Ecological effects of nitrogen and sulfur air pollution in the US: what do we know?

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Four decades after the passage of the US Clean Air Act, air-quality standards are set to protect ecosystems from damage caused by gas-phase nitrogen (N) and sulfur (S) compounds, but not from the deposition of these air pollutants to land and water. Here, we synthesize recent scientific literature on the ecological effects of N and S air pollution in the US. Deposition of N and S is the main driver of ecosystem acidification and contributes to nutrient enrichment in many natural systems. Although surface-water acidification has decreased in the US since 1990, it remains a problem in many regions. Perturbations to ecosystems caused by the nutrient effects of N deposition continue to emerge, although gas-phase concentrations are generally not high enough to cause phytotoxicity. In all, there is overwhelming evidence of a broad range of damaging effects to ecosystems in the US under current air-quality conditions.

Front Ecol Environ 2012; 10(7): 365–372, doi: 10.1890/110049 (published online 29 Mar 2012)

Oxidized chemical forms of nitrogen (N) and sulfur (S) in the gas phase (NO_x and SO_x, respectively) are regulated under the US Clean Air Act (CAA) of 1970. These pollutants can enter plant stomata, damaging sensitive species. Typically, however, ambient air concentrations in the US are not high enough to cause damage. Instead, it is the deposition of atmospheric N and S onto the landscape that puts ecosystems at risk, through ecosystem acidification and alteration of nutrient balances. Acidification is caused by both wet deposition via precipitation and dry deposition of gases and particles of N and S from the atmosphere. The process of acidification was dubbed "acid rain" and made headlines in the US in the later decades of the 20th century; its conspicuous absence from the news in recent years may lead many to wonder whether acid rain is still a problem in this country. In addition to acidification, N deposition (in reduced, oxidized, and organic forms) can alter the nutrient balance of entire ecosystems, causing a cascade of effects. Furthermore, S deposition can stimulate microbes to methylate mercury (Hg), a process that introduces Hg into the food chain and leads to its bioaccumulation.

In a nutshell:

- Nitrogen oxides (NO_x) and sulfur oxides (SO_x) are emitted to the atmosphere as a result of human activities, including combustion and land-use practices
- These pollutants are regulated through National Ambient Air Quality Standards (NAAQS), which are intended to protect ecosystems from gas-phase effects on vegetation and to minimize impacts on human health
- Current emissions of NO_x and SO_x to the atmosphere contribute to total nitrogen (N) and sulfur (S) deposition, leading to acidification, N enrichment, and S-induced mercury methylation in sensitive ecosystems throughout the US
- Current air-quality standards do not protect ecosystems from the effects of N and S deposition in many parts of the nation

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The US Environmental Protection Agency (EPA) prepared an Integrated Science Assessment (ISA) to review the secondary National Ambient Air Quality Standards (NAAQS) for NO_x and SO_x in response to a court decision requiring a review of the standards (US EPA 2008). Approximately 3000 publications were evaluated in the ISA to determine whether NO_x and SO_x are causing harm to sensitive ecosystems under current conditions. The effects of NO_x and SO_x were also evaluated relative to total N and S deposition. The main results of this review are summarized here, and the policy implications of these findings are discussed. The main effects associated with NO_x and SO_x are illustrated in Figure 1.

■ N and S air pollution policy in the US

The CAA lists NO_x and SO_x as pollutant categories for which NAAQS may be set. Under the CAA, "primary standards" are set for the protection of human health, whereas "secondary standards" are established to protect public welfare. In this usage, welfare includes, but is not limited to, soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on man-made materials, personal comfort, and well-being. In 1971, the

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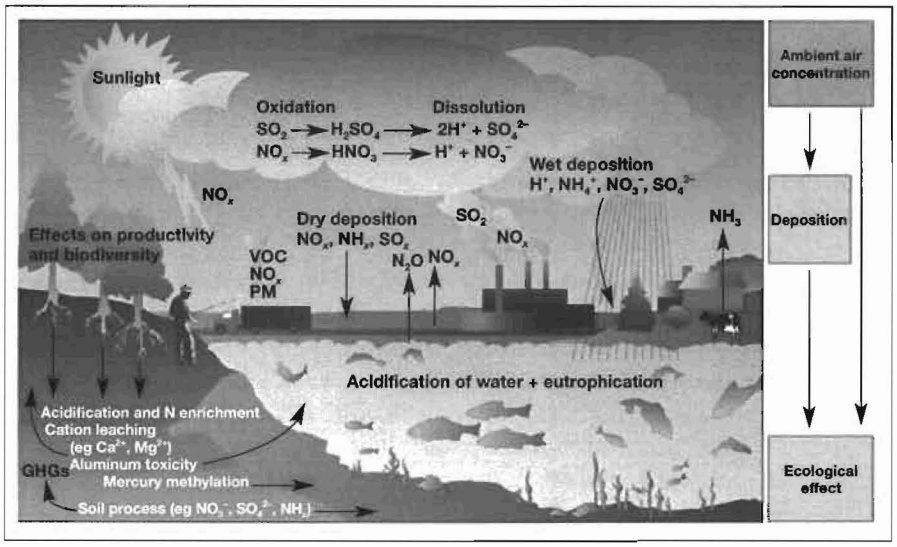

