

**Unit field approach to examining nitrogen export:  
relative importance of land use, land  
management, climate, and groundwater transit  
time on annual chemical yields**

A Thesis

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## **Abstract**

The majority of the 20<sup>th</sup> century saw a marked increase in environmental degradation, and it was not until creation of the Clean Water Act (CWA) in 1972 that the United States took its first major step towards active improvement of the environment. The CWA dictates that all public waters must be fishable and swimmable. To be fishable the water must be clean enough to sustain fish and other aquatic organisms. To be swimmable means the water must be suitable for recreational purposes and not cause illness when humans or animals come into contact with it.

Water pollution can come from many sources and is not just limited to acutely toxic chemicals. Rather, anything that makes the water not fishable or swimmable can be considered a pollutant. A source of water pollution not often considered is agricultural operations as there is a heavy chemical reliance, which can often result in runoff laden with pesticides (insecticides, herbicides, and fungicides) and fertilizers. Pesticides are used to control unwanted organisms that compete with, or are detrimental to, crops. Fertilizers, however, are used to increase the nutrient content of the soil and so pollution from fertilizer use is often referred to as nutrient pollution (USGS Surface Runoff, 2018). To achieve the goal of fishable and swimmable, the Federal government, through the Environmental Protection Agency (EPA), works with states to reduce or eliminate pollution to waters via implementation of Total Maximum Daily Loads (TMDLs).

A TMDL for nutrients and sediment was implemented in the Chesapeake Bay watershed in the late 1990s across Pennsylvania, Maryland, Virginia, District of Columbia, New York, Delaware, and West Virginia (EPA, 2015) The annual limits set in this TMDL were 185.9 million pound of nitrogen, 12.5 million pounds of phosphorus, and 6.45 billion pounds of sediment – reductions of 25%, 24%, and 20%, respectively (EPA, 2015). Since implementation there has been interest in determining whether the goals laid out in the TMDL have been achieved, which has been difficult to definitively determine. One complicating factor in the analysis of real-world observed data has been the year-to-year variation in streamflow and chemical loads created by the annual variation in weather. Other difficulties exist with constantly changing landscape as agricultural and urban land use spread.

This study focuses on the comparison of various factors affecting the loads of a conservative chemical and nitrogen and the relative impact those factors have on the nitrogen load.

Precipitation falling on the surface of land can either be recycled to the atmosphere through evapotranspiration (ET), be stored in the upper soil layers, exit the surface as runoff, or exit the upper soil as recharge to groundwater. The groundwater then moves to a discharge point, a

process that may take years. Precipitation can introduce some nitrogen to the land surface, known as atmospheric deposition, and is the main source of pre-anthropogenic nitrogen. Additional nitrogen is introduced to the environment primarily through urban and agricultural activities. Water movement then carries nitrogen through, and out, of the landscape to either groundwater or surface water.

The first chapter examines how variation in precipitation leads to variation in observed streamflow and water quality. As there may be numerous factors affecting water quality, it was determined that the model would be run with a simple, generic chemical *C* that was conservative, non-sorptive, and non-reactive chemical. The goal was to better understand how the magnitude of groundwater flow and *C* load to the stream, the variation in the flow and load of *C*, and the time it may take the groundwater to reach the stream are all affected by the variation in weather and land use. A standardized field, referred to as a unit field, was used for comparisons between scenarios. A square field was created with sides of 400 m by 400 m, for a total area of 16 hectares (39.54 acres). Annual precipitation was simulated using a random normal distribution with mean of  $1.0 \pm 0.2$  m. From this it was assumed that 0.5 m left the system as ET and 0.25 m as groundwater. The remaining precipitation left the system as runoff. A lumped-parameter model (LPM) was used to model the groundwater. The LPM followed an exponential distribution and the total groundwater discharge to the stream was added to the runoff to create the streamflow. The total load of nitrogen was also accounted for using the LPM and runoff concentrations. Using the model, four basic land use scenarios were examined: natural vegetation, agricultural land use, and agricultural land use with a Best Management Practice (BMPs) reducing the nitrogen levels by 10% and 30%. Results showed that, as in real-world observed data, identifying trends year-to-year was nearly impossible and that the groundwater component of the model greatly increased uncertainty. The model showed that, due to the lag resulting from the groundwater, the stream required four times the groundwater transit time to approach steady state – e.g. a groundwater transit time of 20 years meant the stream required approximately 80-100 years to reach steady state. It also demonstrated a change in load of 25% was not easily identifiable without a large dataset and may take decades to observe (if all the change occurred in a short period).

In the final chapter a second model was used to examine how land use, land management, and climate might affect streamflow and nitrogen load. APEX, Agricultural Policy/Environmental eXtender model, was used to model various land uses (agriculture, urban, perennial vegetation), land managements (BMPs, nitrogen application rates, percent urban), and different climate projections to identify relative importance when it came to streamflow and nitrogen load. A new

stand-alone model in R was then created that combined the APEX output, along with the groundwater model used in chapter 1, and developed a theoretical watershed. The purpose of creating this watershed was to analyze how a change in part of the watershed may impact the streamflow and nitrogen load. This information is useful to water resource scientist and policy decision makers as it helps to emphasize what changes may be most important from a water quality perspective. A by-product of this analysis is that this tool in R is now available for anyone to use as it is a simple model based off of APEX simulations.

First ArcGIS and APEX were used to delineate a field near Bridgeville, Delaware. This would be the unit field for the second chapter and was 13.21 ha (32.64 acres) in size and used for all scenarios. The model outputs for the hydrologic and nitrogen cycles were captured and annual water and nitrogen budgets developed. A standard land use and management was chosen as the basis for comparison: corn with conventional tillage, recommended nitrogen application rates, no BMPs, and historically observed weather. All other scenarios were compared to this. It was identified that reducing nitrogen application rates (where applicable) and implementing buffer strips were most effective at reducing total nitrogen in the stream for all crops. No till increased the amount of water and nitrogen to the groundwater. The timing of rainfall was critical, as uniform increases in rainfall intensity resulted in large increases in nitrogen export, but a single large event did not substantially increase nitrogen loads.

Building the theoretical watershed in R, the watershed can be any size (by number of unit fields) and composition (land use and land management). For purposes of this study, a watershed comprised of 1,000 unit fields was modeled from pre-settlement into the future. While it shows that it is not possible to achieve pre-settlement levels of nitrogen, implementation of BMPs can help reduce nitrogen loads by 25%, the level required in the Chesapeake Bay TMDLs. This information thus allows water resource scientist and policy makers, when they identify regions for improvement, to quickly recommend options and provides background on how they might see their watershed responded to those changes.

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**1 Setting realistic expectations of changes in stream loads of a conservative chemical with a simple land use model**

## **1.1 CHAPTER 1 SYNOPSIS**

Chemical application to land surfaces is prominent throughout the world. Many are taking steps to reduce the amount of chemicals escaping to the environment. A common method to combat this pollution is to implement some form of Best Management Practice (BMP). Quantification of the trends in the effectiveness of BMPs is difficult due to the complex nature of natural ecosystems and identifying real-world trends in observed data has proven to be challenging. One factor that causes issues with this is the annual variability in observed streamflow and chemical loads, which is a result of the year-to-year variability in precipitation. Another is the groundwater and the response in the stream due to groundwater discharge. A model was created that simulated annual precipitation with known chemical characteristics, routed the water movement across the surface as runoff, through the groundwater to the stream as groundwater discharge, and created an overall annual hydrologic and chemical budget. Analysis showed that with normal variability in annual precipitation and limited data, it was nearly impossible to identify any trend. The groundwater transit time resulted in short-term observations that were not representative of the true mean stream load. A period greater than the groundwater transit time is needed to observe chemical loads that approach steady state.

## **1.2 INTRODUCTION**

The use of chemicals in the agricultural industry to prevent or exterminate detrimental or competing organisms (pesticides) or alter of the nutrient content of soil is a common practice throughout the world. While chemical applications are used to increase plant survival or yield, and is often necessary, the chemicals can negatively impact ecosystems. Pesticides can be toxic to non-target organisms and potentially kill beneficial organisms (Aktar 2019). Fertilizer use is related to higher nutrient concentrations in surface waters and groundwater, leading to eutrophication and other issues associated with nutrient-impaired water (Carpenter, 1998). Nutrient impairment is directly linked to fertilizer use, and since the invention of the Haber process in 1908 the use of fertilizer in the US has increased from less than 0.3 Tg-N/yr before 1940 to 11.4 Tg-N/yr in 2015 (Cao, 2018).

Most chemicals used in agriculture are applied to crops and/or directly to the soil surface. From there they are then taken up by organisms, are transported by runoff, or travel deeper into the soil with recharge. When precipitation exceeds the saturation point of the surface soil, the result is runoff (USGA Surface Runoff, 2018) that can transport chemicals, both dissolved and sorbed to particles. Of the remaining precipitation some infiltrates into the soil and transports dissolved chemicals. Over time, some of these dissolved chemicals may enter the groundwater and

eventually make it to the stream. Both recharge and runoff can result in the transport of chemicals to streams, ultimately carrying them to coastal areas. Once there, a chemical that served a purpose growing crops may become detrimental to the marine ecosystem.

A prime of example of such a chemical is nitrogen from fertilizer. Nitrogen fertilizer application has been essential in increasing crop yields to keep pace with growing populations (Cao, 2018). But, as fertilizers enter water systems, they continue to promote vegetation growth often in the form of algae. The sudden growth of algae results in an algal bloom, blocking sunlight from reaching the bottom of water bodies which can kill rooted vegetation. The harmful algal blooms (HABs) often impact water bodies downstream of the point of application. A 2000 study estimated that HABs cost the United States roughly \$50 million a year (Anderson, 2000), a number that will surely increase as the size and severity of HABs increases. To address this issue regulatory agencies may enact control measures such as a Total Maximum Daily Load (TMDL), which can restrict how much of a contaminant may leave a watershed. Sources of contamination are lumped into two categories: point source and nonpoint source. Point source pollution is typically easy to identify and expensive to mitigate, such as wastewater treatment plants and industrial discharge. Nonpoint source pollution is often more difficult to precisely locate, such as agricultural runoff and atmospheric deposition. Methods to reduce nonpoint source pollution from agriculture are collectively referred to as BMPs and can consist of buffer strips, no-till practices, terrace farming, cover crops, etc.. It has been suggested that BMPs can reduce total nitrogen discharge to streams by more than 30% (Capel, 2018).

One example of nutrient pollution is the Chesapeake Bay watershed, which is the context of this study. The Bay is considered impaired due to excess nutrients, leading to algal blooms and water quality issues (EPA, 2019). In accordance with the Clean Water Act's mandate that all waters be "fishable and swimmable", the EPA has set TMDLs for nutrients entering the bay from the region that comprises the Bay's watershed: Pennsylvania, Maryland, Virginia, District of Columbia, New York, Delaware, and West Virginia (EPA, 2015). The goal of the TMDL is to reduce the nitrogen load to the Bay to 185.9 million pounds per year, a decrease of 25%, with full implementation of the TMDL by 2025. This would be done by focusing on improving wastewater treatment plant operations, reducing stormwater pollution, and modifying agricultural practices. The overall TMDL was distributed over the seven states and the District of Columbia. With the implementation of agricultural and urban BMPs throughout much of the watershed, and the improvements in nitrogen removal at wastewater treatment plants, there is great interest in determining how effective the changes have been. But the variability in annual precipitation,

which strongly influences the year-to-year variability in streamflow and nitrogen load, makes detecting changes in annual streamflow and load due to the TMDL incredibly difficult. Adding to the complexity of the situation is the delayed response observed from groundwater. This lag results from the time it takes water, and contaminants it may carry, to enter the aquifer and exit the aquifer. A study (Meter, 2018) found that legacy nitrogen is a primary source of nitrogen to the Mississippi Watershed and that it may require decades for the Mississippi River to fully represent changes that have occurred on the land surface.

Given the expected variability of annual rainfall, the question arises of how much change in land use and implementation of conservation practices is needed to yield an observable change in the annual stream load of a chemical. Stream loading of a generic, conservative chemical (*C*) was modeled. Simple watersheds were then built using combinations of unit fields to examine how land use and BMPs affect the streamflow and annual stream load of *C*. A unit field had uniform land cover and fixed water table. Unit field land cover included naturalized vegetation or cropland. The weather simulated for the watershed in these scenarios consisted of 150 years of annual precipitation which followed a normal distribution with a mean of 1.0 m/yr and standard deviation of 0.2 m/yr. Precipitation was the only water input to the system, while evapotranspiration, runoff, and baseflow were the only water outputs of the system. Evapotranspiration and runoff were observed during the same timestep. Recharge to groundwater was then discharged to the stream in steps following an exponential distribution. Using this modeling framework, numerous combinations of land use distributions, conservation practices, and groundwater transient times were modeled with a given normal distribution of annual precipitation. The resultant variability in the annual stream loads and time to a new steady state were examined to better understand the conditions for which statistically significant changes in stream loads could be observed. This is valuable in understanding when changes to land surfaces may be fully observed, allowing for realistic expectations to be set when implementing new TMDLs.

## 1.3 METHODS

### 1.3.1 Historic environmental observations

Historical precipitation data for select regions of the Chesapeake Bay watershed were obtained from the United States Geological Survey (USGS) (USGS Water Data). The mean and standard deviation are given in table 1.1. Streamflow for select streams in the Chesapeake Bay Watershed were also obtained from the USGS (USGS Water Data) and mean and standard deviation are provided in table 1.2. From this data it is evident that the annual total stream discharge is dependent on watershed size but has streamflow relative standard deviation (RSD) appears to be independent. Finally, the annual nitrogen load in three streams was obtained from the USGS (USGS Annual Loads) was also examined and is provided in table 1.3. The Potomac River and Difficult Run are examined more closely in figures 1.9, 1.10, 1.13, and 1.14. The Potomac River is a larger watershed than Difficult Run, with a variety of land uses while Difficult Run has mostly gone from forested to urban in recent decades.

### 1.3.2 Model structure

A model was developed in R to simulate the annual load of a chemical in a stream flowing through a watershed. A standardized field, referred to as a unit field, was used to build the watershed. The unit field had dimensions of 400 m by 400 m for a total area of 16 hectares (~39.54 acres). This area was chosen because it is approximately the size of a traditional farm field. The land use (forested and agricultural) and land management (agricultural with and without BMPs) for each field was independent of all other fields.

A simplified water budget was created for the model and is shown in figure 1.1 and represented in equation 1.

$$Precipitation = Evapotranspiration + Runoff + Recharge \quad \text{Eq. 1}$$

Precipitation is the only input while outputs for the water budget were evapotranspiration, recharge, and runoff. Precipitation consists of all forms of water condensation from the atmosphere on the land surface. Evapotranspiration (ET) is the water that returns to the atmosphere from plant respiration and evaporation. Recharge is the water that travels through the soil to the groundwater, then eventually to the stream as discharge. Runoff is the water that travels across the surface of the land to the stream. This budget was chosen due to its simplicity and it captures the major components of the water cycle<sup>1433</sup>.

Variability in the hydrology of the model was introduced by varying precipitation. A mean rainfall depth of 1.0 m with an RSD of 20% was used in the model. Although the variability observed in historic precipitation was not this high, the variability in model precipitation was needed to match the observed historic streamflow. A random normal number generator in R(R project) was used to create annual precipitation events over the timespan of 150 years, with mean 1.0 and standard deviation of 0.2 m. Any year with less than 0.75 m in precipitation was fixed at 0.75 m. Evapotranspiration and recharge were fixed at 0.5 m and 0.25 m, respectively. The difference between precipitation and the sum of evapotranspiration and recharge resulted in runoff (Eq. 1).

In the model there are two inputs to the stream leaving the watershed: runoff and groundwater discharge. Runoff is routed straight to the stream and observed the same year when precipitation was greater than 0.75 m, the sum of the annual ET and recharge. Groundwater discharge was set equal to the annual recharge, 0.25 m. The process of the recharge reaching the stream as discharge was not as direct as runoff. Recharge must travel through the aquifer before being discharged, and thus has some transit time that can range up to hundreds of years. To model this groundwater transit time the lumped-parameter model (LPM) from Haitjema (Haitjema, 1995) was used.

$$\mathbf{Groundwater\ age\ distribution} = \frac{\mathbf{1}}{\mathbf{Tbar}} e^{-\frac{\mathbf{T}}{\mathbf{Tbar}}} \quad \text{Eq. 2}$$

$$\mathbf{Tbar\ (mean\ groundwater\ age)} = \frac{\mathbf{n\ H}}{\mathbf{N}} \quad \text{Eq. 3}$$

*T* = number of years since model pulse

*n* = porosity

*H* = saturated aquifer thickness

*N* = areal recharge rate

The LPM creates a frequency distribution of travel times, following an exponential distribution, and was only a function of the aquifer porosity, saturated aquifer thickness, and areal recharge rate. Assumptions for the LPM are that the groundwater is at steady-state and follows Dupuit-Forchheimer flow (Haitjema, 1995). The response curves of the current and prior years are used to determine the current makeup of the groundwater discharge to the stream. For this paper, the mean groundwater age was held constant at either 0, 2, 20, or 30 years.

With the hydrologic balance established, a conservative chemical was incorporated into the model. Conservative refers to a non-sorptive and non-reactive chemical. The chemical, *C*, is thus transported by water at the same speed and therefore also modeled by the LPM. It is assumed to be added to the land surface at a fixed amount annually. Concentrations of *C* were different between land uses, and different between runoff and recharge for those land uses, as shown in table 1.4. Land uses considered were agricultural and natural. Natural was considered to be both pre-agricultural and reverting back to natural land known as CRP (Conservation Reserve Program). Land management was either no BMPs, 10% efficient BMPs, or 30% efficient BMPs, where the efficiency of a BMP resulted in a corresponding drop in *C* concentration in both the runoff and recharge (table 1.4).

### 1.3.3 The model watershed

The model in R created a watershed with a size of 1,000 unit fields (figure 1.2). Each unit field was one of the four land uses and managements: natural (or CRP), agriculture with no BMPs, agriculture with 10% efficient BMPs, and agriculture with 30% efficient BMPs. Each unit field received the same precipitation for the model year. The R model routed runoff same-year, and recharge to discharge following the discharge created by the LPM. The model time length was set to 300 years and a change from one land management to another was simulated halfway through the model at year 150. It was determined this length of time allowed the groundwater to reach steady state both before the change and after. The annual stream load for each scenario was recorded and the results from the modeling were then used to help estimate when real-world observations might indicate actual changes instead of perceived changes from annual variability.

## 1.4 RESULTS

### 1.4.1 Real World Results

The hydrologic cycle of a natural system originates from precipitation, which is typically the sole hydrologic input to that system. Precipitation then drives evapotranspiration, runoff, and groundwater recharge. Therefore, variability in precipitation directly influences observed variability in evapotranspiration, runoff, and recharge. The variability in precipitation used in the model was compared to historical data from the mid-Atlantic region for both precipitation (table 1.1) and stream discharge (table 1.2). For modeling purposes, an annual mean of 1.0 m and relative standard deviation (RSDs) of 20% was used. While this was higher than the RSDs of the historical precipitation data, it was lower than the RSDs of the historical flow data.

Historical precipitation in the Chesapeake Bay watershed (table 1.1) has an overall annual mean of  $1.13 \pm 0.027$  m. Regardless of the mean and standard deviation, all watersheds had similar RSDs over the range of 2.5-2.9%. This variability in rainfall gives rise to the variability and uncertainty observed in streamflow data (table 1.2).

From the observed streamflow data, the annual mean discharge of the stream was proportional to the size of the watershed (table 1.2). Watersheds ranged in size from 62,392 km<sup>2</sup> to 157 km<sup>2</sup>. The relative standard deviation does not have a discernable correlation to watershed size and remains in the mid-30% range for most rivers (1.2), which was greater than the modeled variability. To achieve the desired variability in model streamflow, a RSDs of 20% in annual precipitation was used for the model. Observed total nitrogen loads ranged from 21.8 to 0.1 Million kg-N per year with RSDs of 50.3-39.7%, for the three selected streams (table 1.3).

### 1.4.2 Modeled Results

#### 1.4.2a Effect of land use and groundwater transit times

A very simple scenario (figure 1.3) was examined in which the land was converted entirely from natural to agricultural all at one time, with no variability in rainfall. This resulted in a relatively instantaneous stream load increase with the load immediately after the change 90% of steady state. The lag after the change at year 150 is due to the groundwater transit time, which is visible for about 75-80 years or 4x the groundwater transit time. Most of the difference between final and initial stream load was due to the immediate land use change was from runoff, the stream takes time to reach a new steady state because of the groundwater lag.

Analysis of only the load from the groundwater component of the stream (figure 1.4) highlights the effect that the groundwater transit time has on the stream load, and the time until steady state

is reached. The scenario of zero transit time shows a lack of a lag in the groundwater and steady state was achieved instantly. As the transit time increases, the groundwater responds more slowly to the change in land use. A transit time of two years requires about 10 years for the system to reach steady state. While a transit time of 20 and 30 years requires about 90 and 175 years, respectively, for the system to reach steady state.

#### 1.4.2b Effect of variability in precipitation

The previous example had zero variability in precipitation. The next step looked at stream load with variability in precipitation and carrying that variability throughout the system. A comparison of stream loads for different groundwater transit times for a single unit field (figure 1.5) show that annual variability in streamflow, a result of the variability in precipitation, is a much larger source of uncertainty than groundwater transit time. Immediately after the change in land use at year 150, the groundwater lag does add some uncertainty between scenarios. Comparison of year 152 between scenarios with groundwater transit times of 2, 20, and 30 years reveal very different results. However, as time elapses each scenario approaches a similar steady state value and was nearly identical by year 300.

The comparison of year 152 reveals something else. Year 152 was a “drought” year, a year in which there was no runoff. When there is no runoff, the streamflow is due 100% to groundwater discharge and has the same distribution as the groundwater discharge. It also makes the magnitude of the flow, compared to other non-drought years, much smaller. It also

#### 1.4.2c Scaling up to watershed size

As the size of the model increases from a single unit field to a watershed, the variation observed in the stream load becomes more noticeable. The figure 1.6 shows the stream load of a watershed that went from 100% natural to 100% agricultural at year 150, the mean of years 272-300,  $\pm 10\%$  of the mean, and  $\pm 20\%$  of the mean. From the figure it is noticeable that many of the data points fall outside of the  $\pm 20\%$  of the mean lines. From this it is easy to see that a single, or even multiple, observed loads that represent a 25% reduction from the mean may not indicate a true decrease in load.

The contribution of groundwater to the total stream load is examined more closely in figure 1.7. The figure shows the stream load when the groundwater transit time is 20 years and a change from a natural unit field to an agricultural unit field occurs at year 150. The graph also shows the percent difference in this same stream to a scenario where there is no groundwater lag. Two things can be determined from this data. Initially after year 150 there is a great difference due to

the groundwater lag. This difference quickly disappears though and within a time range of 20 years (a time equal to the groundwater transit time) the difference is minimal. This is because as time elapses, the aquifer approaches the recharge concentration. Second, when there is a drought year, and runoff is minimal or nonexistent, the difference in stream load between a 0-year transit time and a 20-year transit time is the highest, as shown by the vertical line at year 191. This is because groundwater discharge is the only input for the stream without the runoff, resulting in a high load from the 0-year transit time groundwater and a lower load from the 20-year transit time groundwater.

#### 1.4.2d Complex changes

Comparing large changes at the watershed scale, various ratios of forest to agriculture were considered. The mean stream load for each agricultural scenario changes fall within 25% of each other (figure 1.8). This suggests a couple things. First, changes in means between scenarios can be identified after the new steady state is reached, but any amount of change in land use from 25-100% are not statistically significant from each other. The means of the scenario was only 25% of the 1,000 unit fields is agricultural can reasonably interpreted as a data point in the scenario where 100% of the 1,000 unit fields.

