

Effects of Nitrogen Deposition on Greenhouse Gas Fluxes for Forests and Grasslands of North America

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In a nutshell

- Terrestrial ecosystems across much of North America are exposed to elevated rates of atmospheric nitrogen (N) deposition, which has substantially increased carbon dioxide (CO₂) uptake by forests and has likely increased nitrous oxide (N₂O) emissions from soils.
- Ammonia (NH₃) emissions related to agriculture are expected to remain relatively stable over the next 20 years, while NO_x emissions, ozone, and total N deposition are projected to decline.
- The net effect of US N deposition on long-lived greenhouse gas fluxes is currently equivalent to uptake of 170 Tg CO₂ (CO₂ equivalent) per year. Over the next 40 years, this is expected to decrease by 40% due to declining rates of N deposition.

Abstract

Human activities have significantly elevated atmospheric deposition of reactive nitrogen (N) onto terrestrial ecosystems of North America. Some of this N can stimulate carbon (C) storage in terrestrial ecosystems, but the fertilization effect of added N can be diminished by elevated concentrations of tropospheric ozone (O₃) and by chronically high deposition of N. In this review, we discuss spatial patterns and effects of N deposition and tropospheric O₃ on net greenhouse gas fluxes in North American forest and grassland ecosystems. While projected rates of ammonia (NH₃) emissions and deposition are expected to remain unchanged, projected declines in nitrogen oxides (NO_x) emissions within the United States are expected to lead to reductions in total N deposition and O₃. The net effect of these changes in N deposition onto forest and grassland ecosystems will likely lead to declines over the next 40 years in C sequestration attributed to N deposition and decreases in NO_x emissions to the atmosphere.

Introduction

The atmosphere consists largely of N as N₂, yet this form of N is not available to most living organisms. Human activities such as fossil fuel combustion, production and application of N fertilizers, and cultivation of plants with N fixing symbionts have led to increased emissions of reactive N, particularly nitrogen oxides (NO_x) and ammonia (NH₃), to the atmosphere (e.g., Galloway *et al.* 2008). Both NO_x and NH₃ can contribute to the formation of atmospheric aerosols, particles which dim the amount of light available for plant photosynthesis (Chameides *et al.* 1999). NO_x emissions also lead to chemical

reactions that drive the formation of tropospheric ozone (O_3), and the removal of atmospheric methane (CH_4). In the atmosphere, NO_x and NH_3 undergo a series of chemical transformations, resulting in a mix of N compounds that deposit onto downwind ecosystems (Figure 1). Nitrogen can be deposited onto terrestrial and aquatic ecosystems both as dry deposition (particulates and gases) and as wet deposition (in precipitation).

Atmospheric deposition of N affects a range of biogeochemical processes in terrestrial ecosystems that control the production and consumption of several important greenhouse gases, including nitrous oxide (N_2O), carbon dioxide (CO_2), CH_4 , and tropospheric O_3 (Figure 1). First, N deposition increases plant growth, which increases uptake of CO_2 and rate of C sequestration. Scarcity of plant-available N often limits plant growth rates (Vitousek & Howarth 1991), such that N additions typically enhances rates of net primary production (CO_2 uptake) across a range of terrestrial ecosystems, including temperate and tropical forests, tundra, grasslands, and wetlands (LeBauer & Treseder 2008). Nitrogen additions not only affect plant growth, but can also suppress rates of soil decomposition and release of CO_2 to the atmosphere. Furthermore, by enhancing the supply of N to microbes that produce N_2O in soils and sediments, N deposition increases N_2O emissions. Lastly, N additions can slow CH_4 consumption by microbes in upland soils (Aronson and Helliker 2010), and can have variable effects on CH_4 emissions from wetlands (Liu and Greaver 2009). Therefore, some of the benefits attributable to increased CO_2 uptake caused by N deposition are offset by effects on N_2O and CH_4 fluxes (Liu and Greaver 2009; Butterbach-Bahl *et al.* 2011; Zaehle *et al.* 2011). Each of these biogeochemical responses to N deposition is described in further detail below.

In this paper, we summarize the effect of atmospheric N deposition on the consumption and production of greenhouse gases by non-agricultural terrestrial ecosystems in North America. Recent reviews summarize effects of human-driven N enrichment on net greenhouse gas emissions for Europe (Butterbach-Bahl *et al.* 2011), and in the context of overall effects of N pollution and effects on climate for the US (Pinder *et al.* 2012) and modeled for the globe (Zaehle *et al.* 2011). Here, we first discuss spatial patterns of N deposition and tropospheric O_3 exposure in forests and grasslands across much of North America. Second, we summarize the known effects of N deposition on net greenhouse gas fluxes in North American terrestrial ecosystems. Finally, we examine temporal trends and future projections for atmospheric N deposition and discuss their implications for net greenhouse gas fluxes over the next 40 years.

