Spatio-Temporal Patterns in Net Anthropogenic Nitrogen and Phosphorus Inputs Across the Grand River Watershed

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Author’s Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Xiaoyi Zhang
Abstract

Over the last century, human activities have dramatically increased the inputs of nitrogen (N) and phosphorus (P) to land, resulting in increased eutrophication of aquatic systems, and degradation of drinking water quality. Although many changes in management have been adopted to mitigate these impacts, little improvement has been observed in water quality. Multiple N and P mass balance studies have indicated imbalances between inputs and outputs of N and P in anthropogenic landscapes. In this work, historical (1901-2011) N and P budgets for the Grand River Watershed (GRW) in southwestern Ontario were developed using the NANI/NAPI (net anthropogenic N/P input) framework. NANI was calculated as the sum of four different components: commercial fertilizer N application, atmospheric N deposition, net food and feed imports, and biological N fixation. A similar budgeting method was used to estimate NAPI, which includes fertilizer P application, net food and feed imports and detergent P use by humans. Relevant data was obtained from the Canadian agricultural census, Environment Canada, and literature estimates. Our results showed that annual NANI and NAPI values increased approximate 2-fold since 1901, with peak net inputs in 1986 and 1976, respectively. Increases in NANI over time can primarily be attributed to high atmospheric N deposition, fertilizer N application and biological N fixation, while increases in NAPI are primarily due to increased fertilizer P application. Spatially, the hotspots for both NANI and NAPI have since the early 1950s shifted to the central sub-watersheds of the GRW, which can be attributed to greater urbanization and agricultural intensification in the central area. The historical NANI and NAPI estimates obtained for the GRW provide insights into the spatio-temporal patterns in NANI and NAPI, and can facilitate better N and P management strategies.
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Chapter 1 - Introduction

1.1 The Natural Nitrogen and Phosphorus Cycles

Nitrogen (N) and phosphorus (P) are essential elements for all living organisms on earth. There is abundant N gas in the atmosphere, but only small amounts of N are available to organisms (Delwiche 1970; Galloway 1998). The primary production of many terrestrial and marine ecosystems is limited by N because only the reactive N can be taken up by plants. In the natural world, lightning and biological N fixation (BNF) are the important sources of energy to convert N gas to reactive N (ammonia and nitrates) that can be used by plants effectively (Galloway 1998). When animals consume the plants, reactive N is obtained by animals (EHP 2004). After the death of plants and animals, N compounds are released into soils by the decomposition of organisms. Ammonia is produced in this decomposition process, and then is converted to nitrates through the nitrifying bacteria (SLH 2013). Finally, nitrates are converted back to N\(_2\) in the process of denitrification. The whole N cycle is completed.

Bedrock, soils and organic material are the three pools of P in the continental reservoir (Ruttenberg 2003). Apatite (Ca\(_{10}\)(PO\(_4\)\(_6\))(OH,F,Cl)\(_2\)) is the most abundant P-bearing mineral on earth and contains 95% of P in crustal rocks (Smil 2000; Ruttenberg 2003). Weathering of apatite provides phosphates to soils that supports the growth of plants in terrestrial systems (Ruttenberg 2003). Then plants are consumed by animals, and phosphates are incorporated into organisms. After the death and decay of plants and animals, P then is returned to soils. Primarily, P attached to soil particles is transferred into oceans by river flows (Ruttenberg 2003).

1.2 Human Modification of the N and P Cycles

1.2.1 Human Activities Accelerate the N and P Cycles

Over the last century, human activities such as the combustion of fossil fuels, application of fertilizers and cultivation of N-fixing crops have greatly enhanced rates of N fixation on land (Vitousek et al. 1997). Consequently, both the availability and the mobility of N have increased (Vitousek et al.
1997), and the amount of reactive N in the world has doubled (Galloway et al. 2004). The global P cycle has also been dramatically accelerated by a series of human actions over the past 60 years. P is mined at a large scale and is used in fertilizers, animal feeds and other products that are transported to agricultural lands globally (Bennett et al. 2001). The dominant anthropogenic N and P sources are listed as follows:

*Combustion of fossil fuels:* The burning of fossil fuels converts organic N contained in coal, oil and natural gas to NO\(_x\) in the atmosphere (Galloway et al. 1995). It leads to the production of 21 Tg reactive N annually on a global scale (Levy and Moxim 1989). A large portion of the N emission sinks to both the land and sea surface by wet and dry deposition and pollutes our waterways (Smith et al. 1999).

*Application of fertilizers:* One of the most significant transformations in agriculture is the shift from BNF to industrial fixation of N (Crews & Peoples 2004). The Haber-Bosch process is the main industrial procedure to synthesize N fertilizers, which have been largely produced to increase crop yields since the 1940s in order to fulfill demand for food as a result of increasing growth of population (Farrar et al. 2014). N fixed by industries for production of fertilizers is approximately 80 Tg yr\(^{-1}\) and represents the largest source of human-induced reactive N to the global ecosystem (Vitousek et al. 1997). In order to improve crop production and support the growing population, the mined phosphate rocks that used as fertilizers have increased greatly since the late 1940s (Ruttenberg 2003). Excessive application of fertilizers and animal manure to agricultural lands has led to the accumulation of P in soils (Bennett et al. 2001). For example, Fluck et al. (1992) reported that less than 20% of P from fertilizer application was output in agricultural products in the Lake Okeechobee watershed in Florida. Fertilizer P application in excess of P in crop removal in European countries ranged from 0.7 to 57.2 kg P/ha/yr (Runge-Metzger 1995).


* Cultivation of *N*-fixing crops*: Cultivation of legumes and forages associated with the symbiotic *N*-fixing bacteria can convert *N*$_2$ from the atmospheric *N* pool to reactive *N*, which provides a new source of anthropogenically fixed *N* (Galloway et al. 2004; Vitousek et al. 1997). The global-scale estimates of the amount of *N* fixed by legumes and other crops is between 50 and 70 Tg *N* yr$^{-1}$ (Herridge et al. 2008).

### 1.2.2 Serious Environmental and Health Effects of *N* and *P* Pollution

Human alterations of the *N* and *P* cycles have caused severe *N* and *P* pollution in our ecosystems, as described below.

*Eutrophication*: Eutrophication is a one of the most severe water pollution problems where bodies of water receive increasing levels of *N* and *P* suffer from severe algal blooms (Howarth and Marino 2006). The decay of algae deplete oxygen in water that can lead to die-offs of aquatic animals (Anderson et al. 2002; Smith et al. 1999). One of the largest hypoxic zones occur in the northern Gulf of Mexico where the concentration of oxygen can drop to below 2 mg/L (National Oceanic and Atmospheric Administration 2015). This phenomenon occurs every summer mainly due to excess anthropogenic nutrient inputs from the Mississippi River to the Gulf (Goolsby et al. 1997). While *N* is the limiting nutrient implicated for hypoxia in the Gulf of Mexico, *P* is considered to be responsible for hypoxia in Lake Erie (Egerton 1987; Boesch et al. 2006; Jeppesen et al. 2005; Schernewshi and Neumann 2004; Duarte et al. 2009).

*Health effects*: *N* contamination of both surface water and groundwater caused by the widespread use of *N* fertilizers has been identified as a serious health threat (Vitousek et al. 1997). Methemo-globinemia, or blue baby syndrome, has been identified as the most significant health effect associated with the high nitrate levels in drinking water (Knobeloch et al. 2000). Blue baby syndrome can lead to low oxygen in a baby's blood and make the skin turn blue (Knobeloch et al. 2000). The drinking water standard for nitrate in Canada set by Health Canada is 10 mg N/L. For *P*, other than toxic algal blooms,
no direct health effects of P have been identified (Amdur et al. 1991), and therefore there are no drinking water standards for it (U.S. EPA 1990). However, P pollution becomes a problem when total P concentration is larger than 20 µg/L for most freshwater systems (Correll 1998).

*Greenhouse gas N$_2$O:* Human activities have also led to significant increases in the atmospheric concentrations of N$_2$O, a greenhouse gas that has a great global warming potential (Forster et al. 2007). Del Grosso et al. (2008) report that the global emission of N from agricultural systems in the form of N$_2$O is approximately 5.8 Tg annually. According to the Intergovernmental Panel on Climate Change (2007), N$_2$O accounted for 8% of global greenhouse gas emissions in 2004.

*Other effects:* N deposition can damage plants, lead to losses of soil nutrients and increases in soil and water acidity, and cause biodiversity loss of our ecosystems (Diseet al. 2011; Vitousek et al. 1997).

### 1.2.3 Best Management Practices for Reduction of N and P Pollution

Understanding of the detrimental effects of N and P pollution has led to the adoption of several best management practices (BMPs) to mitigate their impacts. Best Management practices often are combinations of practices, generally including soil and water conservation practices, cropping and tillage practices, animal manure management and so on (Sharpley et al. 2006). Many studies have noted little or no nitrate concentration reduction even after well-designed watershed management practices (Hamilton 2012). In several major rivers of Eastern Europe, little water quality improvement was observed in response to significant decline in the application of fertilizers since the late 1980s (Grimvall et al. 2000). For the Yongan River watershed in China, even though the annual net anthropogenic N input declined from 2000 because of the decreased fertilizer N use and BNF, the riverine N flux still increased (Chen et al. 2014). Furthermore, in the Thames River of the U.K., even though fertilizer N application has been controlled to reduce the watershed N inputs since the beginning of the 1980s, nitrate concentration for the Thames remained high (Howden et al. 2010).
Although P-based BMPs have been applied in many areas, the effects of these BMPs may delay due to time lags between water quality improvements and management changes (Jarvie et al. 2013). For example, in one Catskill Mountain watershed, Bioshop et al. (2005) did not find changes of P loading in river runoff in response to BMPs. In the Chesapeake Bay, there were no ecological improvements that have been observed in response to BMPs (Jarvie et al. 2013). Without knowing the fate of P across a watershed, it is hard to reduce riverine P export through the implementation of BMPs (Sharpley et al. 1996; Sharpley et al. 2009). Therefore, in order to understand the role of BMPs in mitigating N and P pollution in our waters, it is important for us to determine the fate of N and P that is applied on landscapes, thus necessitating mass balance studies that are described in the next section.

