Typologies of Nitrogen Surplus Across Continental US: Shifting Hotspots and Dominant Controls

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Statement of Contributions

I would like to acknowledge my co-authors Dr. Kimberly an Meter and Dr. Nandita Basu who contributed to the research described in this thesis.

Abstract

Flows of reactive nitrogen (N) have significantly increased over the last century, corresponding to increases in the global population. The pressures on the N cycle include human waste, fossil fuel combustion as well as increasing food production (i.e., increasing fertilizer consumption, biological N fixation, and livestock manure production). The result is humans causing a 10-fold increase in the flow of reactive N globally. The influx of anthropogenic N into aquatic environments degrades water quality, alters fresh and saline ecosystem productivity, and poses an increasing threat to drinking water sources. In the U.S., decades of persistent hypoxic zones, created by elevated concentrations of nitrate from the landscape, have altered ecosystem trophic structure and productivity. Additionally, increasing N contamination of groundwater aquifers places over 20% of the U.S. population at increased risk of diseases and cancers.

Despite billions of dollars of investment in watershed conservation measures, we have not seen proportional improvements in water quality. It has been argued that delayed improvements in water quality can be attributed to legacy stores of N, which has accumulated in the landscape over many decades. There is considerable uncertainty associated with the fate of N in the landscape; however, studies quantified increasing stores of N in the subsurface, suggesting increasing stores of N in groundwater aquifers, in soil organic nitrogen pools, and the unsaturated zone. Nevertheless, the spatial distribution of legacy N across the conterminous U.S. is poorly quantified.

Here, we have synthesized population, agricultural, and atmospheric deposition data to develop a comprehensive, 88-year (1930 to 2017) dataset of county-scale N surplus trajectories for the U.S. N surplus, defined as the difference between N inputs and usable N outputs (crop harvest), provides insight into the trends and spatial distribution of excess N in the landscape and an upper bound on the magnitude of legacy N accumulation.

Our results show that the spatial pattern of N surplus has changed drastically over the 88-year study period. In the 1930s, the N inputs were more or less uniformly distributed across the U.S., resulting in a few hotspots of N surplus. The following decades had sharp increases in N surplus, driven by the exponential use of fertilizer and combustion of fossil fuels. Contemporary N surplus distribution resembles a mosaic of varying degrees of excess, concentrated in the heavily cultivated areas.

To understand dominant modes of behavior, we used a machine learning algorithm to characterize N surplus trajectories as a function of both surplus magnitudes and the dominant N inputs. We find ten primary clusters, three in crop dominated landscapes, four in livestock dominated landscapes, two in urban dominated landscapes, and one in areas minimally impacted by humans. Using the typologies generated can facilitate nutrient management decisions. For example, watersheds containing urban clusters would benefit from wastewater treatment plant upgrades. In contrast, those dominated by livestock clusters would have more success in managing nutrients by implementing manure management programs.

The estimates of cumulative agricultural N surplus in the landscape highlights agronomic regions that are at risk of large stores of legacy N, possibly leading to groundwater and surface water contamination. In these agronomic regions, the average cumulative N surplus exceeds 1200 kg-N/ha by 2017. Despite having minimal agricultural activity in urban areas, urban fertilizer use has led to an average cumulative N surplus of over 900 kg-N/ha. While our estimates are an upper bound to legacy stores, significant uncertainty remains regarding the magnitude of the estimate of N accumulation. However, our results suggest that legacy N is at varying degrees, impacting most counties in the U.S.

The significant investment and corresponding lack of returns can lead to disillusionment in farmers, watershed managers, and the general public. Developing such N surplus typologies helps improve understanding of long-term N dynamics. Beyond refining the supporting science, appropriately communicating uncertainties and limitations of water quality improvements to the stakeholders, authorities, and policymakers are essential to continuing efforts to improve national water quality.

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1.0 Introduction

1.1 Background: Anthropogenic Nitrogen and the Environment

Unrestricted population growth and consumption have led scientists to coalesce around the idea of a new geological epoch – the Anthropocene – a time marked by the human alterations to the planet (Crutzen, 2016; Subramanian, 2019). One incidence of severe impact to the planet from human, specifically from an increasing population, increasing per capita consumption of energy, and dietary shifts to diets rich in meat and refined fats, is the changes to earth system processes such as the N cycle (Galloway, 1998; Galloway, 2003; Nosengo, 2003; Steffen et al., 2015). Humans have now increased the flow of reactive N globally from 15 Tg N in 1890 to 165 Tg N in 2000 (Galloway et al., 2003). The inputs have increased since the 2000s and are projected to increase even further to meet the growing food demands from an increasing population and shifting to meat-centric diets (Howarth, 2008; Schlesinger & Bernhardt, 2013; P. M. Vitousek, Mooney, Lubchenco, & Melillo, 1997).

N flows from energy and food production in the United States (U.S.), similar to global trends, have increased from 8 Tg in 1961 to 37 Tg by 1997 (Galloway et al., 2003; Houlton et al., 2013).The increase has led to substantial increases in nitrogen flows into the environment, which has contributed to the eutrophication of coastal and freshwater ecosystems and the exceedingly high levels of nitrates in groundwater aquifers (N. M. Dubrovsky et al., 2010; Gurdak, 2009; Harter, Davis, Mathews, & Meyer, 2002; Nolan & Stoner, 2000; Nancy N. Rabalais, Turner, & Wiseman, 2002; N. N. Rabalais, Turner, & Scavia, 2002; Steffen et al., 2015).

1.1.1 Fate and Mobility of Nitrogen

N cycles through ecosystems driven by biotic and abiotic processes (Figure 1). The productivity and community structure of terrestrial, freshwater and marine ecosystems are a product of the availability of N (Galloway, 2003; Ussiri & Lal, 2013; P. Vitousek et al., 1997; P. M. Vitousek et al., 1997). As a result, changes from the natural N cycle can have resounding impacts on the environment.

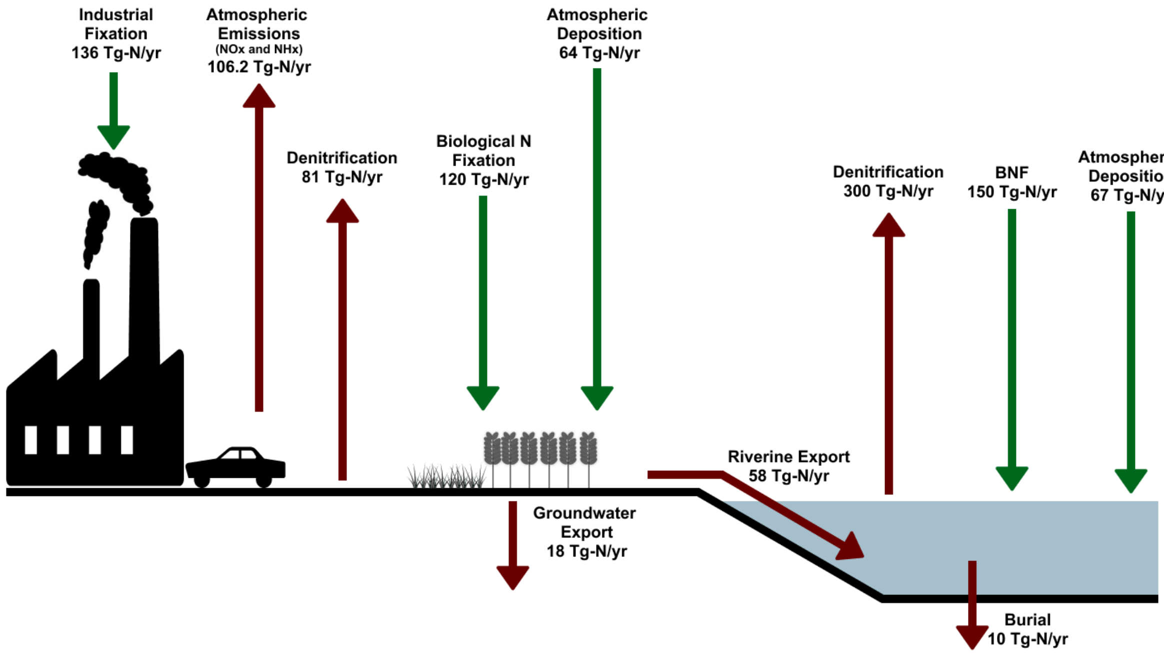

Figure 1. Primary net N cycle fluxes (Tg-N/yr) from terrestrial, atmospheric, and marine reservoirs. Internal cycling is omitted for simplicity unless deemed necessary for context. The contemporary budget does not balance because of omitted fluxes and the large amount of uncertainty in the fluxes and pools of N. The assumption is that terrestrial inputs are increasing while marine N pools are decreasing. Estimates derived from Schlesinger & Bernhardt (2013)**.**

N is abundant in the atmosphere, accounting for 78% of air by volume. Natural mechanisms, including biological N fixation (BNF), a bacteria mediated process, converts the biologically unavailable N_2 to NH_4^+, the bioavailable form preferred by plants. Today, there has been a significant increase in BNF due to the cultivation of N-fixing crops such as soybeans (Galloway et al., 2008; Houlton et al., 2013). Contemporary estimates of N fixation (natural BNF and crop BNF) in terrestrial and ocean pools are estimated to be 120 Tg-N/yr and 150 Tg-N/yr, respectively (Schlesinger & Bernhardt, 2013). Additionally, the Haber-Bosch process is used to convert N2 to NH4 for synthetic fertilizer (Schlesinger & Bernhardt, 2013; Ussiri & Lal, 2013).

Globally, wet and dry atmospheric deposition of nitrogen oxides (NO_x) and volatilized ammonia (NH_3) products contribute a significant source of N to terrestrial landscapes and to the ocean. Annually, total N deposition is estimated at 64 Tg-N/yr and 67 Tg-N/yr on land and ocean, respectively (Schlesinger & Bernhardt, 2013).

Immobilization and mineralization are the processes that govern the fluxes of SON to and from inorganic N. Under appropriate soil moisture and pH conditions, portions of the unused NH_4 in the soil will be immobilized to form the soil organic N (SON) pool. Alternatively, the SON pool can also gain from decomposing plant residue (Meisinger, Calderon, & Jenkinson, 2008). Mineralization, the opposing reaction of immobilization, converts SON from the active pool to NH_4^+. NH_4^+, if not volatilized to the atmosphere, can be converted to nitrite (NO_2^{-2}) and subsequently to nitrate (NO_3^-) through the nitrification process (Galloway, 2003; Schlesinger & Bernhardt, 2013). Under anoxic conditions in the soils, NO_3^- can undergo partial denitrification, producing in gaseous N_2O and NO, or full denitrification producing gaseous N_2, after which are all lost to the atmosphere (Schlesinger & Bernhardt, 2013). The estimate of terrestrial denitrification is approximately 81 Tg-N/yr (Schlesinger & Bernhardt, 2013).

The movement of inorganic N in the landscape is governed by molecular properties. NH_4^+ has a relatively short residence time in soils and is not generally mobile, as it tends to be used by plants, volatilize, or adsorb to soil surfaces (Follet, 1995). If NH_4^+ undergoes nitrification, it converts into the highly mobile species, NO_3^- (Galloway, 2003; Schlesinger & Bernhardt, 2013). The mobility of NO_3^- is caused by the negatively charged ion repelling the negatively charged clay minerals surface in the soils (Follet, 1995). Once NO_3^- is produced, unless it is converted back to NH_4^+ through immobilization, it can easily be leached into the groundwater and transported to nearby surface waters. This process is responsible for the increasing flow of N from the landscape into our water bodies (Follet, 1995; Galloway, 2003; Nolan & Stoner, 2000).

The role of N in an aquatic system is similar to its role in terrestrial systems: it supports the growth and productivity of vegetation. The supply of nutrients, including N, is transferred from land to the coastal ocean by rivers and groundwater (Galloway, 1998; Schlesinger & Bernhardt, 2013). N leaching to groundwater is estimated to be 18 Tg-N/yr, which will eventually flow to rivers or oceans. The flux from the continent to the ocean conveyed through rivers, is estimated to be 58 Tg-N/yr (Galloway, 2003; Schlesinger & Bernhardt, 2013). In the delivery process, sedimentation and denitrification remove a portion of N. With long residence times, particulate N can settle out of the water column in lakes and reservoirs. Once settled, the N can be resuspended or denitrified. Reservoirs and lakes remove approximately 19.7 Tg-N/yr of N (Schlesinger & Bernhardt, 2013). Additionally, under proper conditions (i.e., adequate organic matter and anaerobic conditions) rivers' hyporheic zones and groundwater aquifers can denitrify N, removing it from the system (Schlesinger & Bernhardt, 2013).

N can enter estuaries, the coastal shelf, and oceans through three primary pathways, (1) transport from rivers, (2) fixation from atmospheric N, and (3) atmospheric deposition (Schlesinger & Bernhardt, 2013). Once in the ocean, N can be transferred to the atmosphere through denitrification in sediment or deep ocean, producing N_2O or N_2, or through volatilization of NH_3 (Galloway, 2003; Schlesinger & Bernhardt, 2013). Marine denitrification is responsible for a large flux of N_2O and N_2 to the atmosphere, at the approximate rate of 300 Tg-N/yr (Schlesinger & Bernhardt, 2013). Alternatively, sedimentation removes 10 Tg-N/yr, which is assumed to be a terminal sink on short timescales.

1.2 Consequences of Excess Nitrogen and N Cascade

N cycling sustains life and underpins many essential functions in ecosystems. With anthropogenic perturbation, the disruption of the cycle could lead to excess or insufficient N, resulting in a stressed or over-productive system. When the natural cycle is perturbed, the relative magnitudes of pools and fluxes can change and can result in accumulations of N, threatening both human and ecosystem health.

While N_2 is a stable and inert compound, reactive N (Nr) is the class of biologically, photochemically, and radiatively active N compounds – mainly all N compounds excluding N_2, including NH_4^+, NO_3^-, and NO_x (Galloway et al., 2003). The movement of Nr in the landscape is responsible for:

- Nr causing eutrophication and hypoxia in the coastal ecosystems altering marine trophic structure (Diaz and Rosenberg, 2008);
- Nr in groundwater increasing risks of cancer and methemoglobinemia (Ward et al., 2018); and
- Atmospheric Nr acidifying ecosystems and producing tropospheric ozone and aerosols and destroying stratospheric ozone (Davidson et al., 2011; Lloret & Valiela, 2016; Ravishankara, Daniel, & Portmann, 2009).

As an Nr molecule migrates through the environment, cycling through pools, one single molecule can sequentially cause multiple different environmental and health impacts (Galloway et al., 2003). For example, N from a combustion process can be deposited, migrate to groundwater where it will contaminate drinking water, impacting an individual's health. The same Nr molecule can then migrate to a river through wastewater treatment discharge, where it can contribute to eutrophication in a coastal ecosystem. This cascading effect allows for Nr to have disproportionate effects as is moves through the perturbed N cycle (Galloway et al., 2003).

1.2.1 Nitrogen Contamination and Ecosystem Services

Anthropogenic use of N has changed the transport of excess nutrients, including nitrogen and phosphorus, and the seasonality of the transport regimes, ultimately threatening water quality and ecosystem function (Van Meter, Chowdhury, Byrnes, & Basu, 2019). Specifically, excess nutrients cause algal blooms and eutrophication of freshwater bodies and estuaries (Michalak et al., 2013; Van Meter & Basu, 2017; Vero et al., 2017) and the development of hypoxic zones in estuary and coastal ecosystems (Diaz & Rosenberg, 2008; Michalak et al., 2013; Nancy N. Rabalais et al., 2002; Van Meter, Basu, & Van Cappellen, 2017; Van Meter, Van Cappellen, & Basu, 2018; Vero et al., 2017), all of which result in the general loss of habitat and biodiversity (Orth et al., 2017; P. M. Vitousek et al., 1997).

Eutrophication is the process by which a water body is enriched with nutrients promoting excess growth. Unlike inland water bodies, which have been shown to be phosphorus-limited systems (David W. Schindler, Carpenter, Chapra, Hecky, & Orihel, 2016; D. W. Schindler & Fee, 1974), estuarine and coastal systems are N-limited, and excess anthropogenic N drives widespread algal blooms and subsequent hypoxic zones (Bristow, Mohr, Ahmerkamp, & Kuypers, 2017; Howarth et al., 2011). In addition, some argue that multiple nutrients in concert drive eutrophication and algal blooms, and thus that excess N may also play a role in water quality degradation in inland waters as well as coastal ecosystems (Conley et al., 2009; Lewis, Wurtsbaugh, & Paerl, 2011; Paerl, 2009).

Hypoxia, the condition of low oxygen in the water column, is caused by eutrophication of water bodies. As nutrients promote the growth of excess algae, the aerobic process of decomposition of the organic matter consumes the dissolved oxygen in the water column. Hypoxia is the state in which the oxygen concentration of a body of water is less than 2 mL of O2/L, often occurring below the lower half to two-thirds of the water column (Nancy N. Rabalais & Turner, 2001). In these low oxygen areas, aquatic life is unable to survive and are thus referred to as "dead zones." Globally dead zones have been increasing since 1960 (Diaz & Rosenberg, 2008), and are now reported in more than 400 systems, totaling an area larger than 245,000 km^2 (Figure 2). Incidences have occurred in the Gulf of Mexico, Baltic, Kattegat, Black Sea, and East China Sea (Caballero-Alfonso, Carstensen, & Conley, 2015; Conley et al., 2011; Diaz & Rosenberg, 2008; N. N. Rabalais et al., 2009; Turner & Rabalais, 2018).

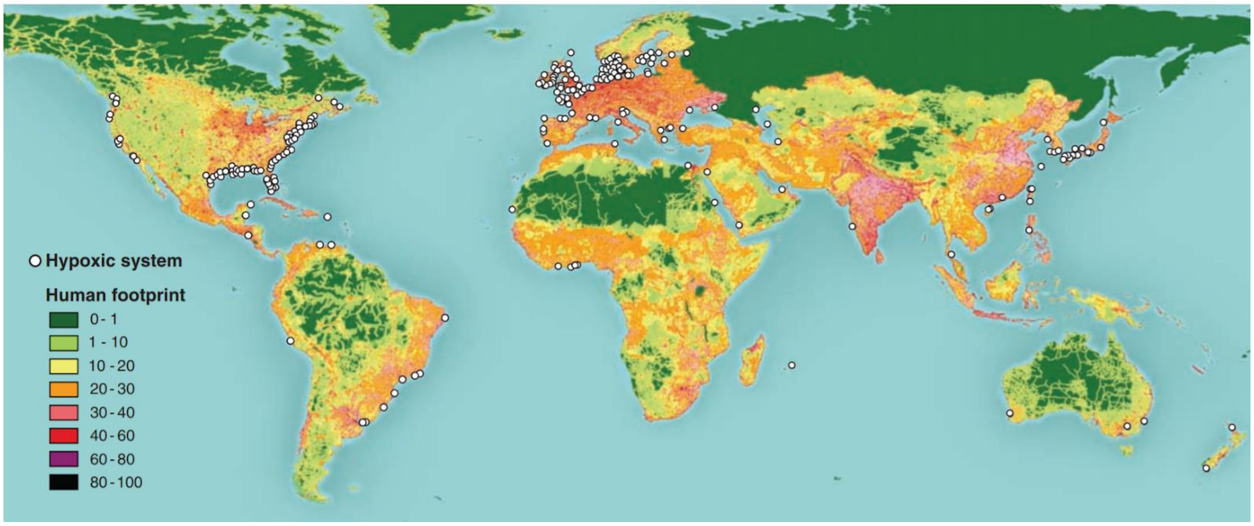

Figure 2. Reported accounts of over 400 eutrophication associated hypoxic zones and excess nutrients (Diaz & Rosenberg, 2008).

Low oxygen areas in coastal waters result in a high mortality rate for aerobic aquatic organisms, a loss of habitat for many bottom-dwelling and benthic fauna, a loss of biodiversity, and a general alteration of trophic structure (N. N. Rabalais et al., 2009). These changes have a direct impact on society and coastal communities as estuaries and coastal environments provide a multitude of services, including tourism, recreation, and provisions from fisheries (Conley et al., 2011; Howarth et al., 2011; N. N. Rabalais et al., 2002).

1.2.2 Nitrogen Contamination and Human Health

In the U.S., 45 million people (14% of the population) receive their drinking water from groundwater wells, any of which are unregulated by the Environmental Protection Agency under the Safe Drinking Water Act. An estimated 15 million people live in areas that have groundwater nitrate levels exceeding 1 mg-N/L, above the threshold of naturally occurring nitrate, and approximately 1.2 million people living in areas with groundwater nitrate levels between 5 mg-N/L and 10 mg-N/L. A national survey of drinking water wells found that 6% of the wells sampled (2,388 domestic wells and 384 public supply wells) exceeded the Maximum Contaminant Level (MCL) of 10 mg-N/L (N. M. Dubrovsky et al., 2010).