Figure 1. Simplified diagram of the ecological effects caused by nitrogen and sulfur air pollution. VOC = volatile organic compound; PM = particulate matter; GHGs = greenhouse gases.

EPA set NO_x and SO_x secondary NAAQS based on gas-phase phytotoxic effects. The NO_x secondary NAAQS was set equal to the primary NAAQS at an annual average nitrogen dioxide (NO_2) concentration of 0.053 parts per million (ppm). In that same year, the SO_x secondary NAAQS was set at sulfur dioxide (SO_2) equal to a 3-hour average of 0.50 ppm, not to be exceeded more than once a year. By the 1970s, European scientists had already documented that deposition derived from atmospheric NO_x and SO_x could cause acidic conditions in sensitive ecosystems, although less was known about such effects in the US. In 1979, the Clean Air Scientific Advisory Committee (CASAC) to the EPA recommended preparation of a comprehensive report on atmospheric deposition as a cause of acidification before regulation was considered. Subsequently, several extensive scientific reports documented the adverse effects of NO_x and SO_x deposition, although it was difficult to quantitatively link deposition to ambient air concentrations. This represented a barrier to regulating these pollutants through the nation's primary legislative mechanism – the CAA – which stipulates that NAAQS be set for ambient air concentrations.

The CAA Amendments (CAAA) of 1990 included Title IV, an amendment relating to acid deposition and control, which was enacted to reduce emissions of SO_2. The EPA's report, *Acid Deposition Standard Feasibility Study: Report to Congress* (US EPA 1995), concluded that, although establishing NAAQS for S and N deposition may become technically feasible at some point in the future, appropriate deposition loads for acidifying chemicals could not be defined with reasonable certainty, and there was no effective method available to quantify the relationship between air concentrations of N and S compounds and N and S deposition at the time of the report. By 1999, seven northeastern states petitioned the EPA to develop secondary NAAQS for NO_x and SO_x. In 2005, the EPA initiated the most recent review of the secondary NO_x and SO_x NAAQS.

■ Current deposition

Atmospheric deposition of N and S compounds varies across the country. Since the passage of the 1990 CAAA, wet S deposition has decreased by 35% or more across the eastern US. Nitrogen deposition, which includes oxidized and reduced (NH_x) forms, changed little between the 1980s and 2000 (Baumgardner *et al.* 2002) but has generally decreased since then. Oxidized N from NO_x emissions, chiefly from fossil-fuel combustion (Elliott *et al.* 2007), typically makes up 50–75% of current total N atmospheric deposition at a distance from sources, but may represent < 10% of total N deposition near sources such as confined animal operations. Ammonia (NH_3) emissions from croplands, animal feeding operations, and increasingly from automobiles are important sources of N pollution in some parts of the country; NH_3 is not a pollutant regulated under the NAAQS.

Several networks monitor chemical constituents of N and S deposition. Wet deposition is routinely monitored at sites distributed across the US by the National Atmospheric Deposition Program's National Trends Network (NADP/NTN). The spatial distribution of the monitoring sites varies and sites are sparse in some areas, especially at high elevations in the mountainous West. Dry deposition is more difficult to measure; it is therefore calculated from air concentration measurements, using a model of the deposition velocity, which is needed to quantify the flux of pollutants from the air onto vegetation surfaces. These methods of quantifying dry deposition rely on assumptions that introduce substantial uncertainty into these estimates. The EPA Clean Air Status and Trends Network (CASTNET) provides estimates of dry deposition at sites throughout the country, but not all important depositing species of N are monitored. Spatial interpolation of data from the monitoring networks is valuable for understanding the ecological effects of deposition. The NADP/NTN-measured values of wet deposition are sufficient to allow for broad, regional interpolation of wet deposition values, at least in the eastern US (Ito *et al.* 2002). In contrast, the CASTNET sites are too widely dispersed to allow for regional interpolation of dry deposition.