Spatial Patterns of Nitrogen Deposition and Tropospheric Ozone Exposure

Atmospheric N deposition is elevated throughout much of the eastern US, averaging $8.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Figure 2). In contrast, much of the western US receives relatively low rates of N deposition ($<4 \text{ kg ha}^{-1} \text{ yr}^{-1}$; Figure 2), but contains hotspots in the California Central Valley and near metropolitan sources, that receive up to $90 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Fenn *et al.* 2003). The eastern US also contains hotspots of N deposition near urban areas and sites of intensive animal management (Templer and McCann 2010; Holland *et al.* 2005), but differences between urban and rural areas are not as pronounced as in the west. Southern Canada also experiences elevated rates of atmospheric N deposition, especially downwind of the agricultural and industrial regions of southern Ontario (Watmough *et al.* 2005; CCME 2011). Measurements of N deposition and O_3 are sparse in Mexico, but exposure levels are likely to be high, especially near urban areas, agriculture, and industry (Fenn *et al.* 2006; de Bauer *et al.* 2007; Molina *et al.* 2010).

Terrestrial ecosystems in North America are exposed to substantial levels of tropospheric O_3 (Felzer *et al.* 2004; Avnery *et al.* 2011; Figure 2). Tropospheric O_3 is a secondary pollutant formed from the reaction of volatile organic compounds (VOCs) and NO_x in the presence of sunlight. A useful metric of O_3 exposure is AOT40 – the hourly O_3 concentration over 40 ppb, accumulated over daylight hours (when plants' stomata are open) from April 1 to September 30 (when most vegetation is photosynthetically active). Effects of O_3 on forest vegetation have been observed for exposures as low as 5 ppm hr (Karlsson *et al.* 2004). Much of the US exceeds these thresholds, especially in and around cities in the Southeast and Southwest US.

To qualitatively identify regions especially exposed to atmospheric N deposition and tropospheric O_3 , we developed an exposure index which is shown in the bottom row of Figure 2. To compute this index, we first normalized rates of atmospheric N deposition and AOT40 by their maximum value to yield a range of 0 to 1. We then calculated the product of these normalized rates of N deposition, normalized AOT40, and the fraction of the landscape covered by forest (Figure 2, left) or grasslands (Figure 2, right). Forests in the eastern US and California Sierra Nevada mountains are among regions that have the highest levels of N deposition and O_3 exposure. The highest exposures for grasslands are in California and the region spanning from central Texas to Kansas.

O_3 . Ozone is a by-product of the atmospheric photo-oxidation of NO_x . It is often co-located with N deposition (Figure 2), is itself a greenhouse gas, and decreases CO_2 uptake by damaging plants (Collins *et*

103 *al.* 2010). As a short-lived greenhouse gas relative to CO₂, N₂O, and CH₄, tropospheric O₃ currently
104 accounts for 22% of the global warming attributed to human activities (Forster *et al.* 2007). Ozone slows
105 plant uptake of CO₂ from the atmosphere. It is a strong oxidant that enters plants through stomata on
106 leaves, initiating a chain of reactions that degrade plants' chlorophyll and reduce rates of
107 photosynthesis. Globally, 50% of forests are expected to be exposed to damaging levels of O₃ by the
108 year 2100 (Fowler *et al.* 1999). Increases in atmospheric CO₂ concentrations and rates of N deposition
109 can stimulate productivity, but high concentrations of O₃ diminish root production and the ability of
110 plants to control stomata, both contributing to reduced rates of plant growth (Grantz *et al.* 2006; Wittig
111 *et al.* 2007) and increased damage from water stress in water limited ecosystems (Fenn *et al.* 2006).
112 Model simulations for northeastern US forests suggest that O₃ reduces rates of net primary production
113 by up to 16% (Ollinger *et al.* 2002). Even though O₃ acts as a greenhouse gas and affects fluxes of CO₂, in
114 this review we did not quantitatively estimate the effects of N deposition on these direct and indirect
115 O₃-related greenhouse gas fluxes.

