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**Quantifying the Role of Agriculture and Urbanization in the Nitrogen
Cycle across Texas**

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**Quantifying the Role of Agriculture and Urbanization in the Nitrogen
Cycle across Texas**

by

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Thesis

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Dedication

For my mother for showing me anything is possible and for my father who showed me science is not just for geeks.

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Abstract

Quantifying the Role of Agriculture and Urbanization in the Nitrogen Cycle across Texas

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Over-enrichment of nutrients in coastal waters has been a growing problem as population growth has enhanced agricultural and industrial processes. Enhanced nitrogen (N) fluxes from land to coast continue to be the result of over fertilization and pollution deposition. This over-enrichment of nutrients has led to eutrophication and hypoxic conditions in coastal environments. This study was conducted along the Gulf of Mexico, through the state of Texas, in order to quantify all agricultural and industrial sources of N in a region which contains a large precipitation gradient, three major metropolitan areas, and one of the top livestock industries in the United States. Nitrogen inputs from fertilizer, livestock, crop fixation, and oxidized deposition from both dry and wet atmospheric processes were quantified and compiled into a Texas Anthropogenic N Budget (TX-ANB). In addition, comparisons and regional enhancements were made to the Net Anthropogenic Nitrogen Input dataset (NANI toolbox), which is a national dataset developed at Cornell University by *Hong et al.* [2011]. These enhancements ultimately will help understand the full pathways of anthropogenic influences on coastal

systems in a regional setting. All three datasets (NANI, NANI Regional, and TX-ANB) indicate agriculture to be the primary contributor to the N cycle in Texas, with TX-ANB showing 38% of inputs from fertilizer, 37% of inputs from livestock, and 2% of inputs from legumes. N input due to atmospheric deposition of oxidized N clearly highlights urban areas, indicating a strong influence of urbanization on the N cycle due to anthropogenic impacts; 23% of N input in Texas is the result of deposition of oxidized N. Quantification of inputs spatially indicates a strong enhancement of N from human influence in the coastal plain where nutrient export is heightened by major storm events. This enhancement of N along a coastal drainage area will likely have a negative impact on downstream environments.

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Chapter 1: Introduction

The chapters of this thesis reflect the motivations and importance of understanding nitrogen cycling while also developing a framework for quantifying all sources of nitrogen in a region where this quantification is critical. All the research presented in this thesis points towards an emphasis of understanding nutrient cycling and accounting for all source and inputs of nitrogen from the earth system.

1.1 THE NITROGEN CYCLE

The world's growing population has led to a strong human influence on the nitrogen cycle [Boyer *et al.*, 2002; Galloway *et al.*, 2004; Howarth, 1998; Smil, 1997]. As human activities have led to an increase in nitrogen inputs, quantification of human influence has become measurable, however transport and retention remains an issue [Galloway *et al.*, 2004]. Nitrogen budgets constructed by previous research works [Boyer *et al.*, 2002; Howarth, 1998; 2004; 2008] point toward human contributions from air pollution through atmospheric deposition, fertilizer inputs from the agriculture industry, food harvesting and consumption through livestock processes, and nitrogen fixation addition from stimulated legume crop growth. A new set of tools developed by Hong *et al.* [2011] provides methods for calculating N budgets anywhere; such tools include accounting for all aforementioned sources.

Sources and inputs however are only part of the cycle; understanding the mechanisms and reactions within the earth system is critical in developing a full pathway framework for N cycling.

1.1.1 The Atmosphere: Species of N and Inputs

In the atmosphere, nitrogen (N) is present naturally in three major forms: reduced, oxidized, and dinitrogen. Reduced N is found the form of NH_x ; this includes NH_3 , NH_4^+ , and NH_2 [Zheng *et al.*, 2002]. Oxidized forms include N_2O and NO_y . NO_y is the sum of two oxides of nitrogen ($\text{NO} + \text{NO}_2$), which generally are denoted as NO_x , as well as all the compounds that are products of atmospheric oxidation of N including HNO_3 , HONO , NO_3 , N_2O_5 , HNO_4 , PAN (Peroxyacetyl nitrate), RC(O)OONO_2 and its homologues, RONO_2 , ROONO_2 [Seinfeld and Pandis, 1997]. NO_y essentially represents all of the chemical processes which occur after the initial oxidation of NO_x ; it is a more accurate way of measuring full oxidized N components and specifically can improve quantification accuracies in rural areas where the influence of other N compounds, such as PAN, can be high. The majority of atmospheric N is unreactive and is dinitrogen (N_2).

Atmospheric N_2 can be transformed to reactive N (N_r) through a number of ways including biological fixation of N (BFN) and oxidation from lightning. Originally oxidation from lightning and atmospheric deposition through wet scavenging were thought to be the two largest sources of N inputs to land, however in 1888 Herman Hellriegel and Hermann Wilfarth published work describing the symbiotic relationship legumes had with micro-organisms which allowed for assimilation of free N in the air through processes of microbes below ground [Smil, 2001]. This marked a change in scientific understanding that later led to cultivation of such legumes through food production processes.

Life and growth are strongly limited by N availability [Vitousek *et al.*, 2002]. This strong limitation developed a need for N in order to produce enough food to match the growing needs of human populations. Legumes crops are able to execute the BFN

process, thus historic records point to cultivation methods of these crops as early as 6,500 years ago [Smith *et al.*, 1997].

1.1.2 The Land: Inputs and Cycling

Legumes were cultivated as early as 6,500 years ago, however synthetic fertilizers have become responsible for about half the nitrogen used by cultivated crops. Fritz Haber and Carl Bosch brought the Haber-Bosch synthesis of nitrogen to life in Germany during the early 1900s and now their impact is responsible for about 130 million tons of ammonia globally. Around eighty percent of that ammonia is used for fertilizers; without it about forty percent of the world's population likely would not exist [Smil, 1999a; b].

Increases in synthetic fertilizer have been observed to have a direct correlation with population increase [Howarth *et al.*, 2002; Jenkinson, 2001]. Large agriculture industries rely heavily on feeding the world through use of synthetic fertilizers. In addition, as synthetic fertilizer use has increased, a matched increase is also evident through livestock production; ultimately leading to 80% of all human's protein originating from the Haber-Bosch process.

Livestock has played a large role in increased N inputs from anthropogenic sources as well. As it has become easier to farm large quantities of food for feed, it also has become increasingly easier to grow animals for food alone. Increased population growth and personal income has enhanced meat demand by over 75% in the last twenty years [Burke *et al.*, 2008]. Cultivated systems, including livestock growth production, occupy close to 25% of the Earth's terrestrial surface [Cassman and Wood, 2005].

1.2 ESTUARIES AND EUTROPHICATION

Substantial evidence from *Boyer et al.* [2002] suggests anthropogenic sources increase N loading in upland river basins, ultimately leading to enhanced nutrient enrichment in downstream estuaries. The increase of N within coastal ecosystems has led to major environmental impacts such as eutrophication, enhanced harmful algae blooms, and hypoxic zones [*Vitousek et al.*, 1997].

Hypoxic zones develop as a result of a stratified water column which contains less dense and warm fresh water on top of more dense cooler salty water. This occurs along shorelines where estuaries exist. A strong flux of nutrients within the incoming freshwater can lead to a nutrient enrichment throughout the estuary [*Goolsby*, 2000]. Algae blooms along the coast are most heavily affected by limiting nutrients; the two most limiting nutrients of marine environments are N and phosphorus (P). A large addition from terrestrial runoff of N and P can lead to a loss of species diversity within a coastal environment, but also leads to large algae blooms [*Tilman*, 1999].

High stream flow events in the spring and summer result in a strong flux of nutrients such as N and P; these high nutrient flux events promote algae blooms which can lead to organic matter from the algae settling to the bottom waters. This organic matter gets decomposed by bacteria which reduce oxygen levels in the process, resulting in low dissolved oxygen within the lower stratified layer of the water column. This decrease in available oxygen creates hypoxic conditions [*Goolsby*, 2000].

Nitrate is easily leached into groundwater and streams as it is the most mobile and soluble form of N. *Goolsby* [2000] studied observations between 1955 and 2000 of nitrate and found the annual flux of nitrate from the Mississippi River Basin to the Gulf of Mexico increased from just below 0.5 million metric tons per year to just over 1 million metric tons per year; peaks in stream-flow during those years directly correlated

with elevated levels of N. During the year of 1993, nitrate levels spiked to 1.6 million metric tons in response to a stream-flow of 27 thousand cubic meters per second (cms), the highest of the full period. In 1973 stream-flow was at a similar maximum of 26 thousand cms, but nitrate levels only reached 0.7 million metric tons per year, suggesting increased anthropogenic input of N from 1973 to 1993. Therefore, an overall increase of nitrate between the fifty years studied clearly demonstrates more available nitrate during higher stream-flow events will result in much higher fluxes of nitrate.

1.3 SUMMARY OF PREVIOUS WORK

Quantifying all sources of N spatially is critical for understanding impact regions which are highly altering downstream ecosystems. *Boyer et al.* [2002] constructed a full N budget based on the work by *Howarth et al.* [1996], for the northeastern U.S. using sixteen watersheds. Their focus was on anthropogenic changes from fertilizers, animal and human waste, fixation from cultivated crops, and atmospheric deposition. These were also the focus of previous work from *Howarth et al.* [1996].

In constructing the aforementioned N budgets, most of the information is available at county level resolution. Census of Agriculture and fertilizer distribution data are used, and field level is not possible.

Within N quantification, numerous uncertainties can be introduced. “Census of Agriculture” data are at a level which does not provide actual location of the animal. The largest counties in Texas span areas between 12 and 16 thousand square kilometers; basing spatial inputs on distribution of N within that large of an area could potentially result in significant error. In addition, fertilizer data using the *Boyer et al.* [2002] method are only distribution data, rather than data based on sales. If a distributor delivers 20 tons

of N from fertilizer to a specific county, it is not guaranteed the fertilizer is actually used. Thus, creating a budget at county level introduces a lot of uncertainty.

Currently *Hong et al.* [2011] have an N input toolbox which uses the Howarth and Boyer methods for the entire United States. Their “Net Anthropogenic Nitrogen Input” (NANI) toolbox accounts for all sources using the county scale approach. In addition, fixation from cultivated crops is accounted for by estimating N inputs from legume crops and pastureland. Pastureland can produce a considerable amount of fixed N from legume growth such as clovers. However, assuming a fixation rate for all pastureland across the entire United States could result in a large overestimation in drier climates, where pastureland may not support favorable conditions for legume growth. In addition, regional sources of input are not considered when using tools for construction of a NANI on a national scale. For this reason, regional N budgets are critical for evaluation of accuracy of NANI.

1.4 REGIONAL MOTIVATIONS

Texas was chosen to represent a regional quantification of all N sources for many reasons. Texas has a highly variable climate, with a large precipitation gradient across the state creating a semi-arid west and a humid east [*Banner et al.*, 2010]. In addition, Texas recently has been subjected to severe to exceptional droughts, including the record-breaking drought of 2011, which has led to changes in land-cover types, specifically in west Texas. Texas also has been projected to be one of the three future climate “hot spots” in North America [*Diffenbaugh et al.*, 2008]. Home to three of the “Top Ten” largest urban areas in the United States, Texas has one of the largest agriculture industries in the Nation. Following the approach by *Golden and Boyer* [2008], this study focuses on analyzing the impacts urban and agriculture areas have on the N cycle in Texas.

1.5 SUMMARY OF WORK PRESENTED

Similar to the well-known water cycle, which represents the flow of water from the atmosphere to the land surface, and the hydrosphere, the nitrogen cycle is the process by which N flows through the environment. Atmospheric deposition of nitrate, organic nitrogen, and ammonia can replenish N in the soil. Microbes can break down the various N compounds to other forms of N which can be used by plants or loss to leaching. Plants can biologically fix their own N through a symbiotic relationship with a root bacteria, animals provide N through their natural excretion process, and N can exist naturally through leaching processes as the result of litter in the forest floor. Currently however, the natural N cycle has been enhanced by anthropogenic influences.

The N cycle was drastically boosted by the Haber-Bosch process in 1909 which created synthetic ammonia through high pressure lab technology. This not only solved the food crisis at the time, it also created the ability to farm immense amounts of food quickly to support a forever-growing population. With an increase in population and the industrial revolution, additional sources of N became apparent in the N cycle through pollution of nitrate from industry.

As the N cycle has become enhanced by human growth and industry, nutrient excess export has developed an overload of opportunities for algae growth in downstream environments like the Gulf of Mexico. Excess fertilization from agriculture, improper care of manure from feedlots, and additional atmospheric deposition of nitrate through dry or wet processes has led to eventual hypoxic conditions in estuaries and a need for quantification spatially of all sources.

Several methods have been developed for spatial quantification of all sources for these conservation purposes. Ultimately all methods have the shortcoming of lack of information/data as well as poor spatial representation. County level information based

on distribution lacks spatial knowledge of input; however, estimating input on known crop acreage may not directly reflect actual current farming practices.

Regional studies are needed in order to refine methods and better understand agricultural practices and local climates. N fixation occurs across pastureland due to legume growth; however, pastureland and legume abundance vary through the United States as the result of dry or wet climates. In addition, farming practices vary from county to county as well. Understanding all sources in a regional context could aid in reducing N inputs based on spatial attributes such as drainage basins and precipitation trends. Quantifying impacts from sources would allow stakeholders and policymakers to focus on reducing sources that contribute most to hypoxic areas. Texas is a prime region for a regional assessment of N inputs due to its diverse climate, its large agriculture industry, and its populous cities.

This thesis will focus on quantifying all sources of N using a hybrid approach that encompasses methods similar to *Boyer et al.* [2002] and *Howarth et al.* [1996], while considering county level information surveyed every five years through the census may not correctly reflect climate variation such as drought impact on pastureland. In order to assess the importance of land use change, more current information from remote sensing datasets will be used to ensure drier years reflect the expected changes in fixation across pasture/barren lands. In addition, this budget, henceforth referred to as the “Texas Anthropogenic Nitrogen Budget” or “TX-ANB”, will quantify the differences between it and national estimates of N inputs from NANI [*Hong et al.*, 2011] in Texas (Figure 1.1). Finally, the new estimates for the Texas region from the TX-ANB will be added to the NANI tools with hopes of improving the already thorough toolset.

Texas N Inputs: TX-ANB

- Net cultivation Input = $\left\{ \frac{N \text{ from fertilizer input}}{\text{crop area in county}} - \left(0.3 \frac{N \text{ from fertilizer input}}{\text{crop area in county}} \right) \right\} * \text{crop area in county}$
- Livestock Inputs = Animal number * N excretion estimates
- Legume Fixation = legume area * fixation estimates
- Atmospheric Dry and Wet Deposition = CMAQ output

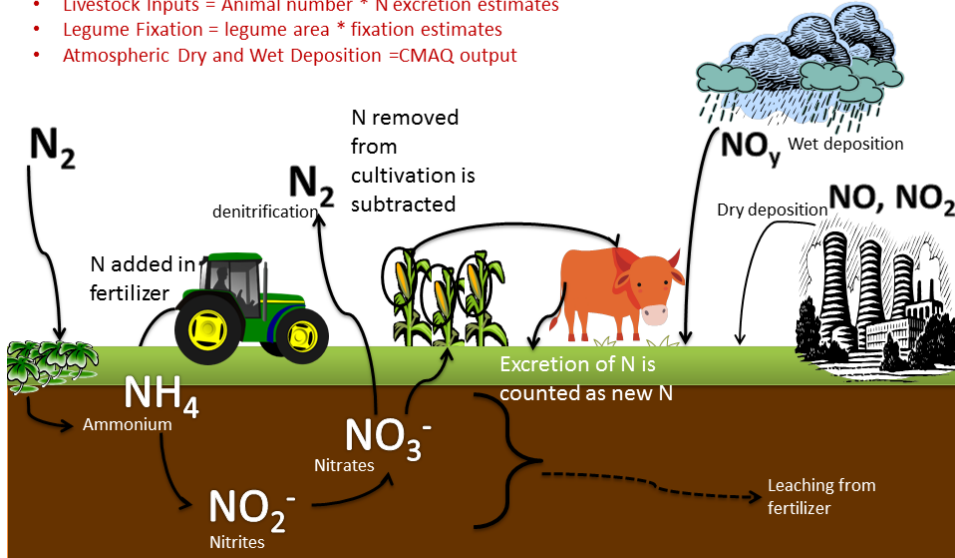


Figure 1.1: The full N cycle, sources, and calculations used in the TX-ANB [Banner et al., 2010]

Chapter 2: Development of a Texas Anthropogenic N Input Budget

2.1 INTRODUCTION: AVAILABLE DATA

Crop cultivation has been essential for matching the food needs of the world's forever-growing population. Cultivation on today's scale would not be possible without the ability to fertilize fields with synthetic N. Applying synthetic N to cultivated crops not only benefits human kind, it also supports the livestock industry. Within Texas a large portion of the crops cultivated are for the purpose of supporting one of the largest livestock industries in the United States [Rundel, 2011]. In order to fully quantify all sources and inputs of N within Texas, it is critical to understand and acquire accurate datasets of fertilizer inputs, crop cultivation area, and livestock populations.

