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The Role of Nitrogen in Climate Change and the Impacts of Nitrogen-Climate Interactions on Terrestrial and Aquatic Ecosystems, Agriculture and Human Health in the United States

A technical report submitted to the US National Climate Assessment

Emma C. Suddick, Woods Hole Research Center

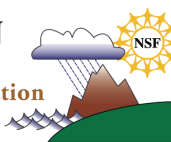
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Preface

This technical report is a product of the North American Nitrogen Center of the International Nitrogen Initiative (NANC-INI; <http://nitrogennorthamerica.org/>). The objective is to provide an in-depth analysis of the cross-cutting issue of climate-nitrogen interactions for consideration by the US National Climate Assessment Development Advisory Committee as they write their 2013 National Climate Assessment report.

Acknowledgments

The authors of this report conducted a workshop at Fort Collins, CO, in July 2012, at the U. S. Geological Survey John Wesley Powell Center for Analysis and Synthesis. The workshop was supported by NSF Research Coordination Network grants DEB-0443439 and DEB-1049744 (<http://nitrogennorthamerica.org/projects.html>) and by the David and Lucille Packard Foundation.

Each chapter in this report has undergone peer review. Documentation of the reviews can be made available by contacting the editors (edavidson@whrc.org). We thank Edith Allen, Richard Alexander, Klaus Butterbach-Bahl, Mike Dettinger, Nancy Dise, Richard Lowrance, Loretta Mickley, Knute Nadelhoffer, Scott Ollinger, Richard Pouyat, Mark Sutton, Sybil Seitzinger, Penelope Whitney, and an anonymous reviewer for their helpful comments on drafts of the chapters in this report.

Disclaimer

The views expressed in this article are those of the authors and they do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency, the U.S. Geological Survey, or any other U.S. agency. Mention of trade names, products, or services does not convey, and should not be interpreted as conveying approval, endorsement, or recommendation by the authors or their institutions.

Preferred citation

Suddick, E.C., Davidson, E.A., (2012). The Role of Nitrogen in Climate Change and the Impacts of Nitrogen-Climate Interactions on Terrestrial and Aquatic Ecosystems, Agriculture, and Human Health in the United States: A Technical Report Submitted to the US National Climate Assessment. North American Nitrogen Center of the International Nitrogen Initiative (NANC-INI), Woods Hole Research Center, 149 Woods Hole Road, Falmouth, MA, 02540-1644 USA.

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The Role of Nitrogen in Climate Change and the Impacts of Nitrogen-Climate Interactions on Terrestrial and Aquatic Ecosystems, Agriculture, and Human Health in the United States

A Technical Report Submitted to the US National Climate Assessment

Chapter 1: EXECUTIVE SUMMARY

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Producing food, transportation, and energy for seven billion people has resulted in massive increases in use of synthetic nitrogen (N) fertilizers and in emissions of N as forms of air pollution. The global N cycle has become more severely altered by human activity than the global carbon (C) cycle. In its numerous chemical forms, reactive nitrogen (Nr) plays a critical role in all aspects of climate change considerations, including mitigation, adaptation, and impacts.

Mitigation: Carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are the most important anthropogenic greenhouse gases in terms of radiative forcing, and N cycling processes affect the atmospheric concentrations of all three gases. Hence, management of the N cycle will not only help mitigate emissions of the N-containing gas N₂O, but will also affect CO₂ and CH₄ in complex ways that are reviewed here. These include how N affects C sequestration in forests and soils, and how atmospheric CH₄ concentrations are affected by the chemistry of nitrogen oxides (NO_x) and ozone (O₃). While some of these N cycling processes have contrasting effects on the atmospheric burdens of greenhouse gases, including a possible net cooling effect on the time scale of a few decades, minimizing Nr releases to the environment would almost certainly help slow the rate of climate change over the long term (e.g., a century).

Adaptation: Understanding interactions of climate with the N cycle will be essential in situations where adaptation to climate change involves changes in energy and water use. Although considerable progress has been made in lowering NO_x emissions from energy, industry, and transportation sectors in the US, this progress could slow or reverse if energy use is increased for climate change adaption, such as additional air conditioning or pumping and treating water. Adaptations to increasing water scarcity may include greater consumptive use of surface and groundwaters, which will likely exacerbate problems of elevated nitrate (NO₃⁻) concentrations in waters draining to rivers, lakes, groundwaters and estuaries, leading to eutrophication, costly drinking water treatments, or increased incidents of NO₃⁻-related disease. On the one hand, improvements in agricultural nutrient management (e.g., properly timed and appropriately balanced nutrient additions) can confer some adaptive capacity of crops to climatic variability, but on the other hand, increased climatic variability will also render the task of nutrient management more difficult. These are only a few examples reviewed in this report of climate-N interactions that would affect or be affected by climate change adaptation.

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Impacts: Climate change will significantly alter N cycling processes, which will affect both terrestrial and aquatic ecosystems, as well as human health. Higher air temperatures will complicate air quality mitigation, because larger reductions in NO_x emissions will be needed to achieve the same reductions of O_3 pollution under higher temperatures, thus imposing further challenges to avoid harmful impacts of O_3 pollution on human health and crop productivity, also known as a “climate penalty.” Changes in river flow, due to summer drought and extreme precipitation events, will affect the loading and processing of N within rivers and estuaries. Lower river flows may reduce the total flux of N entering coastal regions, but would also reduce rates of flushing of estuaries, whereas higher flows will accelerate loading of N from terrestrial to aquatic systems. In either case, more frequent blooms of harmful or nuisance algal species are possible. In addition, rising ambient temperatures will increase ammonia (NH_3) emissions throughout all phases of manure handling and will likely result in lower N use efficiency in livestock production systems and greater losses of N_r to the environment. Both climate change and N inputs from air pollution (i.e., N deposition) can provoke a loss of biodiversity in aquatic and terrestrial ecosystems, due to nutrient enrichment of native ecosystems which favors fast-growing, often non-native species. Less is known about the interactions of climate and N regarding biodiversity, but additive or synergistic effects are indicated. The impacts of climate-N interactions on C sequestration, agricultural productivity, aquatic ecosystems and water quality, biodiversity, and air pollution are analyzed in detail in the chapters of this report.

The climate-N interactions described in the following chapters are too numerous to list exhaustively in this executive summary, but a few of the highlights, organized by chapter topics, are listed here.

Alteration of N flows in the US (Chapter 2)

- Humans introduced about 29 Tg (10^{12}g) of newly formed N_r into the US in 2002 (the most recent year for which the most complete data are available; Figure 1.1). About 65% of N inputs were from agricultural sources (including synthetic N fertilizers and N fixation by legume crops), 20% from fossil fuel sources, and about 15% from industrial sources. Overall in the US, the amount of N_r produced by human activities was approximately five-times larger than all natural processes combined; while at the global scale, human activities produced approximately twice as much N_r as did natural processes (SAB 2011).

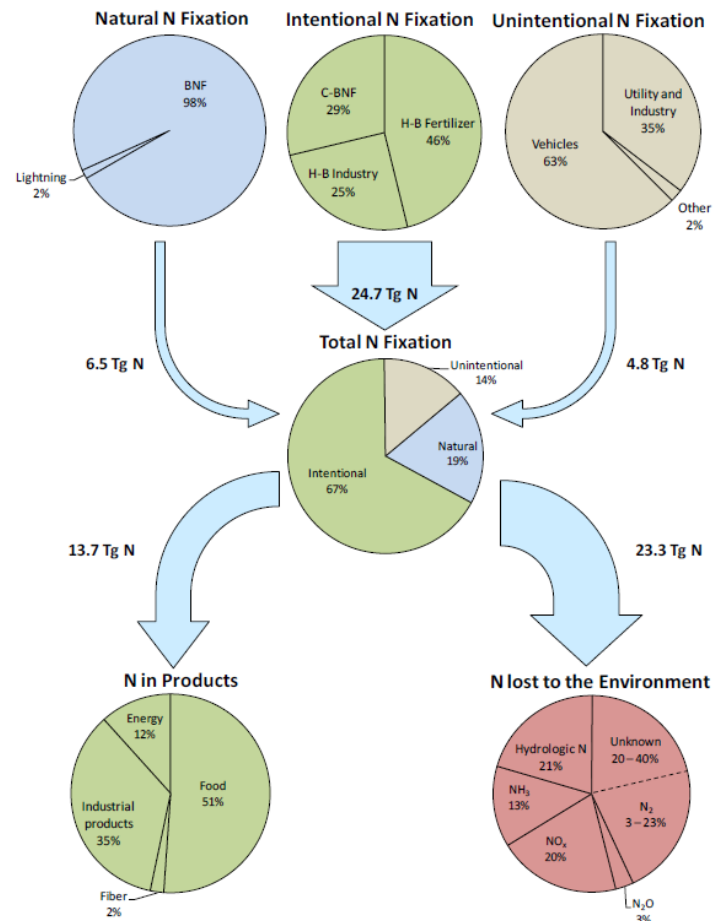


Figure 1.1: N fixation and fates of N in the US for 2007. “BNF” = Biological Nitrogen Fixation; “C-BNF” = Crop BNF; “H-B Fertilizer” = Haber-Bosch Fertilizer; “H-B Industry” = Haber-Bosch Industrial Products; (See also Figure 2.9, Section 2.2.5 in Chapter 2).

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- Human activities have also greatly modified the amount of N that is released from the land to air and water resources. In terms of gaseous N releases, NH_3 and NO_x account for 31 % and 61 % respectively, of a combined flux of 9.3 Tg N/yr. Significant fractions of these N gases are re-deposited on US ecosystems downwind of sources. In contrast, the greenhouse gas N_2O is evenly mixed within the global atmosphere and accounted for approximately 8 % of all US gaseous N_r emissions (Houlton and Bai, 2009).
- Leaching of N to surface waters and groundwater has also increased substantially in the US and around the globe. Our 2002 US budget indicates that leaching to surface waters and groundwater was approximately 4-5 Tg N/yr. Approximately 14-45 % of N entering groundwater as NO_3^- derives from fertilizer and/or manure use and atmospheric deposition (Nolan et al., 2010; Puckett et al., 2011).
- On an annual basis, about 54% of N_r intentionally introduced into the US is converted to food, livestock feed, biofuel (energy), or industrial products; about 27 % of N_r is released to the environment as various forms of air and water pollution, and an uncertain amount (3 - 21%) is converted to inert dinitrogen (N_2) gas. Considering only the agricultural sector, approximately 38% of agricultural N inputs (e.g., synthetic fertilizer and N fixation by leguminous crops) enter the annual food and livestock feed supply. Most of the N that reaches its intended target in consumable human food, animal feed, biofuels, and industrial products is eventually released to the environment as sewage, manure, and other waste products.

Radiative forcing (Chapter 3)

- Nitrogen cycling processes affect radiative forcing directly through emissions of N_2O , a greenhouse gas with long-term warming effects due to a mean residence time in the atmosphere of over 100 years. The US Environment Protection Agency (USEPA 2011) estimates that agricultural activities in the US are directly or indirectly responsible for emissions of about 0.48 million tons of N_2O -N yr^{-1} , which is about 80% of total anthropogenic US N_2O production (the remainder derives from energy and industrial sources), and is about 10% of the global N_2O emissions from agriculture.
- Emissions of NO_x indirectly affect radiative forcing through the effects on atmospheric concentrations of CH_4 , O_3 and aerosol particulate matter (PM). These effects are complex and difficult to quantify (Rypdal et al. 2009, Penner et al. 2010, Myhre et al. 2011). However, they generally result in a cooling effect on time scales of days to decades, becoming insignificant on longer time scales (Boucher et al., 2009).

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- Emissions of NO_x and NH_3 are chemically transformed and eventually deposited onto ecosystems with rain and snow and also as dry particles. This increases the availability of N to ecosystems, which can thus affect the sources and sinks of N_2O , CH_4 , and CO_2 , with the dominant effect being enhanced sequestration of C. The literature reviewed here reports a range of estimates of 20-70 kg C sequestered per kg N deposited onto forests, which are the dominant potential C sinks (Butterbachball et al., 2011; Thomas et al., 2010). Most of the sequestration occurs in aboveground forest biomass, with less consistency and lower rates reported for C sequestration in soils. The permanency of the forest biomass sink is uncertain, but data on forest product fates in the US indicate that only a small fraction of enhanced forest biomass C is sequestered in long-term harvest products or in unmanaged forests.
- The net effect of all of these N cycle processes on radiative forcing in the US is probably a modest cooling effect for a 20-year time frame (although the uncertainty of this estimate includes zero net effect), and a modest warming for a 100-year time frame (Figure 1.2).

Agriculture (Chapter 4)

- Climate-N interactions affect agricultural productivity in part through exposure of crops to elevated O_3 . The O_3 production efficiency per unit NO_x emitted is high in rural areas. Furthermore, increases in temperature can also lead to higher rates of precursor emissions and O_3 formation. Based on large-scale experimental studies in the US (Heagle, 1989; Heck, 1989), the USEPA estimates that the yields of about one-third of US crops were reduced by 10% due to ambient O_3 concentrations in the 1980s (USEPA, 1996). Model simulations of O_3 used with these established concentration and yield response relationships predict larger effects for grain crops for 2000 and 2030 (Avnery et al., 2011a, b). More recent field studies have found similar or larger yield reductions at similar O_3 exposures in a variety of crops (Mills et al., 2007; Emberson et al., 2009).

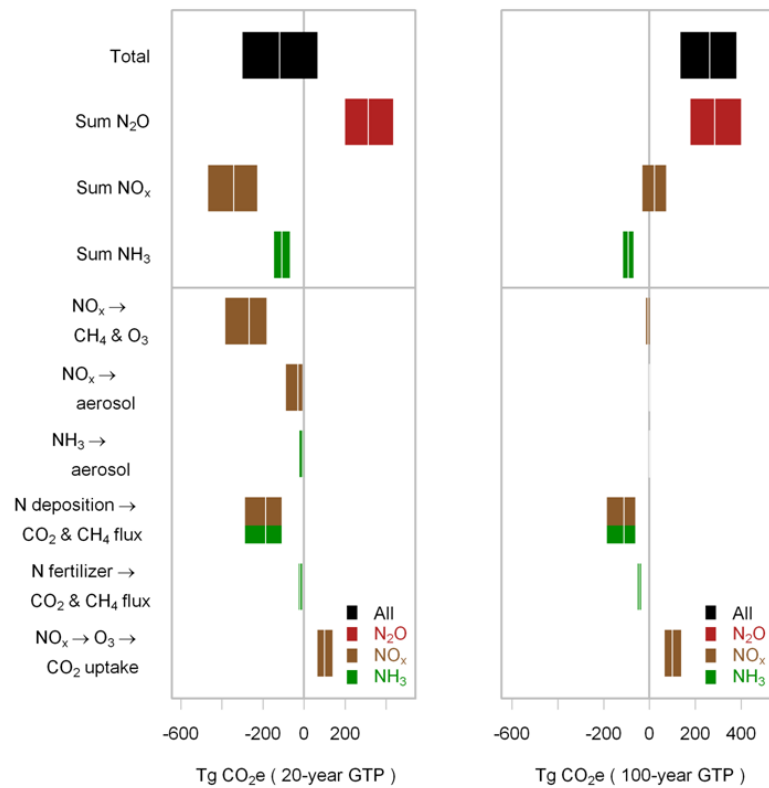


Figure 1.2: The climate change impacts of US reactive nitrogen emissions on a 20-year and 100-year global temperature potential (GTP) basis. (See also Figure 3.1, Section 3.4 in Chapter 3; redrawn from Pinder et al., in review).

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- Increases in drought frequency and intensity from increasing temperatures will also adversely affect crop growth and yield, ultimately impacting nutrient use and uptake efficiency and facilitating unintentional N releases to the environment. Fertilizer N is usually applied at rates expected to produce historically maximum crop yields for a given location. Thus, environmental factors that reduce crop growth and yield, including both drought and excessive moisture, would increase N_r releases to water and air due to reduced crop uptake (Figure 1.3).

- Extreme wet cycles can also result in substantial releases of N_r to the environment, through greater transport of NO₃⁻ as excess water drains from fields, and through gaseous losses of N₂O promoted in wet soils. Nitrate leaching and N₂O production occur when large amounts of soil NO₃⁻ are present after fertilizer application, before the crop has started growing vigorously, and when the soils are wet (Davidson et al., 2012).

- The presence of winter cover crops can reduce N_r losses through mechanisms of plant N uptake and reduced subsurface percolation. Cover crops in some locations have been documented to reduce both N₂O emissions and NO₃⁻ leaching compared with bare fallow systems (McSwiney et al., 2010).

- Rates of NH₃ emissions from livestock operations are also very sensitive to temperature (Montes et al., 2009), such that rising ambient temperatures will also increase this source of N loss throughout all phases of manure handling. Overall, the net effect of changes in the agricultural N cycle in response to higher temperature is likely a reduction in N use efficiency of animal systems, resulting in larger potential releases of N_r to the environment.
- Projected temperature changes will also directly and indirectly affect livestock production, primarily due to heat stress, which causes reduced feed intake, increased water intake, higher body temperatures, increased respiration, decreased activity, and hormonal and metabolic changes. These effects can lead to lower production, lower reproduction, and higher mortality (Nardone et al., 2010). As production is increased elsewhere to make up for this lost productivity, more N will be needed and N_r releases to the environment will increase. Under our current climate, heat stress is

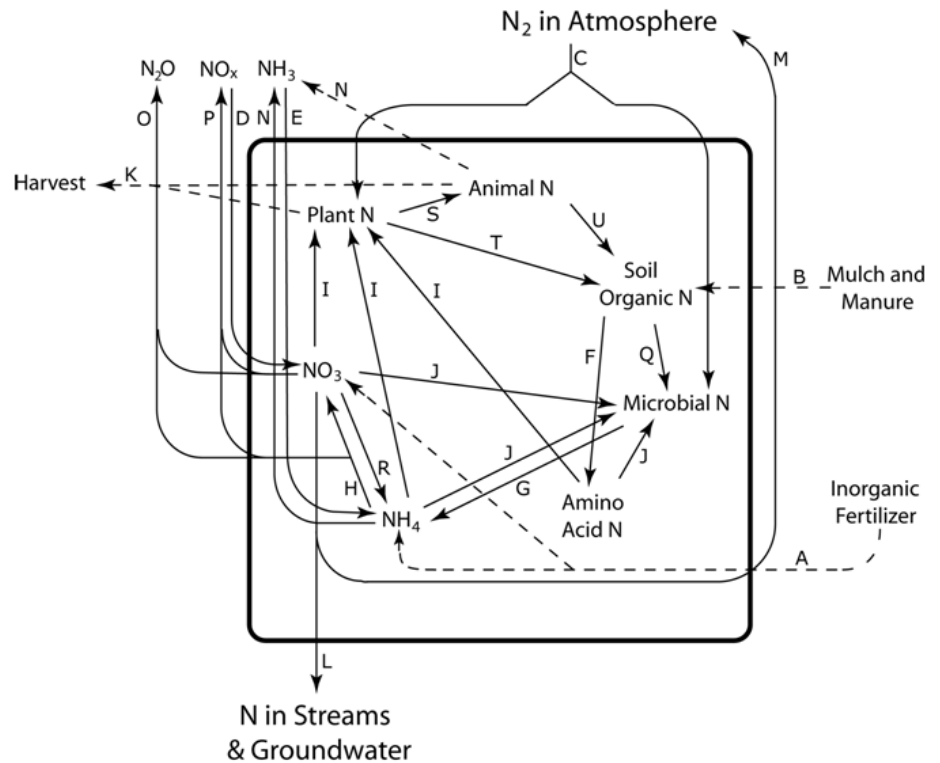


Figure 1.3: Pathways of N cycling in agricultural ecosystems. (See Figure 4.2, Section 4.0 in Chapter 4 for an explanation of the symbols A-T) From Robertson and Vitousek 2007.

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estimated to cause an annual economic loss of 1.7 to 2.4 billion dollars in the US livestock sector (St-Pierre et al., 2003).

- Applying the right source of fertilizer N at the right rate, time, and place is the core concept of mitigation strategies designed to increase crop N use efficiency and to reduce N_2O , NO_x , and NH_3 emissions. However, crop demand for nutrients is highly dependent upon climate and climatic variability, so improved nutrient use management will be increasingly challenging under climate change scenarios of more variable climatic patterns.

Aquatic ecosystems and resources (Chapter 5)

- Nearly all freshwaters and coastal zones of the US exhibit some degree of degradation from inputs of excess Nr. Two-thirds of US estuaries are degraded from N pollution, and effects include anoxia (no oxygen) and hypoxia (low oxygen), loss of critical habitat and biodiversity, and increased frequency of harmful algal blooms (Bricker et al. 2007, SAB 2011).

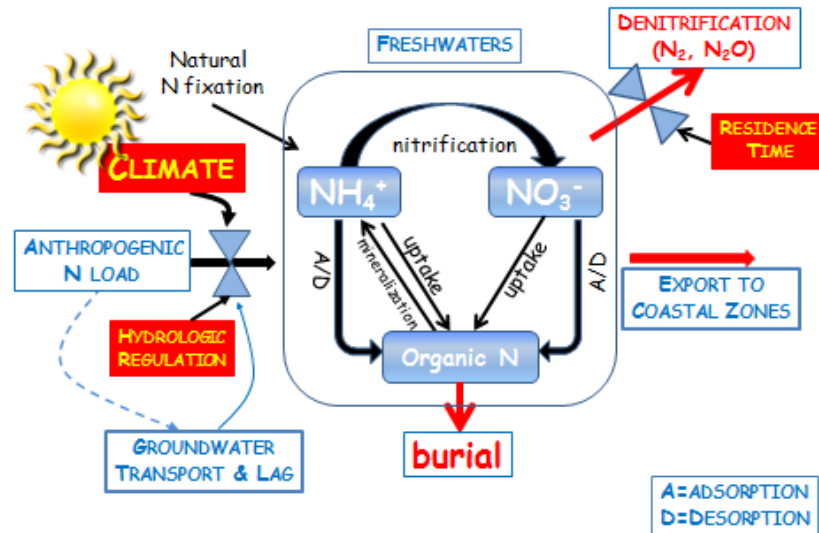


Figure 1.4: Conceptual model of N input, cycling and losses of Nr to inland waters. (See also Figure 5.1, Section 5.2.1 in Chapter 5).

- The loading of N from watersheds and atmospheric deposition has more than doubled the flux of N to estuaries and coastal oceans since the industrial and agricultural revolutions (Howarth et al. 2011a, Boyer and Howarth 2008).
- Inputs to river systems were estimated with the USGS SPARROW model to be 4.8 Tg N yr^{-1} in 2002 (SAB 2011, Alexander et al. 2008). North American riverine N export to the coastal zone, inlands and drylands was estimated at approximately 7.0 Tg N yr^{-1} (Boyer et al. 2006).
- Aquatic ecosystems are critically important denitrification hotspots where Nr can be returned to the atmosphere as un-reactive and harmless N_2 . Denitrification rates per-unit-area are approximately ten-fold the per-unit-area denitrification rates in soils (Seitzinger et al. 2006). One estimate suggests 20% of global denitrification occurs in freshwaters (e.g., groundwaters, lakes, and rivers) (Seitzinger et al. 2006).
- The effect of climate change on N processing in fresh and coastal waters will be felt most strongly through changes to the hydrologic cycle (Figure 1.4). Alterations in the amount, timing, frequency, and intensity of precipitation will speed or slow runoff, thereby influencing both rates of Nr inputs

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to aquatic ecosystems and groundwater and the water residence times that affect Nr removal within aquatic systems. Both hydrologic manipulation by human-made infrastructure and climate change alter the landscape connectivity and hydrologic residence times that are essential for denitrification (Howarth et al. 2011b).

- The reliance of Americans on groundwater for drinking water is likely to increase under future climate change scenarios. In addition, there will likely be increases in costs for treating water to avoid exposure to NO_3^- -related disease. At present, approximately 1.2 million Americans use private, shallow groundwater wells in areas with estimated NO_3^- concentrations between 5 and 10 mg L^{-1} , and about 0.5 million use groundwater in areas with estimated $\text{NO}_3^- > 10 \text{ mg L}^{-1}$ (Nolan and Hitt 2006). A recent study showed that the maximum NO_3^- contaminant level of 10 mg L^{-1} was exceeded in 22% of domestic wells in agricultural areas (Dubrovsky et al. 2010). Model results also suggest that deeper groundwater supplies may be contaminated in the future as NO_3^- in shallow groundwater migrates downward and is slow to respond to changes in management (Nolan and Hitt 2006, Exner et al. 2010, Howden et al. 2010). In addition to the well known NO_3^- related disease methemoglobinemia (blue baby syndrome), NO_3^- from drinking water contributes to the formation of N-nitroso compounds, which have been associated with cancer, diabetes, and adverse reproductive outcomes (Ward et al. 2005).
- Increasing numbers of studies show correlations between N enrichment in waters and pathogen abundance and diseases of both humans and wildlife (Johnson et al. 2010). Many mosquitoes that are carriers of diseases like malaria or West Nile Virus and other parasites associated with warm climates or seasons have increased breeding success in waters high in NO_3^- (Johnson et al. 2010). Occurrence of algal blooms, for which there is also a direct connection to nutrient enrichment and warm waters (Heisler et al. 2008), can cause disease such as swimmers itch, food poisoning, cancer, and paralysis (Johnson et al. 2010). Harmful algal blooms are responsible for massive fish kills and marine mammal kills (Morris 1999).
- Without mitigation, the concurrent impositions of climate change and the increasing load of Nr to freshwater and estuarine ecosystems will most likely have unprecedented additive or synergistic effects on water quality, aquatic biodiversity, human health, and fisheries.

Biodiversity (Chapter 6)

- The strongest drivers of biodiversity loss include habitat loss, overexploitation, invasive species, climate change, and pollution, including pollution from Nr (MEA 2005) (Figure 1.5). Nitrogen enrichment also impacts ecosystems and biodiversity by enhancing plant

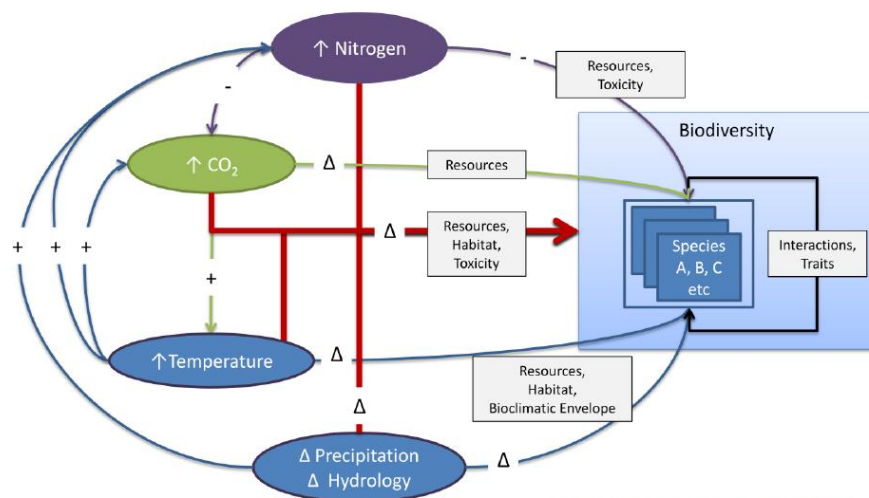


Figure 1.5: Direct and indirect effect of changing climate, N and CO_2 on biodiversity. (See also Figure 6.1, Chapter 6).

Red arrows – Climate-N interaction
 Purple arrows – direct N effect
 Blue arrows – direct climate effect
 Green arrows – CO_2 effect
 Black arrows – Species factors

growth, which has been shown to favor fast-growing, sometimes invasive, species over native species adapted to low N conditions. Results from both empirical studies and modeling indicate that N and climate change can interact to drive losses in biodiversity greater than those caused by either stressor alone.

- For example, controlled experiments in California grassland have shown that increased N and CO₂, separately and in combination, significantly reduced forb diversity (Zavaleta et al. 2003). In arid ecosystems of southern California, elevated N deposition and changing precipitation patterns have promoted the conversion of native shrub communities to communities dominated by a few species of annual non-native grasses. A change in biodiversity can also affect ecosystem function, such as increasing fire risk where fuel accumulation was previously rare (Rao et al. 2010).
- Another example of climate-N interactions on biodiversity involves the combined effects of earlier snowmelt and increased N deposition. Earlier snowmelt in high elevation sites has caused earlier starts to the growing season, thus increasing the exposure of some plants to killing frosts (Inouye 2008). Deposition of N has been associated with greater frost sensitivity in conifer species (Perkins et al. 2000). The combination of more frequent frosts and greater plant sensitivity to those frosts can cause greater mortality of those species.
- Coastal ecosystem biodiversity can become more or less sensitive to N pollution due to climate-driven changes in water residence time, ocean currents, and stratification. For example, the New York Harbor estuary has experienced more occurrences of algal blooms and has become more eutrophic because summer water residence times have increased (less flushing) as a result of less winter snowpack in the Adirondack Mountains (Howarth et al. 1999). The St. Lawrence Estuary and Gulf of St. Lawrence have also become hypoxic in recent years, as their bottom waters now come more from the deep Atlantic water and less from the Labrador Current (Gilbert et al. 2005, Howarth et al. 2011a). Moreover, due to greater stratification, productivity in the Dead Zone area in the Gulf of Mexico has become co-limited by P, causing less N uptake, more N_r loss in coastal environments, and greater transport of N_r to deeper waters (Sylvan et al. 2006, Donner and Scavia 2007).

Air pollution and human health (Chapter 7)

- Nitrogen oxides, O₃, and fine particulate matter (PM_{2.5}) pollution related to atmospheric emissions of N_r and other pollutants can cause premature death and a variety of serious health effects (USEPA 2006; USEPA 2008; USEPA 2009). Recent studies have provided evidence that the adverse health consequences of

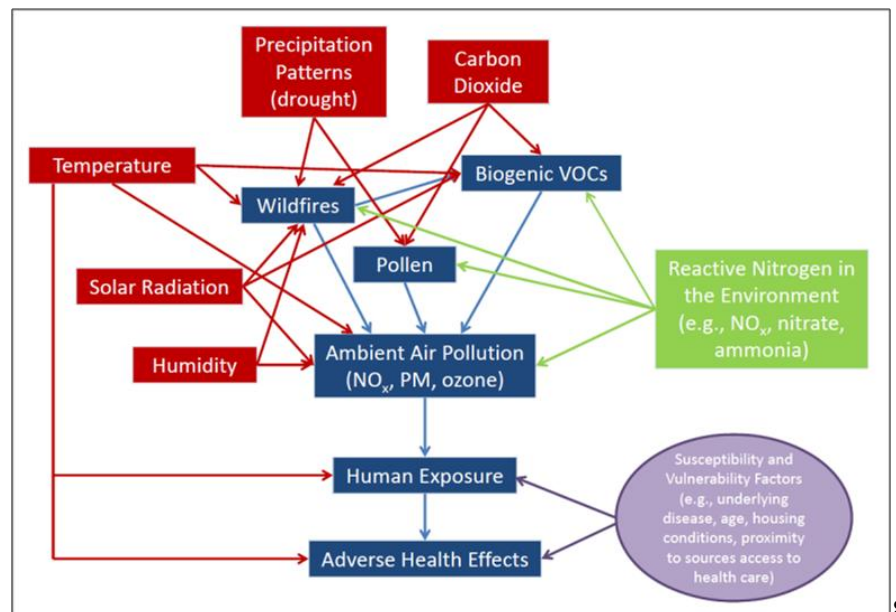


Figure 1.6: Interactions of climate change factors, N_r and their impact on air quality and human health. (See also Figure 7.1, Section 7.0 in Chapter 7).

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ambient O₃ pollution increase when temperatures are higher (Jacob and Winner, 2009). Changes in temperature and precipitation patterns are projected to both lengthen the O₃ season and intensify high O₃ episodes in some areas. A longer O₃ season could result in O₃ exposure overlapping the spring and fall respiratory viral and asthma seasons. In addition, there is evidence that O₃ and other pollutants can enhance the susceptibility to and the severity of respiratory infections and increase sensitization to allergens (Chauhan and Johnson 2003; Ciencewicky and Jaspers 2007; Rusznak et al. 1996).

- Other climate-related changes may increase the atmospheric release of N-containing air pollution precursors and reactants by impacting wildfire regimes, emissions from soil, and volatile organic carbon (VOC) emissions from terrestrial ecosystems. Increases in climate-induced anthropogenic NO_x emissions are more likely during the summer, when extreme O₃ events are most common and when O₃ formation is most sensitive to NO_x emissions (e.g., Jacob 1999; Liao et al 2010; Weaver et al 2009).
- The impact of climate change on PM_{2.5} levels is less clear than for O₃. While climate-induced severe air stagnation events can lead to increased pollutant levels, PM_{2.5} formation is expected to decrease in areas where rainfall is expected to increase and/or become extended. Higher temperatures will also shift the thermodynamic equilibrium away from nitric acid combining with NH₃ to form the ammonium nitrate (NH₄NO₃) aerosol, leading to lower levels of that aerosol product (Stelson and Seinfeld, 1982, Dawson et al., 2007; Mahmud et al., 2010). Accordingly, the impact that climate change will have on PM_{2.5} will likely vary regionally.
- Vulnerability to the joint impacts of N-related air pollutants and global climate change will reflect the non-uniform distribution of human exposures (Morello-Frosch et al. 2011). Furthermore, vulnerability to the impact of both air pollution and temperature is greater in the absence of air conditioning, which has been shown to prevent or reduce infiltration of many ambient air pollutants indoors as well as to affect vulnerability to heat waves. This vulnerability has been shown to covary with socioeconomic status, education, poverty and race, social isolation, age, and pre-existing diseases (e.g., diabetes; Reid et al. 2009).
- Although some components of air quality have been improving in the US and are expected to improve further as NO_x emissions decrease due to current control programs, air pollution may worsen even with future NO_x emissions reduction due to the “climate penalty” (Wu et al. 2008). In other words, the same amount of NO_x reduction may result in less O₃ mitigation in a warmer world.

In addition to analyzing these main points and others, each of the following chapters also provides a list of research needs for improved understanding of climate-N interactions.

Conclusions

Analysis of the drivers of climate change, adaptation options, and the severity of impacts requires in-depth understanding of many interactions between climate change and human alteration of the N cycle. Perturbations of both climate and the N cycle will cause multiple stressors to ecosystem function and human health that are likely to be additive or synergistic. Although our knowledge of those interactions is incomplete, we know a great deal about mitigation of climate change and mitigation of excess N in the environment. As with climate change, political and economic impediments often stand in the way of mitigating releases of excess N to the environment (Davidson et al., 2012). However, we demonstrate in this report that policies aimed at improving N-use efficiencies in agriculture and reducing emissions from transportation and energy sectors would have multiple interacting benefits for climate mitigation and for minimizing climate change impacts on crop productivity, air and water quality, biodiversity, and human health risks.

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Chapter 2: The US Nitrogen Synthesis: N-use Efficiency among Economic Sectors and N by Climate Risks Nationwide

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ABSTRACT

Spillover of reactive nitrogen (Nr) compounds onto the environment heightens the risk of climate change impacts on human health and environmental systems, affecting coastal eutrophication, biodiversity, air quality, and national food security interests. We here seek to identify inefficiencies associated with intentional N use (i.e., creating synthetic N fertilizers and cultivating N-fixing legumes) among the major N-dependent sectors of the US economy by drawing on N inventory data at national and regional scales. We define efficiency of N use as the proportion of N directly incorporated into intended products – i.e., food, fiber, fuel, and industrial goods – versus the pool of initial N feedstocks available. Any N that is not incorporated into a given product is considered “excess N”, and we trace the fate of such excess N through the climatologic, environmental and human health systems. At the national scale, our analysis points to substantial inefficiencies in N use, approximately 45 % of the N that enters the US economy never makes its way into an intended product. Excess Nr spillover is most pronounced in agricultural sectors of the economy, where a substantial fraction of N leakage from croplands leads to poor water quality (nationwide), and hotspots of ozone (O₃) related air quality issues, especially in Midwestern and Northeastern regions of the US. In terms of climate interactions with Nr, agricultural activities in the Midwest are identified as the largest source of nitrous oxide (N₂O) to the atmosphere. Targeted efforts to reduce excess N from agriculture would therefore not only benefit drinking water quality, coastal eutrophication and air quality, but would aid significantly in greenhouse gas mitigation. From a carbon (C) storage perspective, the positive benefits of anthropogenic deposition are most evident in forests growing in the Northeast and Northwest regions of the US. In particular, the large C sink in the Northeastern US is at least partially due to elevated quantities of N in deposition that are associated with power plants in the Ohio River Valley. However, such positive benefits of excess Nr on the environment will not persist indefinitely; chronically high N inputs act to acidify soil-systems resulting in increases in tree mortality and forest declines as already seen for some Northeast hardwood forest ecosystems. Rather, when viewed overall, improved N use efficiency and reduced Nr spillovers would have positive benefits for the economy, US citizen human health, ecosystem services, and climate change. For example, reducing N losses from agriculture and other economic sectors would reduce risks of climate change on coastal eutrophication, smog formation, and warming effects associated with N₂O without negatively affecting food production or economic output.

2.0 INTRODUCTION

An essential resource for life, nitrogen (N) influences many aspects of both natural and managed ecosystems (Vitousek et al. 1997). Historically, N is the nutrient that most often constrains plant productivity worldwide (Vitousek and Howarth, 1991; Lebauer and Treseder, 2008). However, humans have substantially accelerated reactive N (Nr; defined as all N forms other than dinitrogen (N₂)) cycling – supporting dramatic gains in production of food, fiber and industrial goods, more than doubling terrestrial Nr inputs compared to background conditions (Galloway et al. 2003). This substantial biogeochemical perturbation has also produced unwanted consequences, altering the climate system, air and water quality, and the biodiversity of natural ecosystems (Compton et al. 2011). The objective of this chapter is to examine the major flows of N in the US and thereby identify some of the major challenges facing excess N use nationwide. Specifically, we analyze recent trends in N flows, examine efficiencies of N usage among different sectors of the economy, highlight risks of excess Nr in the environment, and identify the kinds of N by climate interactions that are likely to play out across US regions. We base our assessment on the synthesis of several existing data sets and on summary calculations.

Over nearly all of Earth's history, since the evolution of photosynthetic organisms, the conversion of atmospheric N₂ to trace quantities of Nr forms has not kept pace with biological demands, thereby limiting the full productive potential of the biosphere (Falkowski 1997; Vitousek and Howarth, 1991). The first traces of Nr creation were likely associated with lightning storms in the early atmosphere; this conversion was critical to the first organisms on Earth, but it remains today only a small piece of the global N budget (Galloway et al. 2004; Gruber and Galloway, 2008). Owing to the pressure of N scarcity on early life, marine cyanobacteria developed the biochemical machinery to convert N₂ in the atmosphere into amino acids and proteins around 3.5 billion years ago (Falkowski 1997). Biological N fixation (BNF) gave N fixing organisms a competitive advantage over non-N fixing organisms. It also radically altered the cycles of other major elements such as phosphorus (P) and carbon (C), and restructured the global climate system. Nevertheless, the high-energy requirements of BNF, coupled with gaseous N losses mediated by natural bacteria (i.e., denitrifiers), have for eons limited the abundance of Nr on Earth (Vitousek and Howarth, 1991; Houlton et al. 2008; Schlesinger 2009; Houlton and Bai, 2009).

However, anthropogenic activities have altered the N cycle profoundly: human activities result in substantial N fixation, largely via the “Haber-Bosch” process, more than doubling the N flows on land when compared to pre-industrial levels (Millennium Ecosystems Assessment, 2005). Unlike biochemical N fixation, Haber-Bosch fixation combines intense pressure, heat and natural gas to convert atmospheric N₂ into fertilizers and other N-based industrial products. Agricultural expansion has also enhanced biological N fixation in leguminous crops such as soybeans and peas, and human activities fix N inadvertently during fossil fuel combustion (Vitousek et al. 1997). The benefits of anthropogenic N fixation are well documented; it has allowed human populations to grow substantially over the past 100 years, particularly through the increased abundance and worldwide distribution of N fertilizer (Galloway et al. 2003). Many industrial products also require N – especially those associated with the production of plastics and nylon (Galloway et al. 2008). Finally, fiber production in plantation forestry has benefited from fertilizer inputs, as has the biofuel industry, which is also heavily reliant on N fertilization of agricultural fields (Crutzen et al. 2008).

Unfortunately, unwanted risks related to excess Nr spillover are extensive, as can already be seen on land, and in the water and air (Compton et al. 2011; Davidson et al., 2012). Much of the effect of Nr on

the total environment centers on its extreme mobility; N_r mobilizes quickly from land to the air and waterways, meaning that a single atom of fixed N cascades through all of Earth's systems (Galloway et al. 2003). For example, an estimated average of 50% of the N applied to agricultural ecosystems escapes to the broader environment each year (Leach et al., 2012). Our comprehensive analysis here will help to inform N-based management needs, and identifies several win-win options for the economy and environment.

In this chapter, we provide an overview of N flows in the US, and the interactions of N with climate, with implications for environmental quality and human health. We approached our assessment in four primary ways. First, we highlight major aspects of N impacts on climate change, eutrophication, and biodiversity and air quality – and describe potential overlaps among climate x N interactions. Second, we analyze recent trends in N fluxes, evaluating the efficacy of recent N-based policies and research areas of further need. Formulated in large part by a science advisory board report to the EPA (SAB, 2011), this analysis takes advantage of their comprehensive N budget. Third, we compile N flows and budgets associated with the nation and among different economic sectors – including, food, fiber, fuel and industry. Our goal here is to evaluate the efficiency of N use nationally and identify opportunities for improved efficiency gains. Finally, we examine the regional effects of excess N, including N interactions with direct climate change, C sequestration, and air and water quality.

2.1 RISKS OF REACTIVE N AND CLIMATE CHANGE ON THE ENVIRONMENTAL SYSTEM

Both climate and N affect many aspects of the environment and human health. In some cases N x climate effects are additive, in others synergistic. This section focuses on three major interactions involving changes in N and climate– C sequestration, eutrophication, and air quality and it frames the impetus for our nation-wide N assessment.

2.1.1 Interactive effects of N and climate on C sequestration

As a biologically essential element, N influences plant photosynthesis, terrestrial C storage, and the pace and magnitude of global climate change (Field and Mooney, 1986; Vitousek and Howarth, 1991; Hungate et al. 2003; Lebauer and Treseder, 2008; Wang and Houlton, 2009; Erisman et al., 2011). Decades of experiments have shown that N limits carbon dioxide (CO_2) uptake in many terrestrial ecosystems – and the role of N as a key limiting resource is apparent in many streams, rivers, lakes and the sea (Elser et al. 2007). Such widespread N limitation makes logical sense given the fundamental role N plays in DNA, protein, and many cell functions (Sturner and Elser, 2002). Additionally, the preponderance of N limitation is not simply an environmental issue; the billions of dollars spent annually on N fertilizers for food production is a testament to the widespread importance of N. Figure 2.1 presents a model-based estimate of patterns of nutrient limitation on land, revealing especially widespread N (and N plus P co-limitation) of terrestrial processes in areas outside of the tropics, including much of the US (Wang et al. 2010). While the projection of nutrient limitation in Figure 2.1 needs further field verification, it agrees with widespread N and N plus P co-limitation observed for many temperate zone forest and grassland ecosystems (Elser et al. 2007)

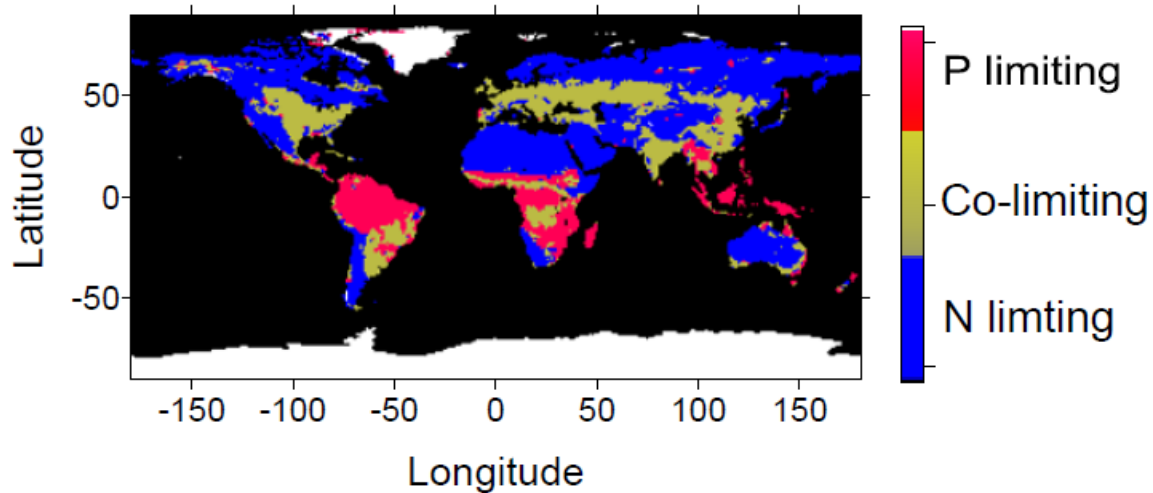


Figure 2.1: Estimates of the geographic occurrence of N limitation, P limitation and N x P co-limitation on land. From Wang et al. (2010).

Over 80% of the N_r produced by human activities occurs via Haber-Bosch production and fossil fuel combustion (Galloway et al., 2004; Gruber and Galloway, 2008). While the airborne fraction of agricultural N remains relatively local to the site of fertilization, N_r produced by fossil fuel combustion can travel far distances from the initial source of creation, and is thus responsible for rising rates of N deposition on many temperate forests globally (Holland et al. 2005; Dentener et al. 2006). Elevated quantities of N deposition have the potential to fertilize plant growth in natural ecosystems, with estimates suggesting an “N fertilization effect” that varies between approximately 0.2 Pg of to 0.6 Pg of C/yr in forests (Thomas et al. 2010). The major source of uncertainty in this calculation, among other factors, has to do with the amount of C storage per unit of N addition; the C/N uptake ratio has been estimated to range between 200 and 20 in temperate forests (Thomas et al. 2010; see Chapter 3).

In addition to the effects of N deposition on C sequestration, changes in climate directly affect the C sequestration potential of ecosystems as well. Globally, as rising temperatures accelerate rates of microbial decomposition during the next 50 to 100 years, the expected C-climate feedback will release some of the stored CO_2 back to the atmosphere (Friedlingstein et al. 2006). In the conterminous US, such climate impacts on C sequestration are likely to vary spatially. For instance, interior continental areas will likely become warmer and drier, which will facilitate fires and release significant quantities of C to the atmosphere (Westerling et al. 2006), as well as increase the incidence of tree mortality from pests such as the mountain pine beetle (Pfeifer et al. 2011) and the hemlock wooly adelgid (Ellison et al. 2005). On average, climate change in US latitudinal bands 35° - 55° N has increased forest productivity over the last 20 years (Slayback et al. 2003), though some forested areas of the western US have exhibited declines in productivity over this same time period owing to the effects of climate change (van Mantgem et al. 2009). Overall, dynamic-global vegetation models suggest a decrease in C storage with climate change compared to cases without climate change; soil decomposition rates are projected to accelerate substantially in the future as the climate warms (Sitch et al. 2008).

The combined effects of climate and anthropogenic N deposition on C sequestration are, on balance, positive, although there are large uncertainties, which are analyzed, in detail in Chapter 3. Moreover, the positive effects of N deposition on C sequestration must be tempered by observations that large,

chronic inputs of N can lead to soil acidification, nitrate (NO_3^-) exports to drainage water, and increased tree mortality (Aber et al. 1998, 2003). Finally, while N deposition x climate effects may increase C storage on average – current estimates suggest that the cooling effects are largely compensated for by the warming effects of increases in N_2O as the result of agricultural fertilizer use (see Chapters 3 and 4).

2.1.2 Eutrophication of aquatic ecosystems

Eutrophication is a global issue that threatens the functioning, sustainability and security of the world's coastal regions and freshwater resources (Vitousek et al. 1997). It is the process whereby nutrient (e.g., N, P) enrichment accelerates plant growth. In the case of aquatic ecosystems, eutrophication is associated with the growth of substantial algal blooms in both fresh waters and in coastal zones. Studies in the 1960s and 1970s found that elevated concentrations of P in detergents were leaching into lakes and thereby promoting the occurrence of massive algal blooms. Lake Erie in the US is a well-documented example of this (e.g., Schindler 1977; Chapra and Robertson 1977). In contrast, the nutrient N plays a principal role in eutrophication of many estuarine ecosystems (Howarth 2008).

Increases in crop N fixation and synthetic N fertilizer applications (see Chapter 4), and increased N fixation via fossil-fuel combustion, have promoted widespread eutrophication of estuaries (Howarth 2008; see Chapter 5). Nitrogen is scarce in many natural estuarine ecosystems, owing to fundamental constraints on natural N fixation inputs in such environments (Vitousek and Howarth 1991). As mentioned earlier, on average only 50% of the N applied to soil to grow crops is in the harvested biomass (Leach et al. 2012). This means that a substantial fraction of the N applied to land leaches to groundwater and surface waters. Moreover, N fixed during fossil fuel combustion enriches aquatic N supplies through transportation via atmospheric deposition on coastal environments (Howarth et al. 1996; Duce et al. 2008).

Once anthropogenic N enters coastal ecosystems, it can fuel large algal blooms (Howarth 2008). Although algal photosynthesis initially produces oxygen (O_2), decomposing organic matter eventually consumes O_2 in the water column leading to hypoxia (little oxygen). The global extent of hypoxic zones (also known as “dead zones”) is highly correlated with human populations and centers of agricultural productivity (Diaz and Rosenberg 2008). In the US, chronically high N fertilizer applications in the Midwest have greatly accelerated algal production in the Gulf of Mexico (Rabalais et al. 2007). Transport of N by the Mississippi River has fueled the hypoxic zone in the Gulf. In contrast, estuaries of the Northeastern US show a high correlation of eutrophication with anthropogenic N deposition associated with fossil fuel combustion and energy generation (Howarth et al. 1996).

Furthermore, climate strongly influences eutrophication and hypoxia (Rabalais et al. 2009). Climate-change driven stratification of estuaries reduces atmospheric O_2 ventilation of deeper water, further intensifying hypoxia (Rabalais et al. 2009). Thus as global temperatures rise, the risk of hypoxia increases, all else remaining equal. Enhanced O_2 deprivation of sub-thermocline waters can also increase the re-suspension of ammonium-N ($\text{NH}_4\text{-N}$) in bottom sediments; this N can become entrained back into the euphotic zone during periods of turnover, feeding back positively on algal growth, eutrophication, and hypoxia (Mee 2006). Finally, changes in global precipitation patterns associated with climate change are likely to reinforce hypoxia, for example, increases in prolonged periods of hypoxia in coastal waters are likely to occur as larger fresh water flows strengthen the density difference between surface and subsurface waters (Rabalais et al. 2009).

2.1.3 Biodiversity

Biodiversity contributes to regulating ecosystem services, such as climate regulation, flood protection, disease mitigation, and water quality regulation. The strongest drivers of biodiversity loss include habitat loss; overexploitation, invasive species, climate change, and pollution, including pollution from Nr (see Chapter 6). Nitrogen enhances plant growth, but particularly favors invasive, fast-growing species over native species adapted to low N conditions. For example, in arid ecosystems of southern California, elevated N and changing precipitation patterns have promoted the conversion of native shrub communities to communities dominated by a few species of annual non-native grasses, which have increased fire risk (Rao et al. 2010). Results from both empirical studies and modeling indicate that N and climate change can interact to drive losses in biodiversity greater than losses caused by either stressor alone (see chapter 6). Reducing inputs of anthropogenic Nr may be an effective mitigation strategy for protecting biodiversity in the face of climate change.

2.1.4 Air quality

An altered N cycle contributes to air pollution in several ways, and has significant socioeconomic consequences. Concentrations of nitrogen oxides (NO_x) in the atmosphere are a key control over the formation of tropospheric ozone (O_3 ; Jacob 1999) and both NO_x and ammonia (NH_3) in the atmosphere react with other atmospheric constituents to elevate air pollution due to fine particulate matter (PM) aerosols. Such constituents have a variety of negative consequences for human health, for example NO_x is a component of indoor air pollution (Wolfe and Patz 2002; Chauhan et al. 2003; see Chapter 7). Therefore, because of their health risks, both PM and O_3 are regulated pollutants in the US, but exceedance of regulatory standards occur in multiple locations every year, causing increased morbidity and mortality in humans (see Chapter 7) (Bell et al. 2007; Fann et al. 2012). Moreover, higher O_3 levels not only cause direct health damages to humans, they reduce crop and forest growth (see Chapter 4), resulting in both economic and potential food security consequences (Chameides et al. 1994; Compton et al. 2011; Birch et al. 2011; Shindell et al. 2012). In the US alone, the costs of N-related air pollution exceeded an estimated \$15 billion per year (USD_{2002}) (Muller and Mendelsohn 2007), with most of this cost attributed to direct health impacts.

Air pollution related to N is also sensitive to both temperature and precipitation, thus air pollution is one of several important interactions between the N cycle and climate change. For example, largely due to the Clean Air Act, NO_x emissions and concentrations are declining in many regions of the US (See Figure 2.2 described below); this trend alone should lessen the risks of O_3 exposure. However, O_3 formation is also strongly temperature sensitive (Jacob and Winner 2009), thus rising temperatures can exact a so-called "climate penalty" on the air pollution gains made by reducing NO_x emissions (Wu et al., 2008; see Chapter 7). Temperature and moisture also affect the rates of NO_x and NH_3 emissions from multiple sources, as well as their subsequent reactions in the atmosphere (Jacob and Winner 2009). In addition, the atmospheric lifetime and the transport distance of particulate air pollution are strongly affected by precipitation patterns (Fang et al. 2011). Thus, future risks from N-related air pollution in the US will not only be a function of N cycle dynamics, but of their interactions with a changing climate.

From a climate-change perspective, these interactions also highlight an important opportunity for mitigating the risks of climate change. Air pollution is one such risk: multiple studies predict that human and crop exposure to damaging forms of air pollution will increase under expected climate change trajectories (Van Dingenen et al 2009; Avnery et al. 2011). However, significant mitigation of Nr releases to the environment would reduce at least some of these risks (Townsend et al. 2012).

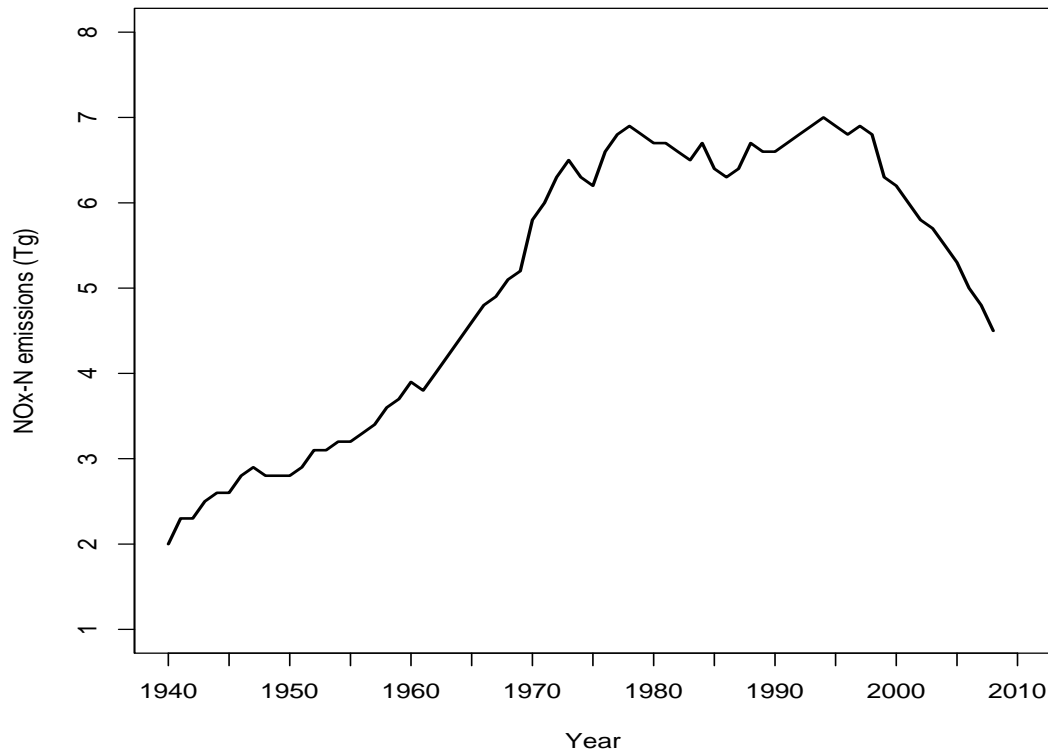


Figure 2.2: Gaseous emission of nitric oxides (NO_x) in the United States, 1941 – 2007. Source: EPA National Emissions Inventory (USEPA 2011a).

2.2 US N INVENTORY

This section describes the major N flows and fluxes in the US, including recent trends, contemporary budgets, and imports and exports of N in goods, and calculates efficiencies in N use among the major N-based sectors of the economy.

2.2.1 Conceptual framework: The N cascade

We base our nationwide assessment of Nr in the US on what is referred to as the N cascade. This concept points out that the creation of a new molecule of Nr can, in sequence, interact with the total environment – thereby contributing to a suite of environmental problems (Galloway et al., 2003). In the context of accounting for N inputs and losses nationwide, this is a useful model for synthesizing the various aspects of N cycling that we quantified and their potential effects. The conceptual model presented here (Figure 2.3) is taken from a recent report of the US Environmental Protection Agency (after USEPA 2011, where the N cascade illustration was designed by co-authors Boyer & Galloway).