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118 **CO₂.** Nitrogen inputs from atmospheric deposition can affect atmospheric CO₂ concentrations by
119 enhancing CO₂ uptake by plants and by reducing CO₂ release from soils by decomposition. Analysis of
120 forest growth along gradients of N deposition revealed that N deposition has stimulated forest growth
121 across the northern and central hardwood forests of the eastern US (Thomas *et al.* 2010). This growth
122 enhancement amounts to an increase in regional tree carbon gain of approximately 60 kg C ha⁻¹ yr⁻¹ per
123 kg N ha⁻¹ yr⁻¹ received in deposition. Yet, N deposition enhances growth for only half of the region's tree
124 species: it has no effect on growth of many tree species; it slows growth for a few conifer species, and it
125 decreases survivorship of one-third of the species examined (Thomas *et al.* 2010). These responses
126 reflect the net response of eastern forests to both N deposition and to potential covarying damage from
127 O₃ or sulfur deposition. Yet, long-term N addition experiments show that chronic exposure to N
128 additions of 16 to 50 kg N ha⁻¹ yr⁻¹ can induce forest decline (e.g., McNulty *et al.* 2005, Magill *et al.* 2004,
129 Wallace *et al.* 2007). The relatively moderate rates of N addition received by most North American
130 forests (Figure 2) likely place the majority of the continent's forests in the range for growth stimulation
131 rather than decline, although concurrent declines can occur in some tree species, older forests, and
132 forests in N deposition hotspots.

Compared to understanding of the effects N deposition on eastern US ecosystems, significantly less is known about the response of western ecosystems (Fenn *et al.* 2003). Co-limitation by water availability (e.g., Nemani *et al.* 2003) could yield small growth enhancements of western forests. In the western US, especially forest ecosystems of Southern California, elevated concentrations of tropospheric O₃ have significantly dampened the positive effects of atmospheric N deposition (Fenn *et al.* 2003). Furthermore, recent evidence points to increased fire frequency and consequent CO₂ release as a result of N deposition-induced shifts from native shrubland to exotic grasslands (Fenn *et al.* 2003).

Nitrogen additions not only affect growth, but can also suppress rates of decomposition in many, but not all, temperate and boreal forests (Janssens *et al.* 2010). The exact causes, magnitude, extent, and persistence of this suppression is not well understood, but may be due to changes in the abundance, species composition, and enzymatic response of microbial decomposers. However, not all soils show suppression of decomposition in response to N addition, and rates of N-induced soil C storage across a range of forest and grassland soils appear to be relatively small, typically averaging 0 to 20 kg of soil C storage per kg of N addition (Nave *et al.* 2009, Janssens *et al.* 2010, Lu *et al.* 2011).

N₂O. Nitrous oxide (N₂O) is a long-lived greenhouse gas, and its abundance in the atmosphere relates directly to human acceleration of the global N cycle. Although its atmospheric concentration is much lower than that of CO₂, N₂O has roughly 300 times the warming potential of CO₂ per molecule (Forster *et al.* 2007). Nitrous oxide is produced by microbes in soils and sediment during the processes of nitrification and denitrification (Venterea *et al.*, this report). The rate of N₂O production typically increases with temperature and with the rate of N cycling through an ecosystem, although it can vary tremendously as the availability of N, oxygen, and organic carbon affect microbial activity (e.g., Davidson *et al.* 2000). Globally, the concentration of atmospheric N₂O has increased rapidly over the last 150 years in direct association with N enrichment of the biosphere through the use of synthetic fertilizers and manure production by livestock (Davidson 2009). To date, most estimates of N₂O emissions induced by N deposition have been extrapolated from measurements of N₂O loss from N addition experiments. In a long-term N addition experiment in a red pine and mixed hardwood forest in Massachusetts, rates of NO and N₂O production increased with increasing rates of N addition, but the response of NO was significantly greater than N₂O, which was negligible in these forests (Venterea *et al.* 2003, 2004). These results are broadly confirmed by a meta-analysis of N addition experiments at 59 forest, 16 grassland, 19 wetland and 3 heathland sites, which found a mean emission rate of 0.9%, or 0.009 kg N₂O-N ha⁻¹ y⁻¹,

emitted for every kg N ha⁻¹ yr⁻¹ of N addition (Liu and Greaver 2009). Using this emission rate and estimates of N deposition onto natural ecosystems in the US, Pinder *et al.* (2012) estimate that N deposition makes a relatively minor contribution to US N₂O emissions. In Europe, estimates of N₂O emissions based on alternative approaches (e.g., using gradients or time-series of N deposition) yield the markedly higher rates of N₂O emissions of 1-6% of deposited N (Butterbach-Bahl *et al.* 2011). All of these approaches measuring N₂O emissions from soil fail to include N₂O emissions produced as excess N flows off-site to downstream water bodies. While most estimates suggest that the enhancement of N₂O emissions from soils due to N deposition is minor, there are considerable uncertainties that require further investigation.