## 1.5 DISCUSSION

The focus of this research, using model results was is it possible to answer the question of “after a change in in land management occurs, how long before changes in stream load can realistically be observed?”. A look at the model data in figure 1.6, where the years 180-190 are higher than average then years 190-200 are around average, demonstrate the high variability that makes interpreting observed data so difficult. The historical flow data suggests a high degree of variability exists (table 1.2). Observations in annual nitrogen loads in the Potomac River indicate declining annual nitrogen loads (figure 1.9) while the stream load in Difficult Run shows an overall increase (figure 1.10). P-values comparing the observed data are provided in the figures.

While examining stream load with no variation (figure 1.3) it was apparent that approximately 90% of the difference between the old and new steady states would be observed immediately due to changes in the runoff load. The remaining 10% change in stream load would be due to changes in the annual loads from groundwater. Given a scenario in which the groundwater has a 20-year transit time, it takes approximately 75 years to reach the new steady state. The groundwater transit time therefore adds a layer of complexity to any stream receiving groundwater discharge.

This variability was explored further (figure 1.4) when considering various groundwater transit times. Short transit times of 0 and 2 years show little to no lag, so a sample following a land use change may likely be near steady state. While the longer transit times of 20 and 30 years show considerable lag. Comparison of the groundwater component of the stream load to the total stream load (figure 1.5) shows that years immediately following a change in land use are the most sensitive to groundwater transit time. Influence of the groundwater on the stream load diminishes during years with higher loads (higher precipitation). This was due to the runoff observed instantaneously and also the higher concentration in the runoff.

Upon adding multiple unit fields to form a watershed, the range in the stream load increases greatly (figure 1.6). While +/- 10 % of the mean was highlighted, data points rarely actually fall into this narrow range. It appears more common to fluctuate around this range and stream loads in wet years are orders of magnitude higher than loads in dry years.

A watershed was created which started with every unit field in agriculture. Over the model life of 300 years, the stream load was reduced by 25% to match the Chesapeake Bay TMDLs. The resulting figure (figure 1.11) shows a decreasing trend in stream load. Comparing the initial 10 years and final 10 years however, it was difficult to distinguish the distributions (figure 1.12) and p-values did not show statistical significance: p-value of first 10 years was 0.92 and the p-value

of the last 10 years was 1. Similar difficulties are encountered when reading the real-world data (figures 1.13 and 1.14). This demonstrates that accurately identifying significant changes using a single, or even multiple data points, is difficult as the variation from one year to another due to the variation in flow may be as high as 50% or double the reduction requirements.

**Chapter 1 figures**

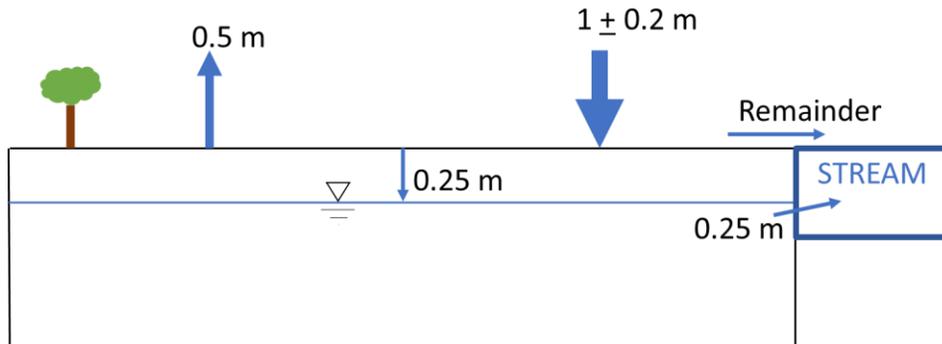


Figure 1.1: Standard unit field with water budget of the model. The surface receives  $1.0 \pm 0.2$  m of precipitation annually. There is a fixed evapotranspiration of 0.5 m and a fixed recharge of 0.25 m. The remainder is then runoff to the stream.

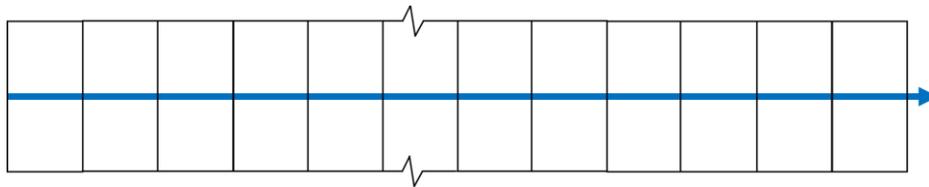


Figure 1.2: Visualization of watershed within the model. Each square represents a unit field, with a total of 500 unit fields on either side of the stream. The watershed is thus 2 unit fields wide by 500 unit fields long.

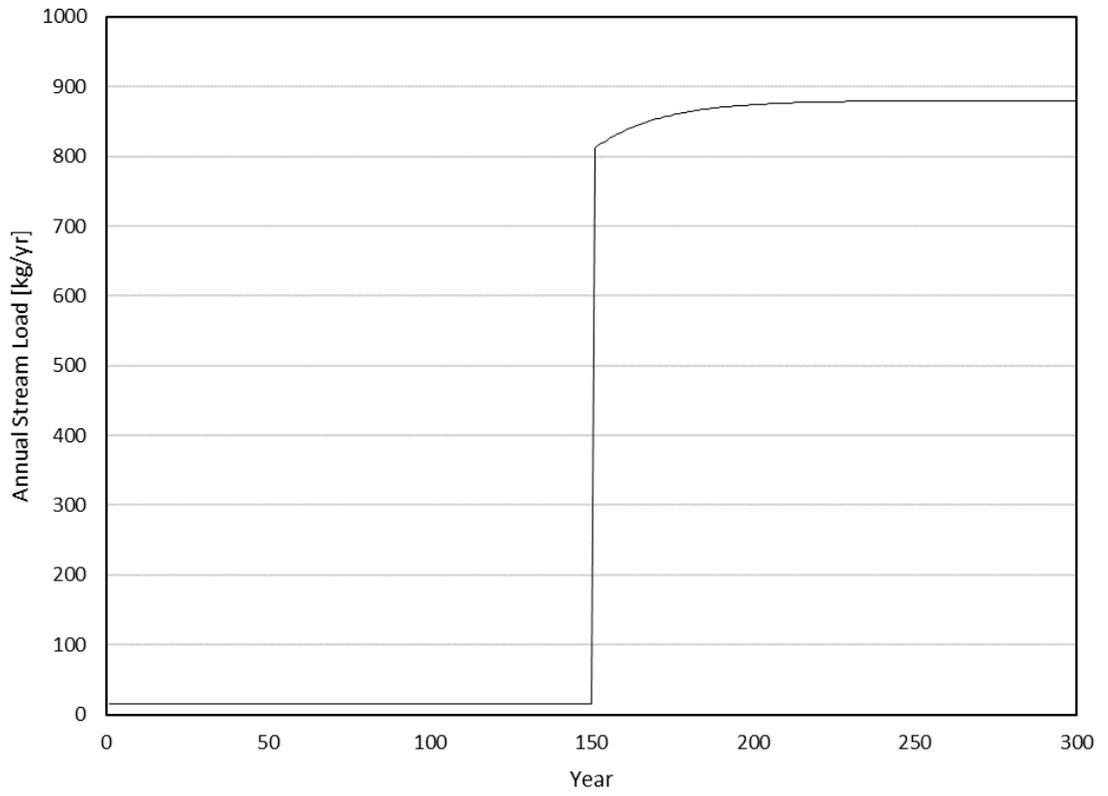


Figure 1.3: Simulated annual stream load for a unit field with a 20-year transit time and no variability in rain. Precipitation was fixed at  $1.0 \pm 0.0$  m/yr. An abrupt change occurs at year 150 from natural to agricultural with no conservation practices.

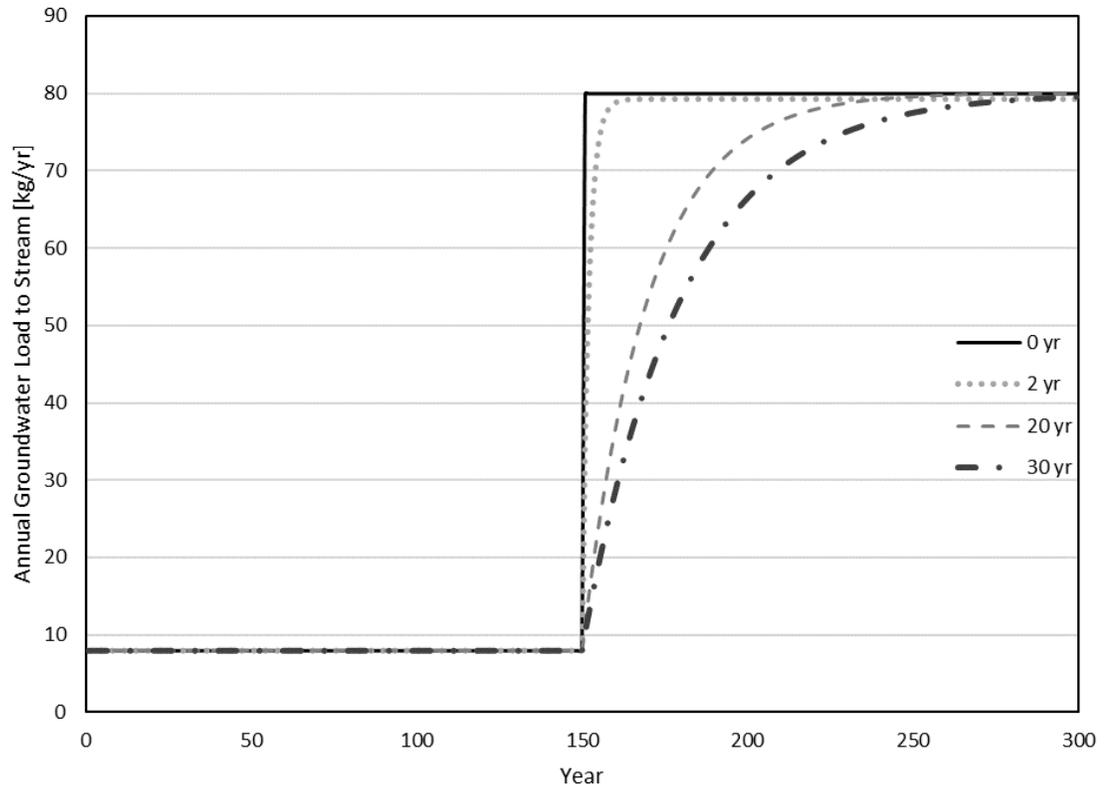


Figure 1.4: Simulated annual groundwater loads to a stream from a unit field are shown for 4 different mean groundwater transit times for the scenario of an abrupt land use change at year 150 from 100% natural to 100% agricultural with no conservation practices. The annual precipitation  $1.0 \pm 0.2$  m/yr. This highlights the effect the groundwater lag time has on the stream's ability to reach steady state.

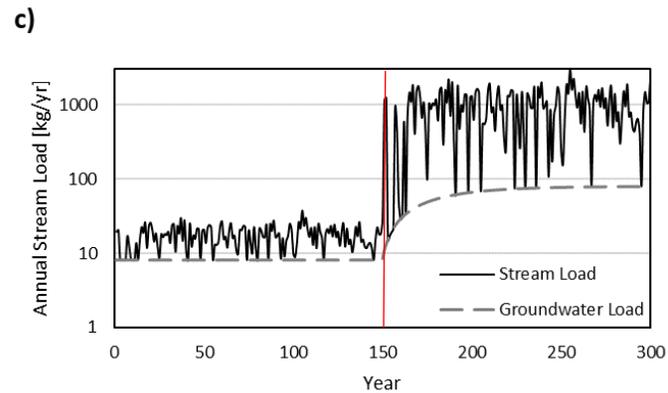
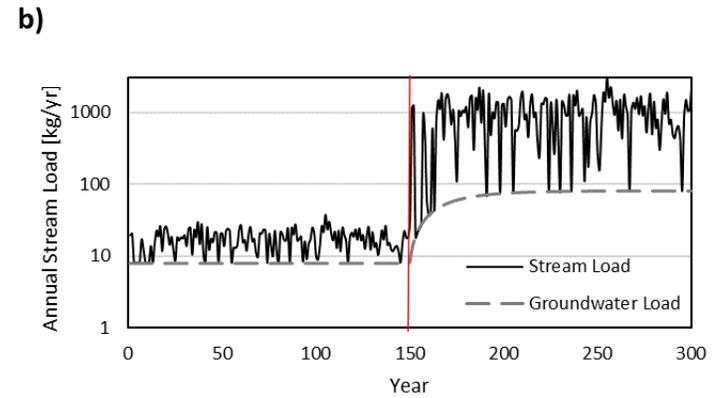
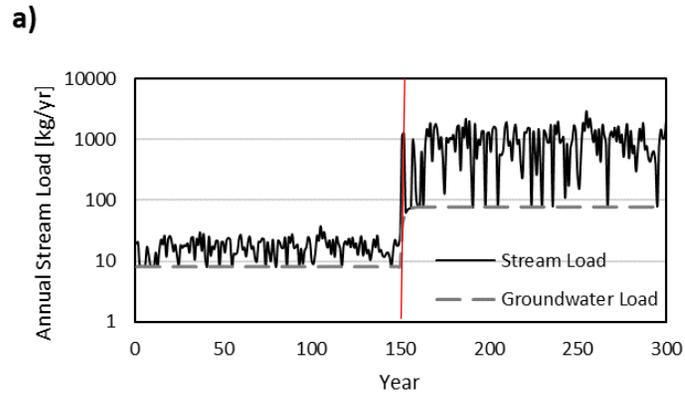


Figure 1.5: Simulated annual stream load and groundwater load plotted over time for the stream from a single unit field with varying transit times a) 2 years b) 20 years c) 30 years. An abrupt change in land use from natural to agricultural occurred at year 150 (vertical line). The same precipitation distribution was used in all scenarios with a mean of  $1.0 \pm 0.2$  m/yr. The load was plotted on a semi-log plot to highlight the difference in contribution to the stream load.

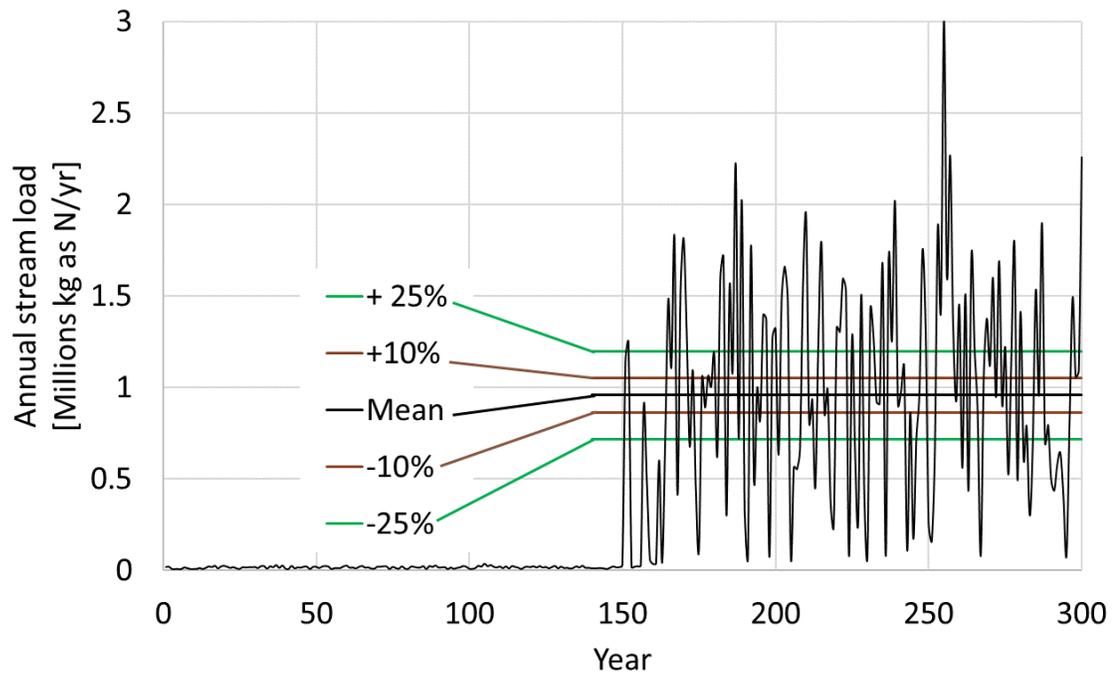


Figure 1.6: Simulated annual stream load for a watershed comprised of 1,000 unit fields with a 20-year groundwater transit time. There was an abrupt change in land use at year 150 from natural to 100% agricultural with no conservation practices. Precipitation variability was  $1.0 \pm 0.2$  m/yr. The five horizontal lines show the mean value at steady state during year 272-300. The  $\pm 10$  and 25% indicate  $\pm 10$  and 25% of the mean.

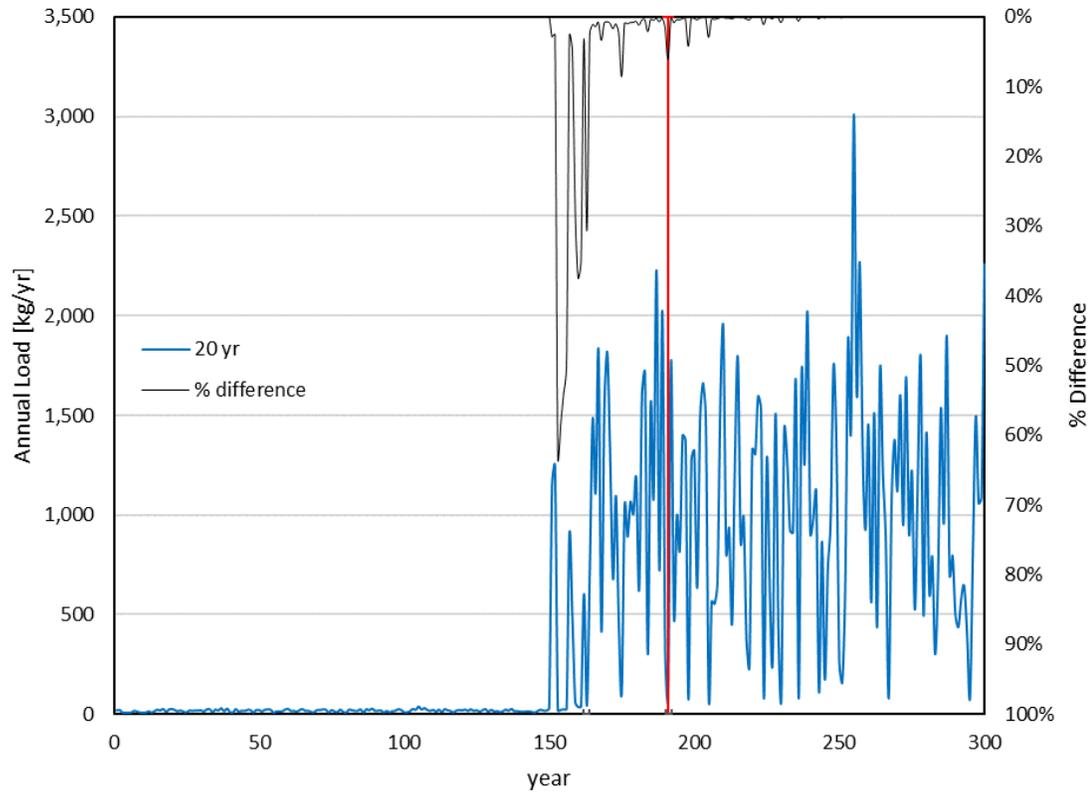


Figure 1.7: Simulated annual stream load for a watershed comprised of a single unit field and 20-year transit time. An abrupt change occurs at year 150 from 100% natural to 100% agricultural with no conservation practices. The left vertical axis corresponds to stream load on the bottom of the figure. The right vertical axis corresponds to the percent difference in stream load (between the stream load for the 20-year groundwater transit time and the stream load for the 0-year groundwater transit time, both of which are also shown in figure 1.4) and is the top line in the figure. The vertical line year ~191 shows a drought year.

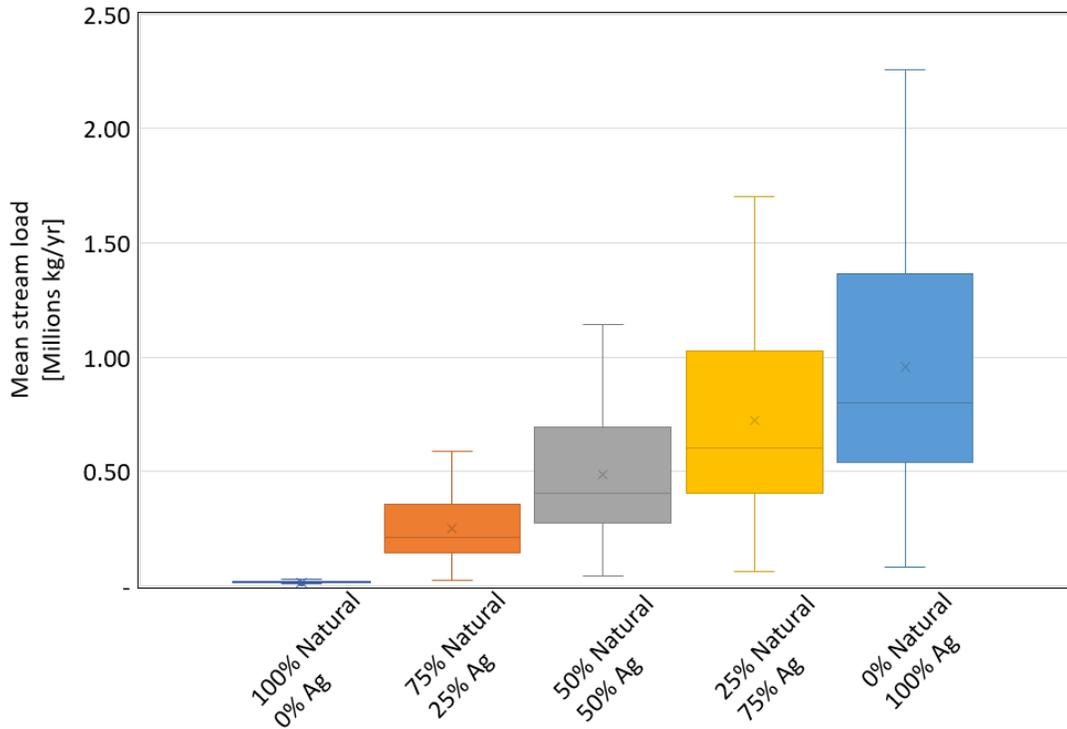


Figure 1.8: Mean stream loads for a modeled watershed comprised of 1,000 unit fields with the type of cover as indicated. Unit fields not in a natural state are agricultural with no conservation practices. Each scenario has an identical precipitation pattern with  $1.0 \pm 0.2$  m/yr, and a groundwater transit time of 20 years. Data was taken when the model was at steady state from years 272-300.