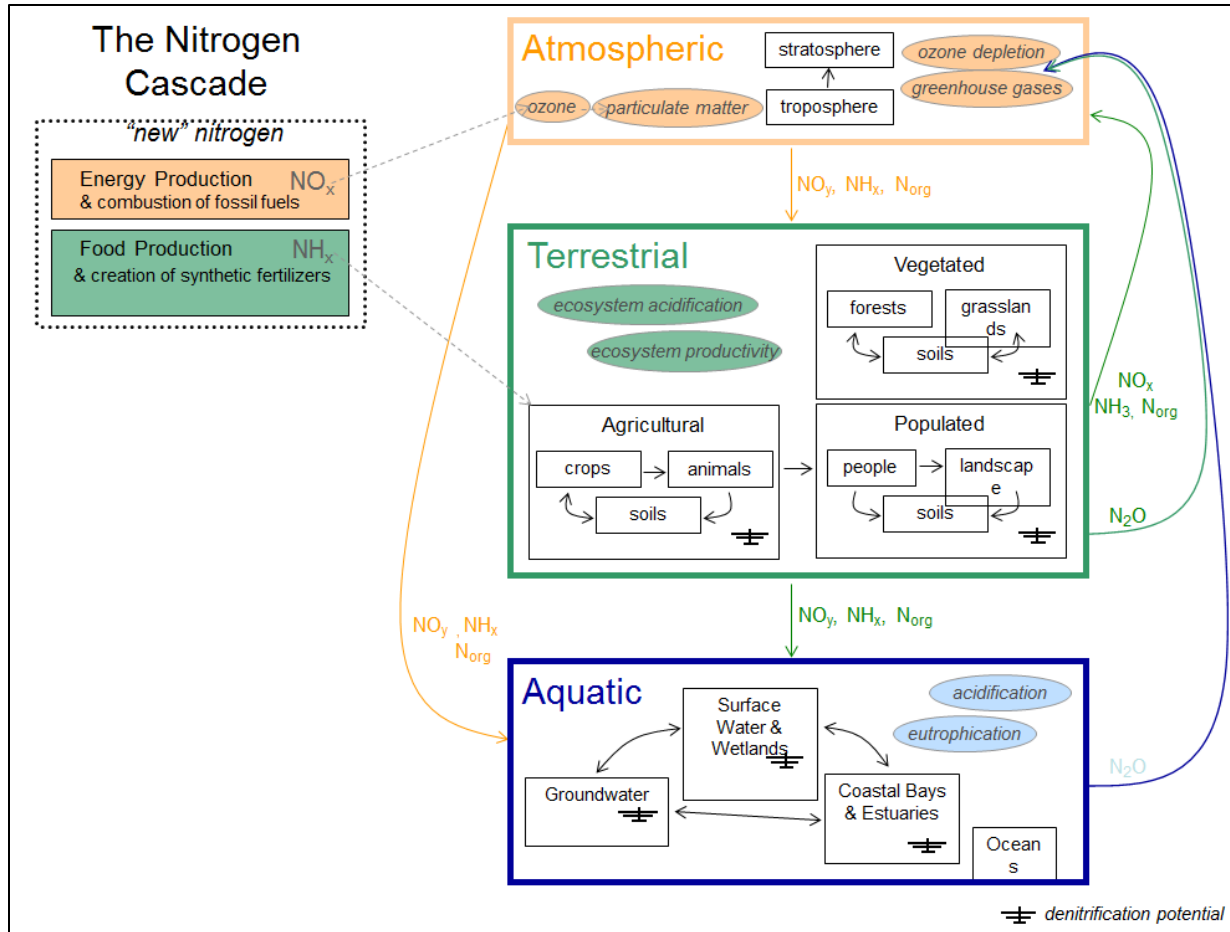


Figure 2.3: The Nitrogen Cascade Model.

The "new" N box depicts the two primary anthropogenic processes through which Nr originates, energy production and food production, and locations where Nr from these sources enter ecosystems. Energy production includes both fossil fuel and biofuel combustion. Food production includes N fertilizer produced in the US, cultivation-induced biological N fixation (C-BNF) in the US, production of animals and crops in the US for human consumption, and imports of N-containing fertilizer, grains and meats to the US.

The **atmospheric** environment box indicates that tropospheric concentrations of both O_3 and PM increase due to emissions of NO_x to the atmosphere. The ovals illustrate that the increase in N_2O concentrations, in turn, contribute to the greenhouse effect in the troposphere and to O_3 depletion in the stratosphere. Except for N_2 , there is limited Nr storage in the atmosphere and losses of Nr from the atmospheric system include total oxidized N ($\text{NO}_y = \text{NO}_x + \text{HNO}_3 + \text{organic nitrates} + \text{inorganic nitrate}$), reduced N (NH_x), and organic N (N_{org}) deposition to terrestrial and aquatic ecosystems. There is little potential for conversion of Nr to N_2 via denitrification in air; however, once airborne deposition of Nr occurs it is subject to denitrification pathways in both soil and water.

The **terrestrial** environment box depicts that Nr enters agricultural lands via fertilizer for food production, and further enters into the entire terrestrial landscape via atmospheric deposition. Within agricultural regions, N cycles among soils, crops and animals, and then a transfer of Nr through food to populated

regions, from which there are also Nr losses to the environment (e.g., sewage, landfills). The ovals showing ecosystem productivity and biogeochemical cycling show that Nr is actively transported and transformed within the terrestrial system and that consequently there are significant impacts on ecosystem productivity due to fertilization and acidification, often resulting in declines in biodiversity. Losses of Nr from this system occur by leaching and runoff of NO_y , NH_x and N_{org} to aquatic ecosystems and by emissions to the atmospheric system as NO_x , NH_3 , N_{org} and N_2O . There is also potential for conversion of Nr to N_2 via denitrification in the terrestrial system. However, there are many opportunities for Nr storage in both biomass and soils.

The aquatic environment box shows that Nr enters via leaching and runoff from terrestrial ecosystems and via atmospheric deposition. Connected with the hydrological cycle, there are fluxes of Nr downstream, eventually moving to coastal zones and the ocean. Within the aquatic system, the ovals highlight two significant impacts of waterborne Nr and include the acidification of freshwaters and eutrophication of both fresh and coastal waters. Except for the accumulation of Nr in groundwater reservoirs, there is limited Nr storage available in the aquatic environment. Losses of Nr from the aquatic system are primarily via N_2O emissions to the atmosphere. There is, however, a large potential for converting Nr to N_2 via denitrification in both water and wetlands.

The process of denitrification to N_2 – defined here to include anaerobic denitrification, nitrifier-denitrification, and ammox pathways – is the only mechanism by which Nr is converted to chemically inert N_2 , thereby completing the continuous cycle (the figure shows only flows of Nr, not N_2). Denitrification has the potential to occur in any of the indicated environments except in the atmosphere.

2.2.2 Recent trends in flows of N nationwide

Prior to the early 1900s, the global inventory of fixed N was controlled (mainly) by the balance of BNF inputs versus N losses to denitrification (Falkowski 1997). Production of food, fiber, fuel, and some industrial products such as nylon and explosives have substantially increased global and US N consumption since World War II (Galloway et al. 2008). This has dramatically altered the structure of the N cycle and transformed the natural flows of N that long-determined ecosystem N availability. In the US, consumption of synthetically fixed NH_3 increased exponentially from 0.4 Tg per year in 1943 to a maximum of 17.1 Tg in 1998 (Figure 2.4). From the 1940s to the 1980s, the rate of fertilizer consumption grew at an average of 11% per annum. Since 1980, however, consumption has leveled off and has remained relatively constant with limited year-to-year variation, converging on a mean value of $14.7 \text{ Tg} \pm 1.2 \text{ Tg}$ per year. Fertilizer consumption accounts for nearly 90% of the N consumed in the US and thus its use is reflected in the overall trend (USGS 2010). Non-fertilizer synthetic N data suggest that non-farm consumption declined 49% from 2.7 to 1.4 Tg per year between 1975 and 2009. However, such a downward trend contrasts with recent global trends (International Fertilizer Association (IFA) 2009 in Winiwarter and Hettelingh 2011).

Nitrogen fixation along symbiotic and nonsymbiotic paths converts atmospheric N_2 into constituents of Nr that are available to all forms of life (see Figure 2.3). Human domestication of crop species that are capable of BNF has increased the magnitude of this N input substantially. Consequently, human appropriation of N fixation is generally proportional to biomass production (productivity) and areal extent of cultivation (Herridge et al. 2008). Sobota et al. (in preparation), using the model presented by Herridge et al. (2008) and data from the USDA Census of Agriculture, estimated the historical quantity and contribution of N fixation by soybeans and alfalfa (Figure 2.5). The fixation of N by soybeans and

alfalfa comprise the majority (greater than two thirds) of C-BNF in the US (Howarth et al. 2002), and thus can be used to analyze long-term trends in C-BNF. In addition, as with synthetic N fixation, there have been substantial increases in the amount of N entering terrestrial ecosystems via BNF. Inputs from C-BNF in the US climbed steadily between 1924 and 2009, and in total increased nearly an order of magnitude, from approximately 1.0 to 9.4 Tg per year. Long-term comparisons of synthetic N fertilizer use and C-BNF records suggest that the US agricultural economy transitioned from one mostly reliant on BNF to one more dependent on fossil fuel-derived N fertilizers in the mid-1960s (Figures 2.4 and 2.5). In itself, C-BNF has undergone a massive transition over the past 100 years (Figures 2.5). Until the 1980s, alfalfa comprised the largest fraction of total C-BNF in the US and beginning around 1990 BNF associated with soybeans has consistently exceeded alfalfa-mediated BNF.

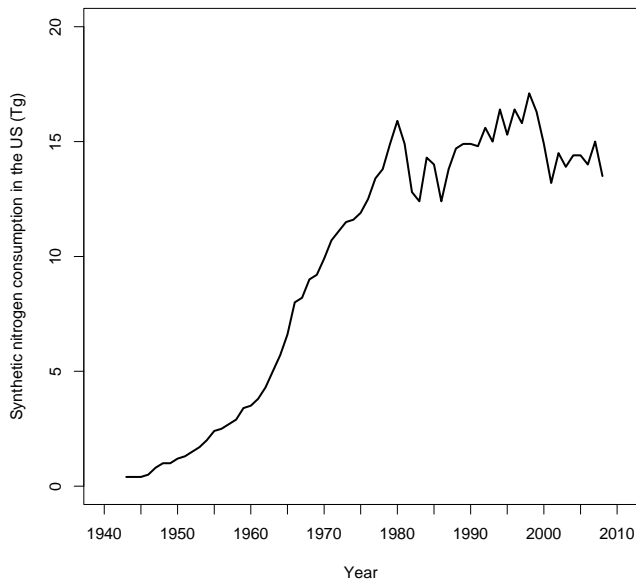


Figure 2.4: Apparent consumption of synthetically fixed nitrogen (ammonia) in the United States, 1943 - 2009. Apparent consumption = production + imports - exports \pm stock changes. Source: USGS (2010).

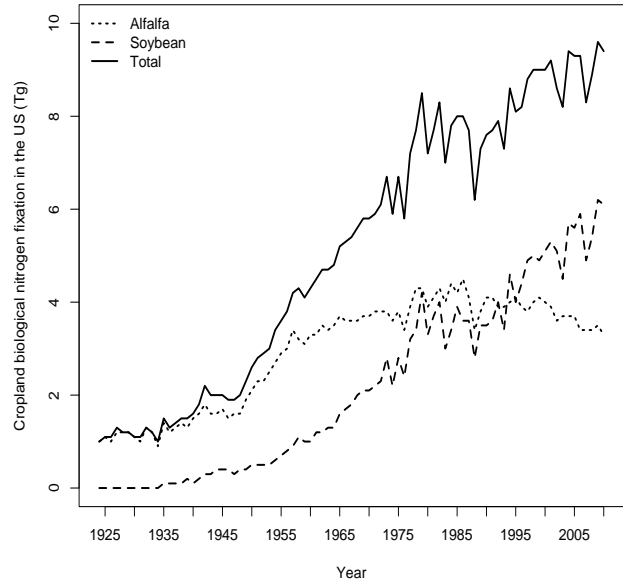


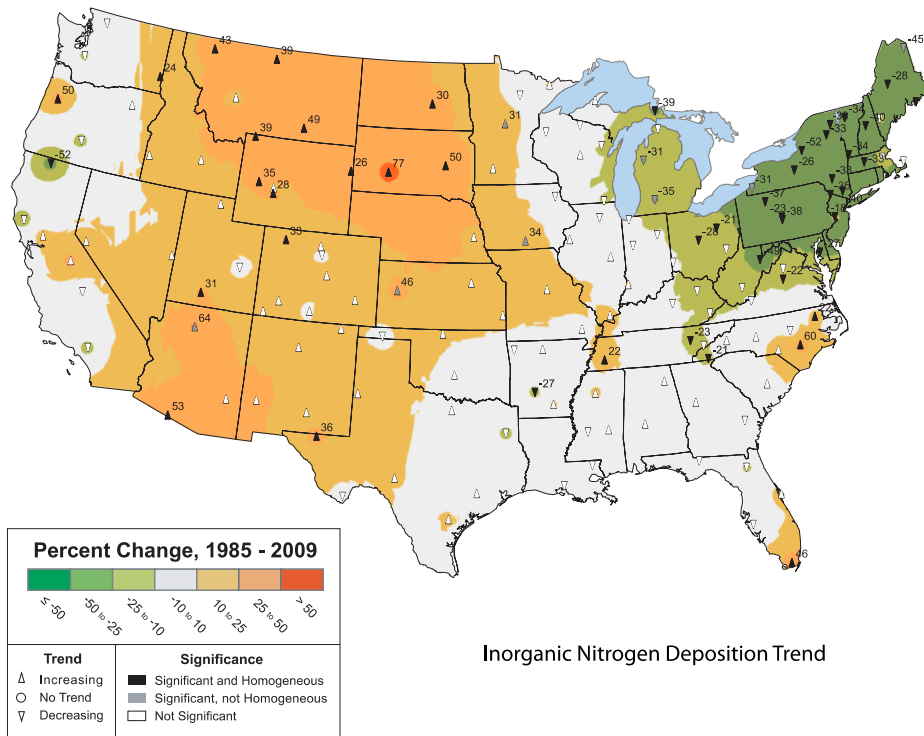
Figure 2.5: Nitrogen fixation by cultivated biological nitrogen fixation (alfalfa + soybean), 1924 - 2009. Source: Sobota et al. (in prep).

Human activities – industrial, transportation, and agricultural – also emit Nr compounds into the atmosphere (see also Figure 2.2). With the growth of industry and increase in the use of the internal combustion engine, emissions of NO_x have risen throughout the middle of the 20th century. Emissions more than tripled, from 2.0 to 7.0 Tg per year, between 1940 and 1970. In the following 25 years, however, emissions stabilized. By the end of the century, the amount of N released into the air as NO_x began to decline significantly, likely due to implementation of the Clean Air Act of 1970 and amendments in 1977 and 1990. In 2008, NO_x emissions accounted for 4.5 Tg, a level equivalent to that of the mid-1960s (Figure 2.2).

Historical trends in N deposition in the US are not as complete as for fertilizer N fluxes, which date back more than 60 years. Monitoring of N deposition began in the late 1970s. Currently a robust nationwide monitoring network with more than 250 sites is in place to monitor N deposition (e.g., National

Atmospheric Deposition Program, NADP). Information characterizing trends in dry deposition is however, meager. Monitoring sites are largely found in the Eastern US, with only sparse data coverage throughout the West (e.g., Clean Air Status and Trends Network), where monitoring beginning in 1987. Limited spatial coverage reduces our ability to draw inferences about historical changes in dry and total deposition at national levels because of the potential bias induced by the skewed distribution of monitoring sites in regions where deposition has been decreasing.

Data collected at NADP sites clearly show significant regional variation in annual deposition rates. From 1985 to 2009, wet deposition of total inorganic N declined by up to 50% in parts of the Northeast (Figure 2.6). However, N deposition increased from 25% to 50% across parts of South- and Mountain-west, which may be partially due to increases in NH_4^+ deposition (Lehman et al. in preparation). Thus, while the Clean Air Act has helped reduce deposition of oxidized N, deposition of reduced forms of N appears to be on the rise. It is of particular concern that the regions seeing the greatest increase in inorganic N deposition contain vast areas of N sensitive ecosystems (Chapter 6).



Inorganic Nitrogen Deposition Trend

Figure 2.6: Trend in wet deposition of inorganic nitrogen, 1985-2009. Source: Lehmann et al. (in preparation).

Finally, while massive increases in N_2O have occurred since pre-industrial times, direct atmospheric measures across the conterminous US are not as extensive as those for the other fluxes mentioned above. Clearly, N_2O has increased substantially with agricultural fertilizer production and increases in denitrification; however, the trend in the US since 2000 has remained relatively constant (Figure 2.7). Agriculture is by far the major source of N_2O in the US (e.g., through soil management and manure use; see Chapter 4).

Moreover, other aspects of the US N cycle have changed but have not been quantified with as much rigor. For example, NH₃ emissions are on the rise and appear to be making up a more significant fraction of N deposition in the US, in addition to being transported to nearby coastal ecosystems (Duce et al. 2008; see also Chapters 4, 6, and 7).

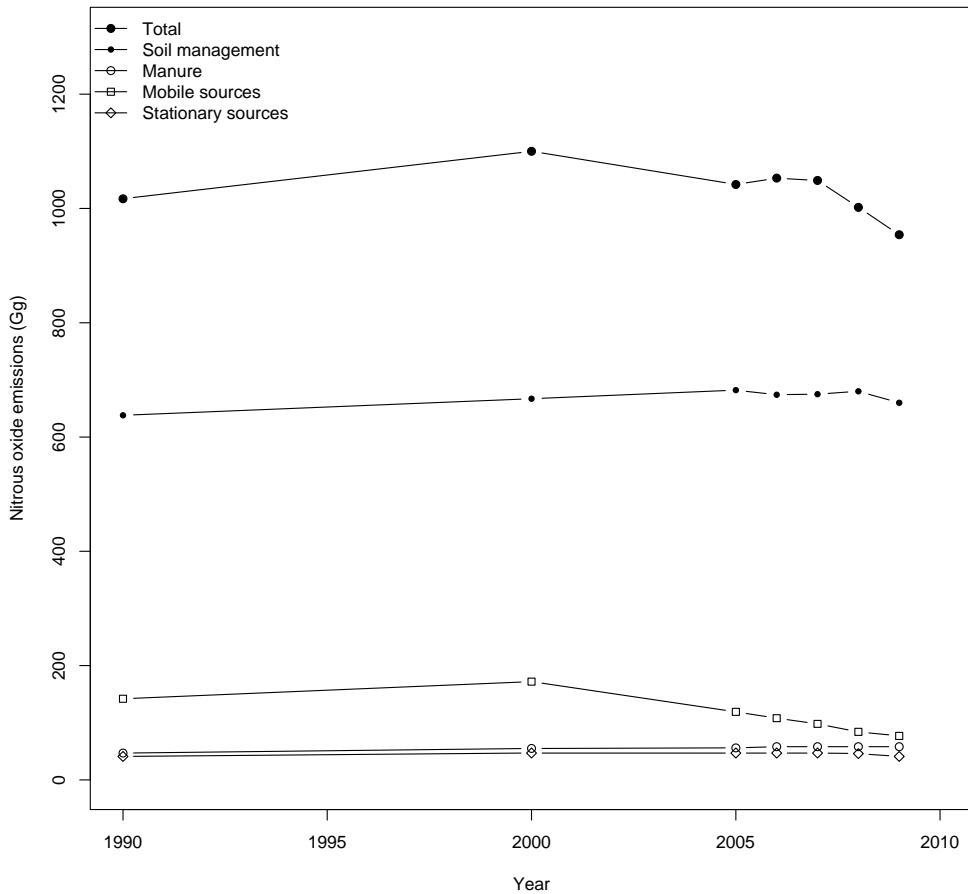


Figure 2.7: Nitrous oxide emissions from major sources. Source: EPA Greenhouse Gas Inventory (USEPA, 2011b)

2.2.3 US N budget for 2002

With temporal trends of Nr in mind, we focus here on the overall N budget for a given point in time for the conterminous US (Figure 2.8; Table 2.1). We present an inventory of Nr in the US for 2002, as the US EPA used this time-slice as a benchmark for contemporary Nr dynamics against which future progress can be assessed amidst changing Nr inputs and implementation of policy and management strategies to mitigate Nr pollution (SAB 2011). The year 2002 thereby provides the most complete and robust assessment of N flows in the US to date. In our assessment, Nr includes all biologically active, chemically reactive, and radiatively active N compounds in the atmosphere and biosphere, and is in contrast to the non-reactive gaseous N₂ which makes up approximately 78.1% of the atmosphere.

As stated earlier, in terms of inputs, agriculture and domestic use of fertilizers to produce food, feed, and fiber (including bioenergy and BNF) and combustion of fossil fuels are the largest sources of Nr released into the environment in the US (Figure 2.8). The largest single source of Nr in the US is the Haber-Bosch process creating synthetic fertilizers, which introduces about 15.2 Tg N/yr (9.4 Tg N/yr from Nr that was produced & used in the US, and 5.8 Tg N/yr from net imports of Nr in fertilizers). The 15.2 Tg N/yr of anthropogenic Nr is used in three ways; (1) 9.9 Tg N/yr is used to produce agricultural crops; (2) 1.1 Tg N/yr is applied to turf grasses; and (3) 4.2 Tg N/yr is used by industry for production of nylon, refrigerants, explosives and other commercial products. Mentioned earlier, the second largest source of Nr introduced into the US is through the enhancement of BNF by cultivating legumes like soybeans and alfalfa that have N-fixing symbionts, or by crops such as wetland rice that have N-fixing bacteria in their rooting zones. These N fixing crops introduce about 7.7 Tg N/yr. Additionally, a small amount of Nr is also imported in commodities such as in grain and meat products; in 2002, this source of added Nr was approximately 0.2 Tg N/yr. Fossil fuel combustion is the third largest source of Nr; it introduces approximately 5.7 Tg N/yr into the environment (almost entirely as NO_x), 3.8 Tg N/yr of which is derived from transportation sources and 1.9 Tg N/yr occurs from stationary sources such as electric utilities, industrial boilers and from certain industrial processes.

Considering just the anthropogenic inputs mentioned, humans introduced 28.6 Tg of newly formed Nr into the US in 2002 (Figure 2.8). About 65% of N inputs were from agricultural sources (including BNF and turf production), 20% from fossil fuel sources, and about 15% from industrial sources. Overall in the US, the amount of Nr produced by human activities was approximately five-times larger than all natural processes combined; while at the global scale, human activities produced approximately twice as much Nr as did natural processes (SAB 2011).

Human activities have also greatly modified the amount of N that is lost from the land. In terms of gaseous N losses, NH₃ and NO_x account for 31 % and 61 % of gaseous Nr emissions, respectively (Table 2.1) – or a combined flux of 9.3 Tg N/yr. However, a significant fraction of these N gases are re-deposited on US soil downwind of the source. Hence, they form large-scale, short-term recycling loops among US regions as opposed to being completely lost from the nation, for example a substantial fraction of NH₃ and NO_x emissions recycle among terrestrial regions. This behavior contrasts sharply with the other two major gaseous N losses, the radiatively important N₂O and the inert N₂, which are long-lived and mix evenly within the global atmosphere. As of 2002, N₂O accounted for approximately 8 % of all gaseous Nr emissions, with N₂ likely equal to twice that of N₂O efflux (Houlton and Bai, 2009), albeit with a high degree of uncertainty (Schlesinger 2009). Globally, N₂O has risen sharply since the industrial revolution and its effective contribution to global warming is expected to double by 2100 (IPCC AR4, 2007), largely owing to the expansion of agriculture and N fertilizers worldwide.

Leaching of N to surface waters has also increased substantially in the US and around the globe. In 2002, N_r gaseous emissions accounted for 10 Tg N/yr whereas N leaching to surface waters was approximately 5 Tg N/yr (Table 2.1). Estimates of groundwater N export are very tenuous and not considered in our assessment. However, previous studies have shown that approximately one third of total annual loads of inorganic N (e.g., NO_3^-) to small streams in the US come from groundwater baseflow (see Chapter 4; Dubrovsky et al. 2010). Also approximately 14-45 % of N entering groundwater as NO_3^- derives from fertilizer and/or manure use and atmospheric deposition (see Chapter 4; Nolan et al. 2010; Puckett et al. 2011).

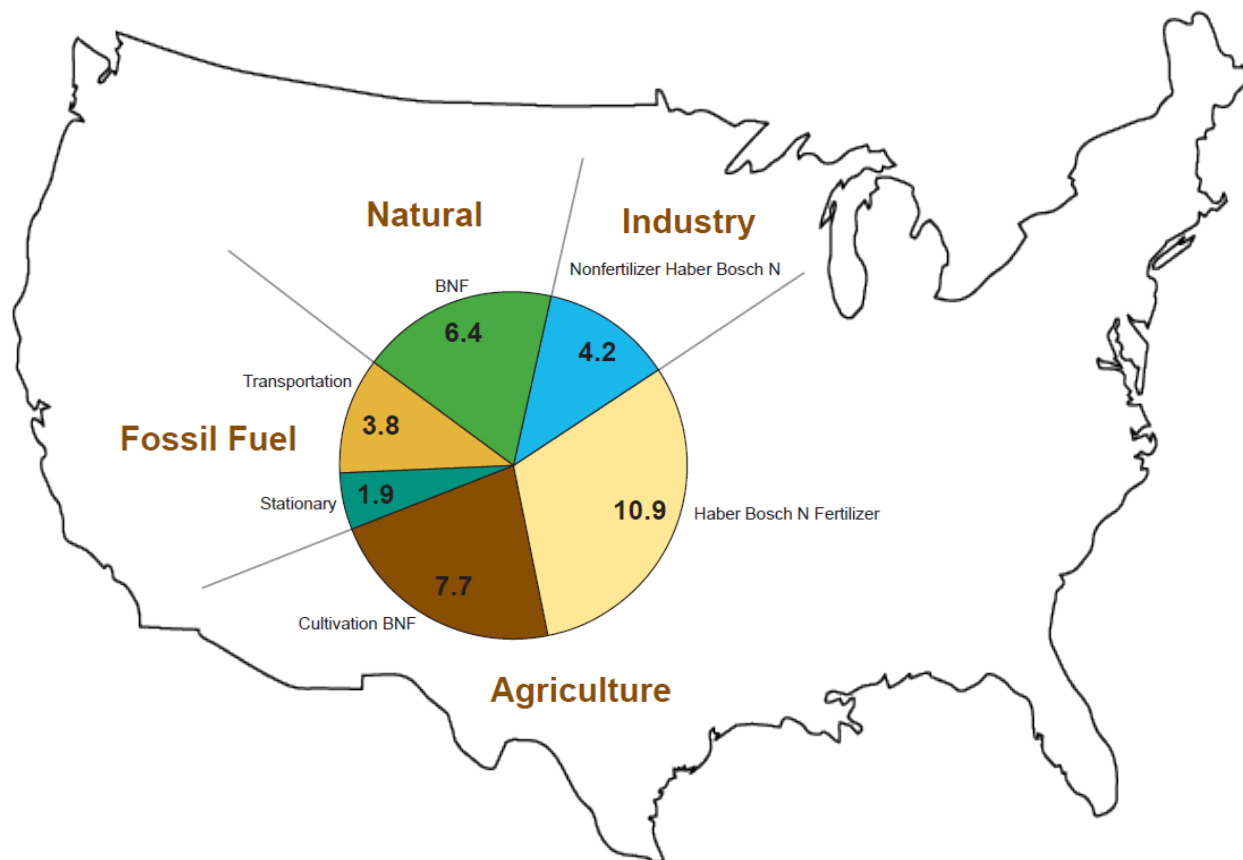


Figure 2.8: Distribution of N inputs in the United States in 2002. Units are in Tg N/yr.

Table 2.1: Reactive nitrogen fluxes for the United States, Tg N in 2002. Nr is reactive nitrogen. Terms with an asterisk indicate Nr that is created, highlighting where Nr is introduced into the environment.

Nr inputs to Atmospheric environment			Tg N/yr	%
N ₂ O-N emissions	Agriculture: livestock (manure) NO ₂ -N	0.03	0.8	8
	Agriculture: soil management NO ₂ -N	0.5		
	Agriculture: field burning ag residues	0.001		
	*fossil fuel combustion: transportation	0.1		
	: miscellaneous	0.1		
NH _x -N emissions	Agriculture: livestock NH ₃ -N	1.6	3.1	31
	Agriculture: fertilizer NH ₃ -N	0.9		
	Agriculture: other NH ₃ -N	0.1		
	*fossil fuel combustion: transportation	0.2		
	*fossil fuel combustion: utility & industry	0.03		
	: other combustion	0.2		
	: miscellaneous	0.1		
NO _x -N emissions	Biogenic from soils:	0.3	6.2	61
	* fossil fuel combustion: transportation	3.5		
	*fossil fuel combustion: utility & industry	1.9		
	: other combustion	0.4		
	: miscellaneous	0.2		
	Total Atmospheric Inputs			
Nr inputs to Terrestrial environment			Tg N/yr	%
Atmospheric deposition	Organic N	2.1	6.9	16
	Inorganic NO _y -N	2.7		
	Inorganic NH _x -N	2.1		
*biological N fixation in cultivated croplands	*soybeans	3.3	7.7	18
	*alfalfa	2.1		
	*other leguminous hay	1.8		
	*pasture	0.5		
	*dry beans, peas and lentils	0.1		
*biological N fixation in non-cultivated vegetation			6.4	15
*N import in commodities (e.g., grain & meat products)			0.2	0.3
*Synthetic N fertilizers produced by Haber Bosch	*fertilizer use on farms & non farms	10.9	15.1	35
	*non-fertilizer uses	4.2		
Manure N production			6.0	14
Human waste N			1.3	3
Total Terrestrial Inputs			43.4	100
Nr inputs to Aquatic environments				
Surface water N Flux	Under average flow conditions in past 3 decades		4.8	

2.2.4 Imports and exports of N in the United States

In addition to the N flows discussed above, N_r embedded in food and fertilizer is traded extensively among countries. Trade has beneficial effects, including economic benefits for exporters and access to a diverse food supply for importers. However, the trade of food and fertilizer N_r also has negative consequences. The producing country that exports an item sustains the environmental burden (e.g., excess N_r released to the environment) while the importer receives the benefit (e.g., the use of the food or fertilizer). The revenue gained from the export reflects production costs, but does not reflect the costs associated with the largely un-priced environmental consequences of producing the exported commodity.

To determine the importance of this for the US, an analysis of the trade of N_r was completed, focusing on the amount of food and fertilizer N_r produced in, imported to, and exported from the US. The analysis does not include the trade of fish, as fish trade data are not available in the FAOSTAT trade application – both food and animal feed are considered, but does not yet distinguish between the two. Food trade data were obtained from FAOSTAT (accessed 6 December 2012), and fertilizer trade data were obtained from the IFA and ICIS (2010). {Food and Agriculture Organization of the United Nations. Updated 2 June 2010. Food Balance Sheets. Accessed 6 December 2012 <<http://faostat.fao.org/site/368/default.aspx>>}. {International Fertilizer Association and ICIS. 2010. Global fertilizer trade flow map.} (See Appendix A for description of methods).

Overall, the analysis of the trade of N_r for the US found that in 2007 (the most recent year for which data from FAOSTAT were available), the US produced 9 Tg N and 11 Tg N embedded in food and fertilizer, respectively, for a total production of 20 Tg N. In addition, it imported 0.4 Tg N embedded in food and 6 Tg N in fertilizer, and exported 3 Tg N in food. These exports from the US resulted in a loss of 3 Tg N to the environment for food that is not consumed in the US, which results in an environmental burden from food exports that is not captured in the price of the exported material.

2.2.5 N use efficiency among major N-based sectors of the economy

In this section, we provide estimates for sources and fluxes of N in the US, calculating efficiencies for the incorporation of fixed N into products (e.g., food, fiber, biofuel, and industrial goods). We classify N inputs as “intentional” vs. “unintentional”, in which intentional N inputs are associated with N fixation in agriculture and Haber-Bosch N fixation and unintentional denotes N associated with fossil fuel combustion. In terms of efficiency, the intentional N not incorporated into the initial product is considered a leak in the system, resulting in N transport to the atmosphere and terrestrial and aquatic environments. The leaks thereby summarize the residual term in our calculation of efficiency, and include gaseous loss vectors such as NO_x, N₂O, NH₃, and N₂ and NO₃⁻ leaching. We recognize that this is a simplification based on set time-domain; as the N cascade model points out, each atom of N that is fixed will ultimately interact with all of earth’s systems (see Figure 2.3). Nevertheless, the emphasis on intentional N creation that does not find its way into the intended product allows us to identify where N is being used optimally versus where efforts could focus to reduce excess N damages on the broader environment. Our analysis focuses on two time points – 2002 and 2007 – providing information on any changes in N over time use as well as overall efficiencies.

Table 2.2 shows the major fluxes of N in our analysis. We observed no major changes in N use between 2002 and 2007; the overall budget suggested only a slight increase in N flows to the US over this time period. Fixation of N currently accounts for 6.5 Tg N yr⁻¹ of total N fixation in the US (SAB 2011), with the

majority (6.4 Tg N yr⁻¹) originating from BNF (Table 2.2). Intentional N fixation includes the cultivation of crops with symbiotic relationships with N fixing microbes (C-BNF) and the fixation of N via the Haber-Bosch process (synthetic fertilizers and industrial N). Intentional N fixation currently accounts for two-thirds (22.8 – 24.7 Tg N yr⁻¹) of total N fixation in the US (Table 2.2; Figure 2.9). Unintentional N fixation occurs during the combustion of fossil fuels, and currently contributes around 15 – 20% (4.8 – 5.9 Tg N yr⁻¹) of total national N fixation (Table 2.2; Figure 2.9). Nearly two-thirds of unintentional N fixation derives from vehicle use, while a majority of the remainder derives from fossil fuel combustion by stationary power plants, industrial boilers, and other similar processes (Figure 2.9). All told, intentional and unintentional N fixation currently exceeds natural N fixation five-fold in the US (Table 2.2).

Table 2.2: N fixation in the United States for 2002 and 2007. All values are in Tg N.

	2002	2007
Natural N fixation		
Lightning ¹	0.1	0.1
Biological N fixation (BNF) ²	6.4	6.4
<i>Subtotal:</i>	6.5	6.5
Intentional N fixation		
Haber-Bosch N		
Synthetic fertilizer ³	10.9	11.4
Industrial production ³	4.2	6.2
N-fixing crop cultivation (C-BNF) ²	7.7	7.1
<i>Subtotal:</i>	22.8	24.7
Unintentional N fixation (emissions)		
Fossil fuel combustion-transportation ⁴	3.6	3.0
Fossil fuel combustion-utility and industry ⁴	2.1	1.7
Other combustion ⁴	0.2	0.1
<i>Subtotal:</i>	5.9	4.8
Grand total:	35.6	37.0

¹Galloway et al. (2004)

²SAB (2011); USDA (2011); 2007 C-BNF estimated using SAB (2011) methods and USDA (2011) data

³FAO (2011)

⁴EPA (2011a)

Approximately 75% of intentionally fixed N enters agricultural systems in the United States for food, livestock feed, energy, and fiber production (Figure 2.9). Synthetic fertilizer comprises two-thirds of N input to agricultural systems, with the remainder originating from leguminous crops. Additionally, industrial products like nylon and explosives use up the remaining 25% of intentionally fixed N (Table 2.2; Figure 2.9).

2: The US Nitrogen Synthesis

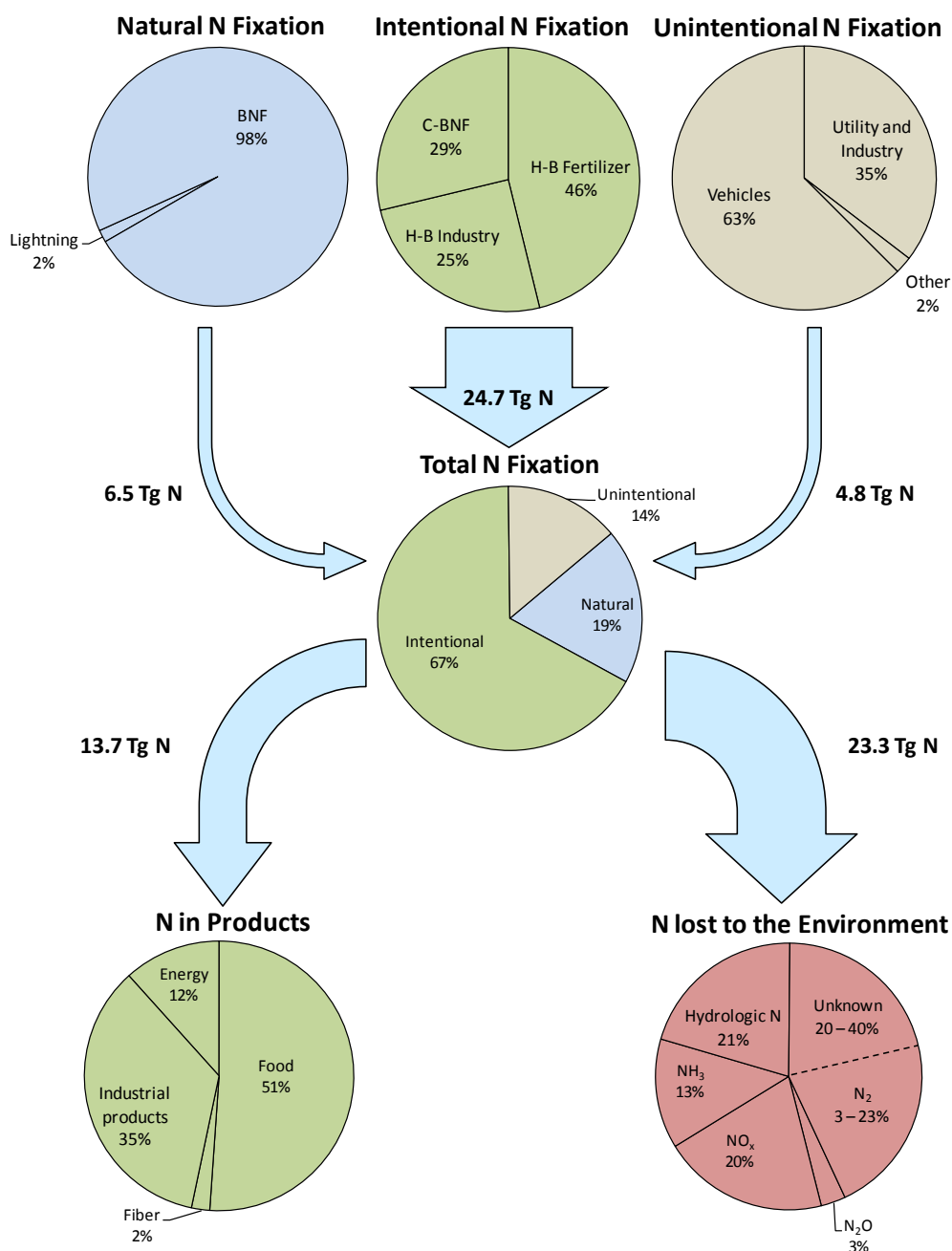


Figure 2.9: N fixation and fates of N in the United States for 2007. BNF: biological N fixation; C-BNF: crop biological N fixation; H-B: Haber-Bosch.

On an annual basis, approximately 30 % of total N fixation (both unintentional and intentional N_r creation) is initially incorporated into products, the same amount is lost to the environment as N_r, approximately 2 to 15 % is converted to inert N₂ gas, and 12 to 25 % is lost to an unidentified sink(s) nationwide (Table 2.3; Figure 2.9). As would be expected, intentional N fixation is more efficiently used, with 54 % entering food, livestock feed, biofuel (energy), or industrial products nationwide. Spillover of intentional N is thus on the order of 45 % with 27 % lost to the environment as N_r along different pathways, and an uncertain amount (3 – 21 %) escaping via inert N₂ gas annually (Figure 2.10). Assuming steady state, approximately 38 % of agriculturally fixed N (synthetic fertilizer and fixation by

leguminous crops) is used for human food and livestock feed, making it the dominant sink for intentional N in the US. Conversion of Nr-N to inert N₂ gas and hydrologic loss of N compose the largest environmental losses of intentionally fixed N in the US (Figure 2.10). Gaseous emissions of NH₃, NO_x, and N₂O are smaller fates of intentionally fixed N in terms of mass (Figure 2.10).

Table 2.3: Fates of N created in the United States for 2002 and 2007. All values are in Tg N.

	2002	2007
Distribution of N by economic sector		
Energy (corn-based biofuel) ¹	1.1	1.6
Agriculture		
Food ²	7.0	7.0
Fiber ³	0.3	0.3
Industrial products ⁴	3.2	4.8
<i>Subtotal:</i>	<i>11.6</i>	<i>13.7</i>
N lost to the environment		
N ₂ O		
Fossil fuel combustion ⁵	0.1	0.1
Industrial goods manufacturing ⁵	0.05	0.05
Agricultural sources ⁵	0.5	0.5
Miscellaneous ⁵	0.05	0.05
NO _x		
Fossil fuel combustion ⁶	5.5	4.4
Agricultural/industrial sources ⁶	0.3	0.3
NH ₃		
Fossil fuel combustion ⁶	0.4	0.4
Agricultural/industrial sources ⁶	2.6	2.7
Surface water N ⁷	4.8	4.8
N ₂ ⁸	0.7 – 5.3	0.8 – 5.4
Unknown ⁹	4.4 – 9.0	4.6 – 9.2
<i>Subtotal:</i>	<i>24</i>	<i>23.3</i>
Grand total:	35.6	37.0

¹Data on corn consumption from the USDA 2011. We assume that 32% of corn devoted to ethanol production enters the animal production system as distillers grain (residue from ethanol production; http://www.ethanolrfa.org/page/-/objects/documents/1898/corn_use_facts.pdf). We note that distillers grain has a higher N content (3.8%; <http://www.ddgs.umn.edu/profiles-current.htm>) than unprocessed corn grain (~1.5%).

²Leach and Galloway, unpublished data (assumed that 2002 is similar to 2007)

³Fox et al. (2006); USDA (2011)

⁴Assumes 22% of N created for industrial uses (FAO 2011) is lost as waste or emissions (derived from data in Febre Domene and Ayres 2001).

⁵EPA (2011b)

⁶EPA (2011a)

⁷SAB (2011)

⁸Lower bound estimated by applying a ratio of 1.7:1 moles of N₂-N:N₂O-N generated via denitrification (Schlesinger 2009) to N₂O emissions listed for denitrification-mediated agricultural sources listed in USEPA (2011) and a ratio of 1.04:1 is assumed for forested land. Upper bound estimates are based on an N₂-N:N₂O-N of 12:1 and derive from comparison of global estimates of soil denitrification (Seitzinger et al. 2006) and Denman et al. (2007). For both lower and upper estimates, 90% of N₂O emissions from agricultural lands are assumed to originate from denitrification; 60% is assumed to originate from denitrification in forest/unmanaged lands (Opdyke et al. 2009).

⁹By difference

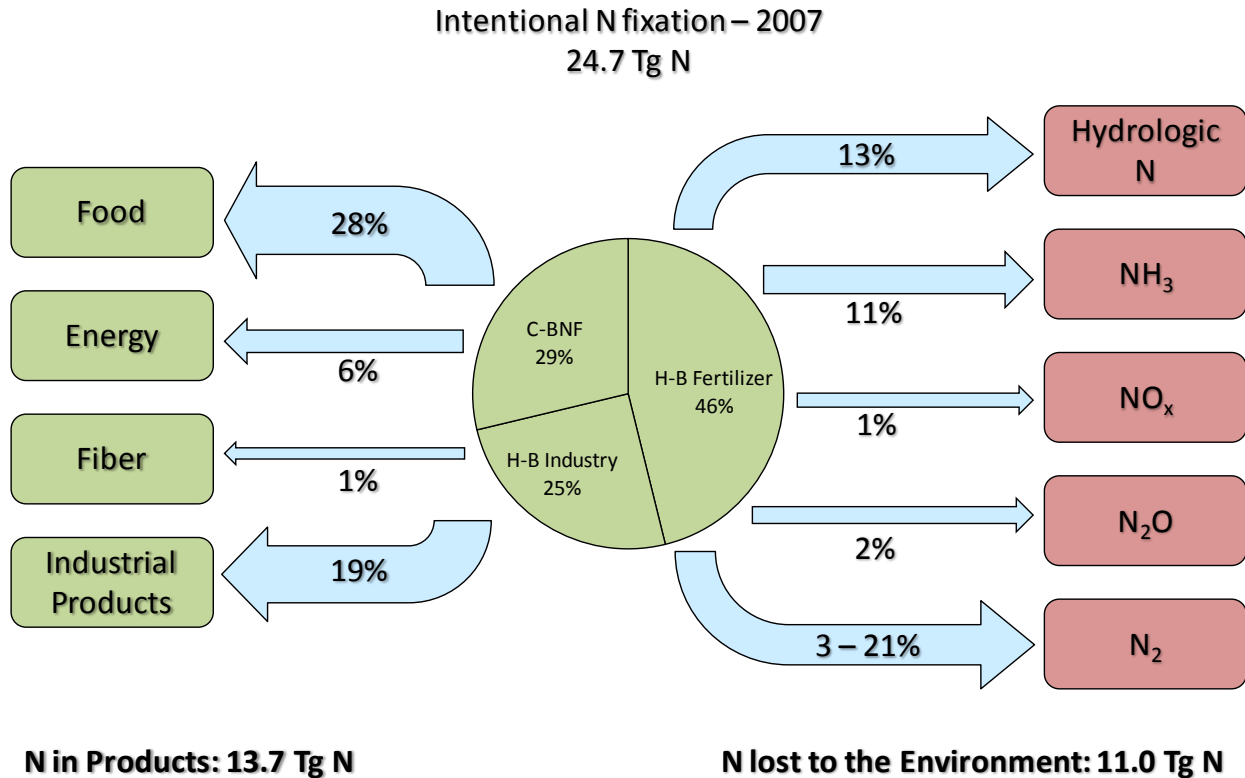


Figure 2.10: Fates of intentional N fixation in the United States for 2007. C-BNF: crop biological N fixation; H-B: Haber-Bosch.

2.3 REGIONAL IMPACTS OF N BY CLIMATE INTERACTIONS

Variation in N flows among US regions are controlled by multiple factors, particularly climate land use, industrial activity, energy production, and population. Similarly, the costs and benefits of the production and use of N_r and the interactive effects of N and climate are not distributed equally across geo-political regions. Here we describe the likely impacts of N across the six regions in the continental US as defined in the National Climate Assessment. This analysis was conducted in two primary ways. First, we quantified the areal rates by region for most of the large N flows in the US: fertilizer and manure use, NO_x and NH₃ emissions, and atmospheric deposition. Second, we evaluated the relative magnitude of indicators of the major ecosystem services affected by N: agricultural production, air quality, water quality, greenhouse gas emissions, and biodiversity.

With the exception of NO_x emissions, N flows are highest in the Midwest (Table 2.4), largely as the result of widespread agriculture and synthetic fertilizer applications in this region. The lowest N flows on a per area basis are evident for the Northwest and Southwest regions while the Great Plains, Southeast, and Northeast fall at intermediate levels. Synthetic fertilizer use in the Midwest is approximately two times that of any other region, owing to both the large area of agriculture and high fertilizer application rates within this region. While rates of NO_x emissions are highest in both the Northeast and Southeast, N deposition was still highest in the Midwest.

Table 2.4: Regional differences in N flows. Fertilizer, manure, and deposition values are from Ruddy et al. (2006) and gaseous emissions are from the 2002 National Emissions Inventory compiled by the Environmental Protection Agency. The flows of N of each state were summed by region and divided by the area of the region to calculate an area-based N flow. All flows are in kg N/ha/yr.

Region	Fertilizer (kg N/ha)	Manure(kg N/ha)	Deposition (kg N/ha)	NH ₃ emissions (kg N/ha)	NO _x emissions (kg N/ha)
Great Plains	14.2	8.9	2.9	3.6	4.3
Midwest	33.5	11.0	5.6	6.9	11.8
Northeast	6.2	6.2	4.4	4.1	15.9
Northwest	7.2	3.7	0.9	2.4	3.1
Southeast	12.9	9.5	3.9	4.9	12.1
Southwest	4.5	3.6	1.5	1.8	3.9

Similar to the flows of N, the Midwest region displays the highest values (both positive and negative) for ecosystem service indicators associated with N use (Table 2.5). Similarly, the Northwest, with smaller N flows than the Midwest, tends to have the best air and water quality. The dollar value of both crop and animal production are highest in the Midwest. However, ecosystem indicators of poor air and water quality are most pronounced in this region, namely, O₃ concentrations and NO₃⁻ contamination of surface water and groundwater. Similarly, our index of N₂O emissions based on fertilizer and manure use and NO_x emission point to the Midwest region as the major hotspot for this potent greenhouse gas nationwide. Overall, these estimates provide an average view of these indicators across the region, but in some cases, the average may not provide a complete picture of the extent of excess N. For example, groundwater NO₃⁻ concentrations are lowest in the Southwest region; however, the average is a combination of large areas of relatively low NO₃⁻ and small regions, especially in the Central Valley and south coast of California which is among the worst regions with groundwater N contamination problems in the US (Nolan and Hitt 2006).

Table 2.5: Regional differences in indicators for ecosystems services related to N use.

Region	Agricultural Production		Air Quality	Water Quality		GHG's	Biodiversity	
	Crop (\$/ha)	Animals (\$/ha)	O ₃ (ppb)	Surface Water NO ₃ ⁻ (mg N/L)	Groundwater NO ₃ ⁻ (mg N/L)	N ₂ O Flux	Forest C Sequestration (kg C/ha)	Critical Loads for Plants Exceeded
Great Plains	66	137	40	0.32	1.69	**	138	***
Midwest	235	203	48	3.47	2.60	***	283	**
Northeast	92	146	47	0.72	1.60	**	430	**
Northwest	118	76	39	0.12	1.03	*	149	**
Southeast	123	180	45	0.31	1.69	**	233	*
Southwest	127	73	46	0.58	0.61	*	211	**

The dollar value of crop and animal production of the states were summed by region and divided by the area of the region to calculate an area-based N flow. Water quality was assessed for surface water and groundwater. Regional surface water nitrate concentrations were estimated by averaging by region the measured concentrations in the 1392 streams available in the EPA Wadeable Streams Assessment database (http://water.epa.gov/type/rs/monitoring/streamsurvey/web_data.cfm). Regional shallow groundwater nitrate was estimated by averaging the spatially explicit modeled concentrations reported by Nolan and Hitt (2006). We used average daily O₃ concentrations as the indicator of air quality related to N. We calculated the average of the maximum daily O₃ value in 2002 for all stations in the EPA's Air Quality System database and calculated a regional average. An index of N₂O emissions was created based the national contribution of fertilizer (40%), manure (40%) and fossil fuel combustion (20%) reported in the EPA greenhouse gas inventory for the sources of greenhouse gas emissions. We estimated emissions for each state based on the weighted average of the areal rates of fertilizer and manure use (Reddy et al. 2006) and the areal NO_x emission (EPA National Emission Inventory 2002). The regional values were calculated by averaging the appropriate state values. Carbon sequestration for forested land was calculated similarly based on the CO₂ uptake reported by state in the EPA's State Inventory Tool. We evaluated biodiversity effects based on a visual examination of the extent of each region in excess of the critical load for plants in Pardo et al. (2011). With the exception of N₂O emissions and critical loads we show the mean values for the indicators by region. However, for the two semi-quantitative indicators we use * to demonstrate the relative magnitude of the indicator such that * represents lower values and *** represents higher values.

2.4 SUMMARY AND RESEARCH NEEDS

Several take-home points from this report point to future research needs. First, the direct effects of excess N on ecosystem and human health, and the benefits of reducing N usage, are well-documented and widespread. Furthermore, reducing the amount of N that circulates in excess of localized N demand has the potential to greatly reduce risks associated with climate change. For example, N fertilizers added in excess of crop demand contribute to eutrophication and hypoxia of the Gulf of Mexico, Chesapeake Bay and other aquatic ecosystems. Climate change worsens hypoxia, as increased temperatures lead to poor O₂ ventilation of deep waters where O₂ is most limiting to estuarine organisms (see Chapter 5). Climate change projections are thereby expected to exacerbate hypoxia in the future. However, if N is used more efficiently in the US – particularly with the development and deployment of new fertilization practices, fertilizer technologies, and more N use efficient plant geno-types – the climate risks of excess N on eutrophication would be reduced, perhaps alleviated altogether. A similar case could be argued for air pollution effects in which elevated NO_x and increased warming greatly catalyze the formation of ground level O₃; without the elevated NO_x in the atmosphere, the effect of rising temperature on O₃ formation is greatly reduced if not ameliorated (see Chapter 7).

Our report highlights a research need that begs further analysis at the interface of biogeochemistry and bioeconomics. We recommend that further work focus on N and climate interactions from the perspective of N as a strategy for reducing the risks associated with climate change. In particular, quantitative socio-economic models that consider the full cost-benefits of reducing N over various scales, coupled to biogeochemical models that include multiple-organism and element interactions with the terrestrial, atmospheric, and aquatic systems are needed. The tools to begin examining questions about N and climate risks are largely available. Future funding opportunities targeting such multi- and inter-disciplinary efforts are highly recommended.

Another summary finding agrees with previous syntheses for the US, which show that the major flows of N in the US are associated with the agricultural/food industry, both in terms of food production in situ and trade of N among regions. The practice of chronically applying synthetic N fertilizers in excess of crop uptake has many deleterious effects, including those on air and water quality and human health. Based on our assessment of nationwide N use efficiency, slightly less than 50 % of the N that enters the US economy never makes its way into the intended product. There are clear opportunities to better manage N without reducing food production (Davidson et al., 2012; see Chapter 4) or other sinks for N such as fiber, fuel and industrial products.

One of the notable uncertainties in our N use efficiency calculation, which also raises a caveat in our broader analysis, has to do with calculating the amount of N₂ spillover from intentional N creation, and this is another important research need. Denitrification is the most uncertain flux in the N cycle; we estimate here that N₂ may account for 3 % to 21 % of intentional N leakage. The level of uncertainty for this flux suggests a major research effort is needed in quantifying N₂ efflux from natural and managed sites. In terms of our calculations, we treat all N that does not find its way into the intended product as an inefficiency term; however, given that N₂ is the best fate for excess N in terms of its effect on the environment, it is reasonable to consider N₂ differently with respect to inefficiencies in N_r management. This conceptualization further reinforces the importance of finding new ways to measure and assess N₂ efflux, perhaps even enhancing this pathway of N loss as a means toward reducing some of the unintended environmental consequences of excess N use (Schipper et al., 2010). Nevertheless, there are clear economic advantages to reducing N spillover no matter the fate of excess N.

Finally, we stress that the effects of N on the broader environment are both temporally and spatially heterogeneous, with consequences varying from region to region in the US. Based on expert opinion and semi-quantitative mapping of N fluxes across regions, we suggest that, whereas all US regions are likely to experience water quality related issues associated with excess N use, O₃ related air quality issues will be most pronounced in the Midwestern and Northeastern regions. In terms of climate with N interactions, the Midwest is by far the largest source of N₂O to the atmosphere. Targeted efforts to reduce excess N from agriculture would therefore not only benefit water quality, decrease coastal eutrophication and improve air quality, but would aid significantly in greenhouse gas mitigation efforts. From a C storage perspective, the possible benefits of excess N are likely to be most associated with forests in the Northeast and Northwest regions; the location of the largest N sink in the Northeastern US is at least partially driven by N that is transported from stationary power plants in the Ohio River Valley and via vehicle emissions of NO_x. This potentially positive benefit of N for C sequestration (and thus CO₂-driven climate mitigation) is likely to diminish in the future as NO_x emissions decline and as the C sink saturates (see Chapter 3). Moreover, chronically high N inputs over decades results in increases in tree mortality as soils become progressively acidic.

Interactions of N and climate are numerous, both as drivers of climate change and regarding impacts of climate change on ecosystems and humans. In the following chapters, we address these interactions in more detail, with respect to climate forcing, agriculture, aquatic ecosystems and water quality, biodiversity in terrestrial and aquatic ecosystems, and human health.

2.5 Appendix A. Food and N Trade

To determine the importance of food and trade for the US, an analysis of the trade of Nr was completed, focusing on the amount of food and fertilizer Nr produced in, imported to, and exported from the United States.

For the trade of Nr embedded in food, a food balance sheet for the US in 2007 was downloaded, which showed total imports, exports, and production of food products for the US. All food-weight trade values (imports, exports, production) were multiplied by the appropriate protein contents, which were obtained from FAOSTAT food supply data, and by 0.16 to calculate the Nr content. The Virtual Nitrogen (e.g., Nr released to the environment throughout a production process, but not contained in the final product) was then estimated by multiplying each calculated food Nr content by the appropriate Virtual N Factor. The Virtual N Factors used in this analysis were developed by Leach et al. (2012).

The total reported trade data include all food categories. This analysis does account for both food and animal feed, but does not yet distinguish between the two.

For the trade of Nr embedded in fertilizer, US trade data for fertilizer were collected from the “Global Fertilizer Trade Flow Map”, produced by the International Fertilizer Association and the ICIS (<http://www.icis.com/>). The reported NH₃ and urea fertilizer weights were converted to N.