The regulatory standard of 10 mg-N/L was established to protect infants from methemoglobinemia (Dubrovsky et al., 2010; Nolan & Stoner, 2000). The ingestion of NO3- from contaminated groundwater can inhibit the oxygen-carrying capacity of the blood through the preferential binding of NO2-2 to hemoglobin in place of oxygen (The World Health Organization, 2010; Mary H. Ward, 2009). Growing evidence suggests that ingesting nitrates can also increase the risk of a range of other illnesses. Ingestion can trigger the in vivo formation of N-nitroso, a compound found to be potent animal carcinogens and is probably carcinogenic to humans (The World Health Organization, 2010; Mary H. Ward, 2009). There have been few mechanistic studies relating nitrate ingestion to cancer and diseases in humans, however case-studies in the U.S. have positively associated high nitrate drinking water concentrations with bladder cancer, breast cancer, ovarian cancer (Dubrovsky et al., 2010; Mary H. Ward, 2009; Mary H. Ward et al., 2018; Weyer et al., 2001), thyroid disease (Aschebrook-Kilfoy et al., 2012; Mary H. Ward et al., 2018), colorectal cancer, birth defects (Mary H. Ward et al., 2005, 2018), and non-Hodgkin lymphoma -- although subsequent studies have also found no link between NO3- and non-Hodgkin lymphoma (Mary H. Ward, 2009; M. H. Ward et al., 1996). While much research is still needed to fully understand the negative impacts of ingesting nitrate-contaminated water, the most current findings suggest that populations may be at risk even at concentrations well below regulatory limits (Mary H. Ward et al., 2018).

1.2.3 N Atmospheric Pollution and Greenhouse Gasses Production

NO_x and ammonia (NH_3) comprise the majority of atmospheric emissions. There are multiple pathways to producing atmospheric gas. NO_x is produced primarily as a byproduct of the combustion of fossil fuels from vehicles, electric power generating units, and other industrial and natural combustion sources. N_2O is from incomplete denitrification in soils and of manure (Schlesinger & Bernhardt, 2013). Similarly, NH_3 is volatilized from fertilizer and manure (Houlton et al., 2013; Lloret & Valiela, 2016; Reis, Pinder, Zhang, Lijie, & Sutton, 2009).

In the combustion process, the introduction of atmospheric N_2 from the air intake, combined with high temperatures in the combustion chamber, will oxidize N_2 and create unwanted byproducts of NO_x (Galloway, 2003). While the denitrification of N_2O is a natural process, increased inputs of N from fertilizer, manure production, and BNF from row crops provide the system with a larger pool of N to be denitrified (Davidson et al., 2011; Galloway, Schlesinger, Hiram, Schnoor, & Tg, 1995; Houlton et al., 2013). The increasing demand for energy and the intensification of agriculture in the last century has resulted in an increase in NO_x and N_2O emissions from 2 Tg-N/yr in 1940 to 7 Tg-N/yr in 1980. Between 1980 and 1990, emissions remained relatively constant, however, had a subsequent decreased by approximately 40% to 50% from 1990 to 2010 owing to point source control in the Clean Air Act Amendments in the 1990s (Houlton et al., 2013; Li et al., 2016; Lloret & Valiela, 2016).

Passage of the U.S. Clean Air Act was driven by concern regarding the acidification of lakes and surface water bodies due to atmospheric sulfur and N deposition (Kahl et al., 2004). In the atmosphere, NO_x converts to HNO_3^- and particulate NO_3^-, which can be deposited to the land surface via rainfall, known as wet deposition, or by gravity in particulate form, known as dry deposition (National Atmospheric Deposition Program, 2000). Acidification can result in shifts of the plant community, can affect plant populations, and can negatively impact overall forest health (Lloret & Valiela, 2016; Marinos, 2018; National Atmospheric Deposition Program, 2000).

NO_x can both create and destroy ozone, depending on where it occurs in the atmosphere (Davidson et al., 2011; Ravishankara, Daniel, & Portmann, 2009). In the troposphere, complex photochemical reactions with NO_x gasses will create ozone and aerosols (Davidson et al., 2011; Galloway et al., 1995). The products of the reaction in the troposphere act as greenhouse gases, which is linked to climate change (Li et al., 2016; Reis et al., 2009). In the stratosphere, NO_x has the opposite effect, where nitrogen oxide-catalyzed processes destroy stratospheric ozone, which can lead to the degradation of the UV-protective ozone layer (Ravishankara et al., 2009; Reis et al., 2009).

Anthropogenic NH_3 can be produced through the volatilization of NH_3 from fertilizer and manure (Davidson et al., 2011; Li et al., 2016; Lloret & Valiela, 2016). Unlike NO_x emissions, NH_3 is not regulated by the Clean Air Act (Davidson et al., 2011). It was estimated that in 2006, 2.8 Tg-N/yr was deposited in the U.S, and this is expected to increase to between 3.3 and 4.2 Tg N/yr by 2050 (Li et al., 2016). Similar to NO_x, NH_3 can produce atmospheric aerosols resulting in an increased greenhouse gas effect (Behera, Sharma, Aneja, & Balasubramanian, 2013; Davidson et al., 2011). Additionally, NH_3 is the primary basic gas in the atmosphere and thus has an essential role in determining the pH of precipitation and can impact the pH of the ecosystem where it deposits (Behera et al., 2013). Unlike NO_x that generally deposits far from the emission source (Lloret & Valiela, 2016), NH_3 has a relatively short residence time in the atmosphere and is often assumed to deposit locally (Hong, Swaney, & Howarth, 2013; Howarth et al., 1996)

1.3 Current Water Quality and Response to Mitigation

The degradation of groundwater, inland, and coastal waters, has led to the establishment of major policy goals to improve water quality by controlling point source and nonpoint source loadings. For example, the 2008 Gulf Hypoxia Action Plan encouraged all stakeholders in the Mississippi/Atchafalaya River Basin (MARB) to develop strategies to reduce nutrient loadings to the Gulf of Mexico. The outcome was 19 members, ranging from federal and state agencies, tribes, and other partners, establishing individual nutrient reduction frameworks specific to state needs. The goal of the Hypoxia Task Force was to decrease the five-year running average areal extent of the hypoxic zone in the Gulf to 5,000 km^2 by 2015 (USEPA, 2017). Two of the states in the Hypoxia Task Force, Illinois and Iowa, are estimated to contribute 16.8 and 11.3% of the total N flux to the Gulf of Mexico, respectively (Alexander et al., 2008). In response to the Gulf Hypoxia Action Plan, Illinois developed a Nutrient Loss Reduction Strategy to quantify and reduce nutrient loss from Illinois watersheds to the Gulf (IEPA, IDOA, & University of Illinois Extension, 2015). The implementation of strategic plans has been considered successful. There has been a doubling of agricultural best management practices between 2011 and 2015, including cover crops, field buffer strips, and wetlands. Similarly, in 2010, the Iowa Nutrient Reduction Strategy (NRS) was drafted. Since 2011, Iowa has installed over 300,000 acres of cover crops and 37,000 acres of engineered wetlands (INRC, 2019). Furthermore, there has been over $1.3 billion in the last three years (2016 to 2018) to NRS-related efforts and best management practices implementation (INRC, 2019).

Despite concerted efforts to control point source and nonpoint source loadings by many organizations and working-groups, water quality threats persist (Ribaudo, 2015). Riverine and aquifer nitrate concentrations are, in many cases, not responding proportionally to changes in management. For example, in Iowa, there has been massive investments of effort and resources, but no decipherable decreases in annual N loads, as per the 2018 report (INRC, 2019). In Illinois, significant progress has been made in implementing of nutrient reduction strategies, but there have only been a 10% decrease in N loads in Illinois rivers compared to 1980 to 1996 baseline (IEPA, IDOA, & University of Illinois Extension, 2017). The size of the Gulf of Mexico summer hypoxic zone demonstrates the lack of response to N management efforts in the Mississippi River Basin. In 2017, the hypoxic zone was declared the largest ever measured, at over 22,000 km^2, more than four times the size of the 2015 goal set forth by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (USEPA, 2017; Van Meter et al., 2018).

The lack of progress is not unique to the MARB. Since 1987, the Chesapeake Bay Program, in partnership with the EPA and state-level government, has been committed to reducing “controllable” nutrients into the Chesapeake Bay by 40% by the year 2000 (Reckhow et al., 2011). In the Great Plains, the USDA Natural Resources Conservation Service has implemented the Ogallala Aquifer Initiative. It has invested over $26 million over 6 years (2011 to 2017) to conserve water resources, part of which is to improve water quality (USDA, 2017). In the Chesapeake Bay, a 2011 report had concluded that efforts did not achieve the nutrient reduction goals (Reckhow et al., 2011). Despite decreases in N loading, the biennial report card in 2018 for the “State of the Bay” in the Chesapeake Bay gave N pollution a grade of F, 5 points lower than the score in 2016 (Chesapeake Bay Foundation, 2019). Similarly, in the Ogallala aquifer, high levels of NO3- persist with concentrations in public wells with some exceeding 20 mg-N/L in 2017 (Juntakut, Snow, Haacker, & Ray, 2019; Nebraska Department of Environmental Quality, n.d.; Reedy & Scanlon, 2017).

1.4 Missing Nitrogen: Accumulation and Legacy N

It has been argued that such lack of success can be attributed to build up of legacy N in the landscape. Indeed, N mass budgets across various watersheds of the world reveal that inputs are routinely greater than the outputs, and the difference between the two is commonly referred to as N surplus (Boyer, Goodale, Jaworski, & Howarth, 2002; Goyette, Bennett, Howarth, & Maranger, 2016; Hong et al., 2013, 2012). These studies have repeatedly demonstrated that exports account for between 20% and 30% of the N surplus (Billen, Thieu, Garnier, & Silvestre, 2009; Boyer et al., 2002; Han & Allan, 2008; Hong et al., 2013; Howarth, Boyer, Pabich, & Galloway, 2002; Van Breemen et al., 2002). However, as implied, the inputs routinely exceed the export. The remaining 70% to 80% of unaccounted N surplus is partitioned to the N retention pool, which has largely been unquantified at watershed-scale.

There are four pathways for the N in the retention pool: (1) loss through denitrification, (2) conversion to SON, (3) stored in the unsaturated zone as dissolved inorganic N, or (4) stored in groundwater aquifers as dissolved inorganic N (Ascott, Wang, Stuart, Ward, & Hart, 2016; Van Breemen et al., 2002; Van Meter, Basu, Veenstra, & Burras, 2016). There is considerable uncertainty about the magnitude of fluxes and pool sizes, however recent studies have quantified the pools in the Mississippi River Basin and the Susquehanna (Van Meter et al., 2017). Prior to this, many studies attributed the N retention primarily to losses through the denitrification processes, converting inorganic N to N2O or N2 (Billen et al., 2009; Bouwman et al., 2013; N. Chen, Hong, Zhang, & Cao, 2008; Filoso et al., 2003; Liu, Watanabe, & Wang, 2008; Quynh et al., 2005; Swaney, Hong, Ti, Howarth, & Humborg, 2012; van Egmond, Bresser, & Bouwman, 2002; Worrall, Howden, & Burt, 2015). To bolster the notion of alternative fates of N in the subsurface, a study of the Mississippi River Basin (MRB) found riverine export accounts for 23% of the net N inputs, and accumulation in the soil as SON accounts for 53% of net N inputs. The remaining 24% of N is lost through denitrification, reservoir accumulation, and groundwater storage (Van Meter et al., 2016). A similar study of Cedar Basin in Iowa found riverine export and denitrification accounts for 28% and 23% of the net N inputs, respectively. Subsurface storage accounted for the remaining 49% of net N inputs, which included groundwater and soil profile storage (Ilampooranan, 2019).

1.4.1 Evidence of Legacy N in Soil and Groundwater Pools

Parallel to mass balance studies that allude to the possibility of a legacy build up in the landscape, there have also been direct estimates of legacy nitrogen storage, as SON, and in soil water and groundwater (Ascott et al., 2016; J. B. Gardner & Drinkwater, 2009; Van Meter et al., 2017). The potential of nitrogen accumulation in the soil organic matter pool was first uncovered by Van Meter et al. (2016).This challenged the existing paradigm that soil organic matter content in agricultural soils was generally decreasing because of continuous cropping and minimal replenishment of nutrients (Arrouays & Pelissier, 1994; Baker, Ochsner, Venterea, & Griffis, 2007; Billen et al., 2009; Gál, Vyn, Michéli, Kladivko, & McFee, 2007). Furthermore, the high solubility and mobility of NO3- also led to the assumption that N stores in the SON pool are unlikely to increase. Through a longitudinal soil sample analysis in the Mississippi River Basin, (Van Meter et al., 2016) found that within the root zone of agricultural soils (top 1m) there was a total yearly TN increase in Iowa and Illinois soils of 30.8 ± 11.4 kg-N/ha/yr, and 70.3 ± 10.0 kg-N/ha/yr, respectively. Comparatively, a 30-year 15N tracer study conducted near Châlons en Champagne, France, in lysimeters simulating agricultural land use had found evidence of soil N storage. After 30 years,12% to 15% of labeled fertilizer was still present, stored in the soil organic matter (Sebilo, Mayer, Nicolardot, Pinay, & Mariotti, 2013).

While it is generally accepted that dissolved nitrate can accumulate in the unsaturated zone, Ascott et al (2016) was the first to quantify the stored mass at a global scale. Areas that coincide with thick unsaturated zones and agricultural land use are expected to have delays in the leaching of N from the soil to groundwater. Long travel times through the unsaturated zone results in large pools of inorganic N, primarily in the form of NO3-, stored in the unsaturated zone (Ascott et al., 2016). The stores increase with time, as the rate of N inputs exceeds the N leaching rate from the zone to the aquifer. Ascott et al found that large amounts of nitrate stores have developed in North America, China, and Central and Eastern Europe from the coincidence of slow travel times and high N loadings. In particular, contemporary modeled unsaturated zone storage estimates in the

U.S. predicted ranges from negligible amounts (approximately 0 kg-N/ha) to over 4000 kg-N/ha. Spatially, the stores of N in the unsaturated zone are primarily in the Great Plains and prairie land (Ascott et al., 2017). Similarly, a total N mass balance study, including denitrification exports, in the Thames, UK catchment had increasing subsurface N stores of 55 kg-N/ha/yr over 35 years (1,925 kg-N/ha) (Worrall et al., 2015).

Lastly, the existence of N storage caused by long travel times in the subsurface is well accepted in the literature (Hamilton, 2012; Meals, Dressing, Tech, Davenport, & Protection, 2010; Sousa, Jones, Frind, & Rudolph, 2013; Tomer & Burkart, 2003). The travel times are estimates of the time required for N to be transported in the subsurface (unsaturated zone and groundwater aquifer), for which the portion of N in transit is considered a storage of N. It should be noted that in areas with shallow groundwater aquifers, the travel time in the unsaturated zone is negligible, thus the travel times refer to travel through the groundwater pool. As unsaturated zone storage was discussed in the previous paragraphs, travel time will be discussed in the context of groundwater travel times.

Estimation of groundwater travel time is a function of hydraulic conductivity and topography gradient, and soil porosity (Schilling & Wolter, 2007). The long hydrologic transport times in the procs of leaching of inorganic N through the unsaturated zone and groundwater delays its transport to the stream. The inherent heterogeneity in watershed results in distributions of groundwater travel times spanning days to decades. An estimate of groundwater travel time of Walnut Creek in Iowa watershed varies from 7 days to a maximum travel time of 308 years, with a mean of 10.1 years (Basu, Jindal, Schilling, Wolter, & Takle, 2012; K. E. Schilling & Wolter, 2007). The South Fork watershed in Iowa had travel times ranging from 32 days to travel times exceeding 50 years in poorly drained clayey soils (Ilampooranan, Van Meter, & Basu, 2019). The mean travel time distribution was 13 years, similar magnitude to the mean travel time in Walnut Creek watershed. Given the long travel times, the average storage of N in the subsurface of 10 years and annual inputs of N from anthropogenic activities, accretion in the groundwater pool is inevitable. In the Thames, UK watershed estimated accumulated groundwater store peaking at 1,571 ktonne (10^6 kg) in the early 2000s (Worrall et al., 2015). In the Mississippi and Susquehanna river basins, the increasing cumulative N stores had almost exceeded 500 kg-N/ha and 1,000 kg-N/ha by 2013, respectively (Van Meter et al., 2017).

1.4.2 Time Lags and Water Quality Response

Storage of N the unsaturated zone, in the SON pool, or the groundwater pool, can all lead to delays in catchment-scale nutrient delivery, thus significantly delaying the response of water quality to changes in the landscape. Large stocks of N, a result of fertilization and organic N inputs, will result in a legacy N providing a constant source of N for multiple decades, even if N inputs are abated (Haag & Kaupenjohann, 2001; Van Meter & Basu, 2017).

Watershed-scale time lags have been estimated in subwatersheds within the Grand River Watershed (GRW) in Southern Ontario in Canada (Van Meter & Basu, 2017) and in the agriculturally dominated Holtemme catchment in Germany (Ehrhardt, Kumar, Fleckenstein, Attinger, & Musolff, 2019). Here, time lag is defined as the delay between changes in annual N inputs and subsequent changes in water quality (Van Meter & Basu, 2017). Time lags have been estimated to range between 7 and 34 for GRW, and 7 to 22 for the German catchment. Time lags were found to depend on climate and landscape controls including season (high flow in winter and spring versus low flow season in summer and fall), anthropogenic N inputs, landscape slope, fractional tile-drained area, percent wetland, and population density (Ehrhardt et al., 2019; Van Meter & Basu, 2017; Van Meter et al., 2017).

Another study of N net input and riverine dynamics was also undertaken in seven predominantly agricultural watersheds (agriculture land use between 74% and 91%) in the Brittany region in western France (Dupas, Minaudo, Gruau, Ruiz, & Gascuel-Odoux, 2018). As in the GRW in southern Ontario, their results show significant nonlinearity between N inputs and N loads. The strong hysteresis effect is indicative of time lags where watershed had periods of stationary or decreasing N inputs with increasing N loads. The study provides evidence of the time lags, as the accumulation in the shallow groundwater in these catchments led to a mean time lag between N net inputs and riverine concentrations of 10 years (Dupas et al., 2018).

1.5 Nutrient Budgets in the U.S.

Existing N surplus budgets are for various spatial scales, for specific periods and at coarse spatial resolutions. Such datasets are compiled at administrative boundaries or watershed boundaries in the U.S. Many studies are based only on snapshots in time, multiyear averaging of N inputs and outputs, or quantify N surplus for limited periods and for limited regions (Table 1). The methodology and coverage of the studies limit the ability to effectively capture long-term responses to changes in inputs. The onerous data compilation and processing required for an N budget have limited the development of long-term datasets with a national spatial scale at a high spatial resolution (Goyette et al., 2016; Green et al., 2004; Van Meter et al., 2017). Furthermore, select datasets compiled at watershed scale have attempted to close the N budgets by accounting for losses in the system through denitrification and N export to riverine. As denitrification is difficult to measure, it is often used as a balancing term. This approach assumes steady state on either on a yearly basis or over a multiyear period (Chen et al., 2018; David & Gentry, 2000; Green et al., 2004; Howarth et al., 2006). Indeed, it is increasingly recognized that there may be decadal-scale time lags between changes in N inputs and measurable changes in water quality.

Table 1. Existing N budgets for the United States. Studies range in different spatial and temporal scale and resolution.

Location/Extent	Spatial Scale	Temporal Scale	Limitation	Citation
Global	Watershed-scale Crop data: 1993 county yields Livestock: 1993 county heads Fertilizer: County use Atmospheric Dep: 2.5º x 3.25º and 10º x 10º	Snapshot year, 1980	Spatial scale is too coarse. Temporally limited.	(Howarth et al., 1996)
Conterminous U.S.	Watershed-scale Crop data: County yields Livestock: County livestock heads Fertilizer: County use Atmospheric Dep: Countour maps	Snapshot year, approximately in the 1980	Temporally limited	(Jordan & Weller, 1996)
Illinois state	State-scale data Crop data: State yields Livestock: State number of heads Fertilizer: State sales Atmospheric Dep: Station data Population: State population	1945 to 1998	Spatial scale is too coarse. Temporally limited	(David & Gentry, 2000)
Northeastern U.S	County-scale data Crop data: County yields Livestock: County number of heads Fertilizer: County sales Atmospheric Dep: Station data Population: County population Forest Land Use: County scale	Average over 1988 to 1993	Spatially limited. Temporally limited.	(Boyer et al., 2002; Van Breemen et al., 2002)
Global	30º Gridded data Crop data: Country yields Livestock: Country number of heads Fertilizer: County fertilizer use Atmospheric Dep: 12 km x 12 km grid Population: 1km x 1km population grid	Snapshot of contemporary values	Spatial scale is too coarse. Temporally limited	(Green et al., 2004)

Conterminous U.S.	Counties and watersheds Crop data: County yields Livestock: 100 km x 100 km density Fertilizer: Country fertilizer use Atmospheric Dep: 12 km x 12 km grid Population: County population	1987 to 2012	Spatially limited. Temporally limited.	(Hong, Swaney, & Howarth, 2011; Hong et al., 2013)
Mississippi and Susquehanna watersheds	Watershed-scale Crop data: State yields Livestock: State number of heads Fertilizer: County fertilizer use Atmospheric Dep: 4 km x 4 km and 100 km x 100 km grid Population: County population	1850 to 2015	Spatially limited. Spatial scale is too coarse.	(Van Meter et al., 2017)
St. Lawrence sub-basin (U.S. and Canada)	Watershed-scale Crop data: County yields Livestock: County number of heads Fertilizer: County fertilizer sales Atmospheric Dep: 12 km x 12 km grid Population: County population	1901 to 2011	Spatially limited.	(Goyette et al., 2016)
Iowa Cedar Basin, IA	Watershed-scale Crop data: County yields Livestock: County number of heads Fertilizer: County fertilizer sales Atmospheric Dep: 250 m x 250 m and 100 km x 100 km grid Population: County population	1949 to 2012	Spatially limited. Temporally limited.	(Ilampooranan, 2019)
North-central United States and southeast Canada	Field Scale, US All data came from meta-analysis of field sites across the U.S.	Annual, prior to 2016	Spatially limited. Temporally limited.	(McLellan et al., 2018)

Over the past two decades, the compilation of N budgets in the U.S. demonstrates the many attempts to quantify N in the environment. However, the resolution, temporal, and spatial scale of existing datasets are limited. Sources of nitrogen have been dynamic spatiotemporally over the past century driven by technological, land use, and economic and policy changes (Brown, Johnson, Loveland, & Theobald, 2005; Dimitri, Effland, & Conklin, 2005; Office of the New York State Comptroller: Division of Local Government Services & Economic Development, 2004; Yu & Lu, 2018). Inappropriate methods, and limited spatial and temporal scales impede the ability to effectively capture long-term trends, and responses to changes in N usage in the U.S. A dataset with a longer record allows for an accurate estimation of the N retention pool and the analysis of the N surplus trend.