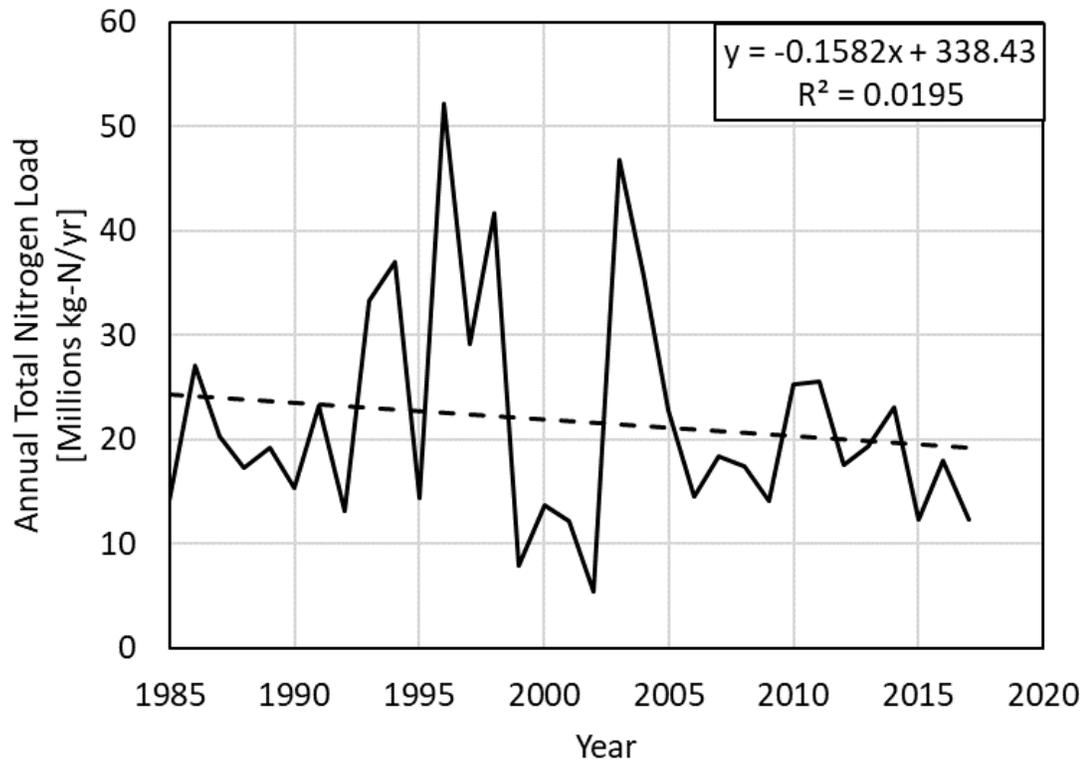


Figure 1.9: Observed annual mean total nitrogen load in the Potomac River from 1985 to 2017 (USGS Water Resources). Data shows an overall decreasing nitrogen load, as shown by the trend line.

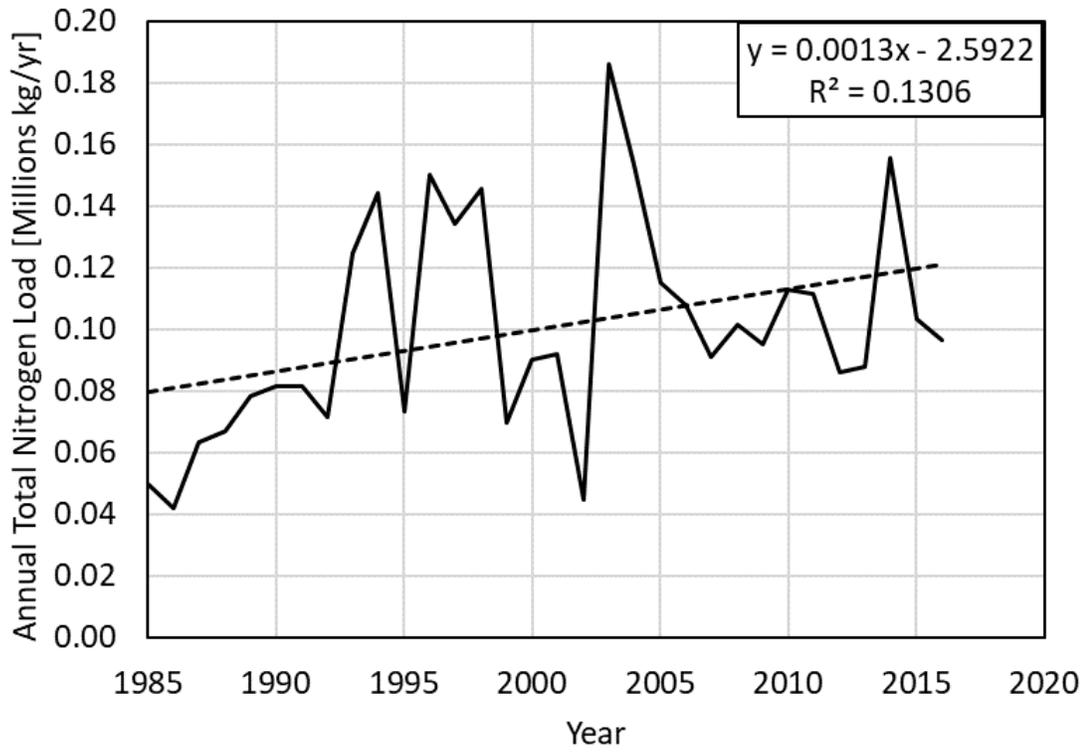


Figure 1.10: Observed annual mean total nitrogen load in Difficult Run from 1985 to 2017(USGS Water Resources). Data shows an overall increasing nitrogen load, as shown by the trend line.

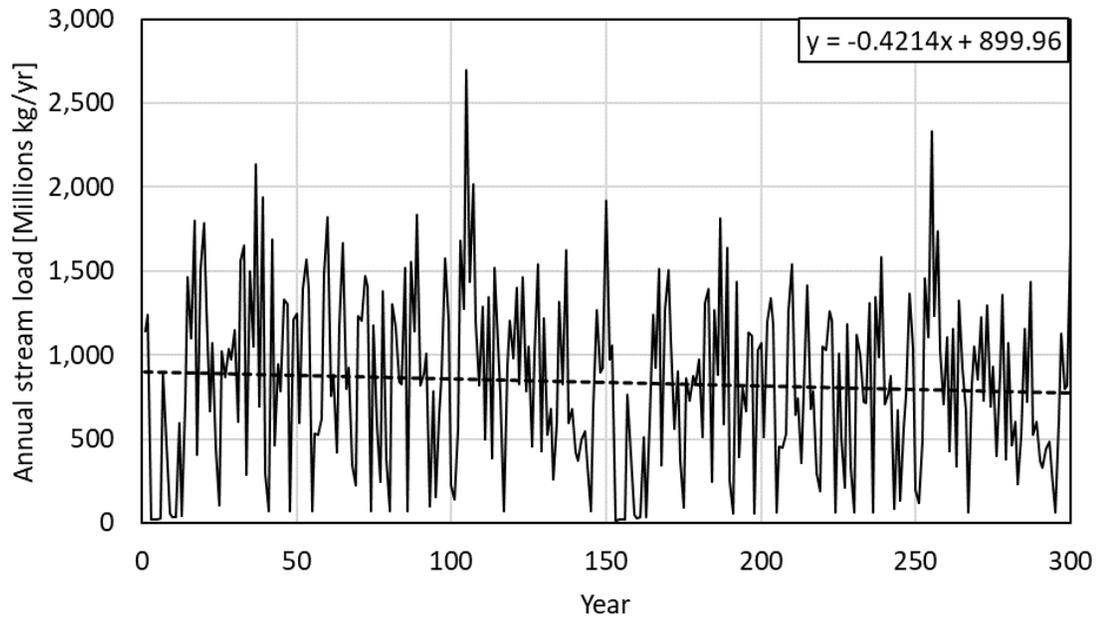


Figure 1.11: Model year 1 starts with a watershed comprised of 1,000 unit fields in agriculture. At random intervals a fraction of the land was converted to agriculture with conservation practices. By the end of the 300-year model run the stream load has been reduced by 25% by changing the land management of 750 unit fields to Ag with 30% efficiency and 250 unit fields to Ag with 10% efficiency.

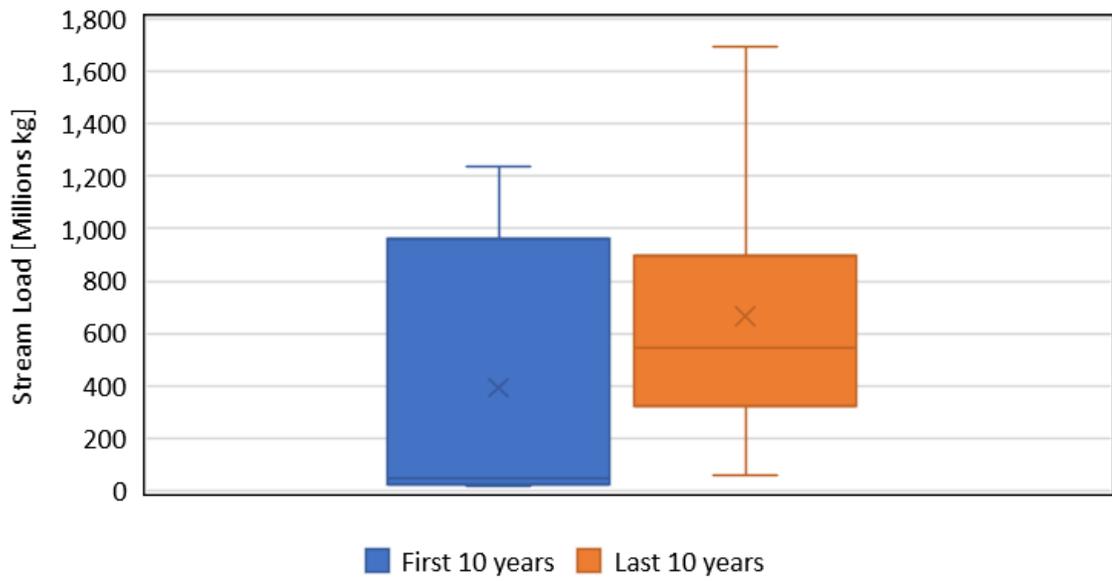


Figure 1.12: Box and whisker plot of the first 10 years (left) of the model and the last 10 years (right).

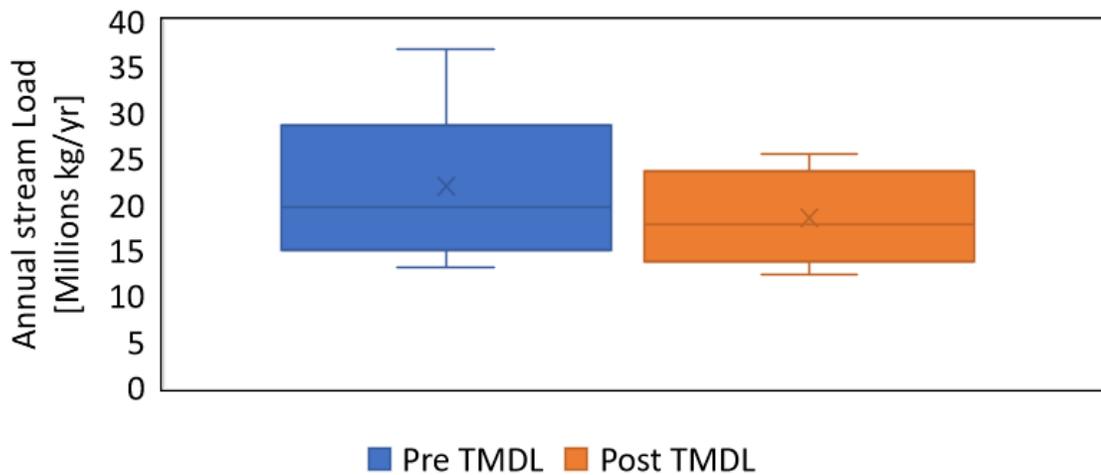


Figure 1.13: Box and whisker plot for the total nitrogen load in the Potomac River. Pre-TMDL (left) was data from the years 1985-1994 and are prior to the implementation of the TMDL. Post-TMDL (right) was data from the years 2006-2015. P-value of the pre-TMDL data was 0.02 and the p-value of the post-TMDL data was 1.0.

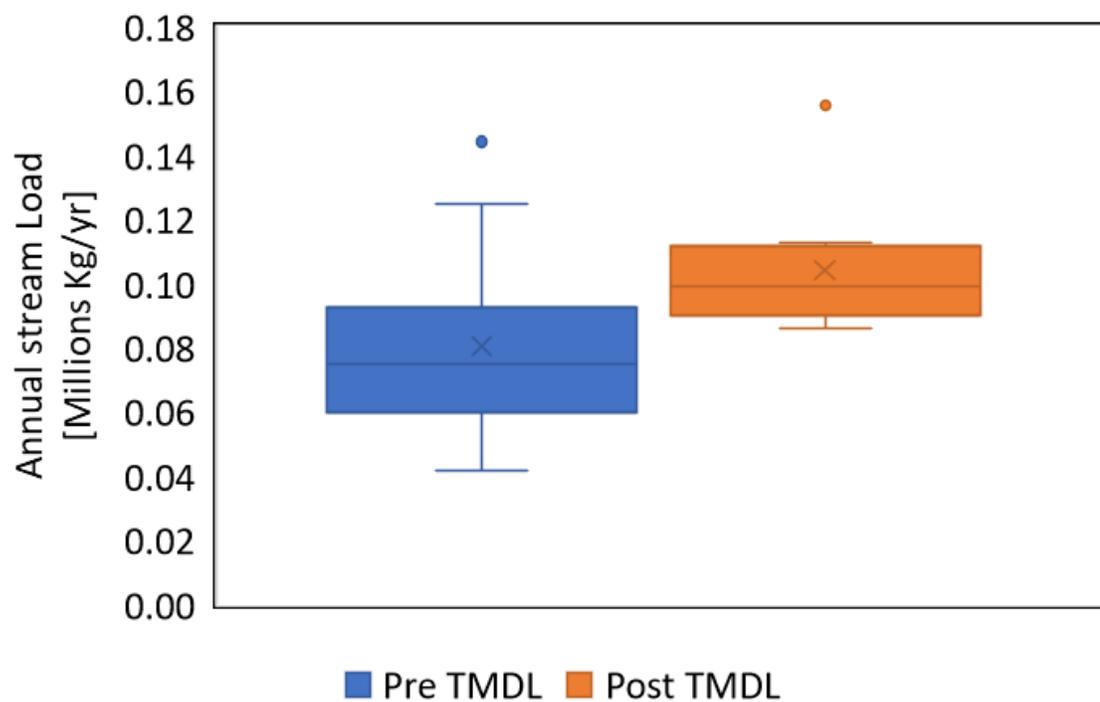


Figure 1.14: Box and whisker plot for the total nitrogen load in the Difficult Run. Pre-TMDL was data from the years 1985-1994 and are prior to the implementation of the TMDLs. Post-TMDL was data from the years 2006-2015. P-value of the pre-TMDL data was 0.02 and the p-value for the post-TMDL data was 1.0.

## Chapter 1 tables

Table 1.1: Historic precipitation data for the years from 1950-2010 for the Chesapeake Bay region over four watersheds are presented below. Average monthly data per watershed was provided by the USGS (NOAA) and annual mean, standard deviation, and relative standard deviation of that data was calculated.

	<b>Mean Annual Precipitation [m/yr]</b>	<b>Standard Deviation Annual Precipitation [m/yr]</b>	<b>Relative Standard Deviation [%]</b>
Upper Chesapeake	1.112	0.031	2.78
Lower Chesapeake	1.108	0.031	2.83
Potomac	1.024	0.029	2.83
Susquehanna	1.037	0.026	2.47

Table 1.2: Historic flow data for selected rivers within the Chesapeake Bay watershed taken from USGS (USGS Water Resources) was presented below. Periods of record for stream flow data range from 1891 to 2017. Average yearly values were used to calculate the mean, standard deviation, and relative standard deviation for each river.

<b>River – USGS Site #</b>	<b>Watershed Area [km<sup>2</sup>]</b>	<b>Mean Discharge [m<sup>3</sup>/s]</b>	<b>Standard Deviation Annual Discharge [m<sup>3</sup>/s]</b>	<b>Relative Standard Deviation [%]</b>
Susquehanna – 01570500	62,392	371.6	195.2	52.5
Potomac– 01646500	29,927	319.4	111.6	34.9
James– 02037500	17,483	194.2	70.2	36.1
Shenandoah – 01636500	7,873	75.9	27.5	36.2
Nanticoke – 02598000	195	2.6	0.9	34.6
Pocomoke – 01485000	157	2.1	0.8	38.1

Table 1.3: Observed annual total nitrogen in given streams for the time period between 1985-2016 with calculated standard deviation and RSD (USGS Water Data).

<b>Stream name</b>	<b>Mean annual TN load [Millions kg-N/yr]</b>	<b>Standard deviation [Millions kg-N/yr]</b>	<b>RSD [%]</b>
Potomac River	21.8	11.0	50.3%
Conococheague River	2.4	1.1	44.6%
Difficult Run	0.1	0.0	39.7%

Table 1.4: Fixed concentrations of C found in runoff and recharge.

<b>Land use</b>	<b>Conc. in runoff [mg/L]</b>	<b>Conc. in recharge [mg/L]</b>
Natural	0.2	0.2
Agricultural	20.0	2.0
Ag. with 10% removal	18	1.8
Ag. with 30% removal	14	1.4

**2 Modeling the effects of change of land use, land management, and climate on the annual export of nitrogen from a watershed: A unit field to watershed approach**

## **2.1 CHAPTER 2 SYNOPSIS**

Increasing concern over excess nutrients and impairment related to nutrient pollution has led to the implementation of Total Maximum Daily Loads in many watersheds throughout the United States. The Chesapeake Bay Watershed is one such watershed with full implementation of measures to meet the TMDL due by 2025. One of the main criteria of the TMDL is a reduction of 25% of the total nitrogen load. To meet this goal both point and non-point sources of nitrogen have to be mitigated. To understand the various approaches to reduce non-point sources of nitrogen, ArcAPEX for annual field-scale water and nitrogen budgets, was combined with a simple lumped parameter model in R to capture groundwater discharge to a stream. Analysis found that many BMPs are effective at reducing nitrogen but reaching the 25% reduction through any one avenue may be difficult. As urban areas expand the overall nitrogen load tends to decrease due to decreasing agriculture.

## **2.2 INTRODUCTION**

There has been increasing concern over excess nutrients (phosphorus and nitrogen) in both freshwater and coastal water systems. Both nutrients are needed for life, but when present at elevated levels in water systems they can cause eutrophication (Schindler, 2006), which impairs water systems by causing excessive plant and algal growth (Chislock, 2013). As the plant and algae die, they decay. As the microbial life feed and grow, they consume oxygen. The oxygen demand can become so high that the microbes deplete all available dissolved oxygen and create what was known as a “dead zone” where organisms that respire oxygen can no longer survive. A 2008 study found that, worldwide, marine dead zones affect an area of more than 245,000 square kilometers (Diaz, 2008). Some algal blooms can also release hazardous toxins (Harmful Algal Blooms or HABs) that can kill animals and cause illness in people, such as blue-green algae in freshwater systems and red-tide organisms in marine environments (Paerl, 1988). Eutrophication and HABs cost the U.S. approximately \$2.2 billion (2010 dollars) annually (Dodds, 2009) and coastal HABs cost the U.S. about \$50 million (2000 dollars) annually (Anderson, 2000) through impacts to public health, fisheries, tourism, the cost to monitor and manage them.

Algal blooms occur in both freshwater and marine environments; however, the nutrient responsible for the bloom was usually different. When the limiting nutrient, the nutrient that was typically present in the lowest levels relative to organism’s needs, was increased it can result in an excessively large bloom. In freshwater systems, phosphorus was typically the limiting nutrient (Schindler, 2006), while nitrogen was usually the limiting nutrient in marine and coastal waters (Goldman, 1976). Since freshwater systems, lakes and rivers, end up discharging to coastal

waters, it was crucial to reduce both nitrogen and phosphorus. To reduce nutrient-impaired waters, steps have been taken to reduce the amount of nutrients reaching those waters.

Inputs to the environment from humans are split into two categories: point and nonpoint sources. Point sources are often characterized by the ability to identify the exact discharge point, such as wastewater treatment plants (WWTPs). Nonpoint sources do not have an exact discharge point, such as runoff to a field, groundwater discharge to a stream, or atmospheric deposition to surface waters.

Since modeling efforts for this study focused on the Chesapeake Bay region, which was a coastal water system, and WWTPs are already regulated and monitored, the rest of this report will focus on nonpoint sources of nitrogen.

While nitrogen occurs naturally, humans have caused nitrogen levels to rise above historic amounts. The primary anthropogenic source of nitrogen was from the agricultural industry where nitrogen application rates have gone from 2.2 kg-N/ha/yr in 1940 to 90.4 kg-N/ha/yr in 2015. The total nitrogen used in agriculture was less than 1 Tg-N/yr (1 million metric tons annually) before 1950 and rose to more than 11 Tg-N/yr (11 million metric tons annually) in the 21<sup>st</sup> century (Cao, 2018). Residential nitrogen use was not as well tracked, but a study found a mean application rate for residential areas of 97.6 kg-N/ha/yr (Law, 2004). According to 2012 USDA estimates there were 28.3 million hectares (69.9 million acres) of urban land (USDA, 2012). Assuming the mean nitrogen application rate was uniform across all urban land results in a total of 2.8 million metric tons applied in urban landscapes across the U.S. Due to the amount of both phosphorus and nitrogen in urban runoff, it was considered the third most important cause of lake deterioration in the U.S. (Carpenter, 1998).

After application, nitrogen was ideally taken up by plants, but may leave the system in runoff or in the recharge to groundwater. If nitrogen was exported from the land surface it most often reaches surface waters where it can cause impairment (figure 2.1).

Generally, water runoff is observed during, or immediately following, a precipitation event, whereas a response in the baseflow due to the recharge takes more time. Water must percolate through the root and vadose zones before reaching the water table and contributing to groundwater, where it slowly travels to some discharge point. The groundwater has some amount of transit time before being discharged to the stream as baseflow. As seen in figure 2.2, the age of the groundwater can vary greatly.

Urban landscapes with impervious surfaces have a drastically different hydrology than do vegetated landscapes. A review of urban hydrology indicates that recharge to groundwater decreases while runoff, total discharge, and nitrogen export all tend to increase (Scott, 2016). The increased water and nitrogen movement out of the unit field was due to a decrease in hydraulic conductivity vertically from the surface down and a smoothing of the land surface so that water flows horizontally more readily. Increasing opportunities for water to infiltrate can combat runoff and nitrogen losses in the urban landscape. It was found that incorporating permeable pavement would result in only 4 mm of runoff from a 121 mm rainfall event (Scott, 2016). Rain gardens may also be implemented to further improve recharge off impervious surfaces.

There are a multitude of approaches to improving water quality and mitigating nitrogen loss in agriculture, these are commonly referred to as Best Management Practices (BMPs). Buffer (or filter) strips are permanent vegetated strips of land between crops and streams or wetlands and serve a couple of purposes. They increase recharge by slowing the velocity of water, allowing more time for recharge to occur (Norris, 1993), and by increasing vertical conduits through which water and nutrients may travel downward more rapidly (Devlin, 2009). Buffer strips can reduce nitrogen in subsurface flow and groundwater when there was flow through the root zone by plant uptake, which may also increase denitrification (Wortmann, 2013). Buffer strips may be comprised of either grassland, riparian, or a combination of the two. A meta-analysis of buffer zones found that they remove 70% of  $\text{NO}_3\text{-N}$  in groundwater, 33% of  $\text{NO}_3\text{-N}$  in runoff, and 57% of total nitrogen (TN) in runoff (Valkama, 2019). The meta-analysis also found that denitrification in riparian zones was between 9-70 kg-N/ha/yr (Valkama, 2019) while a different study showed that riparian buffer zones experienced denitrification rates of 9-200 kg-N/ha/yr and grass buffers a rate of 1.2-32 kg-N/ha/yr (Hefting, 1998).

