a one-day period representing the
 worst-case scenario, continuous corn has the potential for extensive stream
 impairment (77.8 percent of total stream length impaired), due to the increased

pesticide use associated with the large-scale implementation of this intensive row crop. However, impairment for switchgrass results in only 38 percent of total stream length exceeding the human toxicity threshold, whereas base impairs 34.5 percent of stream lengths. These findings indicate that converting a large amount of land into bioenergy crop production may not be suitable in regards to watershed health.

Based on these results, large environmental cost might be associated with future large-scale bioenergy crop expansion. However, the variability of pesticide concentrations between different geographic landscapes suggests that these crops may be suitable if pesticides application managed properly. In addition, due to complexity of pesticide fate in the environment, water quality monitoring is essential to track the potential hazardous conditions. In general, intensive bioenergy crops are the least suitable for large-scale implementation. However, this brings about an important concern: could continuous corn coupled with widespread conservation practices reduce overland pesticide contribution to surface waters enough to avoid such far-reaching water quality impairments? In order to expand our understanding of the effects that large-scale bioenergy expansion may have on aquatic ecosystems and human health, it is suggested that additional studies are performed that include multiple aquatic species assessments in different climatological and physiographic regions to confirm the findings discussed in this paper. In addition, a more widespread collection of observed data is required to obtain adequate model calibration for a more detailed and confident validation of pesticide transport in surface waters. Finally, the authors reinforce the importance of chemical application timing, in which controlling this is perhaps the most cost-effective

and efficient method in directly reducing the amount of pesticides in surface runoff and thus minimizing waterbody impairments.

Acknowledgements

The authors would like to acknowledge Dr. Lizhu Wang, Mr. Sean Woznicki and Mr. Mike Prohaska for their added project support, and Dr. Kurt Thelen, Dr. Wesley Everman, Mr. Dennis Pennington, Dr. Scott Swinton, Ms. Laura James, and Mr. Joseph Duris for their generous contribution of information.

8. CONCLUSIONS

8.1 GENERAL CONCLUSIONS

The research presented here evaluated the potential impacts that large-scale bioenergy crop expansion could have on water quality, aquatic ecosystems, and human health. A comprehensive and physically based hydrologic model, the Soil and Water Assessment Tool (SWAT), was used to predict pollutant loads in a large-scale due to conversion of current landuse to extensive bioenergy crop production. The study area mainly consists of agricultural regions of Michigan with highly variable climatic and physiographic conditions. The model was subject to various landuse scenarios, bioenergy crop rotations, management practices, and time steps. Model output was evaluated based on a comparison with the current scenario (current landcover), which for all purposes of this research, is assumed to represent of future conditions.

In the first section of this research, field studies were conducted in which seven herbicide treatments were applied to field and silage corn to determine the effects on biomass accumulation and glucose percentage for cellulosic ethanol. The second section of this research investigated the effects that management practices have on model output confidence, and the fluctuation in pollutant loads on a temporal scale to demonstrating the extreme fluctuation of pollutant loadings throughout the year. In the third section of this research, a similar approach was taken, only on a much larger scale, which ultimately helped to develop priority areas for focusing conservation implementation efforts. In the last section of this research, predicted pesticide concentration was compared to fish and human toxicity threshold limits to determine the environmental impacts of various bioenergy cropping systems. The results found in these research papers can be concluded in the following:

- Postemergence herbicides can have potentially beneficial biomass and glucose yield effects when applied to corn that will be used as a feedstock for cellulosic ethanol production.
- Perennial grass species are most suitable for large-scale implementation in this study area, whereas traditional intensive row crops should be implemented with caution on such a broad scale as these crops have the greatest potential to detrimentally affect watershed health.
- Only bioenergy crops grown on row crop land experiences significant decreases in total nitrogen load.
- Bioenergy row crops exhibit dramatic pollution load variation caused by differences in climate and physiographic characteristics throughout the study area.
- Traditional intensive row crops such as canola, corn and sorghum may negatively impact aquatic life and in most cases affect the availability of safe drinking water.
- Second-generation lignocellulosic bioenergy crops such as switchgrass show promise in reducing in total impaired stream length that exceeds the threshold criteria for human consumption.

8.2 RECOMMENDATIONS FOR FUTURE RESEARCH

The information presented in this research manuscript is valuable for decision makers regarding the impacts that landuse management has on environmental quality. However there are many opportunities to expand on this work and provide more in-depth research that addresses issues outside of the scope of this project. The following suggestions are recommended for further research:

- Due to climatic and geographic restraints, a number of potential bioenergy crops (i.e. rice, cassava, sugar cane, jatropha) were not examined based on poor suitability for our study region. Additional studies in different climatological and physiographic regions are needed that include such crops.
- In order to expand our understanding of the effects that large-scale bioenergy expansion may have on aquatic ecosystems and human health, it is suggested that additional studies are performed that include multiple specie assessments in different climatological and physiographic regions to confirm the findings discussed in this paper.
- A more widespread collection of observed pesticide data is required to obtain adequate model calibration for a more detailed and confident validation of pesticide transport in surface waters.
- The version of SWAT used in this project does not adequately model static waterbodies such as lakes and wetlands. By incorporating these features in watershed delineation and hydrologic/pollutant transport

processes, the predictions of constituent loads would be a better representation of natural processes.

- Bioenergy crops should maximize efficiency and be cost-effective, while minimizing environmental impact. It would be useful to evaluate many of the ideas presented in this manuscript based on conservation practices such as no-till or edge-of-field filter strips.
- Implement a mass balance approach to determine the amount of nutrients leaving the field through the harvesting of biomass. This may help to demonstrate the effectiveness of bioenergy crops to keep nutrients on site.
- Determine the optimal landuse configuration (percentage and location landuses) to minimize food vs. fuel competition and negative water quality impacts.

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