2.1.1 Fertilizer Data Available

Comprehensive nitrogen (N) budgets require accurate accounting of N within fertilizer applied. Fertilizer distribution data are available from the Office of the Texas State Chemist (OTSC). This dataset keeps record of each county's distributed fertilizer amount and respective N grade within the distributed fertilizer. The data are available online for each county. While distribution information is available from 2005 through 2011, for the purposes of this project it was collected and recorded for 2008 through 2009.

2.1.2 Cultivated Crop and Land-Use Information

When N is applied through fertilizer, it is critical to know how much of that N will be taken up by the cultivated crops within each county. In addition, land use for pastures also can enrich the N cycle as a result of anthropogenic use, thus knowledge of

land use and land cover (LULC) is important in understanding human's impact on the N cycle. Crop coverage and LULC data were obtained from the National Agriculture Statistics Service's Cropland Data Layer project (NASS-CDL). It is available in Texas for 2008, 2009, and 2010 and is an enhanced remote sensing dataset. The NASS-CDL uses data from the Indian Remote Sensing satellite (IRS-P6), data from the Advanced Wide Field Sensor (AWiFs), and MODIS 16-day composite Normalized Difference Vegetation Index (NDVI). A supervised classification is used to differentiate between crop types and ground truth surveying is conducted to ensure accuracy (the NASS-CDL after 2008 may use Landsat 5 TM or Landsat 7 ETM+ satellite imagery to supplement classification) [Jonson and Mueller, 2010]. Typically raw MODIS data products have two classes for crops, while the NASS-CDL contains 36 crop classes for Texas (Figure 2.1). The NASS-CDL focuses on crops and in Texas, it uses its supervised classification system for crops and uses the National Land Cover Dataset (NLCD) to fill in the other land use types. Both the NLCD classes for other lands and the spectrally classified croplands make up the NASS-CDL. For example, corn is classified using the supervised classification methods, and barren land is labeled "NLCD- Barren lands" denoting that this land classification was based on the NLCD classification system. This refinement still provides high-resolution crop area information while maintaining other land classifications within the same dataset. Other land classifications such as legumes land area can be extracted (Figure 2.1) and used for N fixation from vegetated lands. The NASS-CDL information is available at 56 m^2 , which was scaled up to square kilometers for the purposes of accounting for N removal from square kilometer estimates.

2.1.3 Livestock Information: Census of Agriculture

The Census of Agriculture is a county-level available dataset (Figure 2.1), which provides inventory information for animal species within counties, but not specific locations of each animal. Every five years the United States Department of Agriculture sends Census surveys to all farmers regardless of size or production, and collects information including operation characteristics, production costs, and market value of products. Market value of products encompasses numbers of animals within each farm. The Census of Agriculture is the most comprehensive agriculture data available for every state and county [USDA-NASS, 2011]. As its most recent release was 2007, inventory information from 2007 was used for manure calculations.

Inventory information includes many classes of animals not used for total N calculations; selected animal categories for each county are recorded in Table 2.2. N within manure data was calculated based on the animal inventory numbers and suggested excretion rates from *Boyer et al.* [2002].

2.2 METHODS

2.2.1 Net Inputs of Nitrogen (N) from Crop Cultivation: Enhancements of N from Fertilizer and N Removal from Crops

Fertilizer is applied to cultivated crops based on recommended crop N uptake; this is an estimated amount of N needed for specific crops which is crop dependent. In order to accurately represent net N input resulting from crop cultivation, N applied from fertilizer input must be subtracted by the estimated amount crops uptake. Once the crop removes the N that was applied by the fertilizer, the crop is harvested and a percentage of the plant is left behind. The excess N that was not taken up by the plant plus the amount of N left in the plant and left on the field post-harvest, is the total amount expected N

input from cultivation. Therefore, the calculation of net N input from cultivation was completed through a two-step process, accounting of N from fertilizer for each county and estimating crop N removal for each county.

To account for fertilizer N inputs within each county, the OTSC's Annual Commercial Fertilizer Report was used [AgriLIFE Research, 2008]. The report contains fertilizer tonnage distribution and each county's N grade distribution in short tons was converted to kilograms and recorded in an Excel spreadsheet. This spreadsheet was then converted to a text file and imported into ArcGIS. The text file was converted to a database format for compatibility for ArcMap functions and tools. Each county was symbolized based on estimated N application from fertilizer in kg N yr^{-1} (Figures 2.1).

Accounting for N removal required utilizing methods from *Burke et al.*, [2008], which include estimating a certain percentage uptake for crop area present. *Burke et al.* suggests crops remove close to 30% of the N applied once crop harvest is complete. When a crop is harvested, much of the plant is left on the field and only the part of the plant used is removed. For this reason, *Burke et al.* assumes 70% of the plant is left on the field and 30% of it is removed. This method assumes all crops uptake the same amount of N per square kilometer.

The *Burke et al.* [2008] method was applied with use of the NASS-CDL dataset for 2008. In applying this method, scaling the data was important. The NASS-CDL data (field level crop data), downloaded from the NASS website [USDA, 2012] as a .TIFF file, contain attributes for loading in ArcGIS. Within the attributes, a cell count is listed next to each crop type; each cell represents 56 m^2 of the respective crop area. To estimate the quantity of N removed by crops from fertilizer application at county level, scaling the crop data to county level is needed. This can be done through use of tools within ArcGIS.

Once the crops are loaded into ArcGIS, the .TIFF file can be exported to a .GRD file or a “grid file” which ArcGIS can read and operate on more effectively. This grid file still contains all the information; it is just in an easy-to-read format for ArcMap. A function in the ArcToolbox called “Tabulate Area” can be used to transfer the grid squares into county features. A county shapefile for Texas was overlaid with the NASS-CDL dataset and the tabulation was constructed on the NASS-CDL data. The function takes the grids within a bounding county and solves for the area of grids within that county. For example, if there are three grids of corn and two grids of cotton and each grid is 56 m², the tabulate area function would calculate an area of 9,408 m² of corn and 6,272 m² of cotton for example county.

In order to remove the fertilizer N as the result of cultivation, the fertilizer data from the OTSC needed to be converted to an N application rate per crop area (Figure 2.2). Although the OTSC data are only an estimate of N applied within fertilizer to the whole county for all purposes, the assumption was made that any N applied was for the purposes of crop growth. The application of N per crop area was calculated by dividing the total N input from fertilizer applied to each county (kg) by the total crop area estimated from the NASS-CDL for that county (km²).

N removal rate due to cultivation was calculated by taking thirty percent of the respective N fertilizer application rate. The thirty percent of N was then subtracted from the total rate of N applied from fertilizer to estimate the total net N input rate from cultivation practices (Equation 2.1).

$$\text{Net Cultivation Input of N} = \frac{N \text{ from fertilizer input}}{\text{crop area in county}} - \left(0.3 \frac{N \text{ from fertilizer input}}{\text{crop area in county}}\right) \times \text{crop area in county} \quad (2.1)$$

As an example, Andrews County contained 93.87 km² of crops in 2008 and 38,356 kg of N from fertilizer was applied during the same year. This method assumes

all N from fertilizer is for crops thus: $38,356/93.87 = 408.61 \text{ kg N km}^{-2}$ which is the assumed N applied per km^2 of crops. To solve for how much N is removed, 30% of that is 123 kg N km^{-2} , thus if we subtract 30% of what is applied to solve for net input of N from cultivation, $408.61 \text{ kg N km}^{-2} - 123 \text{ kg N km}^{-2} = 285 \text{ kg N km}^{-2}$ is the net N input rate assumed as the result of crop cultivation. Considering this is a rate applied to crop area, multiplying by the area of crops will calculate the total mass of N input (kg) from crop cultivation. In this case $285 \text{ kg N km}^{-2} \times 93.87 \text{ km}^2$ of crops is 26,752 kg N, which is the net total fertilizer remaining on the field after cultivation. Estimated net N from cultivation is displayed in Figure 2.2.

Changes in application rates were apparent between 2008 and 2009, this is further discussed in the methods section. Percent change between 2008 and 2009 was calculated by solving for the difference between 2009's and 2008's N application rate. This difference was then divided by the N application rate from 2008 to show a percent decrease or increase from 2008 to 2009 for every county. The values were mapped using ArcMap symbology tools (Figure 2.2).

The spatial variability of application rates (Figure 2.2) required some assessment of land use in eastern Texas. The fertilizer application rate is based on the idea that all fertilizer applied is for cropland use, thus if there are a lot of crops there will be a lot of N applied, and areas without many crops will not have nearly as much N applied.

This was not the case in east Texas; a lot of N was applied to counties where crop area was small. To select the counties where this was occurring, the selection by attributes tool was used in ArcMap with the threshold of 200,000 kg N km^{-2} of crops for 2008. Once selected, these counties were exported to a new shape file and the tabulate area function was used to determine the land use, based on the NASS-CDL from 2008. The land use and county information was exported to Excel and the land cover types

were summarized by combining NASS-CDL classes into seven main land cover types. All crops were combined into one cropland class, all the urban NLCD classes were added and assigned a class called urban/developed land; the same was done for forested land and barren lands. Pasture and hay needed to be a single category considering the diverse nature of this land cover type. All NLCD aquaculture classes were summed and fallow/idle cropland also was its own class. Once these land area classes were consolidated into the seven types, the area of the county was used to determine the percent area of each land cover type within the county.

For example, Anderson County had high N application with very small crop area. To solve for its total percent area of pasture, the area of pasture (936 km²) was divided by the total area of the county (2,794 km²) to yield the result of 3% of the county lands allocated to pasture. This was done for all of the 26 counties that met the > 200,000 kg N km⁻² threshold in 2008. A table of these counties and their land use percentages can be found in Table 2.3.

2.2.2 Enhancements of N from Livestock

As mentioned before, livestock information was obtained through use of the USDA Census of Agriculture from 2007 that also is at county scale. While the Census is public information, some information is considered “non-disclosed” and denoted as “(D)” within the public information sheets. These numbers of livestock are not disclosed to the public due to protection of information between competing agriculture businesses [Rundel, 2011]). This results in a few types of livestock being under represented. As an example, within the far northeastern counties of Texas large dairy farms are present. Dairy cows excrete the most N of any animal (Table 2.2), however many counties do not disclose their dairy cow numbers. This potentially results in a large amount of N from

excretion in animal waste not being represented when using the raw Census public information. *Boyer et al.* [2002] handled this missing data by developing an interpolation method that replaces the missing animal information with derived values. The interpolated dataset of Census information was obtained from colleagues at Cornell University who now use the *Boyer et al.* [2002] derived animal method for the NANI toolbox [*Hong et al.*, 2011].

Excretion was estimated by using original estimated amounts from *Boyer et al.* [2002] as well and these can be found in Table 2.2. These numbers are based on estimates from *van Horn* [1998] and were chosen because they were estimates based on animal consumption rates from the U.S. Each county's respective animal count was multiplied by the excretion estimation rate for each animal (animal types accounted for are represented in Table 2.2). All the excretion N input estimations were added to produce the estimated N input from animal excretion for each county. These inputs were mapped at county level (Figure 2.3). Some livestock manure can be used to fertilizer crops or can be spread over pasture lands, however, the majority of the transport remains within the county. For this reason, it is reasonable to consider the animal manure N sources remain within the county the livestock population is present in [*Rundel, 2011*].

2.2.3 Enhancements of N from Cultivated N-fixing Crops

Legumes are a unique plant that has a symbiotic relationship with a common soil bacterium called *Rhizobium*. The plant roots of legumes provide nutrients and energy for the bacteria to flourish and within a week of infection, visible nodules are produced which can reach the size of a large pea in plants such as peanuts and soybeans. These nodules take in N_2 from the atmosphere and transform it to NH_4^+ , which can be used by the plant [*Lindemann, 2003*].

Legumes cultivated in Texas were tabulated to each county using methods discussed in section 2.2.2 for crop tabulation from the NASS-CDL. Soybeans, peanuts, and alfalfa are the only legumes cultivated in Texas during 2008 and 2009. The area of cultivation of these crops is relatively small. Within 2008, only 165 km² was allocated for peanut production, 578 km² was cultivated soybeans, and 331 km² was cultivated alfalfa; this area compared to other cultivated crop area in Texas (Figure 2.4) in 2008 miniscule. Soybeans are the only crop represented as a percentage; peanuts and alfalfa when compared to all other cultivation area represent 0% of land. To be complete, cultivated legumes were considered as a source of anthropogenic input and Table 2.4 displays N input from fixation for each cultivated legume.

Not only legumes cultivated fix N however, pastureland and land allocated for hay farming also contain legumes which can fix N (Table 2.4, Figure 2.1). These lands would not likely be allocated for this use without human influence, thus pasture/hay land use is considered an N input from fixation due to anthropogenic activities. Legumes such as clovers can flourish in pasturelands and can provide food for cattle and other range livestock. The presence and abundance of legumes within pasturelands is highly dependent on climate and precipitation variability. Because of this strong coupling between pasture legumes and precipitation, regional annual estimates of this are important to consider as variation of fixation from pasturelands likely varies greatly internally. Gerald Smith at Texas A&M estimated pastures within Texas likely fix 9,000 kg N km⁻² yr⁻¹, and pastureland consist of ~2% legumes coverage. This would suggest ~11,523.06 kg N is input per year from pasturelands.

In order to calculate all the fixation inputs of N from cultivation and pasture/hay lands, each county's area of respective legumes was multiplied by estimated fixation rate (kg N km⁻² yr⁻¹) listed in Table 2.4. The total fixation was calculated for all counties and

maps were created to display spatial variability of fixation spatially. Total area of legumes and respective fixation values are displayed in Figure 2.5.

2.2.4 Atmospheric N Deposition Influence

As urbanization increases across Texas, it is important to account for N deposition from atmospheric sources. N deposition can be the result of combustion processes from cars or power plants volatilizing reactive N (N_r). Reactive N can be in many forms, typically NO_y is considered the source of atmospheric N deposition. In addition, natural sources from the soil may be volatilized and also can result in N deposition through either dry or wet deposition mechanisms. One major volatilization from anthropogenic sources is ammonium (NH_x) from livestock and fertilizer application. NH_x deposition typically correlates well with anthropogenic livestock and fertilizer N sources, thus accounting for NH_x deposition from the atmosphere is omitted when considering atmospheric N deposition as part of a net N input budget [Howarth *et al.*, 1996]. To capture atmospheric fluxes of both oxidized (NO_y) and reduced (NH_x) N, the Environmental Protection Agency's Community Multi-scale Air Quality Model (CMAQ) was used.

CMAQ output data for 2006 was mapped to county level information through use of the Net Anthropogenic Nitrogen Input Toolbox [Hong *et al.*, 2011]. The toolbox approach takes gridded CMAQ output and matches the proportion of grids to a county shape file using ArcGIS. This matching can be done directly in the NANI toolbox. Values were mapped for both oxidized and reduced forms of N deposition (Figure 2.6).

2.3 RESULTS AND DISCUSSION

Choosing datasets is critical in correctly quantifying N inputs. When employing a simple understanding of the N cycle, knowing the sources and inputs is the main limitation on quantifying anthropogenic impacts. Data sources were collected from what

was considered best for Texas. For example, OTSC fertilizer tables were used instead of USGS fertilizer data. The OTSC fertilizer data are based on surveys from county distributors, whereas the USGS fertilizer data are based on estimations of fertilizer distribution from land use. Thus the OTSC's records of distribution likely are more accurate spatially. Field level fertilizer application information is unknown however.