No-till practices are increasing in popularity as it potentially leads to decreases in erosion and soil loss (Daryanto, 2017). However no-till increases macropores and the vertical movement of water and dissolved nutrients (Devlin, 2009). A meta-analysis found that no-till results in an increase in  $\text{NO}_3^-$  load to groundwater, even though the  $\text{NO}_3^-$  concentration remains about the (Daryanto, 2017). The study asserts that the increase in load was due to an increase in water flux downward and implementing a cover crop in addition to no-till practices would help reduce nitrogen losses (Daryanto, 2017).

Cover crops can reduce nitrate in soil water and nitrate leaching to groundwater, along with trap sediment and prevent erosion (Wortmann, 2013). The use of cover crops allows for the retention

of nitrogen as the cover crop uptakes nitrogen in the root zone and assimilates it, then slowly releases it as organic nitrogen as it decays (White, 2017).

Reduction in use of fertilizer inherently decreases nitrogen lost from the land surface. Testing soil nitrogen or plant chlorophyll can help determine whether fertilizer is needed and how much is needed (Waskom, 1996). Subsurface drainage refers to fields with artificial drainage systems that help drain the field of excess moisture and discharge to a nearby stream. As a result of subsurface drainage there was usually less runoff and nitrogen carried in runoff. It also reduces nitrate leaching as the recharge water was intercepted before it reaches groundwater. Subsurface drainage however provides an accelerated mode of transport for water and nitrogen to local surface water (Wortmann, 2013).

Climate is important to consider for planning of water resources into the future as changes in temperature and precipitation affect the hydrologic cycle. Depending on region, climate change is expected to decrease runoff and recharge in currently water stressed regions while increasing runoff and recharge in wetter regions (Kundzewicz, 2008). As temperatures increase in the winter, precipitation type may also change and alter the times of peak flow (Kundzewicz, 2008)

Due to the complexity and interconnectedness of the hydrologic and nitrogen cycles, a model was needed to realistically estimate fluxes through the system. Several pre-existing models meet the requirements of being able to model both the hydrological and nitrogen cycle. SWAT, Soil and Water Assessment Tool, is a watershed model developed by the USDA and Texas A&M. SWAT is capable of simulating surface and groundwater quality and volumes from a small watershed up to river-basin scale (USDA SWAT). APEX, Agricultural Policy/Environmental eXtender, was also developed by the USDA for the field scale, modeling water, sediment, nutrients, and pesticides. For this study APEX was chosen for a couple of reasons. Changes in land use do not occur simultaneously across a watershed, but rather at a field level – a single farmer, or maybe a couple of farmers, may choose to implement a BMP in any specific year. When comparing water quality and quantity from one land use to another, with all other variables kept constant, results from an entire watershed are not needed and may contain too much information. For those reasons it was decided that APEX would be used to model the activity on the landscape. APEX does not model groundwater flow however, only recharge to groundwater, so groundwater discharge to the stream would have to be modeled separately.

The purpose of this work was to compare the relative nitrogen exports from a simple, multi-land use model watershed. Given the wide range of management decisions available, the question

arises of which are the most and least important management decisions in terms of water quality as it relates to nitrogen. By quantifying the relative importance of various land management practices and environmental factors on nitrogen export from a watershed, it was hoped that the most important drivers of change to the nitrogen load exported from a watershed could be identified. This would allow for the most effective conservation practices to be emphasized in future planning of land management within the watershed in order to best improve water quality. A computer model was used to simulate water and nitrogen export from a unit field on a daily timestep, aggregated to an annual timestep, under various land uses and managements using APEX. A program in R was created that consolidated the annual mean hydrologic and nitrogen components into a single file for each scenario. The R program then used a lumped-parameter model to simulate groundwater flow to a stream where it, along with the runoff, contributed to streamflow. The nitrogen in the recharge and runoff was routed along with the water and a total budget was created. This study included the effects of buffer strips, no-tillage practices, and cover crops. Also considered were source reduction (reduction of nitrogen application), installation of subsurface drainage, and variations in climate. As an example of how the model could be used, a simulated watershed was initiated in 1850 with natural land use and followed a development path similar to what may have been observed historically in Minnesota, starting as a mix of forest and wetland, transitioning to agricultural, then urbanization. It was then modeled into the future to demonstrate possible directions the watershed could go and how those different paths might affect water quality.

## 2.3 METHODS

### 2.3.1 ArcAPEX

APEX (APEX 2018), Agricultural Policy/Environmental eXtender model, was used for the surface modeling portion of this experiment. APEX models water, sediment, nutrients, and pesticides at the small watershed or single field level. ArcAPEX was accessed via the APEX website (APEX 2018) on 01 June 2018. ArcAPEX version 10.3.2 was downloaded for use with APEX version 1501 and with ArcMaps 10.3.3 for modeling nitrogen export under various conditions presented in table 2.4. After installation of the default APEX program, additional steps were required to simulate soil and weather local to the Delmarva Peninsula in Maryland.

### 2.3.2 Location and soil

The Chesapeake Bay watershed was the area of interest for this study. ArcGIS was used to delineate a standard unit field near the town of Bridgeville, Delaware, with the watershed outlet located at 38.776635 N, 75.580252 W (figure 2.3). This field was chosen for this study because it was near a USGS well which provided information on soil, aquifer, and groundwater properties. The predominant soil type was Woodstown, a sandy loam soil. The delineation performed by ArcGIS resulted in a total field size of 13.21 hectares, or 32.64 acres. The field was split into two subareas, in case separate land uses within the same field were desired. A request was made to the APEX model developers for a soil file for Woodstown, which they created for us from STATSGO (NRCS, 2018). An overview of the soil properties used can be found in table 2.1. These properties were retrieved from the Microsoft Access file created for the model.

### 2.3.3 Weather

A local weather profile was needed to model the Chesapeake Bay region in APEX. Observed daily temperature and precipitation data for Salisbury Wicomico Regional Airport, located at 38.341574 N and 75.512370 W, in Salisbury, Maryland was used to build the weather profile for the APEX model. This location was chosen due to its proximity to the site and completeness of the data. The daily maximum and minimum temperature, along with precipitation, were retrieved for the Salisbury Regional Airport from the NOAA website<sup>[weather]</sup> for the years 1948-2017. The weather data was then used to create a 28-year normal with a daily timestep from the years 1961 - 1988. A timespan of 28 years was used to account for leap years in modeling. From there the data was repeated six times to create a weather profile of 168 years.

### 2.3.4 Model Scenarios

Default parameters for the various land uses under consideration were used unless specified in appendix A.1. Different land uses considered for modeling were agriculture, various vegetation

not requiring annual plowing and planting (perennial plantings), and urban scenarios. Agricultural land management of these land uses consisted of convention till (CT), no till (NT), no nitrogen application (no N), recommend nitrogen application rates (recom. N), 80% or 90% of the APEX model recommended nitrogen application rates (80% or 90% N), no implementation of Best Management Practices (no BMPs), implementation of a buffer strip (10m Grass Buffer), use of rye or red clover as a cover crop (CC rye/red clover), and presence of subsurface drainage in the field (Tile drainage).

Changes in climate were also considered where increases in temperature and precipitation were modeled. Increases were relative to the 28-year normal used as the basis for the standard weather. They are denoted in table 2.4 and 2.8 by T10 representing a 10% increase in daily maximum temperature and a 5% increase in daily minimum temperature, T20 represents a 20% increase in daily maximum temperature and a 10% increase in daily minimum temperature. In addition to temperature increases, increases in precipitation were also considered. P03 represents a 3% increase in annual precipitation and P06 a 6% increase in annual precipitation. The increases were applied three different ways. P03/06 without a suffix indicates the precipitation was increased uniformly throughout the whole year. A *S* suffix indicates the increase happened in one, single event per year, with the date of that event corresponding to a real historic event (table 2.2) and applied randomly, one per year, to the weather set. The four historic precipitation events were chosen because they were some of the largest on record. A *W* suffix indicates most of the increase in precipitation occurs during the winter months from December to March. Increases in temperature and precipitation were achieved by multiplying the existing weather data by a factor so that mean annual maximum temperature, mean annual minimum temperature, and mean annual precipitation increased to the desired amount. Equation 1 below was used to manipulate the weather data and multiplication factors are given in table 2.3.

$$\text{New weather parameter} = \text{Old weather parameter} + \text{Absolute}(\text{old weather parameter}) * \text{factor} \quad \text{Eq. 1}$$

When creating the future weather scenarios, in the event a temperature was 0° it was changed to 0.01° so that the factor for equation 1 would change the temperature and not result in 0°.

### 2.3.5 APEX model output

ArcAPEX operates on a daily timestep and outputs the results in both a Microsoft Access Database and several output files that can be read using a standard text reader such as Notepad. All files can be found in the TxtInOut folder for each individual scenario. After all the model runs, the mean annual hydrologic and nitrogen components were consolidated from these different files into one CSV file. To do this, a water and nitrogen budget were created and their counterparts within APEX were identified. The tables 2.5t and 2.6 show the budget components, their APEX names, and the file in which they were found. The water budget was then determined to be

$$\begin{aligned}
 \textit{Precipitation} + \textit{Irrigation} = & \textit{Evapotranspiration} + \textit{Groundwater recharge} + \textit{Runoff} + \\
 & \textit{Shallow flow to stream} + \textit{Tile drainage}
 \end{aligned}
 \tag{Eq. 2}$$

The water budget (eq. 2) in APEX terms was then

$$\textit{PRCP} + \textit{IRGA} = \textit{ET} + \textit{PRK} + \textit{Q} + \textit{RSSF} + \textit{QDR}
 \tag{Eq. 3}$$

While the nitrogen budget was determined to be

$$\begin{aligned}
 \textit{Total soil N pool} + \textit{NO}_3^- - \textit{N in root zone} + \textit{NH}_3 - \textit{N in root zone} = & \textit{N fertilizer applied} + \textit{N fixation} - (\textit{N in runoff} + \textit{N in gw recharge} + \\
 \textit{N in drain flow} + \textit{N in crop yield} + \textit{Denitrification} + \textit{N in shallow flow} + & \textit{N volatilization})
 \end{aligned}
 \tag{Eq. 4}$$

The nitrogen budget (eq. 4) in APEX terms was then

$$\begin{aligned}
 \textit{WON} + \textit{ZNMN} + \textit{ZNMA} = & \textit{FN} + \textit{NFIK} - (\textit{QN} + \textit{PRKN} + \textit{QDRN} + \textit{YLDN} + \textit{DN} + \textit{RSFN} + \textit{AVOL})
 \end{aligned}
 \tag{Eq. 5}$$

An R script was then created to find each variable, in their respective file, combine them as indicated in table 2.7, then save the budget components in a CSV file (appendix A.4). There were a total of 13 sets of annual data retrieved from APEX and were recorded in table 2.7.

### 2.3.6 Watershed model with R

A program in R (appendix A.5), which will be referenced as R\_watershed, was then used to assemble a simulated watershed. After simulation of all scenarios in APEX and the summarizing of the water yields and nitrogen loads, R\_watershed took user input to create a watershed by first asking for the number of unit fields (watershed size) and distribution of land uses (composition). It then creates the groundwater portion of the model by using the recharge from APEX as the input and routing that to the stream as discharge using the lumped-parameter model (LPM) described in Chapter 2. The LPM follows an exponential distribution and created a lag between groundwater recharge and discharge, giving the groundwater some amount of transit time. The groundwater discharge was thus a distribution of current and previous year's groundwater recharge. R\_watershed then added the groundwater discharge to the stream, analogous to baseflow, to the current year's runoff, creating the total streamflow.

Every hydrologic component has a corresponding nitrogen component, R\_watershed routes the hydrologic and nitrogen components together. The output of the model was an annual timestep of the streamflow, nitrogen load in the stream, and nitrogen concentration in the stream. These values are then saved in a CSV file along with the watershed characteristics: size, composition, and mean groundwater transit time.

## 2.4 RESULTS

### 2.4.1 Results of the unit field model with APEX

Results of the APEX model scenarios (table 2.8) show that land use and land management strongly influence annual yields of water and nitrogen from the unit field. Results are grouped by crop type or land use: soybean scenarios, corn scenarios, changes in weather, wheat scenarios, perennial vegetation, and urban scenarios. For each different crop, the standard crop scenario (i.e. corn with conventional tillage, recommended nitrogen application, no BMPs, and historical weather) was listed first with variations in land management following. If a crop scenario has a buffer strip, that buffer strip was added to a field with conventional tillage, recommended amount of nitrogen applied, no other BMPs, and historical weather. Different land managements considered included no till instead of conventional tillage practices, reducing the amount of nitrogen applied to 80-90% of recommended application rates, incorporating cover crops such as red clover and rye, implementing a buffer strip, and adding subsurface drainage to the field. The changes in weather were considered only for the standard scenario.

Changes in the nitrogen load of the stream, relative to the standard corn scenario (conventional tillage, recommended nitrogen application, no BMPs, and historical weather), are plotted in figure 2.4. It shows that impervious land uses and perennial vegetation give lower nitrogen loads in the stream. In agriculture, many BMPs lead to a reduction in nitrogen load for all crops considered. Projected increases in temperature and precipitation led to an increase in nitrogen load of the stream.

### 2.4.2 Results of the watershed modeled with R

One of the critical steps in building the watershed in R was creating a transit time for the groundwater, or groundwater lag. This can be seen in a hypothetical scenario (figure 2.5) where the groundwater recharge and nitrogen concentration in the scenario are fixed. The areal recharge rate was set to 0.25 m of precipitation depth over an area of 16 hectares, for a total volume of  $4 \times 10^7$  L. At a specific year during the model, year 150, a change in the nitrogen concentration in the recharge from 2 to 20 mg/L occurred to simulate a change in land use. As seen in figure 2.5, if the groundwater transit time were 0 years (no lag), any change to land use or management would be observed immediately in the groundwater. As the transit time increases, more time was required to observe the full magnitude of any change and more time was needed to reach the new steady state. A period of 4-5 times the transit time was required to reach steady state. This lag in transit time adds another degree of uncertainty when variations in weather, land use, and land management are considered.

Nitrogen export from a watershed with uniform composition was shown (figure 2.5) as an example of the R program's output. There are several factors responsible in the variations observed. The variability in weather was responsible for most of the year-to-year variation and was on a 28-year cycle, resulting in an observable pattern. The pattern repeats, but the magnitude of the load decreases, for example the double peak at years 38 and 40 was also observed in years 66 and 68, but the load was less. This was a result of the APEX model moving towards a steady state, evident in the last three 28-year cycles which experience much less variation between cycles. Finally, there was variation due to the groundwater. Years that experience more recharge also experience a greater nitrogen load to the groundwater, resulting in more nitrogen discharged in the following years, which creates a leveling effect. For these reasons, data from only the last 28-year cycle, for any given watershed, was used in calculations.

## 2.5 DISCUSSION

### 2.5.1 Insights from the unit fields

Land use affects both the overall nitrogen load in the stream and the partitioning of nitrogen between runoff and recharge. A comparison of corn with different tillage, nitrogen application rate, and BMPs (figure 2.6) shows how they change for a single crop. The standard scenario of corn with conventional tillage and recommended nitrogen application rates, no BMPs, and historic weather has a mean annual nitrogen yield of about 16 kg-N/ha, with 38% of that from groundwater discharge to the stream. The next scenario in the figure is a change from conventional till to no till which results in an increase in overall nitrogen load and a decrease in the relative amount of nitrogen due to groundwater. The scenario with red clover cover crop was the only other situation in which there was an increase in the annual nitrogen yield. This was actually determined to be a result of the APEX model not accounting for the decreased need of nitrogen fertilizer due to the nitrogen fixed by the clover, resulting in over-application of nitrogen.

Changes in nitrogen load based on local weather show that with anticipated increases due to climate change that nitrogen loads will likely increase as well. Increases are predominantly due to increases in precipitation. Just a 3% increase in precipitation (~32 mm of rainfall) will result in a yearly increase of about 5 kg-N/ha. When comparing a 3% increase in precipitation to a 6% increase, it becomes evident that the timing of the precipitation event is a major factor. When the precipitation is uniformly increased (scenario 5 of figure 2.7), more nitrogen was exported from the unit field than when the increased precipitation occurs in a single large event occurring in the autumn months (scenario 6 of figure 2.7). This makes conceptual sense as more frequent large rain events are more likely to export recently applied nitrogen while a single large event likely does not coincide with recent nitrogen application.

There was considerably more variation in the annual load at the start of the model (figure 2.5) than in later years. Examining the individual contributions to the stream, it was apparent that the change in nitrogen load between the 28 years cycles was due to a change in the nitrogen load in the recharge (figure 2.8). After analyzing various nitrogen components within APEX, it determined that this high nitrogen load was from various nitrogen storage components of the soil in APEX.

Figure 2.9 shows a scenario of deciduous forest with only natural sources and losses of nitrogen. APEX reaches steady state with respect to nitrogen reserves in about three 28-year cycles, or 84 years. But an agriculture scenario shows the model has a bit more difficulty reaching steady state

(figure 2.10). While the nitrogen storage for a unit field in corn does not appear to asymptote like the storage for a forested unit field, the trendline for figure 2.10 suggests that the nitrogen storage for the last 28 year cycle for this agricultural scenario was very nearly at steady state and, therefore, the nitrogen in the groundwater recharge at the end of the model run is due to land use and land management, and not due to any time lags within APEX.

#### 2.5.2 Insights from the extent of change in watersheds

As the size of the model is scaled up, going from a single unit field to a watershed comprised of 1,000 unit fields, the variety of land management within the watershed increases. The effects of changes in the watershed:land use, crops, management, and climate on the stream load are shown in figure 2.11. Plotted is the mean of the last 28-years of model run for each scenario. Shown is changes from 100% of the 1,000 unit fields in the standard corn scenario (conventional tillage, recommended nitrogen application rate, no BMPs, and historical weather) to 100% of the 1,000 unit fields in the indicated land use and management style.

When considering the TMDL for the Chesapeake Bay Watershed, there are a few land management options that would bring about the required 25% decrease in nitrogen load. Rye cover crop or a nitrogen application rate of 80% of the recommended application rate have similar performances and would require implementation of 50% in an all-corn watershed to achieve the desired reduction in nitrogen. Reducing the nitrogen application rate to 90% of recommended or adding a buffer strip would require 80% and 90% adoption, respectively, throughout an all-corn watershed. As stated before, converting to no till with no additional BMPs would actually increase the overall nitrogen load by more than 50,000 kg-N/yr. Also adding subsurface drainage to a field increases the nitrogen load as results from 100% of the unit fields with subsurface drainage shows. Changing crops, from corn to wheat or soybean, results in an increase in nitrogen load. Similar trends are seen when buffers and rye cover crops are implemented with wheat and soybeans (table 2.8).

Changing land uses throughout the watershed decreases the nitrogen load, an observation that suggest that agriculture is the largest contributor of nitrogen to the environment. Watersheds with 100% urban composition have between 20-25% the total nitrogen load. This is likely a result from the fact that impervious areas receive considerably less fertilizer and does not present a realistic scenario as there has to exist some amount of agriculture to sustain populations. Moving to a watershed with 100% CRP, either wetland or forest shows what could be considered the historic nitrogen load for the watershed, about 30,000 kg-N/yr.

### 2.5.3 Example application of the modeling tool

A watershed was simulated over time from the year 1850 to 2050, with changing land use and management, to replicate how a watershed may have developed in order to examine how that development has impacted nitrogen loads in streams. Table 2.9 shows how the composition (land use and management) of the watershed has changed over time.

Each simulation was run for 168 years, allowing it to reach steady-state. The mean of the last 28 years for each simulation was then calculated and this mean was the theoretical steady-state conditions for the given watershed composition. The mean was then plotted on figure 2.12 to show how the nitrogen load in a stream may have and how it may continue to change in the future.

The early composition of the watershed early was split between forest and wetland. The main source of nitrogen was atmospheric deposition at this time, resulting in relatively low nitrogen loads. As agriculture starts to take over the landscape in 1890, the forest was lost first. The primary crop at the time was corn and the only available fertilizer was in the form of manure. To help simulate this, a reduction from the recommended application rate was used. The results show an increase in the nitrogen load of this second time period, almost doubling the nitrogen load of an “natural” watershed. A similar change in land use occurs between the second and third time periods, where much of the wetland was converted to agriculture. This third time period was meant to simulate early 1900s where most of the crop was corn and wheat with limited use of fertilizer. Nitrogen inputs were limited to atmospheric deposition with some manure sources. This results in a mean nitrogen load about four times that of the pre-agricultural watershed. By the mid-1900s, simulated in the fourth time period, the landscape was dominated by agriculture with widespread chemical fertilizer use. This results in the nitrogen load of the stream increasing to more than ten times the historic levels.

As the watershed comes into the late 1900s, simulated in the fifth time period, several changes to the landscape are occurring. In unit fields with crops, there was an increase in drain tile usage. This greatly decreases the time it takes for water to reach the stream, resulting in an increase in nitrogen delivered to the stream. While drain tiles increase the nitrogen load, urbanization results in less unit fields with fertilizer application and, thus, less nitrogen input to the watershed. The net change was a decrease in total nitrogen load. As the watershed moves into the early 2000s there was an emphasis in increasing water quality. For the model, buffer strips were used to remove some of the nitrogen in the groundwater. The implementation of buffer strips in some of

the fields, along with further urbanization, resulted in further decrease of the total nitrogen load in the stream to a level six times the pre-agricultural loads.

Looking to the future, two scenarios were considered for 2040. Both anticipated further urbanization. One considered the use of buffer strips on all agricultural land to reduce nitrogen loads, while the second had no buffer strips, as a worst-case scenario. The one with buffer strips saw further reduction in nitrogen loads to levels about five times the pre-agricultural levels. The second scenario, with no buffer strips, had nitrogen loads about 40% higher than the first scenario.

#### 2.5.4 Insights into the changes in groundwater

Land use also affects how quickly both the runoff and recharge reach the stream. While runoff can be observed with results immediately readable, groundwater was not as obvious. Following the LPM, the mean groundwater transit time was calculated for each of the watershed composition scenarios considered (figure 2.13).

As large, permanent vegetation was replaced with agriculture, the mean groundwater transit time decreases. The reasons behind this may not be apparent, after all permanent vegetation was supposed to increase recharge by decreasing runoff. However large old growth forests or thick wetlands result in increased plant uptake of water and high evapotranspiration which results in decreased recharge. The mean groundwater transit time was inversely proportional to the recharge, as recharge increases the transit time decreases – conceptually as you increase the volume of water flowing through a pipe, the transit time of that water decreases. Comparing figure 2.13 to table 2.8, it was observed that forest and wetland do indeed have the least groundwater recharge. The groundwater transit time then plateaus starting during the 1980s when the watershed was almost entirely agriculture.

## Chapter 2 figures

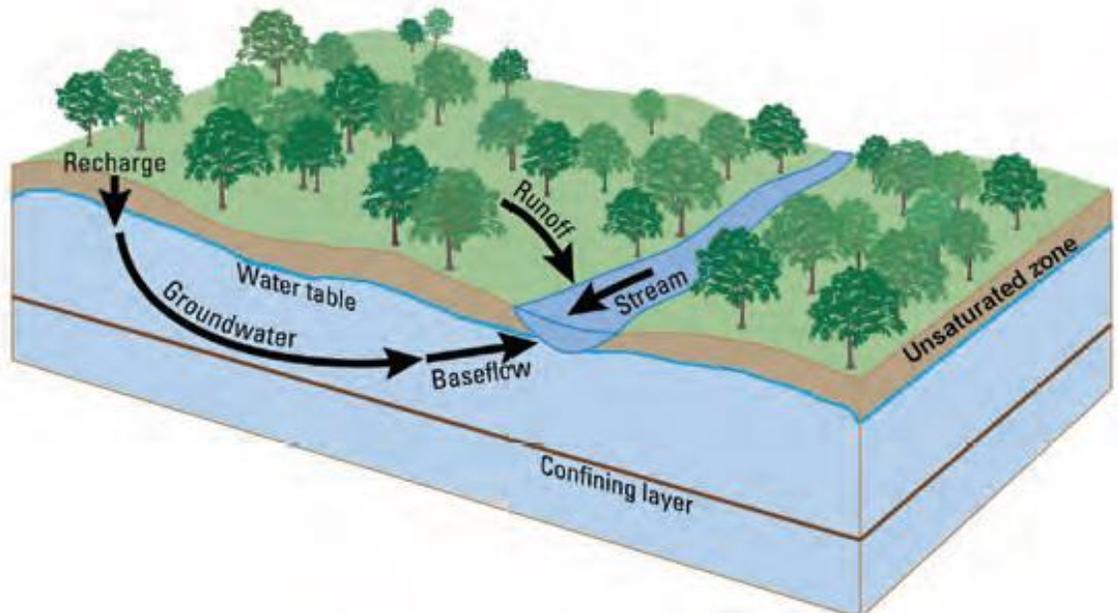


Figure 2.1: Shown was the simplified hydrology of a unit field. Water flowing on the surface of the landscape was runoff. While water that enters the aquifer as recharge eventually ends up in the stream as groundwater discharge. Nitrogen was transported by water and follows the same pathways to surface waters. Figure taken from USGS Circular 1433 (Capel et al, 2018).