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Chapter 3: Impacts of Human Alteration of the Nitrogen Cycle in the US on Radiative Forcing

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ABSTRACT

Nitrogen cycling processes affect radiative forcing directly through emissions of nitrous oxide (N₂O) and indirectly through effects of emissions of nitrogen oxide (NO_x) and ammonia (NH₃) on atmospheric concentrations of methane (CH₄), carbon dioxide (CO₂), water vapor (H₂O), ozone (O₃) and aerosols. The emissions of N₂O are mostly from agriculture and they contribute to warming on both short and long time scales. The effects of current emissions of NO_x and NH₃ on CH₄, O₃, and aerosols are complex, and quantification of these effects is difficult. However, the net result on time scales of decades is likely one of cooling, becoming insignificant on longer time scales. Deposition of N onto ecosystems also affects sources and sinks of N₂O, CH₄, and CO₂; the dominant effect is changes in carbon (C) stocks. Primary productivity in most temperate ecosystems is limited by N, so inputs from atmospheric deposition tend to stimulate plant growth and plant litter production, leading in some cases to significant C sequestration in biomass and soils. The literature reviewed here indicates a range of estimates spanning 20-70 kg C sequestered per kg N in deposition for forests, which are dominant potential C sinks. Most of the sequestration occurs in aboveground forest biomass, with less consistency and lower rates reported for C sequestration in soils. The permanency of the forest biomass sink is uncertain, but data on forest product fates in the US indicate that only a small fraction of enhanced forest biomass C is sequestered in long-term harvest products or in unmanaged forests. The net effect of all of these N cycle processes on radiative forcing in the US is probably a modest cooling effect for a 20-year time frame, although the uncertainty of this estimate includes zero net effect, and a modest warming for a 100-year time frame. We know that N cycling processes are important and that biotic feedbacks to climate change are unlikely to be properly modeled or assessed without including C-N interactions. However, due to the complexity of biological processes involving C-N-climate interactions, biogeochemical models are still poorly constrained with respect to ecosystem responses to impacts of N deposition and climate change. Only recently have N cycling processes been incorporated into Earth system models for C-N interactions, and the robustness of these models remains to be demonstrated. Much work remains for improving their representation in models used to simulate climate forcing scenarios.

3.0 INTRODUCTION

Reactive nitrogen (Nr) emissions alter the climate in many ways, and the importance of the nitrogen (N) cycle in regulating climate is gaining increasing attention. Excess N in terrestrial systems can change the uptake and emission of the three most important anthropogenic greenhouse gases: carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). Many experiments have demonstrated substantial N limitations of CO₂ uptake on land. Therefore, owing to its scarcity, N is a chief player in climate change and the fate of anthropogenic CO₂ emissions. In addition, Nr is a substrate for N₂O production by

nitrifying and denitrifying bacteria in soils, sediments, and water bodies. Microbial production and consumption of CH_4 is also affected by N substrates in complex interactions. In the atmosphere, Nr alters atmospheric chemistry and affects the production and lifetimes of greenhouse gases such as ozone (O_3) and CH_4 , and also leads to the formation of aerosols, which, in turn, affect regional and global climate. This chapter provides an overview on the impacts of Nr on radiative forcing, paying particular attention to the specific interaction between the N and carbon (C) cycles. We present evidence from field studies, meta-analyses, and models of biogeochemical processes within Earth system models.

3.1 RADIATIVE IMPACTS OF REACTIVE NITROGEN

The most direct effect of N on climate is through N_2O production, the third most important anthropogenic greenhouse gas, contributing 6% of total human-induced global warming. It has about 300 times the per-molecule warming potential of CO_2 and it is long-lived in the atmosphere (a “mean residence time” of more than 110 years) (Forster et al. 2007). The concentration of N_2O in Earth’s atmosphere is derived from a variety of sources, mainly from the activity of nitrifying and denitrifying bacteria in soils, sediments, and water bodies. Globally, natural ecosystems release about 10 Tg N yr^{-1} , and anthropogenic sources sum to about 7 Tg N yr^{-1} . One recent study has reported a lower natural contribution (Zhuang et al. 2012). Anthropogenic sources are dominated by the widespread use and subsequent microbial processing of fertilizer in agricultural soils (Forster et al. 2007). Atmospheric concentrations of N_2O have increased rapidly since the industrial revolution, as livestock herds increased globally and as use of synthetic-N fertilizers increased after WWII (Davidson 2009). The natural sink for N_2O in soils is small (Van Groenigen et al. 2011, Syakila and Kroeze 2011). The current rate of increase in the concentration of N_2O is about $0.3\% \text{ yr}^{-1}$, equivalent to the accumulation of 4 Tg N yr^{-1} in Earth’s atmosphere. Global emissions of N_2O are likely to increase as fertilizers are used to boost agricultural productivity.

The US Environmental Protection Agency (US EPA) estimates that agricultural activities in the US are directly or indirectly responsible for emissions of about 0.48 million tons of $\text{N}_2\text{O-N yr}^{-1}$ (USEPA 2011), which is about 80% of total US N_2O production (the remainder from energy and industrial sources) and about 10% of the global N_2O emissions from agriculture. Several mitigation options exist to reduce the emissions of N_2O from agricultural soils (Davidson et al. 2012), and are addressed in more detail in Chapter 4 on agriculture. Associated emissions of N_2O are estimated to negate much of the CO_2 mitigation effect from C sequestration in soils (Schlesinger 2010) or from biofuel production using fertilized crops such as corn (Melillo et al. 2009).

While not a greenhouse gas directly, nitrogen oxides (NO_x) are often a limiting factor in the production of O_3 in the troposphere (the lower atmosphere), which acts as a potent greenhouse gas (Derwent et al. 2008). Nitrogen oxide (NO) reacts with radicals that donate an oxygen atom and convert the NO to nitrogen dioxide (NO_2). In sunlight, NO_2 can give up one of its oxygen atoms as it is converted back to NO by photolysis. The extra atomic oxygen reacts with the molecular oxygen (O_2), which is abundant in the lower atmosphere, and creates O_3 . In the short-term, NO_x emissions contribute to warming by enhancing O_3 concentrations. Furthermore, the short-term increase in O_3 due to NO_x can impact climate indirectly, by damaging photosynthesis and plant CO_2 uptake by as much as 20%, leading to a reduction of atmospheric CO_2 sequestration by plant biomass and resulting in more CO_2 -driven warming (Ollinger et al. 1997, Felzer et al. 2004, Sitch et al. 2007). Carbon storage and Nr are discussed in more detail in the next section.

Another indirect effect of NO_x is through its effect on CH_4 , which is the second-most important greenhouse gas, contributing 15% of total human-induced global warming. With an atmospheric lifetime of 12 years, CH_4 has roughly 27 times the per-molecule warming potential of CO_2 (Boucher et al. 2009). The largest removal process of CH_4 is oxidation by the hydroxyl radical (OH), accounting for 88% of the total sink. Emissions of NO_x can increase atmospheric OH and accordingly, decrease CH_4 concentrations (Boucher et al. 2009). An additional feedback is that the by-products of CH_4 oxidation include radicals that can convert NO to NO_2 . Through this mechanism, CH_4 is also an important contributor to ozone formation (Fiore et al. 2002). Hence, in addition to increasing O_3 on daily time scales, NO_x can lead to decreases in O_3 concentration on a decadal time scale, because it causes an increase in OH radical concentration, which decreases CH_4 concentration, which decreases NO_2 formation, which decreases O_3 formation.

Because NO_x can both increase and decrease O_3 production, the net result of these competing effects depends on where the NO_x emissions occur (Naik et al. 2005, Berntsen et al. 2005). However, the net impact of NO_x on atmospheric chemistry is likely to be cooling, by (i) decreasing the CH_4 concentration, and (ii) decreasing O_3 formation due to lower CH_4 concentrations (Wild et al. 2001, Fuglestedt et al. 2010). Both global, regional, and emission sector-based estimates of the impact of NO_x on CH_4 and O_3 radiative forcing are listed in Table 3.1.

Table 3.1: Change in ozone and methane radiative forcing (mW m^{-2}) due to reactive nitrogen (per Tg N), as calculated in global, regional, and source-specific sensitivity studies.

$(\text{mW m}^{-2} (\text{Tg N})^{-1})$	NO_x to O_3	NO_x to CH_4
Derwent et al. (2008) (global)	+1.0	-2.4
Naik et al. (2005) (North America region)	+0.088	-1.7
Berntsen et al. (2005) (Europe)	+2.0	-1.9
Wild et al. (2001) (Mid-latitudes)	+1.1	-1.9
West et al. (2007) (Anthropogenic)	+2.9	-3.7
Stevenson et al. (2004) (Aircraft)	+1.5	-13.8
Kohler et al. (2008) (Aircraft)	+2.8	-28
Eyring et al. (2007) (Shipping)	+1.3	-4.5
Endresen et al. (2003) (Shipping)	+3.8	-7.7
Fuglestedt et al. (2008) (Shipping)	+5.3	-7.6

In addition to altering radiative forcing from CH₄ and O₃, both NO_x and ammonia (NH₃) also react with other atmospheric constituents to form fine particles called aerosols. Aerosols are powerful cooling agents, both directly by scattering or absorbing light, and indirectly, by affecting cloud formation and lifetime (Forster et al. 2007). Ammonium sulfate ((NH₄)₂SO₄), ammonium nitrate (NH₄NO₃), and organic aerosols are especially important in these processes. Because NO_x influences the rate of oxidation in the atmosphere, it impacts the formation of sulfate and organic aerosols. Ammonia (NH₃) is the most important atmospheric base, and by neutralizing sulfate and nitrate (NO₃), it can enhance the formation of new particles and can condense onto existing acidic particles. Both NO_x and NH₃ alter the chemical and optical properties of the aerosol (Martin et al. 2004), which influences the conversion of aerosol to cloud droplets and ice nuclei (Sorooshian et al. 2008, Abbatt et al. 2006), and alters the lifetime and brightness of clouds. Regionally, these aerosols have important effects on precipitation and temperature patterns. The wide ranges of estimates of the effect of NO_x and NH₃ on aerosol radiative forcing globally are shown in Table 3.2.

Table 3.2: Change in nitrate, sulfate, and ammonium aerosol radiative forcing ($mW m^{-2}$) due to reactive nitrogen, as calculated in global attribution studies

($mW m^{-2}$)	NO _x to NO ₃ ⁻	NO _x to sulfate	NH ₃ to NH ₄ ⁺
Intergovernmental Panel on Climate Change (Forster et al. 2007)	-100±100		
Shindell et al. (2009)	-70	-120	-100
Van Dorland et al. (1997)	-30		
Jacobson (2001)	-50		
Adams et al. (2001)	-22		
Martin et al. (2004)	-40 to -80		
Liao and Seinfeld (2005)	-16		
Bauer et al. (2007)	-60		

Furthermore, O₃ and aerosols cause serious human health effects and contribute to air pollution (see Chapter 7). Interactions between the N cycle and climate change can exacerbate air pollution problems. For example, O₃ formation is also strongly temperature sensitive (Bloomer et al. 2009), thus rising temperatures can exact a so-called "climate penalty" on the air pollution gains made by reducing NO_x emissions (LaFranchi et al. 2011, Jacob and Winner 2009).

Ultimately, the atmosphere tends to convert NO_x and NH₃ to more water-soluble forms that are readily deposited to the Earth's surface. This is a significant source of N available to ecosystems, which influences climate forcing indirectly by altering rates of C sequestration and emissions of CH₄ and N₂O from soils. Deposition of Nr onto ecosystems changes N availability and can increase N₂O emissions and decrease uptake of atmospheric CH₄ by soil microorganisms. Natural well-drained soils (i.e., not wetlands) are an important sink for atmospheric CH₄. However, soil microbes that consume CH₄ often preferentially consume ammonium (NH₄⁺), leading to reduced CH₄ consumption rates in the presence of abundant NH₄⁺ (Mosier et al. 1991). The effects of Nr deposition on plant growth and C storage is described in the next section.

3.2 N EFFECTS ON CARBON STORAGE

Atmospheric deposition of N_r affects terrestrial C sinks by affecting two key processes. First, inputs of N_r from atmospheric deposition can enhance plant growth rates because of the fundamental constraint of N availability on plant productivity and CO_2 uptake into plant biomass, both at present and in the future, in response to rising atmospheric CO_2 concentrations. Second, decomposition is also affected by altering N_r availability in ecosystems receiving N_r . Amendments of N_r have been shown to slow decomposition of plant litter and soil organic matter in many, but not all, forest types. Excess N can also impact C cycling in coastal and marine ecosystems, but this is discussed in Chapter 5.

3.2.1 N effects on plant growth rates

It is well established that net primary production (NPP) is limited by N availability in many terrestrial ecosystems (LeBauer and Treseder, 2008), due to the fact that experimental or fertilizer N additions typically increase C capture and storage. A meta-analysis of 126 N addition experiments evaluated N limitation of aboveground net primary productivity (ANPP) in terrestrial ecosystems by comparing above-ground plant growth in fertilized to control plots (LeBauer and Treseder 2008). The studies incorporated ANPP calculated by multiple methods, including allometric biomass increment plus litterfall, basal area increment, diameter increment, annual litterfall, and allometric volume increment. The results showed that most ecosystems are N limited with an average 29 % growth response to N additions. The response was significant within temperate forests, tropical forests, temperate grasslands, tropical grasslands, wetlands, and tundra, but not deserts (LeBauer and Treseder 2008). The majority of these estimates are based on data from forest ecosystems in northern latitudes, whereas tropical areas and other ecosystem types are not well represented in these analyses (LeBauer and Treseder 2008). While increasing N availability can stimulate plant growth, estimates of the magnitude of this stimulation show greater variation. For example, in a recent synthesis by Butterbach-Bahl et al. (2011), the average increase in above ground C sequestration per unit of N addition is $25 \text{ kg C kg}^{-1} \text{ N}$ (Table 2.3). For eastern US forests, Thomas et al. (2010) estimated a re-growth sink of $61 \text{ kg C kg}^{-1} \text{ N}$. The magnitude of growth stimulation is likely greatest in regions of moderate N_r deposition and slower or even leading to enhanced mortality in regions of highest N_r deposition, due to nutrient imbalances or acidification (Aber et al. 1998). At present, most US ecosystems are probably in the former category, although some high elevation ecosystems in the Eastern US may be in the latter category (Pardo et al. 2011).

It is important to note that the potential for N addition to increase above-ground C biomass is limited in part because only a small portion of added N is actually taken up by vegetation, and thus only a small portion of N contributes to C capture by trees (Nadelhoffer et al. 1999). Recovery in tree biomass (e.g., foliage, woody tissue, and fine roots) of N that was experimentally added to forests has been estimated to range between 7 to 16% (Nadelhoffer et al. 2004) and 0 to 45% (Schlesinger 2009). Nitrogen may be immobilized in the soil, leached out before biological assimilation, or, upon the addition of N, another factor may become limiting to growth (e.g., water or other nutrients). The addition of N has also been shown to increase foliar N concentration (Xia and Wan 2008), which often results in higher photosynthetic rates, but not at high levels of chronic N addition (Bauer et al. 2004). The de-coupling of a photosynthetic-N relationship was observed from numerous chronic N addition studies, mainly because the excess N was invested in amino acids rather than enzymes and proteins associated with the photosynthetic process (Bauer et al. 2004). Foliar N may also increase the albedo of the canopy, enhancing the reflectivity of the Earth's surface, and hence contribute to cooling (Ollinger et al. 2008, Hollinger et al. 2009).

Table 3.3: Current mean estimates of dC/dN ratio for forest ecosystems in North America

Approach	Carbon sequestration (kgC per year/kgN per year)			Scale of application	Authors
	Above ground	Below ground	Total Ecosystem		
Empirical field data Correlation between NEP and total N deposition ⁺	-	-	68-177	Chronosequences in boreal and temperate forests of Eurasia and North America	Magnani et al. (2007) as re-evaluated by Sutton et al. (2008) [#]
Meta-analysis of 9 U.S. studies measuring the effects of N addition on total ecosystem carbon (EC), only included studies of which control and treatment sites experienced the same climatic, soil and vegetation conditions	-	-	24.5	U.S. forests	Liu and Greaver (2009) [#]
Modeled values of N stimulation of above ground C accumulation based on measurements of tree growth along an N deposition gradient*. Below ground values calculated using a biometric relationship	61	12	73	24 common tree species occurring in Northeastern forest in the U.S.	Thomas et. al. (2010) [#]
Synthesis of 14 forest studies (conducted from 1983-2010) including observed measurements and modeled values	25	15	41	Mostly European sites, several North American Sites	Butterbach-Bahl (2011)

⁺ N deposition values from the EMEP model for the year 2000

*N deposition values did not include several chemical species found in dry N deposition and organic N deposition

[#] These studies were not included in the value reported for Butterbach-Bahl (2011).

3.2.2 N effects on Carbon Storage in Soils

While N deposition (N_{dep}) may stimulate productivity and facilitate significant C storage aboveground (LeBauer and Treseder 2008, Xia and Wan 2008), similar trends have not been as clearly observed in soil C storage. With greater productivity, N addition generally increases aboveground litter inputs (LeBauer and Treseder 2008, Xia and Wan 2008, Liu and Greaver 2010), and improves the chemical quality of that litter (i.e., lower lignin: N ratios and greater labile C inputs to surface soils; (Berg and Laskowski 2006), USEPA (2011)). In contrast, N addition decreases fine root production and root respiration (Janssens et al. 2010), and mycorrhizal abundance (Treseder 2004). Although these patterns are not consistent across meta-analyses (see Liu and Greaver 2010), they support the idea that higher plant productivity associated with N_{dep} shifts litter production aboveground as plant investment for nutrient acquisition declines (Aerts and Chapin 2000).

The biochemistry of litter inputs, and especially litter lignin content, influences the effect of N_{dep} on soil C storage. For example, Waldrop and others (2004) report significant soil C losses with N_{dep} in a sugar

maple forest delivering high quality litter, and significant soil C gains with N_{dep} in a nearby oak-dominated forest with lower quality litter. Similarly, root lignin content affects soil C storage in grassland ecosystems receiving elevated CO_2 and N_{dep} (Dijkstra et al. 2004). Concurrently, N_{dep} is known to influence changes in plant species composition (see also Chapter 6). The extent to which climate, N_{dep} , and their interactions may drive changes in species composition that simultaneously alter the quantity and quality of litter inputs have been little explored in the literature (but see Aerts and Bobbink 1999).

Nitrogen deposition also elicits a host of microbial responses that influence organic matter decomposition and, ultimately, influence soil C storage. Microbial responses to N_{dep} include: changes in relative enzyme activity, microbial substrate use, and microbial community composition (Sinsabaugh et al. 1994; Cusack et al. 2011). Notably, N_{dep} accelerates the decomposition of high quality (low lignin) litter by stimulating cellulose degradation, which is typically N limited (Carreiro et al. 2000, Saiya-Cork et al. 2002, Frey et al. 2004, Fog 1988, Berg and Matzner 1997, Sinsabaugh et al. 2002). In contrast, N_{dep} significantly slows decomposition of low quality (high lignin) litter because of decreases in phenol oxidase activity, which reduces rates of lignin degradation (Fog 1988, Hammel 1997, Sinsabaugh et al. 2002). This divergent pattern based on litter quality has significant implications for soil C storage in systems receiving N_{dep} . In some systems, decreases in phenol oxidase activity are attributed to declines in fungal biomass, declining fungal: bacterial ratios, and a reduction of Basidiomycetes, or white rot fungi (Fog 1988, Carreiro et al. 2000, Saiya-Cork et al. 2002, Sinsabaugh et al. 2002, Frey et al. 2004). However, fungal declines with N_{dep} are not ubiquitous in studies reporting changes in microbial community structure (Saiya-Cork et al. 2002, Nemergut et al. 2008, Ramirez et al. 2010). Moreover, the effects of N_{dep} on shifts in microbial community structure and function and their influence on litter decomposition are mediated by substrate quality.

As a result of these changes in microbial community structure and function, rates of litter decomposition generally slow with N deposition, although the consistency of these findings is influenced by ambient levels of N deposition and initial litter chemistry (Fog 1988, Hobbie 2005, Knorr et al. 2005, Janssens et al. 2010). Notably, high rates of N_{dep} ($> 5 \text{ kg ha}^{-1} \text{ y}^{-1}$) slow litter decomposition, whereas low rates of N deposition ($< 5 \text{ kg ha}^{-1} \text{ y}^{-1}$) may actually accelerate leaf litter decomposition (Knorr et al. 2005).

Additionally, N_{dep} may also affect dissolved organic carbon (DOC) export from soil C (Liu and Greaver 2010). Across multiple spatial scales increasing N availability increases DOC export from soils (Aitkenhead and McDowell 2000). Mechanisms to explain these patterns are still unresolved, but generally increased DOC losses result from the combination of higher aboveground litterfall, decreased microbial lignin degradation, and soil acidification (Sinsabaugh et al. 2004, Findlay 2005, Monteith et al. 2007, Evans et al. 2008). Although the magnitude of DOC losses accelerated by N_{dep} may have less impact on ecosystem C storage (Aitkenhead and McDowell 2000), these DOC and Nr inputs will have significant consequences for aquatic ecosystems.

When combined with observations of higher aboveground productivity and litterfall, one might expect significantly greater soil C storage in systems exposed to N_{dep} , but reported rates of accumulation of C in soils are generally modest. Butterbach-Bahl and others (2011) estimate that 15 kg C are sequestered per kg N_{dep} in forest soils (Table 2.3). However, meta-analyses present conflicting results on whether accumulation of soil C occurs consistently (Nave et al. 2009, Janssens et al. 2010, Liu and Greaver 2010). Some of the variation of soil C accumulation reported in these meta-analyses could result from variation in regional and/or ecosystem response to N_{dep} , or the type, duration, and intensity of N additions.

3.2.3 N effects on total ecosystem carbon storage

It is important to consider both the above and belowground C pools in terrestrial ecosystems in order to understand N effects on total ecosystem C sequestration. Various approaches, such as modeling, inventory, and static accounting, have been used to estimate the N induced C sink for different ecosystems (Holland et al. 1997, Magnani et al. 2007, Liu and Greaver 2009, Thomas et al. 2010). The effect of N on net C flux (both above and below ground pools) differs among ecosystems, in general N addition to grasslands and wetlands does not increase C storage; however N stimulates more C storage in forests (Liu and Greaver 2009). In grasslands and wetlands N stimulation of ANPP is offset by other C losses in the system. For example, Bragazza et al. (2006) investigated peatlands across a gradient of N deposition levels and found higher atmospheric N deposition resulted in higher C loss by increasing heterotrophic respiration and DOC leaching. Similarly, Mack et al. (2004) found N fertilization stimulated soil organic carbon (SOC) decomposition more than plant production in a tundra ecosystem, leading to a net loss of ecosystem C. Among terrestrial ecosystems, the response of forests to N availability has been most intensively studied, and more data are needed to better characterize other types of terrestrial ecosystems.

In forests, a wide range of values have been reported for how much additional C is expected to be sequestered per unit of N added. Magnani et al. (2007) published a very high estimate of 725 kg C accumulated per kg N added (dC/dN) to boreal and temperate forests. However, this estimate was quickly contested as biologically implausible by Sutton et al. (2008) who reanalyzed the original data and suggested that 68 dC/dN was more accurate. Since then, attention has been drawn to the requirement that estimates of the stimulation of C sequestration by N at the ecosystem scale need to obey basic stoichiometry of C and N as observed in plant biomass (Schlesinger 2011).

Several studies have evaluated dC/dN ratios in US forests and a meta-analysis (Liu and Greaver, 2009) examined the effect of N fertilization on ecosystem C content (EC), defined as the sum of C content of vegetation, forest floor and soil. To avoid possible confounded variability caused by site conditions, this meta-analysis only included studies of which control and treatment sites experienced the same climatic, soil and vegetation conditions. Studies on N nutrient effects along a deposition gradient were not included. Results show that while there was a great deal of variation in response, overall N addition increased EC by 6% for US forest ecosystems. This study did not find any correlation between the amount of N addition and the response magnitudes of EC. On average, forest ecosystems sequestered $24.5 \pm 8.7 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ per $\text{kg N ha}^{-1} \text{ yr}^{-1}$ (Liu and Greaver 2009). Using a different approach, Thomas et al. (2010) examined tree growth rates over an N deposition gradient in US Northeastern forests. Their results indicate that enhancement of above-ground C storage averaged $61 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ per kg increase in N deposition. When calculating a dC/dN response ratio using values of N deposition, it is very important to consider how N deposition is calculated and whether all relevant chemical species are included. In Thomas et al. (2010) "total" N deposition was calculated using estimates of NO_3 , wet NH_4 , dry HNO_3 gas and particulate NH_4 and NO_3 , it did not, however, include other forms of N deposition, such as dry NH_3 , NO and NO_2 , or organic N. Because all forms of N deposition were not used in the calculation, above ground dC/dN is likely to be over estimated. On the other hand, when a biometric relationship is applied that assumes below-ground tree biomass represents roughly 20% of above-ground biomass, then enhancement of total tree C would increase to $73 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ per kg increase in N deposition. This approach assumes dC/dN in belowground biomass is the same as above ground biomass, which is often not the case (Table 3.3), and does not include other soil pools that affect dC/dN , therefore this is likely an inflated value of dC/dN .

Butterbach-Bahl et al. (2011) recently synthesized and reviewed published dC/dN ratios from studies conducted in Europe and North America (not including Liu and Greaver 2009 or Thomas et al. 2010) and found that average total C sequestration was 41 kg C per kg N addition in forests. Although more research needs to be done to further refine estimates of dC/dN in forests, considering the studies summarized in Table 3 and their caveats, the range of values reported in the literature are between 20-70 kg C ha⁻¹ yr⁻¹ per kg N ha⁻¹ yr⁻¹. Key uncertainties in the sensitivity of ecosystem C sequestration response to N addition include the form and manner of N input, succession status of the forest and prior land-use history (Butterbach-Bahl et al. 2011).

Two factors will likely decrease rates of dC/dN reported for a given forest: N saturation status and stand age. First, N will increase NPP of an N-limited system; however N addition beyond this point may lead to decreases in NPP (Aber et al. 1998). Second, several studies have shown that NPP declines with stand age (Gower 2003, Ryan et al. 2004), which could reduce the potential response to N addition. Furthermore, as NPP decreases due to age, so too will dC/dN . The relative effect of saturation and stand age is varied – a recent flux study found evidence of nitrogen enhanced productivity even in an old growth (200 – 300 years old) forest (Luyssaert et al. 2007).

3.3 BIOGEOCHEMICAL MODELS – C-N INTERACTIONS, C STORAGE, AND N GAS EMISSIONS

3.3.1 Modeling N effects on C sequestration

As climate models evolve into models of the behavior of the Earth system, they have expanded beyond their hydro-meteorological heritage to include biogeochemical cycles and atmospheric chemistry. Early global climate models focused solely on atmospheric physics; later models incorporated the C cycle in order to include feedback with atmospheric CO₂, but did not include C-N interactions. Coupled C cycle-climate models include terrestrial and marine C fluxes so that changes in atmospheric CO₂ concentration are simulated in response to anthropogenic CO₂ emissions (Friedlingstein et al. 2006, Denman et al. 2007). In these models, rising atmospheric CO₂ concentration increases land C uptake by stimulating plant productivity, and this “CO₂ fertilization” is a negative feedback to higher atmospheric CO₂ concentration (the concentration-C feedback). Land C loss through ecosystem respiration increases with warming in a positive climate feedback (the climate-C feedback). Additionally, warming can enhance productivity (negative feedback) in cold regions, but decrease productivity (positive feedback) in warm regions, where greater evaporative demand dries soil.

These predictions for the terrestrial C cycle are found in Earth system models that do not include C-N biogeochemistry. In recent years, some Earth system models have added some representation of the N cycle as a crucial regulator of C-cycle dynamics and related aspects of atmospheric chemistry, but much work is needed to properly incorporate representation of N cycling processes in climate models. Global biogeochemical models of the terrestrial C and N cycles for the Earth build upon a rich heritage of terrestrial ecosystem models (Bonan 2008). They simulate C and N flows among various vegetation and soil components, N inputs for atmospheric deposition and biological N fixation, and N losses from denitrification and leaching.

Carbon cycle-climate model simulations of future climate change with C-N biogeochemistry find decreased C gain with rising atmospheric CO₂ and reduced C loss, or even small C gain, with warming (Sokolov et al. 2008, Thornton et al. 2009, Zaehle et al. 2010). Limited mineral N availability restricts the increase in plant productivity from the concentration-C feedback. Conversely, warming increases decomposition of organic material and N mineralization, stimulating plant productivity. These findings

are generally consistent with results from free-air CO₂ enrichment experiments and soil warming experiments, though few models have been directly compared with experimental manipulations (Melillo et al. 2011).

As mentioned earlier, because N availability restricts plant productivity in many ecosystems; N addition from atmospheric N deposition can enhance C storage. Initial studies of the effect of anthropogenic N deposition on the C cycle reported that the additional N in the system increased global terrestrial C storage from as much as 0.6-1.5 Pg C yr⁻¹ (Holland and Lamarque 1997, Townsend et al. 1997) to as little as 0.25 Pg C yr⁻¹ (Nadelhoffer et al. 1999). More recent model simulations support a smaller C sink of about 0.2 Pg C yr⁻¹ (Jain et al. 2009, Thornton et al. 2009, Bonan and Levis 2010, Zaehle et al. 2011). These models differ in important ecological and biogeochemical processes (e.g., how N affects plant productivity; below-ground C-N dynamics; and denitrification) that determine the amount of N in the system available for plant use and the magnitude of the C sink. Model comparison with results from N deposition gradient analyses (Thomas et al. 2010) or N enrichment experiments (Liu and Greaver 2009) are needed to evaluate the model simulations and to identify deficiencies in model parameterizations. Estimates of N-enhanced C storage, whether derived from observational studies or from models, require knowledge of N deposition rates. These rates can differ greatly among studies in the magnitude and spatial distribution of the deposition, which makes comparison among studies difficult.

A complete understanding of the effects of increased N deposition on terrestrial C storage and radiative forcing requires a multi-disciplinary integration of biogeochemical processes with biogeophysical processes (i.e., energy and water fluxes), and with changes in ecosystem structure and community composition arising from stand dynamics. For example, a more productive forest with higher leaf area index resulting from enhanced N deposition is likely to decrease surface albedo, warming climate with a positive radiative forcing and increasing evapotranspiration (Bonan 2008). Increased evapotranspiration locally cools temperature, but can warm global temperature through increased atmospheric water vapor. The net effect of changes in C storage, surface albedo, and evapotranspiration on radiative forcing is largely unknown for forest ecosystems, and initial estimates of the forcing are quite speculative (Bonan 2008). Another possible biogeophysical forcing is manifested through the effect of foliar N on leaf-, stem-, and canopy-level traits that alter the overall plant reflectance. Canopy N concentration is strongly and positively correlated with canopy albedo, suggesting a possible significant biogeophysical role of N in the climate system through solar radiation absorption and canopy energy exchange (Ollinger et al. 2008, Hollinger et al. 2009).

The long-term sustainability of the N-enhanced C sink is unclear, and C uptake may saturate with future levels of N deposition. The future potential of C storage in terrestrial ecosystems depends on trajectories of climate change and land use, which alter community composition and ecosystem structure. Redistribution of plant species in response to climate change alters patterns of C storage, N uptake, and N mineralization (Pastor and Post 1988, Metcalfe et al. 2011). Enhanced C storage in forest ecosystems arising from atmospheric N deposition becomes less important in a warmer climate where droughts and wildfire are more common. Trajectories of land use (e.g., deforestation, reforestation, and afforestation) driven by socioeconomic needs and policy implementation will also come into play and have competing biogeophysical and biogeochemical impacts on climate. These changes in community composition and ecosystem structure are largely ignored in the current generation of Earth system models, which build on biogeochemical models rather than models of vegetation dynamics.

3.3.2 Modeling N effects on N₂O emissions and other radiative forcing

The atmospheric chemistry models included in Earth system models allow for additional biogeochemical land-atmosphere interactions such as surface N-gas emission and atmospheric N deposition (Lamarque et al. 2011). With the addition of N-gas emissions, the models provide surface N fluxes to atmospheric chemistry models, and can be used to quantify the net radiative forcing due to Nr. This forcing includes the effect of N on terrestrial C storage, the direct radiative forcing from N₂O emissions, and Nr in the atmosphere and its effects on CH₄, tropospheric and stratospheric O₃, and secondary aerosols.

Nitrogen losses associated with nitrification and denitrification are poorly represented in the biogeochemical component of Earth system models and present a large uncertainty in global simulations of climate-N interactions (Schlesinger 2009). Dinitrogen gas (N₂) loss during denitrification is a large term in the global terrestrial N budget (Galloway et al. 2004, Houlton and Bai, 2009, Schlesinger et al. 2009), but there is a high degree of uncertainty regarding the amount of N₂ efflux to the atmosphere (see Chapter 2). A better understanding and further quantification of ecosystem N₂ flux is needed given that this is the best possible outcome for minimizing environmental impacts from excess N.

The DayCENT (Del Grosso et al. 2000) and DeNitrification-DeComposition (DNDC) (Li et al. 2000) models are two commonly used approaches to represent nitrification, denitrification, and associated N-gas emissions. These models have been evaluated for a wide range of environmental conditions, ecosystem types, and N inputs, but are mostly applied only at the site or regional scale. Global terrestrial biogeochemical models for use with Earth system models may not explicitly simulate denitrification and instead include it as a generic N loss term (Melillo et al. 1993, Gerber et al. 2010, Wang et al. 2010). Furthermore, some of the current global models represent denitrification as a fraction of mineralization or mineral soil N (Thornton et al. 2009, Yang et al. 2009). Zaehle and Friend (2010) developed an advanced process-oriented formulation of nitrification, denitrification, and N-gas emissions based on the DNDC model structure, which observed a likely contribution of N_{dep} to C sequestration in forest ecosystems and concurred with ecosystem field studies. Houlton and Bai (2009) used a mass balance approach constrained by observations of ¹⁵N/¹⁴N isotope ratios to estimate NO, N₂O, and N₂ emissions globally and regionally. However, the complexity of trace gas biogeochemistry, the fine-scale spatial heterogeneity of trace gas production, and anthropogenic alterations from agricultural practices makes modeling N-gas emissions an uncertain aspect of global Earth system model simulations.

In addition, a key aspect of climate-N interactions not currently considered by Earth system models is the effect of anthropogenic N on radiative forcing mediated through changes in atmospheric chemistry. Secondary atmospheric aerosols resulting from emissions of NO_x and NH₃ provide a negative radiative forcing that cools climate. None of the currently available Earth system models are able to fully assess these effects, in part because the current generation of global terrestrial C-N biogeochemical models used with Earth system models does not represent N-gas emissions and the anthropogenic and environmental drivers of these emissions.

3.4 NET EFFECTS OF C-N INTERACTIONS ON RADIATIVE FORCING

Reactive N has numerous effects on climate, including N₂O emissions, indirect effects on O₃, CH₄, and aerosols, and C sequestration. To compare these impacts, the effects must be converted in to a common metric. A recent effort in Europe has led to a continental assessment of the contribution of European emissions of Nr to instantaneous radiative forcing, expressed as W m⁻² (Butterbach-Bahl et al. 2011).

3: Alteration of Nitrogen Cycle and Radiative Forcing

Because aerosols have a large effect on short-term radiative forcing, it was found that the net effect of cooling from aerosols and C sequestration outweighed the warming effect of N₂O emissions across Europe. However, the pathways by which Nr impacts climate change do not have the same lifetime – for example, aerosols last for only a few weeks, CH₄ on the order of a decade, and N₂O and CO₂ persist for more than a century. While radiative forcing is a measure of the instantaneous climate change impact, the long-term climate effects depend heavily on atmospheric longevity (Penner et al. 2010).

An alternative approach is the global temperature potential (GTP), which is a measure of the change in global temperature, after a fixed number of years, due to a 1 kg pulse of emissions. The GTP can be calculated on a 20-year basis, to identify Nr impacts likely to change the rate of climate change in the coming decades, as well as on a 100-year basis, to understand the long-term magnitude of climate change. To compare across compounds, the GTP is normalized by the change in temperature due to a pulse of CO₂ and expressed in common units of kg CO₂ equivalence (CO₂e).

The climate change impact of US Nr, on a global temperature potential basis, is presented in Figure 3.1. Each bar represents the climate change impact, in units of Tg CO₂e, due to US Nr emissions, via the processes listed on the left. The length of the bar denotes the range of uncertainty as estimated by a synthesis of the relevant literature. The impacts from changes in O₃, CH₄, and aerosols were calculated as the product of US emissions and the GTP of those compounds as calculated by Fuglestvedt et al. (2010). For the change in greenhouse gas fluxes due to N deposition, the dC/dN values were multiplied by the anthropogenic N deposition calculated by the Community Multiscale Air Quality model (CMAQ; Appel et al. 2010) to each landcover type. A range of 24-65 was used for the dC/dN value for forests. The lower value of this range (24) is from Liu and Greaver (2009) and the upper end of this range is from Thomas et al. (2010). The value 65 results from adjusting the Thomas et al. (2010) value upwards to account for below ground biomass and soil C, and downwards, to account for incomplete measurement of N. For other land cover types, the ranges reported in Liu and Greaver (2009) were used. The permanence of enhanced CO₂ uptake on a 20-year and 100-year timescale was estimated using forestry management data (Heath et al. 2011). The details of these calculations are described in Pinder et al. (*in review*).

The relative impact of each aspect of Nr depends strongly on the time frame of interest. On the left side of Figure 3.1, the impacts are compared on a 20-year basis. Here, the change in O₃, CH₄, and aerosol concentrations due to NO_x contribute substantially to climate change. But on a 100-year basis, these processes are negligible. Emissions of NO_x in the US contribute to cooling on a 20-year basis, but have a very little effect on a 100-year basis. Overall, the cooling effects (i.e., C sequestration enhanced by N deposition, increased lifetime of CH₄, and greater aerosol burden) are slightly larger than the warming effect of N₂O on a 20-year time frame. The error terms on these estimates are large, and the range of uncertainty includes the possibility that the net effect is zero. But on a 100-year basis, the net impact of Nr appears to be one of warming. Putting these estimates into a broader perspective, the modest warming effect US Nr shown in Figure 3.1 is equivalent to less than 10 % of the warming effect of US emissions of CO₂ derived from fossil fuel combustion.

While the net radiative forcing effect of the alternation of the N cycle in the US may be relatively small, there are many offsetting impacts that occur over different time-scales. The long atmospheric half-life of N₂O and uncertainties regarding the permanence of C sequestration mean that there is a risk that the long-term net warming effects may be underestimated. Moreover, the profound effects that excess Nr has on ecosystem processes and biodiversity, which are described in greater detail in Chapters 5 and 6, suggests that assumptions about future radiative forcing of C-N interactions played out in changing terrestrial and aquatic ecosystems must be considered with caution. Despite these uncertainties, we can conclude with confidence that C-N interactions do have important climatic effects that should be included in future measurement and modeling efforts to improve understanding of biological feedbacks to climate change and global change processes.

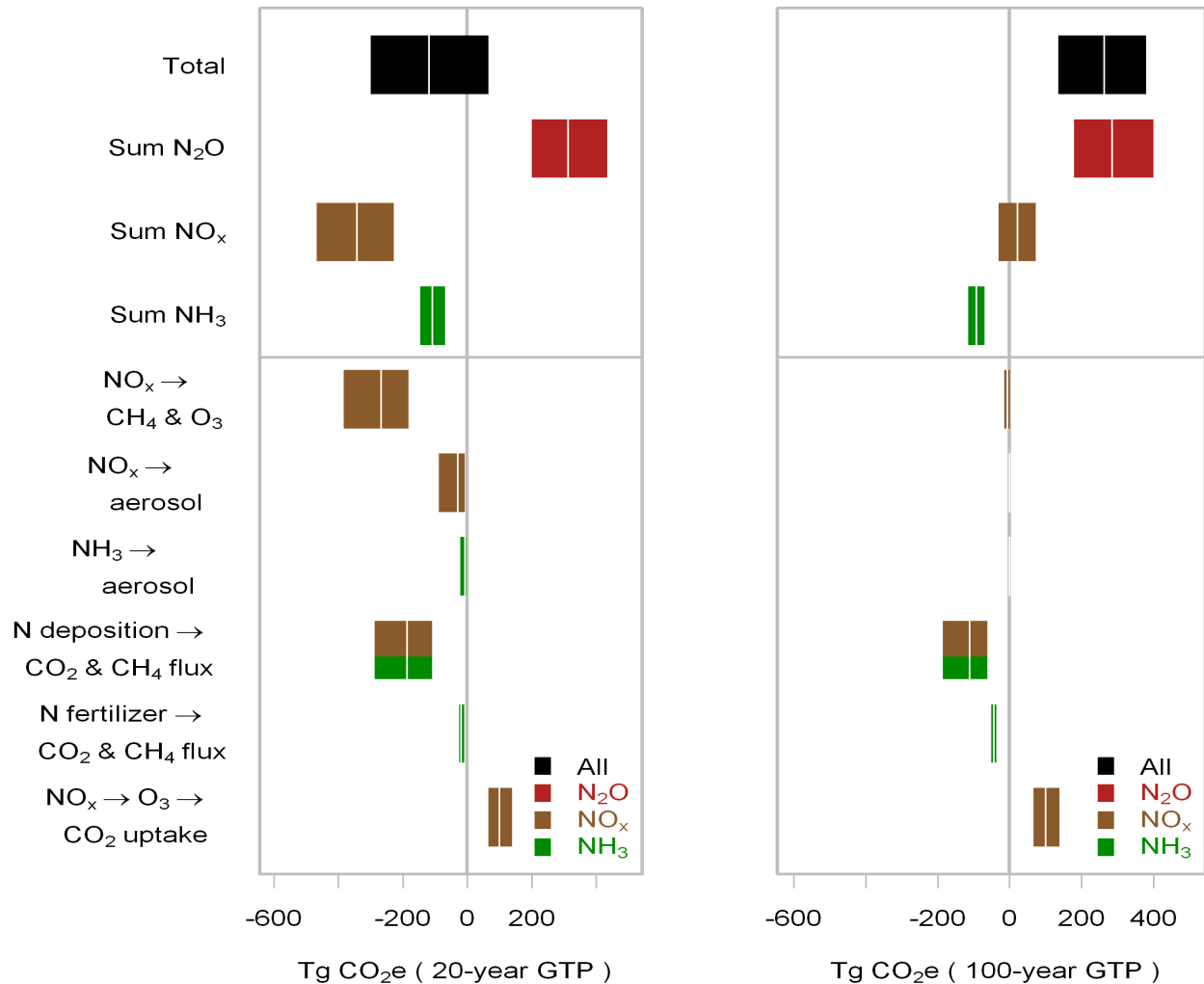


Figure 3.1: The climate change impacts of US reactive nitrogen emissions, by chemical species, in common units of equivalent Tg of CO₂ (Tg CO₂e) on a 20-year and 100-year global temperature potential (GTP) basis. The width of the bar denotes the uncertainty range; the white line is the best-estimate; and the color shading shows the relative contribution of NO_x and NH₃ emissions to nitrogen deposition (adapted from Pinder et al., in review).

3.5 RESEARCH NEEDS

Improved quantification of the effects of excess Nr on radiative forcing will require improvements in our understanding of atmospheric chemical processes, rates of total N deposition, responses of ecosystems to N deposition, and integration of these processes into Earth system models. We identify a number of research needs below:

- The complex nonlinear atmospheric chemistry involving NO, NO₂, O₃, OH, and CH₄ and how it will change with climate and changing sources and sinks requires more research attention to determine impacts at times scales from days to decades.
- The effects of the chemical composition of aerosols on radiative forcing and cloud formation are not well known.
- Improvements are needed in spatially explicit modeling and measurements of all forms of N deposition. Estimates of deposition of organic-N are particularly uncertain.
- Variation in dC/dN responses of ecosystems and the factors that control them are poorly understood for both aboveground and belowground processes. Comparisons between model simulations and results from N addition enrichment studies, gradient analyses, and other field data are needed to validate and identify deficiencies in parameters of both empirical and process-based models.
- Biogeochemical models need improvements to better constrain and reduce uncertainty of estimates of N losses associated with nitrification and denitrification, especially losses of N₂ from denitrification.
- Earth system models need improved representation of C-N interactions in ecosystems and their feedbacks to climate change. This includes feedbacks between vegetation, water vapor, and albedo. Most Earth system models also do not yet include the effects of anthropogenic N on radiative forcing mediated through changes in atmospheric chemistry.

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Chapter 4: Nitrogen – Climate Interactions in Agriculture

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ABSTRACT

Agriculture in the United States (US) cycles large quantities of nitrogen (N) to produce food, fuel and fiber and is a major source of excess reactive nitrogen (Nr) in the environment. Nitrogen (N) lost from cropping systems and animal operations moves to waterways, groundwater, and the atmosphere. Changes in climate and climate variability may further affect the ability of agricultural systems to conserve N. The N that escapes affects climate directly through the emissions of nitrous oxide (N₂O), and indirectly through the loss of nitrate (NO₃⁻), nitrogen oxides (NO_x) and ammonia (NH₃) to downstream and downwind ecosystems that then emit some of the N received as N₂O and NO_x. Emissions of NO_x lead to the formation of tropospheric ozone (O₃), itself a greenhouse gas that can also directly harm crop productivity. There are many opportunities to mitigate the impact of agricultural N on climate and of climate's impact on agricultural N. Some are available today; many await further research; and all await effective incentives to become adopted. Research needs can be grouped into four major categories: (1) an improved understanding of agricultural N cycle responses to changing climate; (2) a systems-level understanding of important crop and animal systems sufficient to identify key interactions and feedbacks; (3) the further development and testing of quantitative models capable of predicting N-climate interactions with confidence across a wide variety of crop-soil-climate combinations; and (4) socioecological research to better understand the incentives necessary to achieve meaningful deployment of realistic solutions.

4.0 INTRODUCTION

Nitrogen (N) is an essential element for plant and animal growth, and our ability to harness N in its reactive forms has fundamentally transformed how we produce food. The Haber-Bosch process, the industrial manufacture of ammonia (NH₃), greatly accelerated the global production and dissemination of synthetic N fertilizers. This development marked the most significant human interference in the natural N cycle by removing a fundamental, natural limit on crop yields, allowing for the adoption of high yielding cultivars and a corresponding increase in global harvests. Today, the approximately 100 Mt of reactive nitrogen (Nr) supplied from synthetic fertilizers is roughly equal to the total N fixed in natural terrestrial ecosystems (see Chapter 2). Global per capita rates of N fertilizer consumption per year have risen from 0.2 kg in 1900 to 2 kg in 1950 to nearly 14 kg in 2000 (Smil, 2001). Inevitably, this huge advance in global N use has been accompanied by considerable growth in Nr loss to the environment, including greenhouse gas (GHG) forcing. For example, emissions of nitrous oxide (N₂O), the most long-lived form of gaseous Nr from US agriculture, have risen 18% since 1750 and stood at 214 Tg CO₂-eq. in 2008 (USDA, 2011).

Fertilizers, manure, and legume dinitrogen (N₂) fixation are the three main inputs of N to US agricultural soils. All three sources have been increasing over the past two decades, while the rate at which N is

removed from cropping systems at harvest has been increasing at a similar rate (Figure 4.1), resulting in a slightly greater proportion of input recovery in 2007 than in 1987 (USDA-ERS, 2012). The major forms of fertilizer used in the US are granular urea, fluid urea-ammonium nitrate (UAN), and anhydrous ammonia, with the use of urea-based fertilizers increasing and the use of anhydrous ammonia decreasing over time. Fertilizer N use in North America is forecast to grow 2.3% per year from 2010 to 2016 (Heffer and Prud'homme, 2011), and has been projected by one group to double to 28 Tg by 2030 (Tenkorang and Lowenberg-DeBoer, 2009).

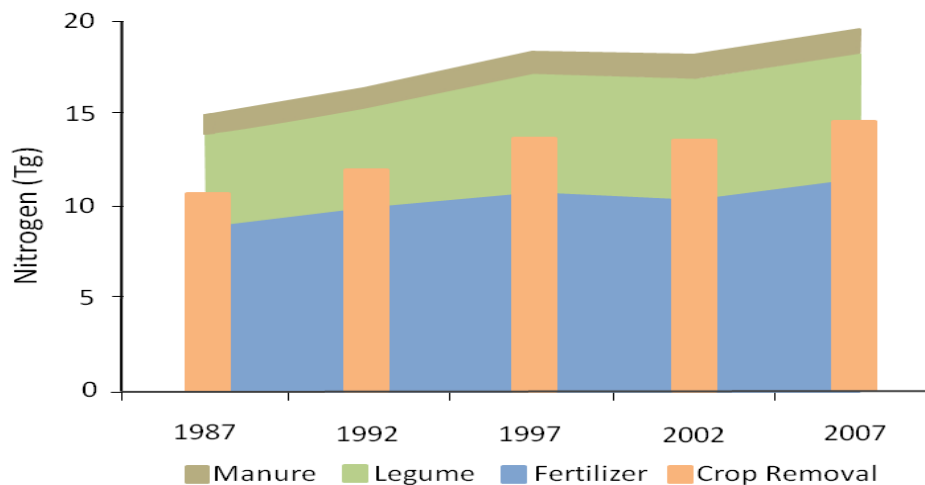
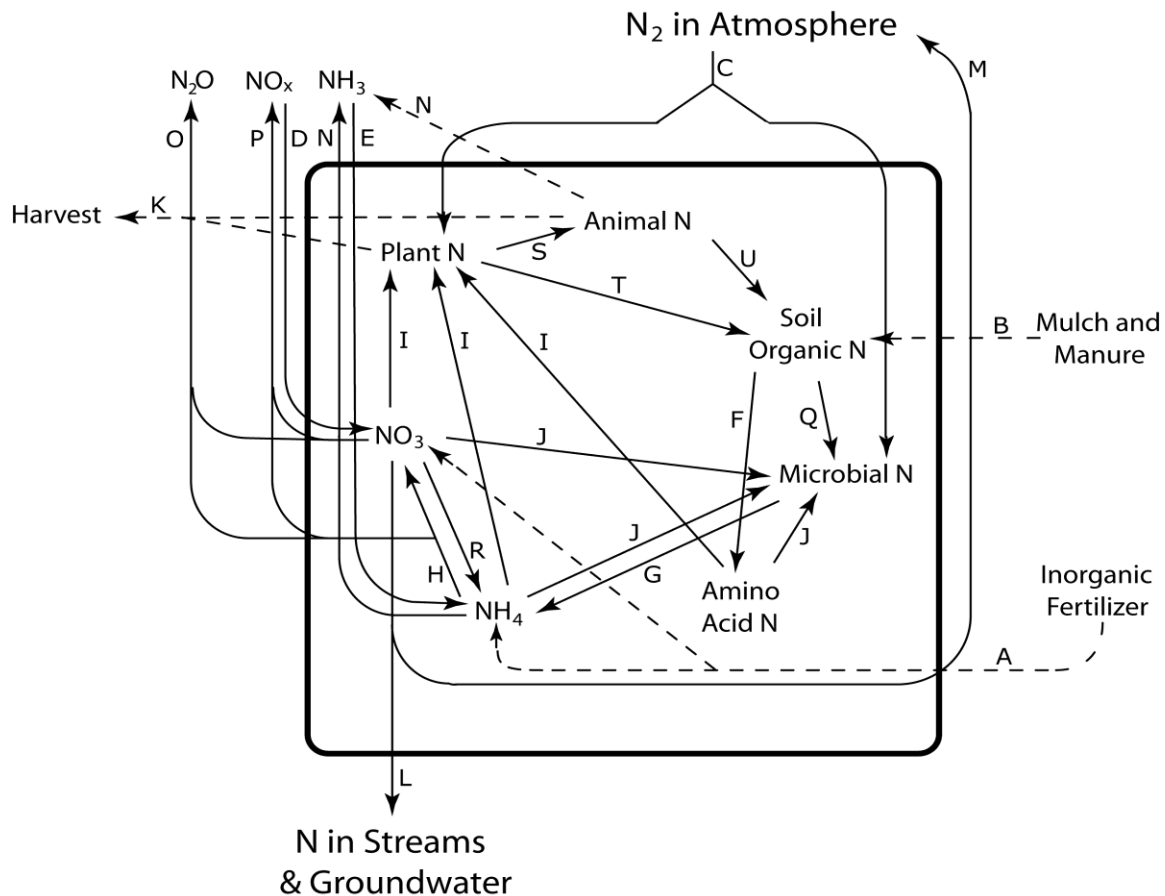


Figure 4.1: Inputs of N to US agricultural land, including recoverable manure, legume fixation, and commercial fertilizers, as compared to removal by crops (adapted from IPNI, 2011).

Nitrogen can take nine forms in terrestrial ecosystems based on different oxidative states (Robertson and Groffman, 2007; Figure 4.2). It is lost from agricultural systems in several of these forms; most of it less than a year after it enters the system (Galloway et al., 2003). Atmospheric emissions can occur as nitrogen dioxide (NO_2), nitric oxide (NO), N_2O , N_2 or NH_3 (see Chapter 3 for the radiative forcing impacts of these compounds), while waterways receive inputs of NO_3^- and dissolved organic nitrogen (DON) via leaching. Reactive N lost in one form can be converted to other forms of Nr and can “cascade” through several media and systems, contributing to a number of types of environmental pollution before returning to its original atmospheric form, N_2 (Galloway et al., 2003; see Chapter 2). Therefore any policy tackling N pollution must note the myriad of potential environmental sources and fates of N in the agricultural N cycle (Figure 4.2) and attempt as holistic an approach as possible to avoid unintended outcomes.

Major factors sustaining demand for N fertilizer use in the US include the outlook for continued large areas of corn cultivation, supported now by biofuel production goals and in the future by burgeoning food demand. At the same time, higher prices for fertilizer and pressures on producers for higher environmental performance are encouraging increased adoption of emerging technologies such as precision agriculture and enhanced-efficiency fertilizers in controlled-release form or formulated with inhibitors of urease or nitrification.



Figur4.2: Pathways of N cycling in agricultural ecosystems. Transformations of N shown in solid lines occur in all ecosystems; those shown with dashed lines are particular to (or particularly important within) agricultural systems. Major fluxes of N include, A, additions of industrial fertilizer; B, additions of organic N in manure and mulches; C, biological dinitrogen (N_2) fixation by microbes symbiotically associated with plants and by free-living microorganisms; D, atmospheric deposition of reactive N in oxidized forms; E, atmospheric deposition of ammonia (NH_3) and ammonium (NH_4); F, mineralization of organic N via mobilization of amino acids through the action of extracellular enzymes; G, mineralization of organic N via release of ammonium by microbes; H, nitrification of ammonium to nitrate; I, plant uptake of available N; J, microbial immobilization—the uptake of biologically available N by microbes; K, losses of N in harvested products; L, losses of N in solution to stream water and groundwater; M, denitrification to dinitrogen; N, NH_3 volatilization from both fields and from intensive animal production systems; O, losses of nitrous oxide (N_2O) produced during nitrification and denitrification; P, losses of reactive oxidized N produced during nitrification and denitrification; Q, uptake of organic N by microbes during decomposition; R, dissimilatory reduction of nitrate to ammonium; S, consumption of plant N by animals; T, flux of N to soil in plant litter; and U, flux of N to soil from excretion or animal death. From Robertson and Vitousek (2009).

Here we first address the sources and fates of N in both cropping systems and animal agriculture and then assess some of the effects of climate change on the US agricultural N cycle as well as the effects of N use on climate forcing. We then summarize a number of mitigation opportunities and current policy efforts before concluding with future research needs.

4.1: SOURCES AND FATES OF N IN AGRICULTURE

4.1.1 Cropping Systems

Agriculture in the US encompasses many different cropping systems designed to produce a diverse array of food, forage, fuel, and fiber products. All of these systems require adequate N, the nutrient that most commonly limits crop productivity, and all but a few leguminous crops depend on added N to achieve profitable yields.

4.1.1.1 Cropping system N sources

Legumes acquire their N from the atmosphere via rhizobial symbionts that reduce N_2 to forms that can be used by the plants for protein synthesis. Many legumes – soybeans and alfalfa among them – can meet 100% of their N needs via N_2 fixation, but more commonly a fraction of the N is provided by soil from the microbial conversion of soil organic matter (SOM) to NH_4^+ and NO_3^- . Most of the N_2 that is fixed ends up being assimilated into plant tissue, but some escapes from the roots to soil as root exudates. A portion of the plant-assimilated N is removed in crop harvest; the remainder becomes plant residue and decomposes to become SOM, ready for mineralization and subsequent crop uptake or loss from the ecosystem the following seasons. When legumes are planted as fallow or winter cover crops following the main crop harvest, all of the N_2 fixed becomes SOM as the cover crop is killed prior to planting the subsequent cash crop.

Synthetic fertilizer makes up the biggest source of N added to US cropping systems. Rates of fertilizer N additions typically range from $<100 \text{ kg N ha}^{-1} \text{ y}^{-1}$ for small grains like wheat and perennial biofuel crops like switchgrass, to $>200 \text{ kg N ha}^{-1} \text{ y}^{-1}$ for high-yielding corn and grass forage crops, and some horticultural crops (Ribaudo et al, 2011). Theoretically, only as much N needs to be added as is removed in crop harvest, but crop N use is commonly inefficient. On average, only about 50% of added N fertilizer is removed in annual grain crop harvest, for example (Robertson 1997).

Best practice calls for applying N at a time that is as close to the N need of the crop as possible to avoid excessive loss. In corn, for example, this usually means starter N at planting and the remainder following initial crop growth. In irrigated corn, fertilizer can be applied throughout the season in irrigation water. Often, however, equipment and labor availability together with uncertain weather drive decisions to add N fertilizer well before crop N needs. In 2005, for example, almost one-third of US corn cropland was fertilized the fall before spring planting (Ribaudo et al. 2011), leading to substantial potentials for N loss.

Nitrogen fertilizer additives and slow-release formulations are designed to delay added N from entering the soil's soluble N pool until crop needs are greatest. Additives include nitrification inhibitors, which slow the transformation of NH_4^+ to NO_3^- . As a cation, NH_4^+ is less susceptible to leaching loss than is NO_3^- . Although NO_3^- is the form of N utilized by most crops, it also is the form that is most readily lost to the environment through leaching and denitrification to N_2O , NO_x [$NO + NO_2$], and N_2 . Slow-release formulations usually coat the N fertilizer particle with a slowly dissolving shell of another chemical or

polymer that reacts to soil temperature and moisture. Additives and slow-release formulations are not widely used due to greater cost and inconsistent performance.