1.3 The Fate of Anthropogenic N and P

1.3.1 Mass Balance Studies

Several mass balance studies have been done over the years attempting to quantify the fate of the applied N and P on landscapes (Howarth et al. 1996; Goolsby et al. 1999; Baker et al. 2001; Bouwman et al. 2005; Hong et al. 2012, 2011; Russell et al. 2008; Han et al. 2012, 2011). The most common approaches for doing watershed N and P balances are known as the Net Anthropogenic Nitrogen and Phosphorus Inputs (NANI and NAPI; Howarth et al. 1996; Hong et al. 2012, 2011).

The NANI and NAPI frameworks has been applied in multiple watersheds by numerous researchers (Hong et al. 2012, 2011; Howarth et al. 2006; Janzen et al. 2003; Russell et al. 2008; Han et al. 2011). Hong et al. (2011), for example, calculated county-level NANI in 1992 for the continental United States and found relatively high NANI in the Eastern and Midwest US (>50 kg N/ha/yr). Among the Baltic Sea basin in Europe, NANI in southern regions (~35-50 kg N/ha/yr) was estimated much higher than in northern regions (~4-7 kg N/ha/yr; Hong et al. 2012). For the Chesapeake Bay region in the United States, NAPI was estimated for all the counties with values ranging from 0.02 to
78.46 kg P/ha/yr (Russell et al. 2008). NAPI framework was also applied for the 18 Lake Erie watersheds of the United States from 1935 to 2007 (Han et al. 2012).

1.3.2 N Retention in Anthropogenic Landscapes

The fate of NANI has been explored in various studies. For example, multiple watershed-scale N balance studies have indicated that N export in streamflow accounts for approximately 25% of NANI to the system (Galloway et al. 2004; Howarth et al. 1996; Howarth et al. 2006; Howarth et al. 2011). So this statistic begs the question, where did the remaining 75% of N go? This difference between the net anthropogenic N inputs (NANI) and riverine N export is most commonly referred to as N retention or missing N (Goolsby et al. 1999; Howden et al. 2011; Schlesinger 2009; Van Meter et al. 2015). Chen et al. (2008), for example, calculated the N budget for the Jiulong River watershed in China with total inputs of N exceeding N outputs by 56.4 kg/ha/yr. Within the Mississippi-Atchafalaya River Basin of the United States, annual N residual (N inputs minus N outputs) varied between 0.3 and 3.6 million tons from 1951 to 1996 (Goolsby et al. 1999) after accounting for denitrification, immobilization, and volatilization fluxes. For all agricultural lands in Canada, Janzen et al. (2003) reported that the difference between anthropogenic N inputs and outputs is 1.13 Tg in 1996. All these studies indicate the imbalance between N inputs and outputs on the landscapes.

This missing N is most likely stored within the subsurface or denitrified, but uncertainty remains regarding the magnitude of these N fluxes (Van Breemen et al. 2002). In the subsurface environment, the major N pools are groundwater, vadose zones, and soil organic N (Baker et al. 2001; Van Meter et al. 2015). The great increase of human-induced N inputs have caused increasing groundwater nitrate concentrations worldwide over the last decades (Burow et al. 2010; Puckett et al. 2010; Worrall et al. 2015). The nitrate legacy in groundwater has been suggested as the reason for the increase of nitrate in some rivers of both the United States and United Kingdom, even though total N inputs to the lands have decreased (Sprague et al. 2011; Worrall et al. 2009). However, it is difficult to determine the
amount of accumulated N in groundwater directly because of complex groundwater flow systems and rapid fluctuations of water levels (Baker et al. 2001). Extremely high dissolved nitrate concentration has been observed in the vadose zone below farmlands in the Salt River Valley in Arizona of the United States (Rice et al. 1989). Lastly, organic N in the soil is the largest pool of N, but the understanding of it is generally poor (Van Meter et al. 2015). In one study, Van Meter et al. (2015) reported the soil N accumulation across the Mississippi River Basin accounted for 65% of net anthropogenic N input from 1980 to 1996. Baker et al. (2001) show that the total accumulation of N within the Central Arizona-Phoenix ecosystem was 21 Tg/yr. In order to understand N accumulation in these different pools, it is important to do N mass balance studies over time.

1.3.3 P accumulation in terrestrial ecosystems

The application of P fertilizers and animal manure in excess of crop requirements in agricultural lands can cause P accumulation in landscapes and increase the risk of P pollution in surface waters (Carpenter et al. 1998). The accumulation of P in soils has been observed in many studies and has already became a big challenge for the management of agricultural practices and water quality (MacDonald et al. 2011). For example, in the P mass balance study of the upper Potomac River Basin in the United States, Jaworski et al. (1992) found that over 60% of P was stored in the watershed. In the Maumee Basin, Powers et al. (2016) reported that there were more than 200 kiloton P accumulation in the basin during the 1970s and 1980s. In addition, riverine P export accounted for about 5% of NAPI in the St. Lawrence basin on average, and the rest NAPI was accumulated in the watershed (Goyette et al. 2016). Therefore, it is important to understand the patterns of long-term P accumulation in landscapes by doing P mass balance studies over time, which can facilitate better BMPs and water quality improvements.
1.4 Canada's N and P Pollution

More and more N and P is transported from the terrestrial system to the oceanic system over the world. It was estimated that there were 0.3 million tons of N released to Canadian water bodies from anthropogenic sources in 1996 (Schindler et al. 2006). In Ontario, 30% of water use is extracted from groundwater, and multiple studies from 1950 to 1992 have shown that 5%-20% of rural wells have a concentration of nitrates exceeding the maximum accepted drinking water standards (10 mg nitrate-N/l) (Goss et al. 1998). For example, at the Venison Creek watershed in Ontario, high nitrate concentration has been observed in both shallow and deep aquifers (Egboka 1984). The Great Lakes, located at the boundary between Canada and the United States, has had serious water quality problems since the 1960s. Excessive algal blooms were observed in the Great Lakes as a consequence of great amounts of P inputs (ECCC 2013). In particular, Lake Erie algal blooms have impacted human activities and wildlife habitats negatively (ECCC 2013).

Lake Erie is the smallest (by volume), shallowest and most productive lake of the Great lakes (Environment Canada 2010). The main inflow of the lake comes from St. Clair River via Superior, Michigan, and Huron Lakes. The drainage basin of the lake covers about 78,000 Km² and has the highest population density of the five Great lake basins (Great Lakes Information Network 2015). Agriculture is the major land use in the Erie lake basin. During the 1960s, eutrophication became a very severe pollution problem in Lake Erie due to excess inputs of P and N from agricultural activities and human sewage (Egerton 1987). The P loads to Lake Erie decreased about 60% until the early 1980s (U.S. Environmental Protection Agency 2011), and the algal blooms were controlled after a series of attempts to reduce P in Lake Erie. However, the concentrations of nitrates in the tributaries of the agricultural lands still increased 0.06-0.10 mg/l annually from 1977 to 1993 even after implementation of agricultural management practices (Baker 1993). Unfortunately, algal blooms came back again to Lake Erie in 2011, which were the largest blooms in the recorded history of Lake Eire (Michalak et al.
The increase in P loading to Lake Erie due to the changes of land use and agricultural practices may lead to the exacerbation of this recent bloom (Michalak et al. 2013).

In Canada, agriculture is the primary contributor to N and P pollution. Fertilizer sales in Canada have increased from 210,000 tonnes in 1966 to 2.4 million tonnes in 2013. The sales in Ontario rapidly increased from 68,000 tonnes in 1966 to 237,000 tonnes in 1985, followed by a 41% decline from 1985 to 1994, and then the sales have remained more or less steady (Figure 1.1). In Alberta, Quebec, Manitoba, Saskatchewan, and British Columbia, livestock and poultry populations have increased several times since the 1950s (Schindler et al. 2006). There are significant amounts of manure applied to land in the areas that have high livestock populations (Schindler et al. 2006). The lack of management for discharge of animal waste and disorganized manure application has caused high ammonia emissions and surface water N and P pollution in most of Canada (Schindler et al. 2006).

1.5 Objectives

Understanding N and P input and output trajectories at the watershed scale is critical to quantifying the legacies of N and P that might contribute to time lags between land use change and water quality improvement. The overall objective of this thesis is to characterize the historical trends in (1901-2011) the sources and sinks of N and P across the Grand River watershed (GRW) in southern Ontario. A related objective was to understand the spatial patterns in N and P inputs and outputs across the GRW to identify the hotspots that would potentially have poor water quality.

The GRW is the largest watershed in southwestern Ontario that drains into Lake Erie and is known to have significant N and P pollution issues. This thesis contains four chapters: Chapter 1 introduces N and P pollution problems around the world and in Canada, chapter 2 is the description of the detailed methodologies for calculating Net Anthropogenic Nitrogen and Phosphorus Inputs (NANI and NAPI) for the Grand River watershed, chapter 3 contains the results and discussion about the spatio-temporal patterns of NANI and NAPI over the GRW and Chapter 4 provides a summary and recommends future work.
Chapter 2 - Materials and Methods

2.1 Overview

In this chapter, I describe the methodologies to estimate the Net Anthropogenic Nitrogen and Phosphorus Inputs (NANI and NAPI) in the Grand River watershed. The study area is described in Section 2.2, data sources are described in Section 2.3, methodologies for calculating NANI and NAPI are described in Section 2.4 and 2.5 respectively, uncertainty analyses are summarized in Section 2.6, and downscaling NANI and NAPI estimates from the county to the sub-basin scale is described in Section 2.7.