To generate regional estimates of total wet plus dry atmospheric deposition of S and/or N, an atmospheric

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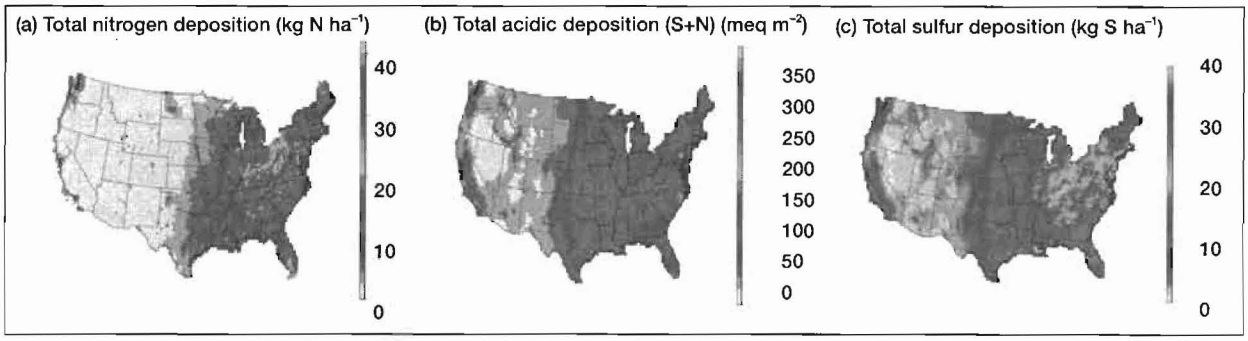

Figure 2. *Maps of CMAQv4.7.1 estimates of annual (a) sulfur, (b) inorganic nitrogen, and (c) acidic deposition for 2002 for a 12-km grid over the continental US, where wet deposition is adjusted by the ratio of observed to modeled precipitation and then regionally corrected for wet deposition bias, and where observed precipitation is from the Parameter-elevations Regressions on Independent Slopes Model.*

transport model, such as the Community Multiscale Air Quality (CMAQ) model (Byun and Schere 2006), is commonly used. The CMAQ estimates of total S and N deposition are as high as 40 kg S ha^{-1} yr^{-1} and 24 kg N ha^{-1} yr^{-1}, respectively, in some hotspots within the US. In general, estimated deposition is heterogeneous across the landscape (Figure 2). CMAQ dry deposition values tend to be higher than estimates developed from CASTNET data but are similar to estimates provided by the Canadian Air and Precipitation Monitoring Network. Considerable uncertainty remains regarding the overall estimation of total S and N deposition; this is an area of active research.

■ Acidification

The effects of N (NO_x and NH_x) and S deposition on aquatic and terrestrial ecosystems have been well studied over the past several decades, leading to the identification of vulnerable regions, and the development of ecological indicators and robust biogeochemical models. Vulnerable and affected areas typically result from (1) inherent ecosystem sensitivity and (2) exposure to acid deposition. Sensitivity is primarily governed by surficial geology, topography, and interactions between drainage water and soil. Of particular importance is the weathering of base cations that can counterbalance acidic anions from deposition. Other factors that contribute to the sensitivity of soils and surface waters to acid deposition include landscape position, vegetation, soil characteristics, land use, and hydrologic flowpath (Lawrence *et al.* 1999; Sullivan *et al.* 2007b).

Acidity develops naturally in soil, but this process is both altered and accelerated by acid deposition from anthropogenic sources. Areas in the US that are most sensitive to terrestrial effects of acid deposition include forests in the Adirondack Mountains of New York State, the Green Mountains of Vermont, the White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the central and southern Appalachian Mountains (Driscoll *et al.* 2001; McNulty *et al.* 2007). The biological effects of acidification on terrestrial ecosystems are often attributable to aluminum (Al) toxicity and the decreased ability of plant roots to take up nutrient base cations (Cronan and Grigal 1995). There are widespread areas of ongoing acidification in forest soils in the northeastern US, despite recent decreases in acid deposition and the recovery of some surface waters (Bailey *et al.* 2005; Warby *et al.* 2009).