Manure represents the third major source of exogenous N to most US cropping systems. Approximately 6 Tg of manure N are produced annually in the US (USEPA, 2011a). Because manure is often produced by livestock consuming grain imported from long distances and is expensive to transport, only a small percentage is returned to the field of origin; most manure is applied to nearby fields close to animal feeding operations. This regional N imbalance leads to less efficient nutrient cycling with greater losses to the environment (Figure 4.3; Lanyon and Beegle, 1989). Domestic animals are the largest source of US NH₃ emissions, accounting for ~1.6 Tg N y⁻¹ (USEPA, 2011a). Certain forms of manure are more susceptible to volatilization than others because of their pH and NH₃ content. Typical annual emissions of NH₃ range from 40-1000 kg N/Mg from cattle and swine and 64-160 kg N/Mg from poultry, depending upon the type of housing and manure handling system used (Rotz, 2004).

Soil organic matter is a fourth source of N in US cropping systems. While important on an annual basis – about 50% of the N needs of fertilized crops are met by SOM mineralization – in most long-cropped soils SOM levels are stable because mineralized N is replaced by N in new crop residues as they decompose to SOM. Thus, SOM is not generally an important source of N_r in the environment except on recently converted lands or on high SOM soils such as drained Histosols, which may quickly lose C and N on conversion to agriculture (Gelfand et al., 2011). There is some evidence, however, that soils once thought to be equilibrated are newly losing SOM, perhaps because of climate change (e.g. Senthilkumar et al. 2009).

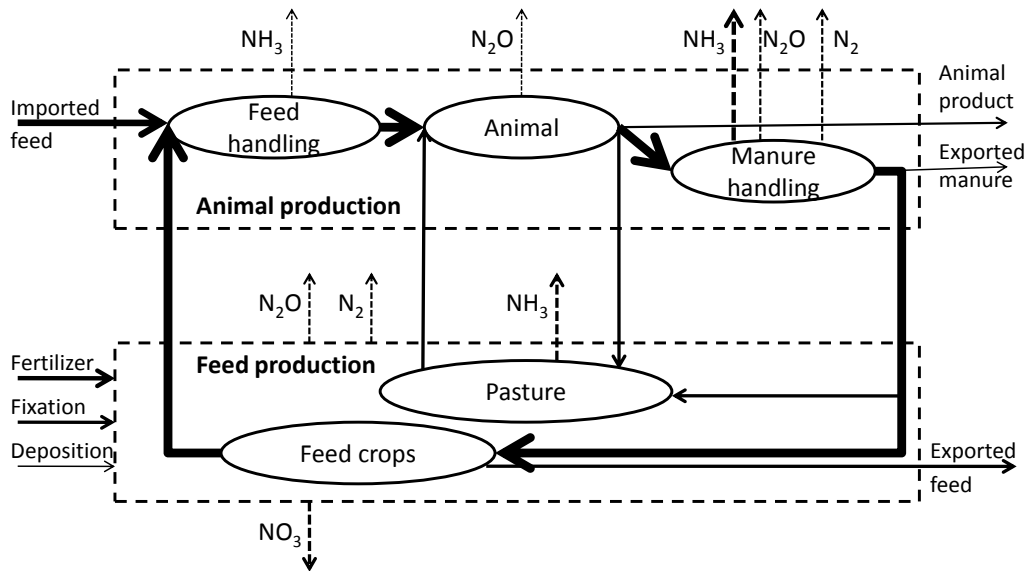


Figure 4.3: Nitrogen flows through an integrated feed and animal production system where line weights represent the relative amounts of flow among pathways.

4.1.1.2 Cropping system N fates

The fate of N applied to cropland depends on many factors, some under management control and others related to soil, climate, and other environmental attributes. Once applied to soil, added N goes through a number of complex transformations, mostly biological, that lead to four major alternative fates (see Figure 4.2): 1) plant uptake and subsequent removal in harvest; 2) loss to surface and groundwater via hydrologic flow as NO_3^- , DON, and particulate N; 3) loss to the atmosphere as N_2O , NO_x , NH_3 , or N_2 ; and 4) storage in the cropping system as inorganic N, in SOM derived from crop residues and microbial biomass, or, for perennial grass or tree crops, in long-lived plant parts such as roots and wood.

The hydrologic loss of NO_3^- is the major vector of N lost to the environment from cropping systems that receive rainfall in excess of evapotranspiration. This loss of NO_3^- can also be high from irrigated systems in drier climates when water applied exceeds crop transpiration need by only a few percent (Gehl et al, 2005). Hydrologic DON loss is minor in most cropping systems (van Kessel et al, 2009), as is particulate N loss, which usually represents the translocation of organic N from one part of the landscape to another rather than loss to the environment – although in areas of high erosion particulate N can be lost to surface waters via direct runoff.

Ammonium loss from cropland tends to be important only when manure is applied to surface soils or when anhydrous ammonia or urea fertilizers are misapplied to dry soil, such that the NH_3 that is added as anhydrous ammonia or formed from urea escapes to the atmosphere before it can be dissolved in the soil solution as NH_4^+ . Fertilizer misapplication in this way is inefficient and is more likely to occur during extended dry periods.

Nitrous oxide and NO are produced in soil by both nitrifying and denitrifying bacteria (Robertson and Groffman, 2007). Nitrification is the oxidation of NH_4^+ to NO_3^- with NO and N_2O being metabolic by-products that escape to the atmosphere. Denitrification is the reduction of NO_3^- to NO, N_2O , and N_2 . The rates of N_2O and NO production are highly variable in most soils, and are related both to the factors that affect rates of nitrification (mainly NH_4^+ availability) and denitrification (mainly NO_3^- , C, and low O_2 availability) as well as soil factors such as pH that affect the proportion of the end products that are emitted as NO and N_2O (Robertson and Groffman, 2007).

An important control on the rate of N gas production is the amount of N available to the bacteria that carry out the reactions. In almost all but very sandy soils, rates of nitrification and denitrification increase with increasing pools of inorganic N (e.g., NO_3^- , NH_4^+), and likewise, the rates of N_2O and NO formation are best predicted by inorganic N availability. In unfertilized soil, N available to the bacteria that produce these gases is largely controlled by rates of N_2 fixation, SOM turnover, and N deposition. In most cropped soils this N is largely controlled by rates of fertilization and SOM turnover. Because plants are good competitors for inorganic N, plant uptake can reduce the amount of N that would otherwise be available for N gas production or hydrologic loss.

Nitrogen use efficiency (NUE) – and in particular N-fertilizer use efficiency – is therefore a good general metric of N conservation in cropping systems. Maximizing the fertilizer N that makes it into the crop will, in general, minimize the N that is free for loss to the environment. The objective of crop N management is to improve the efficiency of plant usage of N fertilizers. Strategies to improve system-wide fertilizer use efficiency are therefore of utmost importance for both reducing the impact of climate on crop N use and for reducing the impact of agriculture on climate, as discussed later.

4.1.2 Animal Systems

Animal agriculture in the US today encompasses a number of different domesticated animals raised for meat, fiber, milk, and eggs in a variety of housing arrangements ranging from high-density confined-animal feeding operations (CAFOs) to extensive rangeland. All systems have in common the provision of high quality feed and forage that contains protein-N in excess of the animals' N need. Excess N is excreted and subsequently available for loss to the environment, where it has a number of potential fates.

4.1.2.1 Animal System N sources

Animal agriculture in the US produces about 131 Tg of meat, eggs, dairy and other animal products using production systems that vary widely by animal species, type of product, and the economic, geographic and cultural characteristics of the production region (USDA-ERS, 2011). The manure produced by farm animals is considered the major source of gaseous NH_3 emission in the US (USEPA, 2011a). Manure is a significant contributor to N_2O and NO_x fluxes both during handling and following soil application (CAST, 2004), where it is subject to the same potential fates as synthetic N additions. Manure applied to fields without growing crops is susceptible to substantial N loss when the manure N is transformed from organic to inorganic (e.g., NH_4^+ and NO_3^-) forms. At a very general level, animal production systems involve the production of feed, preparation and delivery of feed rations to the animals, and the removal and recycling of manure nutrients. The overall production strategy greatly affects the efficiency of N use and its influence on the environment.

The major animal species used for animal agriculture in the US include dairy and beef cattle, swine and poultry. Cattle are ruminant animals that require a different feeding strategy than non ruminants such as swine and poultry (Hristov et al., 2011). Most swine, poultry and beef feedlot systems are managed as independent feeding operations (top half of Figure 4.3), where most or all feed is imported, often from long distances. The production of all confined animal species requires large amounts of N for feed. For all species, protein requirements must be met for maximum production. Protein is comprised of amino acids required by all organisms for maintenance, growth, and reproduction (NRC, 1994; NRC, 1998; NRC, 2000; NRC, 2001). Animals require 20 essential amino acids in amounts that vary with animal age and productivity. Proteins on average contain 16 % N; therefore matching amino acid levels in rations to those required by the animal is complex and bears strongly on efficient N use. Unused protein and non-protein N in animal diets is excreted in manure where it can be lost to the environment as N_r .

During harvest and storage, a small portion of the protein in feed is lost and the remainder can be transformed to different forms (Rotz and Muck, 1994). For example, a large portion of the forage fed to cattle is preserved through ensiling, which breaks down plant proteins to forms that are used less efficiently by the animals (Rooke and Hatfield, 2003).

Much progress has been made in recent years in determining the nutrient requirements of animals and matching those requirements to that available in feed rations in order to maximize production (NRC, 1994; NRC, 1998; NRC, 2000; NRC, 2001). For ruminant animals, suitable fiber levels must be maintained for proper rumen function, which enforces the use of forage in diets and limits the amount of grain and other concentrate feeds that can be used. Some amino acids are required to meet the requirements of microorganisms in the rumen while others are needed in the intestinal tract and must make it through the rumen intact (NRC, 2000; NRC, 2001). Preparing rations that supplement available forage with the proper amino acids to meet animal requirements is difficult due to varying amounts and types of forage

available though the year along with their varying nutrient concentrations. Grazing animals provide an additional challenge since the producer has less control over their diets. Pasture forage tends to have more protein and more rapidly degrading protein than is required, which leads to less efficient N use and greater N excretion (Van Soest, 1994). A study on grazing dairy farms in the northeastern US has shown total protein was being overfed by 20 to 80% (Soder and Muller, 2007).

Non ruminant animal feeding does not have the complication of fiber requirements. Grains and other concentrate feeds have a more consistent concentration of protein and other nutrients, so protein requirements can be met more precisely. Synthetic amino acids are also commonly used to meet nutritional requirements with greater accuracy throughout animal growth cycles (Keshavarz and Austic, 2004).

4.1.2.2 Animal System N Fates

In general, 65 to 90% of the N consumed in feed is excreted in manure with the remainder retained in body tissue and the milk, eggs, or other products produced (Hristov et al., 2011; Rotz, 2004). With good feeding practices for cattle and swine, about 50% of the N excreted in feces is in a relatively stable organic form. The remainder, including most of the excess N consumed, is excreted in urine as urea. For poultry, a large portion of the excreted N is uric acid, which decomposes to form urea. When deposited on the floor of the housing facility, the urea comes in contact with urease enzymes, which rapidly transform the urea N to NH_4^+ . At a rate dependent upon temperature, pH and other manure characteristics, the NH_4^+ forms NH_3 , which is readily volatilized (Hristov et al., 2011; Montes et al., 2009).

On a barn floor, for example, where manure is removed at least once per day, NH_3 emissions vary with temperature and are relatively low in cold winter weather (Montes et al., 2009). In warm weather or on a surface such as an open lot where manure is not removed, nearly all of the urea-N can be lost to the atmosphere as NH_3 (Hristov et al., 2011; Rotz, 2004). Another common housing system uses a bedded pack, whereby manure and bedding materials accumulate on the barn floor. With this strategy, a portion of the NH_4^+ is absorbed into the bedding material, emitting more NH_3 than if it were deposited on a scraped floor, but less than if it were deposited in an open lot. Bedded pack and open lot surfaces both provide aerobic and anaerobic conditions to support both nitrification and denitrification, creating emissions of N_2O and N_2 (Rotz, 2004).

Manure removed from barns can be handled in solid, semi-solid, slurry or liquid forms. Solid manure is relatively dry, often scraped from open lot surfaces where most of the labile N has been emitted as NH_3 (Hristov et al., 2011). Semi-solid manure is formed using bedding material to absorb manure moisture. This type of manure is typically not stored for long periods and may be spread on crop and pastures each day of the year as it is produced. Slurry is formed by scraping manure from the floor of free stall and similar barns designed to use less bedding material. Liquid manure is typically formed by using a solids separator to remove a major portion of the manure particles, leaving the manure solution with less than 5% dry matter content. Manure solids can be composted and used as bedding material, with most of the NH_4^+ remaining in the liquid portion (Meyer et al., 2007). Both slurry and liquid manure are typically stored for 4-6 months and in some cases up to a full year to allow the nutrients to be applied to fields at a time when they are best used by growing crops or grassland. However, this requires a storage capacity that many operations lack and consequently it is not unusual for manure to be spread on frozen fields or pastures during the winter.

During long term manure storage, the organic N portion in the manure slowly decomposes, producing NH_4^+ . If semi-solid manure is stored, it is placed in a stack where NH_3 emissions occur and nitrification and denitrification processes generate N_2O , NO_x and N_2 emissions. About 10-20% of the N entering storage is lost mainly as NH_3 (Rotz, 2004). Slurry manure is typically stored in a tank. When manure is continually added to the surface of the tank, up to 30% of the N can be lost as NH_3 , but little or no emissions of N_2O escapes, because anaerobic conditions inhibit nitrification, thus preventing conversion to NO_3^- and subsequent denitrification. When manure is pumped into the bottom of the tank, a crust of manure solids can form on the surface reducing emissions of NH_3 by up to 80%. However, nitrification and denitrification can occur within this crust, thus emitting N_2O (Peterson and Miller, 2006). Liquid manure is commonly stored in a lined earthen basin or lagoon where NH_3 , N_2O and N_2 losses are relatively high (Harper et al., 2004). When a multiple stage lagoon (e.g., flow from a facultative to anaerobic lagoon) is used, up to 90% of the N can be lost or removed between the inlet and outlet.

Most manure is applied to crop or grassland as fertilizer. Methods of manure application include broadcast application to the field surface, subsurface injection, and irrigation. When manure is broadcast spread, any remaining NH_4^+ in the manure is rapidly volatilized to NH_3 (Génermont and Cellier, 1997), although at least half can be retained if the manure is tilled into the soil within several hours of application (Rotz et al., 2011). Subsurface injection can also greatly reduce or even eliminate NH_3 emission depending upon injection depth (Rotz et al., 2011; Ndegwa et al., 2008). Irrigation is often used to apply liquid manure, and a portion of manure-N content is lost as NH_3 during irrigation. However, if the manure infiltrates rapidly into the soil, N will be retained as NH_4^+ (Sommer et al., 2003). Application losses vary from 2% of the manure N applied through deep soil injection to 30% of the N applied through surface spreading without soil incorporation (Rotz, 2004).

4.2 CLIMATE – NITROGEN INTERACTIONS

Climate and agricultural N interact in complex ways. Some of the interactions are direct, such as changes in climate patterns that prompt farmers to adapt their cropping systems to higher temperatures and changes in rainfall patterns. Some of the interactions are indirect, such as changing consumption patterns of oil and natural gas (used as feedstocks for NH_3 production) as a result of climate policies, which may subsequently affect fertilizer prices and, thus, fertilizer consumption and consequently N_r escape. However, agriculture is not only affected by climate change, but also contributes to climate change by contributing GHGs to the atmosphere. We consider both climate effects on N cycling and farm N cycle effects on climate change in the sections below.

4.2.1 Climate effects on agricultural N cycling

Climate change affects agricultural N cycling mainly through its impact on changing patterns of temperature and rainfall. Effects also occur due to changes in the chemical climate – in particular via changes in atmospheric concentrations of ozone (O_3) and carbon dioxide (CO_2).

4.2.1.1. O_3 , climate, and agricultural yield impacts

Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) are key precursors of tropospheric O_3 . Ozone harms crops and thereby affects crop N use and N_r escape. Ozone is produced in the troposphere by the catalytic reactions of NO_x with carbon monoxide (CO), methane (CH_4), and non-methane volatile organic compounds (NMVOCs) in the presence of sunlight (photolysis). Production of O_3 is a highly non-linear function of the emission of these precursors (NRC, 1991), some of which (NO_x and CH_4 in particular) are

produced by agriculture (Yienger and Levy, 1995; Karl et al., 2009; Hudman et al., 2010). Due to these non-linearities, the O₃ production efficiency per unit NO_x emitted is high in rural areas. Furthermore, increases in temperature can also lead to higher rates of precursor emission and O₃ formation.

Field experiments in the US, Europe, and Asia have shown that surface O₃ causes substantial damage to many plants and agricultural crops, including increased susceptibility to disease, reduced growth and reproductive capacity, increased senescence, and reductions in crop yields (Mauzerall and Wang, 2001). Based on the large-scale experimental studies of the National Crop Loss Assessment Network (NCLAN) conducted in the US in the 1980s (Heagle, 1989; Heck, 1989), the US Environmental Protection Agency (USEPA) estimated that the yields of about one third of US crops were reduced by 10% due to ambient O₃ concentrations during this time (USEPA, 1996). Model simulations of O₃ used with the established NCLAN concentration and yield response relationships predict larger effects for grain crops for 2000 and 2030 (Avnery et al., 2011a, b).

Agricultural soils are a minor but significant source of atmospheric NO_x (Robertson and Vitousek, 2009), with NO_x emissions (“P” in Figure 4.2) typically enhanced following fertilizer application, precipitation, and elevated temperature (Butterbach-Bahl et al., 2009). In a recent top-down analysis, emissions from agricultural soils summed to about 14% of global surface emissions (Jaegle et al., 2005). Hence, increasing fertilizer use in response to a growing global population requiring food and biofuel in a warming climate may lead to higher soil NO_x emissions and consequently increased O₃ production with resulting adverse impacts on crop yields. Emissions of NO_x from industrial and vehicle sources are expected to decrease in the US over the next several decades, increasing the relative contribution from agriculture to total US NO_x emissions (see chapter 7). Thus NO_x emissions from agricultural regions will likely have a proportionally larger impact on rural O₃ concentrations, and hence on crop yields, in the future.

Large-scale, comprehensive field studies in the US and Europe in the 1980s/90s showed a wide range of crop sensitivities to O₃, both among different crops and within cultivars of the same crop (Heagle, 1989; Heck, 1989; Krupa et al., 1998). Crop varieties used today appear to exhibit sensitivity to O₃ that is on average at least as great as that seen in earlier field studies (Long et al., 2005; Emberson et al., 2009). Ozone sensitivity may thus be an overlooked factor in cultivar choice, especially if variety development and breeding trials are conducted in areas of low or moderate O₃ impact.

The observed correlation between surface O₃ and temperature in polluted regions points to a detrimental effect of warming. Although there is regional variability, observations in the US have shown higher surface O₃ concentrations as temperatures increase (see Figure 4.4). In addition, coupled chemistry – climate model simulations indicate that with no change in the emission of O₃ precursors, climate warming itself will likely result in increased surface O₃ concentrations in many parts of the US (Jacob and Winner, 2009). This is frequently termed the “climate penalty” and it applies to penalties both for agricultural productivity and human health (see Chapter 7). Projected increases in O₃ vary among models, but are typically in the 1–10 ppb range over the next several decades, implying that stronger emission controls will be needed in order to meet a given O₃ air quality standard. Although higher water vapor in the future climate is expected to decrease O₃ over remote oceanic regions, the opposite may occur for polluted continental regions (Jacob and Winner, 2009).

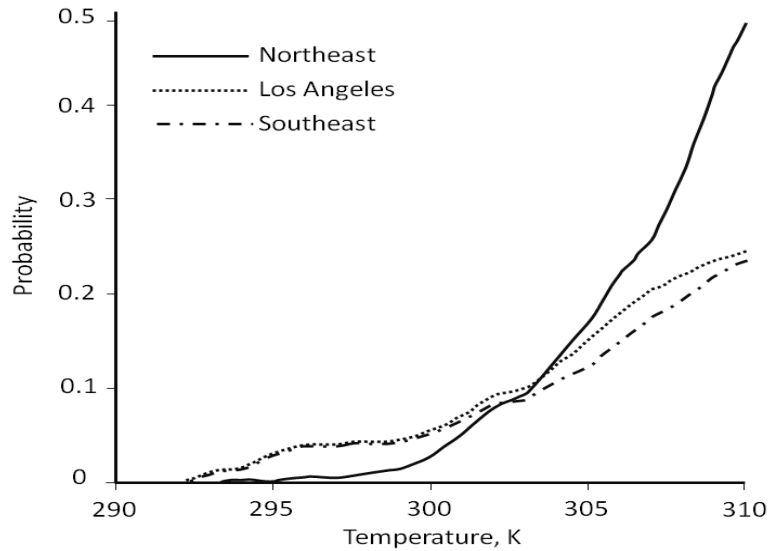


Figure 4.4: Observed probability that maximum daily average ozone will exceed 80 ppb for a given daily maximum temperature (1980-1998 data) for different parts of the US. Adapted from Jacob and Winner (2008).

4.2.1.2 Temperature effects

Temperature will affect both crop and animal production systems. Warming temperatures will affect crop productivity, mainly because most physiological processes related to crop growth and yield are highly sensitive to temperature, and crops have a specific temperature range for maximum yields (Hatfield et al., 2008, 2011; Avnery et al., 2011c). The response of crops to temperature may be complex, non-linear, and exhibit threshold effects. Maximum crop yields for corn, soybeans, and cotton are found at temperatures of 29°C, 30°C, and 32°C, respectively. The slopes of the decline in yield above optimum temperatures are significantly steeper than the incline in yield below optimal temperature (Schlenker and Roberts, 2009).

There is debate over the effect of temperature on agricultural yields. Recent research indicates that from 1980 to 2008 global yields of maize and wheat declined by 3.8 and 5.5%, respectively, relative to a counterfactual without climate trends (Lobell et al., 2011). However, these trends were driven by responses in low latitude countries, where temperatures in tropical locations may exceed optimal ranges, resulting in a significant reduction in yields. In contrast, higher temperatures may benefit crop productivity in some mid- to high latitude regions by increasing the length of the growing season as well as the amount of land suitable for cultivation. Fischer et al. (2005) project an increase in potential agricultural land of 40%, 16%, 64%, and 10% in North America, Europe, Russia, and East Asia, respectively, driving potential global cereal production improvements of 1.9-3.0 Gt by 2080 depending on the climate change scenario considered. However, temperature also affects the rate of plant development, and even brief exposure to higher temperatures may shorten growing periods and threaten yields if exposure occurs during important development stages such as flowering and grain filling (Wheeler et al., 2000; Wollenweber et al., 2003).

Higher temperatures, may also accelerate SOM turnover, leading to lower soil C stores (Davidson and Janssens, 2006; Knorr et al., 2005, Conant et al., 2008) even in arable soils. In some cases (e.g., Senthikumar et al., 2009), accelerated C loss has been attributed to higher wintertime temperatures,

which in cropped systems would release additional N to the soil at a time when plants are not available to immobilize it.

The balance between warmer temperatures and increasing/decreasing rainfall will be important for determining whether there is an increase or decrease in emissions of gaseous N (N_2O , NO_x ; “O” and “P” in Figure 4.2) per unit of fertilizer applied to cropping systems. More research is needed to illuminate these changes on both a regional and global basis.

Projected temperature changes will also directly and indirectly affect animal production. The primary direct impact will be related to heat stress due to increasing ambient temperatures. Heat stress causes reduced feed intake, increased water intake, higher body temperatures, increased respiration, decreased activity and hormonal and metabolic changes, which in turn leads to reduced production, reduced reproduction, and increased mortality (Nardone et al., 2010). Under our current climate, heat stress is estimated to cause an annual economic loss of 1.7 to 2.4 billion dollars in the US (St-Pierre et al., 2003). Future shortages of water may also directly impact animal production and exacerbate the heat stress issue. Indirect effects include changes in feeding practices due to the adaptation of crop type, yield, and nutritive content to changes in climate. Furthermore, adaptation to new feeds may also affect feed value and N use efficiency. Rates of NH_3 emissions are also very sensitive to temperature (Montes et al., 2009), such that increasing ambient temperatures will also increase this source of N loss throughout all phases of manure handling. Overall, the net effect of these changes in the agricultural N cycle in response to heat stress is likely a reduction in N use efficiency of animals systems.

4.2.1.3 Precipitation impacts on crop response to and recovery of N

The quantity, frequency, and intensity of precipitation and evapotranspiration throughout much of the world will likely be altered due to rising global surface temperatures (Meehl et al., 2007). Precipitation increased by 7-12% in the middle to high latitudes of the northern hemisphere during the 20th century, particularly during autumn and winter when rains and snowfall were more intense. However, these increases varied both spatially and temporally (IPCC, 2001). Areas that experience increases in mean precipitation, particularly tropical and high latitude regions are also projected to have an increased intensity of precipitation events. Geographic regions where precipitation decreases (e.g., most subtropical and mid-latitude regions) are expected to have increased sporadic precipitation events of increased strength, with longer dry periods between events. Projected increases in summer dryness from increasing surface temperatures also indicate a greater risk of probable drought. Notable changes in precipitation extremes have already been observed, and projected changes would extend trends already underway (USGCRP, 2009; Meehl et al., 2007).

Intensification of precipitation in spring and excessively wet winters can delay crop planting, increase plant diseases, retard plant growth, and cause flooding, runoff, and erosion – all of which can harm crop production and reduce crop yields. Additionally, extreme wet cycles can result in substantial losses of N to the environment, through transport and leaching of NO_3^- (“P” in Figure 4.2) in regions where artificial subsurface drainage (e.g., tiles) removes excess soil water from fields, and through gaseous losses of N_2O (“O” in Figure 4.2) in regions where drainage is less effective. Nitrate leaching is a problem that is exacerbated when large amounts of soil NO_3^- are present after fertilizer application and before the crop has been planted or before the period of peak N demand (“I” in Figure 4.2) (Davidson et al., 2012). Increases in drought frequency and intensity also adversely affect crop growth and yield, ultimately impacting nutrient use and uptake efficiency. Drought also increases the demand for irrigation which affects regional water resources as well as N movement in the soil system. Fertilizer N is typically

applied prior to or shortly after crop planting (“A” in Figure 4.2), and is usually applied on the basis of expected yields – at rates to produce historically maximum crop yields for a given location. Thus, environmental factors that limit crop growth and yield during the growing season, including both drought and excessive moisture, would result in especially high N_r loss due to reduced crop uptake, particularly when significant precipitation events or prolonged wet periods occur after the growing season.

Occurrences of drought or excessive moisture affect not only crop growth and subsequent nutrient use, but also soil N turnover within agricultural systems (“F”, “G”, “H”, “J”, “R”, and “Q” in Figure 4.2). Short- and long-term fluctuations in precipitation are closely tied to the spatial and temporal N dynamics of the system. During periods of drought or seasonal water deficit, an overall decrease in N turnover typically follows as a result of shifts in soil and atmospheric N dynamics.

Ecosystem N loss mechanisms are highly sensitive to fluctuations and variability in both precipitation timing and amount (Larsen et al., 2011). Seasonal and periodic droughts affect net primary productivity, plant N uptake, soil microbial activity, N₂O flux, NO₃⁻ leaching, and denitrification (Emmet et al., 2004; Davidson et al., 2008; Sardans et al., 2008; Larsen et al., 2011). Further, drought reduces net soil respiration and when soil is wetted following a drought, large fluxes of NO and N₂O rapidly occur (Davidson, 1992; Bergsma et al., 2002; Borke et al., 2006). The pronounced effects of extreme precipitation fluxes and drought on soil N_r dynamics thus affect soil N availability to planted crops and the response of crops to fertilizer N sources.

4.2.1.4 Effect of increased ambient CO₂ on crop N demand

Atmospheric CO₂ concentrations have increased from 270 to 384 ppm_v since the Industrial Revolution. Numerous studies have evaluated crop response to rising CO₂ concentration, sometimes referred to as the CO₂ fertilization effect. Many crop plants, including wheat and soybeans, demonstrate increased growth and seed yield in response to increased CO₂. Elevated CO₂ may also improve crop water use efficiency and drought tolerance by reducing conductance of CO₂ and water vapor through stomatal leaf pores.

Larsen et al. (2011) report increased C to N (C/N) ratio in aboveground plant biomass of a semi-natural ecosystem with elevated CO₂. However, they conclude that the effects of drought dominated plant response compared with elevated CO₂, and that the reduced N turnover stemming from drought and warming may act to reduce the potential plant growth response to rising atmospheric CO₂.

Crop response depends in part on the major photosynthetic pathway employed by a given crop. Plants with a C₃ metabolism have different CO₂ and temperature response curves than those with a C₄ pathway. Most crops grown in the US are C₃ plants, but several C₄ crops are economically important including corn, sorghum, sugar cane, and warm season grasses proposed for biofuel feedstock, such as switchgrass (*Panicum virgatum*) and giant miscanthus (*Miscanthus × giganteus*).

Leakey et al. (2009) recently summarized the results of 15 major Free-Air CO₂ Enrichment (FACE) experiments that measured the impact of elevated CO₂ on plants over multiple seasons and/or crop life cycles. They reported several important effects stemming from the FACE experiments, including:

- Photosynthetic C uptake of C₃ plants is enhanced by elevated CO₂ despite acclimation of photosynthetic capacity, with an expected C gain of 19-46% for plants grown at CO₂ levels projected for the mid-century;

- For C₃ plants, photosynthetic N use efficiency (PNUE), determined as the net amount of CO₂ assimilated per unit of leaf N, increases with increasing CO₂. The observed increase is primarily driven by enhanced CO₂ uptake and not by redistribution of foliar N.
- Plant water use consistently declines with increasing CO₂, resulting in greater soil moisture availability. The decline in water use is driven by reduced stomatal conductance coupled with decreased canopy evapotranspiration with elevated CO₂.
- Carbon uptake in C₄ plants is not directly stimulated by elevated CO₂ except in drought situations. However, there is a potential for increased C₄ plant growth at elevated CO₂. Decreased water use and reduced drought stress at elevated CO₂ improves C₄ plant water relations and indirectly enhances photosynthesis, growth, and yield.
- The increase in C₃ photosynthesis stemming from elevated CO₂ in FACE experiments was greater than the increases in biomass or crop yield, suggesting that photosynthetic response cannot itself predict crop performance. Prior predictions of crop growth based on theory and observations in laboratories or growth chambers systematically overestimated yields of major food crops compared with FACE experimental results.

Cumulatively, the effects of elevated CO₂ impact the response of crop growth and potential yield. The impact of these changes on crop N uptake and demand and crop response to fertilizer N warrants further investigation.

Elevated CO₂ may also directly affect soil N transformations and gaseous Nr loss due to increased soil C availability and changes in soil-plant water relations (Luo and Mooney, 1999). Soil processes that involve Nr may be altered indirectly through changes in plant biomass, root exudates, and microbial community structure (Cantarel et al., 2011).

4.2.2 GHG forcing due to use of N in agriculture

Agricultural N contributes to GHG forcing in several ways. Farming results in the direct release of several GHGs and GHG precursors, including CO₂, N₂O, NO_x, and CH₄. Some of these gases are also released indirectly by farming – in downwind and downstream ecosystems that receive Nr initially in the form of NH₃ volatilized and NO₃⁻ leached from farm systems. Tillage also has a well-known and direct effect on CO₂ release from farmed soils (Reikosky, 1997; Grandy and Robertson, 2006), and there may be an interaction with N use. Additionally, the manufacture of N fertilizer emits CO₂ directly to the atmosphere.

4.2.2.1 N₂O emissions

Nitrous oxide is not reactive in the troposphere but is a powerful GHG – approximately 300 times more potent than CO₂ on a molar basis, and atmospheric concentrations have increased consistently from 270 ppb_v during pre-industrial times to today's concentrations of approximately 320 ppb_v. This increase in N₂O has contributed about 6% of the total GHG forcing that drives climate change (Forster et al., 2007). While this is not a large percentage, the anthropogenic N₂O flux is equivalent to 1.0 Pg C y⁻¹ when converted to C equivalents using 100-year global warming potentials, (Robertson, 2004; Prinn, 2004), which is a magnitude similar to the contemporary net atmospheric CO₂ increase of 4.1 Pg C y⁻¹ (Canadell et al., 2007).

About 80% of the N₂O added to the atmosphere annually by human activities is associated with agriculture. About 60% of this is emitted from agricultural soils, 30% from animal waste treatment, and 10% from burning crop residues and vegetation cleared for new agricultural activities (Robertson, 2004; Houghton et al., 2001). Row crop agriculture is thus responsible for about 50% of the global anthropogenic N₂O flux (Robertson, 2004). Due in part to its high global warming potential, N₂O is a major target for offset projects that can be included in cap and trade markets due to the high payback associated with the mitigation of N₂O emissions (Millar et al., 2010).

Fluxes of N₂O are highest where inorganic N is readily available (Bouwman et al., 1993). Thus soils fertilized with N are major sources of N₂O, although fluxes can also be high in soils with high SOM stores that are rapidly mineralizing N, such as drained organic soils (e.g., Histosols in the USDA soil taxonomy nomenclature). Hundreds of field experiments have shown the amount of N fertilizer applied to be the strongest manageable predictor of N₂O fluxes in all major cropping systems. Although secondary influences such as fertilizer formulation, timing, and placement can magnify or attenuate the general influence of N rate, tillage, residue management, and other agronomic practices can also interact with fertilizer N rate in some soils and cropping systems.

On average, about 0.5 – 3% of N applied to cropped soils is emitted as N₂O to the atmosphere (Stehfest and Bouwman, 2006; Linnquist et al., 2012). The range is due mainly to variation among sites and is well-recognized and expected based on soils, climate, and fertilizer practices. Furthermore, emission rates may be even higher where N input levels exceed the demand of the crop (e.g., Hoben et al., 2011). The Intergovernmental Panel on Climate Change (IPCC) Tier 1 methodologies for national GHG inventories (de Klein et al., 2006) assume an emission factor (EF) for N₂O emissions from cropped soils to be 1% of the N inputs from fertilizer, crop residues, and SOM mineralization where SOM is changing, with an additional premium from drained organic soils (Histosols). Recent evidence suggests that these rates may be even higher at N input levels that exceed the crop demand for N (McSwiney and Robertson, 2005; Ma et al., 2009; van Groenigen, 2010; Hoben et al., 2011).

So-called indirect emissions of N₂O are emitted from downwind and downstream ecosystems when N_r escapes to areas where conditions for N₂O production are favorable. Indirect emissions are even more difficult to estimate than direct emissions because there is uncertainty in both the amount of N_r that escapes and the portion of N that is then converted to N₂O. IPCC Tier 1 methodologies assume that 0.75% of the N that is leached from cropped systems and 1% of the N that is volatilized and subsequently deposited to downwind ecosystems are emitted later as N₂O (de Klein et al., 2006). Recent results suggest that the EF for leached N depends on the type of waterway (Beaulieu et al., 2011), and it is also likely that the EF's for volatilized and re-deposited N will vary depending on the N status (e.g., limiting or non-limiting) of the receiving ecosystem.

4.2.2.2 NO_x emissions

Emissions of NO_x have increased substantially due to human activities, including agriculture (see chapter 2). In the mid-1990s, agricultural sources, broadly defined to include residue burning and land clearing, in addition to direct fluxes from soils, were equivalent to all natural sources and comprised about 25% of all anthropogenic NO_x emissions (Robertson and Vitousek 2009).

In soil the NO that is produced is rapidly oxidized to NO₂ in the atmosphere. Soil NO can be produced by chemodenitrification when HNO₂ spontaneously decomposes to NO, but more commonly, NO is produced by nitrification and denitrification, when NO is produced as a metabolic intermediary and

escapes to the atmosphere (Robertson and Groffman, 2007). Cropland NO_x emissions tend to be highly episodic, and in some cropped systems (e.g., Matson et al., 1998) the magnitude of NO_x emissions can rival those of N_2O . Stehfest and Bouwman (2006), however, estimate that global NO -N emissions from cropland and grassland are less than half of the global N_2O -N emissions. Most NO is formed from the same biological sources as N_2O (i.e., nitrification and denitrification); therefore, NO emissions are also affected by the same environmental and agronomic factors, including fertilizer application rate and soil moisture.

Although NO_x is not a GHG, it plays a substantial role in tropospheric photochemistry (see Chapter 3 and 7), affecting atmospheric concentrations of the GHGs O_3 and CH_4 . Eventually NO_x is deposited on downwind ecosystems in gaseous, particulate, or dissolved forms, where it undergoes the same fate as other Nr inputs, including potential transformation to N_2O .

4.3.2.3 CH_4 fluxes

Lowland rice cultivation represents the only major source of CH_4 from established cropping systems; about 40 Tg y^{-1} are emitted from rice soils worldwide (Sass et al., 1999). About 142 Tg y^{-1} of CH_4 associated with agriculture are also produced by ruminant livestock, animal waste treatment, and when agricultural residues and land cleared for agriculture are burned (Robertson, 2004). However, these sources are not much affected by the use of N in agriculture. In contrast, the application of organic N amendments such as farmyard manure, specialty mixes of organic fertilizer, and incorporated cover crops to rice fields generally increase CH_4 emissions (Qin et al., 2010), although the influence of synthetic fertilizers on CH_4 emissions from rice fields are less consistent and not well understood (Zou et al., 2005).

Methane consumption in soil (CH_4 oxidation or methanotrophy), in contrast to CH_4 production (methanogenesis), is broadly affected by agricultural N use. Methanotrophic bacteria capable of consuming atmospheric CH_4 are found in most aerobic soils, including arable lands, making the uptake of CH_4 globally important: The size of the global soil sink of CH_4 (about $30 \text{ Tg CH}_4 \text{ y}^{-1}$) is the same magnitude as the annual atmospheric increase of CH_4 (about $37 \text{ Tg CH}_4 \text{ y}^{-1}$). In unmanaged ecosystems on well-drained soils, CH_4 uptake is largely controlled by the rate at which it diffuses to soil microsites inhabited by active methanotrophs. Diffusion is regulated by physical factors – principally moisture but also temperature, soil structure, and the concentration of CH_4 in the bulk soil atmosphere.

Agricultural management typically diminishes soil CH_4 oxidation approximately 10-fold (Mosier et al., 1991; Robertson et al., 2000; Smith et al., 2000) for at least as long as the soil is farmed. The mechanism for this suppression is not well understood; likely it is related to soil N availability as affected by enhanced N mineralization, fertilizer, and other N inputs (Stuedler et al., 1989; Suwanwaree and Robertson, 2005). Ammonium is known to competitively inhibit CH_4 monooxygenase, the principal enzyme responsible for oxidation at atmospheric concentrations. Recent evidence suggests that microbial diversity may also play an important role (Levine et al., 2011).

While additional agricultural N use will not much affect CH_4 oxidation in already-cropped soils, Nr that escapes from agricultural to downwind and downstream ecosystems may inhibit CH_4 oxidation in those systems, attenuating a significant CH_4 sink that would otherwise continue to absorb atmospheric CH_4 . The degree to which current natural ecosystems are affected is unknown, mainly because most CH_4 oxidation experiments to date have been conducted with relatively high levels of N addition.

4.1.2.4 Tillage and soil C storage

Nationally, US croplands are in approximate C balance (CAST, 2011). An estimated increase of 13 Tg C on cropped mineral soils is largely balanced by emissions from cultivated organic soils (Histosols) and from land recently converted to cropland (Ogle et al., 2010; USEPA, 2011b). Increases appear to be due to a long-term trend of increasing crop residue production, reductions in tillage intensity (Horowitz et al., 2010), and conversion of annual cropland to perennial grasslands for hay, pasture, and conservation set-asides (CAST; 2011).

The influence of N fertilizer use on cropland soil C storage is unclear and currently under active debate. On the one hand, the argument is that N fertilizer increases soil C because increased above- and belowground residue production parallels increased yields. In addition, because residue C:N ratios have not changed, the additional crop residues should contribute to additional soil C stores (Glendinning and Powlson, 1995; Powlson et al., 2010). On the other hand there are studies that document variable effects of inorganic N on SOM oxidation (see chapter 3; Neff et al., 2002), with recent studies noting declines in soil C storage in well-equilibrated, fertilized, long-term plots despite large and steady increases in crop residue inputs (Khan et al., 2007). An additional consideration is the increase in N₂O fluxes from added fertilizer, which together with the associated CO₂ cost of fertilizer manufacture (see next section), can readily and negatively offset the net CO₂-eq benefit of additional soil C storage.

4.2.2.5 GHG cost of fertilizer manufacture

The production and transport of fertilizer generates a significant proportion of the GHG emissions associated with crop production (Robertson et al., 2000). Estimates of actual emissions from current industrial fertilizer production vary considerably. Snyder et al. (2009) note estimates that range from 2.2 to 4.5 kg of CO₂-eq kg⁻¹ of NH₃-N. The lower value is for NH₃ production only, using best available technology and the higher end of the range is for the current mix of N fertilizer sources used in the US, including the average GHG cost of transport. Production of ammonium nitrate (NH₄NO₃) entails greater GHG emissions than for anhydrous NH₃ or urea.

Only small increases in the efficiency of NH₃ production are expected in the short-term. In the long-term, however, if a C-free method can be found to generate hydrogen for the Haber–Bosch process, NH₃ could be produced with a much smaller C footprint.

In Europe, a large fertilizer producer has provided figures for the C footprint of its N fertilizer (Yara, 2010). They report that manufacture of NH₄NO₃ generates 3.6 kg of CO₂-eq kg⁻¹ of N (2.2 for the NH₄⁺ component plus an additional 1.4 for the NO₃⁻, using best available technology). The transport of the fertilizer adds a further 0.1 kg of CO₂-eq kg⁻¹ of N. In the US, if fertilizer plants were operated with the same best available technology for NH₃ manufacture, a lower C footprint would be expected since NH₄NO₃ comprises only a small fraction of total N fertilizer use. North American producers of N fertilizers have demonstrated improvements in efficiency and have also committed to reducing the C footprint of N fertilizer manufacture to the extent possible.

4.3 OPPORTUNITIES FOR CLIMATE MITIGATION/ADAPTATION WITH N USE

Much of the GHG forcing in agriculture by N can be reduced, avoided, or offset by N management practices that minimize GHG emissions and N_r escape, sequester C, and decrease the likelihood of converting land elsewhere to agricultural production. Many of the effects of these practices interact, so it is important to consider them in concert, from a systems perspective. While many effects are additive, they are combinable to different degrees in different crop and animal systems.

4.3.1 Agricultural intensification

Agricultural intensification can reduce GHG emissions by reducing the need to newly convert non-farmed areas to agricultural production. Burney et al. (2010) estimate that gains in crop yields since 1961 have, globally on a net basis, spared emissions of 320 to 590 Gt CO₂-eq. They note that while emissions per unit area of intensified crops (i.e., a cropping system's GHG intensity) are higher than those of lower-input crops, the emissions from land conversion associated with extensification are considerably larger. Converting land to crop production entails very large GHG emissions, for instance vegetation removal and the oxidation of SOM upon cultivation releases CO₂ and may also affect the N cycle by increasing N₂O production for several years following clearing, even in the absence of N fertilizer.

Burney et al. (2010) further noted that crop yields per unit area increased by more than two-fold from 1961 to 2005, which has limited the expansion in cropland area to 27%. Without these yield increases, they estimated that approximately 300% more land would have been required to attain the crop production levels of 2005. This foregone GHG release is an important benefit of intensification, especially as intensification could provide opportunities for management interventions not as easily provided in more dispersed systems. The authors demonstrated that investment in research toward agricultural intensification (primarily higher crop yields) was a cost-effective approach to GHG mitigation, with overall costs of approximately US \$4 per Gg of CO₂-eq.

4.3.2 N Management Interventions for GHG Mitigation in Cropping Systems

A variety of N management practices are available to reduce GHG forcing in cropping systems. These range from the way in which N fertilizer is applied, such as its rate, timing, placement, and formulation, and to changes in human diets. Many appropriate technologies are available now, and require only appropriate incentives to adopt. Other technologies are promising but unproven or not as generalizable. We identify research needs in section 4.4.

4.3.2.1 Fertilizer rate, timing, placement, formulation, and additives

Applying the right source of N at the right rate, time, and place is the core concept of the 4R Nutrient Stewardship, supported by a wide range of industry and government organizations (IFA, 2009; Bruulsema et al., 2009). The 4R strategy is designed to increase crop NUE. In general, it is assumed that any practice that increases crop NUE is expected to reduce N₂O, NO_x, and NH₃ emissions, because fertilizer N taken up by the crop is not available to the soil processes that lead to N emissions, at least in the short term. Thus, strategies to reduce losses of N are generally associated with improved fertilizer use efficiency.

Practices that improve NUE do not always reduce N emissions, however. Different fertilizer formulations, for example, can result in different N₂O emissions regardless of putative NUE effects. Likewise, banded fertilizer placement can increase NUE but in some cases also increase N₂O emissions, whereas tillage management can increase NUE without affecting N₂O. Thus NUE is generally important but is not sufficient by itself to reduce N emissions. As mentioned earlier, fertilizer rate, timing, placement, and formulation can all affect NUE and N gas emissions independently.

Fertilizer rate: More than any other factor, the amount of N fertilizer applied to soil affects the amount of N₂O and NO_x emitted – in many cases timing, placement, and formulation provide their benefit by effectively reducing fertilizer N in soil. In this sense, fertilizer rate is a good integrator for multiple practices.

Fertilizer timing: Synchronizing soil N availability with crop N demand is a major challenge for efficient fertilizer management. Typically fertilizer is applied well ahead of peak demand, sometimes as much as 6-8 months ahead of crop demand for fall-fertilized corn in the Midwest. Even when side dressing of fertilizer shortens this lag to weeks, there is still a period when N_r is more available to microbes than to roots. Moreover, N emissions are almost always greatest immediately following fertilization when soil N levels are high and temperature and moisture are sufficient for microbial activity.

Fertilizer placement: How fertilizer is applied to soil can affect its availability for crop uptake and also its susceptibility to soil transformations that produce N₂O and NO_x. Placement includes three broad strategies: (1) broadcast application vs. within-row banding; (2) the soil depth to which liquid fertilizer is injected; and (3) uniform application vs. application at different rates within the same field based on the variability of soil fertility across the field. The effects of banding and injection on N gas emissions are equivocal. Although banding can increase NUE, it can also create zones of highly concentrated soil N that can increase rather than decrease the production of N₂O. Deep injection of liquid N almost always reduces volatilization of NH₃ compared with the surface application of manure, urea, and other urea or NH₃-containing fertilizers. However, effects on N₂O production are inconsistent. Variable rate application uses different N rates for different areas of a field based on expected variations on crop N demand. This is a new technique and will be discussed more fully in section 4.3.2.2.

Fertilizer formulation and additives: Anhydrous NH₃ is the most commonly used synthetic fertilizer in the US (35% of total use), followed by liquid formulations including urea ammonium nitrate (29%) and urea (24%). Early studies found inconsistent effects of fertilizer formulation on N gas emissions; consequently IPCC GHG inventory guidelines (de Klein et al., 2006) make no distinctions among different formulations or between inorganic and organic forms, although recent cross-site research suggests higher N₂O emissions with anhydrous ammonia than with broadcast urea (e.g., Venterea et al., 2010). Chemical additives such as urease and nitrification inhibitors delay the transformation of urea and NH₄⁺, respectively, to improve the synchrony between soil N availability and crop N demand. Delayed-release chemical formulations such as polymer coated urea slowly release N with increasing soil temperature and water to achieve the same effect. To date, effects of additives and chemical formulations on N₂O emissions have been inconsistent, although recent meta-analyses (e.g., Akiyama et al., 2010) suggest that broader experimentation will provide greater clarity.

Integration: The 4R Nutrient Stewardship concept noted earlier is designed to provide farmers a management paradigm that increases the sustainability of the plant system to which it is applied (Figure 4.5). For any given system, performance includes the productivity and profitability of the system (the economic dimension of sustainability), its impacts on soil, water, air and biodiversity (the environmental

dimension), and its impacts on quality of life and employment opportunities (the social dimension). Farmers ultimately choose the combination of practices that are judged to have the highest probability of meeting economic and environmental goals based on site-specific soil, weather, crop production, and local regulatory conditions. The 4R Nutrient Stewardship is a program that is a central component of the Alberta N₂O Emission Reduction Protocol for C offset trading (Alberta Environment, 2010).

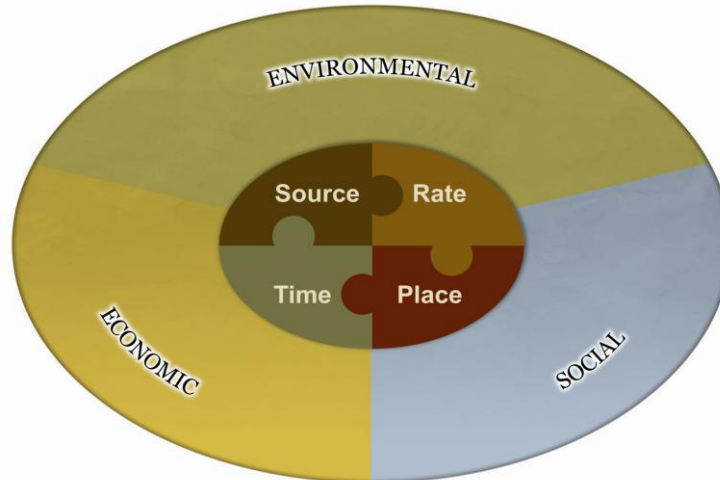


Figure 4.5: The 4R nutrient stewardship concept defines the right source, rate, time, and place for N application within an economic, social, and environmental sustainability framework. Used with permission from the International Plant Nutrition Institute (IPNI, 2011).

4.3.2.2 Precision fertilizer application technologies

Although not new concepts to US agriculture, precision technologies and site-specific N management continue to gain attention as potential methods to improve N fertilizer use and efficiency. Typically, these methods attempt to address field-scale spatial and temporal variations in system characteristics, such as soil chemical and physical properties and crop growth or yield patterns. Farmers can now micro-manage their farms using tools such as global position systems (GPS) and geographic information systems (GIS) software. When combined with geo-referenced sampling and variable rate application technology, farms are able to more closely match fertilizer applications with crop requirements and minimize N_r environmental losses.

An example of the potential impact of precision farming technologies on N management is the growing interest in crop canopy sensor use. Recently, numerous investigations have explored the use of remotely-sensed crop spectral data as a means to understand plant growth characteristics and improve N management for several crops (e.g., Raun, 2002). The remotely-sensed normalized difference vegetative index (NDVI) is a measure of total above-ground green biomass and is an indicator of crop growth and health. Use of canopy reflectance and NDVI as an in-season assessment of crop yields can be a valuable tool to fine-tune N management, optimizing crop N fertilizer recovery. Historically, published reports of NDVI data have been remotely-sensed using passive sensing methods such as aerial and satellite imagery. More recently, numerous studies have specifically reported the use of active-light, crop canopy reflectance sensors as a promising tool to improve N use efficiency by estimating N requirements and yield potentials for crops including corn, wheat, and sugar beets (Raun et al., 2002; Raun et al., 2005; Girma et al., 2006; Freeman et al., 2007; Dellinger et al., 2008; Barker and Sawyer, 2010; Kitchen et al., 2010; Gehl and Boring, 2011).

Beyond in-season N management, NDVI has also been used as a predictor of N management zones for subsequent crops. Franzen (2004) describes the widespread use of satellite NDVI images for sugar beet canopy N credits to develop N management zones for adjusting N rates for the next crop in the rotation. Continued improvements and advances in available site-specific technologies will increase future opportunities for N_r mitigation at the farm field-scale by more closely matching inputs with crop needs.

4.3.2.3 Tillage practices

The effect of changes in tillage management on soil N emissions is variable and not fully understood. Short-term studies have documented increases, decreases, and no changes in soil N₂O emissions with the adoption of no-till, with responses being principally related to soil texture and structure, climate, fertilizer placement, and time since adoption. In a recent meta-analysis, Six et al. (2004) found that N₂O emissions are in general higher in the first 10 years after adoption of no-tillage, but over time emissions tended to be lower in humid climates and the same in dry climates. However there are many sites where this generalization does not fit and clarity awaits further research.

4.3.2.4 Ozone resistant crop cultivars and methane mitigation

Increasing evidence points to elevated O₃ concentrations as being an important and usually an overlooked stress in the deceleration of global crop yield increases (Avnery et al., 2011a; Fishman et al., 2010; van Dingenen et al., 2009; Zhu et al., 2011; Wang and Mauzerall, 2004). Recent model simulations quantified the present and potential future (year 2030) impact of surface O₃ on the global yields of soybean, maize, and wheat given both upper- and lower-boundary projections of reactive O₃ precursor emissions (Avnery et al., 2011a,b). Avnery et al. (2011b) projected substantial future yield losses globally for these crops even under a scenario of stringent O₃ control via traditional pollution mitigation measures (i.e., reductions in NO_x, VOCs, and NMVOCs): 10-15% for soybean, 3-9% for maize, and 4-17% for wheat.

Given the potential for significant future O₃-induced yield losses, two additional strategies to reduce O₃ impacts should be considered: (1) O₃ mitigation through CH₄ mitigation, and (2) adoption of ozone-resistant cultivars. Methane is both a GHG and an O₃ precursor and reductions in CH₄ thus provide benefits to human health and vegetation including crops. Avnery et al. (2011a) found that gradual reductions in CH₄ emissions between 2005 and 2030 could increase global production of soybean, maize and wheat by 23-102 Tg in 2030, which is the equivalent of an approximately 2-8% increase over year 2000 production, worth US \$3.5-15 billion worldwide (USD₂₀₀₀). A wide variation in O₃ sensitivity exists both between crops and among crop cultivars. As noted earlier, analyses using minimum and median concentration-response relationships to O₃ exposure obtained from the US National Crop Loss Assessment Network (Heck, 1989) found that the use of existing cultivars with minimum sensitivity to O₃ could increase global yields of corn, wheat and soybean 12% over year 2000 production by 2030 (Avnery et al., 2011a). Combining CH₄ mitigation with O₃-resistant cultivars would yield the greatest gains to agriculture, although benefits are less than fully cumulative given the nature of the effect of O₃ on crops. In any case, there appears to be significant potential to improve global agricultural production without further environmental degradation by reducing O₃-induced crop yield losses via reductions in O₃ precursors (i.e., NO_x, CO, VOCs, and CH₄) and the development and utilization of O₃ resistant crop cultivars.

4.3.2.5 Perennialization of fields and landscapes

The winter and early spring fallow period common to row crop agriculture creates a significant opportunity for Nr loss (Blevins et al., 1996; Wagner-Riddle and Thurtell, 1998; Strock et al., 2004; Dusenbury et al., 2008). Nitrogen that remains in the soil after the summer annual crop is removed is susceptible to loss by leaching (as NO_3^-) or denitrification (N_2O , NO_x), particularly if no crop or vegetation is present for N uptake during the off-season and when precipitation and/or freeze-thaw cycles are adequate to influence N cycle dynamics (Dorsch et al., 2004). Shifting crop production from annual to perennial systems may include the use of winter cover crops, which provides nearly year-round plant production, or the use of perennial rather than annual biofuel crops.

The presence of living plants during the winter season can reduce Nr losses through mechanisms of plant N uptake and reduced subsurface percolation. Cover crops have been documented to reduce both N_2O flux and NO_3^- leaching compared with bare fallow systems (McSwiney et al., 2010). This effect is especially pronounced where manures have been applied after the primary crop growing season (Parkin et al., 2006). However, recent research has indicated that N fertilizer rate may be more influential to N_2O emissions when compared with the presence of a cover crop, regardless of cropping system and manure application (Dusenbury et al., 2008; Jarecki et al., 2009)

The establishment of perennial vegetation on cropland can also reduce Nr losses. Whether established for conservation purposes such as the US Conservation Reserve Program (CRP) or established for cellulosic biofuel production, perennial grasses and short-rotation trees conserve both N and soil C. The rooting system of some C_4 perennial grasses can contribute up to $2.65 \text{ Mg C ha}^{-1} \text{ yr}^{-1}$ to the top 5 cm of soil (Lemus and Lal, 2005; Schmer et al., 2011). For example, estimated total C mitigation for giant miscanthus was estimated at 5.2 to $7.2 \text{ Mg C ha}^{-1} \text{ yr}^{-1}$ over the course of a 15 year study in Ireland (Clifton-Brown et al., 2007).

Proposed perennial biomass crops generally require relatively low fertilizer N additions for maximum crop growth and consequently can exhibit low N_2O emissions (Jørgensen et al., 1997) and other N cycle benefits such as lower NO_3^- leaching (Robertson et al. 2011). Davis et al. (2011) estimate, using the DAYCENT model, that conversion of US cropland currently used for corn grain ethanol production to perennial cellulosic feedstocks would increase both ethanol and feed production while reducing NO_3^- leaching 15-122% and reducing GHG emissions 29-473%. Research is needed to further improve our understanding of the effects of landscape-level land conversion to perennial biofuel feedstocks on Nr system dynamics.

Perennialization can also occur as the result of strategic conservation plantings in the landscape. Grass or other vegetative buffer strips in specific parts of the landscape can intercept NO_3^- flowing to groundwater and streams, as can natural or restored wetlands, avoiding its conversion to N_2O and NO_x further downstream (Robertson et al. 2007). Although some N_2O is likely to be produced at the point of interception, the presumption is that this will be less than would occur were the Nr allowed to proceed unabated.