2.2 Watershed Description

The Grand River is 300 kilometers long extending from the village of Dundalk to Lake Erie and drains approximately 6,965 Km² of southwestern Ontario (Grand River Conservation Authority 2015; Figure 2.1). The Grand and Detroit Rivers are the two major tributaries of Lake Erie (Singer et al. 2003). There are 925,000 people living in the Grand River Watershed, but most of them live in the five cities of Waterloo, Kitchener, Cambridge, Guelph, and Brantford (GRCA 2015). Agriculture, forested land and urbanized land make up 75%, 19% and 5% of the total land area respectively (Grand River Watershed Characterization Report 2008). Major crops include small grains, corn, hay and beans.

The north region of the Grand River watershed is formed of low permeable till plains (Holysh et al. 2000). A large portion of it is covered by agriculture and wetlands, and a relatively small fraction is urbanized land (Loomer and Cooke 2011). The region encompasses the four rivers that are Conestogo River, Nith River, Upper Grand River, and Speed River (Cooke 2010). In the Upper Grand River, the water quality is acceptable, but the nutrient levels tend to be high in the Belwood reservoir downstream (Loomer and Cooke 2011).

The central parts of the watershed are characterized by highly permeable sand and gravel (Holysh et al. 2000). Significant groundwater is used for drinking water supplies in the central area. Most of the
urban areas are focused in the central region and 64% of the land area is used for agriculture (Grand River Water Management Plan 2013). Complex intrinsic geology, land use and human activities greatly influence the water quality in the central region (Cooke 2006). Irvine Creek, Canagagigue Creek are the two tributaries of the Grand River in this area that have nitrate concentrations two to three times higher than other river systems (Loomer and Cooke 2011). High P concentrations were also observed during the spring season (Loomer and Cooke 2011).

**Figure 2.1.** Map of the Grand River Watershed, obtained from GRCA (2015)

The southern region of the Grand River Watershed is comprised of low permeable clay plain (Holysh et al. 2000), generating great amounts of highly turbid runoff (Cooke 2006). Pollution tolerant
species can survive in low light, low oxygen and high turbid environments, and they are dominant in Cayuga of the lower Grand River in 2003-2005 (Cooke 2010). The water quality is generally poor in terms of high nutrient and periodic low levels of dissolved oxygen in the southern region (Cooke 2010). The P concentrations are very high (> 0.12 mg/l) at Dunnville located in the lower Grand River and are considered as the major sources of P flowing into eastern Lake Erie (Loomer and Cooke 2011).

Agriculture is the dominant land use in the Grand River watershed, and it covers 75% of the total land area. Since the 1950s, the Grand River has received much attention, as it offers drinking water and other important services (e.g. fisheries and tourism) to many of its residents (Loomer and Cooke 2011). In recent years, there has been increased concern of the ecological conditions of the river and its tributaries with continued population increase, intensification of farming and climate change (Loomer and Cooke 2011). High levels of nitrates have been observed in some tributaries of the Grand River, especially during the winter months (Cooke 2010), whereas phosphorus levels tend to be high during the spring (Cooke 2006).

2.3 Data sources

Data for estimating the annual NANI and NAPI budgets for the census years from 1901 to 2011 for the Grand River watershed was obtained from the agricultural census (Statistics Canada) and other relevant sources of the 11 counties (Table 2.1 and Table 2.4).

2.4 Net Anthropogenic Nitrogen Input (NANI) Calculation at the county scale

NANI is made up of four components (Figure 2.2): atmospheric N deposition, fertilizer N application, biological N fixation, and net food and feed N imports or exports. The latter has four subcomponents, namely, crop N production, animal N production and consumption, and human N consumption (Hong et al. 2011). In this approach, animal manure is not included in this analysis since it is considered largely recycled within one region and does not provide new N (Howarth et al. 1996). In addition, N inputs from wastewater discharges are not considered as input terms because N in wastewater is from food originally, which has N from fertilizer application or biological N fixation
Further, ammonia is also not considered in this method since it is assumed that it is redeposited within the same watershed where it is emitted from animal manure (Howarth et al. 1996; Howarth et al. 2002).

Figure 2.2. Overview of NANI and its components as described in Hong et al. (2011). (adapted from Howarth et al. 1996).

A historical N budget for the Grand River Watershed was developed for the period 1901-2011 using the Net Anthropogenic Nitrogen Input (NANI) framework as described by Hong et al. (2011). NANI is calculated as the sum of four components (equation 2.1):

\[
\text{NANI} = \text{FERT}_N + \text{DEP} + \text{NFFI}_N + \text{BNF}
\]  

(2.1)

where \(\text{FERT}_N\) (kg N/ha/yr) is commercial N fertilizer, \(\text{DEP}\) (kg N/ha/yr) is atmospheric N deposition, \(\text{NFFI}_N\) (kg N/ha/yr) is N contained in net food and feed imports, and \(\text{BNF}\) (kg N/ha/yr) is biological N fixation. Quantification of these subcomponents of NANI is described below.
**Fertilizer N application (FERT\(_N\)):** One important component of NANI is Fertilizer N use, which only includes the application of commercial fertilizer N and does not include animal manure fertilizer in this analysis. Fertilizer N application was calculated using a combination of provincial-level fertilizer sales and fertilizer use data together with cropped area data at both the county and provincial levels (Alexander and Smith 1990; Table 2.1), as shown below:

\[
FERT_N = F_{sales} \times \frac{CA_{county} \times A}{CA_{province} \times B} \times U
\]  
(2.2)

where \(F_{sales}\) (kg) is N contained in annual fertilizer sales in Ontario (Korol and Rattray 2002; Canadian Fertilizer Institute 2015; Statistics Canada 2014), \(CA_{county}\) and \(CA_{province}\) are the county- and province-level cropped areas (ha), \(A\) and \(B\) are the ratios of the fertilized cropland area to the total cropped area at the county- and provincial-levels respectively, and \(U\) is a use parameter, corresponding to the estimated fraction of fertilizer sold that is actually applied to cropland. The use parameter \(U\) was calculated as 90.6% for the year 1986, the only year for which direct use total fertilizer sales and total applied fertilizer data (Statistics Canada) was available for Ontario. The use value was assumed to remain constant throughout the study period.

**Atmospheric N Deposition (DEP):** Wet deposition data for nitrates from 1978-2011 at different stations within or near the Grand River watershed was obtained from the NatCHEM database, Environment Canada (2014; Table 2.1). These stations were mapped (Figure 2.3) using GIS software, and deposition values over the GRW were estimated from the point data using the Thiessen polygon method (ESRI 2014). There is no measured data before 1978 and very little data available for stations between 1978 and 1980, and the data that was available was unusually high. Thus to get pre-1980 data we used the modeled deposition values provided by Dentener (2006). The latter provided global gridded estimates of nitrate deposition for 1860 and 1993. In this analysis, we used the modeled 1860 values, and estimated deposition from 1901 to 1976 by assuming a linear relationship between the modeled deposition in 1860 and the measured nitrate deposition data in 1981.
<table>
<thead>
<tr>
<th>NANI Components</th>
<th>Data Type</th>
<th>Data Sources</th>
<th>Temporal Resolution</th>
<th>Spatial Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Net Food and Feed N Imports</strong></td>
<td>Crop N Production</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td>Cropland Area</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1961-2011 (every 5 years)</td>
<td>Ontario</td>
</tr>
<tr>
<td></td>
<td>Animal N Production</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td>and Consumption</td>
<td></td>
<td>1961-2011 (every 5 years)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Human N Consumption</td>
<td>Census of Population, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1961-2011 (every 5 years)</td>
<td></td>
</tr>
<tr>
<td><strong>Agriculture N Fixation</strong></td>
<td>County-level</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td>Cropland Area</td>
<td></td>
<td>1961-2011 (every 5 years)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cropland Area</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>Ontario</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1961-2011 (every 5 years)</td>
<td></td>
</tr>
<tr>
<td><strong>Atmospheric N Deposition</strong></td>
<td>Wet Deposition of</td>
<td>NatCHEM, Environment Canada (2014)</td>
<td>1978-2011</td>
<td>Station data</td>
</tr>
<tr>
<td></td>
<td>NO$_3^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.1.** Summary of data used for NANI calculation, and their sources and spatio-temporal resolution.
Figure 2.3. The monitoring stations for wet nitrate deposition located along with the years of record available for each station.
**Net Food and Feed N Imports (NFFI_N):** Net food and feed N imports to the watershed are calculated as follows:

\[ NFFI_N = C_a - P_a + C_h - P_c \]  \hspace{1cm} (2.3)

where \( C_a \) (kg N/ha/yr) is the animal N consumption, \( P_a \) (kg N/ha/yr) is the animal N production, \( C_h \) (kg N/ha/yr) is the human N consumption, and \( P_c \) (kg N/ha/yr) is the crop N production.

Quantification of these subcomponents of NFFI is described below.

Animal and Human N consumption (\( C_a, C_h \)): In the NANI calculations, it is assumed that livestock and humans first consume crops produced within the watershed. If crop production within the watershed does not meet livestock and human demand, additional consumption requirements are met by imports to the watershed. The equations for calculating consumption (Hong et al. 2011) are as follows:

\[ C_a = A \times N_c \]  \hspace{1cm} (2.4)

where \( A \) is the numbers of animals (Statistics Canada) and \( N_c \) (kg N/animal/yr) is a parameter for animal N intake (calculated from Russell et al. 2008 & Hofmann et al. 2006). For each of the 11 counties, the numbers of each of the ten animal groups (Table 2.2) were obtained from the inventory data of the Census of Agriculture, Statistics Canada. Human consumption was calculated by multiplying population, obtained from the Canada Census of Population (Statistics Canada) by the estimated human N consumption rate, 5 kg N/person/yr (Boyer et al. 2002; Hong et al. 2011).