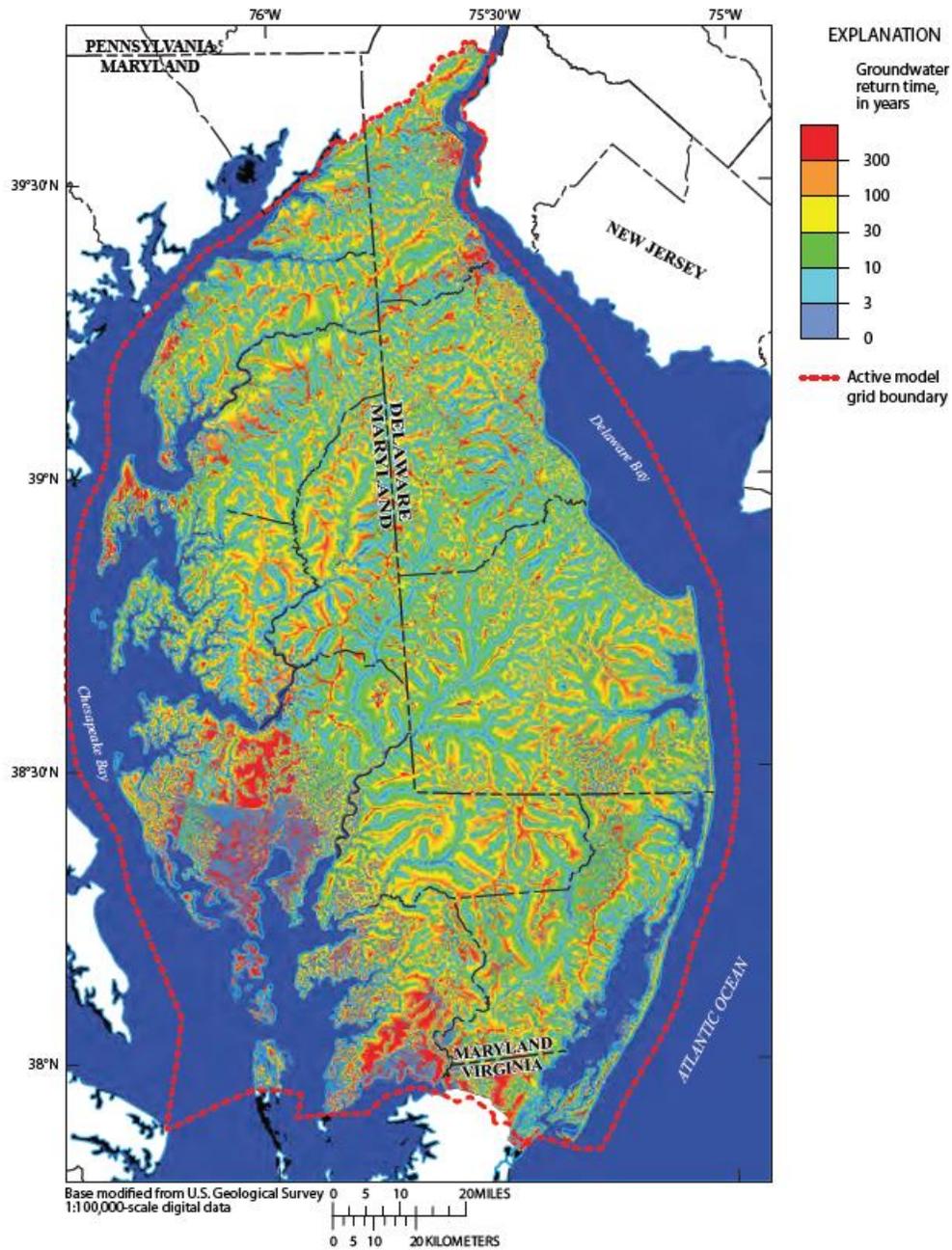


Figure 2.2: Simulated groundwater return time of water traveling from water table to discharge point. Figure is from U.S. Geological Survey (Sanford, 2012) and shows how long it may take groundwater to be discharged.

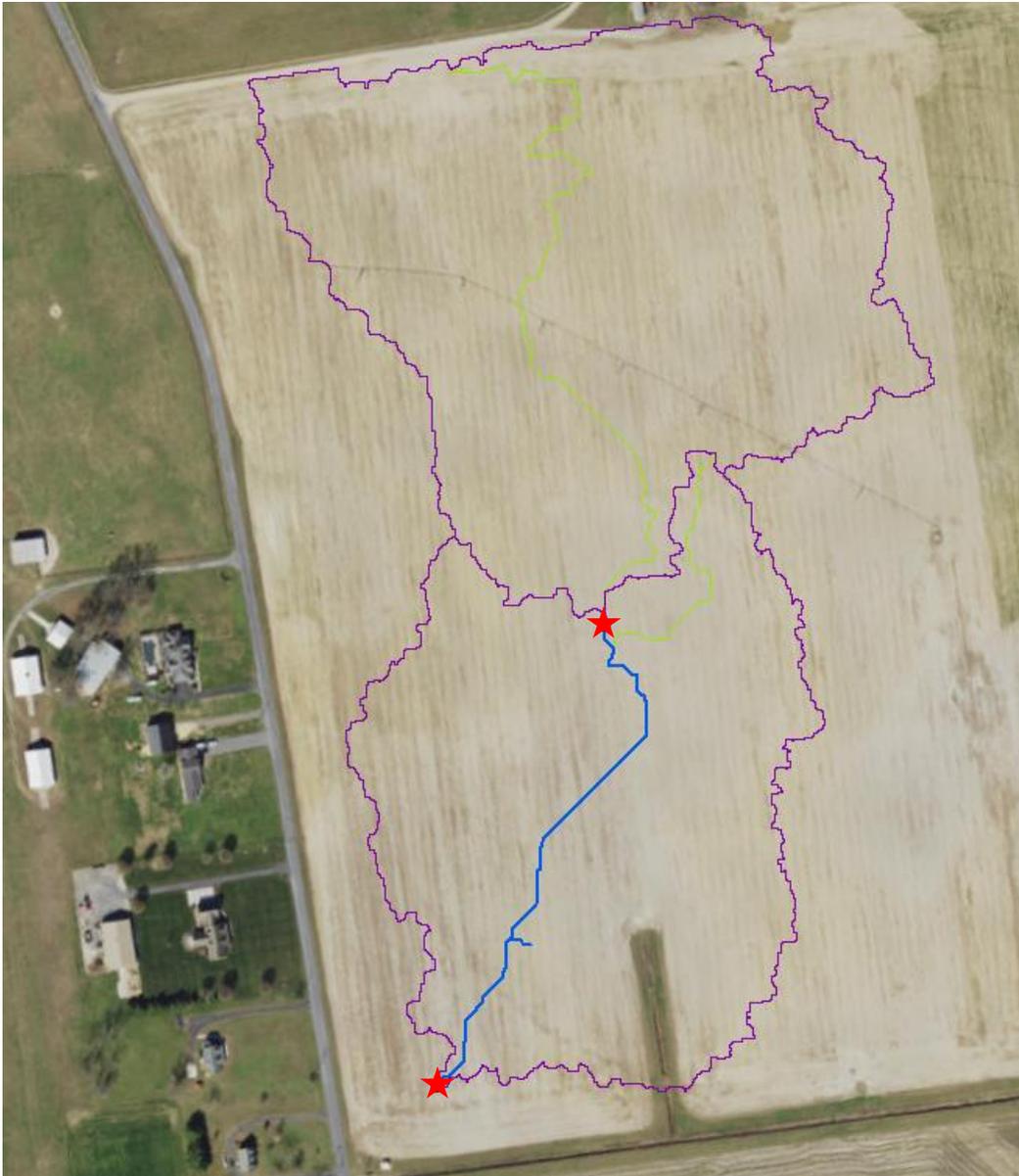


Figure 2.3: The unit field was shown with the delineated watershed, orientation of the picture was such that the top was north, and the bottom of the picture was south. The watershed was outlined with the flow path shown, the stars indicate watershed outlet(s). The southern watershed outlet was the pour point for the unit field and was located at 38.776635 N, 75.580252 W.

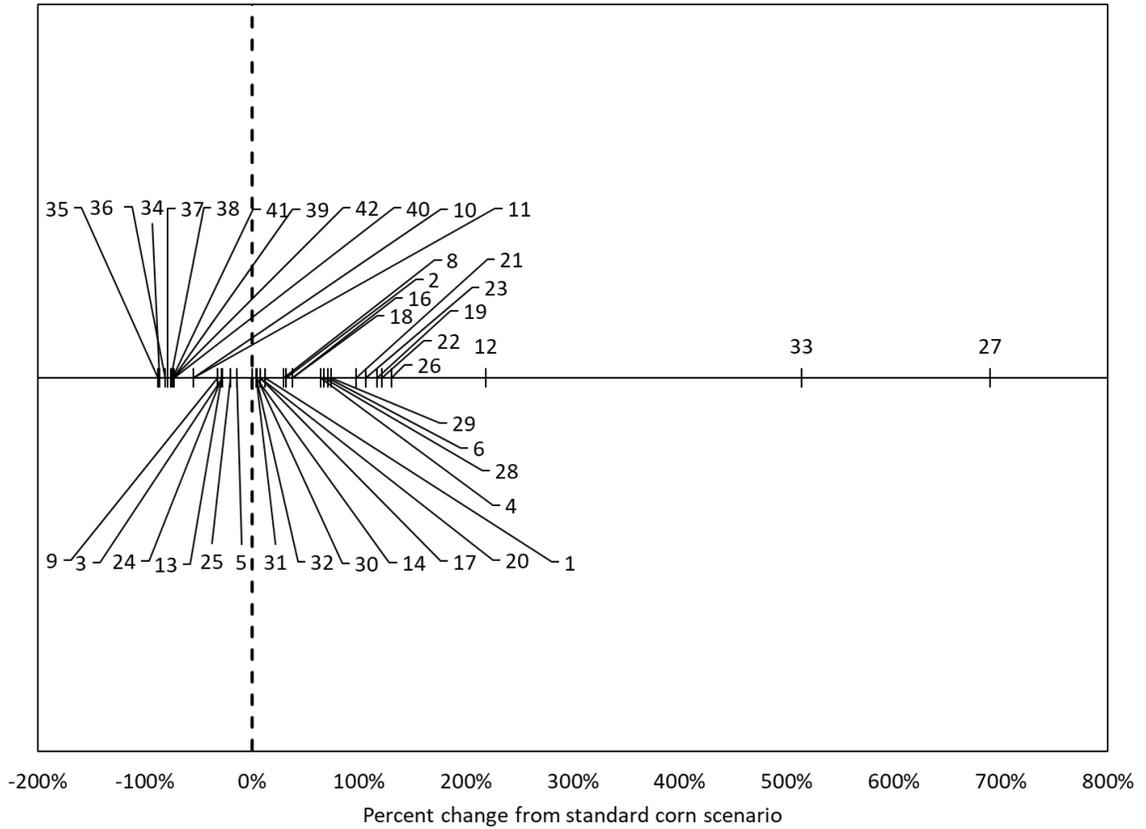


Figure 2.4: The average of the last 28 years for each scenario modeled in APEX was plotted as the percent difference from the standard scenario: corn, conventional tillage, recommended nitrogen application, no BMPs, and historical weather (indicated by the dashed vertical line at 0%). Numbered labels correspond to the left column of table 2.8.

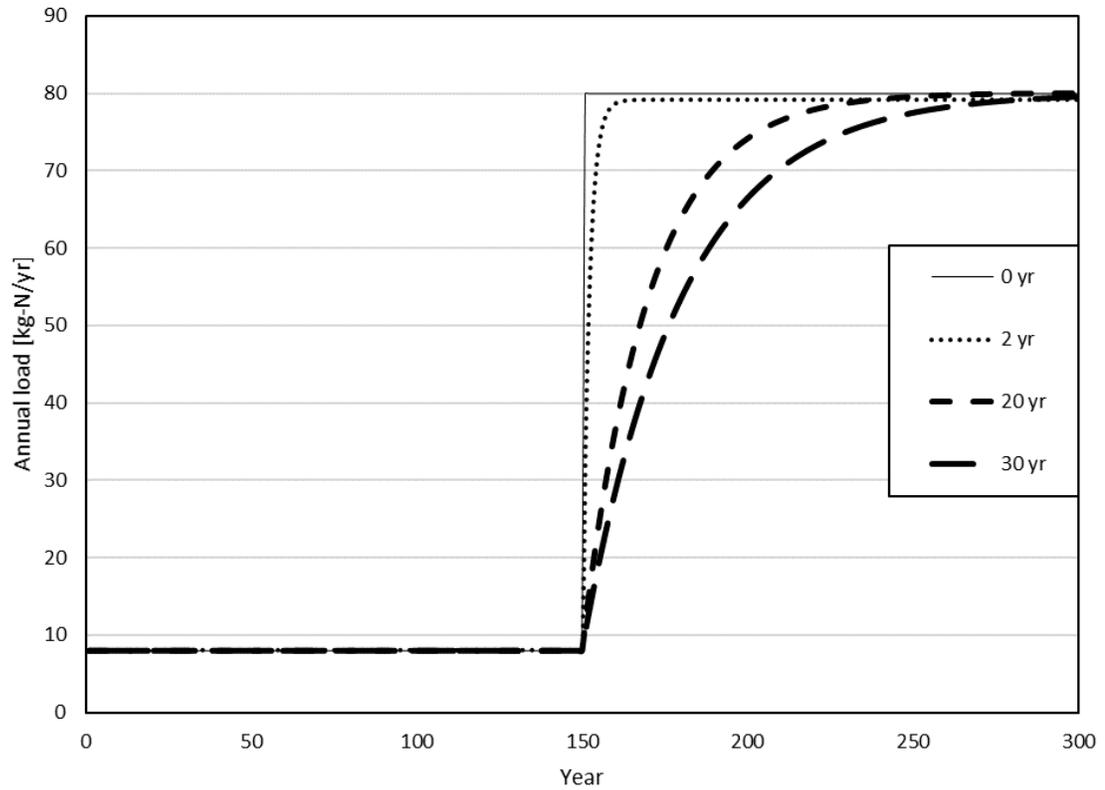


Figure 2.5: This hypothetical scenario highlights the lag observed in groundwater discharged to a stream with no variation in discharge volume or total load. The figure shows a change in land use occurring at year 150. Prior to year 150, the nitrogen load was 8 kg-N/yr. After year 150 the nitrogen load was 80 kg-N/yr. The response curve for 0, 2, 20, and 30-year groundwater transit times was shown, all of which reach the same steady state value.

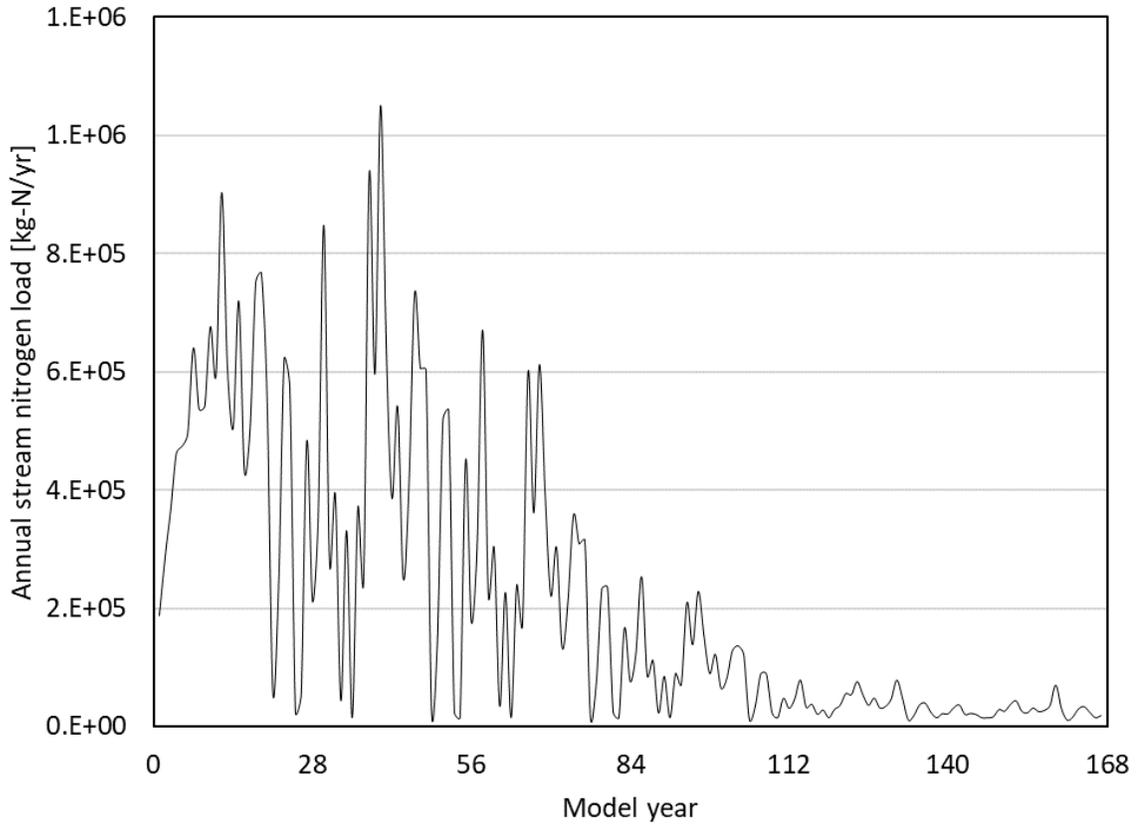


Figure 2.5: Total annual nitrogen exported from the watershed in the stream. Watershed was comprised of 1,000 unit fields. Land use and management for all 1,000 unit fields was the same: deciduous forest and a 10-meter saturated aquifer thickness resulting in a groundwater transit time of 25.7 yrs. Nitrogen load was a result of both surface runoff and groundwater discharge to the stream.

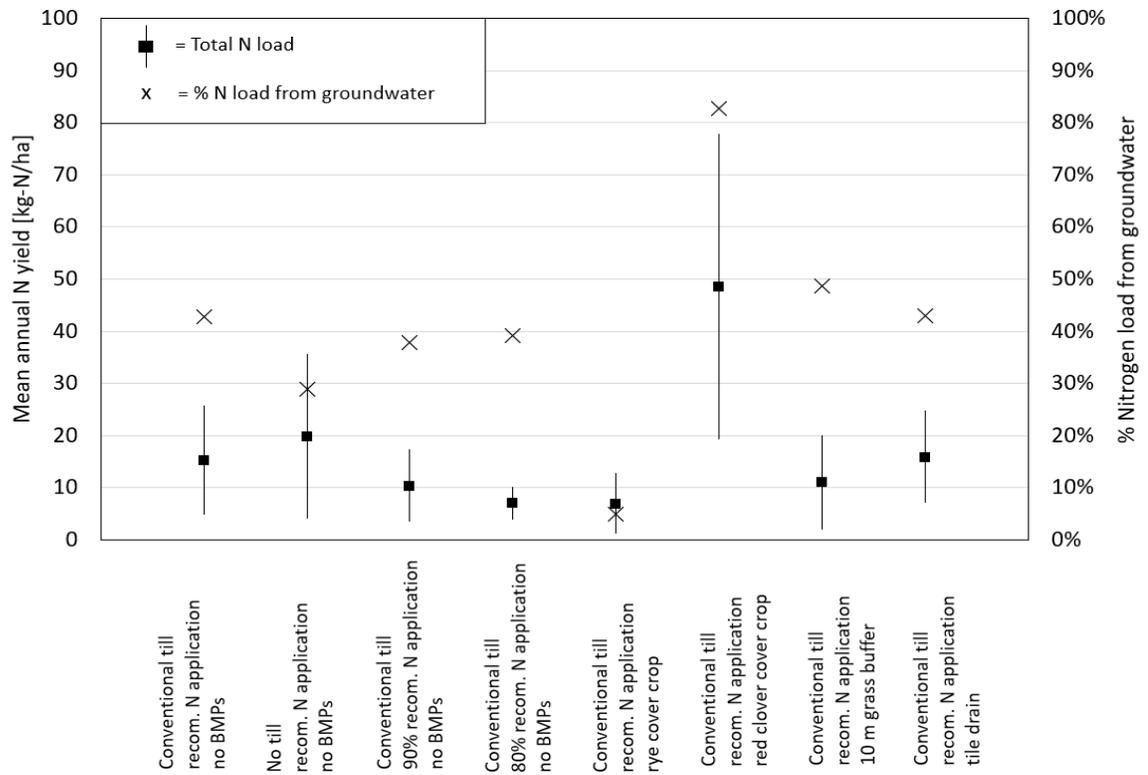


Figure 2.6: Total nitrogen load from a single unit field in corn with the indicated tillage, nitrogen application, and BMPs. Values are the mean of the last 28 years for each scenario with the vertical bar the mean  $\pm$  standard deviation. The 'x' for each land management indicates the % of the total nitrogen load in the stream that comes from the groundwater, calculated as % gw load from mean stream load.

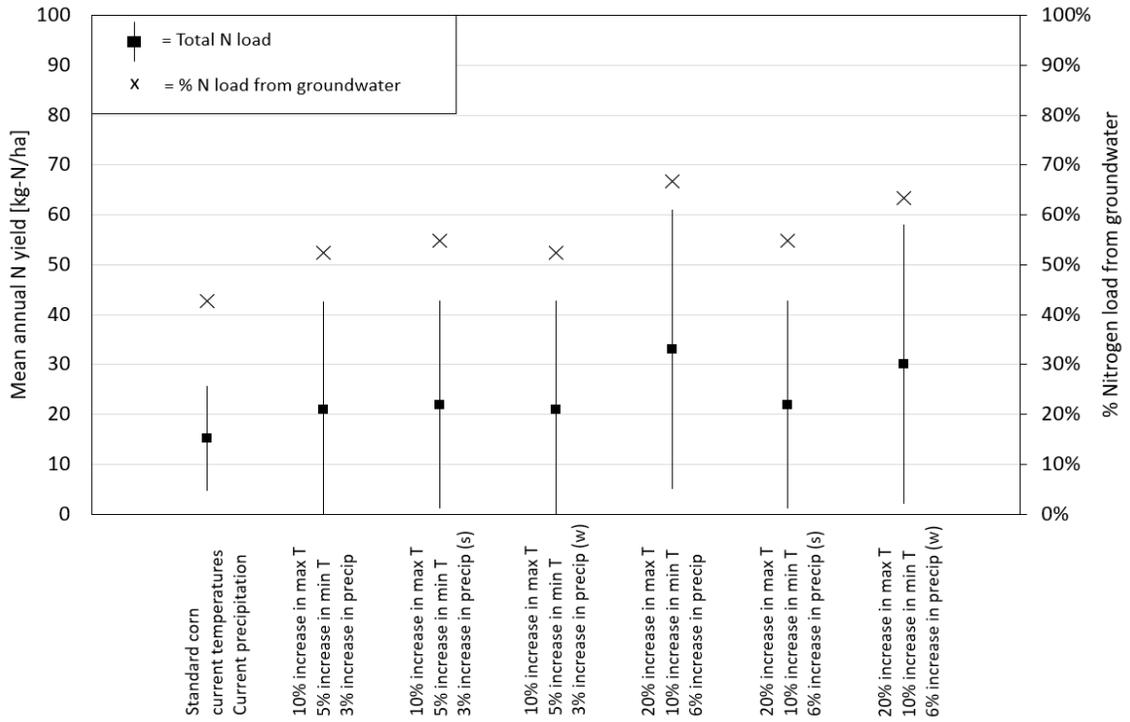


Figure 2.7: Total nitrogen load from a single unit field in corn with conventional tillage, recommended nitrogen application, and no BMPs. Each scenario has the indicated weather. Values are the mean of the last 28 years for each scenario with the vertical bar the mean  $\pm$  standard deviation. The 'x' for each land management indicates the % of the total nitrogen load in the stream that comes from the groundwater, calculated as % gw load from mean stream load.