4.3.2.6 Models and other decision support tools

The complexities of the processes that govern soil Nr transformations complicate N fertilizer management decisions for the grower. These processes are both dynamic and site-specific, requiring growers to make decisions based on past experience while anticipating likelihoods for the current

growing season. In essence, growers must plan and manage N fertility programs that are most likely to give the greatest yield but still maintain economic viability. As such, a system of support tools becomes critical to assist growers with N fertilizer decisions.

Crop response to applied N varies spatially, both among and within fields, and temporally, from one year to the next. The shape of the crop response curve determines the appropriate fertilization rate. For many crops, the most economic N rate prevents loss of large surpluses and comes close to minimizing emissions of N₂O per unit of crop produced (van Groenigen et al, 2010).

The crop response curve to N additions is unknown at the time of fertilizer application, because of uncertain rates of N mineralization from SOM. Therefore, the decision on the appropriate N rate must be made using tools or systems that forecast the most likely response given soil, crop and weather conditions. Recommendation systems in the US are typically state-specific and vary in approach. Historically, recommendations were primarily based on predicted yield models, but more recently many states have moved toward economic response models that may or may not include predicted yield. An example is the maximum return to N (MRTN) recommendation tool recently adopted by seven Midwest states. The MRTN approach uses recent response trial data from individual state or local regions to determine the N fertilizer rate where economic net return to N application is greatest (Sawyer et al., 2006). The MRTN is a regional model based on historic response curves for specific geographies. As a decision support tool, the factors used in generating the recommendation include fertilizer and crop prices.

An approach that goes further toward including additional factors relevant to N rate prediction are process-based models such as Maize-N (Setiyono et al, 2011) and System Approach to Land use Sustainability (SALUS) (Basso et al., 2011). While this approach is more deterministic and less empirical than MRTN, it is still based on historical climate data and could be adapted to anticipate dynamic weather conditions that influence the prediction of potentially attainable yields and yields without N fertilizer.

Weather controls a great deal of the variation in a crop's response to N. The application of models integrating soil water flow, soil N dynamics, and plant uptake can potentially improve the prediction of crop N needs in response to weather conditions. An example of a model that includes dynamic weather factors is Adapt-N (Mobius-Clune et al., 2011).

Nutrient management becomes more complex when animal manure is used in the cropping system. Since the relative concentrations of manure nutrients (e.g., the N:P ratio) are fixed, it is more difficult to match available nutrients to crop needs. Nutrient management plans are often required to assure that manure nutrients are applied at the appropriate time and rates for crop use, thus reducing losses to the environment. Software tools such as the Manure Management Planner (Joern, 2010) assist producers in the development of nutrient management plans that make best use of available manure nutrients along with inorganic fertilizers.

4.3.3 Animal System N Management Practices that Mitigate GHG Forcing

Mitigation of N loss from animal agriculture must begin with improved utilization of feed protein and then continue with the reduction of emissions from manure. More precise feeding of the amount and type of protein (amino acids) needed to meet the animal's requirements at each stage of production is necessary to reduce the excretion of manure N while maintaining or improving animal production. Even

with a good feeding strategy, large amounts of N are excreted, so further mitigation must be obtained through strategies that reduce N losses from manure. The final opportunity is to capture N compounds before they escape to the environment.

4.3.3.1 Animal nutrition

For precision feeding, the protein and other nutrient requirements of the animals must be known, and then a diet must be prepared that meets that requirement without feeding in excess. Implementing precision feeding strategies is challenging, particularly for ruminant animals as noted earlier. The first challenge is discerning the nutrient content of available feeds. While the ability to measure the chemical and physical characteristics of feeds on-farm is improving, feed sampling and analytical procedures are still relatively imprecise, particularly for forages (Moore et al., 2007). With imprecision in measuring the major feed ingredients, there is error in knowing the amounts of supplemental protein needed to balance rations. The second challenge is proper mixing and delivery of the feeds so that the animals consistently receive the nutrients needed (Rippel et al., 1998). Inconsistencies in the diet can reduce NUE, reducing animal productivity and increasing nutrient losses to the environment.

Reducing the total protein in the diet can have a major impact on the environmental effects of N. For example, multiple studies with dairy and beef animals have shown that N excretion and its potential loss to the environment decreases 10-20% for every percentage unit of protein removed from the diet (Hristov et al., 2011; Rotz, 2004; Erickson and Klopfenstein, 2010). To effectively remove that protein, the remaining feed protein must better meet the requirements of the animal at a particular stage of development. This can only be achieved through precise blending of available feeds. Phase feeding can help by dividing and feeding animals according to their stage in development (Erickson and Klopfenstein, 2010). However, as the diet becomes more finely tuned to the animal's requirements, the animal becomes more sensitive to inconsistencies in the feed. Thus, producers tend to reduce their risk by over feeding protein and other nutrients to assure that the requirements of the animals are met. The use of precision feeding is increasing however, and there can be an economic incentive for the producer through a reduction in feed costs.

Synthetic amino acids can be also fed for further precision in meeting animal protein requirements. Different amounts of each amino acid are required, and these amounts vary with animal age and other characteristics. As we learn more about amino acid requirements and we learn to produce these compounds cost effectively for feed use, more precise diets can be created to match the animals' requirements throughout their life cycle. The use of synthetic amino acids has become common in non-ruminant animal production, but their use in ruminant diets is more complex (Han and Lee, 2000; Hristov et al., 2011).

4.3.3.2 Manure handling

Even with very precise feeding, the majority of N consumed is excreted, so further mitigation of N effects on the environment must be achieved through changes in manure handling. This begins in the housing facility. For cattle and swine, floor designs have been developed to separate urine from feces (Ndegwa et al., 2008). When urine has less contact with the urease enzyme in the feces, the transformation of urea to NH_4^+ , and ultimately NH_3 , is reduced. This strategy has reduced the emission of NH_3 from dairy barns by up to 50%. Other strategies such as using a flushing system to remove manure or more frequent scraping may also provide some reduction in NH_3 emission, but this benefit has not been clearly supported through on-farm studies (Ndegwa et al., 2008). On open lots, the use of

organic bedding material, increasing manure removal frequency, and acidifying manure have all shown potential for reducing NH_3 emissions (Erickson and Klopfenstein, 2010). For poultry, the use of catching boards to dry the manure have reduced NH_3 emission by 40-60% (Yang et al., 2000), and the use of belt removal systems have reduced emissions from the housing facility by up to 90% (Groot Koerkamp, 1994).

With long term manure storage, NH_3 emissions can be reduced using a cover. Many cover designs have been evaluated including floating straw, expanded clay pebbles, geo-textile fabric, and other permeable materials. Emissions are reduced up to 80% by impeding emissions and promoting biological activity that transforms gaseous compounds (Peterson and Miller, 2006). However, complete cover must be maintained throughout the storage period, and these covers are often difficult to maintain. The development of a natural crust of manure solids appears to be about as effective as the use of other permeable covering materials. However, with a natural crust or other permeable cover, an environment is created that enhances N_2O production via nitrification and denitrification (Peterson and Miller, 2006). An enclosed tank or impermeable plastic cover provides the most effective mitigation strategy for manure storage, virtually eliminating N emissions (Ndegwa et al., 2008; Rotz, 2004). A floating layer of oil has also been evaluated as an impermeable cover (Ndegwa et al., 2008).

Mitigating N emissions from manure also requires careful management of field applications. Direct injection into soil is the most effective method for reducing NH_3 emission when it is compatible with the cropping system. With deep injection, NH_3 loss can be as little as 2% of the N applied (Ndegwa et al., 2008; Rotz, 2004). With more shallow injection, this loss may be up to a third of that associated with broadcast application (Rotz et al., 2011). However, within the concentrated layer of manure placed in soil, N_2O emission can increase soon after application, providing up to a fourfold increase in average annual emissions (Velthof and Mosquera, 2011). The amount of N_2O emitted is variable and highly dependent on soil characteristics, soil moisture content, and the amount and time of year manure is applied.

Band application is another option, whereby manure is spread on the soil surface in bands, reducing the exposed manure surface compared to broadcast application. Depending upon the width and structure of the bands and the crop receiving the manure, emissions of NH_3 are reduced up to 50% compared to broadcast application (Pfluke et al., 2011). Other techniques that can reduce NH_3 emissions following surface application are to reduce the dry matter content of the manure, which increases soil infiltration, and to apply the manure with fewer but heavier applications (Sommer and Hutchings, 2001; Rotz, 2004). Adding acid to drop the pH of the manure is also effective, but cost prohibitive (Sommer and Hutchings, 2001). Applying manure before rain or irrigation can reduce NH_3 emission, but this may increase nutrient runoff losses in surface water (Vadas et al., 2011).

4.3.3.3 Grazing land management

Management can be used to reduce N loss from grazing animals, but the benefit of these changes may be small and implementation may be impractical. As with confinement fed animals, the first step is to use supplemental protein feeds efficiently, and thus reduce urinary N excretion. These measures are more challenging with grazing animals since there is uncertainty in knowing the amount and type of protein they are obtaining from pasture forage (Fales et al., 1995).

Nitrogen loss from grazing lands can be controlled by avoiding overstocking and importing forage and other supplemental feeds. Furthermore, movement of watering and supplemental feeding areas improves nutrient distribution, thus increasing plant uptake and reducing loss. Volatile loss of Nr may be reduced by irrigating the paddock immediately after grazing to wash the N into the sod and soil. Leaching loss of NO_3^- is best reduced by avoiding grazing in the late autumn or winter when plant uptake of N is low. Removing the autumn growth through silage harvest can help reduce the accumulation of excess soil NO_3^- , which at that time of the year will likely be lost by leaching (Stout et al., 1997). Less use of N fertilizer with greater use of clover and other legumes to supply needed crop N can also reduce soil N levels and leaching loss. Di and Cameron (2002) decreased leaching N loss by 60% and decreased denitrification losses by 82% by applying a nitrification inhibitor, but practical application of this technology is difficult and likely not cost effective for the producer.

4.3.3.4 Animal housing

Adaptation to climate change will require changes in animal housing facilities, including better insulation and greater use of evaporative cooling systems. Coping with increasing temperature in outdoor facilities and pastures may require greater use of shading systems to protect animals from solar radiation and water spray systems for increasing the evaporative cooling of animals. Genetic manipulation of animals to develop greater tolerance to heat may also help in this adaptation (Nardone et al., 2010). If animals cannot be fully adapted to future climate changes, decreases in the efficiency of production will increase losses of N per unit of production.

After N compounds are created and released from the manure, there can be an opportunity to capture the compounds before they disperse into the environment. For example, biofilters and scrubbers can be used to remove NH_3 from the ventilation air exiting enclosed housing facilities (Ndegwa et al., 2008). Scrubbers capture the NH_3 in an acid water solution while biofilters biologically degrade or convert trapped compounds into environmentally benign forms.

4.3.3.5 Whole-farm approaches

Management to reduce N losses in animal production requires a whole-farm approach. Many changes can be made to reduce N losses in each step of manure management between animal excretion and crop uptake. However, the benefit for reducing the loss in any one component is low if steps are not taken to reduce losses occurring in other components (Rotz et al., 2005; Rotz and Oenema, 2006). For example, reducing NH_3 emission in the housing facility has little benefit if that retained N is simply lost due to poor management during subsequent manure storage and field application. Reducing NH_3 emissions may also not provide any overall benefit if the conserved manure N not lost as NH_3 leads to the over application of plant needs and thus greater losses through denitrification and leaching in croplands (Rotz et al., 2011). The loss of N_2O to the atmosphere and NO_3^- to groundwater may have a greater long-term cost to society than NH_3 emission. Only by providing similar levels of management to animal feeding, housing, manure storage, and field application can production systems be developed with reduced or optimal environmental impact.

The primary deterrent to the mitigation of N losses and their impacts on the environment in animal agriculture is normally the economic effect on the producer. Often the technology and management changes required increase the producer's cost of production. Whole farm analyses indicate that changes in feeding management, covered manure storages, and the direct injection of manure into the soil can be performed with less cost to the producer than more major changes such as altered barn or housing

design, enclosed manure storages, and manure treatments (Rotz et al., 2006). Since the profit margin is often tight and the product price is beyond the control of the producer, this additional cost usually cannot be absorbed. If further mitigation of N emissions from agriculture is desired by society, then society must bear the cost either through regulations that increase agricultural product prices or government subsidies.

4.3.4 Human Diet

The life-cycle efficiency of N varies greatly between plant and animal food systems. While approximately 70% of N in harvested food crops becomes available for human consumption after processing losses, only about 15% of the original N in harvested feed crops is present in meat, eggs, and dairy products (Smil, 2002). This is both as a direct result of N leakage to the atmosphere and to waters from intensive animal systems, and from the demand for increased crop production for animal feed -- 70% of the annual cereal and legume harvest in the US is fed to livestock (Smil, 2001). Consequently, continued high meat consumption in developed countries and more meat-intensive diets in developing countries over the coming century will lead to the need for greater N inputs and thus greater N losses from agriculture (Mosier et al., 2001).

For the US, less food waste and changes in diet could significantly reduce N fertilizer consumption without comprising nutritional adequacy. Smil (2001) calculates that a reduction in meat consumption by 33% would reduce fertilizer consumption by 25%, with total fertilizer use dropping from 7-7.5 to 5.3 – 5.6 Tg N.

4.3.5 Current Policy Initiatives

4.3.5.1 US Policy

Policy in the US regarding N mitigation inadvertently began in the 1930s as part of the New Deal. The New Deal National Industrial Recovery Act (1933) authorized the USDA to work on soil erosion control as a means of unemployment relief through the Civilian Conservation Corps (Cox, 2007; Rasmussen, 1982). Soon following, the Soil Conservation Act (1935) established a permanent federal agency, the Soil Conservation Service (SCS). The SCS provided direct assistance to farmers with the help of state legislation. Subsequent acts such as the 1936 Soil Conservation and Domestic Allotment Act began to provide payments to farmers to produce soil-conserving legumes and grasses. The Act also provided payments to farmers to incorporate productivity-enhancing practices on land that was already in production. Financial support for conservation was a means to increase profitability, manage supply, and raise prices.

The shift in agricultural policy from resource conservation to environmental benefits began with the 1977 Food and Agriculture Act. The Act specified that eligibility under the Agricultural Conservation Program (ACP) be based on the presence of an environmental problem that either reduced the productive capacity of a farm's land and water resources or caused environmental degradation. Specifically, the ACP required that the Secretary of Agriculture consider the need to control erosion and sedimentation, water resources, and pollution from animal wastes, in order to encourage voluntary compliance in solving environmental issues, and to consider the degree to which the ACP assistance would contribute to a continuous supply of food and fiber and improve water quality in rural America (Rasmussen, 1982; Cox, 2007).

The Food Security Act of 1985 accelerated the shift from agricultural resource conservation with on-

farm benefits to environmental management with off-farm benefits. Off-farm benefits included clean water and air, biodiversity, and other ecological services. The Act also authorized the Conservation Reserve Program (CRP), which was designed to control the supply of surplus crops and to take highly erodible land out of production. The CRP would later go beyond erodible land to include conservation priority areas such as the Chesapeake Bay, Long Island Sound, and Great Lakes watersheds, as well as state water quality priority areas, and critical areas suitable for high-priority conservation practices such as buffers (Barbarika, 2001; Cox, 2007). The Chesapeake Bay Watershed Initiative, for example, assists with conservation practices that improve water quality and quantity and restores, enhances and preserves soil, air, and related resources. Provisions of subsequent farm bills (1990, 1996, 2002, and 2008) reflected a change in the conservation agenda. Provisions of the farm bill such as the Environmental Quality Incentives Program (EQIP) also include natural resource concerns related to poultry and livestock production. Eligible practices under EQIP include nutrient management, integrated pest management, irrigation water management, and wildlife habitat management.

The US Department of Agriculture (USDA) has been the leading federal department, with the Natural Resource Conservation Service (NRCS) and the Farm Service Agency (FSA) being the leading federal agencies for agricultural conservation and environmental management on private land. Of the 20 programs currently managed, CRP and EQIP represent 64% of the \$5 billion FY2011 appropriations (Stubbs, 2011). The 20-year history of CRP has provided a wealth of knowledge regarding the impact of conservation practices at the field level, and is therefore the most studied conservation program. However, few research studies have been designed to measure the larger effects of conservation practices. Current efforts to quantify the impacts of conservation practices in the US have been under the banner of the national Conservation Effects Assessment Project (CEAP), which was established to quantify environmental benefits of conservation programs on agricultural landscapes at the national, regional and watershed scales. It is an ongoing mix of data collection, model development, model application, and research. Since its inception in 2003, CEAP has grown into a multi-agency, multi-resource effort.

US policy has developed since the New Deal, going beyond the initial focus on reducing soil erosion and increasing farm production. Although these policies were specific to soil erosion, conservation policies have also been important in mitigating N_r losses from agricultural lands. Current efforts now include environmental management and improvements leading to clean water and air.

4.3.5.2 International Policies

There are several existing regional and international policy efforts that attempt to limit N leakages to the surrounding environment. However, only a few deal directly with N emissions related to climate change. One is the United Nations Framework Convention on Climate Change Kyoto Protocol. Nitrous oxide is in the Kyoto basket of controlled GHGs. However, there are no specific controls on N₂O, and to date no emission credits under the Clean Development Mechanism have been issued for agriculture-related N₂O projects. The handful of N₂O emission reductions projects that exist, are associated with industrial applications such as nitric acid plants.

Another policy is the Alberta Quantification Protocol for Agricultural N₂O Emissions Reductions, which issues C offset credits for on-farm reductions of N₂O emissions and fuel use associated with the management of fertilizer, manure, and crop residues for each crop type grown. Presumed reductions are achieved via Beneficial Nitrogen Management Practices (BNMPs) that implement the 4R-Consistent (Right Source at the Right Rate, Right Time and Right Place) Nitrogen Stewardship Plan. Other N₂O

emission reduction protocols (e.g., Millar et al., 2010) are being considered for the Verified Carbon Standard, the American Carbon Registry, and the Climate Action Reserve.

There are also two policy initiatives that deal indirectly with N leakages related to climate change. The EU Nitrates Directive sets limits on the use of fertilizer N and animal manure N (limited to 170 kg N/ha/year) in NO_3^- vulnerable zones, which are declared by member states where surface or ground water concentrations of NO_3^- exceed 50 mg/l, or where NO_3^- concentrations are increasing over time. These requirements in turn reduce the potential for denitrification and thus N_2O emissions in waterways downstream of leaching.

The Convention on the Long Range Transport of Air Pollution & its Gothenburg Protocol set national limits for NO and NH_3 emissions for its Parties with an aim to limit eutrophication, acidification and tropospheric O_3 pollution, which in turn impacts the effects of Nr on climate change (see section 4.2.2). While some of these efforts are more successful than others, an over-arching critique applies to all of them: by examining only specific parts of the N cycle, these efforts could control one form of N pollution while exacerbating another. For example, one of the consequences of the EU Nitrates Directive is more prevalent winter manure storage. However, there is evidence that suggests that this leads to more NH_3 volatilization, detrimental to air quality. The central lesson that should be drawn from these efforts is that any effort to limit N pollution should be done in as holistic a manner as possible so as to minimize potential negative side effects. A useful concept to apply here is the economic N cascade, which is an evaluation of the costs and benefits of reducing Nr pollution at various points of the cascade as recently applied in the Chesapeake Bay watershed (Birch et al., 2011).

4.4 RESEARCH NEEDS

We identify four major research needs for a better understanding of the impact of climate-N interactions in agriculture. First is an improved understanding of agricultural N cycle responses to changing climate. This includes the response of N emissions both direct and indirect to changes in the frequency and intensity of rainfall; the response of N emissions to changes in regional temperature patterns, and in particular to warmer winters and longer and hotter growing seasons; and the response of crop N cycles to O_3 -tolerant crop varieties.

The second research need is for an integrated, systems-level understanding of important crop and animal systems sufficient to identify key interactions and feedbacks. This understanding will allow us to design interventions that maximize synergies and minimize liabilities, and above all avoid unanticipated outcomes with unpleasant surprises.

Third is a need to further develop and test models capable of predicting N-climate interactions with confidence across a wide variety of crop-soil-climate combinations. Models will include biogeochemical estimators for important N species such as N_2O and NO_x . Currently needed are model intercomparisons and a sufficient number of data sets to validate and further refine existing models. Models should also include decision support tools for growers and animal managers to improve N management decisions based on available practices and best possible outcomes.

Finally, socioecological research is needed to better understand the incentives necessary to achieve meaningful deployment of realistic solutions. In many cases knowledge and technology are available to abate and even mitigate effects of agricultural N \times climate interactions. Currently missing are the policy or market incentives that will lead farmers towards adoption.

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Chapter 5: The interactive effects of excess reactive nitrogen and climate change on aquatic ecosystems and water resources of the United States

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ABSTRACT

Nearly all freshwaters and coastal zones of the US exhibit some degree of degradation from inputs of excess reactive nitrogen (Nr). Sources of which are runoff from fertilizer applications and N-fixing crops, atmospheric N deposition, and imports of food and feed. Some of the major adverse effects include harmful algal blooms, hypoxia of fresh and coastal waters, ocean acidification, long-term harm to human health, and increased emissions of greenhouse gases including nitrous oxide (N₂O) and methane (CH₄). While N fluxes to coastal areas and emissions of N₂O from waters have increased in response to N inputs, denitrification and burial of organic N are important processes that return N to the atmosphere or store it in sediments, respectively. Aquatic ecosystems are particularly important denitrification hotspots, both nationally and globally. Carbon (C) storage in sediments is enhanced by Nr, but whether C is permanently buried is unknown. Transport, denitrification, and burial of Nr in the US is influenced by the human-made infrastructure that increases the flushing rate of N-rich waters to groundwaters, streams, rivers, lakes and estuaries from tile drains, canals, and impervious urban surfaces in many areas, and slows the movement of water downstream with dams in other areas. The effect of climate change on N transport and processing in fresh and coastal waters will be felt most strongly through changes to the hydrologic cycle, which will fluctuate in response to precipitation, whereas N loading is mostly climate-independent. Alterations in the amount, timing, frequency, and intensity of precipitation will increase and decrease seasonal and event-driven runoff, thereby influencing both rates of Nr inputs to aquatic ecosystems and groundwater and the water residence times that affect Nr removal within aquatic systems. Both hydrologic manipulation by human-made infrastructure and climate change alter the landscape connectivity and hydrologic residence time that are essential to denitrification. While both Nr inputs to and removal rates from aquatic systems are influenced by climate and management, reduction of N inputs from their source will be the most effective means to prevent or to minimize adverse environmental and economic impacts of excess Nr to the nation's water resources. Without mitigation, the concurrent impositions of climate change and the increasing load of Nr to freshwater and estuarine ecosystems will most likely have unprecedented additive or synergistic effects on water quality, human health, inland and coastal fisheries, and greenhouse gas emissions. Research is greatly needed to identify how the magnitude and effects of current and projected inter- and intra-annual changes in hydrology interact with Nr inputs to surface and ground-waters, how to reduce the transport of N from agricultural landscapes to freshwaters and estuaries, the biologic consequences of Nr interactions with other nutrients under climate change, and the societal and economic risks associated with Nr and climate interactions.

5.0 INTRODUCTION

Climate change effects on US water resources are already evident, caused by alterations in precipitation patterns, intensity, and type, occurrence of drought, increased evaporation, warming temperatures, changes in soil moisture and runoff, and changes in ocean circulation (Karl and Melillo 2009). At the same time, the nation's waters are biologically and chemically responsive to the influx of reactive nitrogen (Nr) that now pervades most freshwater and coastal ecosystems (Howarth et al. 2011b, Smith et al. 2003). The input of Nr to the conterminous US has been increasing over time; recent estimates from an Environmental Protection Agency Science Advisory Board 2011 report (US EPA 2011) suggest the total terrestrial Nr inputs in 2002 to the US were 28.5 Tg N yr⁻¹ (US EPA 2011). Of that, some proportion runs off, leaches, or is deposited on US water resources, which we define as streams, rivers, lakes, reservoirs, wetlands, groundwaters, estuaries and coastal waters. Published models and accounting methods for determining inputs to water resources differ depending on their definitions. Further the US EPA states that the amount of N removal from terrestrial systems ascribed to leaching and runoff are highly uncertain (US EPA 2011). For example, the amount of N in 2002 inputs to river systems was estimated with the USGS SPARROW model to be 4.8 Tg N yr⁻¹ (US EPA 2011, Alexander et al. 2008). North American riverine export to the coastal zone, inlands and drylands was estimated at approximately 7.0 Tg N yr⁻¹ by Boyer et al (2006). Other estimates reported by Boyer et al. (2006) for North America ranged from approximately 4.8 to slightly less than 7.0 Tg N yr⁻¹ (Boyer et al. 2006).

Aquatic ecosystems are disproportionately important relative to their areal extent for processing anthropogenic inputs of N (Galloway et al. 2003, Seitzinger et al. 2006, US EPA 2011). At the same time, aquatic biota is highly responsive to Nr additions, with responses ranging from increases in fish production to loss of aquatic biodiversity. Excess Nr in the nation's water can be injurious to human health and promote harmful algal blooms (HABs). In the assessment below, we address the processes by which Nr and climate change together influence aquatic N cycling, and the implications, in turn, for water quality, greenhouse gas emissions, and ecosystem and human health. Nitrogen inputs are the most important determinant of N concentrations and transport in aquatic ecosystems, but N cycling determines how much N is processed, buried, returned to the atmosphere, or passed downstream. Moreover, N cycling processes are strongly affected by climate (and climate change) and the extensive hydrologic manipulation of US water resources that have been ongoing since European settlement (Howarth et al. 2011a, 2011b, Doyle et al. 2008).

5.0.1 Reactive N

Although few if any aquatic ecosystems in the US are intentionally fertilized, the collective removal of N from fertilized fields, human and livestock waste, and industrial activities have added large amounts of Nr. Sixty four percent of shallow wells in agricultural and urban regions were found to have Nr concentrations elevated over background values, and trends in groundwater N loading are linked to N fertilizer use (Dubrovsky et al. 2010). At least one-third of the total annual load of nitrate (NO₃⁻) in most small streams surveyed by the US Geological Survey (USGS) was derived from base flow contributed primarily by groundwater (Dubrovsky et al. 2010, Bachman et al. 1998). The loading of N from watersheds and atmospheric deposition has more than doubled the flux of N to estuaries and coastal oceans since the Industrial and Agricultural Revolutions (Howarth et al. 2011a, Boyer and Howarth 2008). Two thirds of US estuaries are degraded from N pollution, and effects range from anoxia (no oxygen) and hypoxia (low oxygen) to loss of critical habitat and biodiversity (see biodiversity chapter) and HABs (Bricker et al. 2007, US EPA 2011). The potential of aquatic ecosystems to effectively assimilate, retain and denitrify Nr in ecosystems has been substantially reduced by the large net losses

of aquatic habitats with the highest capacity to remove pollutant N through denitrification (e.g., wetlands, small lakes and streams, and floodplains)(Jordan et al. 2011).

5.0.2 Climate Change

Climate change places an additional stress on the nation's already highly managed water resources, by altering precipitation, temperature, and runoff patterns. Climate was identified as a major cause of increased river discharge in the period 1971-2003 compared with 1948-1970 across much of the country (Wang and Hejazi 2011). Direct human-induced change is spatially heterogeneous and regionally distributed; there has been increased discharge in the Midwest and decreased discharge in the High Plains. The arid regions of the western US showed reduced discharge in the 1971-2003 period due to both climate and human-induced land use change (Wang and Hejazi 2011). Increased climate variability will be a significant component of climate change (IPCC 2007), resulting in an increase in storm intensity and also changes in the seasonality of runoff (Karl and Melillo 2009).

Each of these shifts in the hydrologic cycle will alter the interaction between inputs, retention, losses, and effects of human derived Nr. In addition to altering flow regimes, lake levels, and depth of groundwater, there are many mechanisms by which climate change will alter how N is processed in aquatic ecosystems. The concurrent impositions of climate change and the increasing load of Nr to freshwater and estuarine ecosystems will most likely have unprecedented additive or synergistic effects on water quality, human health, inland and coastal fisheries, and greenhouse gas emissions (Table 5.1).

5.1 PROCESSING AND TRANSPORT OF REACTIVE N IN AQUATIC ECOSYSTEMS

Reactive N primarily enters aquatic ecosystems as ammonium (NH_4^+), NO_3^- , or dissolved organic N (DON), which can be incorporated into biomass or transformed in the dissolved phase to additional nitrogenous compounds. Ammonium may be transformed by nitrifying microorganisms under oxic conditions to NO_3^- , nitrous oxide (N_2O , a greenhouse gas with strong warming potential), or nitric oxide (NO), a precursor to tropospheric ozone (O_3). Denitrification takes place under anoxic conditions where NO_3^- is transformed to N_2O or di-nitrogen (N_2), the inert gas that comprises 78% of the atmosphere (Figure 5.1). Dissolved organic nitrogen may be mineralized to NH_4^+ , or transported long distances downstream. The relative balance of these pathways determines the fate of Nr entering the nation's waters and, at the simplest level, is controlled by relatively few important environmental drivers. These include water residence time, the supply of Nr, supply of labile organic C, temperature, redox conditions and additional limiting nutrients. Shifts in climate change concomitant with an increasing supply of Nr interact to affect these processes with important implications for potable water supplies, aquatic emissions of greenhouse gases (e.g., N_2O , carbon dioxide (CO_2), and methane (CH_4)), losses of aquatic biodiversity, eutrophication of inland and coastal waters, and changes in the potential for a C sequestration sink.

5.1.1 Loading and transport of Nr to aquatic ecosystems

While alteration of the hydrologic cycle affects how N is delivered to and processed by aquatic ecosystems, the primary driver of watershed N export is the amount of Nr applied to the watershed (Howarth et al. 1996, 2011b, Hong et al. 2011). There is substantial variation in retention and ecosystem responses related to climate, topography, terrestrial ecosystem demand, and the efficacy of point source treatment, but as N inputs to catchments increase, hydrologic N exports also rise (Howarth et al. 2006, Schaefer et al. 2009, Sobota et al. 2009, Howarth et al. 2011b). The amount of Nr exported from

inland waters to coastal and marine ecosystems is determined by the balance between the inputs and the amount of N retained or denitrified in transit (Figure 5.1). On average, 25% of the human-controlled N inputs to the landscape flow downriver to coastal marine ecosystems (Howarth et al. 1996, 2006, 2011b).

Reactive N enters surface water ecosystems primarily via surface runoff, shallow subsurface flow paths, groundwater exchange, and direct atmospheric N deposition. Inorganic fertilizer and animal manure are the dominant anthropogenic sources of N in many large US river basins (Howarth et al. 2011b, Hong et al. 2011, Puckett 1995). Although N_r removal from individual fields can vary widely, approximately 50% of the N used in agriculture is unintentionally lost to the environment, with a significant fraction of this loss flowing to freshwaters (Sutton et al. 2011, Howarth et al. 2011b, Schaefer et al. 2009). In addition atmospheric N deposition is a sizeable source of N to most US watersheds, and the dominant N_r source to all mountain ecosystems (Hong et al. 2011, Baron et al. 2011). Emissions of nitrogen oxides (NO_x) have decreased greatly since the 1970s, so that now ammonia (NH₃) emissions, which are currently unregulated, comprise the dominant inorganic N_r source in some parts of the country (US EPA 2011, NADP 2011). The majority of the N supplied to cities, suburbs and consolidated animal feeding operations as food is converted to human and animal wastes, a large proportion of which can ultimately leach or leak from the septic, sewage, lagoon and landfill systems designed to contain and process these wastes (Galloway et al. 2007, Bernhardt et al. 2008, Dubrovsky et al. 2010). The relative importance of the major N inputs (fertilizer, atmospheric N deposition, human or animal wastes, biological N fixation) varies widely over time and regionally with land use (Figure 5.2, Hong et al. 2011).

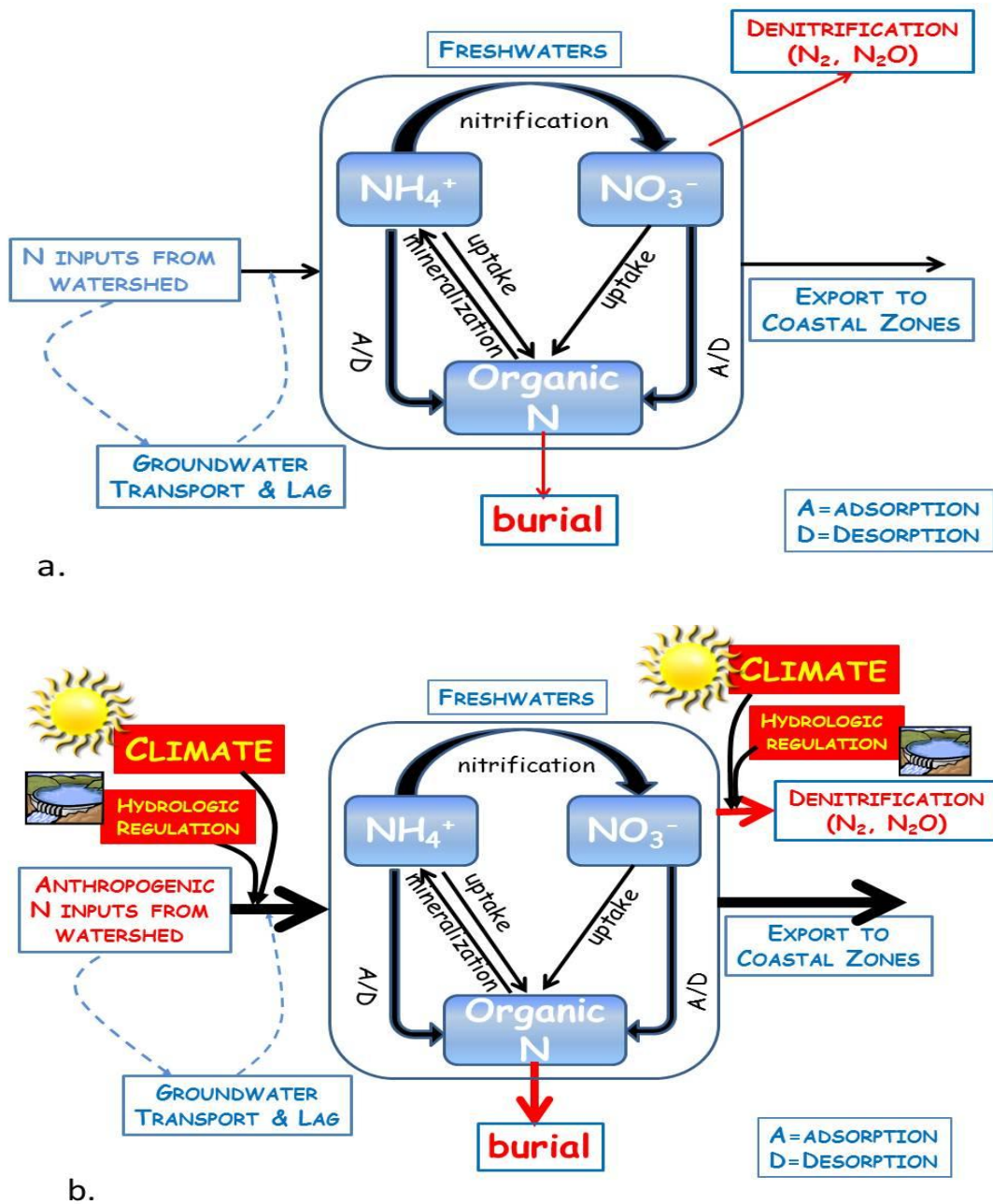


Figure 5.1: Conceptual model of N input, cycling and removal of N_r to inland waters under a) preindustrial conditions and b) with anthropogenic N loading from inorganic fertilizer, manure, atmospheric deposition, and sewage. The movement of N_r into and out of freshwaters is regulated by climate, hydrologic regulation, and residence time, which is designated by bowties. The middle section of this diagram is modified from Bernot and Dodds (2005).

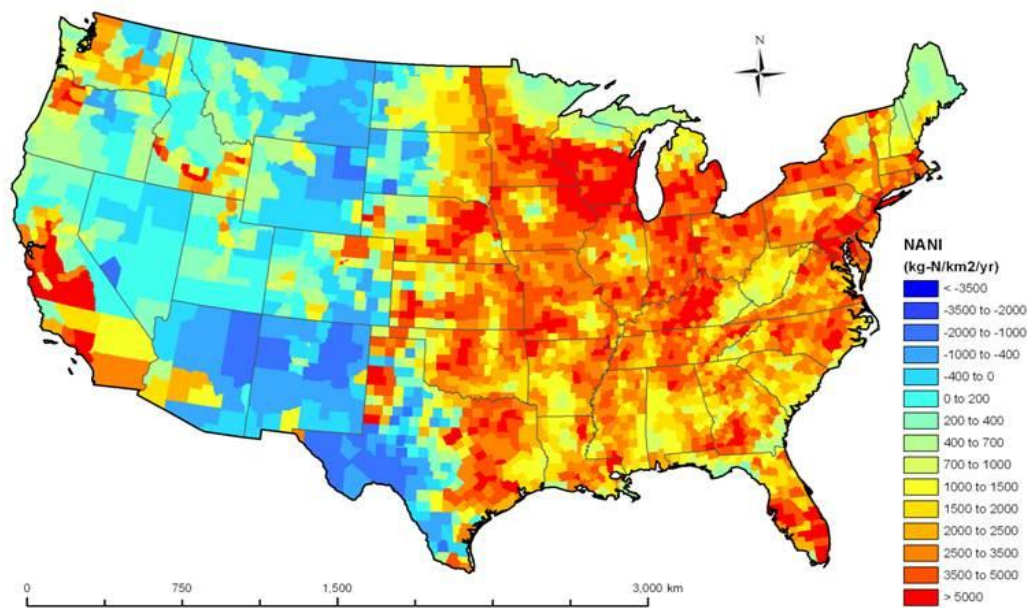


Figure 5.2: County-scale net anthropogenic N inputs (NANI) to freshwaters from different sources for 1992, as determined by the NANI Calculator Toolbox (Hong et al. 2011).

Where the loading of N approximates background levels of approximately $1.0\text{--}4.0\text{ kg N ha}^{-1}\text{ yr}^{-1}$, flushing of terrestrial N and concurrent NO_3^- concentrations are usually low (Baron et al. 2011, Elser et al. 2009). As is the case for agricultural landscapes, net N loading is also the most important determinant of net N export in non-agricultural watersheds, while climate exerts important secondary controls (Figure 5.1; Howarth et al. 2006, 2011b, Smith et al. 2003). This results in the strong relationship between watershed N loading and river N concentrations across major river basins that differ in their population density and land use (Boyer and Howarth 2008, Howarth et al. 2011b). Furthermore, this relationship is also observed across high elevation undisturbed lakes that vary only in the rates of atmospheric N deposition (Bergström and Janssen 2006, Elser et al. 2009, Baron et al. 2011).

5.1.2 Hydrologic alteration in managed ecosystems

The large increases in N loading to aquatic ecosystems over the last century have been matched by ambitious efforts to regulate and manage water movement and storage within the US (Doyle et al. 2008). Furthermore, regulation and management inadvertently alter the processes that regulate microbial and plant N-cycling in these environments.

Efforts to manage US water resources have been far-reaching and diverse. Two effects of water management have been to increase the speed with which stormwaters are routed off land and into surface waters, and to deplete base flows through enhanced water extraction and reduced groundwater recharge. In regions intensively altered for agriculture or human settlement, extensive networks of tile

drains, canals or stormwater pipes have been constructed to route rain and snowmelt rapidly to receiving streams, simultaneously reducing the proportion of precipitation that infiltrates into soils and groundwater and increases the peak flows in surface channels (Dubrovsky et al. 2010). At least half of all freshwater and coastal wetlands in the US have been drained or filled for agriculture, development or waste storage (Mitsch and Gosselink 2007), with some states (CA, IA, IL, IN, KY, MO, OH) having converted >80% of wetland area to agriculture (Zedler 2004). Many larger streams have been channelized or dammed, reducing river residence times and stranding river floodplains while vastly increasing water and sediment storage in reservoirs. Inter-basin transfers have rerouted rivers towards arid cities and farms, while irrigation water withdrawals from surface and groundwaters move an ever larger proportion of water into evaporative losses rather than downstream transport.

This highly intentional water management has had a number of unintended consequences for N cycling by altering aquatic ecosystem geomorphology, hydrologic connectivity, and water residence time and flow rates. When there is less hydrologic exchange there is reduced potential for denitrification, the microbial process by which N_r is returned to the atmosphere as non-reactive N_2 . The converse is also true, whereby; the longer residence times of waters retained by dams enhance denitrification, primary production, and the burial of organic N in sediments. Higher peak flows in managed ecosystems enhance bank erosion and channel incision in receiving streams, reducing the extent of surface and subsurface exchange between streams and their floodplains. At the same time transported sediments can clog streambeds and reduce hydrologic exchange between surface waters and stream sediments and shallow groundwater.

Although sediment loading to river networks has increased dramatically, reservoirs trap sediments and substantially reduce their export to many coastal ecosystems. The result is a net loss of coastal wetlands in the deltas of regulated rivers (Syvitski et al. 2005). In addition, the widespread increases in impervious cover from roads, roofs, and other paved surfaces have dramatically increased overland flow directly from catchment surfaces into river networks. Peak flows were found to be from 30% to more than 100% greater in urbanized catchments compared to less urbanized and non-urbanized catchments of the Southeast US (Rose and Peters 2001).

Even without increases in N applications to watersheds, hydrologic alterations that route rainfall efficiently into receiving streams lead to predictable increases in storm-borne delivery of N to surface water ecosystems (e.g., Shields et al. 2008, Davidson et al. 2010). Collectively, enhanced N loading and highly engineered stormwater routing vastly enhance the loading of N to our nation's waters. For much of the nation, the enhanced storm magnitudes predicted by many climate change models (detailed in section 5.2.3) are likely to further exacerbate this trend.

5.1.3 The effects of climate change on aquatic N dynamics: hydrologic effects

Climate directly affects the rate of delivery of watershed N to waters. Greater N is transmitted to rivers in wetter regions than in drier regions, and more N is transported in years with high discharge compared with years of lower discharge (Caraco and Cole 1999, Seitzinger et al. 2006, Dumont et al. 2005, Howarth et al. 2011b). There have already been regional differences in changes in the seasonality of precipitation across the country, and these trends are expected to continue (Table 5.1). In this section we describe already observed changes in US hydrology that have been attributed to changes in climate, as well as projected changes that are consistent with scientific understanding of increasing atmospheric greenhouse gas concentrations.

Some parts of the US will experience increased drought with climate change. Drought, defined as a transient deficiency in water supply, can be caused by reduced precipitation, transfers of water out of a region, or an increase in the ratio of evapotranspiration to precipitation. Drought, by drying river beds and shrinking flows, can disconnect streams and rivers from their floodplains or active benthic sediments. This reduces opportunities for denitrification and allows reactive N to be transported downstream. By reducing flow rates and water levels, drought also contributes to excess nutrient buildup in waters and algal blooms (Palmer et al. 2009). The occurrence of drought has increased in the Southeast and Western US over the past 50 years, while there has been a decrease in drought in the Midwest and Great Plains (Karl and Melillo 2009). These trends are expected to continue (Milly et al. 2005).

The frequency of heavy precipitation events has increased over the past 50 years, while there has been little change in the occurrence of light or moderate precipitation events (Karl and Melillo 2009). Heavy precipitation events were responsible for most of the increase in precipitation in much of the country during this time period. The greatest increases in heavy precipitation have occurred in the Northeast and Midwest, but the frequency of intense rain and snow storms have also increased in the Southeast, Great Plains, and West (Karl and Melillo 2009). The increasing potential for flooding from intense storms or increased precipitation with climate change will increase the transport of N to the nation's waters (Table 5.1). Intense storms decrease the residence time in unsaturated soil zones leading to faster loading of N to both surface and groundwaters. Flooding from intense rain events may overcome urban or agricultural wastewater treatment facilities, causing rapid release of N and other waste materials downstream (Kirshen et al. 2007). In dry regions such as the Southwest and in heavily developed areas with impervious surfaces, N loading is likely to occur in pulses corresponding to storms or rapid snowmelt (Shields et al. 2008, Schaefer et al. 2009).

Winter, spring, and summer precipitation has decreased in the Southeast, for example, while summer, fall, and winter precipitation has decreased in the Northwest (Karl and Melillo 2009). More than 70% of the N delivered to the Gulf of Mexico is derived from agricultural sources in the Mississippi River Basin, where increased precipitation on cultivated fields may enhance the amount of N that runs off or is leached into groundwater and ultimately downriver (Smith et al. 1997, Alexander et al. 2008, Karl and Melillo 2009, Donner et al. 2007, Brown et al. 2011). In the Mississippi River Basin, climate change is likely to increase winter and spring precipitation. The extensive use of tile drains in this region will make the N removal even greater by reducing the residence time and connectivity of high N waters in soils where plants and microorganisms can assimilate or denitrify reactive N (Dubrovsky et al. 2010). Research is needed to determine the nature of the N transport response to altered seasonality in different regions of the country.

As climate change shifts regional hydrological cycles, the relative importance of groundwater on stream N concentrations may also change, although there has been minimal research to date on the impacts of climate change for groundwaters (Karl and Melillo 2009) (Table 5.1). Reductions in summer and fall surface flows may increase the groundwater contribution to surface flow. Groundwaters are already significant sources of N to streams and strongly influence the amount and timing of N delivery to downstream waters (Wiley et al. 2010). In agricultural regions where precipitation has increased, increased groundwater recharge has been accompanied by high NO_3^- concentrations, as was shown in a recent study from Michigan (Wiley et al. 2010). This was also observed in the High Plains where increased precipitation associated with wet phase Pacific Decadal Oscillation reduced unsaturated zone residence times, which can mobilize large reservoirs of subsoil NO_3^- (Gurdak et al. 2007, McMahon and Böhlke 2006). An additional and indirect consequence of climate change may be increased water supply

demands in arid regions that already rely heavily on groundwaters. In these regions high NO₃ concentrations may have adverse effects on human health, which is discussed further below (Karl and Melillo 2009). With residence times of tens to hundreds of years, groundwaters enriched with N can strongly influence stream and estuarine water quality for many decades. Because of this, downstream water quality responses to management or climate change may lag behind their upstream applications and influences.

Table 5.1: Potential influence of climate changes on water resource N cycling and effects

Climate Change: Warming				
Water Resource Response	Effect on connectivity and residence time	N cycle effect	Consequence	Confidence in logical sequence
Higher maximum, minimum, mean water temperature	Increased	Faster metabolic N cycling (current and anticipated)*	Increased NPP ==> lake and reservoir sediment N and C burial	moderate
<i>Bastviken et al. 2011, Tranvik et al. 2009, Cole et al. 2007, Reay et al. 1999</i>				
Higher maximum, minimum, mean water temperature	Increased	Increased sediment microbial respiration (current and anticipated)	Increased sediment C and N mineralization, reduced C and N sequestration	moderate
<i>Gudasz et al. 2010</i>				
Increased intensity and duration of lake/reservoir stratification	Increased for bottom waters	Increased denitrification (current and anticipated)	Greater N loss to atmosphere, less N transport to coasts, increased N ₂ O and CH ₄ production	moderate
<i>Veraart et al. 2011, Kling et al. 2003</i>				
Increased intensity and duration of lake/reservoir stratification	Decreased for surface waters	Reduced NPP (anticipated)	Greater NO ₃ accumulation, transport to coastal waters	low
<i>Kling et al. 2003</i>				

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Reduced flow	Increased	Increased denitrification, N burial (current and anticipated)	Greater N loss to atmosphere, less N transport to coasts, increased N ₂ O production	low
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Kelley et al. 1987, Dillon and Molot 1990

Reduced estuarine oxygen==> hypoxia and anoxia		Stimulation of N ₂ O production (current and anticipated)	Greater GHG emissions	moderate
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Breitburg et al. 2009

Reduced ocean oxygen==> reduced continental shelf and estuarine oxygen		Increased denitrification (current and anticipated)	Greater GHG emissions	moderate
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Naqvi et al. 2010, Grantham et al. 2004, Brown and Power 2011

Regional water shortages==> greater wastewater reclamation	Increased	Increased denitrification (current and anticipated)	Greater GHG emissions	high
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Townsend-Small et al. 2011

Increased reservoir construction	Increased	Increased denitrification (current and anticipated)	Greater N loss to atmosphere, greater GHG emissions, increased C and N burial, less transport to coasts	high
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Liu et al. 2011, Harrison et al. 2009

Climate Change: Increased precipitation intensity				
Water Resource Response	Effect on connectivity and residence time	N cycle effect	Consequence	Confidence in logical sequence
Pulsed rapid transport of N to freshwaters and estuaries	Decreased	Decreased denitrification opportunity (current and anticipated)	Increased NO ₃ concentrations, increased transport to coasts	moderate
<i>Smith et al. 1997, Alexander et al. 2008, Karl and Melillo 2009, Brown et al. 2011</i>				
Flooding	Decreased	Possible failure of wastewater treatment facilities (current and anticipated)	Increased NO ₃ concentrations, increased transport to coasts	high
<i>Kirshen et al. 2007, Karl and Melillo 2009</i>				
Increased reliance on irrigation, rapid flushing	Decreased	Decreased denitrification opportunity, rapid N transport to groundwaters, streams, estuaries (current and anticipated)	Increased NO ₃ concentrations, increased transport to coasts	poor
<i>Böhlke et al. 2007</i>				
Increased reliance on irrigation	Increased	Stimulation of N ₂ O production (current and anticipated)	Increased GHG production	poor
<i>Böhlke et al. 2007</i>				
Climate Change: Decreasing precipitation				
Water Resource Response	Effect on connectivity and residence time	N cycle effect	Consequence	Confidence in logical sequence
Proportional increase in base flow to streams	Increased	Increased denitrification opportunity	Greater N loss to atmosphere, less transport to coasts	poor

(current and anticipated)

Puckett and Cowdery 2002, Böhlke et al. 2007

Reduced flows, dessication	Decreased	Decreased denitrification opportunity (anticipated)	Increased NO ₃ concentrations, potential for pulsed transport to coasts	poor
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Murdoch et al. 2000

Reduced flows, longer water residence time in estuaries	Increased	Increased denitrification opportunity, greater NPP (current and anticipated)	Eutrophication, hypoxia	high
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Howarth et al. 2011

Climate Change: Increasing precipitation

Water Resource Response	Effect on connectivity and residence time	N cycle effect	Consequence	Confidence in logical sequence
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Greater groundwater recharge	Decreased in unsaturated zone	Increased NO ₃ accumulation in groundwater (anticipated)	Increased NO ₃ to base flow, human health hazard	moderate
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Stuart et al. 2011

Greater groundwater recharge	Decreased in unsaturated zone	Increased NO ₃ contributed to streams (current and anticipated)	Increased NO ₃ concentrations, increased transport to coasts	moderate
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Wiley et al. 2010

Climate Change: Increased winter precipitation				
Water Resource Response	Effect on connectivity and residence time	N cycle effect	Consequence	Confidence in logical sequence
Higher winter flow	Decreased	Rapid N transport from watershed to surface and ground waters (anticipated)	Increased NO ₃ concentrations in surface and groundwaters, increased transport to coasts	moderate
<i>Karl and Melillo 2009, Dubrovsky et al. 2010, Stuart et al. 2011</i>				

**"Current" signifies currently observed with current ranges of variability; "anticipated" signifies an anticipated response with climate change.*

5.1.4 The effects of climate change on aquatic N dynamics: temperature effects

Apart from warmer temperatures that increase soil N mineralization (Melillo et al. 2011) and thus mobilize increasing Nr loads to groundwaters, streams, rivers, lakes, reservoirs, and estuaries, the increase of global air temperatures directly warms lotic and lentic ecosystems in ways that affects their physical, chemical and biological structure and function (Kling et al. 2003, Stuart et al. 2011). This has already been demonstrated to include more limited ice-cover of lakes and rivers, early onset and increased intensity and duration of stratification, higher maximum, minimum, and mean annual temperatures, lower dissolved oxygen levels, and in some cases decreasing or fluctuating lake levels (Magnuson 2000, Kling et al. 2003, Karl and Melillo 2009). Each of these changes has the potential to affect aquatic N cycling (Table 5.1). For instance, a longer ice-free season will result in enhanced summer stratification wherein both hypolimnion and epilimnion will have extended periods of warmer temperatures. Persistent warm epilimnion temperatures will be accompanied by reduced nutrient availability due to prolonged separation from the benthos, a key source of dissolved nutrients.

Within the water column, there is evidence for strong temperature dependence of both heterotrophic and autotrophic microbial NO₃⁻ utilization (Reay et al. 1999). Several studies have shown that N is currently accumulating as NO₃⁻ in the water column of cold, oligotrophic environments (Finlay et al. 2007, Sterner et al. 2007, and Baron et al. 2009). Isotopic evidence suggests some of the NO₃⁻ was microbially-converted, or mineralized, from atmospherically-deposited NH₄⁺ (Finlay et al. 2007, Campbell et al. 2002). Multiple mechanisms that include temperature and organic C have been proposed to explain why water column NO₃⁻ is going unused, and this is an area of active research (Taylor and Townsend 2010).

Intensified stratification will also increase the extent of hypoxia and anoxia in the hypolimnion of lake ecosystems. Rates of denitrification may increase in the sediments and hypoxic water column of stratified lakes, reducing the amount of N exported to coastal zones (Table 5.1). However, it is equally reasonable to think that increased stratification will actually decrease denitrification by limiting the amount of contact NO₃⁻ rich water has with denitrifying sediments in hypolimnia. Although it is difficult to infer how microbial communities will respond to gradual, long-term, climate-change induced

temperature increases based on short-term studies, a recent synthesis of empirical and modeling results suggests denitrification could increase as much as 2-fold with a temperature increase of 3°C (Veraart et al. 2011), well within the range of temperature projections over the next 50 years for aquatic ecosystems of North America (Kling et al. 2003).

Temperature is also likely to affect N cycling by altering stoichiometric ratios of nutrients available to biota. While a mechanism for shifting C:N with temperature is not clear, biomass C:N of a wide range of organisms including many plankton is generally thought to increase with increasing temperature (Woods et al. 2003). Biomass C:N ratio is inversely proportional to the amount of N that is retained in biomass (Elser and Urabe 1999). Thus, increasing C:N of planktonic biomass should decrease N demand of planktonic organisms and increase the amount of N that is recycled to the dissolved pool. In the absence of adaptation to changing thermal regimes this will further exacerbate the amount of N_r in these ecosystems.

There is a need for further research into the mechanisms by which changing temperatures will alter aquatic stoichiometry and microbial processes, but the indications are that microbial N transformation pathways and planktonic N-demand will be altered as temperature warms.

5.1.5 The effects of climate change on aquatic N dynamics: denitrification and burial

Denitrification, an important process by which N_r is removed from ecosystems and returned to the atmosphere, requires low oxygen levels, NO₃⁻, labile organic C, and sufficient residence time to interact with microbes (Figure 5.1; Seitzinger et al. 2006, Mulholland et al. 2008). These conditions occur where NO₃-rich water comes into contact with saturated soils and sediments of lakes, reservoirs, small streams, floodplains and wetlands (Seitzinger et al. 2006). As a result, aquatic ecosystems are critically important denitrification hotspots, with per-unit-area denitrification rates approximately ten-fold (on-average) the per-unit-area denitrification rates in soils (Seitzinger et al. 2006). One estimate using spatially-distributed global models suggests 20% of global denitrification occurs in freshwaters (e.g., groundwaters, lakes, and rivers), compared with 1% in estuaries, 14% in ocean oxygen minimum zones, 44% in the continental shelf, and 20% in terrestrial soils (Seitzinger et al. 2006). Aquatic systems and associated deltas and floodplains are also critical sites for sediment burial of particulate N. Using methods described below and in Table 5.2 we estimate that US aquatic systems retain or remove 11.25 Tg N yr⁻¹ (Table 5.2). We also estimate that US aquatic systems release 0.58 Tg N₂O-N yr⁻¹ to the atmosphere, an amount of N₂O that is significantly higher than other estimates which do not explicitly include individual aquatic ecosystem types (US EPA 2011) and of the same order as N₂O production from all other US sources. Hence, to the extent that aquatic N loading and climate changes affect N₂O production, denitrification and N burial rates, these perturbations are also likely to strongly influence GHG production, downstream N transport fate, and the integrity of freshwater and coastal ecosystems.

In the sections that follow we briefly summarize estimates and how we derived them, of aquatic N removal and N₂O production by aquatic system type in order to evaluate current understanding of the role of inland waters in relation to denitrification in the US (Table 5.2) and the potential for N loading and climate to alter these processes.

Wetlands:

Both natural and constructed wetlands have great capacity for N removal via denitrification (Richardson 1985, Seitzinger 1988). Total N_r removal by wetlands in the contiguous US has been recently estimated as 5.8 Tg N yr⁻¹ (Table 2; Jordan et al., 2011), more than any other single aquatic ecosystem type in this analysis, and more than half the rate of annual inorganic N fertilizer application in the US (approximately 11Tg N yr⁻¹; US EPA 2011, Sobota et al., submitted). Although the method of calculating N removal by wetlands employed by Jordan et al. (2011) (i.e., multiplying average wetland N retention efficiency by average wetland N loading rate) may somewhat overestimate N retention by such systems due to a bias in the literature toward high N-input systems, it is likely that wetland systems are very important sites for N storage and removal at local, regional, and national scales.

Despite their evident importance to N cycling and transport, responses of wetlands and wetland-associated denitrification to climate change and N loading are uncertain and not well understood. Although wetlands do generally increase N storage and removal in response to N loading, and evidence for N saturation of wetlands is scant (Jordan et al. 2011), it is also not clear how N and climate will interact to influence wetland N storage. If wetlands dry out as a result of less available soil moisture due to increased evapotranspiration or decreased precipitation that is anticipated in some regions, their capacity to store and remove N will be reduced. On the other hand, increased frequency and severity of pulsed hydrologic events associated with heavy rains could either decrease the efficiency of wetland N removal by decreasing N and water residence time in such systems, or increase wetland N retention by wetting up a greater proportion of watersheds, thereby promoting the formation of anaerobic sites where denitrification can occur. Interactions between climate, N loading, and wetlands are not well constrained, but, given the efficiency with which wetlands can remove N, constitutes an area of critical future research.