Animal N Production (\( P_a \)): Animal N production is calculated as the difference between animal N consumption (\( C_a \)) and animal N excretion (\( E_a \)), as follows:

\[ P_a = (C_a - E_a) \times 0.9 \]  \hspace{1cm} (2.5)

\[ E_a = A \times N_e \]  \hspace{1cm} (2.6)

where \( N_e \) (kg N/animal/yr) is a parameter corresponding to the N in animal excretion. A 10% loss of N is assumed for the animal production term due to losses incurred in the processing of animals.

Animal data was obtained from the inventory data of the Census of Agriculture, Statistics Canada.
<table>
<thead>
<tr>
<th>Animals</th>
<th>Animal N Intake (kg N/animal/yr)</th>
<th>Animal N Excretion (kg N/animal/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beef cows</td>
<td>102</td>
<td>78.80</td>
</tr>
<tr>
<td>Milk cows</td>
<td>151</td>
<td>122</td>
</tr>
<tr>
<td>Heifers</td>
<td>76</td>
<td>52.20</td>
</tr>
<tr>
<td>Steers</td>
<td>104</td>
<td>78.80</td>
</tr>
<tr>
<td>Bulls</td>
<td>143</td>
<td>90.10</td>
</tr>
<tr>
<td>Calves</td>
<td>30</td>
<td>25.30</td>
</tr>
<tr>
<td>Hogs and pigs</td>
<td>15.36</td>
<td>7.20</td>
</tr>
<tr>
<td>Sheep and lambs</td>
<td>10.62</td>
<td>7.00</td>
</tr>
<tr>
<td>Hens and chickens</td>
<td>0.77</td>
<td>0.42</td>
</tr>
<tr>
<td>Turkeys</td>
<td>2.87</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Table 2.2. Parameters used to calculate animal N production, calculated from Hofmann et al. (2006).

Crop N production \( (P_c) \): N harvested in crops is calculated as follows:

\[
P_c = Q \times \% \text{ dry matter} \times \% \text{ N in dry matter} \times 0.9 \quad (2.7)
\]

where \( P_c \) is crop N production, \( Q \) is the quantity of harvested crop (kg). The crop parameters (% dry matter and % N in dry matter) are summarized in Table 2.3. Crop N production is assumed to incur 10% losses during the production of food and feed (Hong et al. 2011) including losses caused by spoilage and consumption by pests and insects (Pimentel et al. 1975; Jordan and Weller 1996). For the Grand River watershed, a total of 14 crops (Table 2.3) were included in the estimation of crop N production. County-level crop production was calculated based on county-level areas for each crop, as reported in the Canadian Census of Agriculture and Ontario crop production data available from either the Census of Agriculture (1961-1976) or OMAFRA (1981-2011). For 1901-1951, county-level crop production data for each crop was available from the Canadian Census of Agriculture.
<table>
<thead>
<tr>
<th>Crops (kg)</th>
<th>N content</th>
<th>Distributed to human</th>
<th>Distributed to animal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>0.0183(^a)</td>
<td>61%</td>
<td>39%</td>
</tr>
<tr>
<td>Buckwheat</td>
<td>0.0183(^a)</td>
<td>61%</td>
<td>39%</td>
</tr>
<tr>
<td>Rye for grain</td>
<td>0.0191</td>
<td>17%</td>
<td>83%</td>
</tr>
<tr>
<td>Oats for grain</td>
<td>0.0183</td>
<td>6%</td>
<td>94%</td>
</tr>
<tr>
<td>Barley</td>
<td>0.0188</td>
<td>3%</td>
<td>97%</td>
</tr>
<tr>
<td>Mixed grain</td>
<td>0.0188</td>
<td>3%</td>
<td>97%</td>
</tr>
<tr>
<td>Corn for grain</td>
<td>0.016(^a)</td>
<td>4%</td>
<td>96%</td>
</tr>
<tr>
<td>Canola</td>
<td>0.03</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>Soybeans for beans</td>
<td>0.064(^a)</td>
<td>2%</td>
<td>98%</td>
</tr>
<tr>
<td>All hay</td>
<td>0.02(^a)</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>Other fodder crops</td>
<td>0.0036</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>Total dry field beans</td>
<td>0.0593</td>
<td>2%</td>
<td>98%</td>
</tr>
<tr>
<td>Potatoes</td>
<td>0.0036</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>Tobacco</td>
<td>0.02996</td>
<td>100%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Table 2.3. Crop parameters used to calculate crop N production. \(^a\) derived from David et al. (2010); the rest values are derived from Hong et al. (2011).

**Biological N Fixation (BNF):** BNF, defined as the process whereby atmospheric N\(_2\) is converted to ammonia by the nitrogenase enzyme contained in the symbiotic bacteria of leguminous plants, was calculated using a yield-based method (Hong et al. 2013), as follows:

\[
BNF = P_{N-fixing} \times \% \text{ N attributed to fixation} \times 1.5 \tag{2.8}
\]

The mean percent N attributed to fixation was obtained from Han and Allan (2008) (74\% for soybeans and 82\% for hay). N in the harvested product was multiplied by 1.5 to take into account both above- and below-ground inputs (Hong et al. 2013).

2.5 Net Anthropogenic Phosphorus Input (NAPI) Estimation at the County Scale

The Net Anthropogenic Phosphorus Inputs (NAPI) in the Grand River watershed are estimated using the same budgeting methods as in NANI. NAPI is composed of three components: fertilizer P
application, net food and feed P imports and detergent P use (Russell et al. 2008; Hong et al. 2012). Since P inputs from atmospheric deposition occupies less than 1% of NAPI, this component is assumed negligible in most studies (Goolsby et al. 1999; Russell et al. 2008; Hong et al. 2012). The calculation of NAPI in the GRW was based on the framework from Russell et al. (2008). Data used for NAPI calculation, and their sources and spatio-temporal resolution is summarized in Table 2.4. NAPI is calculated as the sum of the following three components (equation 2.9):

\[ \text{NAPI} = \text{FERT}_P + \text{NFFI}_P + \text{Detergent P} \]  
(2.9)

where FERT\(_P\) (kg P/ha/yr) is commercial P fertilizer application, NFFI\(_P\) (kg P/ha/yr) is P contained in net food and feed imports, and Detergent P (kg P/ha/yr) is detergent use of P by human.

**Fertilizer P application (FERT\(_P\))**: Fertilizer P application was calculated using a combination of provincial-level fertilizer sales and fertilizer use data together with cropped area data at both the county and provincial levels (Alexander and Smith 1990), as shown below:

\[ \text{FERT}_P = \text{F}_{sales} \times \frac{CA_{\text{county}} \times A}{CA_{\text{province}} \times B} \times U \times 436.4 \]  
(2.10)

where \(F_{sales}\) (tons) is P\(_2\)O\(_5\) contained in annual fertilizer sales in Ontario (Korol and Rattray 2002; Canadian Fertilizer Institute 2015; Statistics Canada 2014). In this calculation, tons P\(_2\)O\(_5\) contained in annual sold fertilizers in Ontario were converted to kg P in fertilizers by multiplying by 436.4 kg P per ton P\(_2\)O\(_5\) (Russell et al. 2008). \(CA_{\text{county}}\) and \(CA_{\text{province}}\) are the county- and province-level cropped areas (ha), \(A\) and \(B\) are the ratios of the fertilized cropland area to the total cropped area at the county- and provincial-levels respectively, and \(U\) is a use parameter, corresponding to the estimated fraction of fertilizer sold that is actually applied to cropland. The use parameter \(U\) was calculated as 90.6% for the year 1986, the only year for which direct use total fertilizer sales and total applied fertilizer data (Statistics Canada) was available for Ontario. The use value was assumed to remain constant throughout the study period.

**Net Food and Feed P Imports (NFFI\(_P\))**: The calculation of net food and feed P imports to the watershed is identical to that of N and can be expressed as the following equation:

\[ \text{NFFI}_P = C_a' - P_a' + C_h' - P_c' \]  
(2.11)
Animal P consumption, Animal P Production and Crop P Production (\(C_a', P_a', P_c'\)):
The formulas for calculating these three components are same to calculating those of N (Equation 2.4, 2.5 and 2.7). Animal parameters (animal P intake and animal P excretion) were obtained from Russell et al. (2008), who estimated animal P intake by dividing the animal P excretion by the proportion of P that is excreted by livestock and poultry, as summarized in Table 2.5. P content for each of the harvested crops and percentages of crop distributions between humans and livestock are summarized in Table 2.6.

Human P consumption (\(C_h'\)):
Human consumption was calculated by multiplying population, obtained from the Canada Census of Population (Statistics Canada) by the estimated human P consumption rate, 0.64 kg P/person/yr (Han et al. 2011).
<table>
<thead>
<tr>
<th>NAPI Components</th>
<th>Data Type</th>
<th>Data Sources</th>
<th>Temporal Resolution</th>
<th>Spatial Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net Food and Feed P Imports</td>
<td>Crop Production</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td>Cropland Area</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ontario Ministry of Agriculture, Food and Rural Affairs</td>
<td>1961-2011 (every 5 years)</td>
<td>Ontario</td>
</tr>
<tr>
<td>Animal P Production and Consumption</td>
<td>Animal Inventory</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1961- 2011 (every 5 years)</td>
<td></td>
</tr>
<tr>
<td>Human P Consumption</td>
<td>Population</td>
<td>Census of Population, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1961- 2011 (every 5 years)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cropland Area</td>
<td>Census of Agriculture, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>Ontario</td>
</tr>
<tr>
<td>Detergent P Use by human</td>
<td>Population</td>
<td>Census of Population, Statistics Canada</td>
<td>1901-1951 (every 10 years)</td>
<td>County-scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1961- 2011 (every 5 years)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4. Summary of data used for NAPI calculation, and their sources and spatio-temporal resolution.
Animals | Animal P intake (kg P/animal/yr) | Animal P excretion (kg P/animal/yr)
---|---|---
Beef cows | 27.68 | 21.30
Milk cows | 33.16 | 26.80
Total heifers | 15.24 | 10.51
Steers | 17.54 | 13.28
Bulls | 40.21 | 25.38
Calves | 5.01 | 4.29
Hogs and pigs | 7.06 | 3.31
Sheep and lambs | 2.20 | 1.45
Hens and chickens | 0.19 | 0.11
Turkeys | 0.93 | 0.74

Table 2.5. Parameters used to calculate animal P production, calculated from Russell et al. (2008) and Hofmann et al. (2006).