1.6 Objectives

While recent work has shown evidence of legacy nitrogen accumulation in various subsurface pools, and quantified time lags to water quality response due to these legacy stores, there remains a significant gap in quantifying legacy accumulation at continental to global scales. Mass budget studies done over multiple decades provides an upper bound of legacy accumulation. One of the primary knowledge gaps lies in quantification of the time trajectories of N mass budget at large scales. Most mass budget studies, as shown before, are either spatially limited (regional or watershed scale), or regional but temporally constrained (last few years). The study addresses this knowledge gap. The overall objective of this research is to compile a conterminous U.S. scale N surplus dataset beginning before anthropogenic N began to grow exponentially to understand the temporal and spatial distribution of N and legacy N in the U.S.

Objective 1: Reconstruct historical N inputs and outputs from 1930 to 2017 to quantify the N retention pool to facilitate the temporal and spatial analysis of trends of legacy N.

Objective 2: Develop typologies based on N surplus time series, identify drivers to provide a tool for nutrient management decision-making, and identifying areas with potentially high N accumulation.

2.0 Methods

In Section 2 the methods for the data compilation and analyses conducted in the study are presented. Section 2.1 describes data and methods compilation of the N surplus dataset. It includes the sources and process flow of pulling together disparate data sources. Section 2.2 describes the clustering technique used to explore trends and drivers and develop typologies.

2.1 Estimation of N Surplus

We used a simple mass balance approach to quantify the nitrogen surplus (N surplus) in each county in the CONUS. We estimated county-scale nitrogen surplus across the CONUS as the difference between N inputs and N outputs into the landscape. This mass balance approach is adapted from the conceptual framework in previous studies (Boyer et al., 2002; Goyette et al., 2016; Hong et al., 2011, 2013). The methodology also expands on the common anthropogenic sources of nitrogen mass balance (Boyer, Goodale, Jaworski, & Howarth, 2002; Hong et al., 2011) approach by expanding crop types to better represent states with dominant non-field crops. N surplus is a partial mass balance defined as the difference between the inputs and usable outputs of N in the following equations (Ehrhardt et al., 2019; Van Meter & Basu, 2017).

$$N_{SURPLUS} = N_{in} - N_{out} \quad \text{Equation 1}$$

$$N_{IN} = DEP + FERT + BNF + PROD_{LIVESTOCK} + PROD_{HUMAN} \quad \text{Equation 2}$$

$$N_{OUT} = CROP_{HARVEST} \quad \text{Equation 3}$$

Here, DEP is atmospheric nitrogen deposition (kg-N/ha/yr) FERT is inorganic nitrogen fertilizer inputs (kg-N/ha/yr), BNF is biological nitrogen fixation (kg-N/ha/yr). The two waste production components from livestock and humans are referred to as

$PROD_{LIVESTOCK}$ and $PROD_{HUMAN}$. The only removal term in the N surplus calculation is the nitrogen removed from crop biomass harvest and pastureland grazing ($CROP_{HARVEST}$). It is not intended to outline internal pathways of N, nor is it complete quantification of N in the soil because N not removed through crop uptake can either be stored or exported. However, the advantage of N surplus is that the data are available at county level and with higher degree of certainty (Norton et al. 2015).

It should be noted that N in the body mass of livestock and N consumed by livestock is captured in the $PROD_{LIVESTOCK}$ term (Eqn. 4).

$$PROD_{LIVESTOCK} = N_{CONSUMED} - N_{BODY\ MASS} \qquad \text{Equation 4}$$

Here $PROD_{LIVESTOCK}$ is the waste produced by the animal, $N_{CONSUMED}$ is the portion of N consumed by the animal, and $N_{BODY\ MASS}$ is the N that is stored in the animal.

The temporal and spatial resolution of the input datasets are provided in Table 2. The following section describes the calculation of the various components of N surplus. The following section describes the calculation of the various components of N surplus.

The system boundary over which this analysis is done is the county and, the inputs are calculated at the county-scale. The three other components of the mass balance are denitrification in soil, river, or WWTP, and riverine and groundwater export out of the county boundaries. Theses losses are very difficult to estimate, may not be practice (i.e stream export at a county scale), and have large uncertainties. Given the significant uncertainty in computing these fluxes without a process base we have here focused our analysis on N surplus which is the most certain parts of the budget.

County boundaries were not static throughout the time period, as documented in the Atlas of Historical County Boundaries (Long, 2010). To generate a static county map, counties that had merged or separated between 1930 and 2017 were merged for the entire time period (Supplemental Table 2).

Table 2. Data types and sources used to estimate the N surplus in the CONUS.

N Surplus Component	Data Type	Data Source	Temporal Resolution	Spatial Resolution
Human Waste (+)	Human Population	U.S. Census Bureau	1930 to 1990 (decadal) 1990 to 2017 (annual)	County-scale
Crop Removal (-)	Crop Production	USDA Agriculture Census	1930 to 2017 (5-year)	County-scale
	Cropland and Pastureland	Ramankutty and Foley (1999)	1700 to 2007 (subset 1930 to 1945)	0.5° by 0.5°
Biological N Fixation (+)	Crop Production	USDA Agriculture Census	1930 to 2017 (5-year)	County-scale
Livestock Manure (+)	Animal Inventory	USDA Agriculture Census	1930 to 2017 (5-year)	County-scale
	Broiler Consumption		1930 to 1969 (5-years)	National
Fertilizer (+)	County Fertilizer	USDA ERS	2017	National
	County Fertilizer	USGS	1987 to 2012 (annual data corresponding to census years were selected)	County-scale
	County Fertilizer	USGS	1945 to 1987 (annual data corresponding to census years were selected)	County-scale
	Raster Fertilizer	Cao et al. (2017)	1930 to 1945 (annual data corresponding to census years were selected)	1 km by 1km
Atmospheric Deposition (+)	Wet N Deposition Grid	NADP TDEP	1986 to 2017	4 km by 4 km
	Dry N Deposition Grid	CASTNET	2000 to 2017	4 km by 4 km

	National NO_x Emission	EPA, Houlton et al. (2013)	1940 to 1986	National
	Global N Deposition	Dentener (1999)	1930 to 1940	5º by 3.75º

2.1.1 Human Waste Inputs

Human waste inputs were estimated using population census data and information on annual N excretion rates (5 kg-N/cap/yr) (Hong et al., 2011). Decadal county-scale population census data were available from 1930 to 1990 (U.S. Census Bureau, 2007), and annual data were available after 1990 (U.S. Census Bureau, 2016). Between 1930 to 1990, we interpolated decadal census data to estimate annual data. The N excretion rates were then used to convert annual county-scale population numbers to human N waste input.

2.1.2 Crop Uptake

Crop N uptake was estimated using the information on crops harvested in each county and the N content in each crop (USDA-NASS, 2017). We identified the most common crops in each county, by selecting crops such that we covered 97% of the county-scale cropped area (USDA National Agricultural Statistics Service Cropland Data Layer, 2010). Consequently, a total of 65 crops, including field crops, fruit and nut trees, fruits, and vegetables, were used in the N budget. The set of crops is much broader than accounted for in other studies such as (Hong et al., 2011) with 16 crops (including pasture) for uptake and six crops for fixation or Boyer et al. (2002) with eight crops for uptake and five crops for fixation. While field crops do dominate the crop uptake at the country scale, fruit, vegetables, and nuts are locally significant. For example, fruit and nut trees are significant in the southern U.S.

The harvested unit of each crop is available in either area (acres) or mass (bushel, lbs, cwt, tons) units for each census year between 1930 and 2017. For fruit and nut trees, information is available as either the number of trees or acres of trees. Various assumptions were made to convert these to a mass of N in uptake across the years. First, when crop data was available in area unit (acres), crop yield (kg/acre) (Table XX) is used to convert the area into mass units. Given the lack of adequate data on temporally varying yields, we used a constant yield across the years, at the state or national scale, based on data availability. The mass of crop harvested was converted into kg N by multiplying it with the N content of each crop.

Another challenge was the conversion of fruit trees to a consistent unit. Between 1930 to 1997, excluding 1969 and 1978, the census reports the number of trees. In all other years (1969, 1972, and 2002 to 2017), the census reports the acreage of trees. The compiled N uptake information for trees is available in units of kg N per tree. Thus, the acreage of trees was converted into the number of trees. To do this, we estimated the ratio between the number of trees and acres available at the county scale for the nearest census year and used this ratio to convert acreage to the number of trees. The number of trees was then converted to kg-N by multiplying with the N uptake of each tree obtained from the literature (Supplemental Table 3)

Two of the 65 crops used in our national scale analysis were “cropland pasture” and “all pasture,” however, certain assumptions are made to address inconsistencies in the definitions of these two data types over time. Specifically, after 1945, cropland pasture is defined as “land that has been plowed within the last seven years and was used as pasture at the time of the census,” while in the earlier census years, this category did not exist. Non-cropland pasture after 1945 is defined as the “difference between all pasture and cropland pasture and includes areas such as woodland pasture and other low-quality pasture.” In order to estimate the cropland pasture and the non-cropland pasture values prior to 1945, we used a global dataset of pasture and cropland available annually from 1700 to 1992 (Ramankutty and Foley, 1999). First, we clipped the global cropland and pastureland dataset to each county. We then used the percent change in cropland to scale the 1950 census cropland pasture values to 1930, and the percent change in pastureland to scale the non-cropland pasture, over the same time frame.

Another challenge that we encountered while estimating crop N removal is the suppression of county-scale data, used to avoid disclosing data for individual operations. Specifically, if a county contains less than three farms growing a specific crop, the data is withheld at the county-scale, but included in the aggregated state totals. Missing data were estimated using methods developed in previous studies (Hong et al., 2011; Van Meter, 2016). First, the sum of the missing data (mass, acres of crop harvested, or the number of trees) for all the suppressed counties in a state was estimated as the difference between the state-scale value, and the sum of all available county-scale data within that state. This missing data (or the difference) was then apportioned to all the counties with suppressed data using one of two methods. If data was available for that county for the previous census years, we apportioned the missing data as a function of the ratio between the county-scale and state-scale values. We used up to the three nearest past census years available. For example, to appropriation 1997 missing data, we would use ratios first from 1992. If 1992 county data were unavailable, it would subsequently use 1987, then 1982. This method assumes that the relative proportion of crops in the counties with concealed data has remained the same. However, if the data was not available for that county for the previous census years, we used the current year ratio between the harvested cropland at the county and state-scale to apportion the missing data. Here, we assume that counties with a higher fraction of harvested cropland will have a higher probability of containing the crop being distributed. After the counties with concealed data were populated, we used linear interpolation to convert census data into annual data. Figure 3 contains the process flow diagram of the steps outlined to generate our dataset.

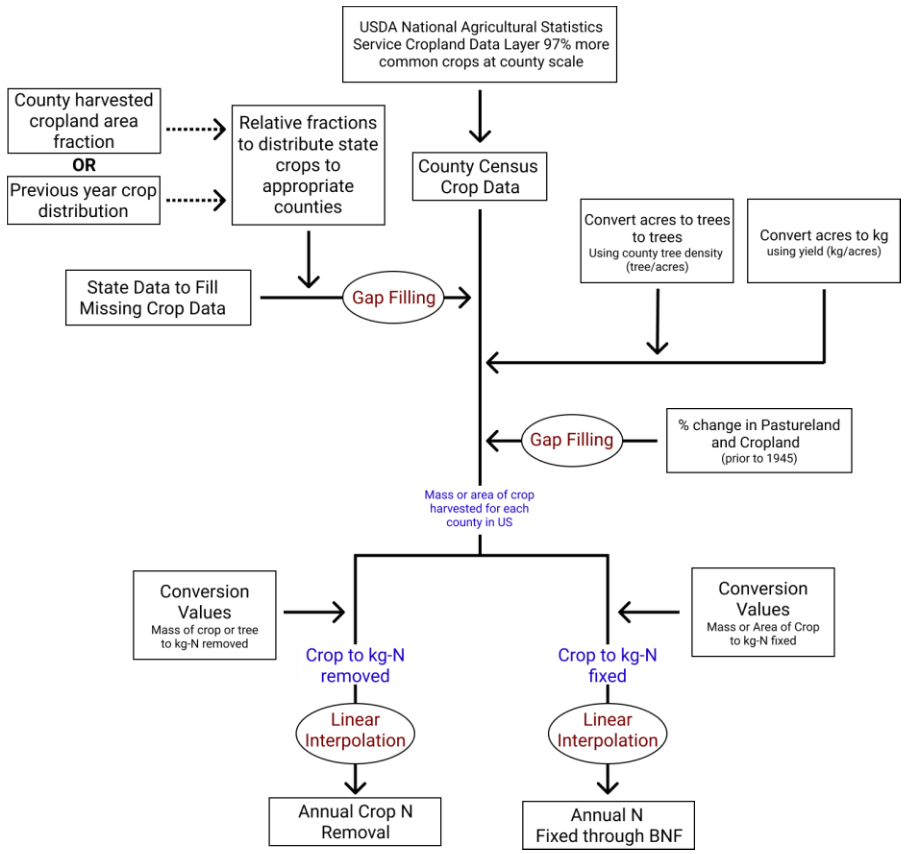

Figure 3. The process flow diagram to estimate crop uptake (kg-N/yr) and crop fixation (kg-N/yr). Black is data used, red is process step, and blue are unit conversions.

2.1.3 Biological N Fixation

We estimated biological N fixation using nine crops, expanding on the crops that included in past studies. In addition to those used in Hong et al. (2011), we also included lentils and dried beans because of their local importance in select counties. BNF was estimated using the methodology developed by previous studies (Han & Allan, 2008; Hong et al., 2013; Meisinger & Randall, 1991), converting harvested mass or area to mass of N fixed.

BNF for crop harvest reported in mass units (ex. bushels, tons, pounds, hundredweights) was estimated using the harvested mass. Specifically, the conversion is the product of harvested mass and the fraction of N content in the crop derived from N fixation (kg-N/kg), including the non-harvested portion. The fraction of N derived from N fixation was 74%

for soybeans and peanuts and 82% for alfalfa and clover. The non-harvested fraction of the crops was assumed to be 50%, based on the values used in Hong et al. (2013). As in Hong et al. (2013), non-alfalfa hay was assumed to have 25% leguminous plants such as clover that can fix N. For bean and lentil crops we assumed that the crop would derive 66% of their N from BFN (Smil, 1999b) (Supplemental Table 4).

For cropland pasture and snap-peas, only harvested area units were available (kg-N/acre). Due to this limitation, the product of acreage harvested and area-based fixation rates (kg-N/acres) was used to estimate BNF (Supplemental Table 4).

BNF has tremendous variability rates, both spatially and temporally, and introduces uncertainty when estimating BNF quantities (Galloway et al., 2004; Hong et al., 2013). As a result, there is considerable uncertainty associated with the estimates for the N surplus calculations.

2.1.4 Livestock Inputs

To estimate the N input from livestock manure, county-scale, livestock inventory numerated at five-year intervals was used (USDA National Agricultural Statistics Service Agriculture Census). We selected 11 different livestock categories, similar to other studies (Boyer et al., 2002; Goyette et al., 2016; Hong et al., 2011). We ensured that these livestock categories contributed over 95% of all manure produced in each state based on 2012 livestock inventory estimates (USDA National Agricultural Statistics Service, 2019). Livestock category definitions for cattle and chicken changed over the 88-year timeframe, and to maintain consistency in category definitions, we aggregated and disaggregated categories, as described in Supplemental Table 1.

Once consistent categories of livestock were established, N excreted was calculated using the product of reported heads of livestock and N content in manure generated per animal (kg-N/animal/yr) reported in previous publications. Cattle is one of the largest contributors of livestock manure. We assumed the manure produced by cattle changed over time, to account for the larger body weight and high protein feed types of modern cattle compared to earlier populations (Smil, 1999b) (Supplemental Table 5).

Lastly, as with crops, USDA agricultural census suppresses data to avoid disclosing data for individual operations. To estimate the suppressed heads of livestock in counties, we used the same methods as described previously for crops (Section 2.1.2). However, to apportion the suppressed data, we used the feed sold at the state scale, instead of the crop harvested data. As in other studies, we do not consider losses through ammonia volatilization from manure in our calculations. We assume that the volatilized ammonia redeposits locally within the county. Figure 4 contains the process flow diagram of the steps taken to generate our dataset.

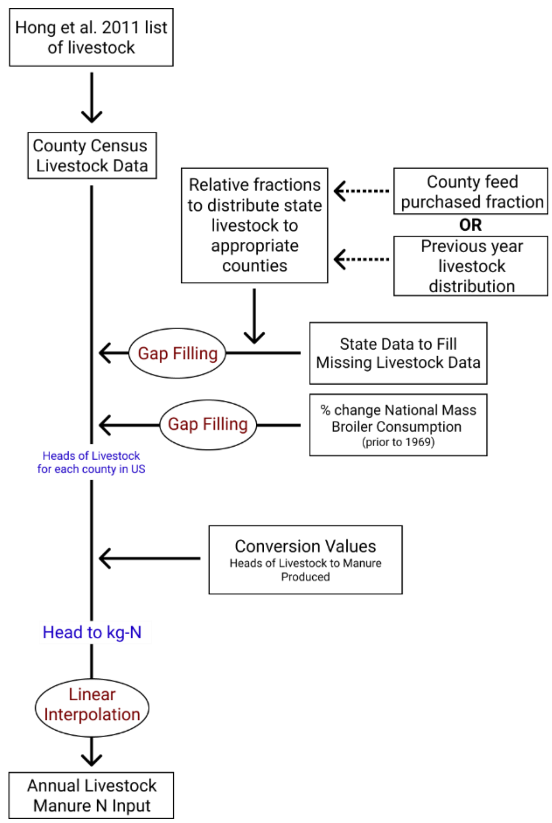

Figure 4. The process flow diagram for the livestock census data (kg-N/yr). Black is data used, red is process step, and blue are unit conversions.

2.1.3 Atmospheric Deposition

Atmospheric deposition is estimated using four datasets at different spatiotemporal resolution. Gridded data (4 km x 4 km) on wet deposition (HNO_3^- and NO_3^-) is available from 1986 to 2017, while similar data on dry deposition (NO_3^-) is available only from 2000 to 2017 (National Atmospheric Deposition Program, 2018). In order to estimate wet and dry deposition over the entire time-period (1986 to 2017), we used the information in the overlapping years (2000 to 2017) to estimate the county-scale ratio of dry deposition to wet deposition. County-scale fractions were highly variable and resulted in spuriously high values in a few counties. To smooth this variability, we aggregated the ratios to the state-level and used the median value of the ratio for each state. We then multiplied 1986 to 1999 county-scale wet deposition fraction by the state-scale ratios to generate county-scale dry deposition values for the missing years.

Next, as NADP does not have deposition estimates for either fraction prior to 1986, we used national NO_x emissions to scale county deposition trends from 1940 to 1986 (Houlton et al., 2013). While emissions are not an ideal proxy for emissions, median national deposition rates from 1986 to 2007 had a reasonable correlation with emission data (R^2 = 0.82). Emissions generally are well correlated with deposition rates in the northeast, an area with the highest rates of deposition.

Finally, from 1930 to 1940, we used a global gridded NO_x deposition dataset with a resolution of approximately 450 km by 420 km (Dentener 2006) to interpolate county deposition rates. We did not consider reduced forms of N (NH_x) in our N surplus calculations since it primarily originates from agricultural sources and is redeposited locally (Goyette et al., 2016; Howarth et al., 1996, 2006).