Lakes and reservoirs:

Using the **Nitrogen Retention in Reservoirs and Lakes (NiRReLa)** model (Harrison et al. 2009), we estimate that 5.45 Tg N yr⁻¹ is removed by US lakes and reservoirs (Table 2). This rate of N removal is equivalent to roughly half the annual rate of inorganic N fertilizer application in the US (US EPA 2011, Sobota et al., submitted), and is therefore significant at the national scale. Locally, the capacity for N removal by lakes and reservoirs often matches N inputs to aquatic systems (Harrison et al., 2009). Reservoirs play a particularly important role in trapping and removing N, accounting for over two thirds (68%) of total N removed by all lentic waters in the US despite occupying only 10% of the US lentic surface area. The dominance of reservoirs with respect to N retention is due to their greater N uptake velocities, watershed source areas and greater average N loading rates compared to lakes (Harrison et al. 2009; Table 5.2). Small reservoirs (surface area <50 km²) are disproportionately important in removing N, accounting for 84% of the N removed in reservoir systems. Small lakes (surface area <50 km²) also retain more N than large (surface area >50 km²) lakes (1.1 and 0.59 Tg N yr⁻¹ for small and large lakes, respectively; Table 5.2). This is due to a combination of factors, including the fact that small lakes are much more numerous than large ones (Downing et al. 2008). In addition, rates of N removal by lakes and reservoirs are greater in the eastern US than the West, although there are hotspots for lentic N retention in western regions with intensive agriculture (Figure 5.3).

Together, these insights suggest that lentic systems constitute important sites for N retention and removal at local, regional, and national scales, that small reservoirs (and to a lesser degree small lakes) are particularly important sites for N retention, and that lentic N retention is particularly rapid in agricultural regions. Hence, it is particularly important to understand how small reservoirs in agricultural areas respond to the dual stresses of increased N loading and climate change. However, we are currently able to say very little about how the dual stresses of N loading and climate change will affect these systems with any degree of confidence. It is fairly well-established that, at least up to a point, increased N loading stimulates N retention across a broad range of aquatic ecosystem types, including lakes and reservoirs (Seitzinger et al. 2006). However, the threshold beyond which denitrifying microbes can no longer keep up with N loading in lakes and reservoirs is not well defined, and even the existence of such a threshold is debated (e.g., Jordan et al. 2011). Climate effects on N transformations and interactions between climate and increased N loading are even less well-understood, but almost certain to be important.

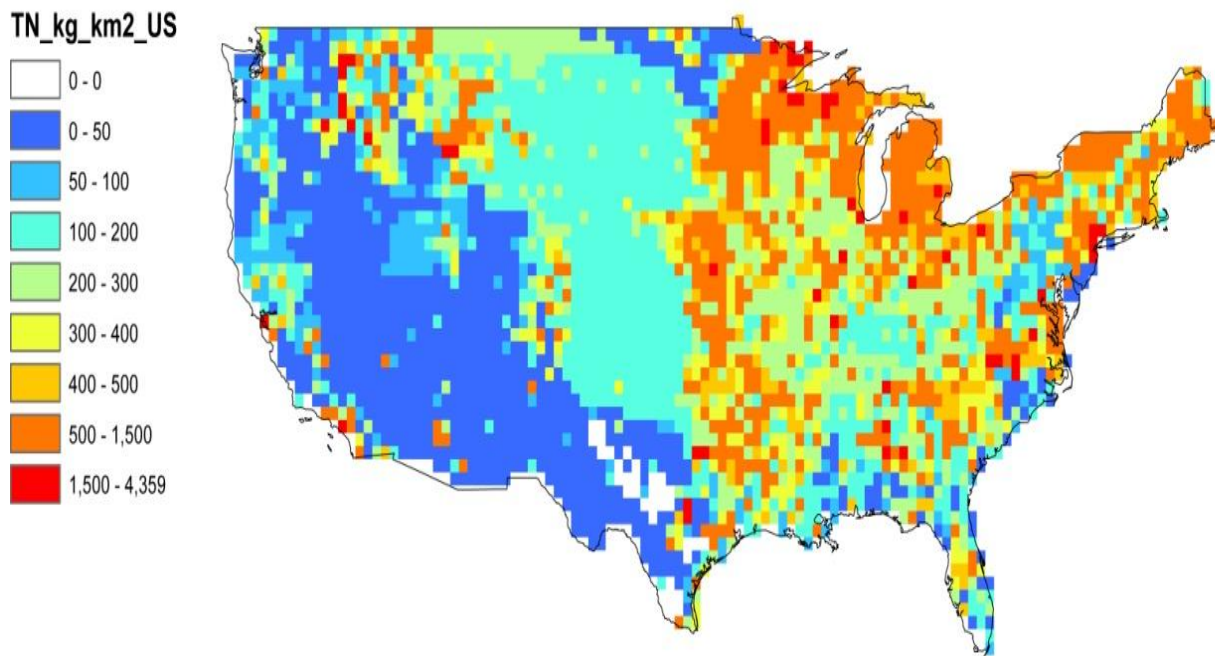


Figure 5.3: Total N retention in lentic systems in the conterminous US ($\text{kg N km}^{-2} \text{yr}^{-1}$). Figure produced with methods from Harrison et al. (2009).

Table 5.2: N budgets for US water resources by ecosystem type.

Water body type	Surface area (km ²)	Nr inputs (Tg N yr ⁻¹)	Nr removal (Tg N yr ⁻¹)	N retained per unit area (Kg N yr ⁻¹)	N ₂ O evaded (Tg N yr ⁻¹)
^a All lakes	1,820,000	5.8	1.73	1.54E+04	0.043
Small lakes	89,100	2.8	1.14	1.28E+04	0.023
Large lakes	23,100	3.1	0.59	2.57E+04	0.21
^a All reservoirs	27,600	4.9	3.72	1.35E+05	0.037
Small reservoirs	4,580	1.7	3.13	6.83E+05	0.013
Large reservoirs	23,000	3.2	0.59	2.57E+04	0.024
^b Streams and Rivers	40,600	4.5	0.73	1.08E+04	0.048
^c All Wetlands	406,300	12.6	5.8	1.43E+04	0.369
Emergent estuarine	18,500	0.3	0.01	4.41E+02	0.001
Palustrine emergent	105,800	10.4	4.7	4.44E+04	0.299
Palustrine forested	210,500	1.8	1.0	4.75E+03	0.064
^d Wastewater treatment		2.0			0.02
^e Estuaries					0.03
^e Continental shelves					0.60
^f All US Waters exclusive of estuaries and continental shelves (this analysis)			11.25		0.58
^g All US Waters (GHG Emissions Inventory)			7.6		0.57

Letters in subscript describe calculations.

^a Inputs to small reservoirs and lakes estimated using Harrison et al. 2009 approach. N retention estimated using Harrison et al. 2009. N₂O production estimated using McCrackin et al. 2011 approach in conjunction with Harrison et al. 2009 N loading estimates

^b US lotic Surface area from Butman and Raymond (2011). Global lotic surface area from Wollheim et al. (2008). TN loading from Van Dreht et al. (2003) (assumes no pre-processing by lakes or reservoirs) TN retention calculated as global retention from Beaulieu et al. (2011) multiplied by fraction of lotic surface area in US. Interestingly, the fraction retained by rivers and streams is 16%, substantially lower than the 80% sometimes attributed to in-stream retention, but still significant and likely to vary in space and time.

^c Surface area from Jordan et al. (2011). TN loading calculated as wetland surface area x average TN loading (from Jordan et al. 2011, Table 3). TN removal calculated as in Jordan et al. (2011). N₂O calculated using average N₂O/(N₂O+N₂) for wetlands reported in SI material associated with Schlesinger et al. (2009).

^d SAB (2011)

^e Kroeze et al. (2005)

^f N retention = Sum of lakes, reservoirs, rivers and streams, and wetlands. N₂O = Sum of lakes, reservoirs, rivers and streams, wetlands, and mid-range sewage treatment estimate

^g US EPA (2011). Numbers are inclusive of rivers, lakes, wetlands, and groundwater

Streams and rivers:

Scaling a recent estimate of global lotic N retention (Beaulieu et al. 2011) to the US using estimates of US and global lotic surface area (from Butman and Raymond 2011) allows us to estimate that US streams and rivers denitrify 0.73 Tg N yr⁻¹. Although substantially less than the amount stored or removed by lakes, this amount of N removal is still significant relative to N inputs (roughly 7% of inorganic fertilizer application in the US), and can be important both spatially and temporally (Peterson et al. 2001, Alexander et al. 2000, Dumont et al. 2005).

The amount of denitrification occurring in streams and rivers is spatially variable, depending on contact time of water with sediments, stream temperature, the supply of biogenic nutrients, and respiration rates (Boyer et al. 2006, Alexander et al. 2009). The NO_3^- removal efficiency (i.e., the fraction of the in-stream NO_3^- flux/concentration) of streams varies seasonally, and is reduced during months with high discharge and NO_3^- flux, and enhanced during months with low discharge and NO_3^- flux (Alexander et al. 2009). This creates a direct connection of NO_3^- removal efficiency with climate change, with reduced denitrification potential during high flows caused by extreme precipitation and flooding events, and enhanced denitrification potential during periods of low discharge. A study of more than 300 stream-reach measurements and experiments concludes that the percentage of stream NO_3^- load delivered to watershed outlets is strongly affected by the cumulative removal of NO_3^- in headwaters, emphasizing the importance of residence time and connectivity of N-rich water with microbe-rich sediments (Alexander et al. 2009). Denitrification generally increases with increasing NO_3^- inputs at low NO_3^- concentrations, but the efficiency with which denitrification removes NO_3^- at higher N concentrations may decrease due to saturation of microbial capacity for NO_3^- uptake (Mulholland et al. 2008, Wollheim et al. 2008). Furthermore, during transport denitrification also occurs in higher order streams (Alexander et al. 2008, 2009).

Groundwater:

Groundwater denitrification rates vary depending on redox state, the availability of electron donors, and aquifer residence time. Some studies show that although groundwater denitrification rates are low, NO_3^- removal can be nearly complete because of long residence times (Puckett and Cowdery 2002). Other studies show irrigation reduces the residence time of water and NO_3^- in groundwater, which reduces the denitrification potential (Böhlke et al. 2007). Riparian buffers provide additional opportunities for denitrification, but their effectiveness varies widely depending on hydrogeologic controls (Puckett 2004). Site-specific denitrification estimates for groundwater have not been scaled up, so national estimates are lacking.

Estuaries and continental shelves:

Estuaries and continental shelves are similar to lakes, rivers, and wetlands in that the surface sediments where denitrification occurs generally contain only a thin layer of aerobic sediments. There is thus a high degree of connectivity between the N load in the form of NO_3^- and denitrifying microbes (Seitzinger et al. 2006). In estuaries that exhibit hypoxia, denitrification is enhanced in suboxic waters (Seitzinger et al. 2006, Codispoti 2010). In addition the percentage of N removed by denitrification is strongly tied to residence time (Harrison et al. 2009), which in estuaries is affected by geomorphology, river discharge, and tidal flushing (Nixon et al. 1996).

Given the ongoing and high contemporary loading of N_r to aquatic ecosystems the current status of N removal by freshwaters is likely to change with shifts in the hydrological cycle due to climate change. In regions where the frequency of high precipitation events increases, or the rate of agricultural irrigation increases to compensate for reduced precipitation, rapid flushing will reduce residence time (Böhlke et al. 2007). This may increase delivery of N_r to estuarine and coastal ecosystems.

5.2 N STIMULATION OF GREENHOUSE GAS PRODUCTION

Although N₂O emissions are estimated to be only ≤1% of the N denitrified in aquatic systems, this amount is important with respect to N₂O budgets (Beaulieu et al. 2011). Production of N₂O increases with N-loading and the N-loading of inland waters is also likely to stimulate production of other greenhouse gases such as CH₄ and CO₂ where N is a limiting nutrient.

5.2.1. N₂O emissions

Nitrous oxide fluxes from all rivers, coastal ecosystems and the open ocean are estimated at 5.5 Tg N yr⁻¹, or 31% of total annual global N₂O emissions, including both natural and anthropogenic sources (Bange et al. 2010, Kroeze et al. 2010, Syakila and Kroeze 2011). Globally, combined N₂O emissions from rivers and estuaries roughly doubled between 1970 and 2000 (Kroeze et al. 2010). Because greater N loading leads to higher rates of N₂O production in all aquatic systems, and because of the potency of N₂O in both planetary warming and stratospheric O₃ depletion, a better quantification of sources and processes is needed (Beaulieu et al. 2011, Verhoeven et al. 2006, McCrackin and Elser 2011).

The 2011 US EPA US greenhouse gas inventory report suggests 0.054 Tg N₂O-N is produced annually from US aquatic systems, and does not partition between lakes reservoirs, groundwaters, streams or wetlands (US EPA 2011). This is roughly 9% of total anthropogenic US N₂O emissions, which, when converted from CO₂ equivalents, were 0.6 Tg N₂O-N for 2009 (US EPA 2011). A number of studies have been published recently that allow a more comprehensive assessment of the N₂O contributions from different aquatic ecosystems (Table 5.2). Summing N₂O estimates for individual aquatic system types, we estimate a cumulative annual aquatic N₂O production rate of 0.58 Tg N₂O N yr⁻¹. This rate is more than 10-fold greater than the US EPA estimate and suggests that aquatic N₂O production is roughly equivalent to all terrestrially-based N₂O sources in the US. Although the values are still poorly constrained, and much work will be needed to better accurately quantify the production of N₂O in US waters, initial calculations suggest a critical role for aquatic systems in the US N₂O budget. Reduction of N inputs to the nation's surface waters may therefore be an effective way to lower aquatic N₂O production and hence emissions of this important greenhouse gas.

Wetlands and Groundwaters:

Based on reported wetland N retention rates and N₂O production efficiencies, we estimate that 0.37 Tg N₂O N yr⁻¹ is produced by wetlands (Table 5.2). This value is several-fold greater than N₂O production from any other single aquatic system type, and, although quite uncertain at this point, suggests that it will be critical to understand wetland N₂O production as climate and N loadings change in coming decades. The proportional yield of N₂O from nitrification can increase under low oxygen conditions in wetlands, while the proportional yield of N₂O from denitrification can increase under conditions of high oxygen or low bioavailable C. It is often hard to determine which process dominates N₂O production, and thus to predict how N₂O emissions may change under future climate scenarios. For groundwaters, the rate of N₂O emissions is highly responsive to both N loading and hydrologic transport. Measurements from aquifer studies and leachate from below root zones display a range of 14-45% of the N applied to the land surface (as fertilizer, animal manure, and atmospheric deposition) is leached to groundwater as NO₃ (Nolan et al. 2010, Puckett et al. 2011).

Freshwaters:

Small headwater streams are active sites for N₂O production, particularly where inorganic N concentrations are elevated by anthropogenic N loading. Globally, N₂O released to the atmosphere from streams and river networks was estimated by Beaulieu et al. (2011) to be equivalent to 10% of the global human-caused N₂O emission rate, a value three times larger than that estimated by IPCC (Beaulieu et al. 2011). The US contribution from streams and rivers is estimated at 0.048 Tg N yr⁻¹ (Table 5.2) by multiplying the global estimate by the fraction of lotic surface area for the US. A conservative estimate of N₂O production from lakes based on inputs solely from atmospheric N deposition suggests an additional 0.04-2.0 Tg N yr⁻¹ (McCrackin and Elser 2011). When N loading to lakes (reservoirs are discussed below under engineered systems) from all sources was used instead of only deposition, values for N₂O production from lakes were estimated at 0.043 Tg N yr⁻¹ (Table 5.2).

Estuaries, Continental Shelves, Oceans:

Contributions from North American estuaries to current global N₂O emissions are estimated to be 0.03 Tg N yr⁻¹ (Kroeze et al. 2005). Estuarine N₂O production reflects direct increases in both nitrification and denitrification as more N is being processed through estuaries and continental shelf systems as N_r inputs increase (Seitzinger and Kroeze 1998). Emissions of N₂O can also increase as a consequence of the spread and intensification of eutrophication and hypoxia – conditions that favor denitrification as well as the efficiency of N₂O production during nitrification (Codispoti 2010). Globally and nationally, the rise of estuarine hypoxia is closely tied to increased delivery of N (NRC 2000, Diaz and Rosenberg 2011). The potential increases in N₂O emissions associated with the expansion of estuarine hypoxia is not well quantified but represents an example of indirect linkages between N-cycle alterations and climate forcing.

As with other aquatic ecosystems, N₂O fluxes are spatially heterogeneous - a fact that introduces sizeable uncertainties in estimates of mean fluxes (see Bange et al. 1996). Globally, continental shelves account for an estimated N₂O input of 0.6 Tg N yr⁻¹ to the atmosphere (Seitzinger and Kroeze 1998). Upwelling-dominated shelf systems such as those along the US West Coast represent particularly strong sources of N₂O to the atmosphere (Nevison et al. 2004b). Nitrogen budgets of continental shelves that were historically dominated by oceanic inputs are now heavily influenced by human activities, particularly in the North Atlantic and the Western Pacific (Howarth 1998, Kim et al. 2011). For continental shelves in the North Atlantic, budget estimates of estuarine export and atmospheric deposition of N_r suggest that one-third of N₂O fluxes may be attributable to anthropogenic sources (Seitzinger et al. 2000). For the ocean as a whole, Duce et al. (2008) estimated that by the year 2000 anthropogenic atmospheric N deposition increased N₂O emission by 1.6 Tg N yr⁻¹ (32% of total ocean net flux), with emissions expected to increase to 1.9 Tg N yr⁻¹ by 2030. While these estimates are very preliminary, given the vast size of the ocean, this clearly highlights the dramatic influence that continental N exports have on changes in global ocean N₂O fluxes and the marine N cycle in general.

In addition to increased output in marine N₂O due to anthropogenic N-loading and climate driven shifts in the continental hydrologic cycle, climate change can also modulate marine N₂O fluxes through changes in ocean oxygen inventory. Modeling studies, many reviewed in Keeling et al. (2010), converge on common forecasts of sizeable declines in the oxygen inventory of the ocean in response to greenhouse gas forcing over century and millennial time-scales. Projections of oxygen declines reflect the combined effects of reduced oxygen solubility from ocean warming and reduced ventilation from stratification and circulation changes (Schmittner et al. 2008, Frölicher et al. 2009, Shaffer et al. 2009).

Oxygen reductions due to changes in organic C flux via shifts in organic matter C:N stoichiometry (Oschlies et al. 2008) and settling (Hofmann and Schellnhuber 2009) in response to ocean acidification have also been observed. Recently the sensitivity of oceanic hypoxia volume to climate variability through increases in export production and vertical displacement of oxygen minimum zones into regions of higher respiration potential has been noted (Deutsch et al. 2011). Because oceanic contributions to the oxygen budgets of continental shelves and estuaries can be substantial (Grantham et al. 2004, Brown and Power 2011), climate-dependent changes in ocean oxygen inventories have the potential to both accentuate the impacts of eutrophication and increase the flux of N₂O from coastal systems (Naqvi et al. 2010). It is worth noting that the air-sea flux of N₂O is dependent on both concentration gradients and physical forcing such as wind (Nevison et al. 2004a) and storm-induced ventilation (Walker et al. 2010). Projections of physically-driven changes in N₂O flux are not available, but projected scenarios of strengthened upwelling wind forcing (Bakun et al. 2010), as well as increases in the intensity and/or frequency of storm events (Bender et al. 2010) suggests the potential for further exacerbation of marine N₂O fluxes will result from climate change.

Engineered Systems:

Constructed treatment wetlands and wastewater treatment plants that receive high N loads produce more N₂O than natural ecosystems and contribute a substantial fraction of the total N₂O produced from managed water resources (Kampschreur et al. 2009, Townsend-Small et al. 2011). Existing wastewater treatment plants in the US are estimated to emit 0.02 Tg N yr⁻¹ as N₂O (US EPA 2011), and the N_r in effluents from both treatment wetlands and facilities can stimulate further N₂O production in receiving rivers (Beaulieu et al. 2010).

Most US wastewater treatment plants are not designed to remove nutrients, but by improving the engineered capabilities for biological N removal, the US EPA estimates that removal efficiencies could be improved, thus reducing the downstream N release below standard N effluent loads by 40-60% (US EPA 2011). Wastewater treatment systems currently are estimated by the US EPA to remove 2.0 Tg N yr⁻¹ from treated waters by returning N₂ to the atmosphere via denitrification (US EPA 2011).

Water reclamation projects that cleanse municipal water for re-use as irrigation or surface and groundwater replacement are used in arid parts of the US, such as southern California, and may become more common as water scarcity increases (Gleick 2003). A study conducted in California found that the rates of N₂O production at water reclamation plants may be several orders of magnitude greater than N₂O emissions from agricultural activities or traditional waste treatment facilities (Townsend-Small et al. 2011). As climate change increases water scarcity in arid regions, and the use of technologies to cleanse and re-use water increases over the coming decades, increased N₂O emissions from water reclamation facilities may result in a positive feedback that exacerbates climate warming.

Reservoirs:

The N₂O contribution from reservoirs has been poorly investigated, but the potential is high, especially since many reservoirs are eutrophic and receive N inputs from their surrounding watersheds (Liu et al. 2011). If scaled up from measurements from two China reservoirs using the sum of small and large reservoirs of 248,000 km² (Harrison et al. 2009), global reservoir N₂O fluxes are estimated at 0.02-0.05 Tg N yr⁻¹. This value is similar to the 0.037 Tg N yr⁻¹ calculated by us using the approach of McCrackin and Elser (2011) for estimating N₂O production and the N loading rates provided by Harrison et al. (2009). Liu et al. (2011) found that deep waters of reservoirs used for hydroelectric generation were

supersaturated with N₂O year-round, as was water directly downstream, suggesting that deep waters released for hydropower are additional sources of N₂O produced by reservoirs.

5.2.2 N Stimulation of CH₄ emissions

In addition to stimulating N₂O production, increased N delivery to wetland ecosystems is likely to elevate emissions of CH₄, an important greenhouse gas (with a global warming potential 25 times greater than CO₂), produced by methanogenic microbes during the anaerobic decomposition of plant material (Liu and Greaver 2010). Natural wetlands are an important part of the global CH₄ cycle, contributing 230 Tg CH₄ year⁻¹ (Fletcher 2004). Rice paddies act as manmade wetlands, and emit an additional 110-120 Tg y⁻¹ (Fletcher 2004). Most experimental additions of N to both natural wetlands (e.g., Aerts and de Caluwe 1999) and rice paddies (e.g., Zheng et al. 2006) have induced increases in CH₄ emissions, although a few experiments found no effect (Keller et al. 2005). In a meta-analysis of over 300 field studies, N additions between 30 and 400 kg N ha⁻¹ y⁻¹ caused CH₄ emissions to increase by an average of 95%, with emissions increasing by 0.008 kg CH₄-C ha⁻¹ y⁻¹ per kg N ha⁻¹ y⁻¹ (Liu and Greaver 2010). The mechanisms for these increases are not clear, but several have been proposed. For example, added N can stimulate growth of primary producers, creating more organic material for decomposition, shifting benthic redox states and stimulating CH₄ production. Nitrogen can also stimulate rates of decomposition by relieving N limitation to the decomposer biomass (Schmidt et al. 2004). Finally, NH₄⁺ is an inhibitor of CH₄ oxidation (Bodelier and Laanbroeck 2004), a process that offsets CH₄ production, resulting in increased CH₄ emission rates.

Lake ecosystems are also strong sources of CH₄ to the atmosphere, currently emitting 8-48 Tg C yr⁻¹ from lakes and estimated at 3-10 times greater for reservoirs (Tranvik et al. 2009). Together, lakes and reservoirs are estimated to emit 103 Tg yr⁻¹ of CH₄ to the atmosphere; a flux when expressed in CO₂ equivalents is roughly 25% of the estimated terrestrial CO₂ sink (Bastviken et al., 2011). With climate change, increased lake primary production due to a combination of nutrient loading and warmer waters will increase the prevalence of bottom water anoxia, causing a concurrent increase in CH₄ production and evasion (Tranvik et al. 2009).

5.2.3 N Stimulation of the C cycle

Heterotrophic metabolism and decomposition can increase in response to N enrichment in streams but responses are highly varied. Positive effects of N enrichment on heterotrophic metabolism are observed when detrital C:N is high (Greenwood et al. 2007, Ferreira et al. 2006, Gulis et al. 2004) but not in N saturated systems with low C:N (Simon et al. 2010). Because temperature often increases heterotrophic activity and decomposition, interactive effects on temperature and N on C cycling interactions are likely to be strongest in ecosystems that are not N saturated and currently maintain high C:N detritus. Several authors have suggested that eutrophication speeds the mass loss of litter C, and reduces the availability of food resources to donor controlled aquatic ecosystems (Benstead et al. 2009).

Given that N often stimulates primary production in freshwaters; increased N loading has the potential to increase C burial in lake and reservoir sediments. Few studies have examined the specific effect of N on C burial, but eutrophication, particularly caused by agriculture, generally enhances rates of aquatic C sequestration (Kastowski et al. 2011). The estimated C mass accumulation rate for European lakes in intensively utilized agricultural areas ranged 22 g C m⁻² yr⁻¹ to 80 g C m⁻² yr⁻¹, compared with 3.4 g C m⁻² yr⁻¹ in areas without surrounding croplands (Kastowski et al. 2011). In some agriculturally influenced lakes and reservoirs in the Midwest US, Downing et al. (2008) reported rates of C burial that were

several orders of magnitude higher than this, ranging up to $6987 \text{ g m}^{-2} \text{ yr}^{-1}$. Vanni et al. (2010) showed up to approximately 10-fold greater C burial in response to the alleviation of N limitation and P enrichment in reservoirs. Given the large C sink of freshwater lakes and wetlands (Cole et al. 2007), the influence of N on organic C burial deserves more attention. With projected climate change effects of decreased runoff and increased consumptive water use in many temperate regions the additive effect of decreased lake and reservoir size and increased lake primary production is suggested to yield an increase in organic C burial (Downing et al. 2008, Tranvik et al. 2009).

Sedimentation of organic matter is capable of storing N as well as C. Streams, lakes and reservoirs have light penetration, algal and macrophyte primary production, and interaction between water and benthic sediments that promote biologically-driven nutrient uptake, sedimentation and ultimately burial (Boyer et al. 2006, Brown et al. 2011, Mulholland et al. 2008, Harrison et al. 2009). There is however, great uncertainty in the estimate of how much N is buried as organic matter in lake and reservoir systems. One global estimate is 600 Tg C buried in the sediments of lakes and reservoirs (Tranvik et al. 2009). Global annual C sequestration rates for lakes have been estimated at 22 Tg C yr^{-1} (Kastowski et al. 2011). Assuming a range of sediment C:N of 24-8 based on trophic state and land use (Kaushal and Binford 1999, Duc et al. 2010), 25-75 Tg N could be sequestered in all lake sediments, accumulating at a rate of $0.9\text{-}2.8 \text{ Tg N yr}^{-1}$ (Kastowski et al. 2011). Kastowski et al. (2011) report that the C mass accumulation rates for 66 lakes was greater by 100% in recent sediments than the long-term mean accumulation rate, and these authors suggest it was due to increased primary productivity caused by eutrophication in agricultural and densely populated areas. This implies the rate of N burial has increased commensurate with cultural eutrophication.

However, N and C sequestered in lake sediments are not necessarily permanently buried. Gudasz et al. (2010) found a strong positive relation between temperature and organic C mineralization. They conclude future organic C burial in boreal lakes could decrease 4-27% under Intergovernmental Panel on Climate Change (IPCC) scenarios of warming due to enhanced temperature-dependent microbial activities (Gudasz et al. 2010). This suggests denitrification rates, which are similarly stimulated by warmer temperatures and greater availability of NO_3 , may reduce the quantity of N buried in lakes with climate change.

5.3 CONSEQUENCES OF N X CLIMATE INTERACTIONS ON AQUATIC ECOSYSTEMS

Above we list several mechanisms through which N levels will increase due to the synergistic effects of anthropogenic N loading and climate change over the coming decades. Below are some implications for aquatic ecosystems and the services they provide. Freshwater diversity, which has been altered by a combination of habitat loss, homogenization of flow regimes, and eutrophication, can also be diminished by excess N and changes to thermal properties (addressed in Chapter 6 on Biodiversity).

5.3.1. Economic Impacts

The combined effect of N loading and climate change on the economic value of water resources and related products has yet to be evaluated, and even the separate economic effects of N loading or climate change are difficult to determine. Economic assessments have been conducted for coastal fish harvests, recreational uses of inland and coastal waters, lakefront property values, and water treatment and human health costs (Birch et al. 2010, Compton et al., 2011, Pretty et al. 2003).

Similar to increased productivity on agricultural lands when N is added, N loading to coastal waters increases fish and invertebrate harvests initially. Beyond the initial stimulation of productivity additional N availability has either no effect or a negative effect (Breitburg et al. 2009). There is thus a positive economic outcome of increased fish landings with N fertilization that may be accompanied by an unquantified negative economic effect on recreational activities caused by eutrophication, increased turbidity, and hypoxia and loss of habitat for specific organisms (Breitburg et al. 2009). Hypoxia and hypoxia-related mortality are consequences of nutrient loading, and may increase with a warming climate due to increasing metabolic rates and increased biological oxygen demand (Breitburg et al. 2009). This is highly uncertain, however, because multiple climate drivers can elicit a variety of effects on the extent and severity of hypoxia responses (Diaz and Rosenberg 2011). The economic effects of hypoxia are difficult to quantify, even when there are mass mortality events. Hypoxia in the 1970s in Mobile Bay caused over \$500,000 in lost oyster stocks, and unquantified additional costs in oyster recruitment (May 1973). Another example of a hypoxic event occurred in the New York Bight in 1976 which caused an estimated loss of over \$570 million in commercial and recreational fishing (Figley et al. 1979, Diaz and Rosenberg 2011).

As eutrophication of inland waters increases with warmer water temperatures, there will be costs associated with upgrades of municipal drinking water treatment facilities, the purchase of bottled water, and the health costs of NO_3^- in drinking water leading to toxicity and disease (Compton et al. 2011). Freshwater eutrophication also reduces waterfront lake property values and recreational use across all waters (Dodds et al. 2009, Birch et al. 2010) and the economic costs of upgrading wastewater and drinking water facilities to accommodate sea level rise and flood risks will be substantial (Kirshen et al. 2007). A study of urban climate change impacts and adaptation strategies for Boston noted the interdependencies of urban infrastructure, flood control, water supply, drainage, and wastewater management (Kirshen et al. 2007). The adaptation costs of preventative activities to minimize the disruption of linked municipal services were found in the Boston study to be extensive, but projected to be less than the costs for repair after a flood event (Kirshen et al. 2007). If the expense for upgrading wastewater management infrastructure for N management is included, the costs rise substantially. The US EPA Clean Water Needs Survey (US EPA 2008) identified more than \$200 billion in wastewater management infrastructure needs for addressing nutrient control from traditional and storm water sources (US EPA 2011).

Given that Americans will increasingly rely on groundwater for drinking water under future climate change scenarios (Karl and Melillo 2009), there is a strong potential for increased costs for treating exposure to NO_3^- -stimulated disease. Approximately 1.2 million Americans use groundwater in areas with predicted NO_3^- concentrations between 5 and 10 mg L^{-1} , and about 0.5 million users live in areas with predicted $\text{NO}_3^- > 10 \text{ mg L}^{-1}$ (Nolan and Hitt 2006). Nitrate from drinking water contributes to the formation of N-nitroso compounds, which have been associated with cancer, diabetes, and adverse reproductive outcomes (Ward et al. 2005). In a recent study, the NO_3^- maximum contaminant level of 10 mg L^{-1} as N was exceeded in 22% of domestic wells in agricultural areas (Dubrovsky et al. 2010). A model of deep groundwater used for drinking (50 m simulation depth) predicted that areas with high N input, well drained soils, and lack of attenuation factors commonly had elevated NO_3^- . Model results also suggest that deeper groundwater supplies may be contaminated in the future as NO_3^- in shallow groundwater migrates downward and is slow to respond to changes in management (Nolan and Hitt 2006, Exner et al. 2010, Howden et al. 2010).

5.3.2 Human and Wildlife Health

Johnson et al. (2010) state that with climate warming there is the possibility for more vector-transmitted diseases to migrate to higher latitudes, where their success may be enhanced by high nutrient loading to US waters. Increasing numbers of studies show a correlation between N enrichment in waters and pathogen abundance and diseases of both humans and wildlife (Johnson et al. 2010). The interaction of N and disease can enhance several disease pathways, including direct disease transmission, vector-borne infections, complex life cycle parasites, and non-infectious diseases (Johnson et al. 2010). Many mosquitoes that are carriers of diseases like malaria or West Nile Virus and other parasites that are associated with warm climates or seasons have increased breeding success in high NO_3^- waters (Johnson et al. 2010). West Nile Virus responds strongly to higher temperatures, suggesting an interactive effect of N and warming may lead to greater risks from this disease, although this can be tempered by mosquito control efforts (Gage et al. 2008).

Harmful algae, for which there is a direct connection to nutrient enrichment and warm waters (Heisler et al. 2008), are increasing in outbreak extent, and can also cause a range of diseases from direct dermatitis, such as swimmers itch, to severe food poisoning, cancer, and paralysis (Johnson et al. 2010). Hoagland et al. (2002) reported more than 60,000 incidents of human exposure to algal toxins annually in the US, resulting in about 6500 deaths. Harmful algal blooms are also responsible for massive fish kills and marine mammal kills (Morris 1999).

5.3.3 Ocean Acidification

Future changes in climate and the N cycle will affect the responses of the ocean through additional indirect pathways beyond the direct ecological impacts of N-enrichment. For example, ocean acidification, the perturbation of the ocean calcium carbonate system affecting uptake of anthropogenic CO_2 , will intensify over the coming decades. Because pH, pCO_2 and relative saturation of calcium carbonate play critical roles in controlling biogeochemical cycles and ecological processes in the sea, ocean acidification has the potential to strongly influence and impact the dynamics of the N-cycle in coastal ecosystems (Doney et al. 2009). Impacts on the N-cycle include pH-dependent reductions in nitrification rates (Beman et al. 2011), and enhancement of open ocean N-fixation (Levitán et al. 2007). Climate-driven intensification of eutrophication can also increase the vulnerability of coastal ecosystems to ocean acidification. Oxygen declines in coastal waters are stoichiometrically coupled to inorganic C increases (Howarth et al. 2011a). As a consequence, C chemistry changes from ocean acidification are disproportionately large in hypoxic water bodies. Already, coastal upwelling shelves and estuaries subject to eutrophication exhibit pCO_2 levels in excess of values that are not anticipated to be reached by the mean surface ocean until the next century (Feely et al. 2008, 2009).

5.4 GUIDANCE FOR NITROGEN MANAGEMENT UNDER CLIMATE CHANGE

Water resources in the US are faced with the simultaneous and interactive forcing from two large stressors: climate change and excess Nr. While responses will vary over space and through time, climatic events and warming will almost certainly alter the rates of denitrification and N transport, largely in response to flushing and temperature. Because climate change will alter landscape and in-stream hydrologic connectivity and residence time in response to both flooding and drought, and warmer waters may increase the rates of Nr cycling by biota but may also intensify the limitation of other nutrients due to increased stratification of waters, there is no reason to assume that climate change will compensate for the negative effects of current and anticipated aquatic Nr loading.

The most direct opportunity for mitigation of detrimental effects of N on aquatic ecosystems is to reduce the inputs of N_r to lakes, reservoirs, streams, rivers, wetlands, and estuaries. The Federal Clean Water Act regulates discharges of pollutants into US waters and sets water quality standards. Section 303 of the Clean Water Act requires states to adopt water quality standards and criteria that meet the state-identified uses for each water body (US EPA 2011). “Such standards serve the dual purposes of establishing the water quality goals for a specific water body and serve as the regulatory basis for the establishment of water quality-based treatment controls and strategies beyond the technology-based levels of treatment required by sections 301(b) and 306 of the Act (40 CFR §131.2).” National nutrient criteria guidance has been published for lakes and reservoirs, rivers and streams, estuaries and coastal waters and wetlands, based on eco-regional directions (US EPA 2000a, 2000b, 2007, US EPA 2011), however, relatively few states have adopted numeric criteria to date. Once criteria have been adopted they can be used to identify impaired waters, where management goals like the total maximum daily load (TMDL) or the critical load (CL, described below) can be established.

Nitrogen emissions from fossil fuel combustion, transportation and agricultural sources contribute significant N_r to waters via atmospheric deposition. There are National Ambient Air Quality Standards (NAAQS) for NO_x which protect against gas-phase effects on vegetation and human health (see human health Chapter 7). The US EPA Integrated Science Assessment review of secondary standards indicates these regulations do not yet adequately protect ecosystems from N_r deposition in many parts of the country (US EPA 2008, Greaver et al. in press). Recent advances in modeling demonstrate that atmospheric deposition loads of N_r are related to ambient air quantities of NO_x, which suggest that existing air quality regulations could be used to reduce N deposition in order to protect water resources (Greaver et al. in press). More research on deposition-to-response relationships is needed to identify a level of pollutant that is protective of ecosystems. However, the NAAQS apply only to NO_x emissions, while emissions of NH₃ are mostly unregulated, and NH₃ emissions acts in combination with NO_x to cause nutrient enrichment effects.

Whereas the TMDL represents the maximum amount of a pollutant allowed to enter a water body via surface or ground water by law, the critical load, which is used to evaluate the effects of airborne pollutants on ecosystems, has not yet been formally adopted for management in the US. The critical load (CL) has been defined as the quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge (Nilsson and Grennfelt 1988). Critical loads have been proposed for water quality thresholds overcome by atmospheric deposition (Pardo et al. 2011, Baron et al. 2011), but as yet there is no regulatory framework for enforcement. The CL approach has not yet been formally and broadly applied in the US, although it is widely used in Europe and Canada (Burns et al. 2008, Greaver et al. in press).

While reducing inputs is the approach most likely to have a significant impact there are a series of additional opportunities that have the potential to further mitigate N stress on aquatic ecosystems. Maintaining and restoring extensive riparian buffers and retrofitting engineered landscapes to ensure that polluted waters from highly populated regions and drained agricultural fields are not piped directly into river networks, can ensure longer residence times and more efficient removal of N in watersheds. However, much research is needed on effective restoration practices. There is limited evidence to suggest that large investments in river and wetland restoration over the last decade have been successful at reducing N concentrations (Zedler 2000, Craft et al. 2003, Bernhardt et al. 2008). Capturing a much larger proportion of human and livestock waste would substantially reduce groundwater N

pollution, while investing in more sophisticated wastewater treatment would substantially reduce point source N inputs to rivers. Investing in tertiary treatment of human sewage and expanding the municipal sanitary infrastructure to capture and treat the sewage of the one quarter of American households currently relying on septic systems would substantially improve the water quality in areas where most Americans live, but care must be taken to minimize the N₂O loss to the atmosphere that accompanies such treatment (Bernhardt et al. 2008, Townsend-Small et al. 2011, Kampschruer et al. 2009). Instituting tighter regulations on consolidated animal feeding operations that require better containment and treatment of livestock wastes could reduce point source N loading in agricultural regions (see also the agricultural Chapter 4)(Schlesinger 2009).

Once N enters aquatic ecosystems the options for retaining and removing N pollution rely upon slowing down water and enhancing biological sequestration or denitrification (Mitsch et al. 2001, Craig et al. 2008). The large-scale construction of major reservoirs throughout the US over the last century has likely enhanced the retention and denitrification of N in reservoir sediments, but as new reservoir construction slows and older reservoirs fill with sediment this capacity is likely to be reduced (Langland and Hainly 1997, Doyle et al. 2008, Harrison et al. 2009). Dam construction, while it may enhance N retention and gaseous export, has many negative consequences for aquatic biota (Poff et al. 2007). Similar results may be achieved by increasing the connectivity between long residence time habitats, and thus the retention of material in river floodplains, backwaters and wetlands (Mitsch et al. 2001).

Increasing the efficiency with which water is used for agriculture, industry, and municipal supply will also build some resilience into US water resources that may prove beneficial to freshwater and coastal ecosystems. Preventative actions to upgrade urban infrastructure and locate or relocate N sources from floodplains are estimated to be cost-effective adaptation options for protecting water quality from flooding and sea level increases.

Strategies to reduce the combined impact of N loading and climate change on US water resources will take many years to show results. Long residence times for deep groundwater NO₃⁻ may require decades for benefits from proper N management practices to be realized under current and future climates. Ecosystem restoration is not yet a mature discipline, and research is only now showing that many restoration practices, such as attempting to reduce N removal from agricultural lands with riparian buffers or stream restoration, are ineffective (Puckett 2004, Craig et al. 2008). While there are locations and approaches that might increase the success of restoration efforts, these are no substitute for the direct reduction of N from its sources.

5.5 RESEARCH NEEDS

Research is needed to increase our understanding of the sources and fate of Nr in US waters, how to mitigate the potential adverse effects of climate change, and how to reduce the transport of Nr from terrestrial to aquatic systems. These are itemized below.

- For all aquatic ecosystems a better understanding of the effects of climate change on Nr transport and transformations is needed, including evaluation of existing relationships, continued monitoring, and modeling of current Nr-climate change dynamics and projected future scenarios. Climate change effects should include understanding Nr transport and transformation responses to increased variability and a shift in mean

conditions, in addition to an increase in extreme hydrologic (floods, droughts) and thermal events.

- Comparisons of current and potential future relations between observed inter-annual variability in precipitation, runoff, and temperature with Nr transport and transformation are needed to gauge the magnitude of future changes. This type of comparison will be necessary for management and adaptation considerations for the broad range of land uses (e.g., natural, agricultural, and urban), water resource types (e.g., lakes, reservoirs, rivers, wetlands, estuaries), and time scales (e.g., events, seasons, years, decades).
- Are there critical thresholds associated with the interactions of climate with Nr? More research is needed to identify levels of pollutants that may be protective of ecosystems and societal water resources. Total Maximum Daily Loads, critical loads, and water quality health standards are available, but may need to be refined as more information becomes available.
- The current uncertainties of estimates of N storage and removal in different aquatic ecosystems, including groundwater, highlight the need for a better N mass balance for the US. Experiments and modeling are also important for better quantifying the climate change-induced responses identified in Table 5.1. Quantification of denitrification rates from freshwaters, groundwaters, and estuaries is important for integrating water resource processes into a N mass balance of the US.
- A greater understanding of the N cycle with other element cycles (e.g., C, phosphorus, silica) in aquatic systems is needed. The influence of Nr on C storage in sediments, and the residence time of C and N stored in sediments, should be quantified in order to evaluate their importance to the global C cycle. Along with the need for better evaluation of nutrient stoichiometry, there is a gap in our understanding of dissolved organic N (DON) in aquatic ecosystems. We know much more about how the reactivity and composition of dissolved inorganic N (DIN) will change with climate change than dissolved organic N (DON). For instance, a large proportion of riverine N load can be made up of DON, but has not been fully quantified.
- Stream restoration ecology is not yet a mature field, yet there is an extant literature suggesting restoration of wetlands and riparian zones, construction of vegetation buffers, and other methods can reduce the transport of agricultural or municipal N to waters with these techniques. Additional research and monitoring is desperately needed to understand farm management effects on downstream water quality related to Best Management Practices. We don't systematically know where farm management is taking place nor and how effective it is in retaining nutrients, yet these tools are on the front lines for potentially controlling farm runoff. Further, research into the

effectiveness of restoration techniques under climate change will be important for determining whether or not restoration is useful for future climate change adaptation.

- Assessments of the social and economic risks associated with climate change and water resources will be critical to evaluating whether and how to intervene in order to minimize the environmental and health consequences of excess Nr in US waters.

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Chapter 6: Nitrogen, Climate Change, and Biodiversity

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ABSTRACT

Biodiversity has been described as the diversity of life on earth within species, among species and among ecosystems. Biodiversity contributes to regulating ecosystem services like climate regulation, flood protection, disease mitigation, and water quality regulation. Biodiversity also supports and sustains ecosystem services that provide material goods like food, fiber, fuel, timber and water, and to non-material benefits like education and recreation, and spiritual and aesthetic enrichment. The Millennium Ecosystem Assessment (MEA) estimated that the rate of biodiversity loss due to human activity in the last 50 years has been more rapid than at any other time in human history, and that many of the drivers of biodiversity loss are increasing. The strongest drivers of biodiversity loss include habitat loss, overexploitation, invasive species, climate change, and pollution, including pollution from reactive nitrogen (Nr). Of these stressors, climate change and Nr from anthropogenic activities are causing some of the most rapid changes. Climate change is causing warming trends that result in consistent patterns of poleward and elevational range shifts of flora and fauna. Warming has also resulted in changes in phenology, particularly the earlier onset of spring events, migration, and lengthening of the growing season. In addition to warming, elevated carbon dioxide (CO₂) by itself can affect biodiversity by influencing plant growth, soil water availability, and trophic interactions. Nitrogen enrichment also impacts ecosystems and biodiversity in a variety of ways. When limiting, N enhances plant growth, but has been shown to favor invasive, fast-growing species over native species adapted to low N conditions. Although there have been only a few controlled studies on climate change and N interactions, inferences can be drawn from a variety of field observations. For example, in arid ecosystems of southern California, elevated N deposition and changing precipitation patterns have promoted the conversion of native shrub communities to communities dominated by a few species of annual non-native grasses. In estuaries, increased N loads result in eutrophication and harmful algal blooms that are exacerbated by higher temperatures, lower flows, and increased periods of stagnation. In addition to empirical studies, modeling can be used to simulate climate change and N interactions. The ForSAFE-VEG model, for example, has been used to examine climate change and N interactions in Rocky Mountain alpine vegetation communities. Results from both empirical studies and modeling indicate that N and climate change can interact to drive losses in biodiversity greater than those caused by either stressor alone. Reducing inputs of anthropogenic Nr may be an effective mitigation strategy for protecting biodiversity in the face of climate change.

6.0 INTRODUCTION

Biodiversity is the foundation of the integrity, resilience and beauty of nature. Simply defined, biodiversity is the variety of life on earth, including all species, the diversity of genes in these species, and the communities and ecosystems they inhabit. A more complete definition from the Convention on Biological Diversity states:

Biological diversity means the variability among living organisms from all sources including, inter alia, terrestrial, marine and other aquatic ecosystems and the ecological complexes of which they are part; this includes diversity within species, between species and of ecosystems” (CBD, 1992).

Biodiversity influences either directly or indirectly nearly every ecological process. Changes in biodiversity alter the structure and function of ecosystems which can in turn affect the production of ecosystem services and human well-being in a variety of ways (Chapin 2000, Millennium Ecosystems Assessment (MEA) 2005, Secretariat of the Convention on Biological Diversity 2010). Biodiversity is positively associated with a number of key ecosystem processes, in particular primary and secondary productivity, resistance to invasion and consumption, erosion control, and nutrient cycling (Balvanera et al. 2006). The benefits of biodiversity become more apparent when multiple ecosystem functions are considered because different species often perform different functions in ecosystems, or at different times (Hector and Bagchi 2007, Scherber et al 2010, Zavaleta et al 2010). More biodiverse systems tend to be more stable when processes are measured either through time (Hector et al 2010, Yachi and Loreau 1999, Tilman et al. 1998) or over larger spatial regions (Loreau et al 2003).

Biodiversity is declining globally despite international agreements to stem this loss. In 2002, over 150 nations signed the agreement under the Convention on Biodiversity “to achieve by 2010 a significant reduction of the current rate of biodiversity loss” (Secretariat of the Convention on Biological Diversity, 2003). Recent analyses have found that, despite some notable successes, and the increasing expansion of protected areas globally, these goals are not being met nor are they expected to be met in the coming decades (Butchart et al. 2010, Secretariat of the Convention on Biological Diversity, 2010, Kleijn et al. 2011, Pereira et al. 2010). Biodiversity within the United States (US) is similarly threatened, with the US Fish and Wildlife Service listing 587 animals and 794 plants as threatened and endangered in 2011 (USFWS, 2011). Various analyses, including with the Globio3 model, project significant declines in biodiversity in the future, both in the US and globally, due to human activities (Alkemade et al. 2009, Secretariat of the Convention on Biological Diversity 2006, Pereira et al. 2010).

Land use change has been a major driver of losses in biodiversity, as natural areas have been converted to agricultural or urban uses, patterns of wildfires and other disturbances have been altered, and new species have been introduced into ecosystems (MEA 2005; Sala et al. 2000, McKee et al. 2004, Alkemade et al. 2009, van Oorschot et al. 2010). Land use change often results in increases in nitrogen (N) released to the environment by increased vehicle emissions, agricultural emissions, and runoff. Increasingly, climate change and increases in reactive nitrogen (Nr) are being recognized as significant drivers of ecosystem changes leading to biodiversity losses (MEA 2005; Rockstrom et al. 2009). These stressors interact in important ways that can either amplify or mitigate changes in biodiversity (Sala et al. 2000).

Historically, fluctuations in climate and nutrient availability are common in natural systems, but the magnitude of recent changes over a relatively short time period is unprecedented in the Holocene

(Rockstrom et al. 2009). Changes in climate generally occurred over much longer time scales and over interconnected natural landscapes. Species ranges shifted accordingly, although many went extinct if migration was impeded or if extant species prevented their immigration to new habitats (Pimm et al. 1995; IPCC 2007). Under more rapid climate change, with a highly fragmented landscape, species migrations are even less likely to be successful (IPCC 2007). Changes in average precipitation and in the frequency and intensity of storms are also expected to impact biodiversity, although the effects of these factors are less well understood. The timing of biological activity, including associations with pollinators, pests, and herbivores, are also expected to change. Finally, one of the primary drivers of climate change, elevated carbon dioxide (CO₂), can have a variety of effects on biodiversity through its influence on plant growth, soil water availability, tissue stoichiometry, and trophic interactions (Reich 2009, Reich et al 2006).

Unprecedented increases in N_r are also expected to drive losses in biodiversity. Nitrogen availability has historically been low in many ecosystems, limiting primary production (Vitousek and Howarth 1991). Against this backdrop of low N availability and tight recycling in undisturbed natural ecosystems, globally available N has increased tenfold from 1860 to the early 1990s due to industrial and agricultural activities (Galloway et al. 2004). Indeed, it is estimated that human-derived N_r surpassed all natural processes combined sometime around the 1980s, a trend that is projected to increase N_r another 70 % by 2050 (Galloway et al. 2004, Vitousek et al. 1997). It follows that species distributions that evolved under largely N-limited natural conditions are likely to have changed and will change further.

Nitrogen enrichment impacts biodiversity in a variety of ways. For plants, these are usually categorized into four mechanisms: eutrophication, acidification, direct damage, and through secondary factors (Bobbink et al 2010, Dise et al 2011, Pardo et al 2011a, Pardo et al 2011b). Nitrogen is a commonly limiting resource for autotrophic plants, and excess amounts can lead to eutrophication of ecosystems, thus favoring fast-growing species in terrestrial and aquatic systems. This increased growth can reduce light penetration at the soil layer (or underwater for submerged macrophytes) and reduce belowground nutrient availability for other species, leading to overall declines in biodiversity and shifts in species composition (Hautier et al 2009, Dise et al 2011). Nitrogen enrichment can also acidify soil and water, lead to losses of base cations from the soil, nutrient imbalances, and increases in toxic compounds in the soil (e.g., aluminum, Al³⁺) (Dise et al. 2001), also leading to reductions in biodiversity and selection for acid-tolerant species. Finally, N enrichment can aggravate the impact on biodiversity of secondary stressors such as fire, pests, and climate extremes (including frost and drought). Vulnerable plant communities can become more simplified in structure and less diverse in species than their undisturbed counterparts, harming animals that depend on certain plant species for food, habitat, or other resources (Dise et al 2011, McKinney and Lockwood 1999). Biodiversity of other biota, including soil microbes, can also be directly affected by N_r enrichment, showing shifts in composition and reductions in beneficial populations (Johnson et al 2003).

Nitrogen can interact with climate in several ways to affect biodiversity. *Additive* effects are when N and climate affect biodiversity independently of one another. *Interactive* effects are when the impact of one (e.g., N enrichment) is contingent on the effect of the other (e.g., climate change). When impacts are additive, total effects can be estimated by their sum (even though some may be positive and some negative), whereas, when impacts are interactive, total effects can lead to disturbances not anticipated from considering either separately. *Compensatory* (or antagonistic) effects occur when an interaction causes the combined effect of the two factors (net impact) to be dampened or offset by each other. *Synergistic* effects occur when an interaction causes the net impact from factors to be amplified.

In this chapter, we focus on how interactions between climate change and N enrichment influence biodiversity within the US. Our conceptual model (Figure 6.1) illustrates how changing climate, CO₂ and N can independently affect biodiversity, and also how these factors can interact with each other and with species traits to influence biodiversity. Our discussion is limited by available data and information from research on these topics. As such, there is a focus on biodiversity at the scale of species, especially plants, with somewhat more information available for terrestrial systems than aquatic systems. We describe several major factors affecting biodiversity and how climate and Nr may interact to influence these factors (Section 6.1), using examples from several ecosystems and taxa (Section 6.2). We then discuss to the implications of this research, including evaluating risks to biodiversity from Nr enrichment and climate change using critical loads and other tools (Section 6.3), modeling efforts to assess climate and Nr interactions (Section 6.4), and potential adaptation and mitigation efforts to reduce these interactions (Section 6.5). Lastly, we highlight some recommended areas of research (Section 6.6).

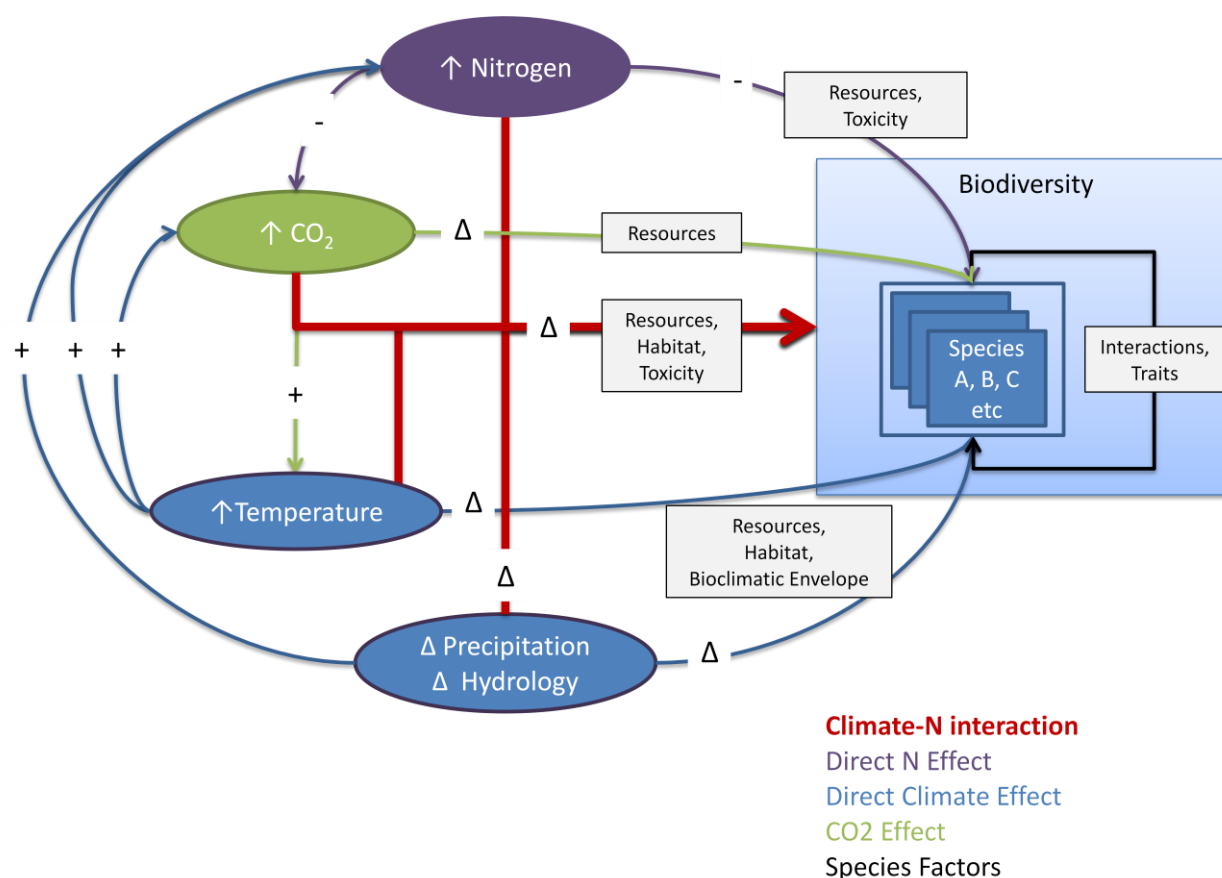


Figure 6.1: Direct and indirect effects of changing climate, nitrogen and CO₂ on biodiversity

6.1 FACTORS THAT DETERMINE BIODIVERSITY

Biodiversity within a given region is determined by complex interacting abiotic and biotic controls (Gaston 2000, Ricklefs 2004), which can be influenced by anthropogenic N enrichment and climate change (Sala et al. 2000, Chapin III et al. 2000). A full account of the factors influencing biodiversity is beyond the scope of this report, but there are some general processes that operate in most systems for most taxa. Generally, for any particular species or individual to survive in an area, it must pass through “environmental filters” (Zobel 1997). Initial filters include the biogeographic distribution of species, and whether local dispersal occurs. Establishment within a site is determined by suitable abiotic conditions (e.g., climate), and biotic interactions that can limit (e.g., competition, predation) or enhance (e.g., presence of pollinators) the abundance of a species. The sections below describe the major factors involved in this filtering process, and how N enrichment and climate change can interactively influence some of these factors. In many cases the influence of one factor accentuates the influence of the other, with the net result being greater changes (usually decreases) in biodiversity.