<table>
<thead>
<tr>
<th>Crops (Kg)</th>
<th>kg P/kg production</th>
<th>% distributed to human</th>
<th>% distributed to animal</th>
<th>% proportion remaining after handling loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>0.003674</td>
<td>61%</td>
<td>39%</td>
<td>90%</td>
</tr>
<tr>
<td>Buckwheat</td>
<td>0.003674</td>
<td>61%</td>
<td>39%</td>
<td>90%</td>
</tr>
<tr>
<td>Rye for grain</td>
<td>0.003149</td>
<td>17%</td>
<td>83%</td>
<td>90%</td>
</tr>
<tr>
<td>Oats for grain</td>
<td>0.003242</td>
<td>6%</td>
<td>94%</td>
<td>90%</td>
</tr>
<tr>
<td>Barley</td>
<td>0.003674</td>
<td>3%</td>
<td>97%</td>
<td>90%</td>
</tr>
<tr>
<td>Mixed grain</td>
<td>0.003215</td>
<td>4%</td>
<td>96%</td>
<td>90%</td>
</tr>
<tr>
<td>Corn for grain</td>
<td>0.002756</td>
<td>4%</td>
<td>96%</td>
<td>90%</td>
</tr>
<tr>
<td>Soybeans for beans</td>
<td>0.005879</td>
<td>2%</td>
<td>98%</td>
<td>90%</td>
</tr>
<tr>
<td>All hay</td>
<td>0.004540</td>
<td>0%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Other fodder crops</td>
<td>0.000480</td>
<td>0%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Total dry field beans</td>
<td>0.005879</td>
<td>2%</td>
<td>98%</td>
<td>90%</td>
</tr>
<tr>
<td>Potatoes</td>
<td>0.000591</td>
<td>100%</td>
<td>0%</td>
<td>90%</td>
</tr>
<tr>
<td>Tobacco</td>
<td>0.004409</td>
<td>100%</td>
<td>0%</td>
<td>90%</td>
</tr>
</tbody>
</table>

Table 2.6. Crop parameters used to calculate crop P production, derived from Han et al. (2011).
**Detergent P Use (Detergent P):** Humans use P in laundry detergents and dishwashing detergents. The total detergent P use is calculated as P detergent consumption per capita multiplied by human population, as follow:

\[ Detergent\ P = (P_{DL} + P_{DD}) \times Population \]  

(2.12)

where \( P_{DL} \) is P laundry detergent consumption per capita, \( P_{DD} \) is P dishwashing detergent consumption per capita. Because little phosphate was contained in the traditional detergents for laundry and dishes in the early 1900s, it is assumed that the detergent P use started effectively from 1935 (Litke 1999 and Han et al. 2012). In addition, P content in laundry detergents decreased from 1975 mainly due to the implementation of P control policies. P laundry detergent consumption per capita (\( P_{DL} \)) and P dishwashing detergent consumption per capita (\( P_{DD} \)) that we used in this analysis are summarized in Table 2.7 and Table 2.8, respectively.

<table>
<thead>
<tr>
<th>Year</th>
<th>Laundry detergent use per capita (kg/per capita/yr)</th>
<th>P content (%)</th>
<th>P laundry detergent consumption per capita (kg P/ per capita/ yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1954-1963</td>
<td>2.27</td>
<td>15</td>
<td>0.34</td>
</tr>
<tr>
<td>1964-1974</td>
<td>5.94</td>
<td>15</td>
<td>0.89</td>
</tr>
<tr>
<td>1975-1978</td>
<td>6.67</td>
<td>8.7</td>
<td>0.58</td>
</tr>
<tr>
<td>After 1978</td>
<td>6.67</td>
<td>2.2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 2.7. The P content of laundry detergent over time, derived from Han et al. (2012).

<table>
<thead>
<tr>
<th>Year</th>
<th>P dishwashing detergent consumption per capita (kg P/ per capita/ yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1934</td>
<td>0.004</td>
</tr>
<tr>
<td>1954</td>
<td>0.018</td>
</tr>
<tr>
<td>1964</td>
<td>0.088</td>
</tr>
<tr>
<td>1974</td>
<td>0.168</td>
</tr>
<tr>
<td>1978</td>
<td>0.241</td>
</tr>
<tr>
<td>1982</td>
<td>0.241</td>
</tr>
<tr>
<td>1987 and after</td>
<td>0.233</td>
</tr>
</tbody>
</table>

Table 2.8. The P content of dishwasher detergent over time, derived from Han et al. (2012).
2.6 Uncertainty Analyses

The estimates of NANI and NAPI developed in the previous section are subject to uncertainty based on uncertainty due to the variability in the input parameters. Monte Carlo simulation methods were used to quantify this uncertainty. Monte Carlo simulation can produce the probability distribution of results by recalculating a model many times using random sampling from input parameters (Chen et al. 2014). Based on previous watershed nutrient mass balance studies (Chen et al. 2014; Ti et al. 2012; Yan et al. 2011), a normal distribution with a coefficient of variation 0.3 was assumed for each of the input parameters. For each year, 10,000 iterations of NANI values were produced using 10,000 sets of input parameters generated from random sampling (Chen et al. 2014). Each parameter is independent and has no correlation with other parameters. In order to get a good indication of the distribution of the simulated NANI and NAPI values, median and interquartile range (IQR) were used in this analysis. The interquartile range is calculated by subtracting the first quartile (25th percentile) from the third quartile (75th percentile) for the data set (Wahi 2013). Therefore, the IQR describes the range of the middle 50% of the data set. The IQR is often considered as a better measurement for spread as it ignored the outliers (Wahi 2013). In this analysis, the first quartile, median and the third quartile for NANI and NAPI values within the Grand River watershed were obtained after the 10,000 simulations.

2.7 NANI and NAPI estimation at the sub-basin scale

The county scale estimates of NANI and NAPI developed in section 2.4 and 2.5 were downscaled to the sub-basin scale using an area-weighting method (Han and Allen 2008; Gao et al. 2014; Chen et al. 2016). The sub-basin map of the Grand River watershed was downloaded online from the website of the Grand River Conservation Authority. In ArcGIS, the sub-basins map layer was intersected with the county-based map layer that has the values of NANI, NAPI and their components over time. The equation for estimating annual sub-basin level NANI is as follows:
Sub – basin level NANI (kg N/ha)

\[= \sum \frac{\text{county} \text{-level NANI (kg N)}}{\text{county area (ha)}} \times \% \text{ of the sub – basin areas} \quad (2.13)\]

The same equation was also used for estimating the different components of NANI, as well as NAPI and its components at sub-basin level in the Grand River watershed.

2.8 Data Limitations and Assumptions

Large amounts of data were collected from various sources for this thesis as shown in Table 2.1 and Table 2.4. Overall the data quality was good, but some issues were faced and dealt with, as described below.

2.8.1 Lack of Data Availability for certain years

For some census years and some counties, harvested crop area data and livestock inventory data was unavailable. To address this issue, we estimated unavailable data by applying the temporal patterns of the adjacent county to the county with the unavailable data. For example, in 2011, the area of rye for grain at Dufferin County was not available and was estimated by applying the temporal trends of Wellington County to Dufferin County. The equation was written as follows:

\[\text{Data C} = \frac{(\text{Data B} - \text{Data A}) \times (\text{Year C} - \text{Year D})}{\text{Year B} - \text{Year A}} + \text{Data D} \quad (2.14)\]

Where Data A and Data B are the data corresponding to years A and B for the Wellington county, Data C represents the unavailable data in Dufferin county in years C, and Data D represents the available data in years D in Dufferin county.

For the harvested crop area, the following data was not available: rye for grain in 2011 for Dufferin County and Halton County; barley for grain for Norfolk County in 1991, 1996 and 2011; alfalfa hay in 1986; other hay in 1996 for Norfolk County; tobacco in 2011; Canola in several counties from 1991 to 2011 and relative more data for rye for grain. For the animal inventory data, the following data was not available: hogs and pigs in 2011 for Halton County, sheep and lambs in 1996 for Norfolk County, total hens and chicken in 1981, 1991 and 1996 for Norfolk County and
relative more data for turkeys. Same estimation method was also used for calculating the amounts of unavailable animal inventories.

2.8.2 Inconsistencies in Category Description for Animal Inventory Data

Animal categories in the Agricultural Census for 1901-1951 differed from those from 1961-2011 with much more detailed animal categories being used from 1961 to 2011. For example, from 1901-1951, cattle and cows were divided into two sub-categories: milk cows and other cows. However, from 1961-2011, this category was divided into six sub-categories, including beef cows, milk cows, heifers, steers, bulls, and calves. Similarly, the "poultry" category for 1901-1951 was divided into two sub-categories for 1961-2011: (1) hens and chicken, and (2) turkeys. Due to such differences, the 1961-2011 categories were simplified to match the earlier data, and consistent N and P intake and excretion parameters were applied across the entire time period.
Chapter 3 - Results and Discussion

3.1. Overview

The main objective of this chapter is to analyze the spatio-temporal patterns in Net Anthropogenic N and P Inputs (NANI and NAPI) over a 110-year frame (1901-2011) in the Grand River watershed. In Section 3.2, we present the spatio-temporal trends in NANI and its different components, namely net food and feed imports, fertilizer N application, atmospheric N deposition, and biological N fixation. In Section 3.3, we present the spatio-temporal trends in NAPI and its different components, namely net food and feed imports, fertilizer P application and detergent P use. In Section 3.4, I did a brief summary of all the results.