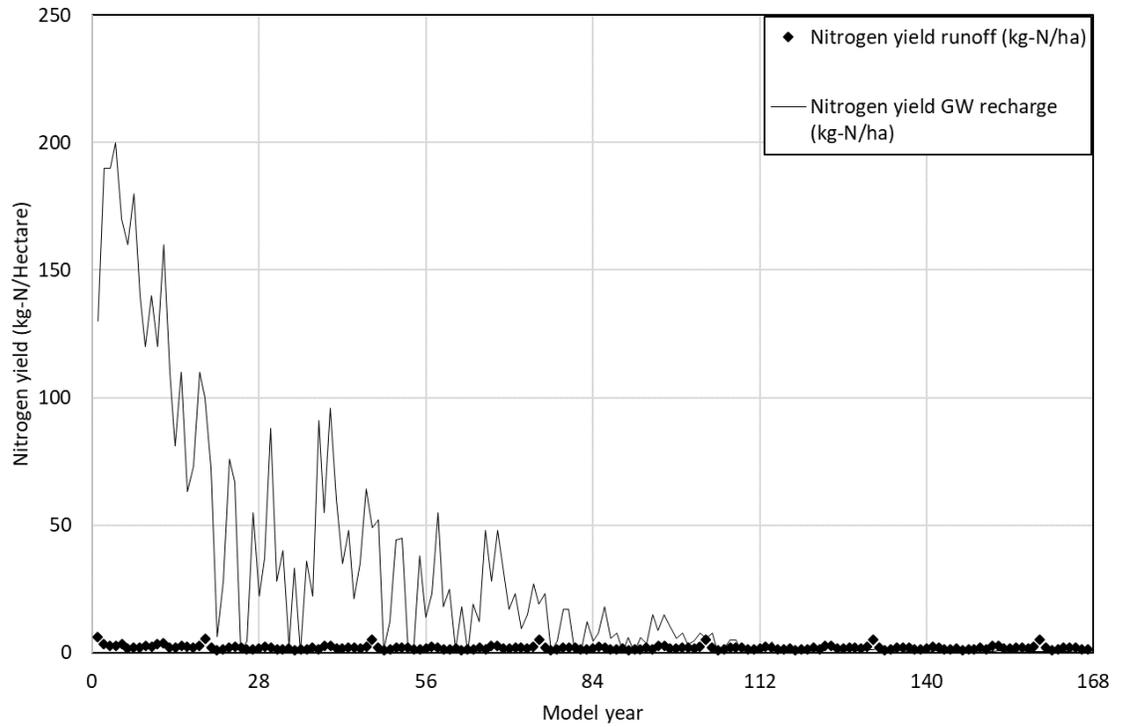


Figure 2.8: Runoff and recharge components from APEX for a single unit field of deciduous forest, no nitrogen application, and no BMPs. Nitrogen in runoff was consistent from one 28-year cycle to another. Nitrogen in groundwater recharge steadily decreases before reaching an asymptote.

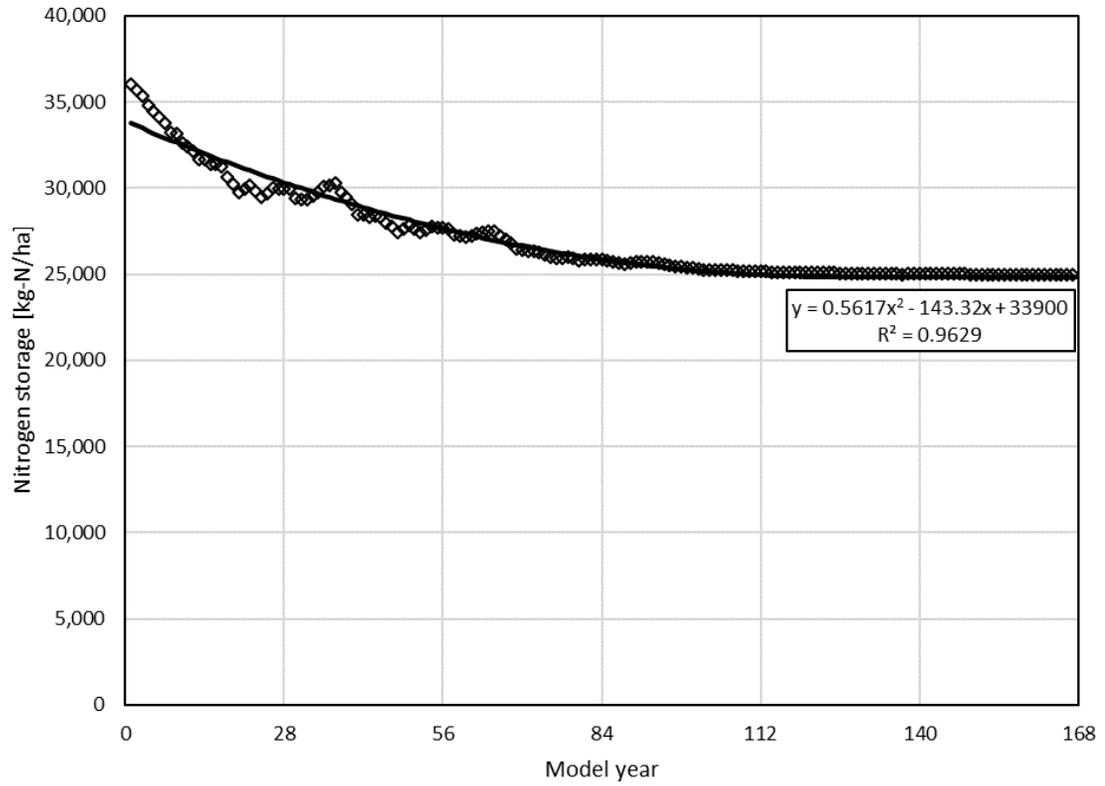


Figure 2.9: The total soil nitrogen storage for a single unit field in deciduous forest with no nitrogen application. Data points show annual nitrogen levels and a trendline was added to show when nitrogen levels reach steady state with the trendline equation shown. Steady state levels for nitrogen storage are about 25,000 kg-N/ha.

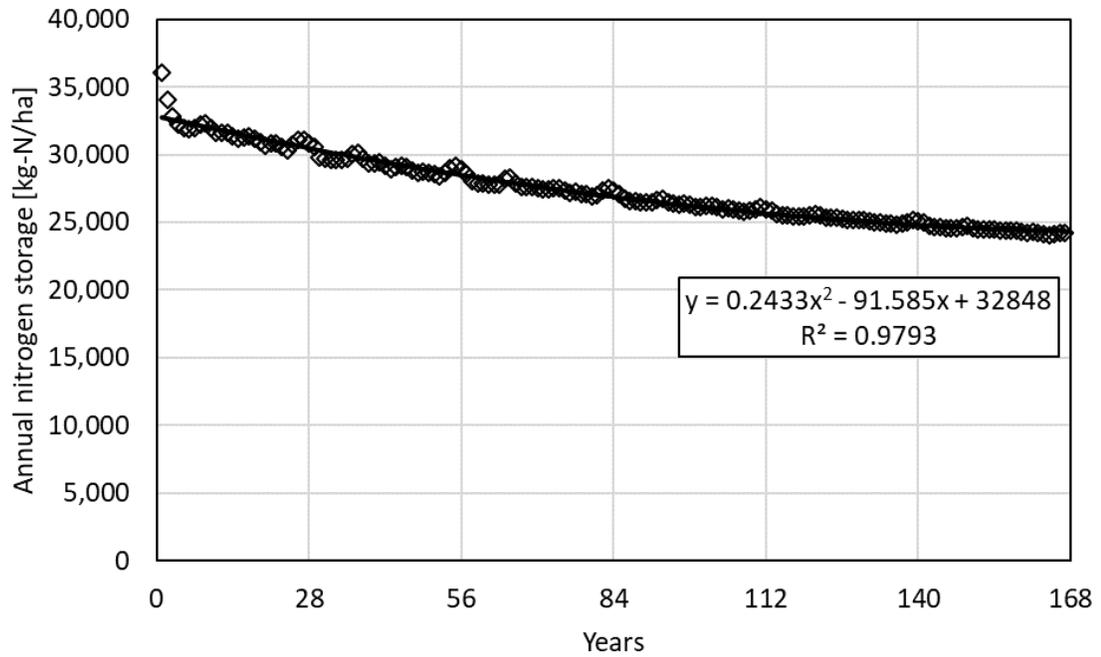


Figure 2.10: The total soil nitrogen storage for a single unit field in corn with recommended nitrogen application and no BMPS. Data points show annual nitrogen levels and a trendline was added to show when nitrogen levels reach steady state with the trendline equation shown. Steady state levels for nitrogen storage are about 24,200 kg-N/ha.

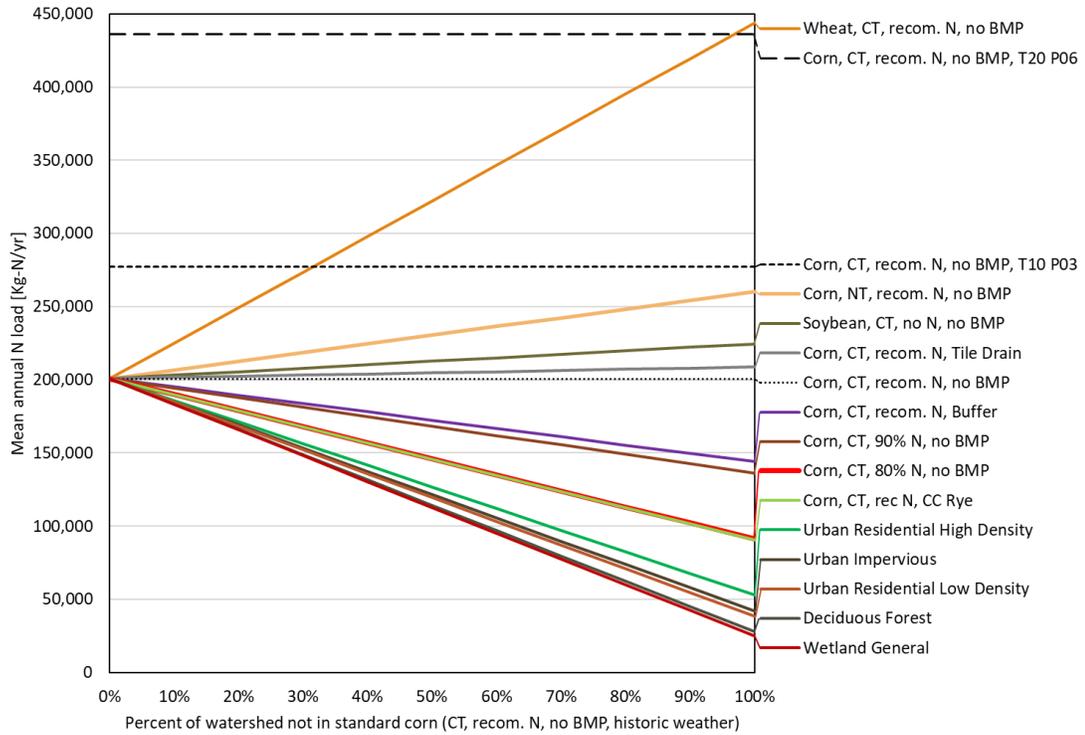


Figure 2.11: Mean nitrogen load of the stream from a watershed of 1,000 unit fields as a function of percent standard corn. Values are the mean of the last 28-years. Left side of the figure represents 100% of the 1,000 unit fields in corn with convention till, recommended nitrogen application, no BMPs, and historic weather observations. Right side of the figure represents 100% (1,000 unit fields) in the indicated land use and management. The labels on the right of the figure are linked to their corresponding lines.

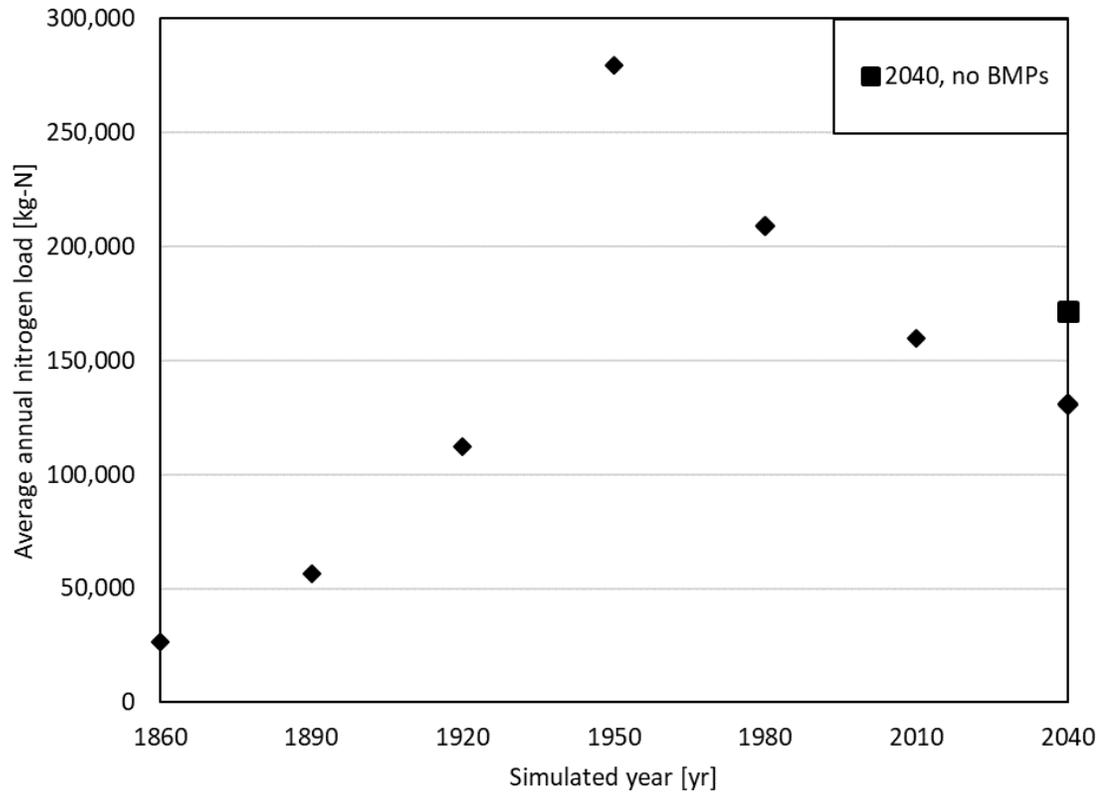


Figure 2.12: Steady-state nitrogen loads in the stream for the simulated watershed over time. Plotted are the mean annual loads for the last 28 years of the watershed for the compositions indicated in table 2.9.

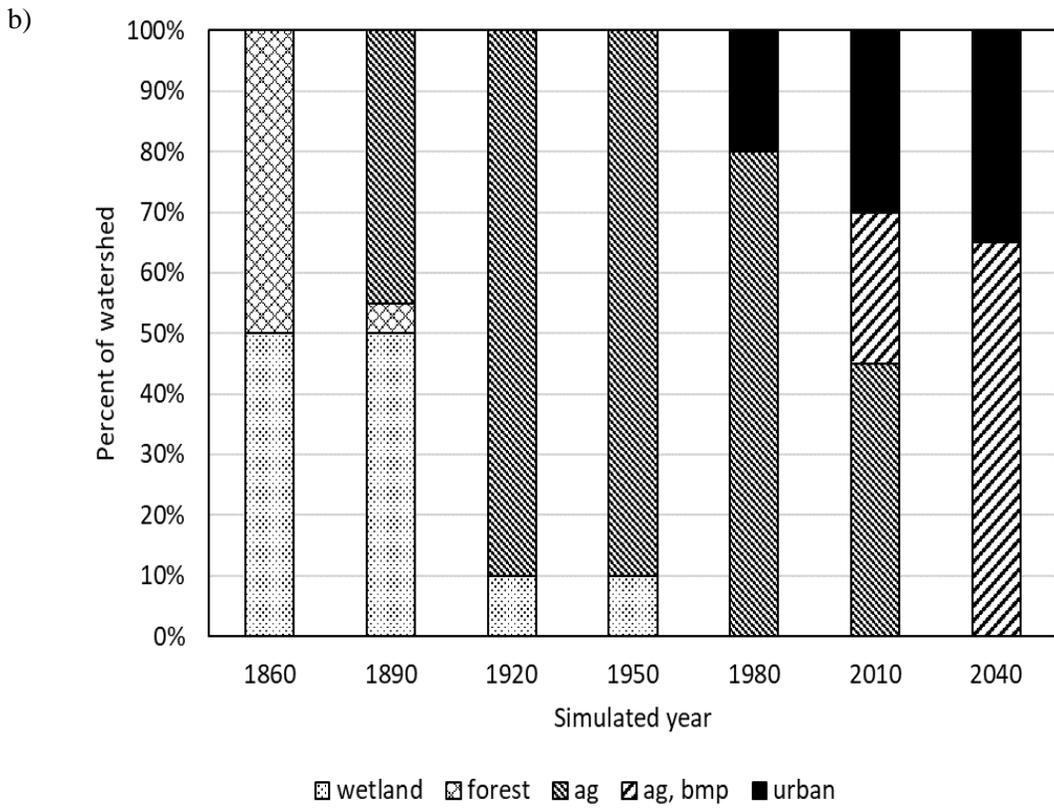
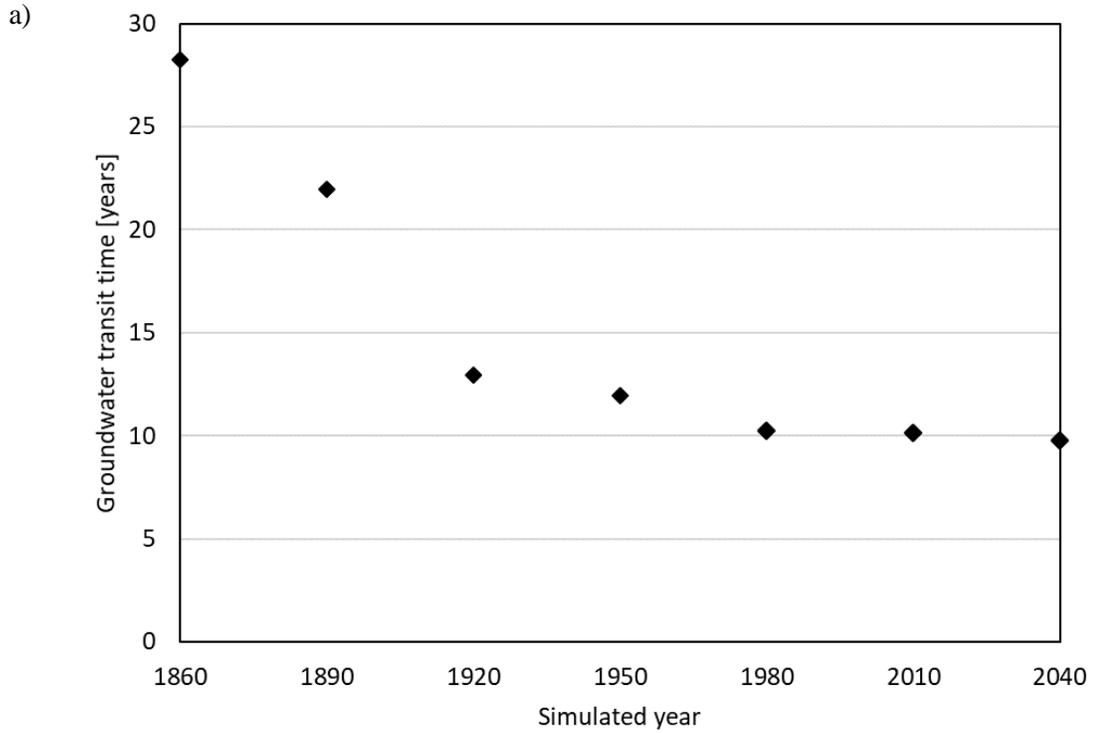


Figure 2.13: Mean groundwater transit times (a) as a function of watershed composition (b). As permanent vegetation was stripped, the mean groundwater transit time decreases.

## Chapter 2 tables

Table 2.1: Soil description and properties for Woodstown soil. Specific soil properties are those used in the model and were retrieved from the Access table.

<b>Taxonomic Class</b>	Fine-loamy, mixed, active, mesic Aquic Hapludults (USDA Woodstown Series)
<b>Moist Bulk Density [g/cm<sup>3</sup>]</b>	1.2
<b>Percent Sand [%]</b>	45.27
<b>Percent Silt [%]</b>	43.23
<b>pH</b>	7
<b>Organic Carbon Concentration [%]</b>	0.87
<b>Coarse Fragment Content [%]</b>	3.54
<b>Saturated Conductivity [mm/hr]</b>	44

Table 2.2: Four historic rain events observed in the Delmarva Peninsula region of Maryland. Events had some of the highest rainfall totals for the area.

<b>Date</b>	<b>Precipitation event</b>	<b>Historic rainfall [mm]</b>
27 August 2011	Hurricane Irene	254
15 September 2003	Tropical Storm Henri	229
16 September 1999	Hurricane Floyd	279
29 October 2012	Hurricane Sandy	317

Table 2.3: Weather scenario identifier and description with the multiplication factor used to attain desired change.

<b>Weather identifier</b>	<b>Description</b>	<b>Multiplication factor</b>
T10	10 % increase in Maximum temp	0.1
	5% increase in Minimum temp	0.039
T20	10 % increase in Maximum temp	0.2
	5% increase in Minimum temp	0.078
P03	Increased uniformly over the year	0.03
P03W	Precipitation increase in December - March	0.05
	Precipitation increase in April - November	0.02
P03S	Single precipitation event	0.03
P06	Increased uniformly over the year	0.06
P06W	Precipitation increase in December - March	0.1
	Precipitation increase in April - November	0.04
P06S	Single precipitation event	0.06

Table 2.4: Land use, land management, and climatic conditions considered by the APEX model. Definition of scenario descriptors: Ct = conventional till, Nt = no till, no N = no nitrogen applied, recom. N = recommended nitrogen applied, 80% N indicates 80% of recommended nitrogen application rates, 90% N indicates 90% of recommended nitrogen application rates, BMP = Best Management Practices, and CC = Cover Crop. Under Climate, historic climate refers to the 28-year normal created with observed daily weather values, T10 = an increase of 10% in the maximum temperature and an increase in 5% in the minimum temperature, T20 = an increase in 20% in the maximum temperature and an increase in 10% of the minimum temperature, P03= an increase of 3% in average precipitation, and P06 = an increase in 6% of the average precipitation.