Crop data can be found from not only the NASS-CDL, but MODIS and the USDA Census of Agriculture as well. The NASS-CDL and Census data contain the finest resolution of crop data. MODIS data only display two classes for cropland and would have limited use in this study. *Hong et al.* [2011] uses Census of Agriculture information for crops. This dataset is available every five years, and thus inter-annual variability analysis is not possible. However, spatial variability is likely more accurate considering it is an in situ form of measurements (survey based) whereas the NASS-CDL is limited by spectral ranges.

Comparing the three options for land use data (MODIS, NASS-CDL, and Census) is difficult because of varying classifications systems. For example, MODIS only has two forms of cropland classified. When comparing it to the cropland coverage from the NASS-CDL, a large swath of cropland appears to be missing for NASS-CDL over the coastal plain (southeastern Texas). This missing crop area coverage is likely due to classification systems for MODIS and NASS-CDL. When producing satellite-derived products, spectral ranges specific to certain crops were chosen. This missing crop area, according to the NASS-CDL and NLCD, contains a lot of pasture/hay lands. When comparing the two products (Figure 2.7), it is evident that much of the missing cropland is likely pasture and hay land. The NASS-CDL does not consider this land cropland, while MODIS categorizes most of it as cropland/natural vegetation mosaic. Thus, MODIS and NASS-CDL do not directly match up when comparing cropland (Table 2.1).

The Census and NASS-CDL are difficult to compare as well for similar reasons. The Census information records crops based on surveys and thus higher-resolution of crop classification is possible (Table 2.1). For example, the NASS-CDL lists the class “pasture/hay”, whereas the Census breaks this land into three classes: non-cropland pasture, cropland pasture, and other hay. Although the NASS-CDL also contains a class for “other hay”, zero area is represented in Texas within this class. The census, however, suggests that Texas contained around 5 million square kilometers of hay in 2007. The NASS-CDL only began in Texas in 2008, and it is unlikely that in one year the state decreased “other hay” areas by 5 million square kilometers. It is more likely that pasture/hay lands were grouped into one area classification and thus are difficult to compare with Census information.

This grouping of classes in the NASS-CDL produces a limitation on legume fixation inputs; other hay lands, according to *Boyer et al.* [2002], contain legumes and fix N at a different rate than pastureland. This fixation rate however, likely varies from region to region and no estimation of this rate is known specifically for Texas. The fine resolution of crop type possible in the Census does produce a more accurate estimation with N fixation assessment, though the main limitation of the Census is time.

The NASS-CDL, although it only dates back to 2008, is an annual assessment of land use that allows for assessment of crops with consideration of inter-annual climate variability. Inter-annual changes in rainfall impact the N cycle greatly, especially with respect to downstream environments. As mentioned in Chapter 1, *Goolsby* [2000] displayed the tightly coupled system of rainfall and N export. Texas’ highly variable climate from year to year provides a need for changing cropland on scales shorter than five years. The drought from 2011 alone displayed how death of vegetation and land cover can change in a season due to scorched landscapes. Pasture/hay lands likely did

not have any N fixation occurring due to legumes during this time when considering the scarcity of water. For this reason, Texas N quantification requires crop/land-use information that spans shorter timescales than five years. This limits use of the Census dataset, despite higher resolution information.

While data choices are important, it is also critical to understand limitations and develop or select methodologies that match what is reasonable for the data available or chosen. Methods for the Texas Anthropogenic N budget (TX-ANB) deviated from *Boyer et al.* [2002] and *Hong et al.* [2011] in calculating N removal and accounting for influences from humans and animals. The deviations in methodologies were based on data selection and regional needs. Although the data were selected with the intention of representing the region best, some assumptions had to be made with respect to cultivation and removal of N due to the data parameters.

2.3.1 Net Inputs of N from Crop Cultivation

Fertilizer application is tied closely to cropland use in most cases. Overlaying NASS-CDL crops with N inputs from fertilizer displays similar patterns (Figure 2.8). These similar patterns suggest the majority of N from fertilizer is used for crops. From this relationship, fertilizer application rates can be assessed as kilograms of N per square kilometer of crops. While this makes sense in areas where cropland is high, an anomalous pattern exists in the east where high N application is exhibited, specifically in 2008 (Figure 2.2, top left). Many of the counties in the east do not contain much crop growth; percent area allocated to crops is zero (Table 2.3). Rate of fertilizer N applied, however, is greater than 200,000 kg N km⁻² of crops. When assessing the land coverage of these counties (Table 2.3), the majority of them have close to 1% developed lands and forested lands typically makeup the remaining land use. It is likely that fertilizer

distributed to those counties either is not used or is used for residential purposes, but it is important to consider what N application rate represents.

The method for calculating N input from fertilizer application per crop area was derived from the county-scale limitation of the OTSC fertilizer. It may be intuitive to divide the county value of N from fertilizer into even grid squares of 1 km by 1km and assume the N applied was evenly distributed throughout the total area of the county, however when considering crop removal this even division of N application is meaningless. The purpose of developing a N application rate per crop area from fertilizer was to calculate how much N is removed by crops. For this reason, dividing fertilizer use evenly would result in an underestimation of crop uptake. Crops uptake a certain amount of N based on need not what is available. If a crop is over fertilized, it does not uptake the extra. If a county was more heavily fertilized in one year, it is important to not assume the N removed will be higher. Considering crop fertilization of N normalized by crop area removes this shortcoming.

The method chosen for calculating N removal was selected for the aforementioned reason; uptake is based on the rate applied not the amount. Essentially, the fertilizer spread was normalized for the crop area that existed within the county. Subtracting 30% as uptake, therefore, is more accurate and can be compared from year to year. This method worked well if all N was being applied to crops, but the OTSC fertilizer N input data were limited in this regard. Application of N, therefore, was extremely high with respect to crop area in places that were using N for personal uses that were not classified as crop production. Because the application rate was mainly used for crop removal, the eastern counties highlighted in Figure 2.2 display high removal *rates* of N. Comparing the *quantity* of N actually removed in counties with a large percentages allocated to crops, with the quantity of N removed in counties with low percentages of

crop area indicated the quantity remaining after cultivation is much less. When the final inputs are calculated, and mass is considered, the counties with large input rates yield a contribution to the N cycle from cultivation that is low.

In summary, Figure 2.2 shows input rates which are crop-area dependent. Gaines County had an N input rate after crop removal of N of $9,433 \text{ kg N km}^{-2}$ of crops and it contained $1,704 \text{ km}^2$ of crops. As a result, the total input of N for Gaines was $16,073,832 \text{ kg N}$. Montgomery County's N input rate from fertilizer after crop removal of N was $419,915 \text{ kg N km}^{-2}$ of crops, although the total cropland for Montgomery County was 1.68 km^2 for that same year. The input of N from fertilizer due to cultivation was $705,457 \text{ kg N}$. The application rate of N due to cultivation was high, but the area that rate was applied was small. Consequently, minimal N is input for that county due to cultivation, which is accurate. The question remains though; what is the N applied for fertilizer in Montgomery county used for? The OTSC estimates $707,150 \text{ kg N}$ is distributed to the county, the method presented here removes N only due to cultivation, thus almost 100% of it is considered to be excess. It is being distributed to the county; therefore, it likely has a purpose that is not captured within the methods of this quantification.

Ultimately, the N input from crop cultivation has a strength of only removing N which is applied for crops and much of the N applied fits well to crop area. Limitations arise when crop area is not the use for the fertilizer N being distributed to the county.

2.3.2 Livestock N Inputs

When quantifying inputs of N from livestock, similar spatial patterns exist (Figure 2.3) to crop spatial variability. This is likely the result of the crop cultivation in Texas being mainly for livestock feed. Other budgets such as *Hong et al.* [2011] suggest N

removed from the fields through crop cultivation gets consumed by animals, and then animal mass is produced and sold for consumption by humans. However in Texas, much of the crop area is for the purpose of growing feed for animals only; much of the harvested crops in Texas are not for human consumption. Humans essentially consume N from livestock and produce excretion which is the input resulting from the N cultivated and removed. For this reason, the *Hong et al.* [2011] sequence may not be as practical in Texas. In Texas, considering animal excretion and omitting human consumption likely is a better way of quantifying how some of the N removed during harvest makes it back into the ground through manure excretion. Human excretion is distributed from where humans actually live to sewage treatment plants, or else is deposited in localized septic systems which treat the waste as well. Because of this structure, it is inaccurate to represent human waste as a direct input spatially.

Excretion rates for animals are highest in the southern panhandle and the northern half of eastern Texas (Figure 2.3). The panhandle contains a large industry of beef production that is highly concentrated into feed lots and the northern Dallas-Fort-Worth area contains farmland which is allocated for dairy cows. These two animal types contribute most to the N cycle through excretion. The N from the excretion also produces volatilized NH_3 as well. The lifetime of NH_3 within the atmosphere is on the order of a few days, and thus the N excretion quantities match similar patterns to the NH_3 deposition (Figure 2.6, atmospheric deposition of reduced N from 2006 CMAQ results).

2.3.3 N Fixation Inputs

The majority of legumes in Texas are represented by pastureland. Peanuts, soybeans, and alfalfa are present in a few areas close to the panhandle and some along the central coastal plain (Figure 2.1). The large area of pasturelands with legumes present

likely varies greatly depending on climate. Clover growth within these lands is the primary contributor to the N cycle. As a result, in times of drought when pastures are starved for rain, clovers likely do not grow. During these times, fixation influence from pasture/hay lands likely decreases as discussed in the previous section.

2.3.4 Atmospheric Deposition N Inputs

Atmospheric deposition plays a strong role in the N cycle in Texas, specifically as the result of urbanization. Figure 2.6 displays the strong correlation between urban areas and oxidized N atmospheric deposition. Also when considering the N cycle contributions in total oxidized N atmospheric deposition plays a large role (Figure 2.9 and 2.10). It is important to consider residence time and sources of N deposition.

Manure resulting from animal excretion contains a lot of NH_4 ; this ammonium gets volatilized and results in high concentrations of NH_4 present in the air close to feedlots. The residence time of NH_4 in the atmosphere is about one day, as a result much of the NH_4 or reduced N deposition represented in the CMAQ output, is directly correlated to manure. These results were tested by *Howarth et al.* [1996]. For the purposes of a total N input quantification in TX-ANB it is important to note the accounting of manure through animal excretion input assessment has already been considered. Thus choosing to also add reduced N as a source from N deposition potentially could lead to accounting for the same source of N twice. For this reason, TX-ANB only considers N deposition for oxidized forms of N.

2.4 CONCLUSION AND SUMMARY

Quantifying all sources of N spatially is critical for understanding impact regions, which are highly altering downstream ecosystems. Available datasets are the main limitation in constructing full comprehensive N budgets through Texas. Choosing

datasets which are region specific is important; understanding what is best for representing climate variability is critical in regions such as Texas, where drought can be present. MODIS data did not contain information on crop types which did not enable legume analysis for fixation influences, in addition assessment of cropland versus pastureland is difficult as a result of the low resolution classification of “cropland/natural vegetation mosaic” within the MODIS dataset. The Census data, while type specific, is only collected every half-decade. This results in the inability to quantify changes of N input from legume fixation through climate variability on an inter-annual scale. The NASS-CDL not only is produced annually, but also has 36 crop types for Texas. Its high resolution allows for legume N fixation input analysis and climate variability assessment.

The majority of the fertilizer distributed and accounted for is likely to support crops, thus all the N input from fertilizer is assumed to be at a rate dependent on crop area within the county. The county level fertilizer information is unable to be scaled down, thus the crop information is scaled up from field level to county level in order to take 30% of the N applied and account it as removed. This is the estimated amount removed due to crop cultivation; the remaining amount of N is left on the field and considered excess N that is not used. The calculation of remaining N is limited to crop cultivation. Since this is not the case, the result is a likely overestimation of N input due to cultivation. The counties that have sizable N distributed in fertilizer but almost no cropland indicate that high N application rates are present. These counties, specifically in the east, are most likely overestimated when considering N input from crop cultivation.

Much of the crops grown in Texas are for the purpose of supporting the large livestock industry. For this reason, the spatial trends of animal population match closely with the crop production. TX-ANB assumes a portion of the N that is removed from the field due to harvest gets input again due to animal excretion. These N excretion estimates

provide information spatially of how much livestock is impacting the N cycle across Texas.

The main legumes in Texas are found in pasturelands; peanuts, soybeans, and alfalfa are grown as well. These legumes take in N_2 and “fix” it for use. Much of this pastureland is for grazing and is the result of farming; consequently pasture/hay lands are considered anthropogenic impacts on the N cycle. These lands are estimated to have ~2% clovers which are responsible for fixing $\sim 180 \text{ kg N km}^{-2} \text{ yr}^{-1}$. This results in a sizable N input in parts.

In general, the major impact to the N cycle on the land is from fertilizer, the second largest impact is livestock and atmospheric deposition of oxidized N follows closely behind. Only a small fraction of the N inputs are from legume fixation. Much of the livestock and fertilizer inputs in the panhandle do not have direct impacts on the coastal environments due to their proximity to the Ogallala aquifer (Figure 2.11). Much of the N recharges into the aquifer there. The coastal plain, where large inputs of N are occurring, has an impact on nutrient levels in the Gulf of Mexico. In addition to proximity, these areas are located in the humid east and see more rainfall which directly correlates to higher potential for N loading in streams. These areas are ones which should be carefully monitored.

All of the analysis done here is extremely limited on data sources available and estimations of N inputs from each source. Of the data available, much of it is at county level thus spatial analysis is difficult. In addition, errors are likely to be introduced when considering N removal from cultivation. Unknown use of the N input from fertilizer likely results in overestimation of excess N. Quantifying N is critical, specifically in wet areas; therefore, improved data resolution in these areas would be most effective.

Data Type	Crop Types for Texas	Data Source
MODIS	2	MODIS Satellite
NASS-CDL	36	IRS-P6, AWiFs, MODIS NDVI
Census	15--17	Census of Agriculture Survey

Table 2.1: MODIS, NASS-CDL, and Census data compared, crop types and data sources are represented.

Animal Type	Excretion N Input Estimates (kg N animal ⁻¹ year ⁻¹)
Beef Cattle	58.51
Dairy Cattle	121.00
Pigs & Hogs	5.84
Sheep	5.00
Goats	5.00
Horses	40.00
Chickens (broilers-layers)	0.07--0.55
Turkeys	0.39

Table 2.2: Census of Agriculture classes recorded and used for N input estimates resulting from livestock production. N content within manure for each respective animal was taken from previous research from *Boyer et al.* [2002].

	Cropland (%)	Developed (%)	Forest (%)	Bare (%)	Pasture (%)	Aqua (%)	Fallow (%)
Anderson	0.0	0.1	0.3	0.1	0.3	0.2	0.0
Angelina	0.0	0.1	<i>0.4</i>	0.1	0.1	0.3	0.0
Cass	0.0	0.1	<i>0.6</i>	0.1	0.1	0.1	0.0
Cherokee	0.0	0.1	<i>0.4</i>	0.1	0.3	0.2	0.0
Gregg	0.0	0.3	<i>0.4</i>	0.1	0.1	0.1	0.0
Leon	0.0	0.1	0.2	0.1	<i>0.4</i>	0.1	0.0
Madison	0.0	0.1	0.1	0.0	<i>0.7</i>	0.1	0.0
Marion	0.0	0.1	<i>0.5</i>	0.1	0.1	0.3	0.0
Montgomery	0.0	0.3	<i>0.4</i>	0.1	0.1	0.3	0.0
Nacogdoches	0.0	0.1	<i>0.4</i>	0.1	0.2	0.3	0.0
Polk	0.0	0.1	<i>0.4</i>	0.2	0.1	0.3	0.0
Rusk	0.0	0.1	<i>0.4</i>	0.1	0.3	0.1	0.0
Sabine	0.0	0.0	<i>0.4</i>	0.1	0.0	<i>0.4</i>	0.0
San Augustine	0.0	0.1	<i>0.4</i>	0.1	0.1	0.3	0.0
San Jacinto	0.0	0.1	<i>0.4</i>	0.1	0.1	0.3	0.0
Shelby	0.0	0.1	0.3	0.1	0.2	0.3	0.0
Smith	0.0	0.1	0.3	0.1	<i>0.3</i>	0.1	0.0
Trinity	0.0	0.1	<i>0.5</i>	0.1	0.1	0.2	0.0
Tyler	0.0	0.1	<i>0.4</i>	0.2	0.0	0.3	0.0
Upshur	0.0	0.1	<i>0.5</i>	0.1	0.3	0.1	0.0
Wood	0.0	0.1	<i>0.4</i>	0.1	0.3	0.2	0.0

Table 2.3: Land use percent coverage for counties containing N application rates in 2008 that exceeded 200,000 kg N km⁻² of crops. Italicized numbers represent the majority of land cover type for the county.