3.2 NANI in the Grand River watershed

3.2.1 Spatio-temporal trends in NANI

The temporal patterns in the Net Anthropogenic N Inputs (NANI) and its four major components, namely net food and feed imports, atmospheric N deposition, biological N fixation, and fertilizer N application, across the Grand River watershed from 1901 to 2011 are presented in Figure 3.1 (3.1a and 3.1b). Overall, NANI in the GRW increased approximately 2-fold from 40 ± 3 kg N/ha/yr (26,866 Ton/year) in 1901 to its peak of 85 ± 6 kg N/ha/yr (57,934 Ton/year) in 1986. This increase can be attributed primarily to the increase in atmospheric deposition and the intensification of agricultural activities including biological N fixation and fertilizer N application (Figure 3.1a). At the start of the century, NFFI was the major component of NANI, contributing to 54% of net inputs (Figure 3.1b), while atmospheric N deposition and biological N fixation contributed to 20% and 26% of NANI, respectively. From 1921 to 1951, all these three components of NANI showed an increasing pattern. The next significant shift in the watershed occurred with the introduction of commercial fertilizers in 1951, which became a significant component of NANI within a 20-year timeframe (Figure 3.1b). Intensive synthetic fertilizer use was accompanied by an
increase in acreage of N fixing crops, and this led to the continued increase in NANI from 1951 to 1986. After 1986, NANI showed a declining trend from $85 \pm 6$ kg N/ha/yr in 1986 to $72 \pm 8$ kg N/ha in 2011. The decline in NANI occurred due to a decline in the atmospheric deposition from better control of NOx emissions, and the flip in the net food and feed imports from being positive to negative (Figure 3.1a). This is explained in future in section 3.2.2. In 2011, biological fixation became the largest source of NANI contributing 46% of total inputs. Fertilizer application was estimated to be $29 \pm 2$ kg N/ha/yr, contributing to 30% of NANI, while atmospheric deposition and net food and feed imports contributed 11% and 13% of net inputs, respectively. The magnitude of NANI observed in our study is similar to other work globally. Chen et al. (2015) reported that NANI in the upper Jiaojiang watershed in China increased from 38 kg N/ha/yr in 1980 to the peak of 77.6 kg N/ha/yr in 2000, followed by a decline to 67.3 kg N/ha/yr in 2010. In the Baltic Sea basin, Hong et al. (2012) estimated NANI values of 35-50 kg N/ha/yr. In the 16 major watersheds in northeastern of the Unites States, NANI values for 1998-1993 ranged from 5.6 kg N/ha/yr to 52.8 kg N/ha/yr (Howarth et al. 2006).
Figure 3.1a. Temporal variation of Net Anthropogenic N Input and its different components from 1901 to 2011 for the Grand River Watershed. The grey area represents the 25th and the 75th percentile of the NANI values estimated based on the Monte Carlo Analysis.

Figure 3.1b. Net Anthropogenic N Inputs across the Grand River Watershed from 1901 to 2011.
Spatially the hotspot in NANI shifted from being in the northern sub-watersheds of the GRW in 1901 and 1951 to the central basins in 1991 and 2011 (Figure 3.2). This is largely due to the impact of agricultural intensification and urbanization in the central basins. While at the GRW scale, NANI increased only 2-fold in the 20th century, locally in sub-basins the increase was more dramatic, with about 3-fold increase from 1901 to 1991 in the central watersheds. The NANI values

Figure 3.2. The spatial patterns of NANI in 1901, 1951, 1991 and 2011.
were lower in 2011 compared to 1991, but the spatial patterns in NANI did not vary significantly over the 20-year period. In order to explore the underlying causes of the observed spatio-temporal patterns in NANI, I have analyzed the various components of NANI, and their spatial trends in the next few sections.

We compared our NANI values with NANI estimated for watersheds around the world (Table 3.1). NANI values showed a wide variation, which can be attributed to differences in land use, fertilizer application rates and climate conditions. The average NANI values for the 18 catchments of the Lake Michigan Basin were estimated to range between 8 and 93 kg N/ha/yr between 1974-1992 (Han and Allen 2008). NANI values for the Mississippi watersheds and northeastern watersheds of the United States were estimated be 23 and 31 kg N/ha/yr for the 1990s, respectively (Hong et al. 2013 and Boyer et al. 2002). NANI values for China and Europe were relatively higher due to the much more extensive application of commercial fertilizers and higher population density (Chen et al. 2008; Chen et al. 2016; Billen et al. 2009). The NANI values of our study were in the range of NANI values observed by different researchers.
<table>
<thead>
<tr>
<th>Watershed name</th>
<th>Area (km²)</th>
<th>% Cropland</th>
<th>NANI (kg-N/ha/yr)</th>
<th>Time Period</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Michigan Basin of the U.S.</td>
<td>85,050</td>
<td>5% - 82%</td>
<td>8 - 93</td>
<td>Averaged over five census years from 1974 to 1992</td>
<td>Han and Allen 2008</td>
</tr>
<tr>
<td>Mississippi River Basin of the U.S.</td>
<td>3,208,700</td>
<td>27%</td>
<td>23</td>
<td>Average of 1987, 1992 and 1997</td>
<td>Hong et al. 2013</td>
</tr>
<tr>
<td>Somme basin in the NW Europe</td>
<td>76,370</td>
<td>53%</td>
<td>46</td>
<td>2000</td>
<td>Billen et al. 2009</td>
</tr>
<tr>
<td>Scheldt basin in the NW Europe</td>
<td>19,860</td>
<td>39%</td>
<td>89</td>
<td>2000</td>
<td>Billen et al. 2009</td>
</tr>
<tr>
<td>The Jiulong River basin in the S.E. China</td>
<td>14,700</td>
<td>18%</td>
<td>118</td>
<td>2004</td>
<td>Chen et al. 2008</td>
</tr>
</tbody>
</table>

**Table 3.1.** Summary of NANI values estimated for different watersheds from the previous literatures
3.2.2 Net Food and Feed Imports (NFFI)

The net food and feed N imports have been very constant and stayed at about 20 ± 2 kg N/ha/yr from the early 1900s to 1976. After this period, the pattern has changed gradually, and the net N food and feed changed from imports to exports for the whole watershed in the early 2000s. Thus, the watershed changed from being a net importer of food and feed to sustain its human and animal population to being a net exporter of these commodities. In order to understand this switch, we plotted the temporal trajectories of the components of net N food and feed (Figure 3.3a). Crop and animal N production within the watershed started meeting livestock and human demands in the early 2000s, and exceeded watershed needs leading to net export after 2001. This occurred primarily due to the dramatic increase in crop N production, which arose from both an increase in crop yields and an increase in the acreage N fixing crops (Figure 3.3b). Corn, hay and soybeans are the three major crops in the watershed and accounted for 42%, 21% and 15% of the total crop production in 2011, respectively. The production of soybeans showed a great increase since the early 1980s, and this increase has continued until now (Figure 3.3b). N produced by hay increased from 6,000 tons in 1901 to 14,253 tons in 1986 and comprised 45-60% of all crop N production during 1901-1986 (Figure 3.3b). However, after 1986, N produced by hay showed a decreasing pattern to 8,955 tons in 2011.

Animal farming has been an important component of agricultural activities since the early 1990s in the watershed. Cattle and cows, pigs as well as poultry are the dominant animal groups that provided N in the form of manure in the GRW. Generally, cattle and cows produce more manure than the smaller animals, and thus generate more N in their manure (Hofmann 2006). N in feed consumed by the animals increased from 52 ± 2 kg N/ha/yr in 1901 to 62 ± 2 kg N/ha/yr in 2011. Population growth in the GRW has led to a steady increase in the human consumption of N in food from 1.6 ± 0.2 kg N/ha in 1901 to 7.5 ± 0.9 kg N/ha in 2011. However, the magnitude of this flux is much smaller than the animal N consumption (Figure 3.3a).
Figure 3.3a. Four different components of N net food and feed imports within the GRW.

Figure 3.3b. N production of various crops over the GRW from 1901-2011.
The spatial variation of NFFI is relatively small across the watershed in 1901 and 1951 (Figure 3.4). During this time-period, the entire watershed imported food and feed from outside of the watershed to meet the N requirements for humans and animals. Gradually with the increase in crop and animal production, the northern and southern sub-watersheds shifted from a net importer to a net exporter of food and feed in 1991. The central part of the basin still remained a net importer of food and feed due to its high human and animal population density (Figure 3.4). Comparing the NANI maps (Figure 3.2) with the NFFI maps, we can see that NFFI has the most significant impacts in the spatial variation of NANI.

**Figure 3.4.** The spatial patterns of N in net food and feed imports in 1901, 1951, 1991 and 2011.
3.2.3 Fertilizers

Commercial fertilizer started being applied in 1951 and increased 13.5-fold over a 35-year period, from $2 \pm 0.1$ kg N/ha/yr in 1951 to $27 \pm 2$ kg N/ha/yr in 1986 (Figure 3.1a). After this increase, it remained relatively stable until 2006, but then had an increasing trend reaching $29 \pm 2$ kg N/ha/yr in 2011. This is analogous to the 20-fold increase in fertilizer N from 1951 to 1991 in the St. Lawrence river basin (Goyette et al. 2016). The reduction in NANI, despite the increase in fertilizer use, is interesting, and occurs due to decreasing atmospheric deposition and NFFI that overcompensate for the trend in fertilizer increase. The factors contributing to the NFFI trend has been discussed in section 3.2.2.