CH₄. Methane is another important greenhouse gas, currently second in importance only to CO₂, and increases in NO_x emissions and N deposition can affect atmospheric CH₄ concentrations in three ways. First, increased NO_x increases photochemical oxidation, which is the largest CH₄ removal process, accounting for 88% of the total CH₄ sink (Boucher *et al.* 2009). By increasing the photochemical removal of CH₄, NO_x decreases the atmospheric concentration of CH₄. Second, in soils, N enrichment with NH₄⁺ can slow the consumption of atmospheric CH₄ by aerobic soil microbes, which favor consumption of NH₄⁺ rather than CH₄ when NH₄⁺ becomes abundant (Steudler *et al.* 1989; Aronson and Helliker 2010). Third, in wetlands, N enrichment can enhance CH₄ production by increasing the supply of organic C to CH₄-producing microbes, but it can also slow microbial production of CH₄ when enrichment with nitrate (NO₃⁻) increases the redox potential above that most favorable for methanogenesis. However, the effects of N additions on net CH₄ emissions from soils and wetlands tend to be very small relative to effects of N additions on C sinks and N₂O production (Liu & Greaver 2009, Butterbach-Bahl *et al.* 2011). Of these three processes by which N deposition can affect atmospheric CH₄, the net response of atmospheric processes dominates by far (Pinder *et al.* 2012).

A recent assessment quantified the greenhouse gas fluxes due to N deposition in both agricultural and natural ecosystems in the US (Pinder *et al.* 2012). The enhancement in the uptake of CO₂ is estimated to range from 110 to 290 Tg CO₂ (1 Tg = 1 Mt = 10¹² g). Nitrogen deposition causes N₂O emissions to increase by 30 to 90 Gg (1 Gg = 10⁹ g) N₂O and atmospheric CH₄ to increase by 40 to 110 Gg CH₄. When N₂O and CH₄ are converted to Tg CO₂e (CO₂ equivalent) on a common global temperature potential basis, our best estimate of the net change in the annual long-lived greenhouse gas flux due to US N deposition is sequestration of 170 Tg CO₂e. This includes sequestration of 190 Tg CO₂, offset by warming

of 18 Tg CO₂e from N₂O and warming from 2 Tg CO₂e from CH₄; Figure 4). This is equivalent to 3.2% of the US fossil fuel CO₂ emissions (equal to 170 Tg CO₂e divided by 5,400 Tg CO₂e released via fossil fuel combustion; USEPA 2012) and approximately 19% of the total forest sector C sink (equal to 170 Tg CO₂e divided by 900 Tg CO₂ stored by the US forest sectors; USEPA 2012).

Future Trends: Atmospheric Deposition and Implications for Greenhouse Gas Fluxes

Because of the serious human health effects of O₃ and atmospheric particulates, the US Environmental Protection Agency (USEPA) has enacted a series of regulations designed to reduce NO_x emissions from power plants and vehicles (USEPA 2010). This has resulted in substantial reductions in NO_x emissions over the past decade (Russell *et al.*, 2010; Pinder *et al.* 2011). The effect of these emission reductions have been observed in the measurements of wet deposition of NO₃⁻ across the US (Figure 3). While NO_x reduction trends show improvement, the trend in NH₃ emissions and deposition is less clear. There does not appear to be a downward trend in measurements of wet deposition of NH₄⁺ (Figure 3). Accordingly, there are many locations in the western US where N deposition has not declined in the last decade, such as Rocky Mountain National Park (Morris *et al.* 2011).

In the coming decades, combustion sources of NO_x are expected to continue to decrease as stricter standards are implemented (Moss *et al.* 2010). The representative concentration pathways (RCP), scenarios developed in support of the Intergovernmental Panel on Climate Change Fifth Assessment Report, project substantial reduction in NO_x emissions. Figure 4 displays one of these scenarios (RCP4.5), which includes NO_x emission reductions of 47% and 67% in 2030 and 2050, respectively, relative to 2006. Given these emission reductions, the resulting expected changes in N deposition and greenhouse gas uptake are shown in Figure 4. On average in the US, N deposition due to NO_x emissions is likely to decrease. Lower rates of N deposition will likely lead to lower CO₂ uptake by plants and less N₂O emitted. Unlike NO_x, NH₃ emissions are not expected to decline. Because NH₃ is emitted primarily from agriculture, these emissions are not expected to decrease without substantial change to food demand and production (Howarth *et al.* 2002, Davidson 2012).