Legume Name	Fixation N Input Estimates (kg N km⁻²yr⁻¹)
Peanuts	8,000
Soybeans	9,600
Alfalfa	22,400
Pasture/hay	180

Table 2.4: Estimations for legume N fixation rates; estimates for peanuts, soybeans, and alfalfa are from *Boyer et al.* [2002]. Estimates of fixation in pasture/hay land are from personal communication with *Gerald Smith* of the University of Texas A&M [2012].

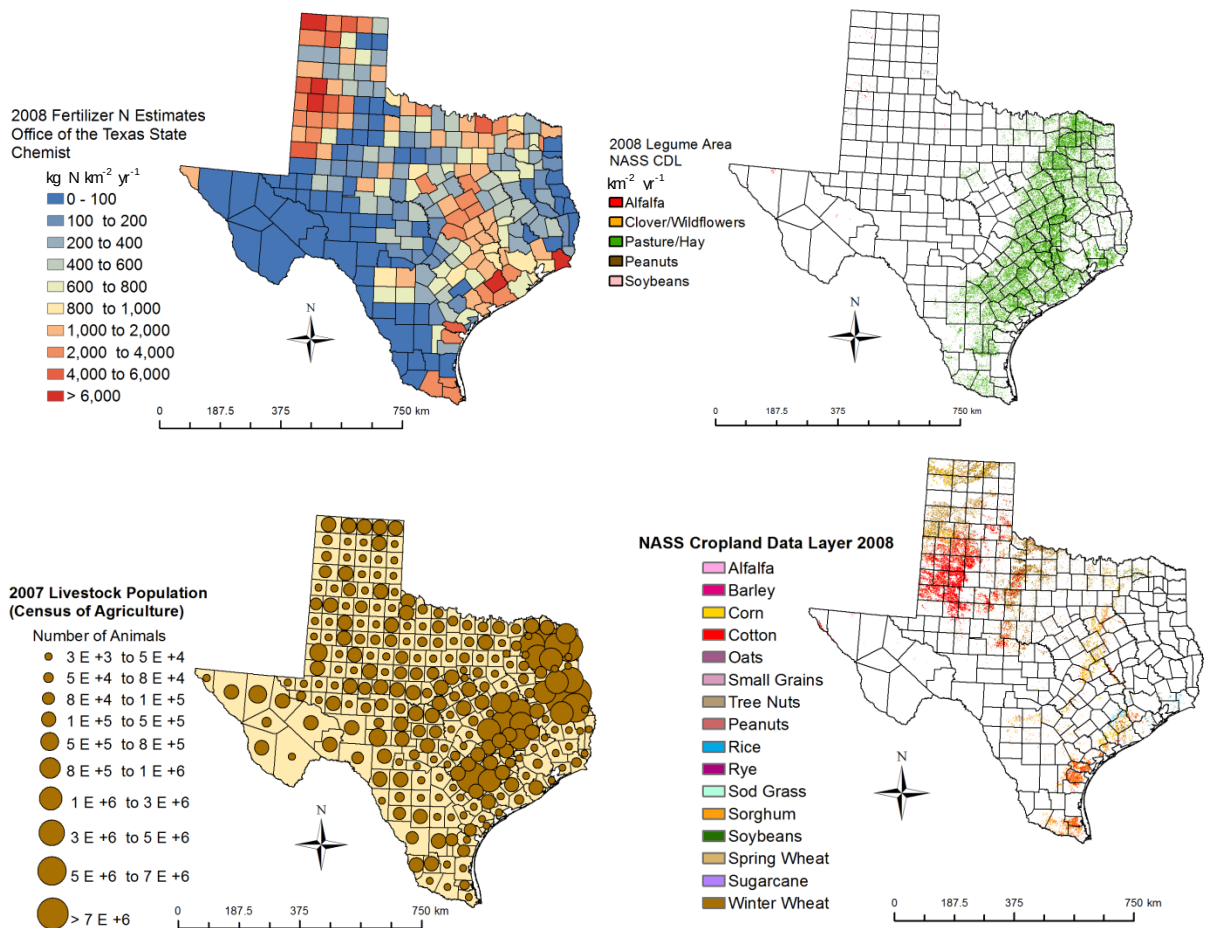


Figure 2.1: All the collected data used in calculating TX-ANB: Fertilizer data from the OTSC 2008 (top left), legume area extracted from the NASS-CDL from 2008 (top right), livestock population density from the USDA Census of Agriculture in 2007 (bottom left), and the NASS-CDL crop area for 2008.

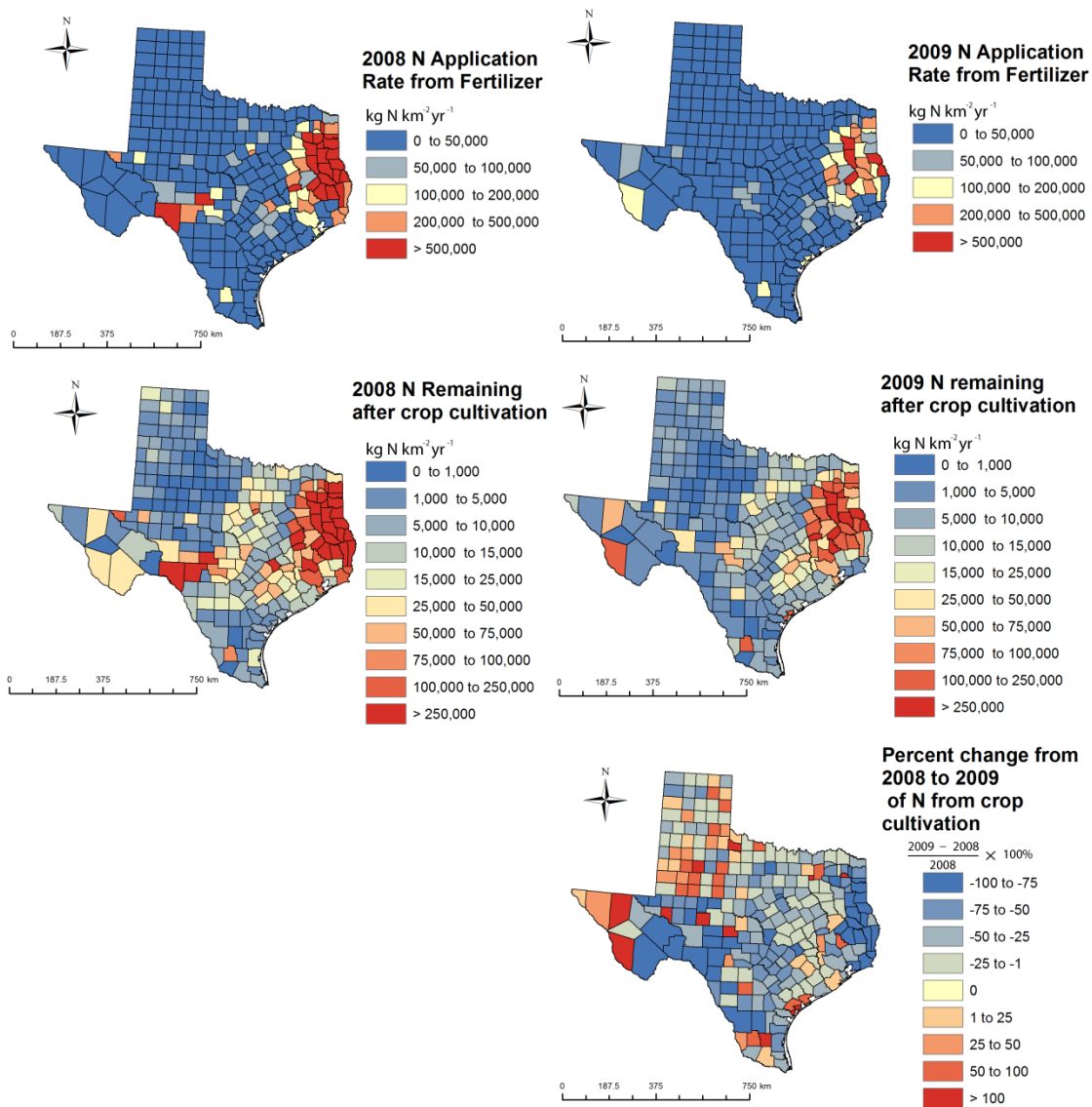


Figure 2.2: Total 2008 and 2009 NASS-CDL crops with N application rates from fertilizer (kg N km^{-2} of crop area yr^{-1}) (top two) and N remaining per crop area after N removal from crops (middle two). Percent change from 2008 to 2009 of total N resulting from crop cultivation (bottom right).

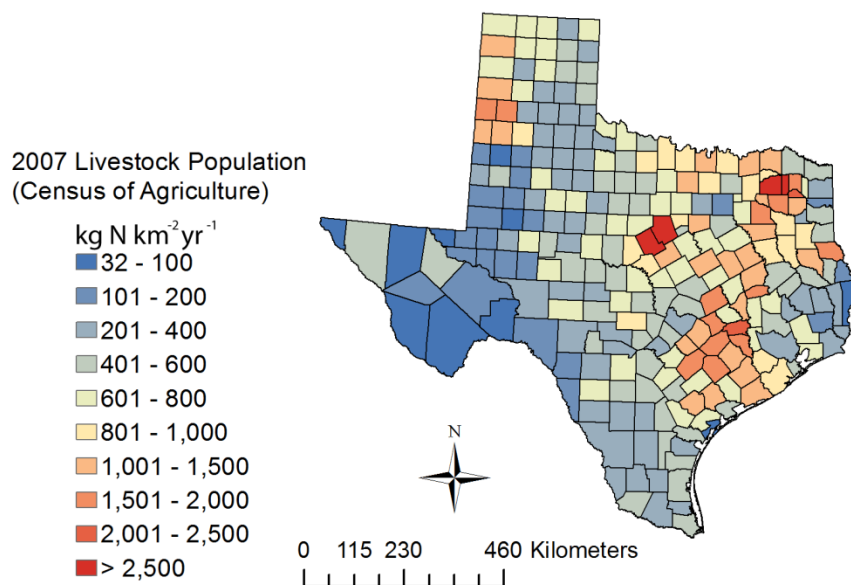


Figure 2.3: Total N input (kg N km⁻² yr⁻¹) from livestock excretion, excretion estimates are based on *Boyer et al.* [2002] and animal numbers are from the USDA Census of Agriculture.

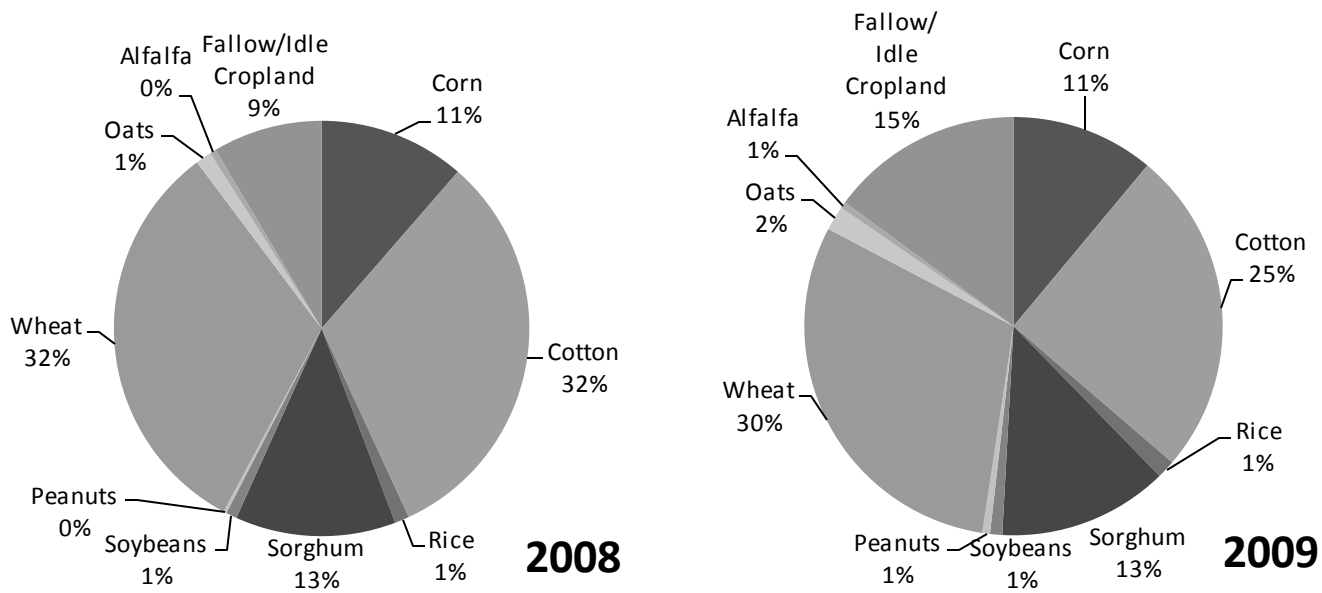


Figure 2.4: Total crop distribution and percent area in 2008 (left) and 2009 (right) from Texas based on crop area information in the NASS-CDL.

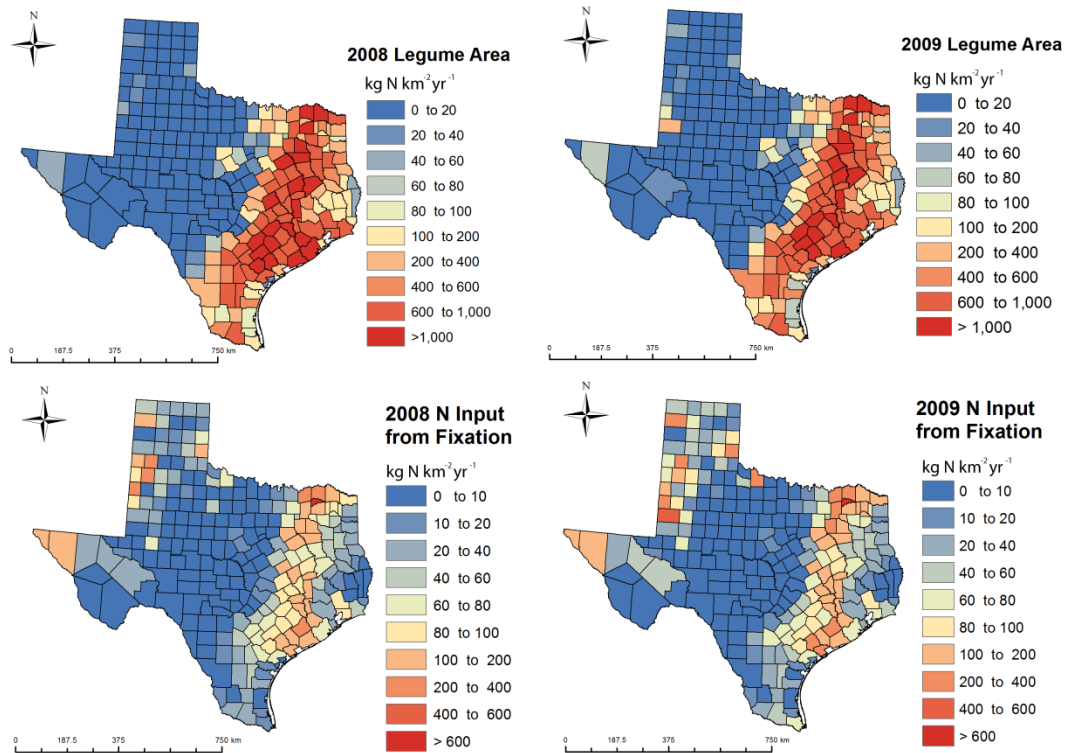


Figure 2.5: County scale legume coverage and N inputs from fixation of legumes for TX-ANB 2008 and 2009.