Spatially the hotspots in fertilizer application were consistent over the 60-year timeframe (1951 to 2011) (Figure 3.5). Fertilizer N application rates are generally low across the whole watershed in 1951, while in 1981, 1991 and 2011, the hotspots of fertilizer N application rates are located along the Nith River and Whitemans Creek. This is an area of intensive agriculture, with a
large number of crops are grown, including corn for grain, rye for grain, oats for grain, barley for grain as well as tobacco. Fertilizer N application rates in these hotspot areas decreased from 1981 to 1991 but increased from 1991 to 2011. This pattern is closely associated with the changes of fertilizer sales from 1981 to 2011. The spatial variability in fertilizer N application rates was the greatest in 2011, ranging from about 15 kg N/ha/yr to as high as 45 kg N/ha/yr. Similarly, across the Lake Michigan catchments, Han and Allen (2008) reported that fertilizer N application ranged from 0.35 kg N/ha/yr to 60.9 kg N/ha/yr.

3.2.4 Atmospheric N Deposition

Atmospheric nitrate deposition increased approximately 3-fold in the GRW from 8 ± 0.5 kg N/ha/yr in 1901 (20% of NANI) to 26 ± 1.7 kg N/ha/yr in 1986 (30% of NANI) (Figure 3.1). Then it showed a decline pattern from 24 ± 1.5 kg N/ha/yr in 1991 to 10 ± 0.6 kg N/ha/yr in 2011. The increase is attributed to increasing NOX emissions, while reductions occurred since the early 1990s because of the implementation of the Air Quality Agreement to reduce NOX emissions (Environment and Climate Change Canada 2013). Atmospheric N deposition for each of the census years is relatively homogeneous across the watershed, therefore the spatial patterns for this component are not discussed here.

3.2.5 Biological N Fixation

Biological N fixation increased steadily from 10 ± 1 kg N/ha/yr in 1901 to 27 ± 3 kg N/ha/yr in 1986. It accounted for 22% and 32% of NANI in 1901 and 1986 respectively, and then greatly
increased to 63% (45 ± 4 kg N/ha/yr) of NANI in 2011 (Figure 3.1). These biological N fixation numbers are in the same range as the study reported for the upper and middle Mississippi River agricultural watersheds (19.3 to 34.7 kg N/ha/yr, Goolsby et al. 1999). The main N-fixing crops in the GRW are hay and soybeans. Biological N fixation in the watershed remained relatively stable from 1901 to 1951 because the production of soybeans and hay did not change much during the same time period (Figure 3.3b). In terms of proportions of the two N-fixing crops, hay accounted for over 95% of total biological fixation inputs before 1981. However, since then, the proportion of N fixed by soybeans increased dramatically from 5% in 1981 to 67% in 2011 due to the massive expansion in the cultivated area of soybeans in these last 30 years.

A shift in the hotspots for BNF was observed from the northern sub-watersheds before 1991 to the central and southern Grand River watershed in 2011 (Figure 3.6). The higher BNF in northern

![Figure 3.6. The spatial patterns of biological N fixation in 1901, 1951, 1991 and 2011.](image)
parts of the watershed occurs due to higher acreage of hay in that area since the early 1900s. The increase in BNF after 1991 in the central and southern sub-watersheds occurred due to the intensification of soybean cultivation in these areas. In 2011, the southern sub-basins had the largest BNF values at over 50 kg N/ha/yr.

3.3 NAPI in the Grand River watershed

3.3.1 Spatio-temporal trends in NAPI

The temporal trends of NAPI, including its three different components, over the last century in the Grand River watershed are shown in Figure 3.7 (3.7a and 3.7b). The Net anthropogenic P inputs to the Grand River Watershed increased approximately two-fold from 6.9 ± 0.5 kg P/ha/yr in 1901 to the peak of 14.5 ± 1 kg P/ha/yr in 1976, and then declined to 7.8 ± 1 kg P/ha/yr by 1996, after which it remained approximately steady till 2011. Interestingly, NAPI values in 1951 and 2011 are the same (9.3 ± 0.7 kg P/ha/yr) (Figure 3.7a), despite the significant increase in the human and animal population in the basin. This occurred primarily because of increase in crop yields and P use efficiency. The dominant components of NAPI are the fertilizer P and net food and feed imports, while the detergent P component is only a small fraction, and thus its ban in 1971-72 (Maki et al. 1984) did not significantly alter the watershed scale P budget. However, detergent P ban significantly impacted the water quality, since wastewater treatment plants directly discharge into streams, and thus do not get filtered through the landscape. The temporal patterns of NAPI we observed is similar to the changes of NAPI across 18 Lake Erie watersheds from 1935 to 2007. Han et al. (2012) reported that NAPI in the Lake Erie watersheds increased from 4.56 kg P/ha/yr in 1935 to 13.51 kg P/ha/yr in the middle of 1970s, followed by a decline to 4.63 kg P/ha/yr in 2007.
Figure 3.7a. Temporal variation of Net Anthropogenic P Inputs and its different components from 1901 to 2011 for the Grand River Watershed. The grey area represents the 25th and the 75th percentile of the NAPI values estimated based on the Monte Carlo Analysis.

Figure 3.7b. Net Anthropogenic P Inputs across the Grand River Watershed from 1901 to 2011.
Spatially hotspots in NAPI are similar to that of NANI (Figure 3.2). This is largely caused by the effects of intensification of agricultural activities, which have influences on both elements. The hotspots of NAPI shifted from the northern sub-watersheds of the GRW in 1901 to the central basins in 1951. Over the next 50 years, the P inputs in the central basins increased, while that in the northern basins decreased. The higher NAPI in the central parts of the watershed can be attributed to the urban and animal farming intensification in this region. NAPI values increased about three-fold in these central sub-watersheds, compared to the two-fold increase at the GRW scale. In order to understand the reasons for the observed spatio-temporal patterns in NAPI, the different components of NAPI and their spatial trends have been analyzed in the next few sections.

**Figure 3.8.** The spatial patterns of NAPI in 1901, 1951, 1991 and 2011.
NAPI values for different watersheds around the world are summarized in Table 3.2. The temporal trends in NAPI across the Grand River watershed are similar to the changes of NAPI across the 18 Lake Erie watersheds of the United States from 1935 to 2007 due to the similar land uses (Han et al. 2012). The NAPI values of the 18 Lake Michigan watersheds for the average of 1974, 1978, 1982, 1987, and 1992 were 6 kg P/ha/yr (Han et al. 2011).

### 3.3.2 Net Food and Feed Imports

P in net food and feed imports was positive over time in the GRW, which means that P consumed by animals and humans was always larger than crop and animal P production from 1901 to 2011, or in other words, the GRW has always been a net importer of P (Figure 3.9). The magnitude of the imports has however declined over time, primarily due to increase in crop yields, and thus crop P production, from 3.9 ± 0.3 kg P/ha/yr in 1901 to 9.6 ± 0.7 kg P/ha/yr in 2011, over the basin. Human P consumption increased almost 5-fold from 0.2 ± 0.02 kg P/ha/yr in 1901 to 1 ± 0.1 kg P/ha/yr in 2011, primarily due to population growth in this area, however this is a small part of the watershed scale P budget. P consumed by livestock and poultry has increased slightly over time with values ranging from 13.9 ± 0.6 kg P/ha/yr in 1901 to 16.2 ± 0.7 kg P/ha/yr in 2011. It is interesting to note that while GRW switched from being a net importer to a net exporter of N, the results are different for P where it continued to be a net importer. This is probably because of the intensification of soybean acreage which are N fixing crops.
<table>
<thead>
<tr>
<th>ID</th>
<th>Watershed name</th>
<th>Area (km²)</th>
<th>% Cropland</th>
<th>NAPI (kg-P/ha/yr)</th>
<th>Time Period</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Root</td>
<td>510</td>
<td>77%</td>
<td></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Milwaukee</td>
<td>1,818</td>
<td>74%</td>
<td></td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Sheboygan</td>
<td>1,106</td>
<td>82%</td>
<td></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Fox</td>
<td>15,825</td>
<td>51%</td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Oconto</td>
<td>2,543</td>
<td>28%</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Peshtigo</td>
<td>2,797</td>
<td>21%</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Menominee</td>
<td>10,541</td>
<td>7%</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Ford</td>
<td>1,165</td>
<td>7%</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Escanaba</td>
<td>2,253</td>
<td>5%</td>
<td></td>
<td>0.4</td>
<td>Han et al. 2011</td>
</tr>
<tr>
<td>10</td>
<td>Manistique</td>
<td>883</td>
<td>5%</td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Manistee</td>
<td>4,343</td>
<td>18%</td>
<td></td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Pere-Marquette</td>
<td>1,764</td>
<td>18%</td>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Muskegon</td>
<td>6,941</td>
<td>34%</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Grand</td>
<td>14,292</td>
<td>75%</td>
<td></td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Kalamazoo</td>
<td>5,164</td>
<td>75%</td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>St. Joseph</td>
<td>12,095</td>
<td>80%</td>
<td></td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Trail Creek</td>
<td>153</td>
<td>50%</td>
<td></td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Burns Ditch</td>
<td>857</td>
<td>64%</td>
<td></td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lake Erie watersheds</td>
<td>54,114</td>
<td>66%</td>
<td>5 - 14</td>
<td>1935 - 2007</td>
<td>Han et al. 2012</td>
</tr>
<tr>
<td></td>
<td>Chesapeake Bay region</td>
<td>165,759</td>
<td>6%</td>
<td>4 - 5</td>
<td>1987 - 2002</td>
<td>Russell et al. 2008</td>
</tr>
</tbody>
</table>