2.1.4 Fertilizer

We compiled 88-years of fertilizer data (1930 to 2017) using a variety of sources with different spatiotemporal resolution. County-scale annual fertilizer use data between 1945 to 1985 was obtained from Alexander & Smith (1990), and between 1987 to 2012 was obtained from Gronberg et al. (2017). Some counties had significant discrepancies in fertilizer use data between the two time-periods (1945 to 1985 and 1987 to 2012) due to changes in estimation and downscaling methodologies. Given that the 1987 to 2012 methodology was more rigorous than the earlier methodology, we scaled the dataset from 1945 to 1985 to obtain a smoother transition between the two timeframes. The scaling factor was generated using the county-scale N fertilizer use for 1987 divided by a 10-year average (1975 to 1985) county-scale N fertilizer use. It should be noted that the USGS 1987 to 2012 fertilizer use dataset partitions the fertilizer use into farm and non-farm. For this study, total fertilizer was estimated as the sum of the farm and non-farm use.

USGS data is not available prior to 1945. Thus, for the period 1930 to 1944, we used a fertilizer use dataset generated by Cao et al. (2018) compiled from a series of sources (Mehring, Adams, & Jacob, 1957; USDA, 1971, 2018). Fertilizer use was reported at the 1 km x 1 km resolution for 1850 to 2015, disaggregated based on land-use and crop type. We found that generally, the magnitudes of fertilizer use in the Cao dataset tended to be lower than the USGS dataset. Thus, to integrate the pre-1945 Cao data with the USGS data post-1945, we scaled USGS county fertilizer use data by the gridded dataset. We used the percent change between census years to scale the USGS 1945 fertilizer-use values to 1930.

The 1945 to 1985 dataset also did not have information on fertilizer use for “independent cities” in Virginia. Thus, we used a similar method as outlined above, using the Cao et al. (2018) dataset to scale the 1987 USGS county fertilizer-use values to 1930.

Finally, at the time of writing, the USGS has not published 2017 fertilizer-use estimates. Thus, we estimated the 2017 county-scale fertilizer inputs using the national fertilizer use data (1994 to 2014), national-scale data on fertilizer applied to corn (1994 to 2016), and the county-scale fertilizer use data between 2007 to 2012 (USDA, 2018). To extend the national fertilizer use data to 2016, we developed a regression relationship between national-scale datasets on fertilizer use and fertilizer applied to corn between 1994 to 2014 (Supplemental Figure 1). We then extrapolated the average national fertilizer use between 2011 to 2016 to estimate 2017 national use. The 2017 national estimate was then downscaled to the county-scale by apportioning it to the counties as a function of the ratio between the county-scale and national fertilizer use in previous years (averaged from 2007 to 2012). This method assumes that the relative usage of fertilizer in the counties has remained the same.

2.2 Clustering Techniques

To explore if there are characteristic trends of N surplus and its components in the county-scale time series, we used a clustering analysis of different N trajectories. Section 2.2.1 explains the background of the clustering methodology. Section 2.2.2 elaborates on the specific methods we used to determine cluster the N component trajectories as well as develop the N surplus typologies.

2.2.1 K-Means Clustering

K-means is an unsupervised learning algorithm that partitions a data set into a prespecified k number of clusters. Before running the algorithm, the data has to be summarized into features (or metrics). Features are chosen or measured metrics from the data that can be used to partition the data into distinct clusters. For example, two metrics for the N surplus dataset could be the mean magnitude and slope of the time series. The datasets are clustered based on those two metrics; thus, we can expect to have clusters representing k different modes of behavior of magnitude and trend direction.

The algorithm takes an iterative approach that optimizes the intra-clusters variance by minimizing the sum of squared Euclidean distances (referred to as the total squared Euclidean distance) (MacKay & Mac, 2003). The user does the first step of selecting k. A commonly used approach for k selection is the elbow method (Dugan et al., 2017; Gardner, Pavelsky, & Doyle, 2019; Steinley, 2006). For the elbow method, the k-means algorithm is run for a range of k values, and the algorithm returns the total squared Euclidean distance for iteration. When plotted, the increasing number of k will result in an exponentially decreasing total squared Euclidean distance, resulting from smaller clusters and improved cluster partitioning. Often, there is a point of a significant decrease in total squared Euclidean distance when incrementally increasing k, which is referred to as the "elbow." By visual inspection of the plotted results (k versus total squared Euclidean distance), the user can select the minimum number of clusters (k value) that resulted in the most significant decrease in total squared Euclidean distance (Dugan et al., 2017; J. R. Gardner et al., 2019; Steinley, 2006).

After selecting k, for the first iteration, the centroid is placed arbitrarily. A distance measure quantifies the distance of every data point to each cluster centroid, at which point data is assigned to the nearest centroid. A standard distance measure for continuous data is the Euclidean distance. For simplicity, assume a dataset has two features and t elements (X: {x^t_N} where N = 2). The following is the Euclidean distance equation for two features data set.

$$Dist_{Eucledian} = \sqrt{(x_1^t - C_1)^2 + (x_2^t - C_2)^2} \quad \text{Equation 5}$$

For the subsequent iterations, the centroids will readjust to the mean of the cluster, and data are reassigned. This process is repeated until the assignments do not change. This process can be summarized in four iterative steps (Figure 5).

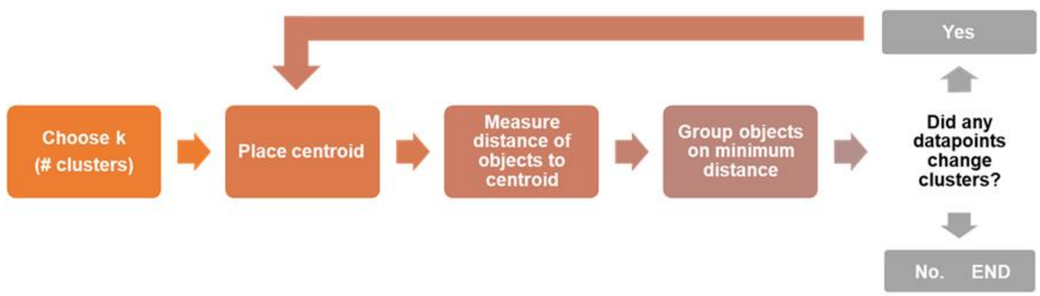

Figure 5. The process flow of k-means algorithms (MacKay & Mac, 2003; Steinley, 2006).

As the algorithm is initiated randomly, it is only able to find a local optimum. As such, once the assignment of clusters has converged, the process is repeated entirely. A new random starting point is selected, and the dataset is clustered again (Steinley, 2006). The total squared Euclidean distance in each cluster is recorded after each convergence. The iteration with the smallest squared total squared Euclidean distance is selected as the cluster partitioning.

Another standard time series clustering methods, dynamic time warping, is far more computationally expensive and also is limited in what features can be used for clustering (Berndt & Clifford, 1994; Keogh & Pazzani, 1999). The benefit of a simple algorithm as k-means is that it is computationally economical, easy to implement (MacQueen, 1967), and is used in similar studies for typology generation (Ascott et al., 2017; Dugan et al., 2017; Gardner et al., 2019). Our implementation of the algorithm allowed for the measurement of the different time series features that were deemed meaningful for our analysis.

2.2.2 Using K-Means for Typology Delineation

To explore spatiotemporal trends of N inputs and output components, as well as N surplus trajectories, we used clustering analysis. Specifically, we used k-means clustering for county-scale N surplus trajectories, as well as the component trajectories of fertilizer, BNF, livestock manure, atmospheric deposition, human waste, and crop output.

For the N surplus component trajectories, we used ten features measured over five distinct periods (1930 to 1940, 1941 to 1960, 1961 to 1980, 1981 to 2000, and 2001 to 2017). In each period, we characterized the mean N input or output of the component and the linear slope of the component trajectory. The periods were of unequal lengths and specially selected to capture the known transitions in the U.S. agricultural systems, for example, the rise in fertilizer use.

For the N surplus trajectory, we used 15 features, which included the mean N surplus and its slope in each period, as described above. Also, we included the mean contributing percentage of each input component (fertilizer, BNF, livestock manure, atmospheric deposition, and human waste) to the total N input over the entire of the time series. The selection of these features ensured that the clustering was based on its trend, as well as its components. Capturing these metrics is important because the components of N surplus would drive critical management decisions.

The features for the clustering algorithms are significantly different in magnitude, which necessitates normalization to prevent the unintended weighting of certain features. For all features except human waste and N surplus, we used a simple linear min-max normalization, scaling the features between ±1. The human waste input and the N surplus magnitudes had significant outliers due to dense urban areas with populations exceeding 80 pp/ha having N surplus magnitudes ranging from 400 - 1400 kg-N/ha/year, in contrast to counties with agricultural inputs with N surplus <200 kg-N/ha. Since the k-means algorithm is sensitive to outliers, we used the error function to normalize the human waste input and N surplus magnitudes. We first divided by 100, and then normalized using the error function, resulting in data exceeding ±180 kg-N/ha approaching the ±1 asymptote.

The elbow method was used to determine k for both clustering exercises. The method yielded five clusters for atmospheric deposition, fertilizer, and crop uptake output, and six clusters for human waste, livestock manure, and BNF. When clustering the N surplus trajectories, there was not an evident elbow in the elbow plot. Therefore, the selection of the number of clusters was based on having less than a 5% improvement in the cluster's squared Euclidean distance by adding a cluster. Indeed, no distinct trends were apparent by increasing the number of clusters beyond 10, and thus we selected 10 clusters for the N surplus trajectories.

3.0 Results and Discussion

The following section outlines the results of our analysis and discussions of our findings. Section 3.1 presents the spatiotemporal trends of N surplus. Section 3.2 presents our results from clustering the individual N surplus components. Section 3.3 presents our results on the typologies of N surplus. Lastly, section 3.4 presents the cumulative N surplus and discusses the implications of legacy N in the landscape.

3.1 N Surplus across the Conterminous United States (CONUS)

The spatiotemporal distribution of N surplus across the CONUS over the last 88 years (1930 to 2017) highlights a 24 fold increase from an average of 0.7 kg-N/ha/yr in 1930 to 16.7 kg-N/ha/yr in 2017, with specific areas emerging as hotspots over time (Figure 6). Spatially, N surplus magnitudes in the 1930s varied from -16 to 1134 kg-N/ha/yr, with the largest N surplus magnitudes (>200 kg-N/ha/yr) concentrated in the urban areas, such as New York City, Boston, St Louis City, and San Francisco County. Much of the cropland at this point in the century had minimal mineral fertilizer use and low livestock density. There is an east-west gradient in N surplus, with the higher N surplus magnitudes in the Northeastern and Mid-Atlantic states driven by N in atmospheric deposition and livestock manure.

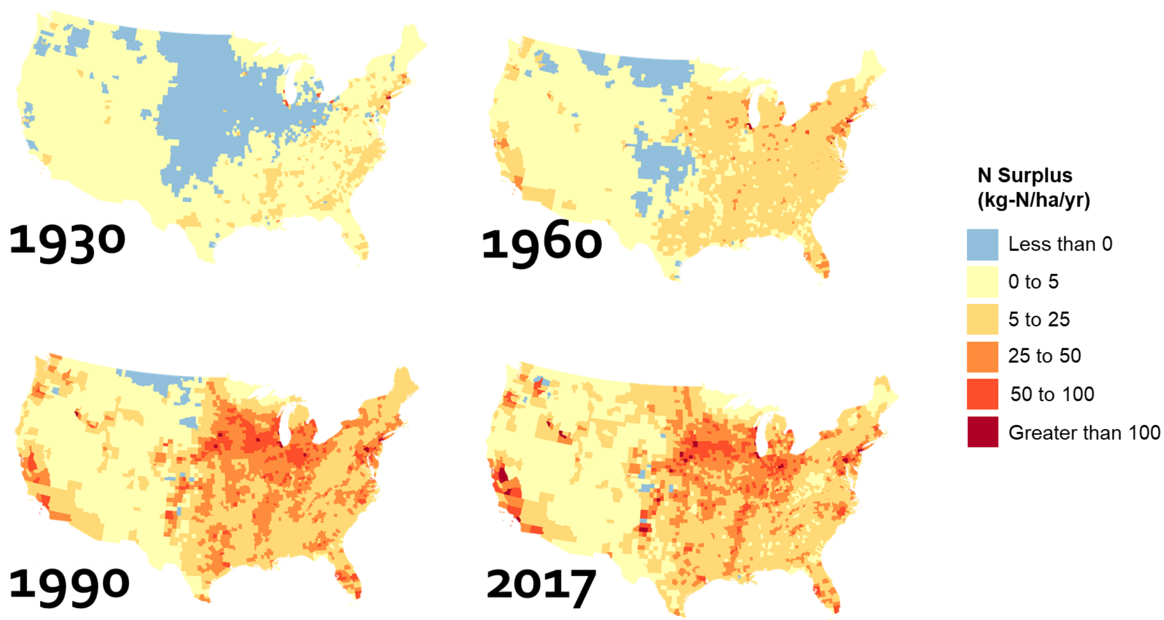

Figure 6. County-scale nitrogen surplus (kg-N/ha/yr) for (a) 1930, (b), 1960, (c) 1990, and (d) 2017.

We see a progressive intensification of agricultural practices, with a dramatic increase in the use of mineral fertilizer after 1945, and the conversion of native prairie soils in the Midwest to row crop agriculture (Cao, Lu, & Yu, 2018; Ramankutty & Foley, 1999; Yu & Lu, 2018). Increases in N surplus by the 1960s were apparent in the three major agricultural regions of the U.S. – the Midwest, Florida, and the Central Valley in California. N surplus increased steadily across the country between 1960 to 1990; however, between 1990 to 2017, there appears to be a decrease in the eastern part of the country. The decrease is possibly due to decreases in atmospheric deposition, and cropland abandonment. In the next section, we explore the various components of the N surplus to understand these patterns.

3.2 Components of the Nitrogen Surplus

We used a cluster analysis to understand the dominant modes of behavior of the six N surplus components across the CONUS: (a) h uman waste N, (b) atmospheric N deposition, (c) livestock manure N inputs, and (d) crop N uptake, (e) fertilizer inputs, and (f) biological N fixation (BNF). By considering the trajectories of these individual components, we can better our understanding of the evolution of N surplus across the CONUS and the extent to which humans have changed the spatiotemporal distribution of N surplus (Figure 7).

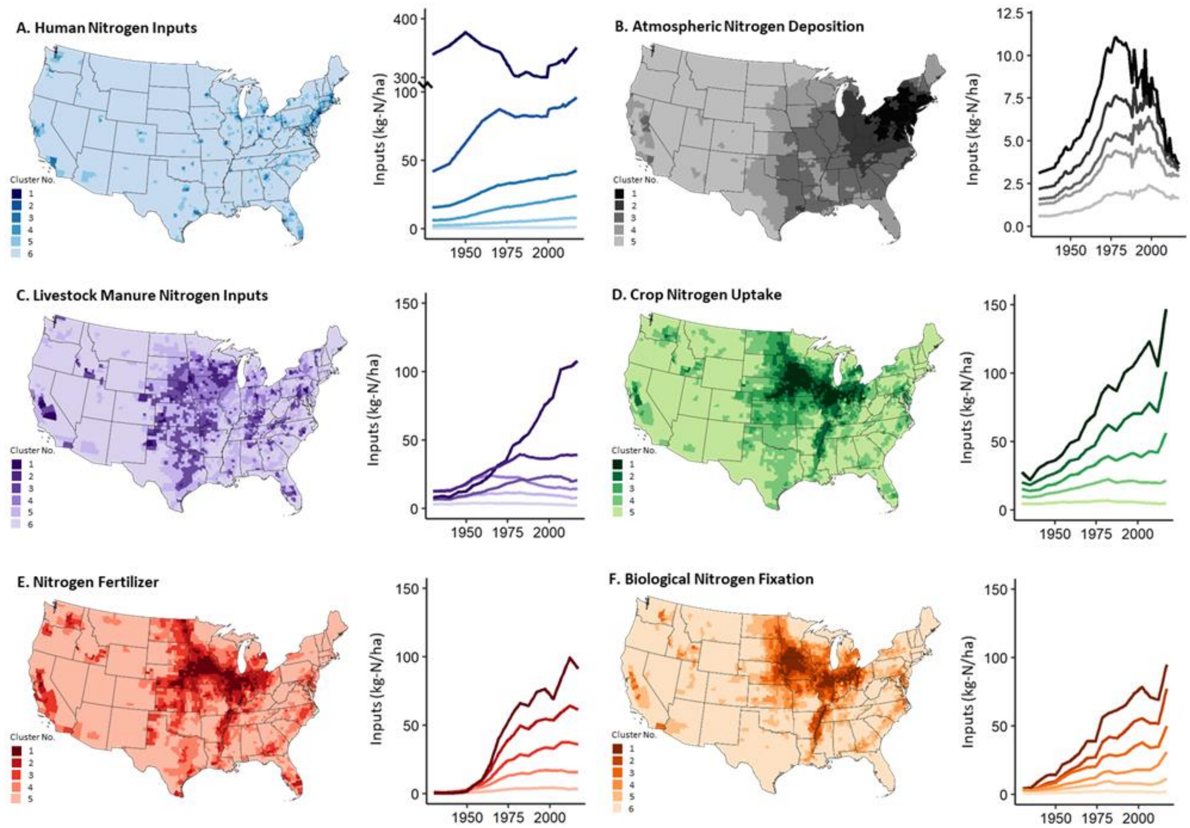

Figure 7. Cluster results for the six N Surplus components. In order to capture both spatial patterns and temporal trends, we have the CONUS map with the clusters and the associated time series in corresponding colors. (A) Human waste nitrogen inputs, (B) atmospheric nitrogen deposition, (C) livestock manure nitrogen inputs, and (D) crop nitrogen uptake, (E) nitrogen fertilizer, and (F) biological nitrogen fixation. Cluster labels are in ascending order of 2017 magnitudes, (1) having the highest magnitudes to (5-6) having the lowest magnitudes.

Clusters of human waste N inputs across the CONUS reveal interesting migration patterns over the last eight decades (Figure 7a), with mean N surplus magnitudes ranging from 330 kg-N/ha/yr for cluster 1 to 0.9 kg-N/ha/yr for cluster 6. Clusters 1 and 2 include counties that contain large to medium-sized cities (e.g., New York, Atlanta, Dallas-Fort Worth, Washington D.C., Chicago and San Francisco), and accounts for 19.6% of the human waste N inputs in 1930, despite covering only 0.16% of the total area. Counties in cluster 1 have maintained high population densities, and thus N input, across the entire time frame of analysis, with some migration out of the metropolitan areas evident after World War II. In contrast, counties in cluster 2 have seen higher rates of migration into the urban centers resulting in a rapid increase in population until the 1970s, after which there is a similar migration pattern out of the urban areas (Brown et al., 2005; Johnson, n.d.). Counties in clusters 3, 4, and 5 are characterized by heterogeneous land-use, often with high-density urban cores surrounded by lower density peri-urban areas or rural landscapes. These clusters correspond to regions such as the metropolitan area sprawling from New York to Washington and surrounding St. Louis, Denver, and San Francisco, Los Angeles, Maricopa, and Davidson County. Finally, cluster 6 includes rural areas that cover 90.8% of the country but contribute to only 31.6% of the human waste inputs in 2017.

While migration patterns are apparent in the human waste signals, the atmospheric N deposition trends show patterns consistent with NO_X emissions, and Clean Air Act Regulations that addressed these emissions (Figure 7b). There is an evident east-west gradient in deposition rates with the lower deposition clusters occurring in the western states. This can be attributed to the higher population density and emission rates in eastern U.S., and the prevalent west to east wind direction that transports significant amount of NO_X from vehicular emissions and power plants (Gschwandtner, Gschwandtner, Eldridge, Mann, & Mobley, 1986; Howarth et al., 2002; Jaworski, Howarth, & Hetling, 1997; Lloret & Valiela, 2016). The highest rates of deposition (Cluster 1 with the peak exceeding 10 kg-N/ha in 1980) occurs in the northeastern states of New York, New Jersey, and Pennsylvania. High deposition rates in Northeastern U.S. have severely impacted the ecosystem, causing the degradation of forested land, the acidification of surface waters, and perturbation of the natural nitrogen cycle (Kahl et al., 2004; Lloret & Valiela, 2016). Temporally, atmospheric deposition has been decreasing across the CONUS since the mid-1990s, primarily due to regulations on NO_X emissions, such as the Clean Air Act amendments in 1990 (Houlton et al., 2013; Lloret & Valiela, 2016). The rate of decline is highest for the eastern states with the highest deposition rates and the lowest in the western states. A 62% decrease in atmospheric deposition in the eastern states corresponds to a decline in N surplus magnitudes over the last two decades in these regions (Figure 2).

The trends in livestock N excretion across the CONUS show a clear transition from a more diversified agricultural landscape, where small farms and livestock operations coexisted across the country (Dimitri et al., 2005), to more concentrated animal operations that characterize the current landscape (Figure 7c). This transition is especially apparent in clusters 1 and 2 that corresponds to 4% of the area but 26% of the inputs in 2017. Both clusters 1 and 2 document the increase in inputs over time, with cluster 2 plateauing after the 1980s, while cluster 1 increases continuously over the entire timeframe. This trend is indicative of the industrialization of the agricultural system towards more concentrated animal feeding operations (CAFOs), as well as shifts in cattle diets from traditional (free-range and poorly fed animals) to modern operations (confined and well-fed animals). In contrast to these increasing trends, magnitudes of inputs in clusters 3, 4, and 5 are lower, and they are decreasing over time. This increasing trend in clusters 1 and 2, coupled with a decreasing trend in clusters 3 to 6 has contributed to a greater range of livestock N inputs in 2017 (0 to 172 kg-N/ha) compared to a more homogenized landscape in 1930 (0 to 23 kg-N/ha). Cluster 1 and 2 include counties in Wisconsin, Iowa, Nebraska, Texas, and California. Clusters 3 and 4 are most common in Texas, Iowa, Missouri, and Kansas, specifically counties that have smaller livestock operations or that contain livestock that produces manure with lower N content. Whereas, counties in clusters 5 and 6 that have little to no manure N inputs are most common in the Great Plains states and much of the south and southeast.