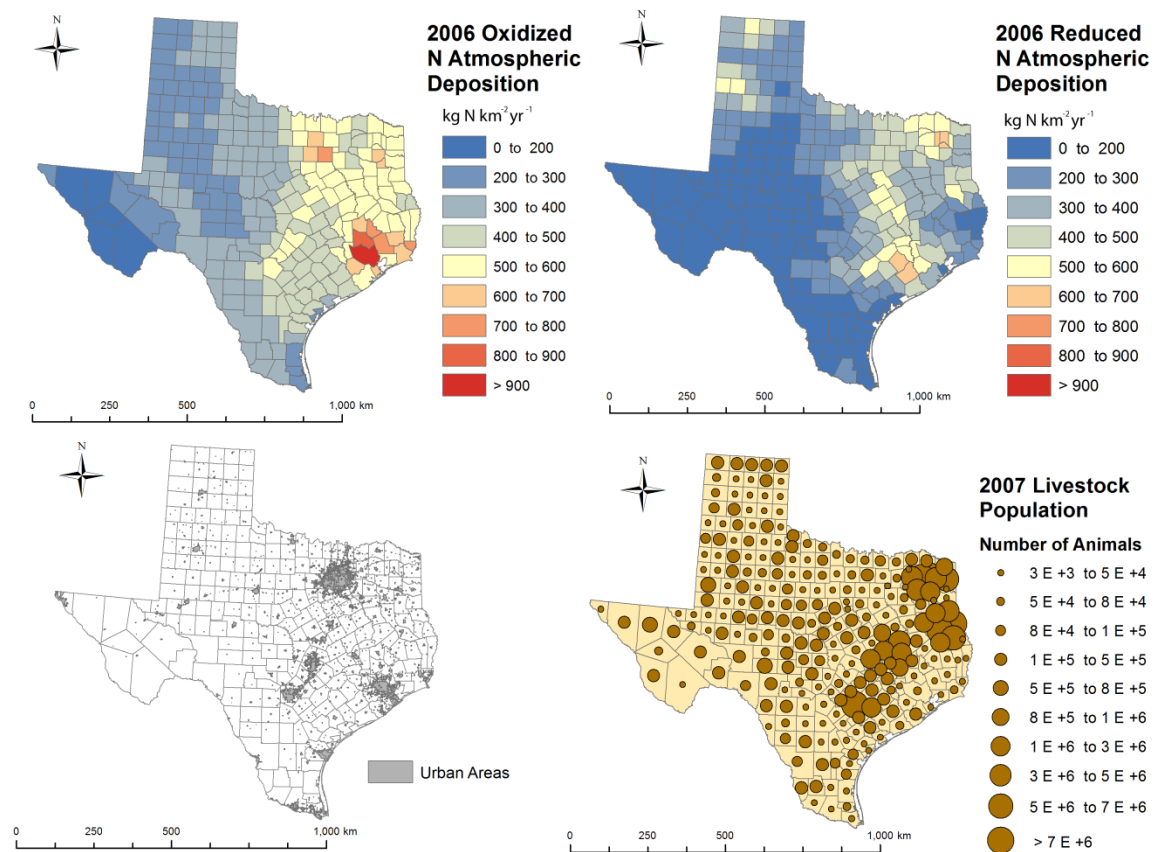


Figure 2.6: Atmospheric Deposition of Oxidized and Reduced N from the Community Multi-scale Air Quality Model (CMAQ) from 2006 (top two maps) and the respective implied sources, urban areas and livestock land (bottom two maps).

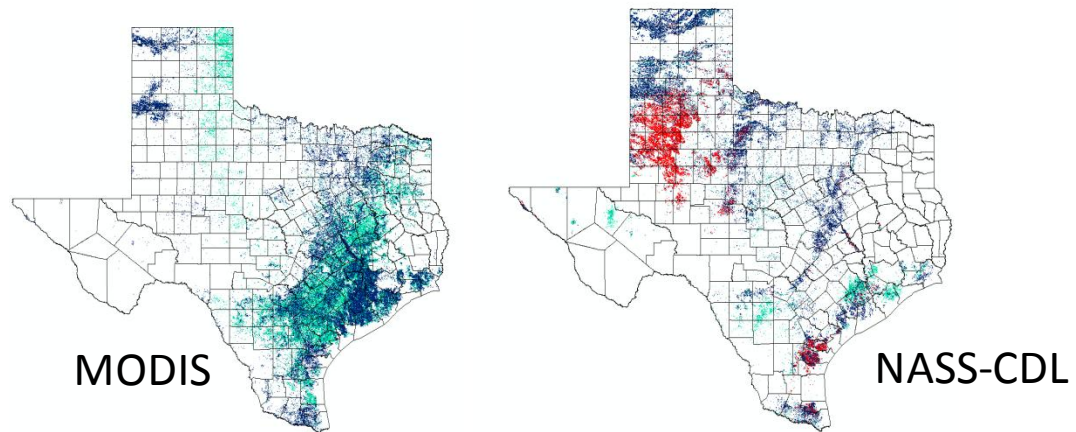


Figure 2.7: MODIS product has two cropland categories : “Cropland” denoted as blue and “Cropland/Natural vegetation mosaic” denoted as green. The Cropland Data Layer product produced by the National Agriculture Statistics Service (NASS-CDL) for research pertaining to crop area and specific types of crop coverage has fifty cropland categories in Texas which are specific to each crop. Here red denotes cotton, blue is grouped cropland, and green is fallow/idle cropland.

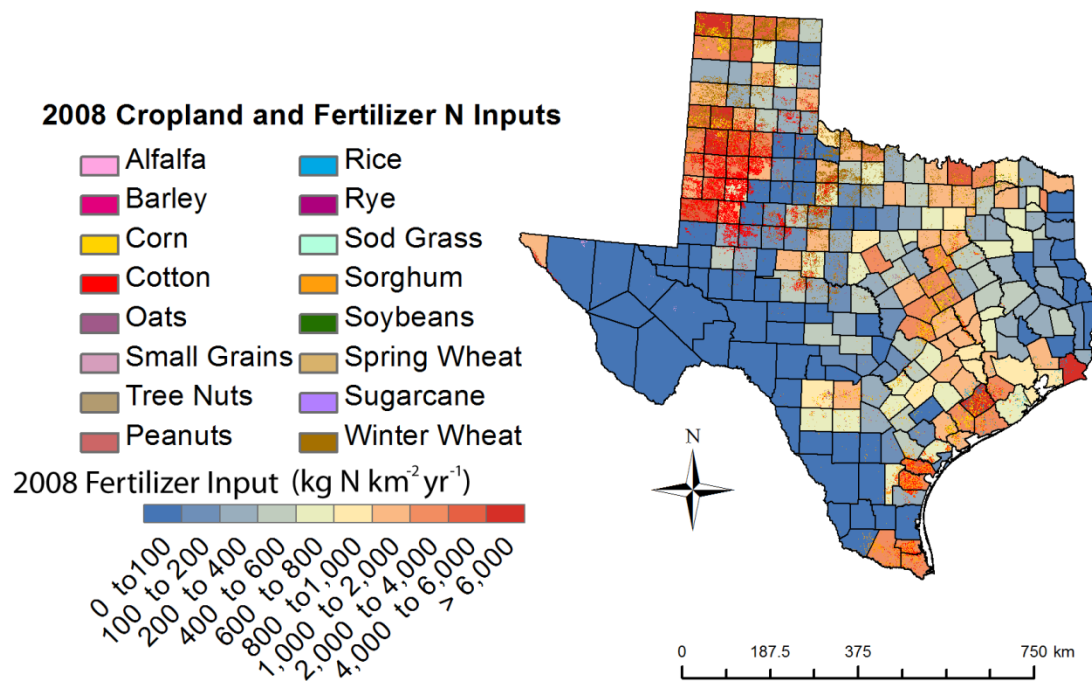


Figure 2.8: Fertilizer application of N per county area (km^2) in Texas with NASS-CDL cropland overlaid at field level (1 km^2 grid cells).

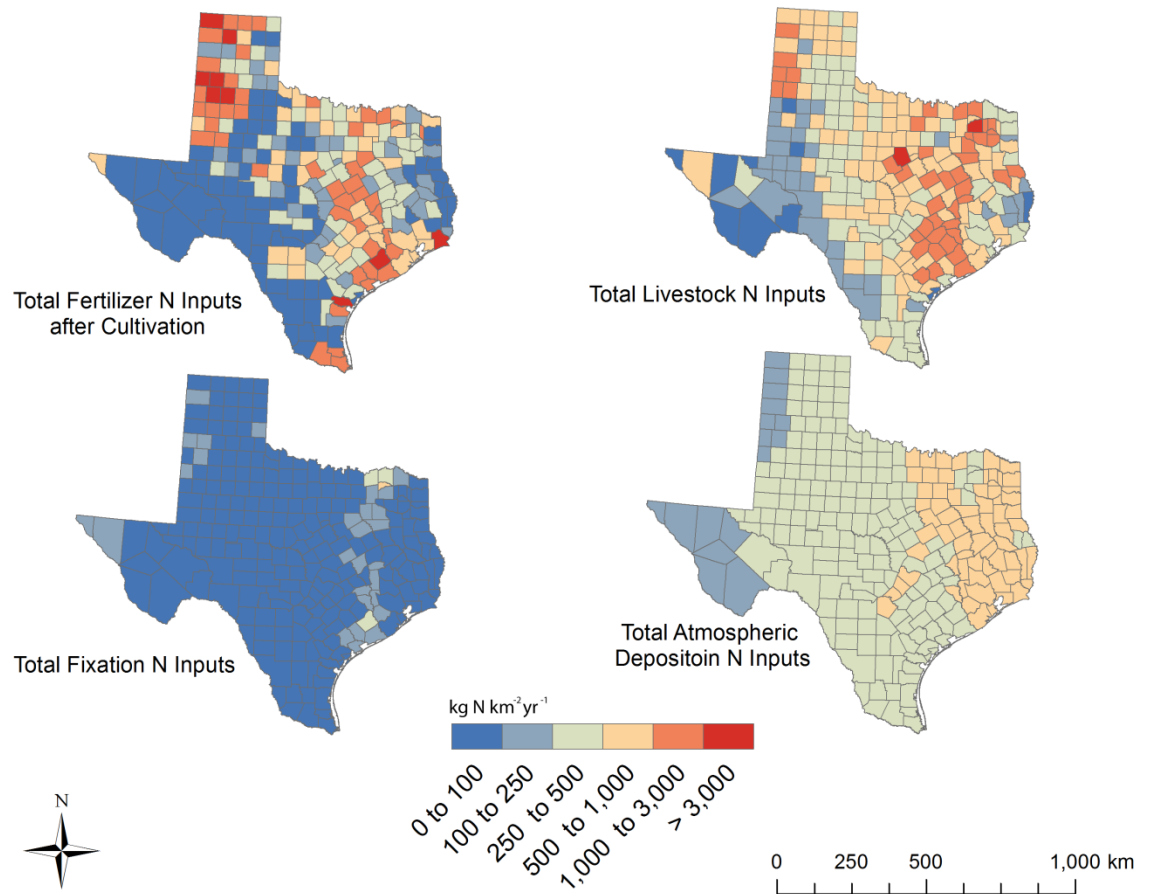


Figure 2.9: Total N inputs accounted for in TX-ANB; fertilizer N input after cultivation has removed N (top left), total N inputs from livestock due to animal excretion (top right), total N fixation inputs (bottom left), total atmospheric oxidized N deposition (bottom right).

Source Disbribution in Texas

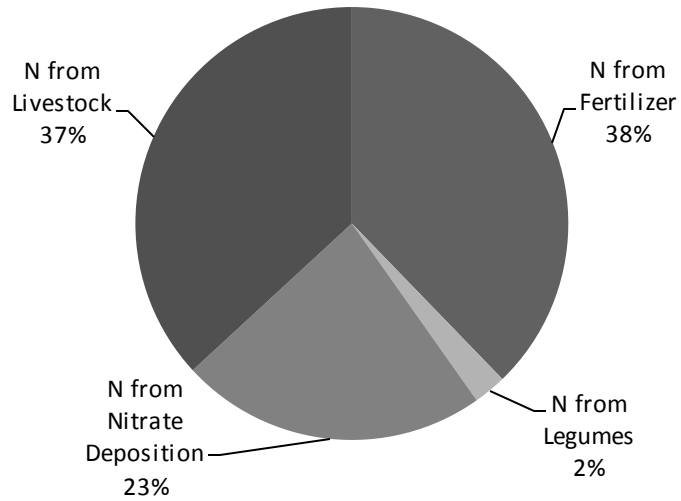


Figure 2.10: Total source distribution from TX-ANB; fertilizer data from 2008 OTSC, Legume area data from NASS-CDL, N deposition data from 2006 CMAQ, Livestock number data from Census of Agriculture 2007.

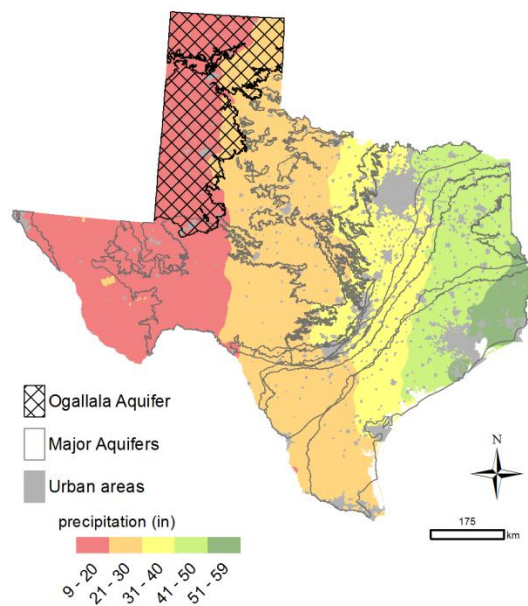


Figure 2.11: Texas' precipitation gradient and major aquifers. The Ogallala Aquifer is highlighted with cross-hatches.

Chapter 3: National and Regional Nitrogen Budgets: Implications for Riverine Nutrient Export

TX-ANB can be compared to a national dataset developed at Cornell University and documented by *Hong et al.* [2011] called the Net Anthropogenic Nitrogen Input Toolbox calculator. Some comparisons were discussed in chapter 2 between the two datasets, while this chapter will focus on directly comparing the two budgets (TX-ANB and NANI) as well as discuss how regional data have the potential to enhance NANI. Comparisons to measured and model results will be used to assess the accuracy of each dataset.

3.1 NET ANTHROPOGENIC NITROGEN INPUTS TOOLBOX: THE NANI TOOLBOX

NANI is designed to estimate anthropogenic N inputs for every state in the United States. The toolbox was developed as a continuation of work done by *Boyer et al.* [2002] and later *Howarth et al.* [2006], which quantified N inputs for states in New England. When creating the toolbox, estimates of N input was based on regional expectations, therefore the toolbox was set up to be enhanced with regional information.

NANI is broken into four main input sources: atmospheric N deposition, net food and feed imports, fertilizer N application, and agricultural N fixation from legumes. Each component relies on data available online and is available to the public. This makes it easy to use in any state in the U.S. The toolbox is a set up in ArcGIS and Microsoft Excel with the intention of a wide user base. The toolbox calculates N input values based on county information. To represent the county data on river basin scale, NANI

calculates the proportion of each county within its respective river basin in order to create a way to measure N inputs on basin levels.

A set of extraction tools was utilized to grab N input data from online sources such as the EPA, USGS, and USDA Census of Agriculture. The extraction tools obtain the data, the Toolbox that contains the NANI algorithms and functions operates on the data. The final output of N inputs from the NANI toolbox is calculated for all counties and river basins within the selected region.