<b>Number Identifier</b>	<b>Land Use</b>	<b>Land Management</b>	<b>Climate</b>
1.001011	Soybean	CT, no N, no BMP	Historic
1.001013	Soybean	NT, no N, no BMP	Historic
1.001031	Soybean	CT, no N, CC Rye	Historic
1.001032	Soybean	CT, no N, CC Red Clover	Historic
1.001041	Soybean	10 m Grass Buffer	Historic
1.001051	Soybean	Ct, no N, Tile Drainage	Historic
1.002011	Corn	Ct, recom. N, no BMP	Historic
1.002011	Corn	Ct, recom. N, no BMP	T10 P03
1.002011	Corn	Ct, recom. N, no BMP	T10 P03S
1.002011	Corn	Ct, recom. N, no BMP	T10 P03W
1.002011	Corn	Ct, recom. N, no BMP	T20 P06
1.002011	Corn	Ct, recom. N, no BMP	T20 P06S
1.002011	Corn	Ct, recom. N, no BMP	T20 P06W
1.002011	Corn	Ct, recom. N, no BMP	Historic
1.002013	Corn	Nt, recom. N, no BMP	Historic

Table 2.4 cont.

1.002022	Corn	Ct, 10% N, no BMP	Historic
1.002024	Corn	Ct, 20% N, no BMP	Historic
1.002031	Corn	Ct, recom. N, CC Rye	Historic
1.002032	Corn	Ct, recom. N, CC Red Clover	Historic
1.002042	Corn	10 m Grass Buffer	Historic
1.002052	Corn	Ct, recom. N, Tile Drain	Historic
1.010011	Wheat	Ct, recom. N, no BMP	Historic
1.010013	Wheat	Nt, recom. N, no BMP	Historic
1.010022	Wheat	Ct, 10% N, no BMP	Historic
1.010024	Wheat	Ct, 20% N, no BMP	Historic
1.010031	Wheat	Ct, recom. N, CC Rye	Historic
1.010032	Wheat	Ct, recom. N, CC Red Clover	Historic
1.010041	Wheat	10 m Grass Buffer	Historic
1.010051	Wheat	Ct, recom. N, Tile Drain	Historic
1.081001	Perennial	Apple Tree, recom. N, CC Ryegrass	Historic
1.081002	Perennial	Apple Tree, 20% N, CC Ryegrass	Historic
1.081004	Perennial	Apple Tree, 10% N, CC Ryegrass	Historic
1.123011	Perennial	Pasture, Ct, recom. N	Historic
1.127001	Perennial	Deciduous Forest	Historic
1.128001	Perennial	Evergreen Forest	Historic
1.129001	Perennial	Wetland, General	Historic
1.130001	Perennial	Wetland, Non-forested	Historic

Table 2.4 cont.

1.133001	Perennial	Forest, Mixed	Historic
1.134001	Perennial	Wetland, Forested	Historic
1.300001	Urban	High density residential	Historic
1.301001	Urban	Medium density residential	Historic
1.302001	Urban	Medium-low density residential	Historic
1.303001	Urban	Low density residential	Historic
1.304001	Urban	Commercial	Historic
1.305001	Urban	Downtown industrial	Historic
1.306001	Urban	Institutional office parks	Historic
1.307001	Urban	Impervious	Historic

Table 2.5: The water budget, corresponding APEX variables, and file each variable was located in. All files are found in the TxtInOut folder for each respective scenario. Units for APEX hydrologic components are in mm.

<b>Water Budget</b>			
<b>Budget component</b>	<b>Input/output/storage</b>	<b>APEX variable name</b>	<b>File</b>
Precipitation	Input	PRCP	Site2.MSA
Irrigation	Input	IRGA	Site2.MSA
Evapotranspiration	Output	ET	Site2.MSA
Groundwater recharge	Output	PRK	Site2.MSA
Runoff	Output	Q	Site2.MSA
Shallow flow to stream	Output	RSSF	Site2.MSA
Tile drainage	Output	QDR	Site2.MSA

Table 2.6: The nitrogen budget, corresponding APEX variables, and file each variable was located in. All files are found in the TxInOut folder for each respective scenario. Units for APEX nitrogen components are in kg-N/hectare.

<b>Nitrogen Budget</b>			
<b>Budget component</b>	<b>Input/storage/output</b>	<b>APEX variable name</b>	<b>File</b>
Nitrogen fertilizer applied	Input	FN	Site2.MSA
Nitrogen fixed	Input	NFIX	Site2.MSA
Total soil nitrogen pool	Storage	WON	Site2.AC�
Nitrate-N in root zone	Storage	ZNMN	Site2.MSA
Ammonia-N in root zone	Storage	ZNMA	Site2.MSA
Nitrogen in runoff	Output	QN	Site2.FSA
Nitrogen in gw recharge	Output	PRKN	Site2.FSA
Nitrogen in tile drain flow	Output	QDRN	Site2.FSA
Nitrogen in crop yield	Output	YLDN	Site2.FSA
Denitrification	Output	DN	Site2.MSA
Nitrogen in shallow flow	Output	RSFN	Site2.MSA
Nitrogen volatilized	Output	AVOL	Site2.MSA

Table 2.7: Table details the outline of the CSV file containing the combined APEX results for each model run. Hydrologic components have units of mm and nitrogen components have units of kg-N/hectare.

<b>CSV Column</b>	<b>Parameter</b>	<b>Definition/APEX Variables</b>
1	File Name	
2	Model year	Annual time step
3	Precipitation	PRCP
4	Evapotranspiration	ET
5	Quickflow	Q + RSSF + QDR
6	Groundwater recharge	PRK
7	Nitrogen yield runoff	QN + QDRN + RSFN
8	Nitrogen yield GW recharge	PRKN
9	Total N load in quickflow	(QN + QDRN + RSFN)*AREA
10	Total N load in GW recharge	PRKN*AREA
11	Nitrogen fertilizer	FNO + FNMN + FNMA
12	Other N sources	NFIX
13	Other N losses	AVOL + DN + YLDN
14	N storage	WON + ZNMN + ZNMA

Table 2.8: Results taken from ArcAPEX output files. Values are the average annual value of the last 28 model years, taken from model run years 141-168. Hydrologic components are normalized per square meter. Nitrogen values are presented as yield [kg-N/hectare] with a total field size to 13.21 hectares. Definition of scenario descriptors: Ct = conventional till, Nt = no till, no N = no nitrogen applied, recom. N = recommended nitrogen applied, 80% N indicates 80% of recommended nitrogen application rates, 90% N indicates 90% of recommended nitrogen application rates, BMP = Best Management Practices, CC = Cover Crop, T10 = an increase of 10% in the maximum temperature and an increase in 5% in the minimum temperature, T20 = an increase in 20% in the maximum temperature and an increase in 10% of the minimum temperature, P03= an increase of 3% in average precipitation, and P06 = an increase in 6% of the average precipitation.

	<b>Land Management</b>	<b>Mean annual runoff [mm]</b>	<b>Mean annual recharge [mm]</b>	<b>N yield in runoff [kg-N/ha] Mean ± SD</b>	<b>N yield in recharge [kg-N/ha] Mean ± SD</b>	<b>Total N yield [kg-N/ha] Mean ± SD</b>
<b>Soybean</b>						
1	CT, no N, no BMP	280	400	6.7 ± 2.9	10 ± 4.5	17 ± 7.4
2	NT, no N, no BMP	290	450	7.7 ± 3.6	12 ± 5.5	20 ± 9.1
3	CT, no N, CC Rye	270	370	5.2 ± 2.5	6 ± 2.6	11 ± 5.1
4	CT, no N, CC Red Clover	270	380	9.7 ± 4	15 ± 7.3	25 ± 11
5	10 m Grass Buffer	250	450	6 ± 2.7	6.8 ± 3.2	13 ± 6
6	Ct, no N, Tile Drainage	330	320	18 ± 6.5	7.5 ± 3.5	26 ± 10

Table 2.8 cont.

<b>Corn</b>						
7	Ct, rec N, no BMP	310	480	$8.7 \pm 8$	$6.5 \pm 2.5$	$15 \pm 11$
8	Nt, rec N, no BMP	330	530	$14 \pm 14$	$5.7 \pm 1.8$	$20 \pm 16$
9	Ct, 10% N, no BMP	320	490	$6.4 \pm 5.8$	$3.9 \pm 1.2$	$10 \pm 7$
10	Ct, 20% N, no BMP	370	380	$4.2 \pm 2.4$	$2.7 \pm 0.8$	$6.9 \pm 3.2$
11	Ct, rec N, CC Rye	280	380	$6.5 \pm 5.6$	$0.3 \pm 0.2$	$6.8 \pm 5.8$
12	Ct, rec N, CC Red Clover	280	380	$8.4 \pm 5.3$	$40 \pm 24$	$48 \pm 29$
13	10 m Grass Buffer	290	530	$5.6 \pm 5.9$	$5.3 \pm 3.1$	$11 \pm 9$
14	Ct, rec N, Tile Drain	370	380	$9 \pm 4.7$	$6.8 \pm 4.1$	$16 \pm 9$

Table 2.8 cont.

<b>Corn, Weather variation</b>						
15	Ct, rec N, no BMP	310	480	$8.7 \pm 8$	$6.5 \pm 2.5$	$15 \pm 11$
16	Ct, rec N, no BMP, T10 P03	330	470	$10 \pm 14$	$11 \pm 7.6$	$21 \pm 22$
17	Ct, rec N, no BMP, T10 P03S	320	470	$9.8 \pm 13$	$6.6 \pm 2.8$	$16 \pm 16$
18	Ct, rec N, no BMP, T10 P03W	330	470	$10 \pm 14$	$11 \pm 7.7$	$21 \pm 22$
19	Ct, rec N, no BMP, T20 P06	350	470	$11 \pm 14$	$22 \pm 14$	$33 \pm 28$
20	Ct, rec N, no BMP, T20 P06S	320	470	$10 \pm 13$	$6.4 \pm 2.5$	$16 \pm 16$
21	Ct, rec N, no BMP, T20 P06W	350	460	$11 \pm 15$	$19 \pm 13$	$30 \pm 28$

Table 2.8 cont.

<b>Wheat</b>						
22	Ct, rec N, no BMP	310	450	$30 \pm 27$	$3.6 \pm 2.3$	$34 \pm 29$
23	Nt, rec N, no BMP	320	490	$27 \pm 25$	$4.4 \pm 2.7$	$31 \pm 28$
24	Ct, 10% N, no BMP	310	450	$7 \pm 5.4$	$3.9 \pm 2.2$	$11 \pm 7.6$
25	Ct, 20% N, no BMP	310	450	$9.5 \pm 9.7$	$2.6 \pm 1.5$	$12 \pm 11$
26	Ct, rec N, CC Rye	290	420	$32 \pm 29$	$3 \pm 2.3$	$35 \pm 31$
27	Ct, rec N, CC Red Clover	320	530	$10 \pm 3.3$	$110 \pm 29$	$120 \pm 32$
28	10 m Grass Buffer	280	500	$23 \pm 24$	$2.4 \pm 1.4$	$25 \pm 25$
29	Ct, rec N, Tile Drain	360	370	$23 \pm 21$	$3.4 \pm 1.7$	$26 \pm 23$
<b>Permanent vegetation</b>						
30	Apple Tree, rec N, CC Ryegrass	210	240	$1.9 \pm 0.9$	$14 \pm 4.8$	$16 \pm 5.7$
31	Apple Tree, 20% N, CC Ryegrass	210	240	$1.8 \pm 0.8$	$14 \pm 4.7$	$16 \pm 5.5$
32	Apple Tree, 10% N, CC Ryegrass	210	240	$1.8 \pm 0.8$	$14 \pm 4.7$	$16 \pm 5.5$
33	Pasture, Ct, rec N	190	140	$5.3 \pm 2.7$	$88 \pm 74$	$93 \pm 77$
34	Deciduous Forest	200	140	$1.8 \pm 0.8$	$0.3 \pm 0.2$	$2.1 \pm 1$
35	Wetland, General	190	130	$1.8 \pm 0.8$	$0.1 \pm 0.1$	$1.9 \pm 0.9$

Table 2.8 cont.

<b>Urban</b>						
36	Low density residential	230	570	$1.5 \pm 0.5$	$1.4 \pm 0.5$	$2.9 \pm 1$
37	Medium-low density residential	250	540	$1.9 \pm 0.6$	$1.3 \pm 0.4$	$3.2 \pm 1$
38	Medium density residential	280	480	$2.5 \pm 0.7$	$1.2 \pm 0.4$	$3.7 \pm 1.1$
39	High density residential	330	410	$2.9 \pm 0.8$	$1.1 \pm 0.4$	$4 \pm 1.1$
40	Commercial	390	330	$3.2 \pm 0.8$	$0.9 \pm 0.3$	$4.1 \pm 1.1$
41	Downtown industrial	460	250	$3.2 \pm 0.8$	$0.8 \pm 0.3$	$4 \pm 1$
42	Institutional office parks	340	400	$3 \pm 0.8$	$1 \pm 0.3$	$4 \pm 1.1$
43	Impervious	550	140	$2.7 \pm 0.7$	$0.5 \pm 0.2$	$3.2 \pm 0.9$

Table 2.9: Changes in land use and management for the historical watershed scenario. The watershed was 1,000 unit fields and the composition column identifies how the watershed was laid out. Further descriptions of the land managements may be found in appendix A.1. CT = Conventional till, NT = no till, N = nitrogen, recom. N = recommended nitrogen application.

<b>Time Period</b>	<b>Simulated year</b>	<b>Land management</b>	<b>Number unit fields</b>
1	1860	General Wetland	500
		Deciduous Forest	500
2	1890	General Wetland	500
		Deciduous Forest	50
		Corn, CT w/ 80% of recom. N	450
3	1920	Corn, CT w/ 80% of recom. N	500
		Wheat, CT w/ 80% of recom. N	400
		General Wetland	100
4	1950	Soybean CT no N	100
		Corn CT recom. N	400
		Wheat CT recom. N	400
		General Wetland	100
5	1980	Soybean, CT no N	200
		Corn, CT recom. N	200
		Corn, CT recom. N w/ drain tile	200
		Wheat, CT recom. N	100
		Wheat, CT recom. N w/ drain tile	100
		Low density urban	200
6	2010	Soybean, CT no N 10m grass buffer	100
		Soybean, CT no N w/ drain tile	150
		Corn, CT recom. N	100
		Corn, CT recom. N 10m grass buffer	150
		Corn, CT recom. N w/ drain tile	200
		High density urban	100
		Low density urban	200

Table 2.9 cont.

7	2040	Soybean, CT no N 10m grass buffer	250
		Corn, CT recom. N 10m grass buffer	300
		Wheat, Ct recom. N 10 m buffer	100
		High density urban	100
		Low density urban	200
		Impervious	50

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## **APPENDIX**

### **A.1 Land Management**

Please see supplementary file *Land Management*.

## **A.2 Weather Data**

Please see supplementary file *Weather Data*.

### A.3 R Code: Lumped Parameter Model

```
##### Modelled small watershed with generic, conservative chemical
#####
# Script determines concentration of a generic, conservative chemical in the baseflow from an unconfined
  aquifer to a small stream.
# A small watershed is comprised of a number of standardized unit land volumes. Soil and aquifer
  properties are identical for all unit fields, with above ground
# land use being the only differentiating piece.
#
# Author: John Larkin
# Version 12.27.17
#####
scenarios <- read.csv('scenarios.csv') #reads in table of different scenarios
PPT <- read.csv('PPT.csv')$Rainfall #Extract precipitation .csv file and convert to a single vector.
year <- 0:149 + 0.5 #Run time starting at year 0 for a length of 300 years, the 1/2 is added to allow for
  calculations during the middle of the year.
yr <- length(year)

## Constants of watershed
areaField <- 400*400 #Area of standardized unit field in meters, equivalent to 16 hectare or ~39.5 acra
m3toL <- 1000 #Convert m3 to Liters
mgTOkg <- (10^-6) #Convert mg to kg

## Variables of Watershed
numberFields <- 1000 #number fields(unit fields) in watershed

for(i in 1:yr){
  if(PPT[i] < 0.75){
    PPT[i] <- 0.75
  }
}
ET <- 0.5 #meters
recharge <- 0.25 #meters
runoff <- PPT - (ET + recharge) #meters

aveHistoric_C <- 0.2 # initial concentration of CHEMICAL in GW, mg/L
aveRunUndev_C <- 0.2 #ave annual conc of CHEMICAL in runoff from UNDEVELOPED land, mg/L
aveRunAg_C <- 20 #ave annual conc of CHEMICAL in runoff with agriculture w/o BMP, mg/L
aveRechUndev_C <- 0.2 #ave annual conc of CHEMICAL in recharge from UNDEVELOPED land, mg/L
aveRechAg_C <- 2 #ave annual conc of CHEMICAL in recharge from agriculture w/o BMP, mg/L

##### tbar 2 #####
tbar <- 30 #mean groundwater transit time

# Cumulative frequency distribution (Ft) and probability distribution function (Et)
# of watershed with constant areal recharge and mean GW residence time
Ft <- 1 - exp(-year/tbar)
Et <- (1/tbar)*exp(-year/tbar)

gwData <- matrix(0,yr,yr)
for (i in 1:yr){
  if(tbar != 0){
    gwData[i,i:yr] <- Et[1:(yr + 1 - i)]*recharge
  }
  else{

```

```

    gwData[i,i] <- recharge
  }
}

depth <- c()
for (i in 1:yr){
  depth[i] <- sum(gwData[,i])
}
newGwVol <- depth*areaField*m3toL
historicGwVol <- (recharge - depth)*areaField*m3toL

#### Baseflow ####
baseflowVol <- recharge*areaField*m3toL
# Loads are in mg
undevBaseLoad <- (newGwVol*aveRechUndev_C + historicGwVol*aveHistoric_C)
AgBaseLoad <- (newGwVol*aveRechAg_C + historicGwVol*aveHistoric_C)
AgBmp10BaseLoad <- (newGwVol*aveRechAg_C*0.9 + historicGwVol*aveHistoric_C)
AgBmp30BaseLoad <- (newGwVol*aveRechAg_C*0.7 + historicGwVol*aveHistoric_C)

#### Runoff ####
runoffVol <- runoff*areaField*m3toL
undevRunoffLoad <- runoffVol*aveRunUndev_C
agRunoffLoad <- runoffVol*aveRunAg_C
agBmp10RunoffLoad <- runoffVol*aveRunAg_C*0.9
agBmp30RunoffLoad <- runoffVol*aveRunAg_C*0.7

#### Scenarios ###
a <- dim(scenarios)[1]
numUndev <- c()
numAG <- c()
numAGbmp <- c()
bmpEff <- c()
for(i in 1:a){
  numUndev[i] <- scenarios$Number.fields.UNDEV[i]
  numAG[i] <- scenarios$Number.fields.AG.wo.BMP[i]
  numAGbmp[i] <- scenarios$Number.fields.AG.with.BMP[i]
  bmpEff[i] <- scenarios$Efficiency.of.BMP[i] #Removal efficiency of BMP
}

scenarioBaseLoads <- matrix(0,dim(scenarios)[1],2*yr)
scenarioRunoffLoads <- matrix(0,dim(scenarios)[1],2*yr)
scenarioVol <- (baseflowVol + runoffVol)*numberFields
scenarioNames <- c()
yr_1 <- yr + 1
yryr <- yr*2
for(i in 1:a){
  scenarioBaseLoads[i,1:yr] <- numberFields*undevBaseLoad
  scenarioRunoffLoads[i,1:yr] <- numberFields*undevRunoffLoad
  scenarioNames[i] <- paste(numUndev[i],',',numAG[i],',',numAGbmp[i],',',bmpEff[i])
  if(bmpEff[i] == 10){
    scenarioBaseLoads[i,yr_1:yryr] <- numUndev[i]*undevBaseLoad + numAG[i]*AgBaseLoad +
      numAGbmp[i]*AgBmp10BaseLoad
    scenarioRunoffLoads[i,yr_1:yryr] <- numUndev[i]*undevRunoffLoad + numAG[i]*agRunoffLoad +
      numAGbmp[i]*agBmp10RunoffLoad
  }
}

```

```

else{
  scenarioBaseLoads[i,yr_1:yr] <- numUndev[i]*undevBaseLoad + numAG[i]*AgBaseLoad +
    numAGbmp[i]*AgBmp30BaseLoad
  scenarioRunoffLoads[i,yr_1:yr] <- numUndev[i]*undevRunoffLoad + numAG[i]*agRunoffLoad +
    numAGbmp[i]*agBmp30RunoffLoad
}
}

scenarioStreamLoads <- (scenarioBaseLoads + scenarioRunoffLoads)*mgTOkg
scenarioStreamConc <- matrix(0,dim(scenarios)[1],2*yr)
for(i in 1:a){
  scenarioStreamConc[i,] <- (scenarioBaseLoads[i,] + scenarioRunoffLoads[i,])/rep(scenarioVol,2)
}

write.csv(cbind(scenarioNames,scenarioBaseLoads*mgTOkg),file='Chem baseload, 30 .csv')
write.csv(cbind(scenarioNames,scenarioRunoffLoads*mgTOkg),file='Chem Runoff Load, 30 .csv')
write.csv(cbind(scenarioNames,scenarioStreamConc),file='CHEM Stream Conc, 30 .csv')
write.csv(cbind(scenarioNames,scenarioStreamLoads),file='CHEM Stream Load, 30 .csv')