Surface waters in the US that are most sensitive to acidification are largely found in the East, Florida, the Upper Midwest, and the mountainous West (Figure 3; Omernik and Powers 1983; Baker *et al.* 1991; Driscoll *et al.* 2001; McNulty *et al.* 2007; Nanus *et al.* 2009). Surface-water acidification from atmospheric deposition affects aquatic biota by altering surface-water chemistry and can cause the loss of acid-sensitive biota; the greater the acidification, the more species are lost (Driscoll *et al.* 2001). These effects on aquatic biota directly affect ecosystem services, including water-based recreational activities and tourism. Changes in water chemistry associated with acidification include alterations in the concentrations of sulfate (SO_4^{2-}), nitrate (NO_3^-), inorganic Al, and calcium ions (Ca^{2+}); surface-water pH; the sum of base cations; acid-neutralizing capacity (ANC); and base cation surplus (Lawrence *et al.* 2007), although not all of these chemical indicators have direct effects on biota. Acid-neutralizing capacity is commonly used as an indicator of acidification; decreases in pH and increases in inorganic Al concentration co-vary with decreasing ANC and can cause toxic conditions that lead to declines in sensitive species of phytoplankton, zooplankton, macroinvertebrates, and fish (Rago and Wiener 1986; Driscoll *et al.* 2001). Adverse biological effects may be seen at pH levels < 6.0–6.5 and inorganic Al concentrations >30–50 μg L^{-1} (Baker *et al.* 1990). Aluminum effects vary substantially by organism, life stage, and type of surface water. Calcium ameliorates some of the effects of acidity and Al on biota. Most organisms can tolerate lower pH levels and greater Al levels at higher Ca^{2+} concentrations.

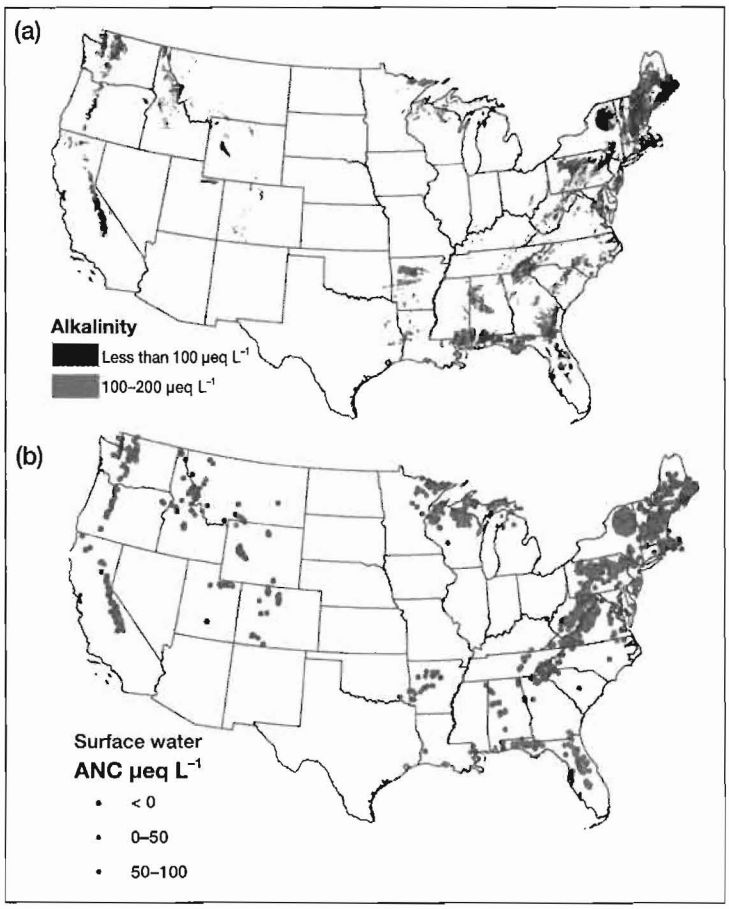

Figure 3. *A synoptic illustration of surface-water sensitivity to acid deposition in the conterminous US. Maps of (a) total alkalinity classified by Omernik and Powers (1983), which is based on available measurements of the acid-neutralizing capacity (ANC) of surface waters from data collected before 1980, and (b) surface-water measurements of ANC less than 100 μeq L^{-1} from water-quality data since 1984. Although the actual sensitivity of a water body depends on many watershed characteristics and processes, the low-alkalinity and ANC areas on the map indicate where sensitive surface waters are most likely to be found.*

Although both N and S deposition can cause aquatic acidification, S deposition is generally the primary cause of chronic acidification, with secondary contributions from N deposition. By 2000, one-quarter to one-third of the lakes and streams in the US that were chronically acidic (ANC ≤ 0 microequivalents per liter [μeq L^{-1}]) in the late 1980s and 1990s had shown increases in ANC in response to decreased S deposition and were no longer acidic during baseflow (streamflow derived from groundwater seepage into the stream) (Kahl *et al.* 2004). However, several lakes and streams remain acidic, even though wet SO_4^{2-} deposition has been decreasing since about 1989. Nitrate pulses into aquatic ecosystems, resulting in part from N deposition, are a main cause of episodic acidification and short-term decreases in ANC that in turn affect biota in some sensitive surface waters (Lawrence *et al.* 2008). In both the mountainous West and the Northeast, the most severe acidification of surface waters generally occurs episodically, during spring snowmelt.