3.2 NANI vs. TX-ANB: METHODS AND DATA

The major difference between NANI and TX-ANB lies in the methodologies accounting for the input of fertilizer, the treatment of human consumption, and animals' consumption and excretion data. The methods and data chosen in NANI were for purposes of representing the whole nation best and TX-ANB data and methods were chosen with the purposes of modeling nutrient export and best representing the Texas region.

The calculation of inputs for humans and animals within NANI is the result of "Net Food and Feed Imports". In addition, calculation of legume N fixation within TX-ANB is calculated with a regional estimate for uncultivated lands, and the NANI calculation is based on fixation estimates from the Northeast with respect to pastureland. Pastureland legume fixation depends highly on percent coverage of clovers within the land. The estimate of fixation is likely different from region to region, but a blanket estimate is used in NANI. In addition, different datasets are used for NANI than are used in TX-ANB; fertilizer data used in the NANI calculation is from the USGS sales and distribution estimates and TX-ANB considers data from the Office of the Texas State Chemist (OTSC). Schematics for both TX-ANB and NANI can be found in Figure 3.1.

3.2.1 Data Differences

NANI considers fertilizer data from the USGS as fertilizer N inputs for the U.S. The data [Ruddy *et al.*, 2006] are based on sales of fertilizer for the entire state and estimates of input for crops within counties recorded to be grown. For example, the state of Texas has purchased 1,000 tons of fertilizer with N grade of 850 kg/T. According to the USGS estimates, where the fertilizer is distributed is based on how many crops are grown in counties. If Anderson County does not have high crop growth, little is allocated to that county.

TX-ANB uses data from the Office of the Texas State Chemist (OTSC). The data are based on sales and distribution to specific counties. If Anderson County purchases and distributes a certain amount of fertilizer containing a certain N grade, that amount is recorded regardless of crop growth within that county. This results in a more accurate estimation spatially of N inputs from fertilizer.

Crop data and land use information also vary between the two budget calculations; NANI uses USDA Census of Agriculture information for crop growth and TX-ANB uses the NASS Cropland Data Layer (NASS-CDL) product as cropland and land use information. Census information is collected by survey every five years and is considered to be the most accurate farmland/land use information available [USDA-NASS, 2011]. However, remotely sensed data used in the NASS-CDL is expected to be accurate as well considering its highly refined supervised classification system. The land classification system of both datasets vary, thus difficulty arises when attempting to make direct comparisons.

The differences in data classification between the Census, which the NANI calculation relies on, and NASS-CDL, which TX-ANB utilizes, result in differences of N input calculations. In addition, methodology differences between the two budgets result

in different calculations of NANI as well. The variations of methods and the results will be discussed below.

3.2.2 Methods for Legume Fixation Estimation in Pasturelands

Legumes in pastures are highly climate dependent. Legumes such as clovers cover much of the pastureland in a region. Depending on the amount of precipitation, coverage can be dense or sparse. NANI has estimated fixation in pasturelands to be $1,500 \text{ kg N km}^{-2} \text{ yr}^{-1}$, while TX-ANB uses estimations based on Texas coverage of clovers in pasturelands. Regional estimations for Texas legume coverage within pasturelands suggest about ~2% of pastureland are covered by legumes, thus the fixation rate in pasturelands is significantly less ($180 \text{ kg N km}^{-2} \text{ yr}^{-1}$) than what is expected in NANI. While legume fixation is a small contributor to the N cycle in Texas as a whole, specific river basins do not show the same distribution. As discussed later, the Guadalupe basin, which borders the Gulf of Mexico, is greatly affected by N from legume fixation in pasturelands. For this reason, obtaining an accurate fixation rate is critical for understanding downstream impacts.

3.2.3 Net Food and Feed Imports

Quantifying the net input from humans, animals, and agriculture is a difficult task which NANI and TX-ANB attempt very differently. The NANI calculation combines these inputs and uptakes into one net calculation called net food and feed imports. The calculation considers human and animal consumption of food a positive flux and animal and crop production a negative flux (Equation 3.1). The sum of all the fluxes makes up the net food and feed import of N from agriculture and humans.

$$Net\ Food\ and\ Feed = \left(\frac{Human\ N\ consumption}{+ livestock\ N\ consumption} \right) - \left(\frac{Livestock\ N\ production}{+ crop\ N\ production} \right) \quad (3.1)$$

Each flux within the NANI food and feed imports calculation is treated as a separate term in order to decrease the impact of imports of food for humans or exports of crops from land. The negative flux of animal production is based on the difference of estimated animal consumption and animal excretion. Crop production is calculated from kilograms harvested and percent N in dry matter as well as percent loss in processing for food/feed.

The result of this net calculation can lead to negative values in areas where production is high and consumption is low. Production is considered a negative flux, therefore if a crop production is high in a non-populated area (few humans or animals), the resulting value of net food and feed can be negative. The final NANI calculation is a net value; if net food and feed is a large negative number, it can essentially remove the impacts from other sources. For example, Hill County, located south of the Dallas Ft. Worth area along the I-35 corridor, is estimated to have 530 kg N km⁻² yr⁻¹ input as the result of oxidized N atmospheric deposition. The net food and feed import however, is estimated to be -1,396 kg N km⁻² yr⁻¹. This is the direct result of the negative fluxes of livestock and crop production estimated to be greater than the human and livestock consumption within the area. When NANI is calculated, the resulting net input from anthropogenic sources is -681 kg N km⁻² yr⁻¹. This negative flux implies all the N input is less than the N removed from the area. This is a weakness of NANI, and a limitation for use as nutrient modeling input data. A negative flux might be possible in areas where atmospheric N deposition could be used by crops, however, in the case of Hill County; the net result of the negative flux is an artifact of NANI methods and is not realistic.

TX-ANB was created with a budget framework, rather than a net calculation. With nutrient modeling in mind, TX-ANB was calculated to only have positive fluxes result. Crop production within TX-ANB is calculated based on how much fertilizer is applied. Thirty percent of fertilizer applied to crop area is removed due to production; however a negative net flux never is the result (equation 2.1). In addition, “animal production” is not something that is considered for this reason. Animals are consuming N within their food, and the N consumed is assumed to be from harvested crops since many of the crops in Texas are farmed specifically for animal feed. Consequently, the removal of N from crop production is accounted for and the animal consumption of that N is accounted for through excretion estimations. Human consumption, however, is not accounted for; human consumption and excretion is difficult to represent accurately spatially in Texas. Waste water treatment plants clean waste water and export the waste associated with it. Septic systems exist in Texas, but leakage and leaching from them is difficult information to obtain. As a result, human direct input of N is not accounted for. As mentioned, TX-ANB was developed for nutrient modeling input data, thus spatial input of sources is the primary concern.

In summary, TX-ANB does not account for human direct input, and NANI and TX-ANB consider animal input and crop removal differently. Despite the differences, NANI and TX-ANB produce similar total inputs for Texas as a whole. TX-ANB estimates $454,951 \text{ kg N km}^{-2} \text{ yr}^{-1}$, which is comparable to NANI’s input at $467,889 \text{ kg N km}^{-2} \text{ yr}^{-1}$.

3.3 METHODS FOR NANI REGIONAL: TX-ANB WITH NANI TOOLBOX

The NANI toolbox is set up to be modified, thus any new information can be added to the NANI toolbox. NANI calculations can be done separately and the results

can be calculated using the total NANI calculator. Essentially, one can change the input data and still use the algorithms and toolset. In order to assess the impact of using different input data, changes to the input data within the NANI toolbox were made and the results were compared with NANI's original input estimates. The final NANI calculation was done with all of the different input data (input data from TX-ANB) and was called NANI Regional.

The three main differences between TX-ANB and NANI were the fertilizer information, fixation in pastureland estimations, and the difference in cropland information. Fertilizer data can easily be replaced in NANI; the fertilizer data within the NANI toolbox was replaced with information from the OTSC. NANI then was calculated and compared to NANI with USGS fertilizer information.

Changing the fixation was also simple to do within the NANI toolbox; the fixation rate for pasturelands was changed from $1,500 \text{ kg N km}^{-2} \text{ yr}^{-1}$ to $180 \text{ kg N km}^{-2} \text{ yr}^{-1}$ and the NANI calculation was completed again. The values for NANI were recorded and compared to NANI with previous fixation estimates (Figure 3.2).

Accounting for differences in cropland information was more difficult. NANI uses the Census for crops and TX-ANB employs NASS-CDL. Cropland information is used in NANI and is imbedded in the calculation. Thus comparisons of cropland were directly made outside of NANI and the resulting main differences were noted. The main difference that would readily affect the NANI calculation was the difference in land allocated to "other hay". NANI has "other hay" as a source of N due to fixation inputs. The NASS-CDL does not show any "other hay" represented in their land classification all across Texas. In order to represent this difference in N inputs from fixation in "other hay", zero was used for the other hay fixation value in the NANI toolbox. The toolbox contains algorithms that use the fixation rate and area for specific types of legumes to

calculate the N inputs from fixation. When the “other hay” fixation rate was replaced with zero, the toolbox obtained a zero value for “other hay” fixation N inputs. As a result, the calculated NANI values displayed what NANI would be without the contribution of N fixation from “other hay”. These values were compared with NANI values that included other hay (Figure 3.2).

To obtain the NANI Regional output, two versions were calculated. For NANI Regional 1, the fixation for pastureland was changed to the regional expected fixation rate for pastureland, fertilizer input data were from the OTSC, and “other hay” was removed by replacing the fixation value of this land to zero. These results were compared with NANI original information. NANI Regional 2, used the same calculation as for NANI Regional 1 except that the Census crop information was employed to represent “other hay” (Figure 3.2). A bar graph comparing total input for Texas was also made showing TX-ANB, NANI, and NANI Regional 1 and 2 (NANIR-1 and NANI-R2)(Figure 3.3). It is important to consider TX-ANB was not able to be fully represented in the toolbox

In addition, the output from NANI can be directly linked to river basins through functions in the toolbox. This was done for NANI, NANI-R1, and NANI-R2(Figure 3.4). Note that the toolbox functions are not modified to directly represent TX-ANB.

3.4 RESULTS AND DISCUSSION

Comparing all four results of N inputs from anthropogenic sources, some common characteristics are noted. NANI-R1 suggests significantly smaller inputs of N in total. NANI contains the highest amount of input of N; however, a significant gradient is seen from east to west. TX-ANB also indicates the same gradient, but the difference between the two regions is less. As mentioned previously, TX-ANB does not have any

negative values of N fluxes. If N is available from oxidized N deposition from the atmosphere, it is not assumed that the plant will use that N. While this may not be the case for plants, this assumption accounts for inputs from N deposition in areas where crops are not present but animals are. Within NANI, animal production is accounted for as a negative flux; if there is a lot of N deposition and animal production within a county, NANI would remove the input of N deposition through the net calculation as the result of the county producing a lot of livestock. Animals do not eat N that is atmospherically deposited, and as a result TX-ANB does not have this shortcoming.

The main shortcoming within NANI is the aforementioned issue, but on the whole, NANI is a well-developed and widely used dataset for budgeting. Regional enhancements can be made to improve it, as demonstrated by NANI-R1 and NANI-R2. In order to assess the validity of NANI, NANI-R1, and NANI-R2 comparisons were made between measurements of N concentrations exported to the Gulf of Mexico. The overall trends, estimated leaching of NANI, NANI-R1, and NANI-R2, and the ratio of N inputs to measured concentrations helped assess the validity all the NANI results. Direct comparisons of the NANI results to the measured concentrations are not reasonable; as a result *Hong et al.*, [2011] and *Howarth et al.* [2008] developed the above mentioned methods of comparing inputs to N concentrations. The measurements for the comparison came from the University of Texas Marine Science Institute for two river basins: The San Antonio (SA), which was considered the urban assessment, and the Guadalupe (GA) which was considered for the rural assessment (Figure 3.5). The measurements were taken within close proximity to the coast without being at the mercy of tidal influences.

The overall trend was assessed by considering the total mass of N, expected to be input from NANI, NANI-R1, and NANI-R2, compared with the total mass of N measured for a wet year (2008) and a dry year (2009) at two gauge stations: San Antonio

at Goliad and Guadalupe at Victoria (Figure 3.5). A wet year (2009) resulted in higher measured concentrations of N whereas the dry year (2008) resulted in lower measured concentrations of N (Figure 3.6). This trend is consistent with the expectation that increased rainfall results in increased N loading (Table 3.1 and 3.2). The basin measured comparisons for 2008, between the SA and GA, however, was not consistent with the NANI result. NANI-R1 and NANI-R2 show that SA has greater expected N concentrations, which matches the measured output for the wet year. In the dry year GA's measured concentration of N was higher than SA; this is consistent with the NANI result, but not NANI-R1 and NANI-R2.

The interesting point of note is the SA River Basin is significantly smaller in area than the GA. During the wet year the GA was measured to have more discharge, but the concentrations of N were higher in the SA River basin than in the GA. The main source contributions in the SA are from NO_3 which likely originate from urban inputs such as oxidized N deposition (Table 3.1). These results imply that in wetter years, oxidized N deposition could be enhanced from greater precipitation followed by an increase in wet scavenging. In addition, the general trend is apparent: in wetter years concentrations of N are higher on the whole. Not only is deposition enhanced, but also leaching is heightened. Expected leaching was assumed to be ~45% of the total N applied [Howarth, 2008].

When comparing NANI estimated leaching results to these measurements during the dry year of 2008 (Figure 3.7), neither NANI, NANI-R1, nor NANI-R2 was consistently close. It appears that NANI-R1 was the most successful at capturing the GA N export; however it underestimated the SA export. NANI-R2 was close to capturing the SA export, but was much greater than the GA export. NANI estimated leaching was too

high for the dry year; however in 2009 when wetter conditions were present, NANI estimated leaching was the closest at capturing the SA export.

In addition to comparing estimated leaching, assuming 45% of the total N input is leached, Hong et al. [2011] has shown through regression analysis that typically 20% of N makes it from inputs to export in rivers. This analysis is typical on a national scale. The assumption is ~20% of N exported in rivers are from anthropogenic sources, the remaining anthropogenic inputs are denitrified. While this may work well on a national scale, rainfall amounts and regional loading variation may play a role in how much N is exported. Table 3.2 displays the percent of NANI, NANI-R1, and NANI-R2 estimated to be loaded based on the ratio of the inputs to the measured mass of N, within the SA and GA basins for the wet and dry year. From the data available, the results indicate an increase in loadings during the wet year (2009). Both NANI and NANI-R1 suggest loading during wet years is greatest in the SA basin, however, NANI-R2 suggests the GA receives the highest percent of N from anthropogenic sources.

The NANI toolbox uses data that are publically available; but comparing NANI results to the measured results may not be an appropriate comparison. NANI data contain livestock and land-use information from 2007, and fertilizer and atmospheric deposition data from 2006. Thus, inputs are not directly accurate for 2008 and 2009 when measurements are available. For this reason, the source of N for the measured N exported is critical. If agriculture is the primary source for what is exported, NANI or NANI-R2 may better estimate the export due to its enhanced fixation lands. NANI-R1 contains no “other hay” land contributing to the N cycle, and consequently a smaller result is present than in NANI-R1.

The only difference between NANI-R1 and NANI-R2 is fixation; NANI-R1 removed “other hay” from fixing N. Figure 3.7 shows a large difference between NANI-

R1 and NANI-R2 in the GA basin. This indicates “other hay” is a large input within the region. NANI-R1 agrees better with the measured during both years, thus perhaps at least in the SA basin, the “other hay” fixation is overestimating N inputs. When considering Texas as a whole, legume fixation is not a significant component of anthropogenic N impacts, however specific basins, such as the GA in this case, may largely be impacted by N from legumes.

3.5 CONCLUSION AND FUTURE WORK

Quantifying N inputs regionally is important, specifically when considering N export and protection of coastal environments. Although this quantification is possible; data are the main limiting factor in estimating N fluxes. Through enhancing a national dataset (NANI) with regional input, it became clear that understanding exact land use coverage and legume fixation rate is most important. In addition, specific types of data can greatly affect the expected N sources. As such, when constructing an N budget choosing data available annually is important.

NANI is a good toolset, which works well at estimating general input on national scales. On regional scales, however, it is important to consider regional sources. Much of Texas contains lands where livestock and crops are being produced within close proximity to urban areas. While atmospheric N deposition could potentially enhance available N for crops, animal production does not uptake N from the atmosphere. For this reason, NANI’s approach of Net Food and Feed Imports is not the strongest in regions where livestock have a strong presence.