Crop uptake is the only N output pathway in our analysis, and the spatiotemporal patterns of uptake closely mimic fertilizer and BNF patterns (Figure 7d). We identified 5 clusters of the crop uptake output component, with clusters 1 and 2 having the largest crop removal magnitudes of 148 kg-N/ha/yr and 100 kg-N/ha/yr in 2017 and accounting for 22.6% and 24.5% of uptake at the U.S. scale, despite occupying only 3.6% and 5.8% of the overall area, respectively. Counties in these clusters also show a significant drop in uptake in 2012 induced by reduced yields from the drought (Rippey, 2015). Cluster 4 contains the low productivity cropland areas, with N outputs increasing from a median of 9 kg-N/ha/yr in 1930 to 20 kg-N/ha/yr in 2017. Cluster 4 corresponds to the Great Plains and eastern inland counties. Whereas, cluster 5 also contains low productivity counties; however, cluster median magnitudes are significantly lower, ranging from 3.7 kg-N/ha/yr to 6.4 kg-N/ha/yr. Cluster 5 is the dominant cluster in the interior western U.S., and the area outside of the dominant agricultural areas (Midwest, Mississippi Alluvial Plains, Great Plains, and the Central Valley in California).

Fertilizer N input is the second-largest component of the N budget after human waste, and has significantly increased since the 1940s, following the use of the Haber Bosch process for fertilizer production and the increased demands on food and feed (Figure 7e) (Dimitri et al., 2005; Houlton et al., 2013; Cao et al., 2018). This component is described by five modes of behavior (Figure 7e), with cluster 1 and 2 with the largest inputs also showing some of the steepest increase in N since the 1940s (1.42 kg-N/ha/yr/yr and 0.29 kg-N/ha/yr/yr for cluster 1 and 2, respectively). Spatially, clusters 1 and 2 are found in the highest density in the Mississippi River Basin (corn belt in the Midwestern U.S. and Mississippi Alluvial Plain) and the Central Valley in California. These areas have seen an almost exponential increase in area under cultivation agriculture owing to the presence of highly productive soils and climate suitable for agricultural intensification (Yu & Lu, 2018). The other clusters with lower inputs surround these highly productive areas and contain counties in Delaware, Virginia, Alabama, Georgia, and South and North Carolina, Texas, California, and Washington. Finally, the last cluster corresponds to the inland Western U.S. grassland and shrubland that have limited agriculture due to unfavorable conditions and water limitations. They also correspond to forested areas, protected reserves, and mountainous terrain (Waisanen & Bliss, 2002).

Trends in BNF are similar to fertilizer inputs, with increasing trends apparent in all 6 clusters (Figure 7f), corresponding to increasing land under the N fixing crops, particularly soybean. The crops contributing to BNF have changed over time; however, BNF nationally dominated by soybeans and alfalfa hay in 1930 through to 2017. While alfalfa hay BNF has doubled since 1930, soybean BNF has increased 500 times from 1930 to

2017. The national landscape dominated by alfalfa hay in the 1930s accounts for 54% of total BNF, while currently, soybean accounts for 79%, and it was only in 1968 where mass fixed by soybean exceeded that of alfalfa hay. There is a sudden drop in BNF values in 2012, and this corresponds to the drought in the Midwest that reduced the yield of N-fixing crops (Rippey, 2015). It is interesting to note that the magnitude of BNF can be as high as fertilizer N inputs, with maximum values being greater than 120 kg-N/ha for both categories. Given the recent expansion of N fixing crops, it is thus critical to better understand the uncertainty in these BNF estimates, as well as the role of these crops to N pollution.

3.3 Typologies of Nitrogen Surplus across the U.S.

We found four dominant modes of behavior for N Surplus trajectories across the CONUS - crop dominated, livestock dominated, human waste dominated, and minimally impacted (ex. forests or desert) (Figure 8 and Figure 9). Our machine learning algorithm identified 10 clusters of county-scale N surplus trajectories, with three clusters that are crop dominated, four that are livestock dominated, two that are urban dominated, and one that has minimal impact.

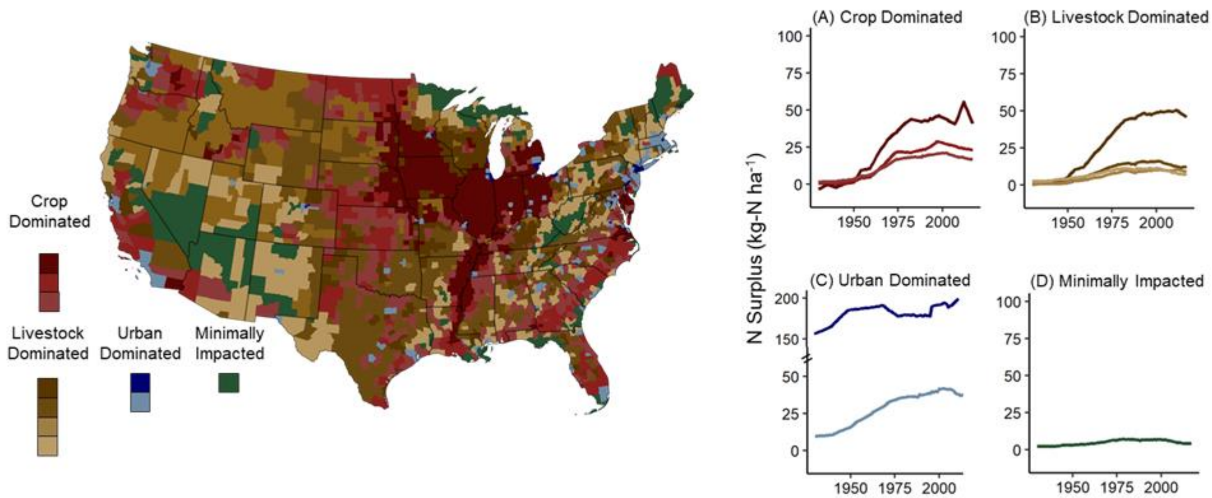

Figure 8. N Surplus clusters across the Conterminous U.S. Our results suggest 10 primary clusters, with the clusters differentiated by N surplus magnitude and the dominant input component. Three of the clusters are dominated by crop production (a), four by livestock production (b), two by human waste flows in more urban counties (c), and one by atmospheric deposition in relatively less disturbed landscapes (d). The typologies are not based on any quantitative comparison; however, when coupling patterns of inputs and land use across the clusters, clear patterns emerge**.**

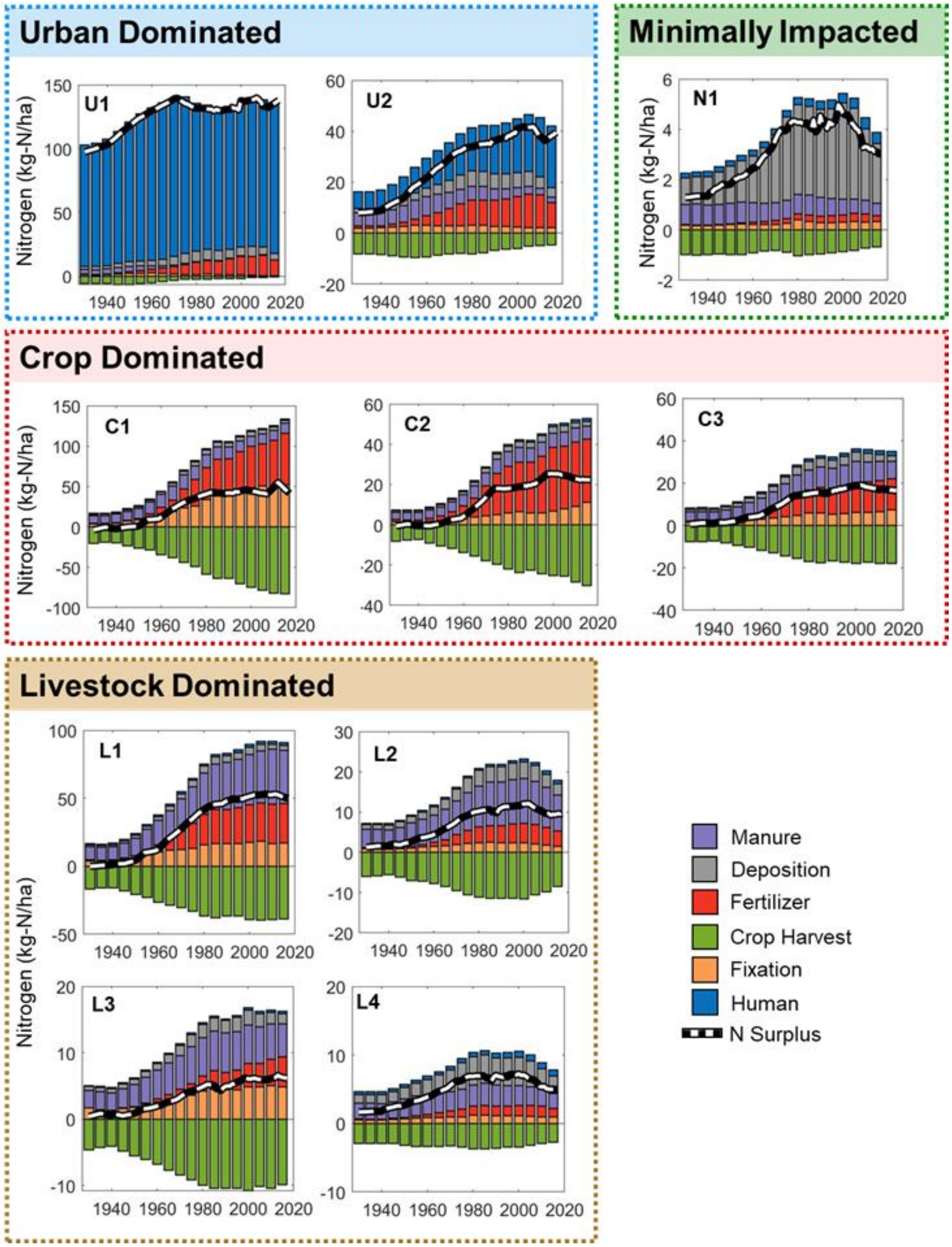

Figure 9. Cluster component time series aggregated into the four typologies. Each bar is an average of 5 years of data, and N surplus (black and white line) is the annual N surplus for the cluster. Shorthand or the clusters include U corresponds to urban dominated, M corresponds to minimally impacted, C corresponds to crop dominated, and lastly, L corresponds to livestock dominated.

Human waste comprises 87% and 44% of the N inputs for the two urban dominated clusters U1 and U2. Cluster U1 encompasses large urban centers like New York, Cleveland, Chicago, Denver, and San Francisco, while cluster U2 comprises counties with urban cores, such as Los Angeles, Miami, Houston, and Dallas and Fort Worth, surrounded by more peri-urban areas. The magnitude of N surplus for U1 is three times greater that of U2, and it has remained relatively constant over the last two decades. The stable N surplus is a reflection of the stable population trends (U.S. Census Bureau, 2016). Cluster U2, however, shows a slight decrease in N surplus over the last decade, and this can be attributed primarily to the decrease in atmospheric deposition in this cluster. The effect of the decrease in atmospheric N deposition is even more apparent in the trajectories of the minimally affected cluster M1, where the N surplus magnitudes are low and dominated by atmospheric deposition. The cluster M1 characterizes counties that are minimally impacted by anthropogenic nitrogen sources, including forested areas in Michigan or Vermont, or unproductive arid land in southern Nevada and east of the Sierra Nevada mountain range.

N surplus magnitudes are the largest in C1 (mean N surplus of 41.3 kg-N/ha/yr in 2017), followed by C2 (mean N surplus of 22.2 kg-N/ha/yr in 2017) and C3 (mean N surplus of 16.4 kg-N/ha/yr in 2017). The lower N surplus in C3 is driven by less productive agricultural areas or mixed land-use in the counties. The trajectories in all these clusters show an increasing trend after the 1940s (Section 3.2), and a plateauing, or even a slight decrease in N surplus values in the most recent years. The cropland cluster C1 encompasses counties dominated by corn and soybean production in Illinois, Indiana, and Iowa. Cluster C2 includes counties in a slightly less productive area or have heterogeneous land use areas in California, Florida, southeastern states, North Dakota, and Kansas. Cluster C3 is found across the country and is generally not localized as with the C1 and C2. Fertilizer and BNF are the principal inputs for clusters C1 and C2 (74.8% for C1 and 70.2% for C2), while the inputs in cluster C3 are split equally between livestock and cropland.

Counties in the livestock dominated clusters (L1, L2, L3, L4) are found in larger proportions in the Great Plains and the eastern states. Cluster L1 is a mixed input cluster, with manure contributing 44%, and fertilizer and BNF contributing 25.6% and 19.9% of the inputs, respectively. This cluster is distributed across the country but has a higher density in the states of Wisconsin, Texas, Kentucky, and Iowa. N surplus magnitudes are the highest in L1 (37.7 kg-N/ha/yr in 2017), followed by L2 (11.5 kg-N/ha/yr in 2017), L3 (7 kg-N/ha/yr) and L4 (6.9 kg-N/ha/yr). Counties in cluster L2 are in the Great Plains and Southeast, predominantly in Texas and Oklahoma, and has a higher contribution by manure with an average 51.5% of total inputs. Finally, counties characterized by L3 and L4 are primarily in the arid inland western U.S., particularly in Arizona, Colorado, Utah, and New Mexico, and parts of eastern U.S. These clusters are dominated by low productivity agricultural or pastureland with manure contributing 40% and 33% of total inputs. For Cluster L4, atmospheric N deposition rates contribute to 36% of N inputs. Along with low magnitudes and mixed inputs, L4 can be considered a transition cluster between livestock dominated typology and the minimally impacted typology.

Clustering of the dominant modes of N input across the conterminous U.S. helps provide insight into primary causes for N pollution and can guide better management decisions. For example, to reduce N load in a watershed dominated by cluster H1 (human dominated), one would need to focus on upgrades to wastewater treatment plants (WWTP). Whereas manure management would possibly yield the maximum benefit in a watershed dominated by cluster L1 and L2. The close spatial proximity of the livestock dominated cluster L2 and the cropland clusters C1 and C2 highlight opportunities for manure redistribution on croplands. Usage of manure as a nutrient source as opposed to waste reduces the demand for inorganic fertilizers and provide an end-use for manure. Indeed, recent studies have shown the economic feasibility of manure redistribution (Werenka, 2019). Instead of an ad hoc approach to implementation of nutrient reduction strategies, watersheds could optimize returns on investment by approaching strategy implementation based on the dominant typology. Approaching management through typologies framework can also provide insight into timelines of response. Areas with non-point sources found in as crop dominated and livestock dominated, typologies are at higher risk of lag times between management practice implementation and achieving improvements in water quality.

3.4 Addressing Risk and Legacy N with Cumulative N Surplus

The N surplus trajectories were then used to estimate the cumulative N surplus, which provides an upper bound for legacy N accumulation over the timeframe 1930 to 2017. Such cumulative surpluses are commonly estimated for phosphorus, while for N, the prevailing paradigm has been that the annual N surplus is lost through riverine export and denitrification, such that there is no net surplus accumulation (Billen et al., 2009; Bouwman et al., 2013; Swaney et al., 2012; Arrouays & Pelissier, 1994; Baker et al., 2007; Billen et al., 2009; Gál et al., 2007). This paradigm has been challenged in recent papers that have provided evidence of organic nitrogen build up in the soil root zone, vadose zone, and groundwater pools (Ascott et al., 2017, 2016; J. B. Gardner & Drinkwater, 2009; Kroeze et al., 2003; Sebilo et al., 2013; Van Meter et al., 2017, 2016; Worrall et al., 2015).

We focused specifically on the agricultural N surplus in our cumulative surplus estimation since it excludes human waste that is mostly treated in WWTPs and directly discharged into streams (Figure 10). Studies in the Mississippi River basin, Lake Michigan drainage basin, and in eastern U.S. watersheds have estimated N loss to riverine export to be between 20% and 29% of total inputs (Boyer et al., 2002; Han & Allan, 2008; Hong et al., 2013; Howarth et al., 2002, 2006; Ilampooranan et al., 2019; Swaney et al., 2012; Van Breemen et al., 2002). By removing the fraction of N removed annually through riverine export, it improves our estimates cumulative mass in the landscape. While accounting for denitrification could further improve estimates, denitrification rates are highly uncertain and spatiotemporally variable. Thus, we have omitted this step. As a result, the estimate is an upper bound of the mass of legacy N that can accumulate in our soil and groundwater.

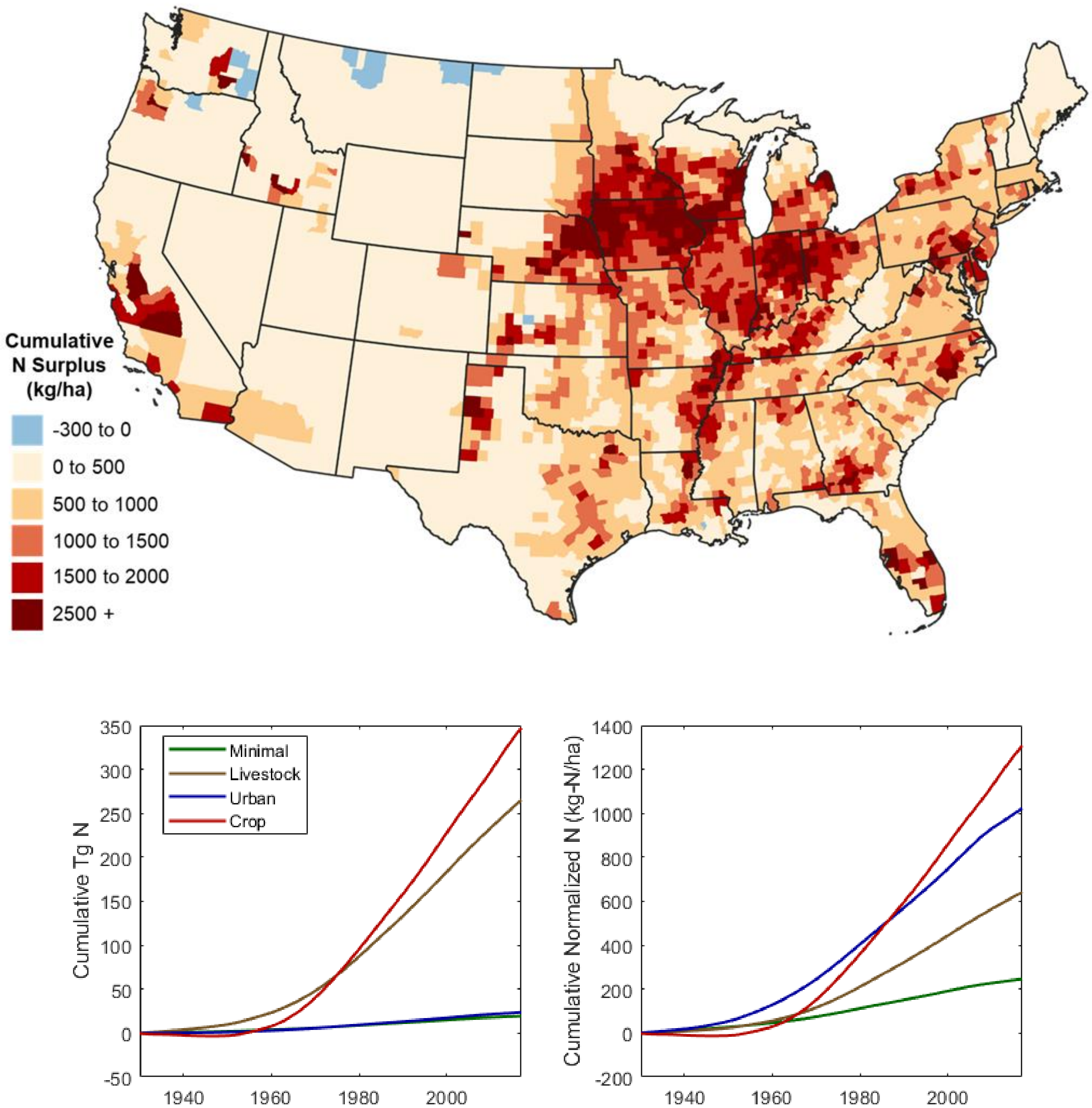

Figure 10. Cumulative agriculture N surplus includes N inputs of fertilizer, fixation, atmospheric deposition, and livestock manure, with the only output value as the crop uptake N removal. (a) The spatial distribution across the CONUS of cumulative agricultural N surplus, (b) the cumulative mass and normalized mass for the typologies outlined in Section 3.3.