Trends in the condition of ecological indicators of aquatic acidification have varied over the past two decades, with some sites showing recovery and others showing little change. Figure 4 shows time-series data for SO_4^{2-}, NO_3^-, Ca^{2+}, Gran ANC (that is measured by the Gran titration method), and pH in Dart Pond, New York (Adirondack region) and Meadow Run, Virginia (a stream in the Shenandoah region). Dart Pond's recovery is indicated by decreasing SO_4^{2} and NO_3^- and increasing pH and ANC, whereas Meadow Run shows little to no change due to soil conditions that inhibit recovery in this area.

Process-based mathematical models calibrated to Adirondack lake watersheds suggest that the number of acidic lakes may increase in the future under continued current deposition loads (Sullivan *et al.* 2007a). This is largely because soils continue to acidify under these loads (Warby *et al.* 2009).

■ Nutrient effects of N deposition

The effects of N deposition on ecosystems can range from fertilization that stimulates plant growth and forest carbon (C) storage, to nutrient imbalances that reduce plant productivity, alter species assemblages, and diminish biodiversity, to acidification of soils and waters (Figure 5; Fenn *et al.* 2003; Bricker *et al.* 2008; Lovett and Goodale 2011; Pardo *et al.* 2011). Through its many chemical forms and biogeochemical pathways, N may simultaneously act as a nutrient and as a strong acid anion in some ecosystems, causing a range of effects that may be considered both positive and negative (Compton *et al.* 2011). The full extent of ecosystem nutrient effects is still unknown. Substantial empirical information has been collected from selected ecosystems and for specific indicators. However, given the complexity of the N cycle, a broadly applicable and well-tested predictive model of the ecological effects of N deposition is not yet available. Although the sensitivity of ecosystems to N deposition across the US varies, a large body of evidence clearly demonstrates a broad range of ecological effects.

The contribution of N deposition from the atmosphere to total N load varies among ecosystems; it is the main source of new N to most high-elevation lakes and headwater streams (Fenn *et al.* 2008). Terrestrial, wetland, freshwater, and estuarine ecosystems receive N through multiple pathways (eg biological N-fixation, agricultural run-off and wastewater effluent), with variable contributions from the atmosphere. There are multiple biogeo-

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chemical indicators of N deposition effects. The onset of NO_3^- leaching is one of the best documented biogeochemical indicators that a terrestrial ecosystem is receiving more N than it is able to retain (Aber *et al.* 2003). Nitrogen retention by terrestrial ecosystems represents a valuable ecosystem service by regulating water quality. When atmospheric deposition of N impairs the ability of terrestrial and aquatic ecosystems to retain and remove N, NO_3^- leaching occurs, which can lead to degradation of water quality (Aber *et al.* 2003; Bergström and Jansson 2006; Bricker *et al.* 2008). The level of N deposition associated with both the onset of N saturation and the associated NO_3^- leaching, as well as increases in foliar, soil, and streamwater N concentrations, has been shown to range from 5 to 18 kg N ha^{-1} yr^{-1} in different ecosystems (Figure 5; Aber *et al.* 2003; Fenn *et al.* 2008).