```

#### A.4 R Code: APEX Results Read-In

```
# Author: John Larkin
# Last revised: 15 December 2019
# For the USGS
# In support of Masters of Science in Civil Engineering with an emphasis in Environmental Engineering
from
# the University of Minnesota

## Script consolidates hydrologic and nitrogen components from various APEX output files for every
scenario.

setwd('~')
setwd('../Desktop/Apex Scenarios') #normal scenarios
# setwd('C:/Users/John Larkin/Desktop/Weather Changes') #Weather scenarios

filesAvailable <- list.files()
# filesAvailable <- list.files('../Desktop')

numberFiles <- length(filesAvailable)

avgLoadParamaters <- 7
avgLoad <- matrix(NA,numberFiles + 1,avgLoadParamaters)
avgLoad[1,2:avgLoadParamaters] <- c('Avg annual runoff [mm/sq m]', 'Avg annual recharge [mm/sq m]',
                                     'Avg annual N yield in runoff [kg-N/hectare]', 'Std dev annual N yield in runoff [kg-
N/hectare]',
                                     'Avg annual N yield in recharge [kg-N/hectare]', 'Std dev annual N yield in recharge
[kg-N/hectare]')

for(j in 1:numberFiles){
  setwd('~')
  setwd(paste('../Desktop/Apex Scenarios/',filesAvailable[j],'/TxtInOut',sep = "))
  initialApexN <- tail(read.delim('SITE2.FSA',stringsAsFactors = F,skipNul = T),-8)
  initialData <- tail(read.delim('SITE2.MSA', stringsAsFactors = F),-9)
  soilN <- tail(read.delim('SITE2.ACN',stringsAsFactors = F),-8)

  if(sum(strsplit(filesAvailable[j],split = "\\s+")[1] == 'Buffer')){
    area1 <- 13.2
    area2 <- 0.01
    buffer_eff <- 0.5
  }else{
    area1 <- 7.3
    area2 <- 5.91
    buffer_eff <- 0
  }
  areaTot <- area1 + area2

  sn1 <- c()
  sn2 <- c()
  wlsn1 <- c()
  wlmn1 <- c()
  wbm1 <- c()
  whsn1 <- c()
  whpn1 <- c()
  wlsn2 <- c()
  wlmn2 <- c()
}
```

```

wbnm2 <- c()
whsn2 <- c()
whpn2 <- c()
f <- 1
sn <- 28
i1 <- 1
i2 <- 1
while(f < dim(soilN)[1]){
  if(as.numeric(tail(strsplit(soilN[f,],split = "\\s+")[1],1)) == 1){
    sn1[i1] <- as.numeric(tail(strsplit(soilN[sn,],split = "\\s+")[1],1))
    wlsn1[i1] <- as.numeric(tail(strsplit(soilN[sn - 5,],split = "\\s+")[1],1))
    wlmn1[i1] <- as.numeric(tail(strsplit(soilN[sn - 4,],split = "\\s+")[1],1))
    wbnm1[i1] <- as.numeric(tail(strsplit(soilN[sn - 3,],split = "\\s+")[1],1))
    whsn1[i1] <- as.numeric(tail(strsplit(soilN[sn - 2,],split = "\\s+")[1],1))
    whpn1[i1] <- as.numeric(tail(strsplit(soilN[sn - 1,],split = "\\s+")[1],1))
    i1 <- i1 + 1
  } else {
    sn2[i2] <- as.numeric(tail(strsplit(soilN[sn,],split = "\\s+")[1],1))
    wlsn2[i2] <- as.numeric(tail(strsplit(soilN[sn - 5,],split = "\\s+")[1],1))
    wlmn2[i2] <- as.numeric(tail(strsplit(soilN[sn - 4,],split = "\\s+")[1],1))
    wbnm2[i2] <- as.numeric(tail(strsplit(soilN[sn - 3,],split = "\\s+")[1],1))
    whsn2[i2] <- as.numeric(tail(strsplit(soilN[sn - 2,],split = "\\s+")[1],1))
    whpn2[i2] <- as.numeric(tail(strsplit(soilN[sn - 1,],split = "\\s+")[1],1))
    i2 <- i2 + 1
  }
  f <- f + 31
  sn <- sn + 31
}
SN <- (sn1*area1 + sn2*area2)/areaTot

WLSN <- (wlsn1*area1 + wlsn2*area2)/areaTot
SLMN <- (wlmn1*area1 + wlmn2*area2)/areaTot
WBMN <- (wbnm1*area1 + wbnm2*area2)/areaTot
WHSN <- (whsn1*area1 + whsn2*area2)/areaTot
WHPN <- (whpn1*area1 + whpn2*area2)/areaTot

scenarioLength <- dim(initialApexN)[1]
dataRange <- dim(initialData)[1]

qn <- c()
prkn <- c()
qdrn <- c()
yldn <- c()
PRKN1 <- c()
QN1 <- c()
QDRN1 <- c()
YLDN1 <- c()
PRKN2 <- c()
QN2 <- c()
QDRN2 <- c()
YLDN2 <- c()
a1 <- 1
a2 <- 1
for(i in 1:scenarioLength){
  qn[i] <- as.numeric(strsplit(initialApexN[i,],split="\\s+")[1][26])
  prkn[i] <- as.numeric(strsplit(initialApexN[i,],split="\\s+")[1][28])
}

```

```

qdrn[i] <- as.numeric(strsplit(initialApexN[i,],split = "\\s+")[1][35])
yldn[i] <- as.numeric(strsplit(initialApexN[i,],split = "\\s+")[1][59])
if(i%%2 == 0){
  QN2[a2] <- qn[i]
  PRKN2[a2] <- prkn[i]
  QDRN2[a2] <- qdrn[i]
  YLDN2[a2] <- yldn[i]
  a2 <- a2 + 1
} else{
  QN1[a1] <- qn[i]
  PRKN1[a1] <- prkn[i]
  QDRN1[a1] <- qdrn[i]
  YLDN1[a1] <- yldn[i]
  a1 <- a1 + 1
}
}
QN <- (QN1*area1 + QN2*area2)/areaTot
PRKN <- (PRKN1*area1 + PRKN2*area2)*(1 - buffer_eff)/areaTot
QDRN <- (QDRN1*area1 + QDRN2*area2)*(1 - buffer_eff)/areaTot
YLDN <- (YLDN1*area1 + YLDN2*area2)*(1 - buffer_eff)/areaTot
#### Using SITE2.MSA
prcp <- matrix(0,2,167)
irga <- matrix(0,2,167)
et <- matrix(0,2,167)
prk <- matrix(0,2,167)
q <- matrix(0,2,167)
rssf <- matrix(0,2,167)
fn <- matrix(0,2,167)
nfix <- matrix(0,2,167)
dn <- matrix(0,2,167)
rsfn <- matrix(0,2,167)
qdr <- matrix(0,2,167)
nitr <- matrix(0,2,167)
avol <- matrix(0,2,167)
fno <- matrix(0,2,167)
fnmn <- matrix(0,2,167)
fnma <- matrix(0,2,167)
gwsn <- matrix(0,2,167)
umn <- matrix(0,2,167)
znmn <- matrix(0,2,167)
znma <- matrix(0,2,167)

for(i in 1:dataRange){
  x <- strsplit(initialData[i,], split = "\\s+")[1]
  i2 <- as.numeric(x[4]) - 2060

  if(x[2] == 1){
    if (x[6] == 'PRCP'){
      prcp[1,i2] <- as.numeric(x[19])}
    if (x[6] == 'IRGA'){
      irga[1,i2] <- as.numeric(x[19])}
    if (x[6] == 'ET'){
      et[1,i2] <- as.numeric(x[19])}
    if (x[6] == 'PRK'){
      prk[1,i2] <- as.numeric(x[19])}
    if (x[6] == 'Q'){

```

```

q[1,i2] <- as.numeric(x[19])}
if (x[6] == 'RSSF'){
  rssf[1,i2] <- as.numeric(x[19])}
if (x[6] == 'FN'){
  fn[1,i2] <- as.numeric(x[19])}
if (x[6] == 'NFIK'){
  nfix[1,i2] <- as.numeric(x[19])}
if (x[6] == 'DN'){
  dn[1,i2] <- as.numeric(x[19])}
if (x[6] == 'RSFN'){
  rsfn[1,i2] <- as.numeric(x[19])}
if (x[6] == 'QDR'){
  qdr[1,i2] <- as.numeric(x[19])}
if (x[6] == 'NITR'){
  nitr[1,i2] <- as.numeric(x[19])}
if (x[6] == 'AVOL'){
  avol[1,i2] <- as.numeric(x[19])}
if (x[6] == 'FNO'){
  fno[1,i2] <- as.numeric(x[19])}
if (x[6] == 'FNMN'){
  fnmn[1,i2] <- as.numeric(x[19])}
if (x[6] == 'FNMA'){
  fnma[1,i2] <- as.numeric(x[19])}
if (x[6] == 'ZNMN'){
  znmn[1,i2] <- sum(as.numeric(x[7:18]))}
if (x[6] == 'ZNMA'){
  znma[1,i2] <- sum(as.numeric(x[7:18]))}
if (x[6] == 'UMN'){
  umn[1,i2] <- sum(as.numeric(x[7:18]))}
if (x[6] == 'GWSN'){
  gwsn[1,i2] <- sum(as.numeric(x[7:18]))}

}else{
if (x[6] == 'PRCP'){
  prcp[2,i2] <- as.numeric(x[19])}
if (x[6] == 'IRGA'){
  irga[2,i2] <- as.numeric(x[19])}
if (x[6] == 'ET'){
  et[2,i2] <- as.numeric(x[19])}
if (x[6] == 'PRK'){
  prk[2,i2] <- as.numeric(x[19])}
if (x[6] == 'Q'){
  q[2,i2] <- as.numeric(x[19])}
if (x[6] == 'RSSF'){
  rssf[2,i2] <- as.numeric(x[19])}
if (x[6] == 'FN'){
  fn[2,i2] <- as.numeric(x[19])}
if (x[6] == 'NFIK'){
  nfix[2,i2] <- as.numeric(x[19])}
if (x[6] == 'DN'){
  dn[2,i2] <- as.numeric(x[19])}
if (x[6] == 'RSFN'){
  rsfn[2,i2] <- as.numeric(x[19])}
if (x[6] == 'QDR'){
  qdr[2,i2] <- as.numeric(x[19])}
if (x[6] == 'NITR'){

```

```

    nitr[2,i2] <- as.numeric(x[19])}
  if (x[6] == 'AVOL'){
    avol[2,i2] <- as.numeric(x[19])}
  if (x[6] == 'FNO'){
    fno[2,i2] <- as.numeric(x[19])}
  if (x[6] == 'FNMN'){
    fnmn[2,i2] <- as.numeric(x[19])}
  if (x[6] == 'FNMA'){
    fnma[2,i2] <- as.numeric(x[19])}
  if (x[6] == 'ZNMN'){
    znmn[2,i2] <- sum(as.numeric(x[7:18]))}
  if (x[6] == 'ZNMA'){
    znma[2,i2] <- sum(as.numeric(x[7:18]))}
  if (x[6] == 'UMN'){
    umn[2,i2] <- sum(as.numeric(x[7:18]))}
  if (x[6] == 'GWSN'){
    gwsn[2,i2] <- sum(as.numeric(x[7:18]))}
  }
}

PRCP <- (prcp[1,]*area1 + prcp[2,]*area2)/areaTot
IRGA <- (irga[1,]*area1 + irga[2,]*area2)/areaTot
ET <- (et[1,]*area1 + et[2,]*area2)/areaTot
PRK <- (prk[1,]*area1 + prk[2,]*area2)/areaTot
Q <- (q[1,]*area1 + q[2,]*area2)/areaTot
RSSF <- (rssf[1,]*area1 + rssf[2,]*area2)/areaTot
FN <- (fn[1,]*area1 + fn[2,]*area2)/areaTot
NFIK <- (nfix[1,]*area1 + nfix[2,]*area2)/areaTot
DN <- (dn[1,]*area1 + dn[2,]*area2)/areaTot
RSFN <- (rsfn[1,]*area1 + rsfn[2,]*area2)/areaTot
QDR <- (qdr[1,]*area1 + qdr[2,]*area2)/areaTot
NITR <- (nitr[1,]*area1 + nitr[2,]*area2)/areaTot
AVOL <- (avol[1,]*area1 + avol[2,]*area2)/areaTot
FNO <- (fno[1,]*area1 + fno[2,]*area2)/areaTot
FNMN <- (fnmn[1,]*area1 + fnmn[2,]*area2)/areaTot
FNMA <- (fnma[1,]*area1 + fnma[2,]*area2)/areaTot
GWSN <- (gwsn[1,]*area1 + gwsn[2,]*area2)/areaTot
ZNMN <- (znmn[1,]*area1 + znmn[2,]*area2)/areaTot
ZNMA <- (znma[1,]*area1 + znma[2,]*area2)/areaTot
UMN <- (umn[1,]*area1 + umn[2,]*area2)/areaTot

quickflow <- Q + RSSF + QDR
quickflow_load <- QN + QDRN + RSFN
Nfert <- FNO + FNMN + FNMA
otherNinput <- NFIK
otherNloses <- AVOL + DN + YLDN
Nstorage <- GWSN + SN + ZNMN

yearRange <- c(1:length(PRCP))

matrixRows <- length(yearRange) + 1
scenarioR <- matrix(NA,matrixRows,16)
scenarioR[,1] <- filesAvailable[j]
scenarioR[,1:2:16] <- c('Year','Precipitation (mm/sq m)','Evapotranspiration (mm/sq m)','Quickflow
(mm/sq m)','Groundwater recharge (mm/sq m)',

```

```

        'Nitrogen yield runoff (kg-N/ha/yr)', 'Nitrogen yield GW recharge (kg-N/ha/yr)', 'Total N
yield (kg-N/ha/yr)',
        'Total Nitrogen load in Quickflow (kg-N)', 'Total Nitrogen load in GW recharge (kg-
N)', 'Total N load exported (kg-N/yr',
        'Nfert [kg-N/HA]', 'Other N sources [kg-N/HA]', 'Other N losses [kg-N/HA]',
        'N storage [kg-N/HA]')
scenarioR[2:matrixRows,2] <- c(1:length(yearRange))
scenarioR[2:matrixRows,3] <- signif(PRCP,2)
scenarioR[2:matrixRows,4] <- signif(ET,2)
scenarioR[2:matrixRows,5] <- signif(quickflow,2)
scenarioR[2:matrixRows,6] <- signif(PRK,2)
## work with Yields [kg-N/hectare/yr]
scenarioR[2:matrixRows,7] <- signif(quickflow_load,2)
scenarioR[2:matrixRows,8] <- signif(PRKN,2)
scenarioR[2:matrixRows,9] <- signif(quickflow_load + PRKN,2)
scenarioR[2:matrixRows,10] <- signif(quickflow_load*areaTot,2)
scenarioR[2:matrixRows,11] <- signif(PRKN*areaTot,2)
scenarioR[2:matrixRows,12] <- signif((quickflow_load + PRKN)*areaTot,2)
scenarioR[2:matrixRows,13] <- signif(Nfert,4)
scenarioR[2:matrixRows,14] <- signif(otherNinput,4)
scenarioR[2:matrixRows,15] <- signif(otherNloses,4)
scenarioR[2:matrixRows,16] <- signif(Nstorage,4)

avgLoad[j+1,1] <- filesAvailable[j]
avgLoad[j+1,2:avgLoadParamaters] <-
c(signif(mean(quickflow[140:167]),2),signif(mean(PRK[140:167]),2),
    signif(mean(quickflow_load[140:167]),2),signif(sd(quickflow_load[140:167]),2),
    signif(mean(PRKN[140:167]),2),signif(sd(PRKN[140:167]),2))

setwd('~')
setwd('../Desktop/APEX_R_outputs')
write.csv(scenarioR, file = paste(filesAvailable[j],'.csv',sep="))
print(j)
}

write.csv(avgLoad,file = 'Average Steadystate load.csv')

```

## A.5 R Code: Chapter 2 LPM and Watershed Builder

```
##### Watershed_Builder #####
# Author: John Larkin
# Last revised: 15 December 2019
# For the USGS
# In support of Masters of Science in Civil Engineering with an emphasis in Environmental Engineering
from
# the University of Minnesota

# This stand-alone model builds a theoretical, user-designated, watershed. It accesses results from APEX
# (Agricultural POLicy/Environmental eXtender model) that are stored in '.csv' files.

setwd('~') # sets working directory to default location (documents folder is default)
setwd('../Desktop/APEX_R_outputs')

directions <- readline(prompt='Read directions for model (yes/no)? ')
if(directions == 'yes'){
  cat("This model creates a user-specified watershed(both size and composition)
  and calculates the annual watershed stream flow and total nitrogen load.
  There are several prompts to follow as the watershed is built:

  First, the user is prompted for the land use and management. A list of available land
  uses and managements is printed. The index number corresponding to that unit field is typed
  for the response. If more than one type of unit field is used place a space between
  the different index numbers.

  Second, the user will be asked to add the number of each land unit to the watershed. Type the
  Type the number of fields you wish to add of each unit field.

  FOR EXAMPLE: 'scenario indices'= 1 5 22 THEN '# land units' = 250 100 150
  would result in
  Scenario 1 @ 250 fields
  Scenario 5 @ 100 fields
  Scenario 22 @ 150 fields

  The number of land units currently in the watershed is printed for the user's own knowledge
  before being prompted to continue, then asked whether or not
  additional land units are to be added to the watershed.

  The model will provide a range of aquifer thickness and the resulting composite groundwater age.
  The user can then indicate their desired aquifer thickness.
  The model will request concentrations of nitrogen in groundwater before the model period,
  if 0 then must indicate 0.")
}

readline(prompt = 'Press [Enter] to continue')
setwd('C:/Users/John Larkin/Desktop/APEX_R_outputs')
filesAvailable <- list.files()

##### User interface #####
Ws_comp <- c()
Ws_comp_num <- c()
i = 1
```

```

# while (readline(prompt = 'Add to the watershed(yes/no)? ') == 'yes'){
  print(filesAvailable)
  ws_comp <- strsplit(readline(prompt = 'Scenario indices (type each index followed by a space,
    then press"enter" when done)? '),split = ' ')[[1]]
  ws_comp_num <- strsplit(readline(prompt = 'How many of the land units in that land management
    (type number of each land unit followed by space,
    then press "enter" when done? '),split = ' ')[[1]]

  for(i in 1:length(ws_comp)){
    Ws_comp[i] <- as.integer(ws_comp[i])
    Ws_comp_num[i] <- as.integer(ws_comp_num[i])
  }

  print(paste("Number of land units designated: ",sum(Ws_comp_num)))
  readline(prompt = 'Press [Enter] to continue')
#### Gw calculations ####
yearRange <- c(1:167)
porosity <- 0.45

areaHA <- 13.21
area <- areaHA*100*100
kg_to_mg <- 1e6
mg_to_kg <- 1e-6
mm_to_m3 <- 1e-3
m3_to_l <- 1e3
L_to_m3 <- 1e-3

runoff <- matrix(0,nrow = length(Ws_comp), ncol = 167)
runoff_load <- matrix(0,nrow = length(Ws_comp), ncol = 167)
gw_recharge <- matrix(0,nrow = length(Ws_comp), ncol = 167)
gw_load <- matrix(0,nrow = length(Ws_comp), ncol = 167)

for(i in 1:length(Ws_comp)){
  runoff[i,1:167] <- as.numeric((read.csv(filesAvailable[Ws_comp[i]],colClasses = 'character')[2:168,6]))
  gw_recharge[i,1:167] <- as.numeric((read.csv(filesAvailable[Ws_comp[i]],colClasses =
'character')[2:168,7]))
  runoff_load[i,1:167] <- as.numeric((read.csv(filesAvailable[Ws_comp[i]],colClasses =
'character')[2:168,10]))
  gw_load[i,1:167] <- as.numeric((read.csv(filesAvailable[Ws_comp[i]],colClasses =
'character')[2:168,11]))
}
mean_gw_recharge <- c()
for(i in 1:length(Ws_comp)){
  mean_gw_recharge[i] <- mean(gw_recharge[i,])
}

buffers_present <- grep('Buffer',filesAvailable[Ws_comp])
buffer_eff <- 0.5
for(i in 1:length(Ws_comp)){
  if (i == buffers_present){
    gw_load[i,1:167] <- gw_load[i,1:167]*buffer_eff
  }
}

# Create a range of groundwater transit times as a fxn of aquifer thickness
H <- c(1,5,10,20,40)

```

```

tbar <- c()
Tbar <- matrix(0,length(H) +1 ,2)
Tbar[1,1:2] <- c('Saturated aquifer thickness [m]', 'Mean transit time [yr] for watershed')
Tbar[2:(length(H) +1),1] <- H

for(j in 1:length(H)){
  for(k in 1:length(Ws_comp)){
    tbar[k] <- (porosity*H[j]/(mean_gw_recharge[k]/1000)) # nH/N, porosity*Saturated aquifer
    thickness/areal recharge rate, convert from mm to m
  }
  Tbar[(j+1),2] <- sum(Ws_comp_num*tbar)/sum(Ws_comp_num)
}
print(Tbar)
H <- as.numeric(readline(prompt='GW TRANSIT TIME AS A FXN OF AQUIFER THICKNESS.
Please indicate the saturated aquifer thickness to achieve desired mean GW transit times. '))

tbar <- c()
for(k in 1:length(Ws_comp)){
  tbar[k] <- mean(porosity*H/(mean_gw_recharge[k]/1000))
}

lengthofRain <- 167
i2 <- lengthofRain
baseflowArray <- matrix(0, length(Ws_comp), ncol = 167)
baseloadArray <- matrix(0,length(Ws_comp),167)
nitrogen_seed <- as.numeric(readline(prompt='Seed groundwater with nitrogen concentration (mg/L)? '))

for (j in 1:length(Ws_comp)){
  baseflowMatrix <- matrix(0, 167, 167)
  baseloadMatrix <- matrix(0,167,167)

  for( i in 1:lengthofRain){
    Et <- ((1/tbar[j])*exp(-c(1:lengthofRain)/tbar[j]))[1:i2]
    GWEt <- Et*gw_recharge[j,i:lengthofRain]
    NEt <- Et*gw_load[j,i:lengthofRain]
    if (i > 1){
      zeros <- 0*c(1:(i-1))
      baseflowMatrix[i,] <- c(zeros,GWEt)
      baseloadMatrix[i,] <- c(zeros,NEt)
    }
    else{
      baseflowMatrix[i,] <- GWEt
      # print("Work")
      baseloadMatrix[i,] <- NEt
    }
    i2 <- lengthofRain - i
  }

  baseflow <- c(1:lengthofRain)*0
  baseload <- c(1:lengthofRain)*0

  for ( i in 1:lengthofRain){
    old_water <- (gw_recharge[j,i] - sum(baseflowMatrix[,i]))
    #Calculates to contribution to baseflow from 'old' water
    baseflow[i] <- sum(baseflowMatrix[,i]) + old_water
  }
}

```

```

# baseflow from recharge + baseflow from already present groundwater
baseload[i] <- sum(baseloadMatrix[,i]) +
old_water*mm_to_m3*m3_to_l*nitrogen_seed*mg_to_kg*area
#nitrogen load from scenario water + n load old water

}
baselflowArray[j,1:167] <- baselflow
baseloadArray[j,1:167] <- baseload
}

#### Watershed compilation ####
scenario_runoff <- c(1:167*0)
scenario_baseflow <- c(1:167*0)
scenario_runoff_load <- c(1:167*0)
scenario_baseflow_load <- c(1:167*0)

for(i in 1:length(Ws_comp)){
  scenario_runoff <- scenario_runoff + runoff[i,]*Ws_comp_num[i]*mm_to_m3*area*m3_to_l
  scenario_baseflow <- scenario_baseflow +
baselflowArray[i,]*Ws_comp_num[i]*mm_to_m3*area*m3_to_l
  scenario_runoff_load <- scenario_runoff_load + runoff_load[i,]*Ws_comp_num[i]
  scenario_baseflow_load <- scenario_baseflow_load + baseloadArray[i,]*Ws_comp_num[i]
}

scenario_flow <- scenario_runoff + scenario_baseflow
scenario_load <- scenario_runoff_load + scenario_baseflow_load
scenario_conc <- ((scenario_runoff_load + scenario_baseflow_load)*kg_to_mg)/(scenario_runoff +
scenario_baseflow)

name_scenario <- matrix(NA,168,10)

name_scenario[1,1:10] <- c('Index #','# of land units','Saturated Aquifer thickness','Mean GW transit time
[yr]','Year',
'GW component flow [L/yr]','Annual flow from watershed [L/yr]','Gw component load [kg-
N/yr]',
'Annual load from watershed [kg-N/yr]','Avg annual N concentration from watershed
[mg-N/L]')
name_scenario[2:(length(Ws_comp) +1),1] <- filesAvailable[Ws_comp]
name_scenario[2:(length(Ws_comp) +1),2] <- Ws_comp_num
name_scenario[2:(length(Ws_comp) +1),3] <- H
name_scenario[2:(length(Ws_comp) +1),4] <- sum(Ws_comp_num*tbar)/sum(Ws_comp_num)
name_scenario[2:168,5] <- 1:167
name_scenario[2:168,6] <- scenario_baseflow
name_scenario[2:168,7] <- scenario_flow
name_scenario[2:168,8] <- scenario_baseflow_load
name_scenario[2:168,9] <- scenario_load
name_scenario[2:168,10] <- scenario_conc

avg_load <- mean(scenario_load[140:167])
avg_flow <- mean(scenario_flow[140:167])
print(paste('Mean annual steady state flow [L/yr]= ',avg_flow," ",
'Mean annual steady state load [kg-N/yr]= ',avg_load))
plot(scenario_load,t='l',xlab = 'Model Year',ylab = 'Annual stream N load [kg-N/yr]')
print(paste(Ws_comp_num,' of ',filesAvailable[Ws_comp]))
final_name <- readline(prompt='Name for scenario? ')
write.csv(name_scenario,file= paste('./Watersheds/',final_name,'.csv',sep=""))

```