Higher risk of legacy N in the landscape corresponds to the intensively cropped area in the U.S (Figure 10a). We found the cumulative N surplus to range from -300 to over 2,500 kg-N/ha, with hotspots concentrated along the Mississippi River, and in the Midwest, Florida, California, and the Northeastern states of Delaware and Maryland. The maximum cumulative N surplus is 5,678 kg-N/ha and 5,147 kg-N/ha in Cuming County, NE, and Sioux County, IA, respectively. Evidence of increases in N stores in the subsurface has been documented in national and global scale studies. A total N mass balance study, including denitrification exports, in the Thames, UK catchment had increasing subsurface N stores of 55 kg-N/ha/yr over 35 years (1,925 kg-N/ha)(Worrall et al., 2015).

Furthermore, soil studies in Iowa and Illinois found that in agriculture areas, SON has been increasing at rates of 30.8 ± 11.4 kg-N/ha/yr, and 70.3 ± 10.0 kg-N/ha/yr, respectively (Van Meter et al., 2016). Similarly, modeling of the Mississippi River Basin found increasing groundwater stores (2.25 kg-N/ha/yr) of N and increasing fluxes of N to the SON (6 kg-N/ha/yr) between 1925 and 2014, both indicating increasing cumulative N in the watershed. A study of global patterns of N storage in the unsaturated zone has estimated N storage of 4,000 kg-N/ha in the U.S., particularly the Great Plains.

N accumulation trajectories show distinct patterns in the four cluster typologies, with maximum apparent in the cropland cluster, followed by livestock, with urban and minimally impacted areas having similar magnitudes. Interesting to note that while the urban dominated cluster does not contain many counties, their normalized area inputs are comparable to those of crop dominated clusters. Approximately 600 kg-N/ha of the total cumulative mass can be attributed to urban fertilizer use. Urban fertilizer use is rarely considered explicitly in mass balance studies; however, it can contribute significant N to surface water and groundwater systems. N budget study of seven urban subwatersheds of the Mississippi River in the Capitol Region Watershed found that domestic use of nutrients dominated urban inputs (Hobbie et al., 2017). In fact, household fertilizer in the watersheds accounted for 37 to 59% of total N inputs. In the study, N export was calculated by using export from storm drains, runoff, and baseflow. Budgets of the watersheds estimated rate of N retention (including denitrification removal) ranging from 19.5 kg-N/ha/yr to 53 kg-N/ha/yr (Fissore et al., 2012; Hobbie et al., 2017). Thus, in urban areas, legacies in groundwater and soil pools can be extensive. While our agriculture N surplus demonstrates legacies in urban counties, improving the estimates of urban fertilization and including other sources is necessary for a more accurate estimate. However, evidently, further investigation into the impacts of urban fertilizer use is crucial when considering N management.

Interestingly, areas that are clustered under minimally impacted in the previous section, particularly in Eastern U.S., have cumulative stock ranging between 500 and 1000 kg-N/ha. Years of elevated N deposition has caused the accumulative in these minimally impacted areas. While cumulative N stock magnitudes is a fraction of those in the intensively cropped area in the U.S., N can still have resounding impact on forested ecosystems by perturbing natural N cycling, decreasing the pH of soils, acidifying surface waters, and altering community of trees (Driscoll et al., 2001; Lloret & Valiela, 2016).

The spatial patterns of cumulative N surplus correspond well with patterns of elevated nitrate concentrations in aquifers (N. Dubrovsky et al., 2010). Based on our cumulative N surplus results, it is evident that many counties within the High Plains aquifer region are at high risk of having legacy N in the subsurface. Groundwater monitoring in the High Plains aquifer from 1999 to 2004 revealed concentrations exceeding background nitrate levels (4 mg-N/L) in 90% of the wells tested in the north, 60% in the central, and 55% in the southern region (Gurdak, 2009).

While significant uncertainty remains regarding the magnitude of the estimate of N accumulation, the present results suggest that legacy N is, at varying degrees, impacting most counties in the U.S. The cumulative N surplus can provide insight into agronomic regions that are at risk of having legacy stores of N that could lead to groundwater or surface water contamination. Outlining such areas can allow for management practices to be adopted to address legacy N in the landscape that can be tailored to have the highest return on investment, both economically and environmentally.

4.0 Conclusions

The overall objective of the study was to compile a conterminous U.S. county-scale dataset of N inputs and outputs, over a relatively long period (1930 to 2017), to understand the temporal and spatial distribution of legacy N across the CONUS. In the last 88 years, the magnitude and distribution of N surplus, quantified as the difference between N inputs and outputs, have changed drastically. In 1930 N surplus hotspots were urban centers, including New York with N surplus rates exceeding 1000 kg-N/ha/yr. Since the 1940s, N surplus has increased in the Midwest, driven by the intensification of agriculture and the concentration of animal operations. Today, national N surplus magnitudes are 24-times greater than magnitudes in the 1930s. While urban areas still have significant N surpluses, wastewater treatment plants remove large portions of N. In contrast, agricultural N inputs result in the accumulation of legacy N.

The magnitudes and hot spots of N surplus can elucidate areas potentially at risk. However, understanding the drivers of the magnitudes and hotspots is essential for decision-making. For that reason, we developed typologies to group counties that have similar N surplus magnitudes and drivers. The four typologies include (1) urban dominated, (2) crop dominated, (3) livestock dominated, and (4) minimally impacted landscapes. Spatially, the Midwest, California, Florida, and Southeastern U.S. are predominant in the crop dominated typology. Livestock dominated counties are generally found more in Wisconsin and the Great Plains. Minimally impacted counties coincide with areas that are too arid to support agriculture or uninhabited forested area. Urban dominated typologies are distributed across the U.S., generally accounting for counties with large cities with high population densities.

Using typologies to cluster counties can provide insight into primary causes for N pollution. Understanding the source of N in the county or watershed can guide better management decisions. For example, reducing N loads in a watershed for the urban typology requires upgrades in wastewater treatment plants. Whereas, in the crop or livestock dominant typologies, agriculture best management practices (i.e., manure management and fertilizer use reduction) would yield the maximum benefit.

We furthermore used the N surplus trajectories to estimate the cumulative agricultural N surplus over the past 88 years, which provides an upper bound of the of the potential legacy N stores in the landscape. Unsurprisingly the highest levels of cumulative N surplus correspond to the areas in agriculture and livestock typologies. Furthermore, the spatial patterns of cumulative N surplus also correspond to many areas with high levels of groundwater NO3-. While significant uncertainty remains regarding the actual magnitude of the estimate of cumulative N, the present results suggest that legacy N is at varying degrees, impacting most counties in the U.S.

Billions of dollars spent on investment in the last few decades on watershed conservation measures, however, we have yet to see proportional improvements in water quality. Outlining such areas can allow for management practices to be adopted to address legacy N in the landscape and set realistic water quality goals by accounting for stores of N. Large investment and minimal returns have already led to disillusionment in stakeholders. Appropriately communicating uncertainties and limitations of water quality improvements to the stakeholders, authorities, and policymakers are essential to inspire confidence.

4.1 Future Work

This dataset allows for extensive analysis and is likely going to contribute to many future works. However, there are two projects in the foreseeable future. The current work focuses solely on spatiotemporal N surplus dynamics. However, coupling the inputs with water quality provides insight into the interaction of N with the landscape. Future work will include processing long term water quality data from over 300 watersheds (Oelsner et al., 2017). Although existing studies have conducted watershed-scale analysis of N surplus and export to understand trends and processes controlling N export (Boyer et al., 2002; Lin, Pearlstein, Compton, Matthews, & Leibowitz, 2016; Mehaffey et al., 2005; K. Schilling & Zhang, 2004; Swaney et al., 2012; Williams, King, & Fausey, 2015), due to the onerous data processing demand, these studies are often limited to fewer than 100 watersheds (Hong et al., 2013). With a dataset that begins before water quality measurements and extensive improved spatial coverage, we can expand on the existing analysis of water quality landscape drivers.

Secondly, this dataset will also be used to estimate time lags in watersheds across the U.S. using a similar approach to the analysis performed of the Grand River Watershed (Van Meter & Basu, 2017). In the Grand River watershed, using N surplus estimates and long-term water quality trajectories, subcatchment with legacy N stores showed nonlinear relationships between N inputs and outputs. The strong hysteresis effect is evidence of legacy N and decadal-scale lag times. We can scale up this approach by coupling water quality trajectories from the 300 watersheds with our N surplus trajectories.

References

Alexander, R. B., Smith, R. A., Schwarz, G. E., Boyer, E. W., Nolan, J. V., & Brakebill, J. W. (2008). Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. *Environmental Science & Technology*, *42*(3), 822–830.

Arrouays, D., & Pelissier, P. (1994). Changes in carbon storage in temperate humic loamy soils after forest clearing and continuous corn cropping in France. *Plant and Soil*, *160*(2), 215–223.

Aschebrook-Kilfoy, B., Heltshe, S. L., Nuckols, J. R., Sabra, M. M., Shuldiner, A. R., Mitchell, B. D., … Ward, M. H. (2012). Modeled nitrate levels in well water supplies and prevalence of abnormal thyroid conditions among the Old Order Amish in Pennsylvania. *Environmental Health: A Global Access Science Source*, *11*, 6.

Ascott, M. J., Gooddy, D. C., Wang, L., Stuart, M. E., Lewis, M. A., Ward, R. S., & Binley, A. M. (2017). Global patterns of nitrate storage in the vadose zone. *Nature Communications*, Vol. 8. https://doi.org/10.1038/s41467-017-01321-w

Ascott, M. J., Wang, L., Stuart, M. E., Ward, R. S., & Hart, A. (2016). Quantification of nitrate storage in the vadose (unsaturated) zone: a missing component of terrestrial N budgets. *Hydrological Processes*, *30*(12), 1903–1915.

Aubert, A. H., Gascuel-Odoux, C., Gruau, G., Akkal, N., Faucheux, M., Fauvel, Y., … Others. (2013). *Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study*. Retrieved from https://hal-insu.archives-ouvertes.fr/insu-00833564/

Baker, J. M., Ochsner, T. E., Venterea, R. T., & Griffis, T. J. (2007). Tillage and soil carbon sequestration—What do we really know? *Agriculture, Ecosystems & Environment*, *118*(1), 1–5.

Basu, N. B., Jindal, P., Schilling, K. E., Wolter, C. F., & Takle, E. S. (2012). Evaluation of analytical and numerical approaches for the estimation of groundwater travel time distribution. *Journal of Hydrology*, *475*, 65–73.

Behera, S. N., Sharma, M., Aneja, V. P., & Balasubramanian, R. (2013). Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. *Environmental Science and Pollution Research International*, *20*(11), 8092–8131.

Berndt, D. J., & Clifford, J. (1994). Using dynamic time warping to find patterns in time series. *KDD Workshop*, *10*, 359–370. Seattle, WA.

Billen, G., Thieu, V., Garnier, J., & Silvestre, M. (2009). Modelling the N cascade in regional watersheds: The case study of the Seine, Somme and Scheldt rivers. *Agriculture, Ecosystems and Environment*, *133*(3-4), 234–246.

Bouwman, A. F., Beusen, A. H. W., Griffioen, J., Van Groenigen, J. W., Hefting, M. M., Oenema, O., … Stehfest, E. (2013). Global trends and uncertainties in terrestrial denitrification and N_2O emissions. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, *368*(1621), 20130112.

Boyer, E. W., Goodale, C. L., Jaworski, N. A., & Howarth, R. W. (2002). Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A. *Biogeochemistry*, Vol. 57, pp. 137–169. https://doi.org/10.2307/1469687

Bristow, L. A., Mohr, W., Ahmerkamp, S., & Kuypers, M. M. M. (2017). Nutrients that limit growth in the ocean. *Current Biology: CB*, *27*(11), R474–R478.

Brown, D. G., Johnson, K. M., Loveland, T. R., & Theobald, D. M. (2005). Rural Land-Use Trends in the Conterminous United States , 1950-2000 Published by : Ecological Society of America. *Ecological Applications: A Publication of the Ecological Society of America*, *15*(6), 1851–1863.

Caballero-Alfonso, A. M., Carstensen, J., & Conley, D. J. (2015). Biogeochemical and environmental drivers of coastal hypoxia. *Journal of Marine Systems*, *141*, 190–199.

Cao, P., Lu, C., & Yu, Z. (2018). Historical nitrogen fertilizer use in agricultural ecosystems of the contiguous United States during 1850–2015: application rate, timing, and fertilizer types. *Earth System Science Data*, *10*(2), 969–984.

Chen, N., Hong, H., Zhang, L., & Cao, W. (2008). Nitrogen sources and exports in an agricultural watershed in Southeast China. *Biogeochemistry*, *87*(2), 169–179.

Chesapeake Bay Foundation. (2019). *State of the Bay 2018*. Retrieved from Chesapeake Bay Foundation website: https://www.cbf.org/about-the-bay/state-of-the-bay-report/

Conley, D. J., Carstensen, J., Aigars, J., Axe, P., Bonsdorff, E., Eremina, T., Zillén, L. (2011). Hypoxia is increasing in the coastal zone of the Baltic Sea. *Environmental Science & Technology*, *45*(16), 6777–6783.

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., Likens, G. E. (2009). Ecology. Controlling eutrophication: nitrogen and phosphorus. Science, 323(5917), 1014–1015.

Crutzen, P. J. (2016). Geology of Mankind. In P. J. Crutzen & H. G. Brauch (Eds.), *Paul J. Crutzen: A Pioneer on Atmospheric Chemistry and Climate Change in the Anthropocene* (pp. 211–215). Cham: Springer International Publishing.

David, M. B., & Gentry, L. E. (2000). Anthropogenic Inputs of Nitrogen and Phosphorus and Riverine Export for Illinois, USA. *Journal of Environmental Quality*, *29*, 494–508.

Davidson, E. A., David, M. B., Galloway, J. N., Goodale, C. L., Haeuber, R., Harrison, J. A., … Others. (2011). Excess Nitrogen in the U.S. Environment: Trends, Risks, and Solutions. *Issues in Ecology*, (15). Retrieved from https://pubs.er.usgs.gov/publication/70032270

Diaz, R. J., & Rosenberg, R. (2008). Spreading dead zones and consequences for marine ecosystems. *Science* , *321*(5891), 926–929.

Dimitri, C., Effland, A., & Conklin, N. (2005). *The 20th Century Transformation of U.S. Agriculture and Farm Policy The 20th Century and Farm Policy: Economic Information Bulletin Number 3* (p. 14). Retrieved from http://www.ers.usda.gov/publications/EIB3/eib3.pdf

Driscoll, C. T., Lawrence, G. B., Bulger, A. J., Butler, T. J., Cronan, C. S., Eagar, C., … Weathers, K. C. (2001). Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management StrategiesThe effects of acidic deposition in the northeastern United States include the acidification of soil and water, which stresses terrestrial and aquatic biota. *Bioscience*, *51*(3), 180–198.

Dubrovsky, N., Burow, K., Clark, G., Gronberg, J., Hamilton, P., Hitt, K., … Others. (2010). Nutrients in the Nation’s Streams and Groundwater, 1992--2004, Circular 1350. *US Geological Survey, Reston, VA, USA*.

Dubrovsky, N. M., Burow, K. R., Clark, G. M., Gronberg, J. M., Hamilton, P. A., Hitt, K. J., … Wilber, W. G. (2010). *The quality of our Nation’s waters: Nutrients in the Nation's streams and groundwater, 1992-2004*. https://doi.org/10.3133/cir1350

Dugan, H. A., Bartlett, S. L., Burke, S. M., Doubek, J. P., Krivak-Tetley, F. E., Skaff, N. K., … Weathers, K. C. (2017). Salting our freshwater lakes. *Proceedings of the National Academy of Sciences of the United States of America*, *114*(17), 4453–4458.

Dupas, R., Minaudo, C., Gruau, G., Ruiz, L., & Gascuel-Odoux, C. (2018). Multidecadal Trajectory of Riverine Nitrogen and Phosphorus Dynamics in Rural Catchments. *Water Resources Research*, *54*(8), 5327–5340.

Ehrhardt, S., Kumar, R., Fleckenstein, J. H., Attinger, S., & Musolff, A. (2019). Trajectories of nitrate input and output in three nested catchments along a land use gradient. *Hydrology and Earth System Sciences*, *23*(9), 3503–3524.

Filoso, S., Martinelli, L. A., Williams, M. R., Lara, L. B., Krusche, A., Victoria Ballester, M., … de Camargo, P. B. (2003). Land use and nitrogen export in the Piracicaba River basin, Southeast Brazil. *Biogeochemistry*, *65*(3), 275–294.

Fissore, C., Hobbie, S. E., King, J. Y., McFadden, J. P., Nelson, K. C., & Baker, L. A. (2012). The residential landscape: fluxes of elements and the role of household decisions. *Urban Ecosystems*, *15*(1), 1–18.

Follet, R. F. (1995). Fate and transport of nutrients: nitrogen. USDA. *Agricultural Research Service, Soil-Plant-Nutrient Research Unit, Working Paper*, (7). Retrieved from https://www.nrcs.usda.gov/wps/portal/nrcs/detail/national/landuse/crops/?cid=nrcs143_014202

Gál, A., Vyn, T. J., Michéli, E., Kladivko, E. J., & McFee, W. W. (2007). Soil carbon and nitrogen accumulation with long-term no-till versus moldboard plowing overestimated with tilled-zone sampling depths. *Soil and Tillage Research*, *96*(1), 42–51.

Galloway, J. N. (1998). The global nitrogen cycle: Changes and consequences. *Environmental Pollution* , *102*(SUPPL. 1), 15–24.

Galloway, J. N. (2003). *The Global Nitrogen Cycle. Chap 8.12* (pp. 557–583; H. Hooland & K. K. Turekian, Eds.). London: Elsevier.

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., & Cosby, B. J. (2003). The Nitrogen Cascade. *Bioscience*, *53*(4), 341–356.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., … Smarty, R. (2004). *Nitrogen cycles: past, present, and future*. Retrieved from https://dornsife.usc.edu/assets/sites/125/docs/Galloway_et_al_2004_BGC.pdf

Galloway, J. N., Schlesinger, W. H., Ii, H. L., Schnoor, L., & Tg, N. (1995). Nitrogen fixation: Anthropogenic enhancement-environmental response reactive N. *Global Biogeochemical Cycles*, *9*(2), 235–252.

Gardner, J. B., & Drinkwater, L. E. (2009). The fate of nitrogen in grain cropping systems: a meta-analysis of 15N field experiments. *Ecological Applications: A Publication of the Ecological Society of America*. Retrieved from https://esajournals.onlinelibrary.wiley.com/doi/abs/10.1890/08-1122.1

Gardner, J. R., Pavelsky, T. M., & Doyle, M. W. (2019). The Abundance, Size, and Spacing of Lakes and Reservoirs Connected to River Networks. *Geophysical Research Letters*, *46*(5), 2592–2601.

Goyette, J.-O., Bennett, E. M., Howarth, R. W., & Maranger, R. (2016). Changes in anthropogenic nitrogen and phosphorus inputsto the St. Lawrence sub-basin over 110 yearsand impacts on riverine export. *Global Biogeochemical Cycles*, *18*(3), 1088–1089.

Green, P. A., Vörösmarty, C. J., Meybeck, M., Galloway, J. N., Peterson, B. J., & Boyer, E. W. (2004). Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on typology. *Biogeochemistry*, *68*(1), 71–105.

Gschwandtner, G., Gschwandtner, K., Eldridge, K., Mann, C., & Mobley, D. (1986). Historic Emissions of Sulfur and Nitrogen Oxides in the United States from 1900 to 1980. *Journal of the Air Pollution Control Association*, *36*(2), 139–149.

Gurdak, J. J. (2009). *Water Quality in the High Plains Aquifer, Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming, 1999-2004*. U.S. Geological Survey.

Haag, D., & Kaupenjohann, M. (2001). Landscape fate of nitrate fluxes and emissions in Central Europe A critical review of concepts, data, and models for transport and retention. *Agriculture, Ecosystems and Environment*, *86*, 1–21.

Hamilton, S. K. (2012). Biogeochemical time lags may delay responses of streams to ecological restoration. *Freshwater Biology*, *57*(s1), 43–57.

Han, H., & Allan, J. D. (2008). Estimation of nitrogen inputs to catchments: comparison of methods and consequences for riverine export prediction. *Biogeochemistry*, *91*(2), 177–199.

Harter, T., Davis, H., Mathews, M. C., & Meyer, R. D. (2002). Shallow groundwater quality on dairy farms with irrigated forage crops. *Journal of Contaminant Hydrology*, *55*(3-4), 287–315.

Hobbie, S. E., Finlay, J. C., Janke, B. D., Nidzgorski, D. A., Millet, D. B., & Baker, L. A. (2017). Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. *Proceedings of the National Academy of Sciences of the United States of America*, *114*(16), 4177–4182.

Hong, B., Swaney, D. P., & Howarth, R. W. (2011). A toolbox for calculating net anthropogenic nitrogen inputs (NANI). *Environmental Modelling and Software*, *26*(5), 623–633.

Hong, B., Swaney, D. P., & Howarth, R. W. (2013). Estimating net anthropogenic nitrogen inputs to U.S. watersheds: Comparison of methodologies. *Environmental Science and Technology*, *47*(10), 5199–5207.