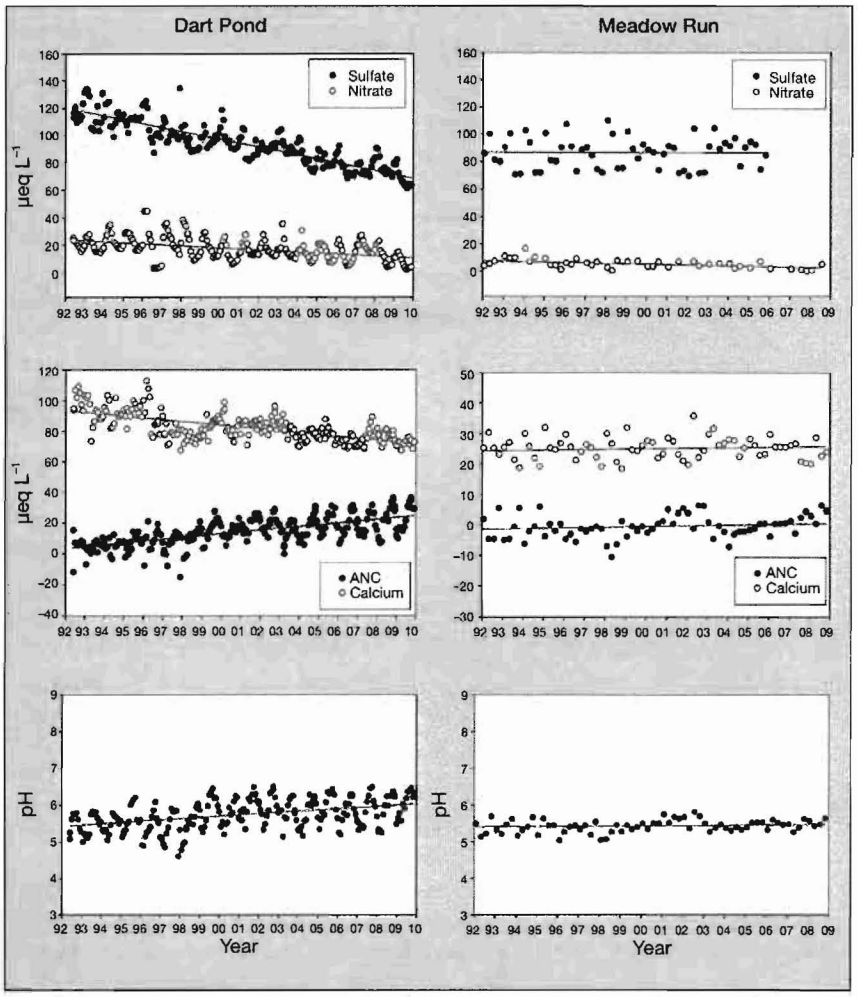

Figure 4. *Time-series data for sulfate (SO_4^{2-}), nitrate (NO_3^-), calcium ions (Ca^{2+}), Gran-acid neutralizing capacity (ANC), and pH in Dart Pond, New York (Adirondack region) and Meadow Run, Virginia (a stream in the Shenandoah region). Data collected as part of two EPA programs: the Temporally Integrated Monitoring of Ecosystems (TIME) project and the Long-Term Monitoring (LTM) project.*

Nitrogen deposition in terrestrial and wetland ecosystems alters biogenic sources and sinks of methane (CH_4), nitrous oxide (N_2O), and two greenhouse gases (GHGs), resulting in increased emissions of these gases to the atmosphere (Liu and Greaver 2009; Butterbach-Bahl *et al.* 2011). The addition of N decreases CH_4 uptake in coniferous and deciduous forests, and increases CH_4 production in wetlands (Liu and Greaver 2009), while increasing the biogenic emission of N_2O in coniferous forests, deciduous forests, grasslands, and wetlands. Although N addition can cause a rise in biogenic CH_4 and N_2O emissions from soils, it is difficult to generalize a dose–response relationship because GHG production is influenced by multiple environmental factors (eg soil, vegetation, and climate) that vary greatly over small spatial and temporal scales (Liu and Greaver 2009).

Nitrogen is often the nutrient that most limits plant growth in terrestrial ecosystems (LeBauer and Treseder 2008). Nitrogen deposition can increase primary productivity, thereby altering the biogeochemical cycling of C and potentially altering ecosystem C budgets. Nitrogen deposition has been shown to increase C sequestration in some forest ecosystems (Liu and Greaver 2009; Thomas *et al.* 2010; Butterbach-Bahl *et al.* 2011). However, the net effect of N on the C budgets of non-forest ecosystems remains unclear (Liu and Greaver [2009]; see additional discussion in WebPanel 1). In addition to total ecosystem C sequestration, N deposition can also change C allocation patterns. Typically, N deposition stimulates aboveground growth more than it does belowground growth, which can increase susceptibility to (1) severe fires, as the biomass becomes fuel under dry conditions, (2) drought, because the lower root-to-shoot ratio results in less water uptake relative to the amount of shoots or foliage, and (3) wind damage, as a lower root-to-shoot ratio decreases the structural anchorage of some plant species. These effects have been shown in studies conducted in the western US and Europe (Braun *et al.* 2003; Fenn *et al.* 2003). Alteration of primary productivity can also alter competitive interactions among plant species. The increase in plant growth in response to increased N supply is greater for some species than others, leading to possible shifts in population dynamics, species composition, community structure, and ecosystem type.