6.1.1 Bioclimatic conditions

To establish viable populations at a site, organisms must be able to physiologically withstand the range of climatic conditions present at that site, including extremes in temperature, solar radiation, and water availability. Climate change has and will continue to alter the range of these conditions, and the survival of species under changing conditions will depend on the pace of change and the biological attributes and phenology of individual species. Much of the available evidence for effects is based on small-scale, short-term experiments and should be interpreted with caution, since biodiversity at the landscape level may respond very differently as species redistribute under new climatic conditions.

The few controlled studies on the impact of changes in precipitation on biodiversity are largely from herbaceous communities, and are of relatively short duration (e.g. a few years). Research from Mediterranean systems (Zavaleta et al. 2003a, Zavaleta et al. 2003c) and tall-grass prairie (Collins et al, in review) found that increased precipitation had a small positive or negligible effect, respectively, on species richness. Similar findings have been reported in China (Yang et al 2011a, 2011b).

A study from California shrub and grass ecosystems indicated that an increase of about 1°C above ambient in temperature applied over three years had a negligible effect on biodiversity (Zavaleta et al. 2003a; Zavaleta et al. 2003c); in contrast, evidence from grasslands in China indicated a decrease with a similar increase in temperature (Yang et al 2011b). These diverging effects likely stem from differing impacts of simulated changes on other factors, such as changes in soil moisture (Zavaleta et al 2003b, Yang et al 2011a).

Extreme changes in temperature (e.g., hot periods and/or cold periods) and water availability (e.g., drought or flood) can subject populations to local extinction. If widespread population extinctions occur, the potential for species extinctions increases (Jeffries 2006, Parmesan 2006, Sinervo et al. 2010, Tilman and Haddi 1992).

Interactions with N and climate

Anthropogenic N input has the potential to change the capacity of species to tolerate altered climatic conditions. For example, earlier snowmelt in high elevation sites has caused earlier starts to the growing season, thus increasing the exposure of some plants to killing frosts (Inouye 2008, Figure 6.2).

Deposition of N has been associated with greater frost sensitivity in conifer species (Sheppard and Pfan 2001), and the combination of more frequent frosts and greater plant sensitivity to those frosts can increase mortality rates. Nitrogen can also increase the capacity of species to tolerate a changing climate, for example, promoting growth and expansion of deciduous shrubs in tundra, while decreasing overall species richness (Chapin et al. 1995). Thus, in general, climate change and N may act synergistically or antagonistically on biodiversity, depending on system-specific and taxa-specific dynamics.

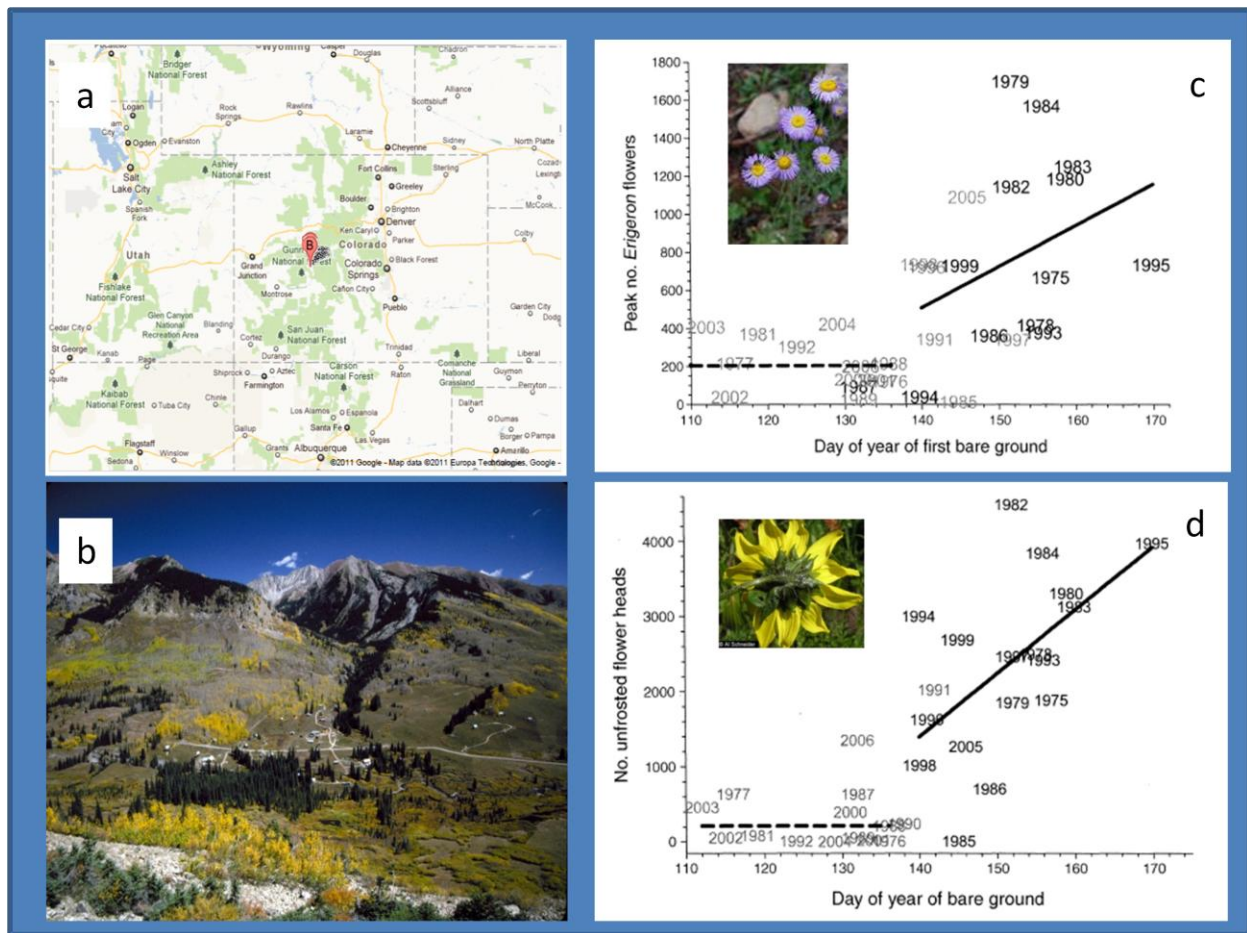


Figure 6.2: Shown below are results from one study in Colorado on the effects of changes in climate on wildflower reproduction. The location and photo (a, b) of the Rocky Mountain Biological Laboratory where the study was held. Researchers found that the peak number of wildflowers (*Erigeron speciosus*) was lower when the season started earlier (c), and that more flower heads were killed (*Helianthella quinquenervis*, d) (modified from Inouye 2008).

6.1.2 Movement of Species

A species must be able to colonize new areas to expand its range, and diversity in a given habitat is strongly influenced by the number of species that can successfully disperse there (Zobel 1997). For example, remote islands generally have fewer species than mainland areas of similar size and conditions, often because of the difficulty of reaching these isolated habitats (Ricklefs 2004, Rosenzweig

and Abramsky 1993, Rosenzweig 1995). Dispersal may limit diversity even in non-isolated areas: for example, the addition of seeds to some plant communities often leads to increases in diversity (Foster and Tilman 2003, Hubbell 2001, Hurtt and Pacala 1995).

Interactions with N and climate

The successful movement of species across landscapes is a complex process, including reproduction (for sessile organisms like plants), dispersal, and establishment in a new habitat. Climate change and N enrichment can alter each of these steps and thus expand or contract the potential range of a species. Overall declines in plant diversity associated with anthropogenic N deposition, described primarily in grasslands (Stevens et al. 2004, Stevens et al. 2010, Clark and Tilman 2008, Dupre et al. 2010, Maskell et al. 2010), will affect dispersal and establishment by decreasing the pool of plant species available to migrate and form new communities as climate change occurs. And although N enrichment tends to increase seed production and nutritional quality in plants (Throop and Lerdaun 2004), species may respond differently. For example, in Minnesota, elevated N increased seed production for C₄ herbaceous species, and decreased seed production for C₃ species (HilleRisLambers et al. 2009). In addition, elevated CO₂ has also been found to increase seed production for many crop and annual species (Ackerly and Bazzaz 1995, Jablonski et al. 2002, Huxman et al. 1999), although other studies suggest that perennial species and undomesticated species may respond differently (Jablonski et al. 2002, Thurig et al. 2003, HilleRisLambers et al. 2009).

Because of these complexities, and because few experiments have examined the effects of global change on reproduction and dispersal, there is little detailed information on how ecosystems will shift with climate in the US or globally. Most modeling efforts assume that species ranges will shift with climate, though researchers acknowledge this is only a first approximation (Guisan and Thuiller 2005, Pereira et al. 2010).

6.1.3 Disturbance

Disturbance, or physical alteration of the habitat, plays an important role for biodiversity at the local and landscape scales. Both the frequency and intensity of disturbance are important. Areas that are either frequently or infrequently disturbed often have lower levels of biodiversity than areas with a moderate amount of disturbance. For example, rivers that experience high levels of flow variability have, in general, reduced food chain length and fewer numbers of species (Sabo et al. 2010). Disturbances influenced by climate, including fires, severe storms, and floods, are expected to change over the next century, although all are anticipated to occur more frequently and be more intense (Karl et al. 2009).

Interactions with N and climate

Nitrogen enrichment has the potential to alter the response of ecological communities to climate change-driven disturbance. As an example, N enrichment and changes in precipitation patterns in the Mojave Desert have been implicated in the success of invasive annual grasses, which increase fuel loadings and carry fires in a native shrub community not well adapted to fire (Rao et al. 2010, Figure 6.3). Similarly, increased fire frequencies in chaparral vegetation, in combination with greater N availability, enhances the replacement of native shrubs with weedy non-native annual grasses (Haidinger and Keeley 1993). Elevated N inputs can shift allocation of plant biomass from belowground to aboveground, which tends to reduce the stabilizing influence of belowground biomass on the soil

(Adair et al. 2009). Conversely, more aboveground biomass coverage can reduce the impact of rain droplets on destabilizing soil, and provide a physical barrier to storm flows in and along riverbanks, thereby reducing the potential for landslides and flooding (Körner 2004).

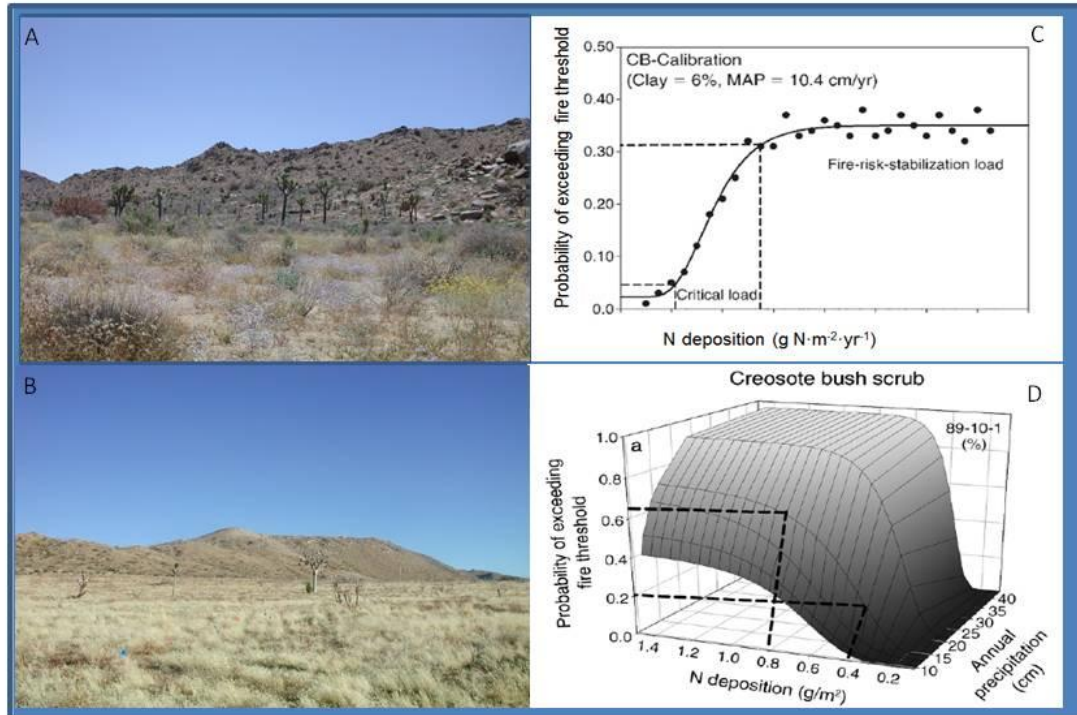


Figure 6.3: Shown is an example of the interactive effects of nitrogen and climate on the probability of fire in the Mojave Desert, CA. N deposition facilitates the growth of invasive grasses in the spaces historically bare between shrubs (low invasion and high invasion/post-fire in A and B respectively; photos courtesy of Dr. Edith Allen). C shows fire risk increasing in the creosote bush scrub community (CB) as N deposition increases; MAP is mean annual precipitation. In D, the probability of fire is enhanced with N deposition and increased precipitation (C and D adapted from Rao et al. 2010).

6.1.4 Hydrology

Climate change is anticipated to increase the duration of low flow periods in streams and rivers and the frequency of extreme events (e.g., drought and flood) across much of the planet (IPCC 2007). During the 20th century approximately half of the world's wetlands have disappeared (Zedler et al. 2001), and freshwater extraction in some regions is so extreme that some major rivers, including the Nile, Yellow, and Colorado Rivers, no longer flow to the sea either seasonally or entirely (MEA 2005). Climate change will alter the delivery of water to many areas by affecting how much rain falls versus snow, changes in snowmelt timing and also changes in water flows to estuaries and coastal zones.

Interactions with N and climate

In alpine lakes, altered snowmelt timing and increases in glacial melting can increase nutrient loading and alter lake diatom communities (Saros et al. 2010). Storms and increases in precipitation increase nutrient loads to coastal zones, and droughts increase residence times, promoting algal growth, including growth of harmful cyanophytes and bloom-forming flagellates (Paerl and Scott 2010). Altered hydrology can cause wholesale shifts in habitat, and if areas dry up, can cut off connectivity in streams or reduce habitat in wetlands.

6.1.5 Resource supply

The supply of resources (e.g., water, light, nutrients) is an important control on biodiversity. The supply of N in many ecosystems is restricted by climatic factors that constrain the turnover of organic matter, including low soil temperature and both high and low soil moisture (Hobbie 1996). Studies across major biomes have found that, in general, increased biodiversity is associated with increased fertility and productivity which is positively correlated with soil N content (Chase and Leibold 2002, Waide et al. 1999). However, in more focused investigations of terrestrial and marine ecosystems and some fresh water ecosystems, diversity has been found to be inversely correlated with N inputs (Stevens et al. 2004, Stevens et al. 2010, Clark and Tilman 2008, National Research Council 2000, Dudgeon et al. 2006). Thus, it appears to be the interplay of resource supply with other factors such as dispersal, scale, species interactions, and others that determine the net effect of resource supply on biodiversity.

Interactions with N and climate

Climate change may increase N availability in many ecosystems, potentially enhancing the effect of additional N enrichment on changes in diversity. For example, melting alpine glaciers are releasing N into receiving streams and lakes, where increasing N has been linked to shifts in diatom species assemblages from oligotrophic to mesotrophic species (Saros et al. 2010, Baron et al. 2009, Wolfe et al. 2001). Warming increases N mineralization in soils, increasing N availability in peat bogs (Keller et al. 2004, Weedon et al. 2012), subarctic heath-lands (Hartley et al. 1999), and New England forests (Butler et al. 2011, Melillo et al. 2011). In tundra, greater shrub cover promoted by N enrichment can enhance the development of an earlier insulating snow cover, increasing decomposition during the winter and thus the supply of plant-available N (Sturm et al. 2005). Elevated CO₂, on the other hand, may decrease N supply to plants due to shifts in the balance of C and N causing a slowdown in decomposition (Hu et al. 2001).

6.1.6 Species Interactions: consumptive and non-consumptive

Species interactions, including non-consumptive functions such as competition and facilitation, and consumptive processes such as herbivory, parasitism, and predation, can influence the success or failure of species within a community, and subsequently influence its biodiversity (Ricklefs 1987). The spatial and temporal extent, intensity, and outcome of these interactions often depend on the climatic conditions and variations in the supply of resources such as N.

Interactions with N and climate

Competition for N by autotrophs could decrease under climate warming and N enrichment scenarios by shifting the limiting resource(s) from N to phosphorus (P) in aquatic systems (Elser et al 2009), and P, light, or water in terrestrial systems (Hautier and Hector 2009). However, the overall intensity of competition could increase as well. In California, simulated elements of a global change scenario (elevated N deposition, temperature, CO₂, and precipitation) influenced diversity, as measured by total grasslands species richness, in different ways. For example diversity increased with elevated precipitation alone, was unaffected by elevated temperature alone, and decreased with increasing N and temperature (Zavaleta et al 2003a, Zavaleta et al. 2003c). All factors in combination caused changes in the relative dominance of forbs and grasses, with decreases in forb abundance. Forbs make up most of the plant biodiversity in these systems (Figure 6A-B). Elevated N and CO₂ reduced the difference in flowering date between the two groups, increasing temporal overlap and leading to greater overall competition between these two functional groups, with the grasses subsequently dominating (Figure 6C). The highly invasive yellow starthistle, *Centaurea solstitialis* L., also benefited disproportionately under altered climate and N regimes (Figure 6D). However, the only other experiment examining the impact of both elevated N and CO₂ on biodiversity in the US (Reich et al. 2009), found that, although N addition reduced diversity in a Minnesota grassland over ten years (-16%), , elevated CO₂ mitigated about half of this loss. Thus, although elevated N reduces biodiversity in general, other global change factors may interact to affect this response.

Climate change and N enrichment may have an additive effect on increasing the amount of consumption and population growth of consumers (e.g., herbivores, carnivores, etc.). Greater consumption rates can increase diversity when a dominant competitor is the preferred target species, or decrease diversity when rare species are preferentially consumed (Olf and Richie 1998). Many consumers, particularly herbivores, are growth-limited by the supply of N (Mattson 1980). Growth may increase substantially in response to N enrichment as forage quality increases with higher N concentrations in plants, lower concentrations of defensive compounds, and shifts to higher dominance of more palatable species (Throop and Lerdau 2004). Climate change in temperate and arctic climates will benefit many invertebrate consumers due to a longer growing season (Bale et al. 2002) that allows some insect herbivore species to complete more than one life cycle in a year (Roy et al. 2009, Mitton and Ferrenberg, in press). The longer growing season is implicated as one factor contributing the outbreak of mountain pine beetles in western North America (Raffa et al. 2008, Bentz et al. 2010).

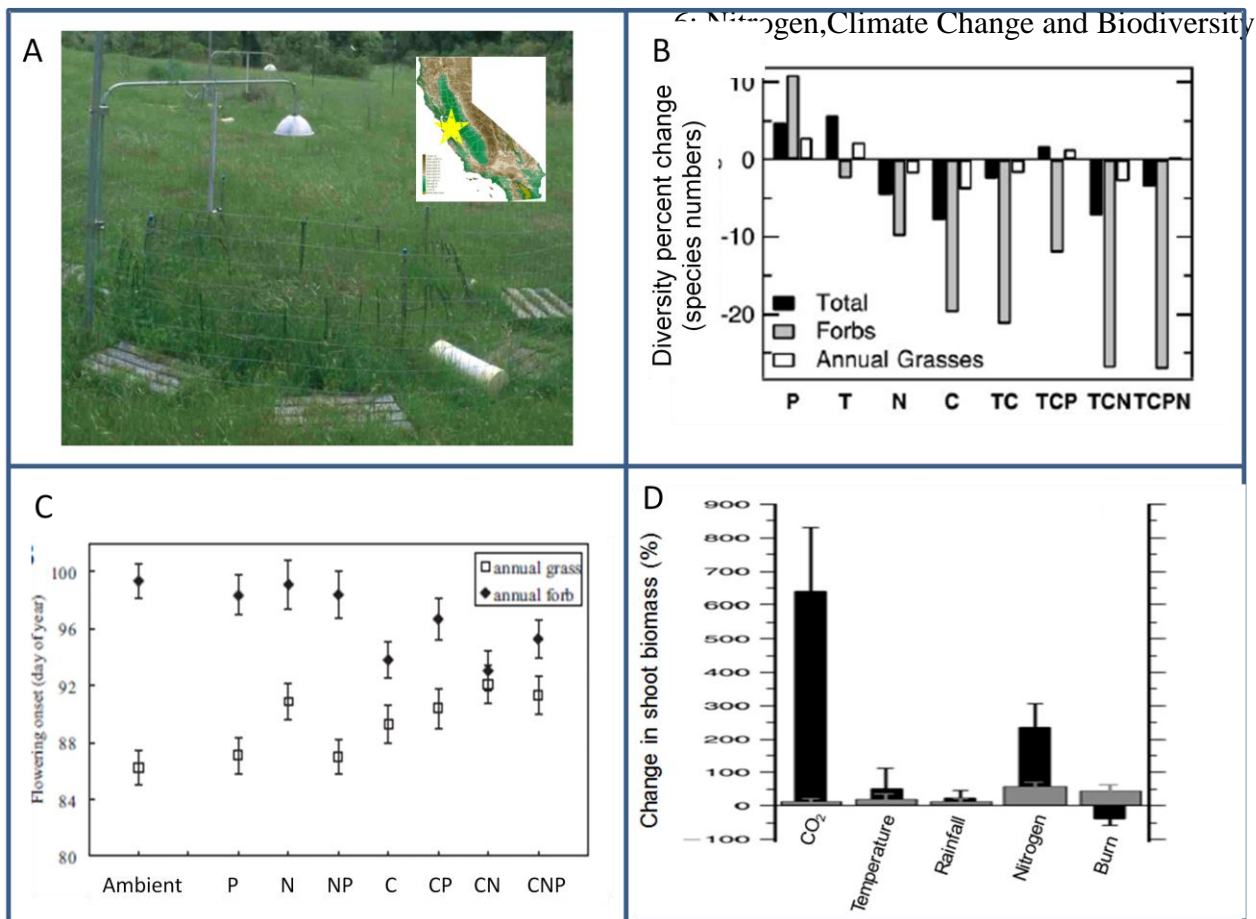


Figure 6.4: Results from a global change experiment in California on the individual and interactive effects on plant diversity from four global change factors (elevated temperature (T), precipitation (P), nitrogen (N), and CO₂ concentrations (C); Shaw et al 2002, Zavaleta et al. 2003a, Cleland et al. 2006, Dukes et al. 2011). (A) Shows a typical plot and the geographic location of the experiment (modified from Shaw et al. 2002). Results of the overall diversity changes are shown in (B) (Zavaleta et al. 2003a) related to individual and combined treatments. Shifts in phenology for annual grasses and forbs are shown in (C) (Cleland et al. 2006). Responses of the invasive star thistle (thin black bars) and the extant community (thick grey bars) are shown in (D) (Dukes et al. 2011).

6.1.7 Habitat heterogeneity

Generally speaking, more heterogeneous habitats, or areas with many different kinds of habitats, can support more species (Ricklefs 2004). For example, mixed forest stands usually support more species than single-species stands, and old growth forests more species than mixed stands.

Interaction of N and climate

Some species preferentially benefit from increases in N, leading to an overall simplification of the habitat. This is often termed “biotic homogenization” and can be driven by a number of factors such as the spread of few numbers of invasive species (McKinney and Lockwood, 1999). In terrestrial ecosystems N deposition can reduce local variation in soil N availability, which is an important contributor to diversity (Gilliam 2006). In grasslands N-addition experiments, reductions in plant diversity led to a reduction in the diversity of insects (Haddad et al 2000). Climate change may exacerbate this simplification, both through its effects on species diversity and habitat diversity.

6.2 SENSITIVITY OF SPECIFIC ECOSYSTEMS TO CLIMATE-N INTERACTIONS

Reviewing the interactions between N and climate change is challenging since many studies address these impacts individually rather than together. Few manipulation experiments alter temperature or precipitation and nutrient availability; fewer still examine the impacts on biodiversity. Reich et al (2006) reviewed all known studies combining N enrichment and elevated CO₂ treatments, and found only eight that they considered representative of natural responses (e.g., field-based, replicated, long term), with none in mature mixed forests. Globally, the Jasper Ridge FACE experiment in Stanford, California (Shaw et al 2002) is the only field experiment examining the impact on biodiversity of increasing N deposition, temperature, CO₂, and precipitation, both singly and in combination. Clearly there is growing recognition of the importance of these interactions, and a need for more information. Complementary approaches exist, however, such as modeling, regional gradient surveys, and re-surveys or retrospective analyses of existing long-term data sets (Table 6.1). In this section we use this combined evidence to examine the sensitivity of different ecosystems and regions to changes in N and climate. The following section (4) will integrate this knowledge with future projections of N deposition and climate to explore risk and vulnerability.

Table 6.1: Case examples of nitrogen and climate impacts and interactions on biodiversity by region.

Region: North East							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Northern Forest	Spruce-Fir	N deposition may decrease Ca availability, limiting the ability to respond to stress, and reducing red spruce cold tolerance	Climate change can cause trees to "deharden" (during mid-winter thaws) predisposing them to freezing injury	Decreased ability to respond to increasing stresses leads to increased freezing injury, increased mortality, shift in species composition	Synergistic	Nutrients-- shift in available N/Ca, [site characteristics, shallow soil; acidification]	Bioclimatic envelope, Species functional traits
DeHayes et al. 1999, Schaberg et al. 2002							
Northern Forest	Northern hardwoods	N deposition reduces Ca availability at Ca-poor sites	Changes in frequency and severity of ice storms caused by warmer winter temperatures	At Ca-poor sites, post-ice storm growth in paper birch was suppressed.	Synergistic	Disturbance--ice storm	Species traits--birch structure, nutrients--Ca depletion
Halman et al. 2011							

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Region: South East							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Eastern Temperate Forests	Red Spruce Forest	Increased basal area (growth) associated with higher N deposition	Increases in drought frequency and severity increases susceptibility to pest outbreak	Increased susceptibility to pest outbreak can follow a drought period, resulting in mortality of spruce on N rich sites	Synergistic	Nutrients	Disturbance-drought, pest outbreak

McNulty and Boggs 2010

Region Midwest, Great Plains							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Great Plains	Northern Prairie	N fertilization enhances growth of grasses, leading to reductions in biodiversity of forb species	Elevated CO2 has little effect on biodiversity when other stressors are absent.	Elevated CO2 reduced the impacts of added N by reducing soil N and increasing soil water, leading to lower species losses under both stressors.	Antagonistic	Nutrients	Soil water, species traits

Reich et al 2009

Great Plains	Short-grass steppe	N fertilization had little effect on plant species but the trend was for diversity reductions	Water addition increased production and triggered changes in composition .	Losses of species and changes in composition with N addition are larger with increased precipitation because systems switch from water to N limitation	Synergistic, Additive	Water	Nutrients
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Lauenroth et al 1978, Clark et al 2007, Gough et al 2000

Great Plains	Tall-grass and mixed grass prairie	N fertilization decreased biodiversity primarily of forb species.	Periodic fire and water additions did not reduce plant biodiversity on their own.	Periodic fire amplified the impact of added N leading to large declines in diversity. Water additions increased diversity	Synergistic	Nutrients	Fire, grazing, water
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Gough et al 2000, Clark et al 2007, Collins et al 1998

Region: Northwest							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Tundra	Alaskan Arctic	Nitrogen increases growth of particular shrub species in arctic tundra	Warming increases growth of particular shrubs in arctic tundra	Shrub cover in increasing in large areas of arctic tundra, shift in ecosystem type. Dominant shrub is N-fixer.	Synergistic	Bioclimatic envelope	N availability

Sturm et al. 2001; Chapin et al. 1995

Region: North and South West							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Marine West Coast and NW Forested Mountains	Western hemlock, Oak savanna, High elevation forest	N deposition shifts species composition from oligotroph to eutroph dominated	Changes in temperature and relative humidity affect lichen composition	Lichen community composition shifts in response to N deposition and climate (T and RH)	Additive	Species traits, species interactions	Bioclimatic envelope, Nutrients -- N availability
Geiser et al. 2010							

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Region: South West							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Mediterranean annual grassland	N fertilization reduced biodiversity of plants, mostly of forb species	Elevated CO ₂ also reduced biodiversity; warmer temperatures had no effect, and elevated precipitation increased biodiversity.	Few interactive effects reported.		Additive	Nutrients	Precipitation, fire, CO ₂
Zavaleta 2003a, 2003b							
North American Deserts	Desert	Fertilization promotes growth of non-native annual grasses and shifts in species composition resulting in increased risk of fire	Altered precipitation patterns allow increased growth of exotic? annual grasses	Drought and increased fuel source lead to increased fire which causes a loss of native shrubs in areas not adapted to fire	Synergistic	Nutrients, changing precipitation patterns, disturbance	Species competition, Species functional traits, N
Rao et al. 2010; Rao and Allen 2010; Fenn et al. 2010							
NW Forested Mountains	Alpine	N deposition has been associated with greater frost sensitivity	Earlier snowmelt and earlier starts to the growing season increases plant exposure to killing frosts	Combination of more frequent frosts and greater plant sensitivity to those frosts can cause greater mortality	Synergistic or antagonistic, depending on system and taxa	Bioclimatic envelope (freezing events)	Species functional traits, N
Inouye 2008							
Mediterranean California	California Coastal Sage Scrub	N fertilization promotes growth of non-native annual grasses that prevent	Altered precipitation patterns allow increased growth of ?exotic annual	N promotes shift from shrubs to grasslands in CA coastal sage scrub communities, resulting	Synergistic	Nutrients	Bioclimatic envelope, Species functional traits, N

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percolation of rainwater to shrub rooting zones suppressing shrub establishment and growth

grasses

in change in hydrological regime that exacerbates shrubland conversion

Wood et al. 2006

NW Forested Mountains	Rockies Lakes	Nitrate released from melting glaciers increases N loading to alpine lakes	Melting of glaciers increases water flux and releases stored nitrate	Increased N loads result in shifts in lake diatom communities	Synergistic	Nutrients	Hydrology, species functional traits
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Baron et al. 2009; Saros et al. 2010

Region: Coastal (Northeast)							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Eastern temperate Forests	New England and Chesapeake Bay estuaries	N loading lead to a significant decline of eelgrass coverage, and almost all eelgrass habitats were lost at high loading levels	Changes in the nitrogen loading and concentrations	N loading changes result in reduction in eel grass communities, which is an important foundation of the estuarine structure and function. Increases in harmful algal blooms in Hudson.	Synergistic	Nutrients	Species functional traits

Latimer and Rego 2010; Najjar et al. 2010

Eastern temperate forests	NE estuary	Increased N loads can lead to coastal eutrophication, harmful algal blooms and hypoxia	Changes in delivery of nutrient loads and concentrations	Eutrophication and HABs in Hudson River estuary during low flow years; Could be accompanied by hypoxia	Synergistic	Nutrients	N, species interactions, bioclimatic envelope
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Howarth et al. 2000

6: Nitrogen, Climate Change and Biodiversity

Region: Coastal (Southeast)							
Level I Ecoregion	Ecosystem	Effect of increasing N	Effect of changing climate	Interactive impacts on Biodiversity	Nature of N x CC interaction	Primary factor	Other Important Factors
Eastern temperate forests	SE Estuary	Increased N loads can lead to coastal eutrophication, harmful algal blooms and hypoxia	Changes in delivery of nutrient loads and concentrations	Eutrophication and HABs in NC estuaries during low flow years; Could be accompanied by hypoxia	Synergistic	Nutrients	N, toxicity, species interactions
Paerl 2006							
Eastern Temperate forests and Great Plains	GOM estuary	Higher flow leads to more delivery of N; higher concentrations during low flow periods	Changes in delivery of nutrient loads and concentrations	GOM hypoxia extent varies with climate and N load; this in turn affects species composition and distribution	Additive - Synergistic	Nutrients	N, toxicity
Donner and Scavia 2007							

Forests:

Some forest ecosystems are sensitive to the interactions between N and climate change, and many of the interactions are synergistic. Anthropogenic increases in N loading to forests are usually mainly via atmospheric deposition, and thus regions with higher N deposition are more at risk (see Section 4 for more specific discussions of risk and vulnerability). Across the Northeastern US, higher N deposition is associated with enhanced tree growth for most species (Thomas et al. 2010). Nitrogen loading preferentially affects certain species as a consequence of species traits, and in some cases alters the bioclimatic envelope of these species, causing them to be more sensitive to climate change. For example, increased N stimulates leaf area growth, which has been speculated to reduce drought resistance (McNulty and Boggs 2010). Increased N also contributes to soil acidification and subsequent loss of base cations, including calcium. Decreased calcium availability can compromise plant cell membrane integrity, thereby decreasing cold tolerance and increasing the potential for freezing injury (DeHayes et al. 1999; Schaberg 2002). Thus N and climate change interact to alter species composition through drought or frost damage, driven by the plants' response to increased N.

Moreover, much of the biodiversity of forests is in the understory herb and shrub layer rather than in the overstory tree layer (Gilliam 2006). These taxa are poorly studied in the literature, but sensitivity to N deposition and interactions with climate change are likely (Gilliam 2006, Wu and Driscoll 2010).

Tundra: In the Arctic, warming has contributed to dramatic increases in shrub cover, as documented by aerial photographs at thousands of locations between the Brooks Range and the Arctic Coast in 1948-1950 and later in 1999-2000 (Sturm et al. 2001). This has led to a shift in community type from more open graminoid ecosystems to areas dominated by shrubs. Experiments at the Toolik Lake Arctic LTER site confirmed that elevated temperature enhanced shrub production and reduced production of nonvascular plants. Elevated N increased growth and production of deciduous shrubs but reduced growth of evergreen shrubs and nonvascular plants, while combined N and temperature treatments reduced species richness 30-50 percent due to loss of less abundant species (Chapin et al. 1995).

Grasslands: Grasslands are likely to be especially sensitive to changes in N and climate for many reasons. Compared with forests, grasslands are dominated by plants that have a strong capacity for rapid changes in growth (Knapp and Smith 2001). Grasslands are often limited by N availability, or co-limited by N and other resources such as water or P (Elser et al. 2007, Hooper and Johnson 1999, LeBauer and Treseder 2008). Changes in growth and increased production from N enrichment are strong predictors of biodiversity decline (Clark et al 2007). Increases in precipitation may increase ecosystem sensitivity to N deposition by enhancing primary limitation from N, suggesting that future N deposition will have a larger effect over those parts of the US that are likely to experience greater precipitation (Rao et al. 2010). Additionally, impacts from N enrichment could be counterbalanced by elevated concentrations of CO₂, which reduce N cycling in ecosystems and enhance soil water availability through reduced plant transpiration (Luo, et al. 2004).

Despite being better-studied than most biomes, empirical evidence is scarce on the interactive effects of different drivers of diversity in grasslands. Generally, experimental N additions to grasslands result in substantial reductions in species diversity and greater losses in areas that are not also limited by other resources such as water (Bobbink et al. 1998; Clark et al. 2007; Bobbink, et al. 2010). In an experiment in annual Mediterranean grassland in California, where N, temperature, precipitation, and CO₂ were altered, the effects of these factors were additive, and the total effect led to a large loss of plant species, especially forbs (Zavaleta et al. 2003c). In an experiment in temperate perennial grassland in northern Minnesota, where CO₂ and N levels were altered, the reduction in diversity (mostly forbs) due to N addition was partly mitigated by elevated CO₂ because elevated CO₂ reduced soil N and increased soil moisture (Reich 2009). Thus, grassland diversity is likely to be sensitive to changes in N and climate, but the exact nature of these changes can vary from system to system.

Drylands: Plant growth is primarily constrained by water availability in arid systems (Noy-Meir 1973). However, when this constraint is lifted by increased precipitation, N limitation becomes increasingly important (Brooks 2003, Allen et al. 2009, Rao et al. 2010). In Joshua Tree National Park, N addition experiments increased non-native grass biomass and, where non-native grass biomass was high, N decreased native forb species richness (Allen et al. 2009). In areas of the Mojave and Sonoran Deserts in southern California, a series of years with higher-than-average rainfall coupled with increased N deposition from the Los Angeles Basin has promoted the growth of invasive Mediterranean grasses, creating a nearly-continuous fuel layer in arid shrublands (Brooks and Minnich 2006, Rao et al. 2010). Fire frequency has increased, as has fire occurrence in areas previously unburned and unadapted to fire (Rao et al. 2010). Native shrubs may not be able to re-establish in these areas, as invasive grasses change the hydrology of the area, removing rainwater from the top layers of the soil thereby preventing its percolation into the root zone of young shrubs (Wood et al. 2006).

Nitrogen can exacerbate drought stress in drylands. In pinyon-juniper woodland of New Mexico, N fertilization decreased mycorrhizae and increased leaf production in pinyon pine, leading to increased drought-induced mortality (Allen et al. 2010).

Wetlands: Changes in N availability and climate may strongly impact species composition and biodiversity in wetlands (Greaver et al. 2011). Nitrogen is the limiting nutrient for plant growth in both freshwater and estuarine wetlands (LeBauer and Treseder 2008). Despite the high biodiversity in wetlands (USDA 2009), the effects of N loading are studied in a limited number of plant species. Increased N availability or inputs may preferentially increase the growth of certain species, and since not all species respond equally, this may cause species dominance and composition to change. Sensitivity to N deposition in wetlands is generally thought to follow the pattern: bogs > fens, marshes, swamps > intertidal wetlands, representing the gradient from very low N conditions to very high N conditions. Because bogs receive nutrients exclusively from precipitation, they tend to be most sensitive wetland type to N deposition (Morris 1991). Other wetland types can be vulnerable to anthropogenic N enhancement from deposition as well as agricultural runoff via subsurface or surface waters. A recent study in a brackish marsh in Maryland found that N-induced shifts in biodiversity from C₃ to C₄ species altered the community response to CO₂ (Langley and Megonial, 2010). It has been shown that N loading can increase decomposition rates of organic matter and therefore, C loss, from salt marsh soils (Wigand et al. 2009). This could lead to degradation of the marsh structure and greater susceptibility to sea level increases.

Freshwater Systems: Human-driven biodiversity declines are expected to be far greater in freshwater than in terrestrial ecosystems (Sala et al. 2000). Aquatic ecosystems receive water and pollutants from the surrounding catchment, and lose water through landscape-scale withdrawals, and thus are particularly sensitive to anthropogenic change (Dudgeon et al. 2006). Freshwater ecosystems have been described as biological assets that are both disproportionately rich in diversity and disproportionately imperiled (Abramovitz 1996), and the combination of habitat loss, homogenization of flow regimes, and eutrophication has had drastic consequences on native freshwater organisms, including fishes, shellfish, and benthic invertebrates. About 37% of aquatic animal and 62% of aquatic plant species are considered at risk in the US (Heinz Center 2008, Baron et al. 2002). Climate change has dramatic consequences for freshwaters because dissolved oxygen levels are sensitive to temperature, and flow changes can alter the concentrations and/or fluxes of nutrients. Many of the examples we identified in Table 6.1 for aquatic ecosystems involve synergistic interactions between N supply and climate change. For example, increases in temperature and changes in the timing and distribution of precipitation may exacerbate eutrophication and hypoxia in many ecosystems, particularly estuaries and coastal receiving waters.

Current levels of N in freshwaters and estuaries are a significant part of the problem by promoting noxious and harmful algal blooms, simplifying food webs, and creating favorable conditions for non-native species (Heinz Center 2008). Warming, too, may promote local extirpation or migration of cold-obligate species and invasion of non-native species (Rahel and Olden 2008). Water temperature directly regulates oxygen concentrations, metabolic rates, and associated life processes. The thermal regime influences fitness and the distribution of species in both space (e.g., latitudinal and altitudinal gradients) and time (e.g., seasonal variation at a single location) (Baron et al. 2002). A survey of remote arctic and alpine lakes of North America and Greenland found that diversity of algal diatom assemblages has changed in these regions more significantly in the 20th century than in the previous 350 years. Hobbs and colleagues (2010) noted that the greatest changes occurred in areas of most rapid warming (i.e., the Arctic) and areas with N deposition rates significantly elevated over natural background rates (i.e.,

alpine lakes), and predicted that diversity in remote lakes will continue to change, particularly in regions where climate change and N deposition interact. Whether from climate change, N availability, or both, the negative effect on biodiversity is expected to continue in the future.

Marine Systems: Climate change can alter the responses of coastal waters to N pollution in the form of hypoxia, eutrophication, and harmful algal blooms (HABs) toxic to marine fish and wildlife and humans. Coastal ecosystems can become more or less sensitive to N pollution due to climate-driven changes in: a) water residence time as it affects the time for phytoplankton blooms to occur; b) ocean currents, as they affect the oxygen levels and nutrient content of water entering estuaries from the ocean; c) stratification, which is driven by changes in temperature, freshwater discharge, winds and storms; and d) ecological structure that is driven by temperature or a-c above. Examples of both enhanced and reduced sensitivity to N have been demonstrated for these cases. For instance, New York Harbor estuary has experienced greater occurrences of algal blooms and become much more eutrophic, as water residence times in summer have increased as a result of less winter snowpack in the Adirondack Mountains (Howarth et al. 1998). The St. Lawrence Estuary and Gulf of St. Lawrence have become more sensitive to N-induced hypoxia in recent years, as their bottom waters now come more from the deep Atlantic water, already low in oxygen, and less from the Labrador Current (Gilbert et al. 2005, Howarth et al. 2011). Due to greater stratification, productivity in the Dead Zone area in the Gulf of Mexico has become co-limited by P, causing less N uptake, -cycling, and -loss in coastal environments and greater transport of Nr to deeper waters (Sylvan et al. 2006, Donner and Scavia 2007).

Several aspects of climate change that favor HABs include: longer periods of warm temperatures, increased intensity of vertical stratification, increased salinization, and increased intensity of storms and drought frequency and duration (Paerl and Scott 2010). Storms can increase nutrient loads to coastal zones, and droughts increase residence times, retaining nutrients and exacerbating algal blooms. A number of estuaries have experienced hypoxia and HABs associated with altered nutrient loads during certain key seasonal periods (Howarth et al. 2000; Paerl 2006). Harmful algal blooms can dramatically alter ecosystem biodiversity, and influence recreation, fisheries and a host of other ecosystem services (Compton et al. 2011).

Oceans are also sensitive to atmospheric CO₂ enrichment and climate change, with acidification and coral bleaching affecting coral reefs and other vulnerable ecosystems. Chronic stresses, such as nutrient loading, may make it more difficult for corals to adapt to climate impacts (Scavia et al. 2002). Eutrophication and warming, and associated hypoxia and anoxia, can greatly exacerbate ocean acidification because the respiration that drives oxygen consumption produces high levels of dissolved inorganic C, including CO₂ gas. The resulting acidification harms calcifying organisms such as mollusks and some crustaceans (Howarth et al. 2011).

6.3 EVALUATING RISKS FROM NITROGEN ENRICHMENT AND CLIMATE CHANGE ON BIODIVERSITY

In order to evaluate the risks from N enrichment and climate change on biodiversity, we must consider both the exposure and the sensitivity of ecosystems or regions to these two drivers. One tool for evaluating the susceptibility of ecosystems to detrimental effects of elevated N deposition is the critical load (CL). A CL is the N deposition below which no harmful ecological effect occurs over the long term, according to present knowledge (UBA, 2004). Empirical CLs (i.e., determined from experiments or observations along N deposition gradients) for N have been defined for specific areas, such as national parks (Baron 2006; Bowman et al. 2006, Rao et al. 2010). Empirical CLs have also been defined for ecoregions across the continental US for various responses including biodiversity or responses which

could influence biodiversity (such as shifts in N availability, tissue N concentration, responses to secondary stressors, etc.) (Pardo et al. 2011a, Pardo et al. 2011b). Exceedance of the CL indicates regions at risk for detrimental effects from N deposition (Figure 6.5). When the CL has been exceeded over many years or by a large amount, initial changes in biodiversity are more likely to have already occurred; the impact of additional N deposition may further alter the species composition and biodiversity. When the deposition is near the CL, the risk of initial changes in biodiversity may be highest as was reported in the European Nitrogen Assessment (Dise et al. 2011). The extent and degree of detrimental impact varies by ecoregion and receptor (i.e., fungi, lichens, herbaceous species), but areas of exceedance occur in each ecoregion for which CLs were reported.

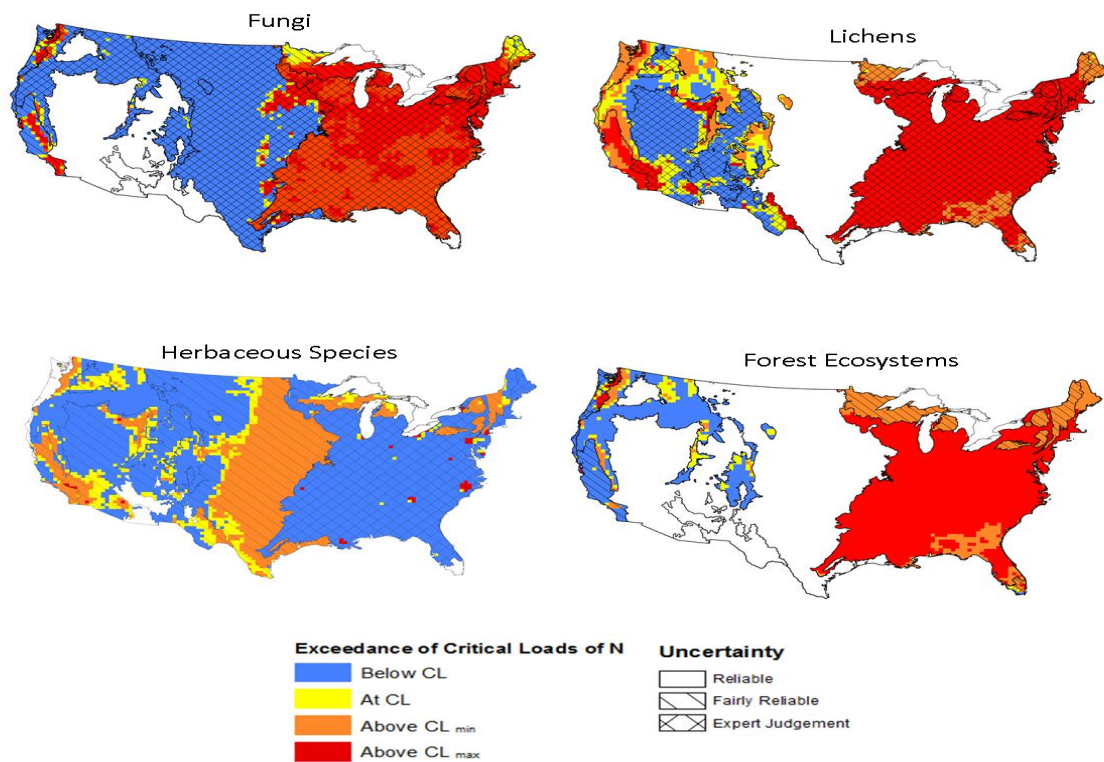


Figure 6.5: Map of exceedance of critical load for nitrogen for mycorrhizal fungi, lichens, herbaceous species and shrubs, and forest ecosystems in the continental U.S. . Exceedance was calculated by subtracting critical loads from modeled nitrogen deposition. Exceedance is shown for several categories: 1) No exceedance (Below CL), when deposition is lower than the critical load range, 2) At CL, when deposition is within +/-1 of the critical load range, 3) Above CL_{min}, when deposition is above the lower end of the critical load range, but lower than the upper end of the range, 4) Above CL_{max}, when deposition is above the upper end of the critical load range. White areas lack data for critical loads determination. The hatch marks indicate increasing level of uncertainty: no hatch marks for the most certain “reliable” category, single hatching for the “fairly reliable” category and cross-hatching for the “expert judgment” category (adapted from Pardo et al. 2011b).

The greatest risks to biodiversity from N and climate change might be expected to occur where exceedance is high, climate change will be greatest, and responses are additive or amplifying. For example, in tundra ecosystems in Alaska where increasing temperature is likely to increase N availability further, impacts on biodiversity are likely to accelerate (Chapin et al. 1995, Chapin and Shaver 1996, Shaver et al. 2001). In addition to increases in temperature and precipitation volume, shifts in seasonal patterns in frequency and intensity of precipitation (including drought) may cause significant interactions with N enrichment and, ultimately, impact biodiversity. Given the complexity both in the types of changes in climate and their interactions with N enrichment in various ecosystems and for multiple species, dynamic modeling will be necessary to assess which ecosystems face the highest the risk of detrimental effects.

6.3.1 Summary of risk by regions to climate-N interactions

This section addresses the risk to biodiversity from climate-N interactions, synthesized by region. The climate information is drawn from the 2009 regional climate impacts section of the National Climate Assessment (NCA 2009). The information on N and climate-N interactions is from Table 2, which presents an overview of the climate, N and climate-N impacts in major ecosystems of the US, with corresponding literature.

Northeast: Forests, lakes, wetlands and a number of estuaries dominate this region, along with a high density of urbanization. Reduced snowpack, longer and more frequent summer droughts, higher mean annual temperatures, higher average total precipitation, and more intense storms are expected for the forest and aquatic ecosystems that predominate the northeastern US. Fire (which is not common in the Northeast) and pest outbreaks are both expected to increase, impacting species composition. Nitrogen deposition is the highest for this US region due to a higher concentration of transportation and power generation activities. Much of the N deposited is in oxidized rather than reduced form, and remains above the critical load even though N deposition has been declining in recent decades.

Changes in terrestrial biodiversity for this ecoregion are likely slow due to the predominance of trees, but alterations in growth and survival due to N deposition have been reported (Thomas et al 2010). Changes in understory species and in soil biodiversity due to N deposition may have already occurred in this area (Gilliam 2006, Hurd et al. 1998). Changes in aquatic biodiversity for this ecoregion also have been reported (e.g., Howarth et al 2011), and will likely continue to shift. Key interactions for the forests in this region include N-driven reductions in freezing tolerance (Schaberg et al. 2002), which will have amplified impacts since the duration and extent of the protective snow layer is expected to decrease under climate change. Finally, higher and more intense precipitation may exacerbate N-induced ion imbalances in terrestrial plants, as more nutrient cations are leached from the rooting zone. In turn these nutrient cations, when leached into surface waters, will exacerbate the eutrophying impact of N on aquatic ecosystems. Eutrophication of lakes and estuaries in this region is currently relatively high: this will likely be amplified under climate change, with a greater extent and duration of hypoxic events in impacted systems.

Southeast: The Southeastern US is dominated inland by broadleaf and mixed forests that are some of the most diverse in North America, as well as by large coastal wetlands and marshes. Climate in this region is expected to continue to warm especially in the winter, and continue to get drier especially in the spring and summer months, with more intense storms overall (Karl et al 2009). Fire, drought and insect outbreaks are expected to be more prevalent with climate change. Despite the fact that N deposition levels are lower than in the Northeast, many regions of the Southeast experience N

deposition at levels that may affect biodiversity (Pardo et al 2011a, Pardo et al. 2011b).

Nitrogen deposition is more balanced between oxidized and reduced forms compared with the Northeast or Midwest because of the combined influences of industry and agriculture in the Southeast, though the majority still falls as oxidized N. Key interactions for terrestrial ecosystems in this region include a potential increase in susceptibility to drought and pests. Increased aboveground growth in N-limited systems may also make them more prone to fire. The Southeast is not expected to dry to levels more common in co-limited (N and water) environments in the western Great Plains, making N limitation likely to continue, and thus N sensitivity to remain.

Key interactions for aquatic ecosystems include a potential decrease in long-term average N loads from decreased precipitation, punctuated with large synoptic flushes of N from increased storm events and intensities. It is unknown how the impacts from these contrasting factors will play out for aquatic biodiversity. Climate change is expected to result in sea level rise and increased flooding of coastal areas in this region, and the interaction with N may exacerbate eutrophication in these areas. Recent work has also shown that eutrophication may exacerbate coastal acidification in these areas (Cai et al. 2011), illustrating a synergistic interaction between climate and N loads.

Midwest and Great Plains: Rangeland, farmland, and grassland dominate much of this region. Because of the favorable conditions for agriculture, many natural systems have been converted for human use, and only fragmented and dispersed natural habitats remain (Pardo et al 2011a, Pardo et al 2011b). The remaining natural ecosystems that are already under stress are anticipated to become warmer and wetter, which could intensify N limitation and sensitivity to N. Deposition of N in this area, is moderate, declining from east to west, and dominated by reduced forms of N, ammonia (NH_3) and ammonium (NH_4^+), due to the abundance of agriculture. Key interactions for these systems include decreased co-limitation by water and N, and increased preponderance of limitation by N (Clark et al 2007). This could increase stresses on plant biodiversity from increased plant growth and competition.

Important wetlands and lakes in this region are expected to undergo synergistic interactions between N and climate change, where warmer, wetter conditions could increase nutrient loading to aquatic ecosystems, leading to higher levels of eutrophication and low oxygen conditions. Many wetlands in this region provide important habitats for migrating waterfowl. Forests and alpine systems dominate the western portions of this region in the mountainous areas of Wyoming and Montana. Earlier snowmelt associated with elevated temperatures has been shown to harm some species of wildflowers through increased frost damage (Inouye et al 2008). Although current N deposition to these regions is generally low, frost damage might be expected to be enhanced with increased N deposition due to increased growth aboveground exposing more tissue to cold stress.

Northwest: Forests generally dominate the Northwestern region with agriculture in many river valleys, and steppe in drylands. Rivers and coastal ecosystems play an important role in the local economy. Elevated temperatures in the Northwest will lead to greater winter precipitation as rain, decreased snowpack, reduced stream flows in the summer, and reduced water availability during peak plant growth periods (Karl et al 2009). These hydrologic changes are expected to alter aquatic communities and drive declines in fish, especially cold-water species such as salmon. Stream networks are likely to constrict with lower summer water conditions, threatening the integrity of aquatic ecosystems, although increased total precipitation may offset some of these changes.

Inputs of N are lower in the Northwest on average than the Eastern US, though some aquatic and terrestrial ecosystems in the region are stressed in areas dominated by agriculture and industry. For example, increasing N deposition in areas around large cities is already affecting lichen community composition in the Northwest (Geiser et al. 2010). Key interactions in this region include the increased frost damage from earlier snowmelt combined with N deposition (already observed in the Rockies as described above), greater total precipitation and storm intensities delivering larger amounts of N to aquatic systems, possible shifts in forest tree composition from longer growing seasons and N deposition as observed in the east (Thomas et al 2010), and increased pest damage from populations feeding on more N-rich tissue in a warmer environment. Changes in climate and in N loading may impact coastal fisheries, although the dynamics of ocean currents play a large role in the coastal ecosystems, and current research indicates that the extent and duration of coastal hypoxic zones are influenced by ocean circulation (Chan et al. 2008). Also, in some Pacific Northwest coastal systems, it has been observed that watershed derived nutrients can acidify coastal waters at a faster rate than atmospheric CO₂ alone (Kelly et al. 2011).

Southwest: Climate change in the forest and desert ecosystems in the Southwestern US is expected to lead to increased temperatures, decreased precipitation, and increased droughts and extreme events (Karl et al 2009). This will likely make them more susceptible to fire and pests. Nitrogen deposition, although not as extensive by comparison with the east, is high nearer to urban and agricultural areas (Fenn et al. 2003), and will likely contribute to climate-driven increases in fire frequency (through increased grass growth in shrub interspaces) and pest stresses (through increased tissue N). An additional key interaction is air quality, which is already poor in this region. Climate change and increased N will continue to result in high ozone levels in the mountains near large cities in California and other Southwestern cities.

Alaska: Alaska is expected to have large changes in climate, but the changes in N loading are not expected to be significant in the future, except possibly in concentrated areas around cities or ports. The potential impacts related to climate-N interactions are likely to be from alterations of the internal N cycle, for example, increasing decomposition rates, increasing N availability and shifting competitive balances. In addition, because critical loads are so low for some of these low- biomass systems, small increases in N deposition could result in significant changes (Pardo et al. 2011a, Pardo et al. 2011b).

Coasts: Aquatic ecosystems, particularly coastal systems, are at high risk for impacts on biodiversity driven by interacting climate change and N inputs. Warmer conditions and higher nutrients will generally lead to increases in aquatic production, eutrophication and decreased dissolved oxygen levels. Eutrophication of N-limited systems in turn will be exacerbated in the warmer conditions with lower water levels. Wetlands and lakes also are at risk for altering biodiversity due to contracting water networks and increased eutrophication. Eelgrass decline has also been associated with high nutrients and eutrophication, and will alter aquatic habitat space and the distribution and abundance of the species that use those areas (Latimer and Rego 2010).

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Table 6.2: Impacts of nitrogen, climate and nitrogen-climate (N_xCC) interactions for major ecosystems in the US.