These estimates of future CO₂ uptake are subject to many other factors that could substantially change the values presented in Figure 4. For example, over the long-term, the effects of N deposition on forest carbon storage depend on future deposition trends as well as patterns of forest disturbance and forest management decisions. Forest N saturation could occur in response to chronic N inputs, especially for

old forests or those in hotspots of N deposition (cf. Aber *et al.* 1998) such as those downwind of Los Angeles (Fenn *et al.* 2003) or projected for regions near tar sand petroleum extraction operations in Alberta (Allen 2004). Total N deposition is likely to decrease, but many locations in the US will experience a shift in the proportion of N deposited from oxidized N to greater NH₃ deposition (Pinder *et al.* 2008), and regional patterns of elevated N deposition are likely to shift from the eastern US to the Midwest. Emissions in other parts of the world, such as Asia, may increase in the future; however previous work suggests that the impact on US N deposition is likely to be small (Sanderson *et al.* 2008). However, rising atmospheric CO₂ concentrations over the next several decades are likely to increase demand for N by vegetation across the continent (e.g., Thornton *et al.* 2007). The projected decreases in deposition of oxidized N onto eastern forests (Figure 3) will likely eventually slow rates of N-induced forest CO₂ uptake. Increases in deposition of reduced N onto grasslands and woodlands will not likely have as large an effect on C storage as on forests, because of the much smaller C storage capacity in vegetation in these ecosystems relative to forests. The long-term fate of N-induced forest C storage depends not only on deposition trends, but also on the fate of the region's woody biomass. Forest disturbances, such as from fire, insects, or hurricanes, return accumulated C to the atmosphere as CO₂, either in rapid pulses through combustion by fires, or more slowly through decomposition in forests killed by insect or wind disturbance. Forests can continue to accumulate C for several centuries, but their capacity to accumulate C slows dramatically as the forest ages. Hence, in unharvested forests, the N-induced stimulation of forest C storage should slow over time. Alternatively, forests that are periodically harvested might sustain N-induced growth enhancements – as long as supplies of other nutrients, such as phosphorus or calcium, do not become limiting. For harvested forests, their capacity to continue to serve as C sinks depends in large part on the fate of their harvested wood and the fraction of it that enters long-lived wood product pools. In short, the relatively high rates of CO₂ uptake due to N deposition cannot be counted on to continue in the future.

Conclusions

Rates of NO_x and NH₃ emissions and atmospheric N deposition are substantially elevated over background levels across much of North America, with important implications for greenhouse gas fluxes. The most important effects of enhanced N deposition are enhanced CO₂ uptake by vegetation and increased N₂O emissions from soils. In the US, the net effect of N deposition on long-lived greenhouse gas fluxes is equal to an annual uptake of 170 Tg CO₂e. However, in the past decade, rates of NO_x emissions have declined and this trend is expected to continue over the next 20 years. In contrast, NH₃

emissions have been relatively stable and are not expected to change significantly in the near future. In total, projected rates of N deposition are expected to decline and climate assessments should anticipate lower rates of forest growth and C storage in the coming decades.

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Figure Legends

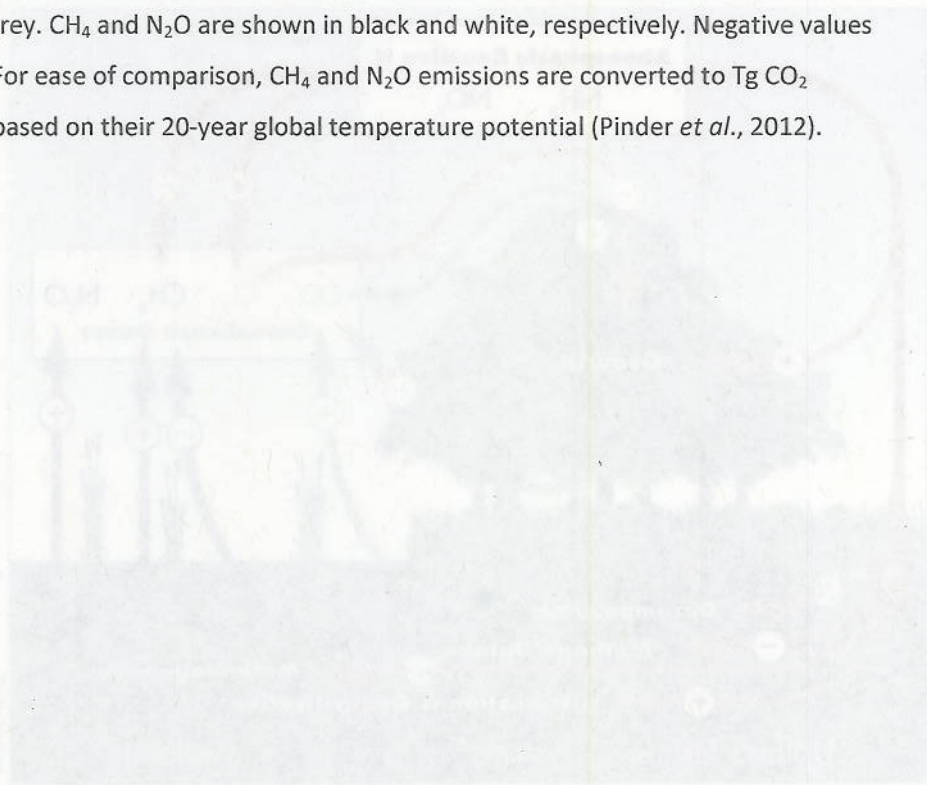
Figure 1. Effects of N deposition on greenhouse gas fluxes. Arrows with “+” indicate where an increase in one factor causes an increase in the next (e.g., an increase in N deposition often increases plant growth); arrows with “-” indicate where an increase in one factor causes a decrease in the next factor (e.g., an increase in growth decreases atmospheric CO₂). A series of chemical reactions with NO_x in the atmosphere lead to formation of tropospheric ozone (O₃) (+), and consumption of atmospheric methane (CH₄) (-). When N deposits on terrestrial ecosystems, it often stimulates plant growth (+), removing CO₂ from the atmosphere (-). Rising CO₂ concentrations can also stimulate growth (+), whereas increasing O₃ concentrations often slow growth (-). Nitrogen deposition not only affects plant growth, but can sometimes slow soil decomposition (-/0) and its release of CO₂ to the atmosphere. Nitrogen deposition can slow CH₄ uptake by microbes in aerobic soils (-), and has variable effects on CH₄ production by microbes in wetland soils (+/-). Nitrogen deposition typically increases microbial production of N₂O through both nitrification and denitrification in a range of aerobic and anaerobic soils (+).