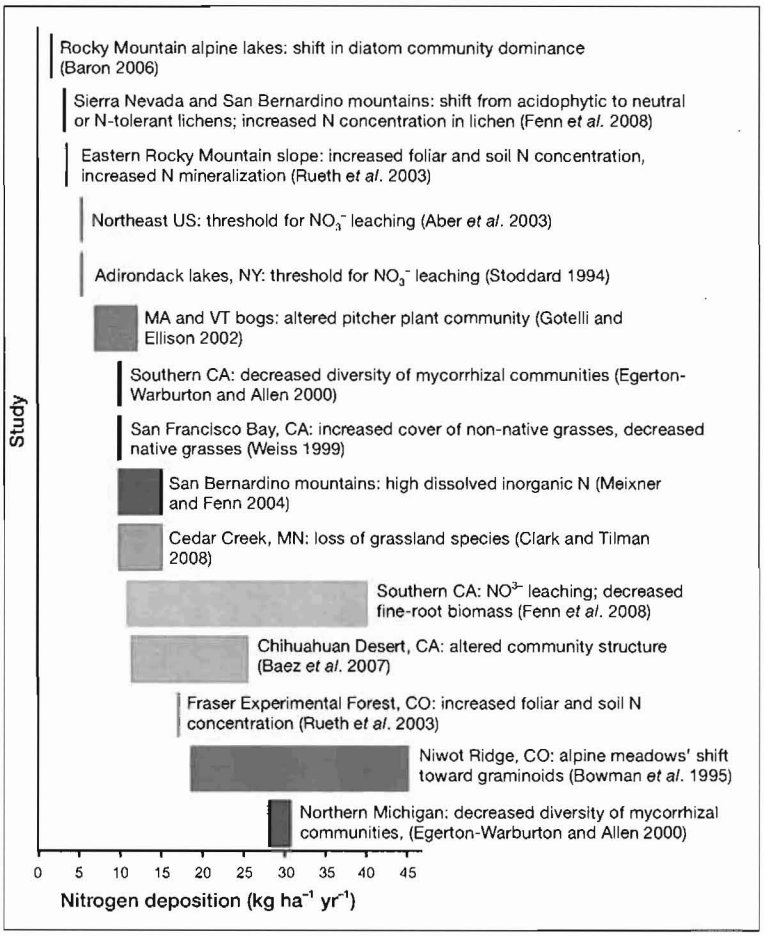

Figure 5. *The continuum of ecological sensitivity to N deposition. Bibliographic information for citations mentioned in this figure can be found in the References and WebReferences.*

Numerous sensitive terrestrial biota and ecosystems are affected by N deposition (Figure 5). Acidophilic lichens are among the most sensitive of these taxa, with adverse effects occurring in response to exposures as low as 3 kg N ha^{-1} yr^{-1} in the Pacific Northwest and southern California (Fenn *et al.* 2008). The decline of biodiversity in grasslands begins to occur at atmospheric N loading of about 5 kg N ha^{-1} yr^{-1} in Minnesota and Europe (Clark and Tilman 2008; Bobbink *et al.* 2010). Altered community composition of alpine ecosystems in the Rocky Mountains and forest encroachment into temperate grasslands in southern Canada have been estimated to occur at deposition levels of about 10 kg N ha^{-1} yr^{-1} (Bowman *et al.* 2006).

The productivity of some freshwater ecosystems is also N-limited (Elser *et al.* 2007). Nitrogen deposition can alter aquatic species assemblages and cause eutrophication of aquatic ecosystems to the extent that N is the growth-limiting nutrient (Elser *et al.* 2009). In the Rocky Mountains, wet deposition loads of approximately 1.5–2 kg N ha^{-1} yr^{-1} are reported to have altered species composition in the diatom communities of some freshwater lakes (Baron 2006).

In estuarine ecosystems, atmospheric and non-atmospheric sources of N contribute to increased phytoplankton and algal productivity, leading to eutrophication (Bricker *et al.* 2008). Water-quality deterioration as a result of estuarine eutrophication can lead to adverse effects, such as hypoxia, species mortality, and harmful algal blooms. Chesapeake Bay, for example, is a large, well-studied, and severely eutrophic estuary that is estimated to receive as much as 30% of its total inorganic N load from the atmosphere (Castro *et al.* 2003; Bricker *et al.* 2008).