Ecosystem	Major Impacts of Climate Change (NCA 2009)	Major impacts of N	Nitrogen References	Impacts of N +CC	N+CC References
Tundra	More rapid climate change that rest of US, Longer growing season, permafrost warming, changes in soil temperature and moisture, increased fire	Increased productivity, shifts towards graminoids and shrubs from bryophytes and lichens, increased decomposition	Shaver et al. 1998; Nowinski et al. 2008; Arens et al 2008, van Wijk et al 2004, Cornelissen et al. 2001	Additive - both increase N availability, warming increases nitrogen mineralization, increasing shrubs trap more snow, wetness decreases sensitivity to N	
Taiga	More rapid climate change that rest of US, Increase in pest outbreaks and fire, Longer growing season, permafrost warming and forest declines, changes in soil temperature and moisture, increased fire frequency increases, drier soils	Increased decomposition, shift in species composition (from shrubs to grasses; lichen community composition)	Aerts and Chapin, 2000, Gough et al. 2000, Nordin et al. 2005, Geiser and Nadelhoffer 2011	Increasing Temperature and N -> increase in green algae	
Alpine	Shorter duration of snowpack, longer growing season, increased exposure to freezing events, movement of invasive species into alpine area	Alteration of species, decreased diversity and whole community composition	Bowman et al 2006, Bowman and Steltzer 1998	Additive - warming will increase nutrient supply, greater species pool combined with higher N makes it a more infeasible system	
Conifer forests	Southeast - Longer growing seasons; Hotter summers and drought; Reduced forest production under drought; Reduced snowpack; Increased fire, pest outbreaks, hurricanes and flooding; Range shifts	Shifts in understory herbaceous species composition, shifts in microbial assemblages	Thomas et al. 2010, Lilleskov et al. 2008	N dep and productivity (C sequestration)--species specific; drought, elevated tissue N and pest susceptibility. N increases susceptibility to disease, to abiotic stresses--> shifts in species composition	McNulty and Boggs 2010

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Hardwood forests	Northeast - Longer growing seasons; Hotter summers and drought; Increased fire, ice storm, heavy precipitation, extreme events; Flooding; Shorter snowpack, increased exposure to freezing events, Range shifts	Shifts in understory herbaceous species composition, shifts in microbial assemblages	Thomas et al. 2010, Gilliam et al. 2006, Hurd et al. 1998	N dep and productivity (C sequestration)--species specific; drought, elevated tissue N and pest susceptibility. N increases susceptibility to disease, to abiotic stresses--> shifts in species composition	Halman et al. 2011
Grasslands	Longer growing season, warmer, wetter--> greater biomass production, potential for increased fire intensity, impacts on dispersal because of prior fragmentation, Range shifts, spread of pests and weeds.	Compositional shifts towards fast-growing (often C3) grasses, structurally simplified, increased competition for light, alter microbial assemblages, reduced insect diversity and shift towards generalists	Tilman 1993, Wedin and Tilman 1996, Clark and Tilman 2008	Warmer, wetter-->intensify N limitation (which could lead to a greater impact if soil N availability is low or a smaller impact if soil N availability increases with CC, reduce water limitation), interaction of elevated CO2 +N may reduce species loss from elevated N input alone	Knapp et al. 1993, 1996, 1998
Deserts	Reductions in water supply. Increased temperature, drought, fire and invasive species will affect the landscape.	Alterations in species composition, increases in exotic species biomass, decrease in native species	Allen et al. 2009, Rao and Allen 2010, Rao et al. 2010	Increased N deposition leading to increased biomass accumulation, increasing fire frequency	Brooks et al. 2004, Brooks and Matchett 2006
Shrublands	Decreased precipitation, increased temperature, more storms, increased fire. Increased die-off of pinyon pine and alteration of pine-rich biodiversity hot spots. Range shifts, spread of invasive species.	N addition decreasing soil moisture in sagebrush steppe. Air quality in the southwest expected to decline. Ozone and other pollutants can impact these ecosystems. Increase in invasive species, decrease in shrub cover and native species.	Inouye 2006, Fenn et al. 2010	NxCC may interact to lead to even drier soils and increased fire	

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<p>Wetlands</p>	<p>Intense droughts in the northeast and especially southeast, leading to local or global extinctions.; flooding and sea level rise; Decline in dissolved oxygen leading to loss of aquatic species.</p>	<p>Nitrogen generally increases production and decreases diversity, particularly in high N load setting like coastal zone (sea grass decline); invasion of non-native species, altered competition, loss of N-sensitive species like eelgrass</p>	<p>Aldous 2002, Bedford et al. 1999, Darby and Turner 2008a, 2008b, Mendelssohn 1979, Tyler et al. 2007, Wigand et al. 2003, Tyler et al. 2007, Crain 2007, Mendelssohn 1979, Wigand et al. 2003, Latimer and Rego 2010</p>	<p>Drying and increases in anthropogenic nitrogen will together strongly alter and likely reduce biodiversity. In freshwater wetlands, N inputs increase CH4 and N2O production</p>	<p>Liu and Greaver 2009</p>
<p>Lakes</p>	<p>Lakes are projected to shrink and become less connected with warming and decreasing flow; so less habitat aquatic habitat overall (happening quickly in Alaska where migrating birds are at risk). Decreases in extent and duration of lake ice; Snowmelt changes and extreme events increase. Residence times and turnover may change as well leading to more intense stratification and fish kills.</p>	<p>In N-limited systems, productivity increases, diatom communities are altered; hypoxia will have even more pronounced impacts on biodiversity</p>	<p>Kelly et al. 2011</p>	<p>NxCC driven shifts in composition and productivity, possible eutrophication and hypoxia</p>	<p>Kelly et al. 2011</p>

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Streams	River networks may shrink and become less connected with warming and decreasing flow; so less habitat aquatic habitat overall. Reductions in snowpack alter runoff timing. Salmon and other coldwater species will experience additional stresses from temperature. Increases in extreme events such as flooding will also affect biodiversity and trophic structure.	In N-limited systems, eutrophication and subsequent alteration of species composition; hypoxia will have even more pronounced impacts on biodiversity	(see Table 1)	NxCC driven shifts in composition and productivity, possible eutrophication and hypoxia	(see table 1)
Estuarine and Near-Coastal Ocean	Changes in flow amount and timing, and estuarine residence time and turnover impact species composition. Ocean acidification. Sea level rise is eroding shorelines. Reduced sea ice in Alaska alters blooms and fish stocks. Displaced marine species and shifts. Changes in currents may increase extent and duration of northern Pacific Dead zone.	N drives eutrophication in many coastal systems, affecting structure and biodiversity	(see Table 1)	NxCC driven eutrophication and hypoxia; Eutrophication can increase the susceptibility to acidification	NxCC driven eutrophication and hypoxia; Eutrophication can increase the susceptibility to acidification

6.4 MODELING

Various approaches have been used to estimate changes in biodiversity due to climate change and typically couple indirect drivers of biodiversity (e.g., population growth, fossil fuel use), direct drivers (e.g., climate, pollution, land-use change), and biodiversity models (e.g., dynamic vegetation models, niche models, and dose-response relationships) (Pereira et al. 2010). Species distribution models (SDMs), that relate field observations to environmental variables, have been widely used to forecast the impacts on biodiversity from a variety of stressors, including climate change. These niche-based models predict the potential distribution of species based on the species' bioclimatic envelope, sometimes integrated with limiting factors of dispersal, disturbance, and resource availability (Guisan and Thuiller, 2005). Process-based models, on the other hand, incorporate the underlying mechanisms that influence species response, such as N and C cycling in soils. Some of these models can also simulate changes in ecosystems over time due to changes in temperature and precipitation, making them useful for studying possible responses associated with climate change (Dise et al. 2011).

Linking process-based models to niche-based models may be particularly important for improving forecasts of plant distribution (Keenan et al. 2011). The ForSAFE-VEG model links the dynamic soil biogeochemistry model ForSAFE with the plant response model VEG to forecast changes in plant communities from impact of N deposition and climate change, and has been tested in the EU in Sweden and Switzerland (Sverdrup et al. 2007; Belyazid et al. 2011) and in the US Rocky Mountains (Sverdrup et al. 2012). For a generalized plant community in the US Rocky Mountains, the model suggests that N has exacerbated reductions in biodiversity expected from climate change alone (Figure 6.6; Sverdrup et al. 2012). In Britain, the MAGIC model (Model of Acidification of Groundwater in Catchments; Cosby et al. 2001), which focuses on acid-base relationships but includes an N module, has been linked with a plant niche model to simulate plant community changes with N and climate change (Rowe et al. 2005). Another biogeochemical model, the PnET-BGC (has been used in the US to simulate soil and vegetation dynamics under various scenarios of N and sulfur deposition and climate change (Wu and Driscoll 2010). In addition the DayCent-Chem (daily version of the CENTURY model) model has also been used to simulate daily surface water and ecosystem responses to N and sulfur and climate change (Hartman et al. 2007).

Models are always limited by available data on ecosystem response, and the scale of that data. But ForSAFE-VEG (a model that simulates soil chemistry, C and N cycling, tree growth, geochemistry, and ground vegetation response) and other models show promise as tools to forecast N and climate change interactions, and are likely to be used more widely as the ecosystem response data needed to calibrate the models become available.

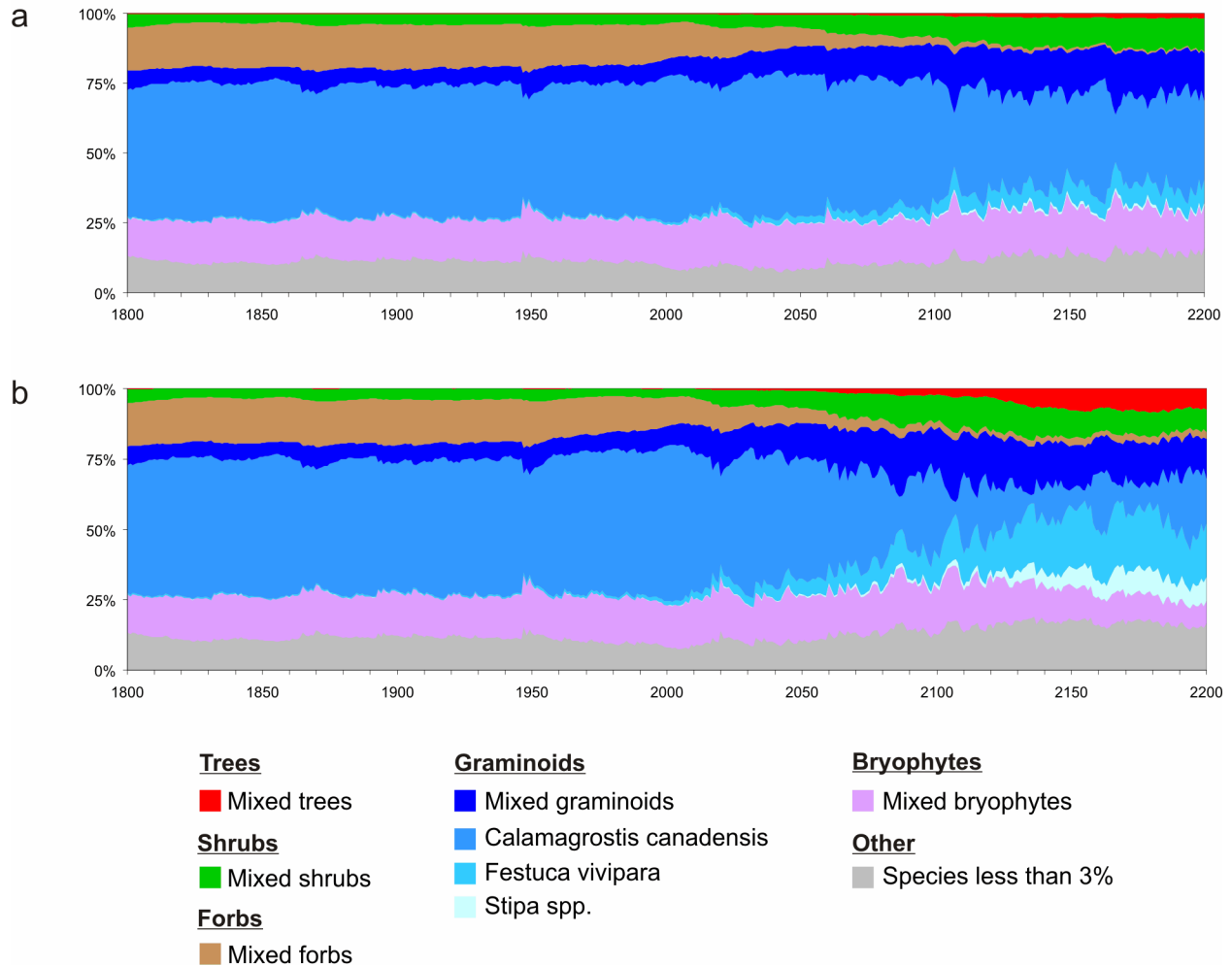


Figure 6.6: ForSAFE-VEG model simulations for plant life form coverage based on the IPCC climate change scenario A2 for the Rocky Mountain region and a) estimated background S and N deposition and b) elevated future atmospheric N deposition (modified from Sverdrup et al. 2012).

6.5 MANAGEMENT AND POLICY OPTIONS FOR REDUCING IMPACTS ON BIODIVERSITY

There are several ways that management and policy may alleviate the interactive effects of climate change and excess N on biodiversity. As a foundation, there must be sufficient understanding of how much and where (1) N is being deposited, and (2) climate is changing. For the former, national monitoring networks (e.g., National Atmospheric Deposition Program – NADP; Clean Air Status and Trends Network -CASTNET) and dynamic atmospheric models (e.g., Community Multi-scale Air Quality - CMAQ), have been developed to generate national estimates of N deposition (Weathers and Lynch 2011). These tools are critical in developing action plans to manage impacts on biodiversity. However, there are still significant limitations including sparse coverage nationally especially for remote and mountainous areas, lack of monitoring for some N species altogether (e.g., organic N), and poor sampling or infrequent sampling for some processes (e.g., dry and fog deposition). Other limitations for the models include incomplete process modeling (e.g., cloud deposition, bidirectional N flows) and incomplete calibration (Weathers et al. 2006, Pardo et al. 2011b, and Chapter 7). For the latter, the US

Global Change Research Program has developed comprehensive reports (in 2000, 2009, and scheduled for 2013) that synthesize the state of knowledge from multiple Agency and non-Agency national and international efforts on how and where climate is changing and expected to change in the future for the US (Karl et al. 2009).

Appropriate actions for managing the interactive impacts on biodiversity from N and climate change depend largely on the dominant mechanism driving biodiversity change. First and foremost is reducing the emissions of N to the environment that are subsequently transported to and deposited on potentially sensitive systems. Several approaches have been proposed (e.g., US EPA 2011) that depend largely on the source of emissions, whether agricultural- or fossil fuel combustion-based. At the other end of the management spectrum are interventions in impacted areas. Reduction of N inputs and the restoration of N and other soil resource conditions will not necessarily guarantee that the original species will return. Species may no longer be present in the degraded habitat or able to disperse there over a fragmented landscape. Seeds of many target grassland species of high biodiversity value are known not to remain viable for more than a few years to a decade in the seed bank (Thompson et al. 1998), suggesting that historical N deposition over the past 50 years could have dramatically altered seed availability to systems thereby necessitating seed addition. This replanting is commonly termed “assisted migration” in the climate literature (IPCC -2007), and may be required for systems where the dominant driver of biodiversity change is climate-induced shifts in range.

In addition to reducing N inputs into ecosystems, several approaches have been proposed to reduce N stores and cycling, including increasing N export through harvesting, turf removal, or fire, increasing N leaching through flushing with aqueous solutions, and decreasing N availability through the addition of C (Bakker and Berendse 1999, Blumenthal et al. 2003, Jordan et al. 2003). Some of these approaches may only redistribute existing N rather than removing it such as through denitrification (Galloway et al. 2003). For systems in which N-induced soil acidification dominates, addition of soil amendments (e.g., lime, magnesium) may be used to increase soil pH, inhibit NH_4^+ accumulation, and restore nutrient balances (Bakker and Berendse 1999, Dise et al. 2011). However, aggressive strategies such as biomass removal and soil amendments have limited usefulness because such treatments require periodic application to be effective and are costly and labor intensive, and in some areas may be prohibited because of land protection mandates (e.g., national parks or wilderness) (Fenn et al. 2010).

Because of the significant problems associated with most forms of aggressive intervention management, reduction of N deposition to ecosystems is the best strategy for long-term success in managing impacts from climate and N deposition on biodiversity (Fenn et al. 2010, Fenn et al. 2011, Bobbink et al. 2010). A review of available N mitigation strategies for California concluded that the ideal management option for reducing effects of N excess is to reduce N deposition by improving air quality (Fenn et al. 2010). Reducing N deposition can occur through many policy approaches, including the establishment of critical loads, and through allowing tradable permits for pollution which are slowly removed from the market, thereby reducing total pollution. In many countries including the US, emissions and deposition of nitrogen oxides (NO_x) have decreased dramatically in the past twenty years as a result of regulatory policies (Fenn et al. 2010). However, similar controls for emissions of NH_3 are less prevalent and the proportion of N deposition occurring in reduced forms (NH_x) is increasing in many areas above levels known to have ecological effects on more sensitive taxa (Clarisse et al. 2009, Fenn et al. 2010). This highlights the importance of selecting the appropriate receptor to use when implementing critical loads. The impacts to plant and lichen biodiversity in terrestrial ecosystems occur at lower air pollution levels than impacts on human health, and effects to nonvascular biodiversity occur at lower air pollution levels than effects to vascular biodiversity (Bobbink et al. 2010, Pardo et al. 2011a, Pardo et al. 2011b). Thus

when air pollution standards are determined primarily or solely by impacts to human health, in many cases sensitive ecosystems and biodiversity will not be effectively protected. And the N-induced loss of ecosystem services has serious consequences for human health and well-being (Compton et al. 2011).

6.6 SUMMARY AND KEY RESEARCH NEEDS

Biodiversity is decreasing worldwide and in the US, with serious consequences for ecosystem services including water quality regulation, production of food and fiber, and disease resistance. Although biodiversity losses have been largely driven by land use changes to date, climate change and increases in Nr are recognized as increasingly important drivers of biodiversity. The interactive effects of climate change and N are just beginning to be understood, and effects may vary across ecosystems. In general, N and climate change separately reduce biodiversity in sensitive systems, and together have the potential to cause even greater losses. In summary:

- Nitrogen is a strong driver of biodiversity loss in many types of ecosystems. The effects of climate change are less certain, although there is evidence that changes in precipitation and temperature increases in drought, floods, and other disturbances can result in simplified, less diverse systems.
- Many areas of the US are now receiving N deposition in excess of critical loads for ecosystem health, including for biodiversity. Some of these areas are also undergoing rapid climate change and are at heightened risk for biodiversity losses from combined N and climate change effects.
- Focused empirical studies are needed to obtain additional response data to changes in N, temperature, precipitation, and CO₂, and the interactions of these stressors in those ecosystems most vulnerable to N and climate change. This response data will improve modeled estimates of future conditions affected by N and climate change interactions.
- Reducing N deposition is likely to be an effective strategy for mitigating climate change impacts on biodiversity.

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Chapter 7: Impact of Nitrogen and Climate Change Interactions on Ambient Air Pollution and Human Health

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ABSTRACT

Nitrogen oxides (NO_x) are important components of ambient and indoor air pollution and are emitted from a range of combustion sources, including on-road mobile sources, electric power generators, and non-road mobile sources. While anthropogenic sources dominate, NO_x is also formed by lightning and wild-land fires and is also emitted by soil. Reduced nitrogen (e.g., ammonia, NH₃) is also emitted by various sources, including fertilizer application and animal waste decomposition. Nitrogen oxides, ozone (O₃) and fine particulate matter (PM_{2.5}) pollution related to atmospheric emissions of nitrogen (N) and other pollutants can cause premature death and a variety of serious health effects. Climate change is expected to impact how N-related pollutants affect human health. For example, changes in temperature and precipitation patterns are projected to both lengthen the O₃ season and intensify high O₃ episodes in some areas. Other climate-related changes may increase the atmospheric release of N compounds through impacts on wildfire regimes, soil emissions, and biogenic emissions from terrestrial ecosystems. This chapter examines the potential human health implications of climate change and N cycle interactions related to ambient air pollution.

7.0 INTRODUCTION

Reactive nitrogen (Nr), including both anthropogenic and natural nitrogen (N) emissions, plays an important role in ambient air quality and subsequent impacts on human health. Here we describe the interactions of Nr and global climate change on ambient air quality and subsequent human health impacts, as displayed in Figure 7.1 We describe the role of Nr in ambient air pollution formation, including nitrogen oxides (NO_x), O₃, and particulate matter (PM). We summarize the evidence regarding the human health effects of these ambient pollutants. Finally, we discuss implications for policy and provide recommendations and key research needs.

Global climate change is predicted to have adverse consequences to human health through many pathways outside of the those described within this chapter; these additional pathways have been previously described (see Confalonieri et al. 2007; Haines and Patz 2004; Houghton et al. 2001; Institute of Medicine 2011). Examples of these predicted adverse health consequences include the following: increased illnesses and deaths due to an increased frequency of heat waves, particularly in traditionally cooler climates; physical injury, infectious disease, malnutrition, and psychiatric disorders due to flooding; malnutrition due to drought; increased pollen concentration leading to increased allergic rhinitis; changes in the geographic patterns of vector-borne diseases; increased indoor allergens and pests due to increased indoor dampness; and reduced indoor air quality due to reduced natural ventilation. Pathways not directly related to ambient air pollution are not discussed further in this chapter.

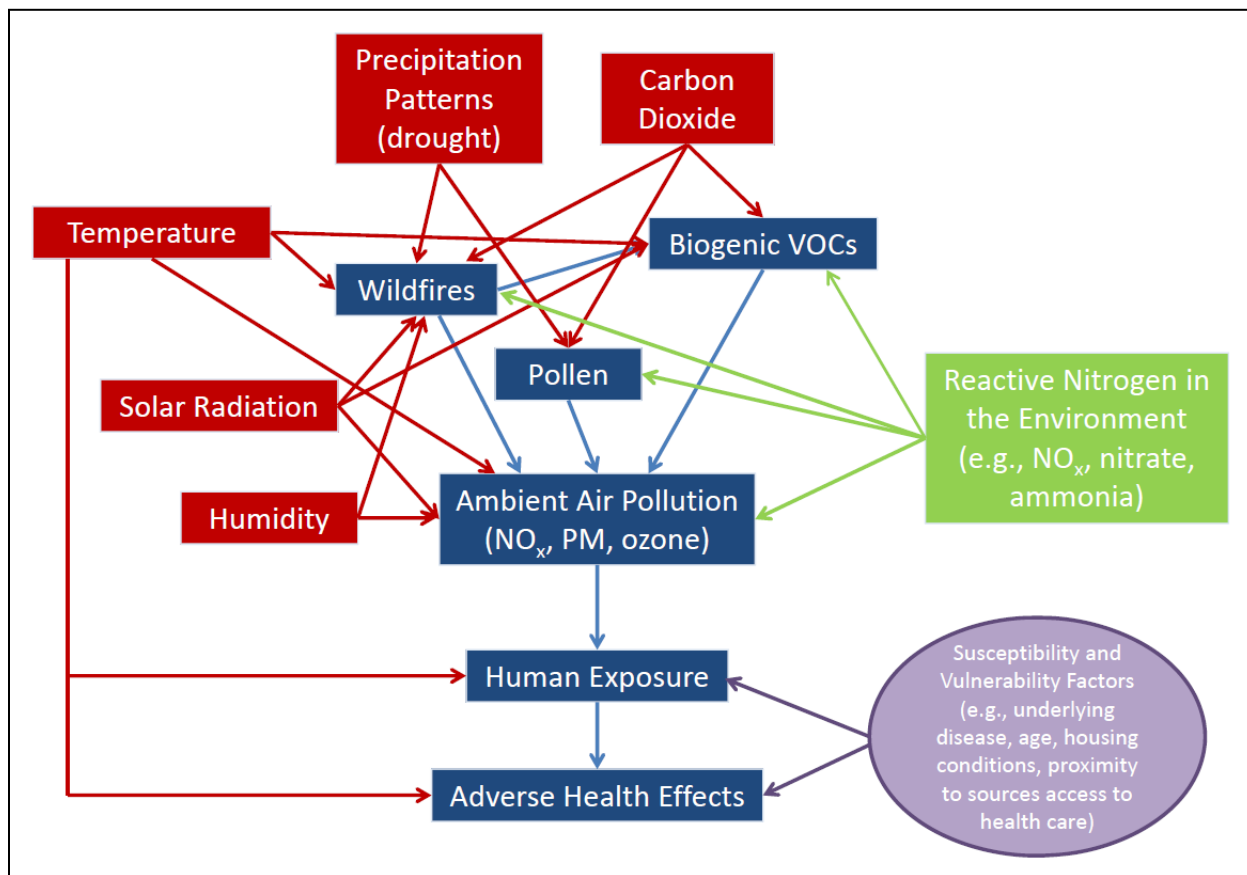


Figure 7.1: Interactions of factors likely to change due to global climate change (red) and Nr in the environment (green) and their impact on ambient air pollution concentrations, human exposure, and subsequent human health effects (blue). Health effects will be influenced by susceptibility and vulnerability factors (purple). Note that the term “temperature” is used for simplicity; this factor will likely act through extreme temperature events (heat waves) and/or stagnation events rather than mean temperature.

7.1 ROLE OF REACTIVE NITROGEN IN AMBIENT AIR POLLUTION

The chemistry of N in the atmosphere is complex. While molecular nitrogen (N_2) and nitrous oxide (N_2O) are essentially inert in the troposphere, Nr species (including nitrogen oxides ($NO_x = NO + NO_2$), nitrate (NO_3^-), ammonia (NH_3), ammonium (NH_4^+), and organic N-containing species such as peroxyacetyl nitrate ($C_2H_3NO_5$), interact with a range of other compounds to form pollutants such as O_3 , and PM (e.g., as ammonium nitrate (NH_4NO_3)). The responsible chemical reactions and the resulting pollutant concentrations are influenced by meteorology, including precipitation, wind speed, the height of the atmospheric boundary layer and solar radiation. These factors, in conjunction with both natural and anthropogenic emissions, make N an important consideration in examining interactions of climate change and the N cycle and its impact on both air quality and human health.

7.1.1 Reactive Nitrogen Emissions and the Nitrogen Cycle.

Understanding the sources of N is critical for determining mitigation strategies and for understanding the impact of climate change. Sources of N oxides to the atmosphere include fossil fuel combustion (e.g., emissions from power plants and mobile sources), biomass burning, agriculture, soils and lightning. The majority of NO_x emissions come from combustion-related activities. Ammonia is derived primarily from agricultural activities (e.g., emissions from fertilized soils and from livestock wastes) with other anthropogenic activities, such as catalytic converters in cars, contributing smaller amounts.

7.1.2 Interactions Between chemistry and meteorology.

Reactive N, particularly NO_x, and carbon monoxide (CO), volatile organic compounds (VOCs) and methane (CH₄), react in the presence of sunlight to form O₃, a pollutant which adversely impacts environmental and human health. Volatile organic compounds are emitted from both vegetation and anthropogenic sources (e.g., mobile and industrial sources). While anthropogenic VOC emissions dominate in most cities, more than 50% of VOCs for some areas of the US, such as in the Southeast, are produced by vegetation (SOS, 2004). The interactions of NO_x and VOCs in the formation of O₃ is non-linear, resulting in areas where the control of one over the other can result in unanticipated consequences depending upon whether the environment is NO_x or VOC limited (Jacob, 1999). As discussed later in this section, the impact of vegetation sources of VOCs on pollution formation is expected to be altered with climate change and N interactions.

Reactions of NO_x also contribute to secondary particulates (e.g., NH₄NO₃) through interactions with NH₃, water vapor and other particles. In addition, secondary organic aerosols (SOA) form in the atmosphere when organic gases react with oxidants, including the nitrate radical (NO₃). Among other sources, the production of SOA also occurs from VOCs, further complicating the N-climate-air pollution system. Thus, the chemical interactions and physical processes involving N is intrinsically linked with meteorology and environmental conditions (e.g., chemicals present, oxidation state). For example, solar radiation increases photolytic activity generating more O₃ during the warmer seasons, and during the warmest hours of the day, yet more PM in the atmosphere causes local scale cooling. Ventilation, caused by higher wind speeds, cleanses the atmosphere, whereas stagnant conditions trap pollutants and their precursors allowing them to react to form photochemical smog and elevated concentrations of ozone and particulates. Precipitation “washes out” particulate N species, causing these ambient particles to deposit to the landscape or onto water bodies (Jacob, 1999). Climate change is expected to alter both long term temperature and precipitation trends (Jacob and Winner, 2009), which in turn, will impact N-related processes and air quality.

7.2 NITROGEN-ASSOCIATED AMBIENT AIR POLLUTION AND HEALTH

A growing body of evidence demonstrates that N-related air pollutants are hazardous for human health. The evidence linking NO_x, O₃ and the fine size fraction of PM (PM_{2.5}), all currently regulated by the EPA, is summarized in Table 7.1 (US EPA 2006; US EPA 2008; US EPA 2009). While the detailed mechanisms are not completely understood and are beyond the scope of this summary, it is thought that pollutants can work through several pathways, including direct pulmonary irritation, suppression of the immune system, disruption of the autonomic nervous system, and through systemic inflammation, oxidative stress pathways. For PM, much of the research has focused on PM_{2.5} because of the ability of the smaller particles to penetrate deeper into the respiratory tract. Despite the growing interest regarding the

health impact of the coarse PM size fraction, relatively few studies have examined the coarse size fraction.

In addition, less is known regarding the health effects related specifically to the NO₃⁻ component of PM_{2.5} and SOA's. For other N-related compounds in ambient air, such as N₂O and gaseous NH₃, there is little or no evidence that they cause health effects at current typical ambient concentrations. There is, however, evidence that gaseous NH₃ can cause health effects at higher concentrations such as those experienced in confined animal feeding operations and other occupational settings (ATSDR, 2011). Furthermore, N₂O indirectly affects human health by leading to stratospheric O₃ depletion, which can impact health by increasing UV radiation able to reach the Earth's surface.

Table 7.1: Summary of existing evidence for a causal determination for the relationship between nitrogen-related ambient air pollutants and human health.

Pollutant/ Assessment	Sufficient evidence to infer a causal or likely causal relationship	Suggestive but insufficient evidence
NO _x (frequently measured as NO ₂) 2008 EPA Integrated Science Assessment (ISA)	<ul style="list-style-type: none"> ➤ Short-term exposure and respiratory morbidity, including: <ul style="list-style-type: none"> ● impaired host defense systems ● increased lung inflammation and sensitivity, particularly among asthmatics ● increased coughing, wheezing, and asthma symptoms ● decreased lung function ● increased hospital visits 	<ul style="list-style-type: none"> ➤ Short-term exposure and increased risk of respiratory and cardiovascular mortality ➤ Long-term exposure and respiratory morbidity, including: <ul style="list-style-type: none"> ● decreased lung function ● decreased lung growth and function in children
Ozone 2006 EPA Air Quality Criteria Document (AQCD)	<ul style="list-style-type: none"> ➤ Short-term exposure respiratory morbidity, including: <ul style="list-style-type: none"> ● impaired host defense systems ● increased lung inflammation and sensitivity, particularly among asthmatics ● increased coughing, wheezing, and asthma symptoms ● decreased lung function ● increased hospital visits ➤ Short-term exposure and increased risk of respiratory mortality 	<ul style="list-style-type: none"> ➤ Short-term exposure and cardiovascular disease morbidity, including decreased heart function and increased hospital visits ➤ Short-term exposure and increased risk of cardiovascular mortality
PM _{2.5} 2009 EPA ISA for PM	<ul style="list-style-type: none"> ➤ Short-term and long-term exposure and respiratory and cardiovascular disease morbidity ➤ Short-term and long-term exposure and increased risk of respiratory and cardiovascular mortality 	<ul style="list-style-type: none"> ➤ Exposure during pregnancy and early childhood and adverse reproductive and developmental outcomes ➤ Long-term exposure and increased risk of cancer

7.2.1 Susceptible and Vulnerable Subgroups

There is growing interest in identifying subgroups in the population that are particularly susceptible and/or vulnerable to the health effects of ambient air pollution. Definitions of susceptibility and vulnerability vary, but generally susceptibility refers to populations or characteristics with an increased risk of adverse health effects due to air pollution exposure (e.g., genetics, age, sex, pre-existing disease), while vulnerability often refers to factors that may increase exposure (e.g., proximity to a source, housing characteristics). The terms susceptibility and vulnerability are often used interchangeably. The issues of susceptibility and vulnerability in relation to the health effects of air pollution have recently been reviewed (Sacks et al. 2011). Populations considered especially susceptible to the health effects of ambient air pollutants include those with pre-existing respiratory and cardiovascular diseases (e.g., asthma, chronic obstructive pulmonary disease, congestive heart failure), those with underlying hypertension or diabetes, children and older adults, and the developing fetus (Sacks et al. 2011). Recent evidence also suggests that obesity may increase the adverse effects of ambient air pollution (Sacks et al. 2011). Additionally, several genetic polymorphisms involved in oxidative stress and other biologic pathways have been shown to increase susceptibility to the adverse effects of air pollutants, although further research is needed to confirm these findings (Sacks et al. 2011). Low socioeconomic status has also been seen to increase susceptibility; mechanisms likely include pre-existing disease, nutritional status, and reduced or differential access to medical care (Sacks et al. 2011). Geographic proximity to traffic and other pollution sources may also influence vulnerability and susceptibility to adverse health effects. For example, there is growing evidence of the increased risk of health effects due to traffic emissions (Health Effects Institute 2010). Vulnerability to cumulative environmental hazards is greater among specific racial-ethnic and socioeconomic groups (Su et al. 2009). The US Bureau of the Census' American Housing Survey for 2009 estimated that 19,612,000 year-round, occupied housing units (17.5% of total units) were within 300 feet (92 meters) of a 4-or-more-lane highway, railroad, or airport; and these percentages were higher for African-American households (25%), Hispanic households (22%), households below poverty level (22%), and renter-occupied housing units (26%) (US Census, 2011).

7.2.2 Mortality, Morbidity, and Economic Impacts

The health effects described above and in Table 7.1 impact a large portion of the US population. A recent analysis (Fann et al., 2011) estimated that 2005 levels of $PM_{2.5}$ and O_3 were responsible for between 130,000 and 320,000 $PM_{2.5}$ -related and 4,700 O_3 -related premature deaths, or about 6.1 % of total deaths from all causes in the continental US (using the lower end of the range for premature deaths). In other words, 1 in 20 deaths in the US were attributable to $PM_{2.5}$ and O_3 exposure. This same analysis attributed almost 200,000 non-fatal heart attacks, 90,000 hospital admissions due to respiratory or cardiovascular illness, 2.5 million cases of aggravated asthma among children, and many other human health impacts to exposure to these two air pollutants. Among populations aged 65–99, the analysis estimated nearly 1.1 million years of potential life lost from $PM_{2.5}$ exposure and approximately 36,000 potential life years lost from O_3 exposure.

Fann et al. (2011) found that the confluence of poor air quality, population size and density, and baseline health status caused the largest number of estimated $PM_{2.5}$ -related premature mortalities to occur within the Northeast, Southeast, and Midwestern US. Among urban areas, the largest estimated impacts occur in Los Angeles, Chicago, Detroit, Pittsburgh, Houston, New York, Philadelphia, and Boston. Among the 10 most populous counties in the US, the percentage of deaths attributable to $PM_{2.5}$ and O_3 range from 3.5% in San Jose to 10% in L.A. The analysis demonstrated that, despite significant recent

improvements in air quality in recent decades, PM_{2.5} and O₃ continue to present significant risks to public health.

The health impacts of air pollution not only constitute a serious societal threat, they also pose a significant economic burden, through hospital admissions, emergency room visits, and lost work and school days. Conversely, reducing air pollution decreases health impacts (Fann and Risley 2010) and results in substantial economic benefits to American society (Chestnut and Mills, 2005). A recent study (US EPA, 2011) calculated the costs and benefits of implementing the Clean Air Act Amendments (CAAA) of 1990. The benefits primarily related to reducing human health effects from exposures to fine particles and ground-level O₃. This study found that the economic value of these improvements is estimated to reach almost \$2 trillion (USD₂₀₀₆) for the year 2020, a value that vastly exceeds the cost of efforts to comply with the requirements of the 1990 CAAA. Moreover, the study also conducted economy-wide modeling to estimate the effect of the 1990 Amendments on overall US economic growth and the economic welfare of American households. When some of the beneficial economic effects of clean air programs were incorporated along with the costs of these programs, economy-wide modeling projected net overall improvements in economic growth and welfare. These improvements are projected to occur because cleaner air leads to better health and productivity for American workers as well as savings on medical expenses for air pollution-related health problems.

7.3 INTERACTION OF NITROGEN AND CLIMATE CHANGE – IMPACT ON AIR QUALITY

As discussed previously, meteorology and Nr both play important roles in ambient air pollution formation. In order to hypothesize about the likely impact of climate change (i.e., changing meteorological patterns) on ambient air pollution, the complex interactions between meteorology and Nr need to be considered (Figure 7.1).

7.3.1 Climate Impact on Emissions

Climate change is expected to impact both anthropogenic and natural emissions of Nr and VOCs. The extent, and even direction, of the impact on anthropogenic NO_x emissions is not certain. For example, higher temperatures are expected to increase the use of air conditioners, while also decreasing the need for heating, both of which would impact electricity demand and generation. Further, NO_x emissions are generally subject to increasingly stringent controls aimed at reducing O₃ levels to meet the National Ambient Air Quality Standards (NAAQS). Thus, the net impact on total anthropogenic NO_x emissions is not known (Grambsch, 2002). However, climate-induced anthropogenic NO_x emission increases (for example, from increased use of air conditioning) would likely occur during the summer, when extreme O₃ events are most common and when O₃ formation is most sensitive to NO_x emissions (e.g., Jacob 1999; Liao et al 2010; Weaver et al 2009).

In terms of natural sources of ambient N concentrations, studies suggest that incidences of lightning will increase, leading to more NO_x formation, although the impact on pollutant concentrations at ground level is expected to be small (Henderson et al., 2011; Weaver et al., 2009; Kaynak et al., 2008). Climate change may also impact soil NO_x emissions and soil and manure NH₃ emissions, although the size of this impact is not clear. Higher temperatures generally lead to increased emissions from soils and from manure, but the supply of Nr is also a prime determinant (see agriculture Chapter 4 for further discussion) (e.g., Pinder et al., 2008; Wu et al., 2008). Volatile organic carbon (VOC) emissions from vegetation are expected to respond to climate change, but they are also linked to N availability, which

affects leaf-level physiology involved in VOC production (e.g., Heald et al., 2008, 2009; Lamarque et al., 2005; Wu et al., 2012).

Wild-land fires, both prescribed and wild, can also be impacted by climate and N. Fires emit particulate matter, NO_x , and VOCs, leading to increased PM (primary and secondary) and O_3 . There is also evidence suggesting that fires lead to increased sulfate (SO_4^{2-}) formation in the plumes (e.g., Buzcu et al., 2006), which can in addition be components of PM. Studies suggest that there will be an increased frequency and severity of fires due to higher temperatures, decreased soil moisture, and extended drought (Easterling et al. 2007; Kinney 2008; Westerling et al. 2006). Nitrogen enrichment could also lead to invasion of fire-prone exotic grasses, further increasing fire risk and emissions (see Chapter 6 on biodiversity) (Rao et al. 2010). Emissions from wildfires in North America can have important consequences for air quality both regionally and at sites thousands of kilometers from the fire (Spracklen et al 2009; Wotawa and Trainer, 2000). Wildfires are a significant direct source of atmospheric pollutants such as CO, NO_x , VOCs and PM. These pollutants are precursors for O_3 production and as a result, wildfires may also lead to increases in O_3 concentrations (Wotawa and Trainer, 2000; Pfister et al 2008).

7.3.2 Climate Impacts on Atmospheric Pollutant Processing

Global climate change is expected to impact both the physical and chemical processing of pollutants in the atmosphere. Higher temperatures will tend to increase the rate of photochemical processing, leading to the faster generation of secondary products, including O_3 , which is sensitive to temperature increases. One of the more dramatic impacts that climate change is expected to have on air pollutant concentrations is through the potential for increased periods of stagnation during the summer, leading to decreased dispersion of O_3 and O_3 precursors. This, alone, is expected to lead to increased levels of O_3 and other secondary species. Most models predict an increased number of days exceeding current regulatory O_3 standards (Kinney 2008; Bell et al. 2007). In addition, this is expected to be more prevalent in certain urban areas already experiencing high O_3 , particularly in the Eastern US. Further, these periods of higher temperature would increase vegetation VOC emissions. Combined, the increased stagnation and VOC emissions are estimated to increase O_3 levels in the more highly impacted US regions by 2-8 ppb, (Weaver et al., 2009; Mickley et al., 2004). Studies suggest that this will make O_3 formation in those areas even more sensitive to NO_x emissions (Liao et al., 2010;).

Furthermore, global warming is expected to extend the O_3 season as higher temperatures increase chemical processing rates and vegetation VOC emissions increase earlier in spring, and continue later in autumn (Nolte et al., 2008). To a degree, this is muted because photolysis rates in early spring and late autumn are not as high as during the middle summer months.

The role of climate change on high wintertime O_3 episodes is less clear. Evidence from a recent study by Schnell et al. (2009) observed elevated diurnal levels of ozone in Wyoming during the winter when high pressure conditions prevailed (e.g., low wind speeds, low clouds, and cold temperatures). It was suggested that these meteorological conditions produced a shallow temperature inversion that trapped high concentrations of O_3 precursors (e.g., NO_x from nearby oil and gas wells) in the lower atmosphere overnight, which were then photolyzed during the next day under high light conditions (including reflection of UV by the snow cover) to produce higher day-time O_3 concentrations (Schnell et al., 2009).

The impact of climate change on $\text{PM}_{2.5}$ levels is less clear than for O_3 . Along with more severe stagnation episodes in some regions, climate change is expected to alter precipitation patterns. While

more severe stagnation events can lead to increased pollutant levels, areas where rainfall is expected to increase and/or become more extended (in part due to increased cloudiness), secondary pollutant formation is expected to decrease. Rain will further reduce levels by removing PM and soluble gases. Higher temperatures will also shift the thermodynamic equilibrium away from nitric acid combining with NH_3 to form NH_4NO_3 aerosol, leading to lower levels of that aerosol product (Stelson and Seinfeld, 1982, Dawson et al., 2007; Mahmud et al., 2010). Thus, the impact that climate change will have on $\text{PM}_{2.5}$, will likely vary, with the potential for some areas to experience increases, and others decreases. Although some recent research suggests that the net impact will be an increase in overall $\text{PM}_{2.5}$ (Tagaris et al., 2007), this remains an area of active research. Increased drought would lead to increases in soil-dust PM, though ground cover changes associated with the N-cycle and climate modification of ground-cover would likewise play a role.

Climate change is also expected to increase atmospheric water vapor concentrations. Water vapor reacts with the excited oxygen radical (O1D) derived from O_3 photolysis to form hydroxyl radicals (OH), increasing the rate of chemical destruction of organics and NO_2 (e.g., reducing CH_4). In radical-limited areas (e.g., areas high in NO_x), this will lead to more rapid formation of secondary pollutants like O_3 . In radical-rich (NO_x -limited) regions, this reaction sequence can lead to reducing O_3 as less O1D is available to, ultimately, re-form O_3 .

While emissions of Nr are expected to decline in North America and Europe, emissions in South and East Asia are expected to first increase and then decline more slowly (HTAP 2010). Despite this potential increase in the sources of pollution for intercontinental transport of Nr and its products, warmer oceanic temperatures are expected to increase water vapor over the ocean, resulting in a reduction in cross-hemispheric O_3 transport from South and East Asia through increases in O_3 loss rates over remote oceanic regions (Jacob and Winner, 2009).

7.4 INTERACTION OF NITROGEN AND CLIMATE CHANGE -IMPACT ON HUMAN HEALTH

As demonstrated in previous sections, Nr and climate change have independent impacts on human health by way of ambient air pollution; N and climate change likely also interact in several ways to impact human health (Figure 7.1). As described in the previous section, while factors associated with climate change would likely lead to a net increase in ambient air pollution, these predictions are often calculated in the absence of any net change in Nr emissions, which is highly unlikely. The changing N cycle along with global climate change will likely result in additional impacts on human health due to ambient air pollution through several mechanisms, including shifting patterns and timing of air pollution exposure and the interaction of increased temperature and air pollution. Furthermore, the changes in Nr and climate will occur in the context of changing susceptibility and vulnerability in the population. Table 7.2 summarizes examples of likely scenarios through which climate change and Nr could interact to impact ambient air pollution and subsequent human health effects.

7.4.1. Health impacts of shifts in pollution exposure

A shift towards higher pollutant distributions with increasing temperatures will also increase the proportion of the population exposed to higher pollution levels. For example, a longer O_3 season could result in O_3 exposure overlapping the spring and fall respiratory viral and asthma seasons, which are known to have increased activity during these periods. While the impact of this overlap is not clear, there is evidence that O_3 and other pollutants can enhance the susceptibility to and the severity of,

respiratory infections and increase sensitization to allergens (Chauhan and Johnson 2003; Ciencewicky and Jaspers 2007; Ruzsnaek et al. 1996).

7.4.2. Health impacts of increased exposure to fire emissions

As previously noted, it is also likely that climate change and increased N deposition will both result in increased frequency and exposure to wildfire emissions, which can be an important source of N-ambient air pollution. Wildfires produce severe local plumes of PM, oxides of N and other air pollutants with resulting human exposures, especially among firefighters (Adetona et al. 2011; Neitzel et al. 2009; Reisen and Brown 2009). Exposures to wildfire smoke have been associated with increased emergency department visits, especially among individuals with pre-existing cardiopulmonary conditions such as congestive heart failure (Rappold et al. 2011; Mirabelli et al. 2009; Hanninen et al. 2009; Delfino et al. 2009). These observational studies have recently been supported by reports of increased inflammatory markers in health volunteers in controlled clinical exposures to wood smoke (Ghio et al. 2011). The general adverse health effects of exposures to wood smoke were also the subject of a recent review (Naehler et al. 2007).

7.4.3. Health impacts of increased exposure to allergens

Increased N deposition and climate change factors are also likely to impact aeroallergen patterns. Allergic diseases are an increasing source of morbidity in the US and other developed countries. Nearly 5 million Americans have asthma and more than 50 million Americans suffer from allergic disease; both conditions are exacerbated by pollen and mold and both have been increasing over the past few decades (Kinney 2008). Increased N deposition has been shown to increase pollen production (Townsend et al. 2003). Climate change, including warmer temperatures and changing precipitation patterns, can lead to longer pollen seasons and increased seasonal pollen production (Kinney 2008; Shea et al. 2008). Furthermore, carbon dioxide (CO₂) another greenhouse gas has been shown to stimulate pollen production and potency (Kinney 2008; Shea et al. 2008).

7.4.4. Health impacts of interaction of heat waves and pollutant exposure

While the independent effects of the N-related ambient air pollutants and temperature extremes (e.g., heat waves, night time temperature, and other temperature extremes; McGeehin and Mirabelli 2001; O'Neill and Ebi 2009; Peng et al. 2011) are well-documented, the joint effects of reduced air quality and temperature have received less attention. Meteorological conditions that produce heat waves are generally high pressure systems with stagnant wind conditions that are accompanied by increased levels of many air pollutants. This natural covariation of heat waves and air pollution limits the ability of observational studies to estimate their joint health effects (McMichael et al. 2001; Thurston and Ito 2001). Recent studies have provided evidence that the health effects of ambient air pollutants, including O₃ and PM, are enhanced when temperatures are higher, particularly in regions with typically cooler temperatures (Ren et al. 2009; Li et al. 2011; Dear et al. 2005).

7.4.5. Health impacts on changing populations of susceptible and vulnerable groups

It is important to recognize that the health impacts predicted to result from changing N emissions and deposition and global climate change will occur in the context of changing population susceptibility and vulnerability. Susceptibility to the joint impacts of air pollutants and global climate change will depend

on the same factors that confer susceptibility to the independent effects of air pollutants and heat stress. Ageing populations, increasing prevalence of respiratory and cardiovascular disease, and increasing prevalence of obesity and type II diabetes will all enhance the health effects described previously. These factors are no longer just concerns of developed countries. Cardiovascular disease, obesity, and type II diabetes are increasingly important in low- and middle-income countries as well; cardiovascular disease is now the leading the cause of death worldwide and the second leading cause of death in low-income countries (Narayan et al. 2010; Reddy 2004; Yusuf 2001, 2004).

Vulnerability to the joint impacts of air pollutants and global climate change will reflect the non-uniform distribution of human exposures (Morello-Frosch et al. 2011). Climate change is predicted to impact food availability, flooding, and drought, all of which may result in population movement to urban areas. This population movement may lead to increased proximity to traffic and other sources of air pollution. Vulnerability to the impact of both air pollution and temperature is also greater in the absence of air conditioning. Air conditioning is known to prevent or reduce infiltration of many ambient air pollutants indoors. Individuals without air conditioning will have much greater vulnerability to aeroallergens (Delfino et al. 1997) and to heat stress (IOM 2011; Ostro et al. 2010; Richard et al. 2011). In a recent study, vulnerability to heat waves was largely determined by socioeconomic status, including education, poverty and race; social isolation; air conditioning prevalence; and general health condition, including advanced age and diabetes (Reid et al. 2009). Adaptation to climate change may also increase the susceptibility factors, especially obesity. A recent study has linked accessibility of urban parks as protective for childhood obesity (Wolch et al 2010). Avoidance of outdoor exercise in response to prolonged heat events will therefore tend to increase obesity and thus susceptibility to ambient air pollutants. The accessibility of urban public recreation resources also raises issues of disparities and environmental justice (Dahmann et al. 2010), and disparities in access to air conditioned facilities may be much greater.

Table 7.2: Examples of the Impact of Nitrogen and Climate Change Interactions on Air Quality and Human Health

Process	Impact on Air Quality	Impact on Human Exposure	Net Impact on Human Health (-adverse; + beneficial)	Confidence (1 higher, 3 lowest)
Increased summertime stagnation events	Increased ozone (the “climate penalty”) and increased sensitivity of ozone to NO _x emissions	Increased ozone exposure	-	1
Increased vegetative growth due to increased CO₂ and Nr	Increased biogenic VOC emissions; potentially increased wild-land fire emissions	Increased ozone and PM (including SOA) exposure	-	1
Increased wild-land fires due to drought and increased temperature	Increased biogenic VOC, PM and NO _x emissions	Increased NO _x , ozone and PM exposure	-	1
Increased absolute humidity	Increased OH, decreased long range ozone transport, increased rate of sulfate and nitrate formation.	Small decrease in ozone transport; could lead to increased local ozone formation and exposure	+/-	3
Increased temperature	Decreased or increased ammonium nitrate formation depending on region	Decreased or increased PM exposure	+/-	3
Longer ozone season due to higher temperatures	Increased ozone levels earlier in season	Extended ozone exposure, potentially to a period when respiratory diseases are more prevalent.	-	3
Simultaneous increase extreme ozone and high temperature events	NA	Increased exposure to simultaneous high ozone and temperatures, particularly for populations without access to central air conditioning.	-	3
Changing precipitation patterns with increased precipitation in some regions, decreased in others (leading to drought).	Precipitation scavenges pollutants (PM and precursor gases), and cloudiness reduces pollutant formation. Drought can increase pollutants (including soil dust).	Decreased PM exposure	+	3

7.5 IMPLICATIONS FOR POLICY

The major routes where climate change and Nr will likely interact to modify pollutant concentrations and have implications for policy and management, particularly implementation of the CAAA have been identified. The CAAA is the primary federal tool for controlling air pollution in the US. Last amended in 1990, the CAAA requires EPA to set NAAQS for widespread pollutants from numerous and diverse sources considered harmful to public health and the environment (Bachmann 2007). The CAAA established two types of NAAQS. Primary standards set limits to protect public health, including the health of potentially susceptible populations such as asthmatics, children, and the elderly. Secondary standards set limits to protect public welfare, including protection against visibility impairment, damage to animals, crops, vegetation, and buildings. The CAAA requires periodic review of both the science upon which the standards are based and the standards themselves.

The NAAQS provide policy drivers for controlling six “criteria” air pollutants and the precursor atmospheric emissions that lead to their formation. In relation to the health effects described above, the most relevant health-based, or primary, standards are those for PM_{2.5} and O₃. For PM_{2.5}, there are two health-based standards. The annual standard is 15 µg/m³, meaning that, to attain this standard, the 3-year average of the weighted annual mean PM_{2.5} concentrations from single or multiple community-oriented monitors must not exceed 15.0µg/m³. The 24-hour PM_{2.5} standard is 35 µg/m³, requiring that the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 µg/m³. For O₃, the primary standard is 0.075ppm, which requires that the 3-year average of the fourth-highest daily maximum 8-hour average O₃ concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm.

Due to the overall decreasing trend in NO_x and sulfur dioxide (SO₂) emissions, related air pollution has changed, with substantial improvements seen in O₃ and fine particle concentrations in many regions (US EPA 2010). Nationally, ground-level O₃ concentrations were 10 % lower in 2008 than in 2001, and the trend showed a notable decline after 2002. In the Eastern US, 2006-2008 air monitoring data showed that O₃ air quality improved in almost all of the 104 areas designated to be in nonattainment for the 1997 8-hour NAAQS. Nationally, annual and 24-hour PM_{2.5} concentrations declined by 17 and 19 %, respectively, between 2001 and 2008. Despite this substantial progress, many air pollution issues remain. For example, even though O₃ concentrations in 2008 were among the lowest since 2002, many areas still measured concentrations above the 2008 NAAQS for O₃. Similarly, some areas remain in non-attainment with the NAAQS for PM_{2.5}. In 2008, more sites exceeded the level of the 24-hour PM_{2.5} standard than the annual PM_{2.5} standard. Eighteen sites exceeded the annual standard and 55 sites exceeded the 24-hour standard, while 14 sites exceeded both.

As described above, air quality has been improving and is expected to improve further as NO_x emissions decrease due to control programs currently in place – however, even with these future emission reductions in place, air pollution may worsen due to the “climate penalty”. In other words, the same amount of NO_x reduction may result in less O₃ mitigation in a warmer world – hence the term “climate penalty” (Wu et al., 2008).

There is a substantial and growing body of literature showing that climate change has the potential to impact the extent, severity, timing, length and geography of O₃ pollution and high O₃ episodes – influencing health and economic burdens across large parts of the country in the future (Racherla and Adams 2009; Mickley et al. 2004; Mickley 2007; Hogrefe et al. 2004; Jacob and Winner 2009). The “climate penalty” has important policy implications. For example, even while changes in US emissions

will continue to be critical for attaining O₃ air quality standards, climate change by itself may significantly worsen the severity and frequency of high ozone events in the US (Racherla and Adams 2009). Thus, higher O₃ levels due to future climate change alone could erode the gains made through future US NO_x emission reductions, meaning that stronger emission controls may be needed to meet a given air quality standard. In addition, policy makers must plan appropriately for background O₃ increases due to projected increases in non-US anthropogenic emissions that, as described above, may also erode the progress made in decreasing pollutant emissions from domestic sources. And, finally, the end result will be continued serious impacts to human health and concomitant economic burdens.

In contrast to the “climate penalty”, there is some evidence that some areas will see increased cloud cover and precipitation, generally leading to overall reductions in pollutants, particularly O₃ and secondary PM constituents (Tagaris et al., 2007), and that climate-related changes could result in reduced air pollution. These aspects of climate change could be a possible countervailing phenomenon leading to better air quality, impacting both human health and the ability of states to attain the NAAQS for O₃ and fine PM. Other mechanisms will play more minor roles, and may increase or decrease pollutant levels; further research is needed in this area.

Another important health-related policy issue at the N-climate nexus involves the potential for changing frequency, intensity, and spatial extent and distribution of fire. The elevated concentrations of air pollution due to wildfire may impact the ability of areas to attain and maintain the NAAQS for pollutants associated with wildfires. In many areas of the country, prescribed fire is an important management tool employed by federal and state land management agencies, often as a means to lower the fuel load in order to lessen the extent and severity of wildfire. To the extent that climate change and N loading influence, either separately or jointly, natural or managed fire in the US, with accompanying impacts on air quality, this will likely have implications for land management and the functioning and budgets of agencies responsible for overseeing federal and state lands.

7.6 SUMMARY AND KEY RESEARCH NEEDS

Global climate change and Nr in the environment will interact through several mechanisms to impact ambient air pollution and may have subsequent adverse effects on human health. Given the complex interactions, changes in local and regional meteorology patterns due to global climate change and changes in the N cycle must be examined concurrently when discussing any likely future impacts on human health (e.g., the “climate penalty”). Among the most important climate change – N interactions in terms of ambient air pollution and human health effects, include the increased number of “high” O₃ days, the increased length of the O₃ season, increased vegetative VOC emissions from plant activity, and increased VOCs, PM and NO_x from fires.

The state of knowledge regarding the likely impact of the interaction of N and climate change on ambient air quality and human health contains some critical gaps. The interaction between climate change and changes in Nr in the environment will likely lead to changes in the levels of vegetation VOC emissions, and potentially the composition of those emissions as well. Oxidation of VOC leads to secondary organic aerosols, however, the potential health implications of SOA's are not known. A better understanding of the health effects of SOA's should be a focus of further study, not only to address the question of the combined impacts of climate and the N cycle, but to better understand the current impact of vegetation emissions on health.

Additionally, NH₃ emissions result primarily from agricultural practices, including the use of fertilizers and large confined livestock operations. Whereas the majority of NO_x emissions fall under air quality regulations, NH₃ emissions from agriculture are mostly unregulated. In contrast to recent decreases in NO_x emissions, which are expected to continue due to air quality regulations, NH₃ emissions are expected to increase. The potential contribution of NH₃ emissions to fine particle formation is an issue of concern. An area for further work involves the impact of NH₃ emissions on our ability to attain fine particulate standards for human health, including the combined effects of NH₃ emissions and climate change on air quality and human health.

One of the areas where climate change and the N cycle may have an effect on health is on the change in pollen emissions. However, we need improved understanding of the combined and interactive effects of climate change and N cycling in the environment on production rates and types of pollen.

Finally, given the relative lack of research in the area, further work is needed to evaluate the interaction of ambient air pollution and temperature (specifically high temperature and heat waves) on human health. Additionally, more research is needed to evaluate potential susceptibility and vulnerability factors, particularly those that are predicted to increase (e.g., obesity, underlying disease, older age, nutritional deficits, proximity to sources) at the same time that population experiences the impacts of global climate change.

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