**Table 3.2.** Summary of NAPI values estimated for different watersheds from the previous literatures
Spatially the patterns of NFFI are similar to NAPI. The hotspots in NFFI spread from the northern sub-watersheds in 1901 to both the central basins in 1951, 1991 and 2011 (Figure 3.10). Although GRW is a net P importer, P import is more dominant in the central sub-basins due to its large human and animal population, while the northern and southern basins are P exporters. Considering the strong similarity in the spatial patterns of NFFI and NAPI, we can concluded that NFFI have the most significant influence on the variation of NAPI across the watershed.
3.3.3 Fertilizer P

The application of P fertilizers increased dramatically from 1.3 ± 0.1 kg P/ha/yr in 1951 to the peak of 8.5 ± 0.6 kg P/ha/yr in 1981, followed by a 56% decrease to 3.7 ± 0.3 kg P/ha/yr by 1996. Then it showed an increasing pattern and reached 6.5 ± 0.5 kg P/ha/yr in 2011 (Figure 3.7). Fertilizer P comprised 50%-70% of NAPI from 1971-1991 and has been the largest P source for the GRW during those 20 years. In many other P budget studies, fertilizer use is also a large source of P. For example, the study done by Bennett et al. (1999) showed that fertilizer P input accounted for over 50% of total P in the Lake Mendota watershed. In the study of P accumulation in Saint Lawrence River watershed soils, MacDonald and Bennett (2009) showed that the use of fertilizer P has been increasing since 1901 and reached its peak in 1981. In summary, all these studies, including our study, have demonstrated that P inputs from fertilizer application comprised significant amounts of total P inputs into watersheds and reached the peak in the 1980s.

Maps showing the spatial distribution of fertilizer P application in the GRW for 1951, 1981, 1991 and 2011 are presented in Figure 3.11. In 1951, Fertilizer P application rates are generally low across the whole watershed. In 1981, 1991 and 2011, the hotspots of fertilizer P application shifted to the western sub-watersheds primarily due to agricultural intensification. A large number of crops, including corn for grain, rye for grain, oats for grain as well as barley for grain are grown in this area. In 2011, the hotspots also covered the areas that located in the Conestoga River and Speed
River sub-watersheds. This is probably due to the great increase in the acreage of wheat, corn for grain as well as fodder crops in these sub-watersheds.

![Image](image1.png)

**Figure 3.11.** The spatial patterns of fertilizer P application in 1951, 1981, 1991 and 2011.

### 3.3.4 Detergent P

Detergent use contributed much less P into the watershed compared to the other two sources. P from detergent use increased from zero in 1934 to its peak at 0.97 ± 0.08 kg P/ha/yr in 1971 (Figure 3.7a). The implementation of the P ban in laundry detergents in 1971-72 was very effective
in reducing P in detergents (Maki et al. 1984). However, the amounts of P inputs to the GRW has not changed too much since the watershed population has almost doubled from 1971 to 2011. The total detergent P use has shown a slight increase from $0.38 \pm 0.03$ kg P/ha/yr in 1981 and reached $0.58 \pm 0.05$ kg P/ha/yr in 2011 (Figure 3.7a). Although detergent use is a small component of watershed scale NAPI, P in detergents has significant impacts of surface water quality.

Maps for detergent P use in the sub-basins of the GRW for 1951, 1971, 1991 and 2011 are shown in Figure 3.12. Small amounts of detergent P were used over the whole watershed in 1951. However, after 20 years in 1971, the hotspots shifted to the central part, where population and urban activities are concentrated. The central sub-watersheds are still the hotspots of detergent use in 1991 and 2011, which are associated well with the locations of population density.

Figure 3.12. The spatial patterns of detergent P use in 1951, 1971, 1991 and 2011
3.3.5 Cumulative NAPI

The 1901-2011 NAPI budgets clearly indicated that human activities have caused P accumulation in the watershed since the beginning of the last century. The cumulative NAPI in the watershed was obtained by adding together the annual NAPI values from 1901 to 2011. The results show large magnitude of P accumulation, from 460-500 kg P/ha in the lower watershed to 1300-1400 kg P/ha in the central sub-watersheds (Figure 3.13). It would be interesting to see if this correlates with soil P levels in these areas, but that is behind the scope of this study. Globally, P accumulation magnitudes were provided by Bennett et al. (2001), they reported the annual accumulation magnitudes of 8 Tg/year from 1958-1998 in agricultural land of the world. In UK, Withers et al. (2001) reported that P accumulation in agricultural soils is about 1000 kg/ha from 1935 to 1965. Understanding these accumulation magnitudes is critical to quantifying lag times between management practices and water quality improvement.

![Cumulative NAPI in 2011](image)

**Figure 3.13.** The spatial patterns of cumulative NAPI in 2011.

3.4 Summary

In this chapter, we analyzed temporal trends in NANI and NAPI, and their different components, across the Grand River watershed from 1901 to 2011. NANI and NAPI reached their peak in the 1980s and 1970s respectively and then showed declining patterns. Agricultural intensification had the strongest influence on the temporal trends of NANI and NAPI. For NANI,
net food and feed N imports and biological N fixation were the dominant N inputs before 1951. Gradually with the changes of agricultural practices, fertilizer N application and biological N fixation became more and more important and reached 30% and 47% of NANI in 2011, respectively. In the case of NAPI, net food and feed import to the GRW provided the largest P input before 1961, after which fertilizer became the dominant source of P. The hotspots of NANI and NAPI both are shifted from northern sub-watersheds in 1901 and 1951 to the central area in 1991 and 2011 mainly due to the intensification of animal farming and urban activities in the central sub-watersheds.
Chapter 4 Conclusions and Recommendations

4.1 Conclusions

The overall objective of this study was to characterize the spatio-temporal trends in net anthropogenic N and P inputs in the Grand River watershed. The net anthropogenic N and P input (NANI and NAPI) framework (Hong et al. 2011; Russell et al. 2008) was used to quantify the N and P budgets over the last 110 years from 1901 to 2011 in the Grand River watershed by tracking the historical changes of fertilizer use, crop production, animal inventory, human population and atmospheric deposition. The budgets helped us get a better understanding of spatio-temporal patterns of net anthropogenic N and P inputs across this agriculture-dominant landscape.

NANI in the GRW increased approximately 2-fold from 40 ± 3 kg N/ha/yr to 85 ± 6 kg N/ha/yr between 1901 and 1986, and then decreased from 78 ± 6 kg N/ha/yr in 1991 to 72 ± 8 kg N/ha in 2011. The decrease in NANI was created primarily by an increase in crop yield, and a rise in the acreage of the N-fixing crop soybean, which transferred the watershed from being a net importer to a net exporter of anthropogenic N. The decrease in NANI since 1986 is encouraging and suggests that we are being more efficient in our use of N.

NAPI exhibited a similar trend as NANI. NAPI in the watershed increased approximately two-fold from 6.9 ± 0.5 kg P/ha/yr in 1901 to its peak of 14.5 ± 1 kg P/ha/yr in 1976, and then declined to 7.8 ± 1 kg P/ha/yr by 1996, after which it remained approximately steady till 2011. The primary difference between NANI and NAPI was the watershed remained a net exporter because of lack of P fixing crops.

Over the last 110 years, the changes of agricultural land use and activities across the watershed have led to the transition in the relative importance of different N and P sources. For N, net food and feed imports and biological N fixation dominated total anthropogenic N inputs to the Grand River watershed before 1951 accounting for 74% (on average) of the net inputs. With the intensification of agricultural activities over time, fertilizer application and biological fixation became the dominant N sources accounting for 77% of the net inputs in 2011. For P, net food and feed imports into the watershed provided the largest amounts of P before 1961. However, since the early 1970s, fertilizer application has been the largest P source accounting for over 50% of the net inputs and reached 70% of NAPI in 2011. Detergent use contributed much less P into the watershed compared to the other two sources, accounting for 1-7% of NAPI over time. Spatially the hotspot in NANI shifted from being in the northern sub-watersheds of the GRW to the central basins since the early 1980s and same shift patterns occurred in NAPI since the early 1950s. These changes can be attributed to faster intensification of urban and agricultural activities in the central area. The central part of the watershed remained N and P importers over the 110 years, while the northern and
southern sub-watersheds shifted from being N and P importer to exporter. Fertilizer N and P application rates are generally low across the whole watershed in 1951, while in 1981, 1991 and 2011, the hotspots of fertilizer application rates are located in the western sub-watersheds, where large numbers of crops are grown. At the cumulative scale, the hotspot in NAPI is at the central sub-watersheds with the magnitude of P accumulation at 1300-1400 kg P/ha.

Animal farming has been an important component of agricultural activities since the early 1990s in the GRW. In order to reduce N and P inputs from animals, dietary N and P can be adjusted to match the needs based on the N and P requirements of livestock and poultry (Carpenter et al. 1998). In our analysis, we also found that atmospheric N deposition decreased after the implementation of Air Quality Agreement in the early 1990s. The P ban in detergents helped reducing P content in detergents, even though the total P amounts didn't change too much due to the population growth.

4.2 Recommendations for Future Work

This study provides a foundation for the future research in transformation or storage of N and P in agricultural watersheds. Future work would involve quantifying N and P exports in river outflows. While stream N and P concentrations do exist in the GRW, they are often really sparsely monitored in time, making it a challenge to quantify annual loads from them. Estimation of annual loads would help us establish relationship between NANI/NAPI and riverine outputs, and quantify how these relationships vary over time.

Our results indicate that the central sub-watersheds are hotspots of N and P pollution. This is in agreement with stream water quality data that also show high N and P concentrations in these areas (Cooke 2006; GRWMP 2013). Thus, monitoring and managing these areas of the watersheds would lead to more effective control of N and P pollution.
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