■ S-induced mercury methylation

Methyl mercury (MeHg) is highly neurotoxic. In 2006, 3000 fish consumption advisories were issued in the US because of high concentrations of MeHg in fish. As of July 2007, 23 states had issued statewide advisories (http://epa.gov/waterscience/fish/advisories/). The majority of Hg in the environment was contributed by historical deposition and accumulation, although some atmospheric emissions and deposition continues. Ninety to 99% of the Hg that is taken up and accumulated in biota is in the methylated form (Harris *et al.* 2003). The production of potentially harmful MeHg is facilitated by the presence of both SO_4^{2-} and Hg. Methylation is accomplished mainly by sulfate-reducing bacteria. Where Hg is present, increased availability of SO_4^{2-} results in increased production of MeHg. The amount of MeHg produced varies with oxygen content, temperature, pH, and supply of labile organic C (Munthe *et al.* 2007). Once methylated, Hg is more readily taken up by microorganisms, zooplankton, and macroinvertebrates and bioconcentrated at higher trophic levels (eg in fish and fish-eating wildlife; Scheuhammer *et al.* 2007). Watersheds with conditions known to be conducive to Hg methylation can be found in the northeastern US and southeastern Canada. Mercury bioaccumulation has also been widely observed in other regions, where a different set of conditions may exist, although these have not been studied as extensively (Evers *et al.* 2007; Shanley *et al.* 2008).

■ Gas-phase effects

Acute and chronic exposure to SO_2 can have phytotoxic effects on vegetation, including foliar injury, decreased photosynthesis, and reduced growth (Winner *et al.* 1985). Acute exposures to NO_2, NO, peroxyacetyl nitrate, and nitric acid (HNO_3) cause plant foliar injury and reduced

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growth (Cape 2003). However, most studies have been performed at concentrations of these gas-phase chemical species that are well above current ambient conditions observed in the US. There is little evidence that current concentrations of gas-phase S or N oxides are high enough to cause phytotoxic effects in this country (US EPA 2008). However, some studies indicate that current HNO_3 concentrations may be contributing to the decline in lichen species in the Los Angeles basin (Nash and Sigal 1999; Riddell *et al.* 2008).

Conclusions and policy implications

There is overwhelming scientific evidence that atmospheric deposition of NO_x, NH_x, and SO_x cause a broad range of detrimental effects and perturbations to ecosystems in the US under current air-quality conditions. The best understood of these effects are aquatic acidification, for which there are well-documented and quantified chemical indicators, and effects on biota. The section of the CAAA known as Title IV led to cap-and-trade of SO_2 emissions beginning in the 1990s, which successfully reduced the magnitude and extent of acidification. Despite this success, acidification remains a problem in many parts of the US. Ecosystem effects attributable to N enrichment are less well-understood. Setting air-quality standards to protect sensitive ecosystems from acidification and the enrichment effects of N and S is one potential policy tool.

Key scientific research areas that will be important for policy making involve the protection of ecosystems from acidification and nutrient effects caused by atmospheric deposition. First, more deposition-to-response relationships are needed, to identify a level of pollutant exposure that is still protective of ecosystems. 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). To date, CLs for acidification are reported for some sensitive areas of the US; however, few CLs have been reported for N and S nutrient effects, although this is slowly changing as the first US assessment of N CLs has recently been published (Baron *et al.* 2011; Pardo *et al.* 2011). The CL approach has not yet been formally and broadly applied in the US, but is widely used in Europe and Canada (Burns *et al.* 2008). Second, ecosystem sensitivity to N and S deposition is heterogeneous across the US landscape; tools will therefore need to be developed to extrapolate site-specific data to inform policies that apply at the national scale.

NH_x is currently unregulated as a "critera" air pollutant under the NAAQS, yet it acts in combination with NO_x to cause nutrient effects, and with NO_x and SO_x to cause acidification. Approaches will need to be developed that consider how a given quantity of NH_x deposition relates to total N deposition or acidic deposition, to determine how much can occur while still ensuring protection of sensitive ecosystems. Finally, in order to regulate NO_x and SO_x via the NAAQS, deposition must be related to ambient air quantities. This is now possible via calculations of deposition velocities from models (eg CMAQ); however, additional research is needed to decrease the uncertainty in the broad-scale application. In all, there have been great advances in our understanding of the pathways and causes of ecological responses to atmospheric N and S deposition over the past several decades, which can be used for environmental protection from these pollutants.

Acknowledgements

We thank S Jordan and T Long for helpful comments on the manuscript. This work was funded by the EPA. The study was reviewed by the National Center for Environmental Assessment, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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