Figure 2. Row 1: Spatial distribution of total atmospheric deposition of nitrogen (wet + dry) and cumulative ozone exposure across the continental US, southern Canada, and northern Mexico. Rates of atmospheric N deposition and ozone exposure (AOT40) were simulated by the Community Multi-scale Air Quality (CMAQ) chemical-transport model with 12 km horizontal resolution (Rao *et al.*, 2011). Row 2: percent of the landscape covered by forest and grassland (Kinnee *et al.* 1997); Row 3: the forested and grassland areas most severely exposed to both N deposition and ozone.

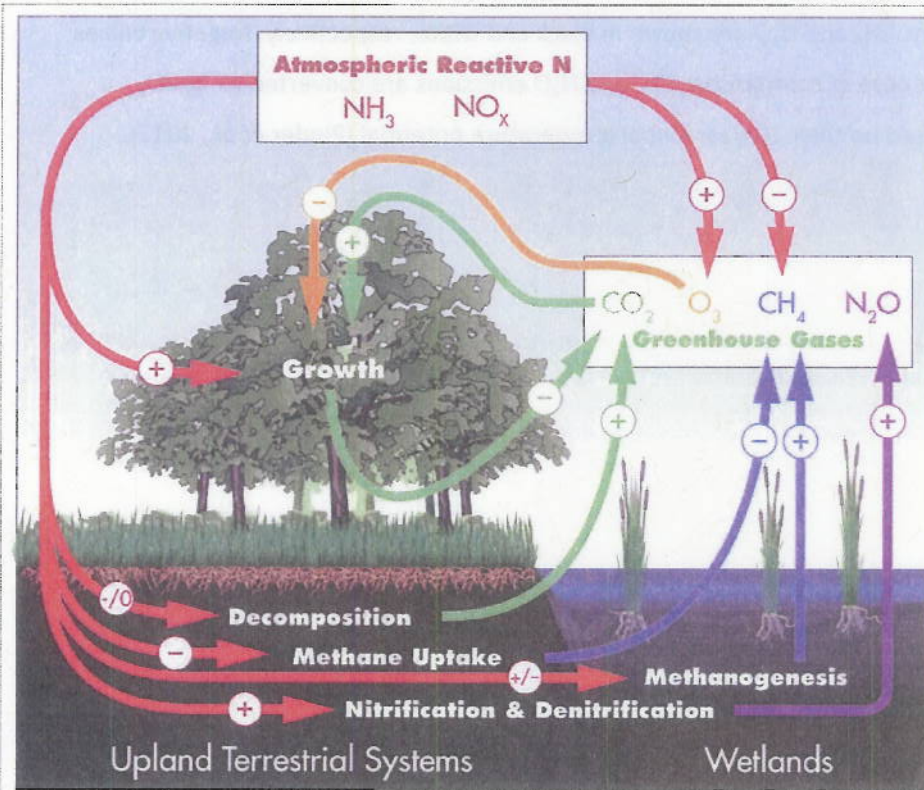
Figure 3. Trends in wet deposition of nitrogen (NADP, 2011) for the US (lines) and emissions of NO_x (USEPA, 2011; bars). NO_x emissions projected from the RCP4.5 scenario. Nitrate deposition is declining at a rate similar to the decrease in emissions, but this is not true for ammonia, nor is it true at all locations, such as Rocky Mountain National Park (Morris *et al.* 2011). The dashed lines denote the future trend as an extrapolation of the least-squares fit to the trend over the period 2000 – 2010.