As expected, N concentrations are enhanced during periods with strong rainfall. This does provide a need for data at a finer scale than the Census of Agriculture. At least in the case of the SA basin, atmospheric N deposition has a large impact on downstream

environments. When considering sources, agriculture plays a large role (more than 50% of sources). When considering what fraction of the sources are not used and thus make it to the Gulf of Mexico via riverine transport atmospheric deposition of N might play a stronger role. Much of the N applied during agriculture is for a purpose; N deposited as the result of pollution is not applied for any purpose and thus does not have an expected remover within the system. For this reason, future work of understanding N deposition is important.

Representing N deposition through multiple modeling studies could potentially improve the understanding of the full pathways of N. While it is tempting to think the largest sources result in the largest fluxes to the Gulf of Mexico, this may not be accurate. For this reason, assessing N deposition full pathways is important for future work.

Basin Name	Year	NH₄	DON	NO₃	Total Mass N measured (mg/L)
San Antonio (Urban)	2008	1.90	5.45	174.96	182.31
	2009	1.98	4.76	110.56	117.30
Guadalupe (Less Urban)	2008	0.61	1.63	8.91	11.16
	2009	2.04	4.91	7.00	13.95

Table 3.1: San Antonio and Guadalupe N measurements for 2008 and 2009 from the University of Texas Marine Science Institute.

Basin Name	Year	Discharge (m³/s)	Total Mass (kg N)
San Antonio (Urban)	2008	415.78	264,020.87
	2009	1,279.63	12,968,855.96
Guadalupe (Less Urban)	2008	390.43	376,327.88
	2009	3,076.39	3,708,252.84

Table 3.2: San Antonio and Guadalupe discharge (cubic meters per second) and respective total mass of N (kg N) for 2008 and 2009 (measurements from The University of Texas Marine Science Institute).

Input type	Year	Input loaded San Antonio	Input loaded Guadalupe
NANI	2008	1 %	1%
	2009	46%	12%
NANI-R1	2008	5%	10%
	2009	262%	94%
NANI-R2	2008	1%	2%
	2009	7%	21%

Table 3.2: NANI, NANI-R1, and NANI-R2 estimated load percentage. Percentages of total load to rivers were calculated based on measured total mass of N for the San Antonio (Urban) and Guadalupe (Rural) river basins. Measurements of N concentrations from 2008 and 2009 were taken by The University of Texas Marine Institute.

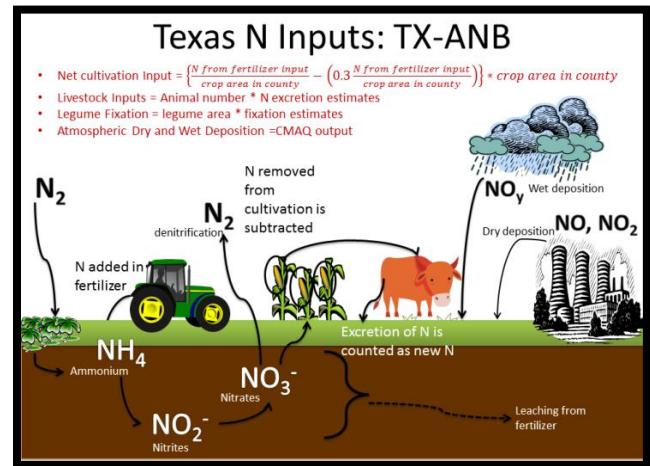
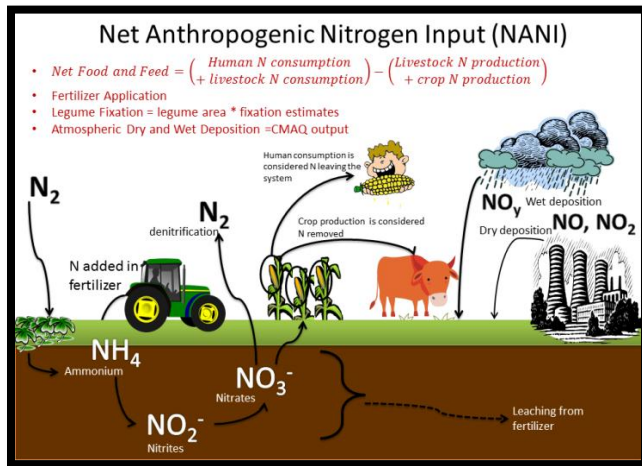


Figure 3.1: The NANI budget (left) and TX-ANB (right) are illustrated with functions and input calculations represented.

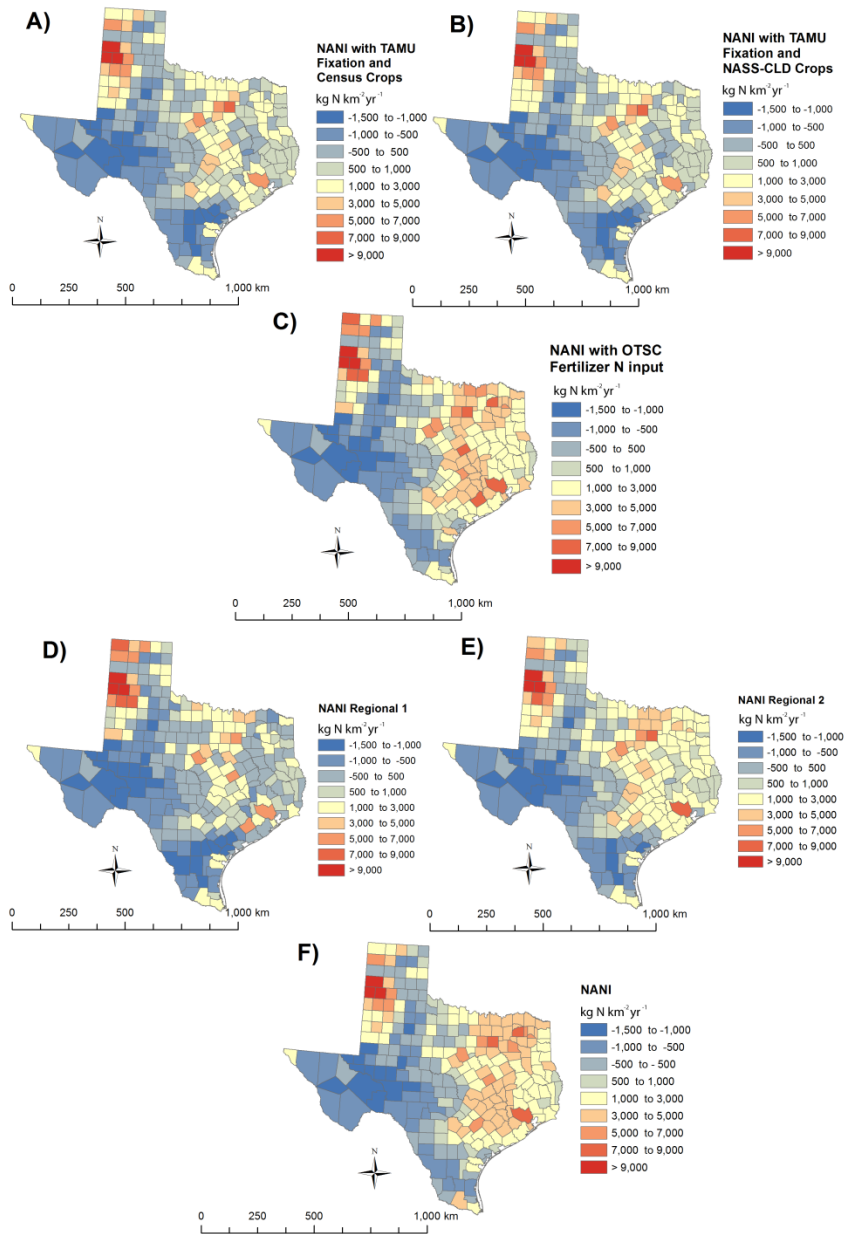


Figure 3.2: Total anthropogenic N inputs from NANI Toolbox calculation with the TAMU regional fixation estimation and Census crop and land cover information(A), with the TAMU regional fixation estimation NASS-CLD crop and land cover information (B), with OTSC fertilizer information (C). NANI Regional 1 (D), NANI Regional 2 (E) and NANI without any modifications (F).

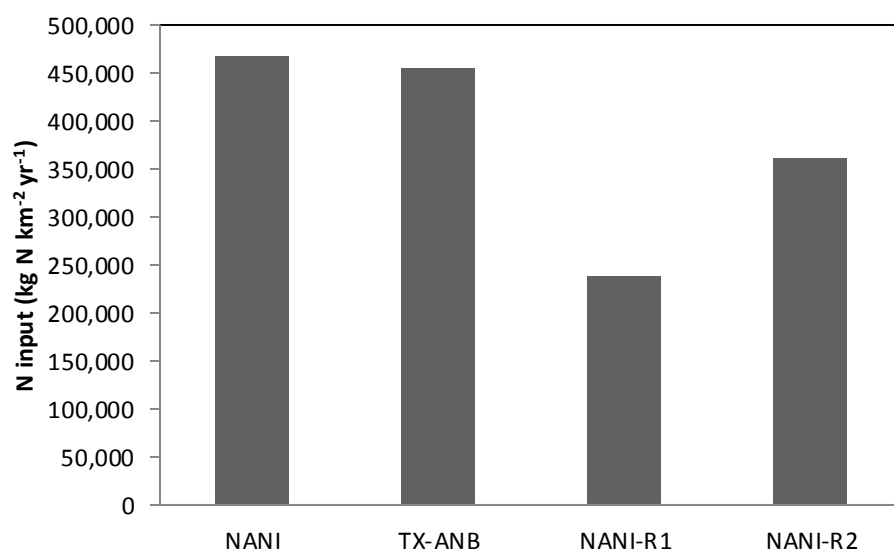


Figure 3.3: NANI, TX-ANB, and NANI Regional 1 and 2 calculated input of N from the NANI toolbox.

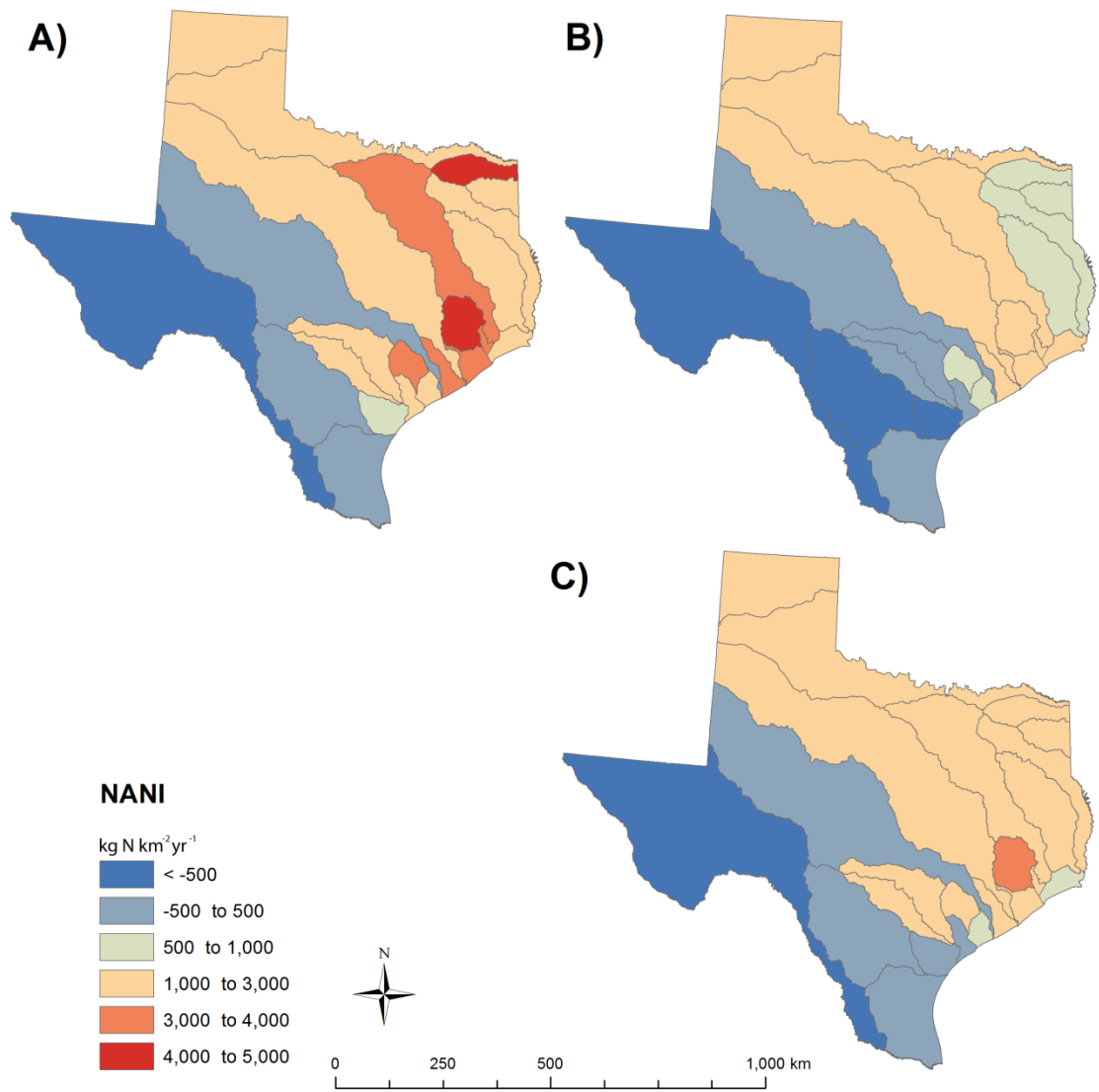


Figure 3.4: NANI (A), NANI Regional 1 (B), and NANI Regional 2 (C) calculations at basin scale.

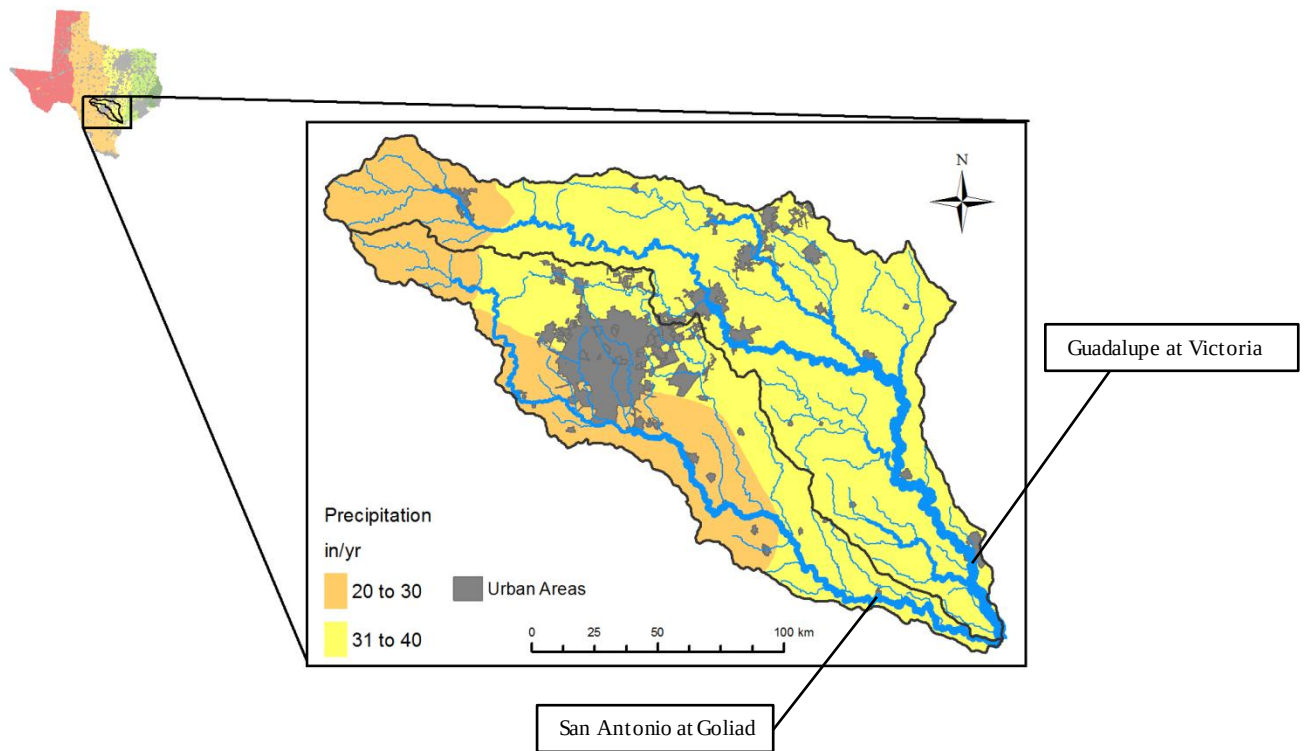


Figure 3.5: The San Antonio Basin (bottom basin) containing most urban area, and the Guadalupe Basin (top basin) containing less urban areas. Two USGS gauges, San Antonio at Goliad and Guadalupe at Victoria are marked as well as mean flow of the major rivers in the basin.