Hong, B., Swaney, D. P., Mörth, C. M., Smedberg, E., Eriksson Hägg, H., Humborg, C., … Bouraoui, F. (2012). Evaluating regional variation of net anthropogenic nitrogen and phosphorus inputs (NANI/NAPI), major drivers, nutrient retention pattern and management implications in the multinational areas of Baltic Sea basin. *Ecological Modelling*, *227*, 117–135.

Houlton, B. Z., Boyer, E. W., Finzi, A., Galloway, J., Leach, A., Liptzin, D., … Townsend, A. R. (2013). Intentional versus unintentional nitrogen use in the United States: Trends, efficiency and implications. *Biogeochemistry*, *114*(1-3), 11–23.

Howarth, R. W. (2008). Coastal nitrogen pollution: A review of sources and trends globally and regionally. *Harmful Algae*, *8*(1), 14–20.

Howarth, R. W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., … Zhao-Liang, Z. (1996). Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Nitrogen Cycling in the North Atlantic Ocean and Its Watersheds*, pp. 75–139. https://doi.org/10.1007/978-94-009-1776-7_3

Howarth, R. W., Boyer, E. W., Pabich, W. J., & Galloway, J. N. (2002). Nitrogen Use in the United States from 1961–2000 and Potential Future Trends. *AMBIO: A Journal of the Human Environment*, *31*(2), 88–96.

Howarth, R. W., Chan, F., Conley, D. J., Garnier, J., Doney, S. C., Marino, R., & Billen, G. (2011). Coupled biogeochemical cycles: Eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. *Frontiers in Ecology and the Environment*, *9*(1), 18–26.

Howarth, R. W., Swaney, D. P., Boyer, E. W., Marino, R., Jaworski, N., & Goodale, C. (2006). The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. *Biogeochemistry*, *79*(1-2), 163–186.

IEPA, IDOA, & University of Illinois Extension. (2015). *Illinois Nutrient Loss Reduction Strategy*. Retrieved from Illinois Environmental Protection Agency and Illinois Department of Agriculture; Springfield, Illinois. website: https://www2.illinois.gov/epa/Documents/iepa/water-quality/watershed-management/nlrs/nlrs-final-revised-093115.pdf

IEPA, IDOA, & University of Illinois Extension. (2017). *Illinois Nutrient Loss Reduction Strategy: Biennial Report (2015-2017)*. Retrieved from Illinois Environmental Protection Agency and Illinois Department of Agriculture; Springfield, Illinois. website: http://www2.illinois.gov/epa/

Ilampooranan, I. (2019). *Modeling Nutrient Legacies and Time Lags in Agricultural Landscapes: A Midwestern Case Study*. Retrieved from https://uwspace.uwaterloo.ca/handle/10012/14652

Ilampooranan, I., Van Meter, K. J., & Basu, N. B. (2019). A Race Against Time: Modeling Time Lags in Watershed Response. *Water Resources Research*, *475*, 65.

INRC. (2019). *Iowa Nutrient Reduction Strategy 2017-18 Annual Progress Report*.

Jaworski, N. A., Howarth, R. W., & Hetling, L. J. (1997). *Atmospheric Deposition of Nitrogen Oxides onto the Landscape Contributes to Coastal Eutrophication in the Northeast United States*. https://doi.org/10.1021/ES960803F

Johnson, K. M. (n.d.). *Reports on America: The Rural Rebound* (No. Vol 3.). Retrieved from Population Reference Bureau website: https://www.prb.org/theruralrebound/

Juntakut, P., Snow, D. D., Haacker, E. M. K., & Ray, C. (2019). The long term effect of agricultural, vadose zone and climatic factors on nitrate contamination in Nebraska's groundwater system. *Journal of Contaminant Hydrology*, Vol. 220, pp. 33–48. https://doi.org/10.1016/j.jconhyd.2018.11.007

Kahl, J. S., Stoddard, J. L., Haeuber, R., Paulsen, S. G., Birnbaum, R., Deviney, F. A., … Urquhart, N. S. (2004). Have U.S. surface waters responded to the 1990 Clean Air Act amendments? *Environmental Science & Technology*, *38*(24), 484A – 490A.

Keogh, E. J., & Pazzani, M. J. (1999). Scaling up Dynamic Time Warping to Massive Datasets. *Principles of Data Mining and Knowledge Discovery*, 1–11. Springer Berlin Heidelberg.

Kroeze, C., Aerts, R., van Breemen, N., van Dam, D., Hofschreuder, P., Hoosbeek, M., … de Vries, W. (2003). Uncertainties in the fate of nitrogen I: An overview of sources of uncertainty illustrated with a Dutch case study. *Nutrient Cycling in Agroecosystems*, *66*(1), 43–69.

Lewis, W. M., Wurtsbaugh, W. A., & Paerl, H. W. (2011). Rationale for control of anthropogenic nitrogen and phosphorus to reduce eutrophication of inland waters. *Environmental Science and Technology*, *45*(24), 10300–10305.

Lin, J., Pearlstein, S., Compton, J., Matthews, W., & Leibowitz, S. (2016). *Nitrogen balance and use efficiency in the Calapooia River Watershed, Oregon, United States*. (December), 2–5.

Liu, C., Watanabe, M., & Wang, Q. (2008). Changes in nitrogen budgets and nitrogen use efficiency in the agroecosystems of the Changjiang River basin between 1980 and 2000. *Nutrient Cycling in Agroecosystems*, *80*(1), 19–37.

Li, Y., Schichtel, B. A., Walker, J. T., Schwede, D. B., Chen, X., Lehmann, C. M. B., … Collett, J. L. (2016). Increasing importance of deposition of reduced nitrogen in the United States. *Proceedings of the National Academy of Sciences*, *113*(21), 5874–5879.

Lloret, J., & Valiela, I. (2016). Unprecedented decrease in deposition of nitrogen oxides over North America: the relative effects of emission controls and prevailing air-mass trajectories. *Biogeochemistry*, *129*(1-2), 165–180.

Long, J. H. (2010). Atlas of historical county boundaries. Retrieved May 1, 2018, from The Newberry Library Dr. William M. Scholl Center for American History and Culture website: http://publications.newberry.org/ahcbp/index.html

MacKay, D. J. C., & Mac, D. J. (2003). *Information Theory, Inference and Learning Algorithms*. Cambridge University Press.

MacQueen, J. (1967). Some methods for classification and analysis of multivariate observations. *Proceedings of the Fifth Berkeley Symposium on Mathematical Statistics and Probability*, *1*, 281–297. Oakland, CA, USA.

Marc Ribaudo. (2015). The Limits of Voluntary Conservation Programs. *Choices* , *30*(2), 1–5.

Marinos, R. E. (2018). *Ecosystem Recovery from Acid Precipitation: Carbon and Nitrogen Cycling in* (Duke University). Retrieved from https://dukespace.lib.duke.edu/dspace/bitstream/handle/10161/16959/Marinos_duke_0066D_14664.pdf?sequence=1&isAllowed=n

McLellan, E. L., Cassman, K. G., Eagle, A. J., Woodbury, P. B., Sela, S., Tonitto, C., … van Es, H. M. (2018). The Nitrogen Balancing Act: Tracking the Environmental Performance of Food Production. *Bioscience*, *68*(3), 194–203.

Meals, D. W., Dressing, S. A., Tech, T., Davenport, T. E., & Protection, U. S. E. (2010). Lag Time in Water Quality Response to Best Management Practices : A Review. *Journal of Environmental Quality*, (39), 85–96.

Mehaffey, M. H., Nash, M. S., Wade, T. G., Ebert, D. W., Jones, K. B., & Rager, A. (2005). Linking land cover and water quality in New York City's water supply watersheds. *Environmental Monitoring and Assessment*, *107*(1-3), 29–44.

Meisinger, J. J., Calderon, F. J., & Jenkinson, D. S. (2008). *Soil Nitrogen Budgets*. American Society of Agronomy Monograph Series.

Meisinger, J. J., & Randall, G. W. (1991). Estimating Nitrogen Budgets for Soil-Crop Systems. In R. F. Follett, D. R. Keeney, & R. M. Cruse, *Managing Nitrogen for Groundwater Quality and Farm Profitability* (pp. 85–124). Madison, WI: Soil Science Society of America.

Michalak, A. M., Anderson, E. J., Beletsky, D., Boland, S., Bosch, N. S., Bridgeman, T. B., … Zagorski, M. A. (2013). Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proceedings of the National Academy of Sciences of the United States of America*, *110*(16), 6448–6452.

Molenat, J., Gascuel-Odoux, C., Ruiz, L., & Gruau, G. (2008). Role of water table dynamics on stream nitrate export and concentration in agricultural headwater catchment (France). *Journal of Hydrology*, *348*(3), 363–378.

National Atmospheric Deposition Program. (2000). *Nitrogen In The Nation's Rain*. Retrieved from http://nadp.slh.wisc.edu/lib/brochures/nitrogen.pdf

National Atmospheric Deposition Program. (2018). NADP Total Deposition Maps. Retrieved February 1, 2019, from http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/

Nebraska Department of Environmental Quality. (n.d.). *2018 Nebraska Groundwater Quality Monitoring Report*. Retrieved from https://clearinghouse.nebraska.gov/CurrentReports/GW_Report_2018.11.29_web.pdf

Nolan, B. T., & Stoner, J. D. (2000). Nutrients in groundwaters of the conterminous United States, 1992- 1995. *Environmental Science & Technology*, *34*(7), 1156–1165.

Nosengo, N. (2003). Fertilized to death. *Nature*, *425*(6961), 894–895.

Oelsner, G. P., Sprague, L. A., Murphy, J. C., Zuellig, R. E., Johnson, H. M., Ryberg, K. R., … Farmer, W. H. (2017). *Water-Quality trends in the nation's rivers and streams , 1972 – 2012 — Data Preparation, Statistical Methods, and Trend Results Scientific Investigations Report 2017 – 5006*. https://doi.org/10.3133/sir20175006

Office of the New York State Comptroller: Division of Local Government Services & Economic Development. (2004). *Population Trends in New York State's Cities*. Retrieved from https://www.osc.state.ny.us/localgov/pubs/research/pop_trends.pdf

Orth, R. J., Dennison, W. C., Lefcheck, J. S., Gurbisz, C., Hannam, M., Keisman, J., … Wilcox, D. J. (2017). Submersed Aquatic Vegetation in Chesapeake Bay: Sentinel Species in a Changing World. *Bioscience*, *67*(8), 698–712.

Paerl, H. W. (2009). Controlling Eutrophication along the Freshwater–Marine Continuum: Dual Nutrient (N and P) Reductions are Essential. *Estuaries and Coasts*, *32*(4), 593–601.

Quynh, L. T. P., Billen, G., Garnier, J., Théry, S., Fézard, C., & Van Minh, C. (2005). Nutrient (N, P) budgets for the Red River basin (Vietnam and China). *Global Biogeochemical Cycles*, *19*(2). Retrieved from https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2004GB002405

Rabalais, N. N., Díaz, R. J., Levin, L. A., Turner, R. E., Gilbert, D., & Zhang, J. (2009). Dynamics and distribution of natural and human-caused coastal hypoxia. *Biogeosciences Discussions*, Vol. 6, pp. 9359–9453. https://doi.org/10.5194/bgd-6-9359-2009

Rabalais, N. N., & Turner, R. E. (2001). Hypoxia in the northern Gulf of Mexico: description, causes and change. *Coastal and Estuarine Studies*, 1–36.

Rabalais, N. N., Turner, R. E., & Scavia, D. (2002). Beyond Science into Policy: Gulf of Mexico Hypoxia and the Mississippi River: Nutrient policy development for the Mississippi River watershed reflects the …. *Bioscience*. Retrieved from https://academic.oup.com/bioscience/article-abstract/52/2/129/341059

Rabalais, N. N., Turner, R. E., & Wiseman, W. J. (2002). Gulf of Mexico Hypoxia, A.K.A. "The Dead Zone." *Annual Review of Ecology and Systematics*, *33*(1), 235–263.

Ramankutty, N., & Foley, J. A. (1999). Estimating historical changes in land cover:North American croplands from 1850 to 1992. *Global Ecology and Biogeography*, Vol. 8, pp. 381–396. https://doi.org/10.1046/j.1365-2699.1999.00141.x

Ravishankara, A. R., Daniel, J. S., & Portmann, R. W. (2009). Nitrous oxide (N2O): the dominant ozone-depleting substance emitted in the 21st century. *Science*, *326*(5949), 123–125.

Reckhow, K. H., Norris, P. E., Budell, R. J., Di Toro, D. M., Galloway, J. N., Greening, H., … Stacey, P. E. (2011). *Achieving Nutrient and Sediment Reduction Goals in the Chesapeake Bay*. Washington, D.C.: National Academies Press.

Reedy, R. C., & Scanlon, B. R. (2017). *Evaluation of Groundwater Nitrate Contamination in Public Water Systems and Major and Minor Aquifers in Texas*. Retrieved from https://pdfs.semanticscholar.org/a2ac/487df42b8e28a1b7dfbf9f1adc12d260191c.pdf

Reis, S., Pinder, R. W., Zhang, M., Lijie, G., & Sutton, M. A. (2009). Reactive nitrogen in atmospheric emission inventories – a review. *Atmospheric Chemistry and Physics Discussions*, Vol. 9, pp. 12413–12464. https://doi.org/10.5194/acpd-9-12413-2009

Rippey, B. R. (2015). The US drought of 2012. *Weather and Climate Extremes*, *10*, 57–64.

Ruiz, L., Abiven, S., Martin, C., Durand, P., Beaujouan, V., & Molénat, J. (2002). Effect on nitrate concentration in stream water of agricultural practices in small catchments in Brittany: II. Temporal variations and mixing processes. *Hydrology and Earth System Sciences*, Vol. 6, pp. 507–514. https://doi.org/10.5194/hess-6-507-2002

Schilling, K. E., & Wolter, C. F. (2007). A GIS-based groundwater travel time model to evaluate stream nitrate concentration reductions from land use change. *Environmental Geology*, *53*(2), 433–443.

Schilling, K., & Zhang, Y. K. (2004). Baseflow contribution to nitrate-nitrogen export from a large, agricultural watershed, USA. *Journal of Hydrology*, *295*(1-4), 305–316.

Schindler, D. W., Carpenter, S. R., Chapra, S. C., Hecky, R. E., & Orihel, D. M. (2016). Reducing Phosphorus to Curb Lake Eutrophication is a Success. *Environmental Science & Technology*, *50*(17), 8923–8929.

Schindler, D. W., & Fee, E. J. (1974). Experimental Lakes Area: Whole-Lake Experiments in Eutrophication. *Journal of the Fisheries Research Board of Canada*, *31*(5), 937–953.

Schlesinger, W. H., & Bernhardt, E. S. (2013). *Biogeochemistry: An Analysis of Global Change*. Elsevier/Academic Press.

Sebilo, M., Mayer, B., Nicolardot, B., Pinay, G., & Mariotti, A. (2013). Long-term fate of nitrate fertilizer in agricultural soils. *Proceedings of the National Academy of Sciences*, *110* (45), 18185–18189.

Smil, V. (1999a). Detonator of the population explosion. *Nature*, *400*(6743), 415–415.

Smil, V. (1999b). Nitrogen in crop production: An account of global flows. *Global Biogeochemical Cycles*, *13*(2), 647–662.

Sousa, M. R., Jones, J. P., Frind, E. O., & Rudolph, D. L. (2013). A simple method to assess unsaturated zone time lag in the travel time from ground surface to receptor. *Journal of Contaminant Hydrology*, *144*(1), 138–151.

Steffen, W., Richardson, K., Rockström, J., Cornell, S. E., Fetzer, I., Bennett, E. M., … Sörlin, S. (2015). Planetary boundaries: Guiding human development on a changing planet. *Science*, *347*(6223). https://doi.org/10.1126/science.1259855

Steinley, D. (2006). K-means clustering: A half-century synthesis. *British Journal of Mathematical and Statistical Psychology*, Vol. 59, pp. 1–34. https://doi.org/10.1348/000711005x48266

Subramanian, M. (2019). Anthropocene now: influential panel votes to recognize Earth's new epoch. *Nature*. https://doi.org/10.1038/d41586-019-01641-5

Swaney, D. P., Hong, B., Ti, C., Howarth, R. W., & Humborg, C. (2012). Net anthropogenic nitrogen inputs to watersheds and riverine N export to coastal waters: a brief overview. *Current Opinion in Environmental Sustainability*, *4*(2), 203–211.

The World Health Organization. (2010). *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans: Ingested Nitrate and Nitrite, and Cyanobacterial Peptide Toxins* (Vol. 94). Retrieved from https://monographs.iarc.fr/wp-content/uploads/2018/06/mono94.pdf

Tomer, M. D., & Burkart, M. R. (2003). Long-term effects of nitrogen fertilizer use on ground water nitrate in two small watersheds. *Journal of Environmental Quality*, *32*(6), 2158–2171.

Turner, R. E., & Rabalais, N. N. (2018). *2017 Forecast: Summer Hypoxic Zone Size Northern Gulf of Mexico*. Retrieved from https://gulfhypoxia.net/wp-content/uploads/2018/06/2018-forecast-4.pdf

U.S. Census Bureau. (2007). *Census U.S. Decennial County Population Data, 1900-1990*. Retrieved from http://www.nber.org/data/census-decennial-population.html

U.S. Census Bureau. (2016). *Census U.S. Intercensal County Population Data, 1970-2014*. Retrieved from https://www.nber.org/data/census-intercensal-county-population.html

USDA. (2017). *Ogallala Aquifer Initiative: 2017 Progress Report*. Retrieved from NRDC website: https://www.nrcs.usda.gov/Internet/FSE_MEDIA/nrcseprd1407817.pdf

USDA. (2018, February 21). Fertilizer Use and Price. Retrieved May 17, 2019, from United States Department of Agriculture Economic Research Service website: https://www.ers.usda.gov/data-products/fertilizer-use-and-price.aspx

USDA-NASS. (2017). *Census of Agriculture*. Retrieved from https://www.nass.usda.gov/AgCensus/index.php

USDA National Agricultural Statistics Service. (2019). Quick Stats Tools. Retrieved 2018, from United States Department of Agriculture National Agricultural Statistics Service Quick Stats website: https://www.nass.usda.gov/Quick_Stats/

USDA National Agricultural Statistics Service Cropland Data Layer. (2010). Published crop-specific data layer [Online]. Retrieved from USDA-NASS, Washington, DC. website: https://nassgeodata.gmu.edu/CropScape/

USEPA. (2017). *Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2017 Report to Congress*. Retrieved from https://www.epa.gov/sites/production/files/2017-11/documents/hypoxia_task_force_report_to_congress_2017_final.pdf

Ussiri, D. A., & Lal, R. (2013). *Global Nitrogen Cycle* (pp. 29–56).

Van Breemen, N., Boyer, E. W., Goodale, C. L., Jaworski, N. A., Paustian, K., Seitzinger, S. P., … Billen, G. (2002). Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern U.S.A. *Biogeochemistry*, *5758*, 267–293.

van Egmond, K., Bresser, T., & Bouwman, L. (2002). The European nitrogen case. *Ambio*, *31*(2), 72–78.

Van Meter, K. J. (2016). *The Nitrogen Legacy: Understanding Time Lags in Catchment Response as a Function of Hydrologic and Biogeochemical Controls*.

Van Meter, K. J., & Basu, N. (2017). Time lags in watershed-scale nutrient transport: an exploration of dominant controls. *Environmental Research Letters: ERL [Web Site]*, *12*(8), 084017.

Van Meter, K. J., Basu, N. B., & Van Cappellen, P. (2017). Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins. *Global Biogeochemical Cycles*, *31*(1), 2–23.

Van Meter, K. J., Basu, N. B., Veenstra, J. J., & Burras, C. L. (2016). The nitrogen legacy: emerging evidence of nitrogen accumulation in anthropogenic landscapes. *Environmental Research Letters: ERL [Web Site]*, *11*(3), 035014.

Van Meter, K. J., Van Cappellen, P., & Basu, N. B. (2018). Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico. *Science*, *360*(6387), 427–430.

Vero, S. E., Basu, N. B., Van Meter, K., Richards, K. G., Mellander, P.-E., Healy, M. G., & Fenton, O. (2017). Review: the environmental status and implications of the nitrate time lag in Europe and North America. *Hydrogeology Journal*, 1–16.

Vitousek, P., Aber, J., Howarth, R. W., Likens, G., Matson, P., Schindler, D., … Tilman, D. (1997). Technical Report: Human Alteration of the Global Nitrogen Cycle: Sources and Consequences. *Ecological Applications*, Vol. 7, pp. 737–750.

Vitousek, P. M., Mooney, H. A., Lubchenco, J., & Melillo, J. M. (1997). Human Domination of Earth's Ecosystems. *Science*, *277*(5325), 494–499.

Waisanen, P. J., & Bliss, N. B. (2002). Changes in population and agricultural land in conterminous United States counties, 1790 to 1997. *Global Biogeochemical Cycles*, *16*(4). Retrieved from https://onlinelibrary.wiley.com/doi/pdf/10.1029/2001GB001843

Ward, M. H. (2009). Too Much of a Good Thing? Nitrate from Nitrogen Fertilizers and Cancer. *Reviews on Environmental Health*, *24*(4), 324.

Ward, M. H., DeKok, T. M., Levallois, P., Brender, J., Gulis, G., Nolan, B. T., & VanDerslice, J. (2005). Workgroup report: drinking-water nitrate and health—recent findings and research needs. *Environmental Health Perspectives*, *113*(11), 1607–1614.