Figure 4. Nitrogen emissions, N deposition, and greenhouse gas uptake from N deposition in 2006, 2030, and 2050 for the United States. Emissions in year 2006 are from the National Emission Inventory (USEPA, 2010). Future emissions are from RCP4.5 scenario (Moss *et al.*, 2011). Future N deposition and greenhouse gas uptake were calculated by scaling the results of Pinder *et al.* (2012) by the projected future emission rates. Nitrogen deposition includes wet and dry deposition to forests, grassland, croplands, and wetlands. Red shading denotes NO_x emissions and N deposition due to

441 NO_x emissions. Green shading denotes NH₃ emissions and N deposition due to NH₃ emissions. CO₂
442 uptake is shown in grey. CH₄ and N₂O are shown in black and white, respectively. Negative values
443 indicate emissions. For ease of comparison, CH₄ and N₂O emissions are converted to Tg CO₂
444 equivalence (CO₂e) based on their 20-year global temperature potential (Pinder *et al.*, 2012).

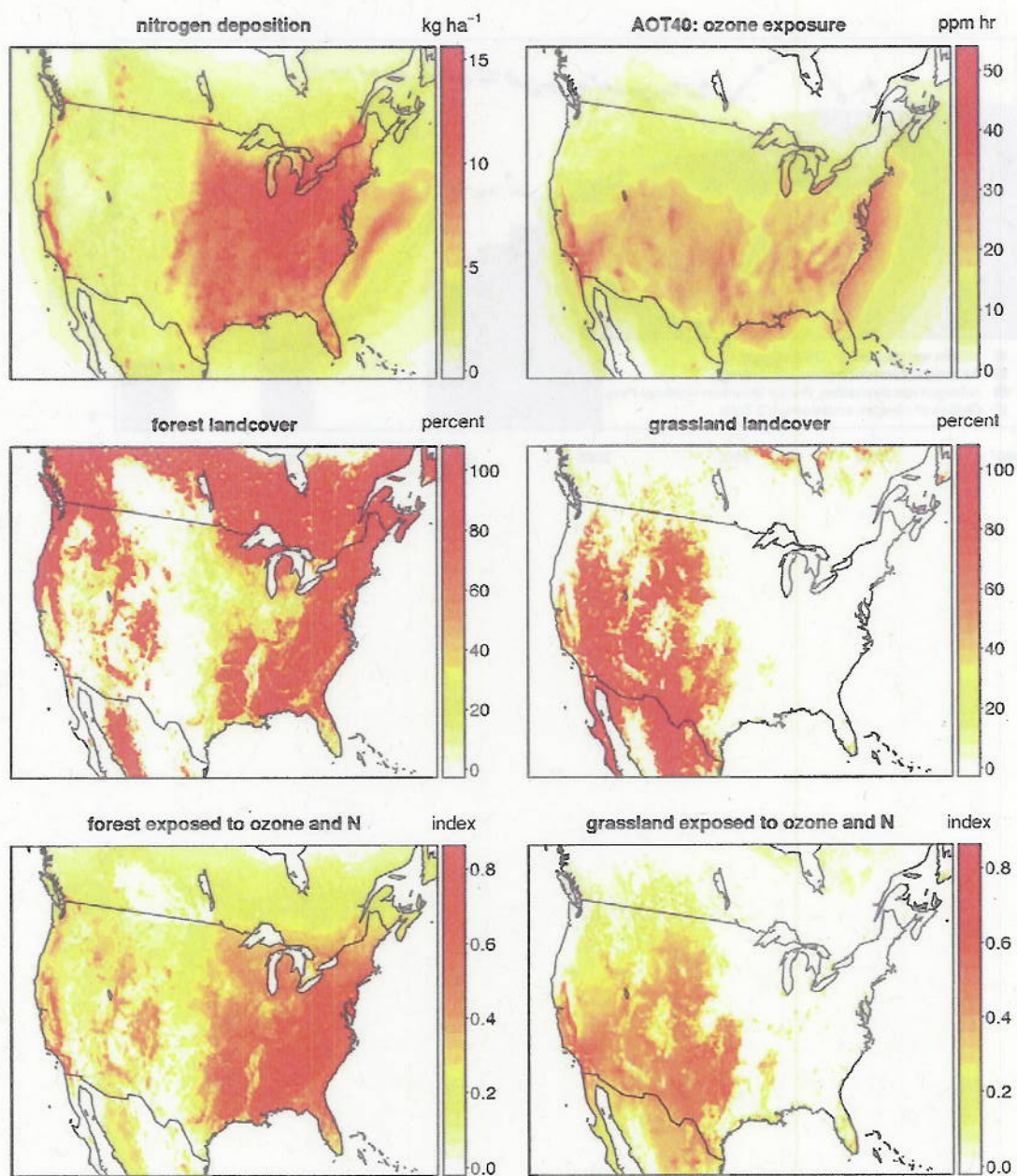


1 Figure 1.



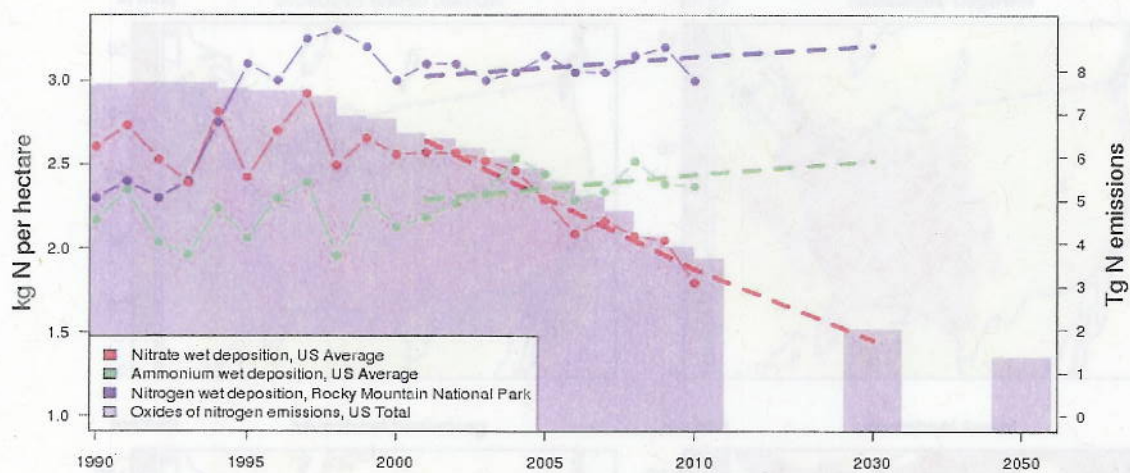
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1 Figure 2.



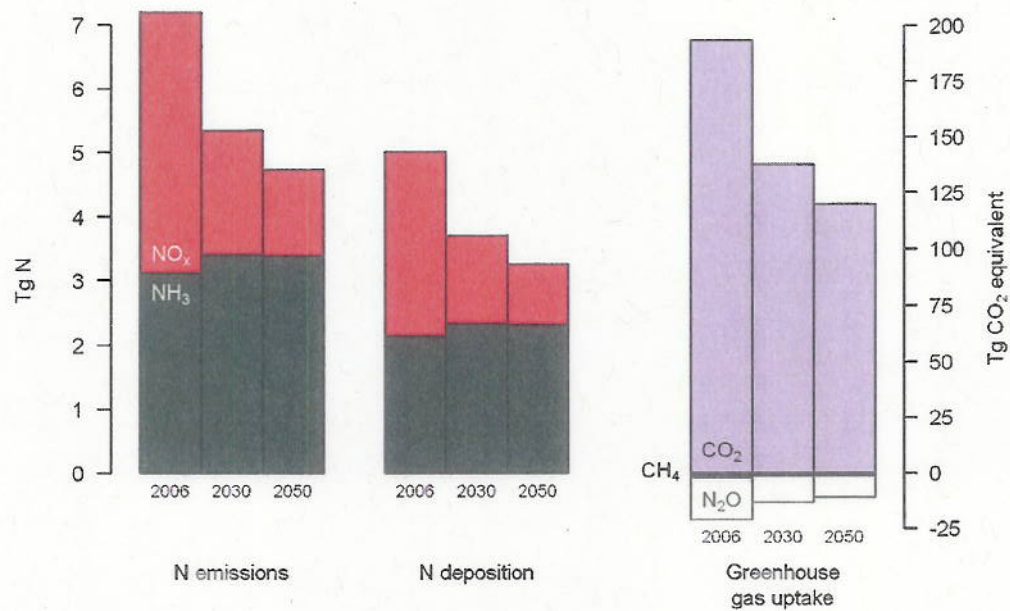
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1 Figure 3.



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1 Figure 4.



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