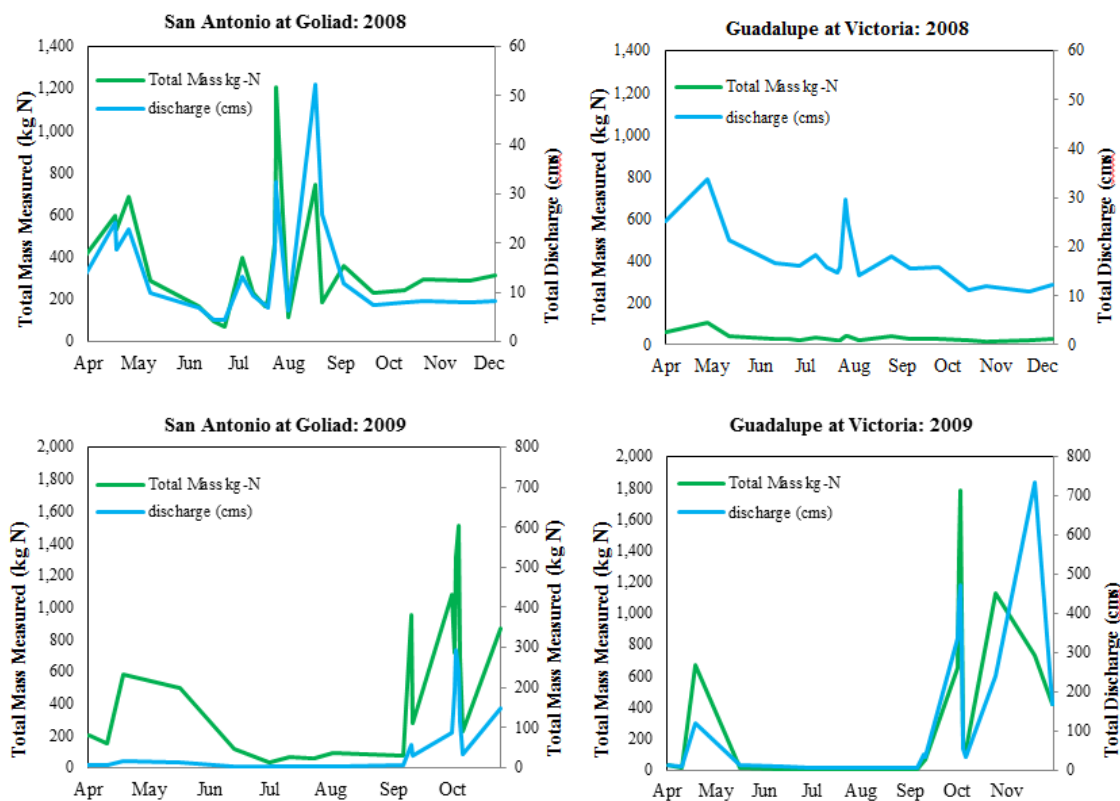


Figure 3.6: San Antonio at Goliad measured discharge (cms) and total mass N (kg N) for 2008 (A) and 2009 (B). Guadalupe at Victoria measured discharge and total mass N for 2008(C) and 2009 (D). Total Mass measured includes concentrations of NO_3 , NH_4 , and DON.

N Inputs, Estimated Leaching, and Measured Mass for the San Antonio and Guadalupe River Basins

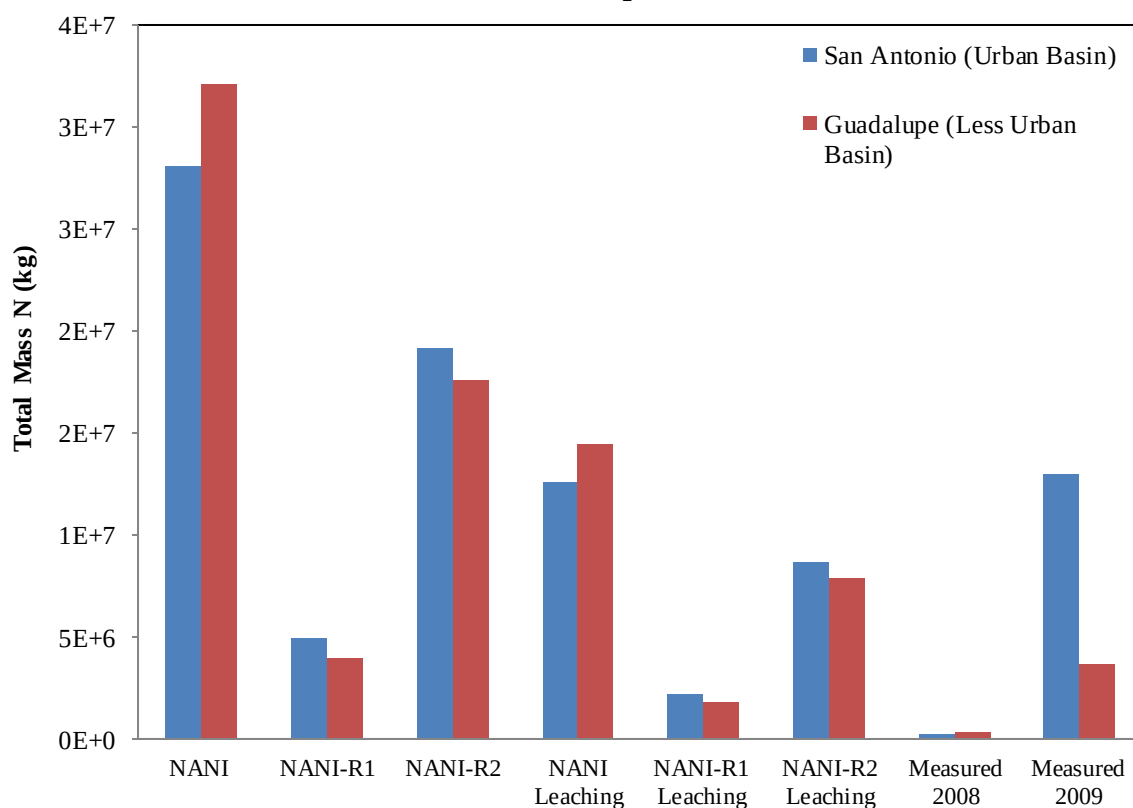


Figure 3.7: N inputs, estimated leaching, and measured mass for the San Antonio and Guadalupe River Basins; NANI, NANI-R1, and NANI-R2 are shown with corresponding leaching estimates. Measured total mass from NO_3 , NH_4 and DON for the year of 2008 and 2009 are also shown.

Chapter 4: Concluding Remarks and Future Work

4.1 CONCLUDING REMARKS

Nitrogen inputs in Texas from atmospheric deposition, fertilizer and livestock input, and legume fixation were compiled and analyzed in a budget called TX-ANB. In general, agriculture played the main role of anthropogenic N inputs for the state; inputs exceed $7,000 \text{ kg N km}^{-2} \text{ yr}^{-1}$ in some counties. Urban influences also played a large role in altering the N cycle; 23% of the inputs of N from TX-ANB came from atmospheric deposition of oxidized N. When comparing regions, the coastal plain (southeastern Texas) was influenced most by anthropogenic N sources. Houston, San Antonio, Austin, and Dallas-Ft. Worth all reside in the east resulting in maximized human input influence. Figure 2.9 clearly illustrates the strong influence urbanization has on the N cycle as much of the I-35 corridor is visible on the atmospheric N deposition influence map. Much of the livestock industry also exists along the coastal plain which results in pasturelands also being present in this area. The legume growth in pasturelands is highly variable from year to year dependent on rainfall. Crops grown in Texas are mostly for the purpose of feeding the livestock industry, and as a result, much of the crops are grown within proximal distance to high animal population density. For this reason, legume, livestock, and fertilizer impacts are greatest throughout the southeast. Land used for these purposes aids in enhancing the natural N cycle.

The measurements for the San Antonio (SA) and Guadalupe (GA) basins indicate (Figure 3.6) that during wet years discharge increases; it is intuitive to conclude as discharge increases there is more water present to dilute the N that is leached, however,

this is not the case. A similar analysis was done through the Mission-Aransas National Estuarine Research reserve by *Mooney and McClelland* [2012, in press]. The results from *Mooney and McClelland* [2012, in press], and the measurements from the SA and GA basin (Figure 3.6) indicate that when discharge increases, concentrations of N also increase. This could be the result of increased N from atmospheric deposition due to wet scavenging, although *Mooney and McClelland* [2012, in press] suggest N concentrations from production of the earth system increase. If the system's production of N is enhanced during wet years, assuming ~45% of N from anthropogenic sources is leached [*Howarth et al., 2002*] is inaccurate. For this reason, leaching estimates from Figure 3.7 may not be accurate.

Greater leaching and heightened atmospheric deposition play a large role in total N concentrations measured downstream of river basins. Enhanced leaching rates could potentially be the reason the GA basin contained higher concentrations of N in 2009 (the wet year). The SA basin also experienced a significant increase in N concentration from 2008 to 2009. When compared to the GA basin in 2009, the SA basin had a much higher concentration of N despite its smaller drainage area. The SA basin's primary source of N, in measured total N concentration, was NO_3 (Table 3.1), which likely originated from atmospheric deposition of oxidized N. If this is the case, the conclusion could be drawn that, in 2009 when precipitation was enhanced, atmospheric deposition was equally heightened resulting in more input to streams directly from the atmosphere. In addition, N atmospheric deposition to the land also was amplified simultaneously with enhanced leaching of N. The heightened impact from the atmosphere directly to the river

combined with the boosted leaching as the result of the washout from rain, ultimately led to the SA basin exporting extremely high concentrations of N with respect to the GA basin.

From these conclusions, it is apparent that data collection across the coastal plain, with respect to N inputs from human influence, is extremely important. Data is the main limiting factor in studying the N cycle. TX-ANB was able to compile data from 2008, 2007, and 2006 for fertilizer and crop data, agriculture data, and oxidized atmospheric deposition data respectively. The inputs from oxidized atmospheric deposition are highly sensitive to weather conditions. Consequently, it is important to consider assessing this portion of the N cycle annually. Fertilizer application and crop cultivation also were variable from 2008 to 2009 as discussed previously. As much as 50 to 100% increase was observed between 2008 and 2009 in select coastal counties. This could indicate fewer crops were grown in the counties that saw an increase, or it could be the result of more N applied to the same crop area. If the latter is the case, it is important to assess if the higher rate of N application is due to a new crop (such as corn or cotton) which needs more N, is now present. Climate assessment would be important in this case.

Forecasted climate would allow farmers to know how much rain may be expected for the subsequent year. Farmers could potentially grow high N needing crops during years when precipitation is lower than average. The crop would utilize the N applied and much of the N would not be leached. During wetter years, crops that do not require as much N could be grown or soil chemistry assessments could be mandatory. Assessing the N content within the already present soil would allow farmers to decrease their use

depending on the net N available prior to planting. In this way, over fertilization could be reduced, resulting in somewhat protected coastal ecosystems. Understanding what is already present within the soil from previous years, as well as, having an idea of the impending weather conditions for the subsequent year could lead to more efficient farming practices and protected coastal environments. This type of assessment could also impact farmers positively on an economic scale. Using what N is already available would lead to a decreased demand for synthetic fertilizer use; as a result less stress related to these purchases would be placed on the farming community.

4.2 FUTURE WORK

As mentioned, data are limiting, but the need for environmental protection is not going to wait for improved methods of data collection. Starting from regional budgets such as TX-ANB, a few improvements could result in the ability to model the full N cycle from the atmosphere to the land and ultimately to coastal environments. In order to achieve this, atmospheric modeling is critical.

Understanding N deposition is important for obtaining an accurate prediction of oxidized N deposition. As seen in the SA basin in 2009, atmospheric deposition of N can have a significant impact on N concentrations downstream. Sophisticated models such as the Weather Research and Forecasting model with online chemistry options (WRF/Chem) are capable of modeling N deposition annually. WRF/Chem uses emissions from the National Emissions Inventory (NEI) dataset which are based on local estimates of point and non-point source emissions. Chemical reactions within the

atmosphere are computed based on the NEI estimated emissions of N for an area, of which meteorological input information is utilized.

When modeling, the flexibility in parameterization schemes can result in heightened accuracy; WRF's ability to utilize schemes that can model high resolution processes results in meteorological output of great accuracy. The accurate meteorological information from WRF is utilized in what is called the SORGAM/MADE model which is a separate driver within the WRF/Chem model that computes the atmospheric chemistry of the model domain. Once the chemistry is computed, the packaged atmospheric data are then used in WRF where atmospheric deposition can be computed.

In addition to point and non-point sources, N emissions can be the result of biogenic volatile organic compounds (BVOCs). For this reason, understanding land surface processes that control the emission of BVOCs, as well as obtaining a dynamic earth system model is important for modeling the full N cycle. WRF is a consistently updated model, which has been recently coupled to the Noah-MP land surface model [Niu *et al.*, 2011; Yang *et al.*, 2011]. This coupling will result in the improved ability for atmospheric forcings to interact with the land surface and hydrologic processes. The enhancements to WRF/Chem from such a coupling will be enormous. For this reason, annually modeling N deposition with WRF/Chem is important.

Utilizing the coupled WRF/Chem–Noah-MP model will enable a dynamic approach for N cycle modeling. The results could potentially provide the ability to forecast N fluxes and know when it is necessary to decrease N inputs from agriculture in

specific sensitive regions. Using TX-ANB as total N applied, plant/crop growth could be estimated. This estimation would aid in forecasting the expected BVOC concentrations. Atmospheric chemistry with enhanced meteorology would give an accurate estimate of N deposition; land use/plant presence would be able to utilize an expected amount of the N deposited and compute what is projected to be as excess N. Livestock influence also would need to be tied in to Noah-MP in some way; this would require further research in livestock population projections. Noah-MP currently is able to produce runoff data for river models such as RAPID [David *et al.*, 2011]. Noah-MP could be enhanced to contain a leaching scheme, resulting in the runoff data containing chemistry information. The leaching scheme could capture all the N fluxes and concentrations which were resulting from a dynamic earth system model (the coupled WRF/Chem-Noah-MP). The chemistry within the runoff data could be input to models such as RAPID, resulting in a full online dynamic model of the N cycle.

Ultimately modeling atmospheric effects on plant growth, plant growth effects on N emissions, urbanization effects from point and non-point source pollution, and over all impacts of humans to N concentrations in streams is possible with the new coupling of WRF/Chem-Noah-MP. For this reason, it is important to enhance Noah-MP with nutrient leaching mechanisms so that the full N cycle can be modeled from the atmosphere to the land to the coasts.

This type of model output theoretically could influence farmer's decisions and planning. Knowledge of expected increased N deposition for a year might indicate a decreased need for N from synthetic fertilizer. This would save the farmer money while

also protecting the environment. To ensure the modeling results are correct, correlations would need to be drawn from a network of measuring stations along the Gulf of Mexico, with a specific focus on N concentrations. Improved measurements of N concentrations will enable assessment of the validity of the proposed work. A calibrated and validated model could lead to an improved knowledge of the earth system, which would only result in better utilization of resources.

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Vita

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