Ward, M. H., Mark, S. D., Cantor, K. P., Weisenburger, D. D., Correa-Villaseñor, A., & Zahm, S. H. (1996). Drinking water nitrate and the risk of non-Hodgkin's lymphoma. *Epidemiology* , *7*(5), 465–471.

Werenka, A. (2019). *Recoupling the Livestock Nutrient Economy: A Path forward for Water Quality Improvement* (University of Waterloo). Retrieved from https://uwspace.uwaterloo.ca/handle/10012/15109

Weyer, P. J., Cerhan, J. R., Kross, B. C., Hallberg, G. R., Kantamneni, J., Breuer, G., … Lynch, C. F. (2001). Municipal Drinking Water Nitrate Level and Cancer Risk in Older Women: The Iowa Women's Health Study. *Epidemiology*, Vol. 12, pp. 327–338. https://doi.org/10.1097/00001648-200105000-00013

Williams, M. R., King, K. W., & Fausey, N. R. (2015). Contribution of tile drains to basin discharge and nitrogen export in a headwater agricultural watershed. *Agricultural Water Management*, *158*(3), 42–50.

Worrall, F., Howden, N. J. K., & Burt, T. P. (2015). Evidence for nitrogen accumulation: the total nitrogen budget of the terrestrial biosphere of a lowland agricultural catchment. *Biogeochemistry*, Vol. 123, pp. 411–428. https://doi.org/10.1007/s10533-015-0074-7

Yu, Z., & Lu, C. (2018). Historical cropland expansion and abandonment in the continental U.S. during 1850 to 2016. *Global Ecology and Biogeography: A Journal of Macroecology*, *27*(3), 322–333.

Appendix A – Supplemental Figures and Tables

Supplemental Table 1. Aggregation and disaggregation of census livestock (cattle and poultry) categories.

Cattle and cows		
Year	**Data Available**	**Description of Process**
1930	Cow & heifers > 2 yr, beef production Cow & heifers > 2 yr, milk production Cow & heifers < 2 yr, beef production Cow & heifers < 2 yr, milk production Heifers, yearlings Bulls > 1yr Steers & bulls, 1 yr Steers, 2 yrs Steers > 2 yrs Calves	Cow and heifers > 2yr for milk and beef were categorized as milk and beef cattle, respectively. Other cattle was calculated by summing remaining categories.
1935	Cows & heifers > 2 yr Heifers < 2 yr Steers & bull > 1 yr Calves	Cows and heifers > 2yrs was split into milk and beef cattle using county-scale fractions (i.e. milk cattle to cows & heifers > 2 yr ratio) from 1940. Other cattle was calculated by summing remaining categories.
1940	All cattle Cow & heifers > 2 yr, beef production Cow & heifers > 2 yr, milk production	Other cattle was calculated by finding the difference between all cattle and milk and beef cattle.
1945	All cattle Cows & heifers > 2 yr	Cows and heifers > 2yrs was split into milk and beef cattle using county-scale fractions (i.e. milk cattle to cows & heifers > 2 yr ratio) from 1940. Other cattle was calculated by finding the difference between all cattle and milk and beef cattle.
1950	All cattle Cows & heifers > 2 yr Cow & heifers > 2yr, milk production	The difference between Cows & heifers that have calved and Cows and heifers > 2yrs, milk production was used to calculate beef cattle. Other cattle was calculated by finding the difference between all cattle and milk and beef cattle.
1954 to 1964	Cows & heifers that have calved Cow & heifers > 2 yr, milk production Steers & bulls, incld. calves	The difference between Cows & heifers that have calved and Cows and heifers > 2yrs, milk production was used to calculate beef cattle. Other cattle was calculated by summing remaining categories.

	Heifers & heifer calves, number	
1969 to 1997	Cow & heifers > 2 yr, beef production Cow & heifers > 2 yr, milk production Steers & bulls, incld. calves Heifers & heifer calves, number	Other cattle category was calculated by summing remaining categories.
2002 to 2017	Cow & heifers > 2 yr, beef production Cow & heifers > 2 yr, milk production Other cattle	No calculations required.
Chicken and Broiler Chickens		
1930 to 1964	Chickens > 3 mths	Chickens > 3 months categorized as other chickens. Broilers were scaled from 1969 to 1930 using rate of change of broiler consumption (kg consumed) and broiler live weight (kg meat/chicken) to establish the percent change of national broiler inventory for each census year.
1969 to 1974	Chickens > 4 mths Broilers & other meat chickens	Chickens > 4 months categorized as other chickens.
1978 to 1992	Chickens > 3 mths Pullets < 3 mths Broilers & other meat chickens	Chickens > 3 mth and pullets < 3 mths are categorized as other chickens.
1997	Layers & pullets > 3 mths Pullet chicks & pullets < 3 mths Broilers & other meat chickens	Layers & pullets > 13 wks and pullet chicks & pullets < 13 wks are categorized as other chickens.
2002 to 2017	Layers > 20 wks Pullet checks for laying flock replacement Broilers & other meat chickens	Layers > 20 wks and pullet checks for laying flock replacement are categorized as other chickens.

Supplemental Table 2. Consolidated County FIPS.

State FIPS	Original County FIPS	Dataset County FIPS	State	County	State FIPS	Original County FIPS	Dataset County FIPS	State	County
4	4012	4027	AZ	La Paz	51	51600	51059	VA	Fairfax
8	8014	8013	CO	Broomfield (new)	51	51640	51077	VA	Galax
8	8001	8031	CO	Adams	51	51595	51081	VA	Emporia
11	11010	11001	DC	District of Columbia (duplicate)	51	51084	51083	VA	South Boston (historical)
12	12025	12086	FL	Dade (historical)	51	51780	51083	VA	South Boston (historical)
13	13041	13121	GA	Campbell County (historical)	51	51683	51153	VA	Manassas
16	16089	16043	ID	Yellowstone National Park (historical)	51	51685	51153	VA	Manassas Park
30	30113	30067	MT	Yellowstone National Park (historical)	51	51775	51161	VA	Salem
32	32025	32510	NV	Ormsby (historical)	51	51678	51163	VA	Lexington
35	35028	35043	NM	Los Alamos	51	51620	51175	VA	Franklin
35	35049	35043	NM	Santa Fe	51	51720	51195	VA	Norton
35	35006	35061	NM	Cibola	51	51735	51199	VA	Poquoson
46	46001	46041	SD	Armstrong (historical)	51	51129	51550	VA	Nokfolk (historical)
46	46131	46071	SD	Washabaugh (historical)	51	51785	51550	VA	South Nokfolk (historical)
46	46133	46113	SD	Washington (historical)	51	51055	51650	VA	Elizabeth City (historical)
46	46102	46113	SD	Ogallala County (new)	51	51189	51700	VA	Warwick (historical)
51	51560	51005	VA	Clifton Forge	51	51123	51800	VA	Nansemond (historical)
51	51580	51005	VA	Covington	51	51151	51810	VA	Princess Anne (historical)
51	51610	51013	VA	Falls Church	55	55083	55078	WI	Oconto
51	51820	51015	VA	Waynesboro	55	55115	55078	WI	Shawano
51	51515	51019	VA	Bedford	56	56047	56029	WY	Yellowstone National Park (new)

Supplemental Table 3. Conversion values for crops uptake included in the N surplus calculations.

Tree Type	Reporting Unit	N Uptake (kg-N/tree)	Citation
Almonds	Trees	0.82	[1,2]
Apple	Trees	0.23	[3,4]
Cherry	Trees	0.23	[5,6]
Grapefruit	Trees	0.31	[7]
Grapes	Vine	0.03	[8,9]
Olive	Trees	0.06	[10]
Orange	Trees	0.31	[7]
Peach	Trees	0.15	[11,12]
Pecan	Trees	1.5	[13,14]
Pistachio	Trees	0.44	[11]
Prune and plums	Trees	0.38	[11]
Walnut	Trees	1.3	[11,15]
Avocado	Trees	1.06	[11]
Apricot	Trees	0.15	[11,12,16]
Pear	Trees	0.23	[3,4]
Crop Type	**Reporting Unit**	**N Uptake (kg-N/acres)**	
Blackberries	Acres	13.50	[17,18]
Blueberry	Acres	10.93	[19]
Cranberry	Acres	18.14	[20]
Raspberries	Acres	16.20	[17,18]

Crop Type	Reporting Unit	Kg per reporting unit	N Content (kg-N/kg)	Citation
Alfalfa hay	Dry tons	907.2	0.025	[21,22]
Asparagus	Acres	756	0.005	[23,24]
Barley	Bushels	21.8	0.019	[21,22]
Beans	Bushels	27.2	0.059	[25]
Beans	Hundredweight	45.4	0.059	[25]
Broccoli	Acres	5130	0.009	[23,26]
Canola	Pounds	0.454	0.035	[25]
Cantaloupes	Acres	9550	0.002	[12,27,28]
Carrots	Acres	15866	0.003	[12,27,29]
Corn, grain	Bushels	25.4	0.013	[21,22]
Corn, silage	Green tons	907.2	0.004	[21,22]

Corn, silage	Acres	7967	0.004	[21,25]
Corn, sweet	Acres	4774	0.013	[25,30]
Corn, total	Acres	6264	0.004	[21,25]
Cotton	Bales	226.8	0.030	[21,22]
Cropland pasture	Acres	907.2	0.025	[21,22]
Flaxseed	Bushels	25.4	0.035	[25]
Non-Alfalfa Hay	Dry tons	907.2	0.011	[21,25]
Hops	Pounds	0.454	0.022	[25]
Lentils	Pounds	0.454	0.039	[25]
Lentils	Hundredweight	45.4	0.039	[25]
Lettuce	Acres	13467	0.002	[12,31–33]
Lima beans	Hundredweight	45.4	0.026	[25]
Millet	Bushels	22.7	0.019	[25]
Millet	Acres	528	0.019	[25]
Noncropland pasture	Acres	min(453.6, cattle uptake*)	0.020	[21,25]
Oats	Bushels	14.5	0.018	[21,25]
Onions, dry	Acres	1679	0.002	[6,34,35]
Peanuts	Bushels	9.98	0.040	[21,25]
Peanuts	Pounds	0.454	0.040	[21,25]
Peppers	Acres	11122	0.001	[27,35]
Potatoes	Hundredweight	45.4	0.004	[21,25]
Potatoes	Acres	11414	0.004	[21,25]
Pumpkin	Acres	9072	0.001	[12,27]
Rice	Hundredweight	45.4	0.013	[21,25]
Rice	Bushels	20.3	0.013	[21,25]
Rye	Bushels	25.4	0.019	[21,25]
Safflower	Pounds	0.454	0.025	[25]
Safflower	Bushels	17.2	0.025	[25]
Safflower	Acres	859	0.025	[25]
Sorghum, grain	Bushels	25.4	0.018	[21,25]
Sorghum, silage	Dry tons	526.2	0.013	[21,25]
Sorghum, silage	Ton, dry	907.2	0.013	[21,25]
Soybeans	Bushels	27.2	0.059	[25]
Squash	Acres	6008	0.001	[12,27]
Strawberry	Acres	15236	0.003	[12,27]
Sugar beets	Tons	907.2	0.002	[21,25]
Sugarcane	Tons	907.2	0.002	[21,25]
	Acres	33109	0.002	[21,25]
Sunflower	Bushels	14.5	0.029	[25]
Sunflower	Pounds	0.454	0.029	[25]
Sweet potato	Bushels	22.7	0.003	[25]
Tobacco	Pounds	0.454	0.032	[21,25]

Tomatoes	Acres	20550	0.001	12,37,38
Triticale	Bushels	25.4	0.027	25
Watermelon	Acres	8417	0.002	27,28
Wheat	Bushels	27.2	0.019	21,25

*Cattle uptakes rates are 66.75 kg-N/animal/yr for beef cattle and 156 kg-N/animal/yr for milk cattle.

1. University of California. University of California Agriculture and Natural Resources. http://ipm.ucanr.edu (2017).
2. Geisseler, D. Nitrogen concentrations in harvested plant parts - A literature overview. *Univ. Calif.* 157 (2016).
3. Neilsen, D. & Neilsen, G. H. Efficient use of nitrogen and water in high-density apple orchards. *Horttechnology* **12**, 19–25 (2002).
4. Neilsen, D., Millard, P., Neilsen, G. H. & Hogue, E. J. Nitrogen Uptake , Efficiency of Use , and Partitioning for Growth in Young Apple Trees. *J. Am. Soc. Hortic. Sci.* **126**, 144–150 (2001).
5. San-Martino, L., Sozzi, G. O., San-Martino, S. & Lavado, R. S. Isotopically-labelled nitrogen uptake and partitioning in sweet cherry as influenced by timing of fertilizer application. *Sci. Hortic. (Amsterdam).* **126**, 42–49 (2010).
6. Mayberry, K. S. & Meister, H. Sample Cost to Establish and Produce Market Onions. (2003).
7. Dagan, S. Nitrogen fertilization in citrus orchards. *Plant Soil* **9**, 1–9 (1987).
8. Peacock, B., Christensen, P. & Hirschfeldt, D. Best management practices for nitrogen fertilization of grapevines. Tulare County UCCE, Pub NG4-96. 1–6 (1991).
9. Hanson, E. J. & Howell, G. S. Nitrogen Accumulation and Fertilizer Use Efficiency by Grapevines in Short-season Growing Areas. *HortScience* **30**, 504–507 (1995).
10. Belguerri, H. *et al.* A Proposal of Nitrogen Balance in a Very High Density Olive Orchard. *J. Fundam. Appl. Sci.* **8**, 639–654 (2016).
11. UC Davis. California Fertilization Guidelines. (2016). Available at: https://apps1.cdfa.ca.gov/fertilizerresearch/docs/Guidelines.html.
12. United States Department of Agriculture. Economics, Statistics and Market Information System. (2010). Available at: http://usda.mannlib.cornell.edu/MannUsda/viewDocumentInfo.do?documentID=1210. (Accessed: 6th May 2018)
13. Kraimer, R. A., Lindemann, W. C. & Herrera, E. A. Recovery of late-season15N-labeled fertilizer applied to pecan. *HortScience* **39**, 256–260 (2004).
14. Kraimer, R. A., Lindemann, W. C. & Herrera, E. A. Distribution of15N-labeled fertilizer applied to pecan: A case study. *HortScience* **36**, 308–312 (2001).
15. Weinbaum, S. a, Muraoka, T. T., Catlin, P. B. & Kelley, K. Utilization of fertilizer N by walnut trees. 317–334 (1991).
16. Sanchez, E. E., Khemira, H., Sugar, D. & Righetti, T. L. R. Nitrogen Management in Orchards. (1995).
17. Rempel, H. G., Strik, B. C. & Righetti, T. L. Uptake , Partitioning , and Storage of Fertilizer Nitrogen in Red Raspberry as Affected by Rate and Timing of Application. **129**, 439–448 (2004).
18. Mohadjer, P., Strik, B. C., Zebarth, B. J. & Righetti, T. L. Nitrogen uptake , partitioning and remobilization in 'Kotata' blackberry in alternate-year production. **0316**, (2015).
19. White, L., Yang, W., Hart, J. M. (John M. & Strik, B. Nutrient management for blueberries in Oregon. (2006).
20. Roper, T., DeMoranville, C., Davenport, J., Service, O. S. U. E. & Hart, J. Nitrogen for bearing cranberries in North America. (2000).
21. Hong, B., Swaney, D. P. & Howarth, R. W. A toolbox for calculating net anthropogenic nitrogen inputs (NANI). *Environ. Model. Softw.* **26**, 623–633 (2011).
22. Hong, B., Swaney, D. P. & Howarth, R. W. Estimating net anthropogenic nitrogen inputs to U.S. watersheds: Comparison of methodologies. *Environ. Sci. Technol.* **47**, 5199–5207 (2013).
23. Doerge, T., Roth, R. L. & Gardener, B. R. *Nitrogen Fertilizer Management in Arizona*. (1991).
24. US Department of Agriculture Economics Statistics and Market Information. U.S. Asparagus Statistics. *2010* Available at: https://usda.library.cornell.edu/concern/publications/d504rk32w?locale=en.
25. US Department of Agriculture Natural Resource Conservation Service. Nutrients Available from Livestock Manure Relative to Crop Growth Requirements (Table A-1). (1998).
26. US Department of Agriculture Economics Statistics and Market Information. U.S. Broccoli Statistics. Available at: https://usda.library.cornell.edu/concern/publications/jd472w44j?locale=en.
27. Bouwman, A. F., Van Drescht, G. & Van der Hoek, K. W. Global and Regional Surface Nitrogen Balances in Intensive Agricultural Production Systems for the Period 1970-2030. *Pedosphere* **15**, 135–55 (2005).
28. US Department of Agriculture Economic Research Service. Fruit and Tree Nut Yearbook Tables. ◘ (2018). Available at: https://www.ers.usda.gov/data-products/fruit-and-tree-nut-data/fruit-and-tree-nut-yearbook-tables/#Melons. (Accessed: 6th February 2018)
29. US Department of Agriculture Economics Statistics and Market Information. U.S. Carrot Statistics. (2011). Available at: https://usda.library.cornell.edu/concern/publications/sx61dm28w?locale=en.
30. US Department of Agriculture Economics Statistics and Market Information. U.S. Sweet Corn Statistics. (2010). Available at: https://usda.library.cornell.edu/concern/publications/1r66j112r?locale=en.
31. Lazicki, P. & Geisseler, D. Melon Production in California. **2013**, 2013–2015 (2013).
32. Geisseler, D. & Horwath, W. R. *Lettuce Production in California*. (2016).
33. US Department of Agriculture Economics Statistics and Market Information. U.S. Lettuce Statistics. (2011). Available at: https://usda.library.cornell.edu/concern/publications/cc08hf60z?locale=en.
34. Lazicki, P., Geisseler, D. & Horwath, W. R. *Onion Production in California*. (2016).
35. US Department of Agriculture Economics Statistics and Market Information. U.S. Onion Statistics. (2011). Available at: https://usda.library.cornell.edu/concern/publications/k643b116n?locale=en.
36. US Department of Agriculture Economics Statistics and Market Information. U.S. Bell and Chile Pepper Statistics. (2008). Available at: https://usda.library.cornell.edu/concern/publications/p5547r38s?locale=en.
37. Le Strange, M., Schrader, W. L. & Hartz, T. *Fresh-Market Tomato Production in California*. (2000).

38. Geisseler, D. & Horwath, W. R. Production of Processing Tomatoes in California. 1–4 (2012).

Supplemental Table 4. Conversion values for crops biological nitrogen fixation included in the N surplus calculations.

Crop Type	Reporting Unit	Kg per reporting unit	Fixation Rates (kg-N/kg/yr)	Citation
Soybeans	Bushels	27.22	0.066	1
Alfalfa Hay	Dry tons	907.18	0.031	1
Peanuts	pounds	0.45	0.045	1
Peanuts	bushels	9.98	0.045	1
Lentils	pounds	0.45	0.039	2
Lentils	hundredweight	45.36	0.039	2
Beans	bushels	27.22	0.059	2
Non-alfalfa Hay	Dry tons	907.18	0.003	1
Crop Type	**Reporting Unit**	**Square kilometers per reporting unit**	**Fixation Rates (kg-N/km2/yr)**	
Cropland Pasture	Acres	0.0040	1500	1
Snap Beans	Acres	0.0040	9000	1

1. Hong, B., Swaney, D. P. & Howarth, R. W. A toolbox for calculating net anthropogenic nitrogen inputs (NANI). *Environ. Model. Softw.* **26**, 623–633 (2011).
2. Smil, V. (1999b). Nitrogen in crop production: An account of global flows. Global Biogeochemical Cycles, 13(2), 647–662.

Supplemental Table 5. Conversion values for livestock manure N excretion included in the N surplus calculations.

Livestock Type	Reporting Unit	N in Animal Excretion (kg- N/animal/yr)	Citation
Poultry, Broiler	Head	0.07	1,2
Poultry, Other Chickens (not broilers)	Head	0.55	1,2
Poultry, Turkey	Head	0.39	1,2
Goat	Head	5.0	1,2
Hog and Pigs	Head	5.8	1,2
Sheep and lambs	Head	5.0	1
Poultry, Turkey	Head	0.39	1,2
Horse and Ponies	Head	40	1,2
Cattle, Beef	Head	58.51	1,2
Cattle, Beef pre-1945	Head	30	1,2
Cattle, Milk	Head	121	1,2,3
Cattle, Milk pre-1945	Head	45	1,2,3
Cattle, Other (Heifer, Bull, Steers, Calves)	Head	58.5	1,2
Cattle, Other pre-1945 (Heifer, Bull, Steers, Calves)	Head	30	1,2,3

1. Hong, B., Swaney, D. P. & Howarth, R. W. (2011) A toolbox for calculating net anthropogenic nitrogen inputs (NANI). *Environ. Model. Softw.* **26**, 623–633.
2. Smil, V. (1999b). Nitrogen in crop production: An account of global flows. Global Biogeochemical Cycles, 13(2), 647–662.
3. Van Meter, K. J., Basu, N. B., & Van Cappellen, P. (2017). Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins. *Global Biogeochemical Cycles*, *31*(1), 2–23.

Supplemental Figure 1. National N consumption and N use on corn