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

Tara L Greaver[1*], Timothy J Sullivan[2], Jeffrey D Herrick[1], Mary C Barber[3], Jill S Baron[4], Bernard J Cosby[5], Marion E Deerhake[6], Robin L Dennis[1], Jean-Jacques B Dubois[1], Christine L Goodale[7], Alan T Herlihy[8], Gregory B Lawrence[9], Lingli Liu[1], Jason A Lynch[10], and Kristopher J Novak[1]

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

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

[1]*US Environmental Protection Agency, Research Triangle Park, NC* [*]*(greaver.tara@epa.gov);* [2]*E&S Environmental Chemistry, Corvallis, OR;* [3]*Research Triangle Institute, Washington, DC;* [4]*US Geological Survey, Fort Collins, CO;* [5]*University of Virginia, Charlottesville, VA;* [6]*Research Triangle Institute, Research Triangle Park, NC;* [7]*Cornell University, Ithaca, NY;* [8]*Oregon State University, Corvallis, OR;* [9]*US Geological Survey, Troy, NY;* [10]*US Environmental Protection Agency, Washington, DC*

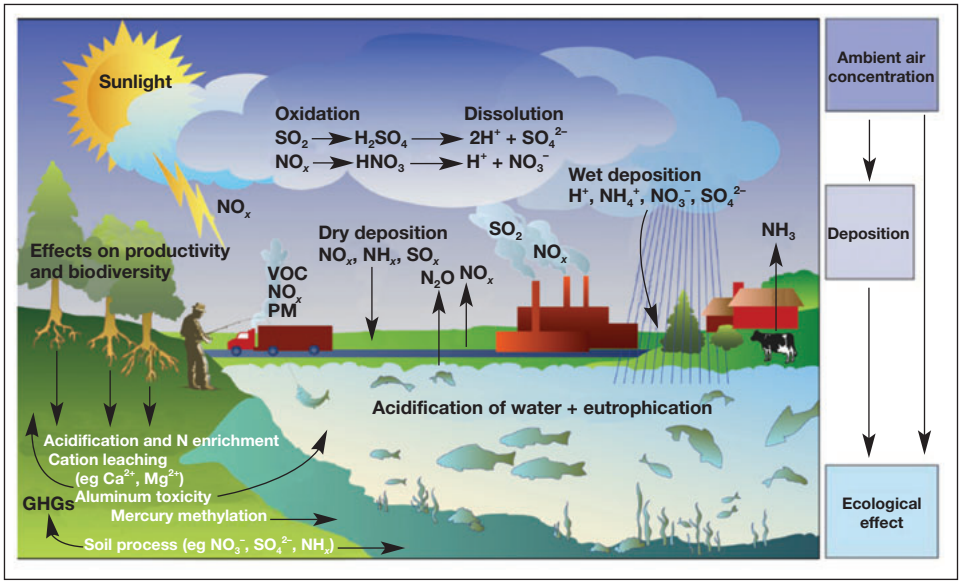

Figure 1. *Simplified diagram of the ecological effects caused by nitrogen and sulfur air pollution. VOC = volatile organic compound; PM = particulate matter; GHGs = greenhouse gases.*

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

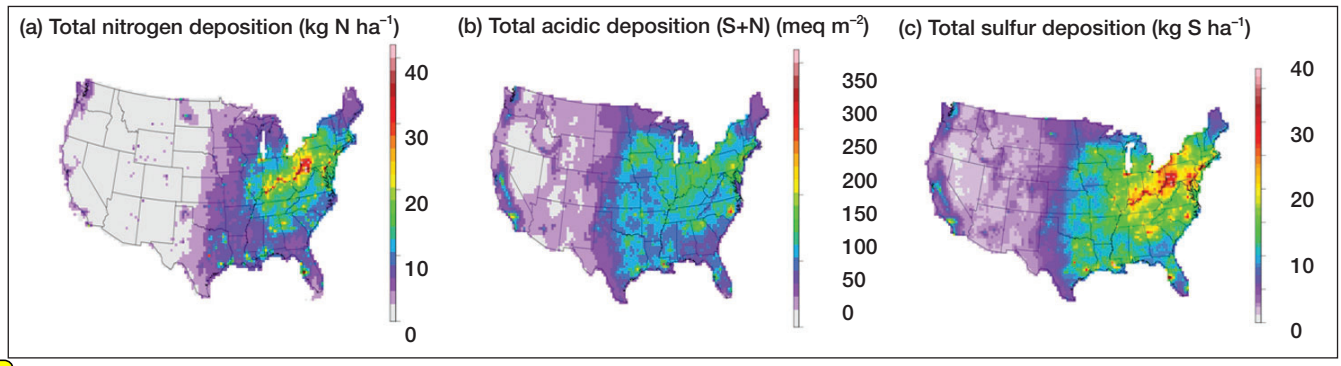

Figure 2. *Maps of CMAQv4.7.1 estimates of annual (a) sulfur, (b) inorganic nitrogen, and (c) acidic deposition for 2002 for a 12-km grid over the continental US, where wet deposition is adjusted by the ratio of observed to modeled precipitation and then regionally corrected for wet deposition bias,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

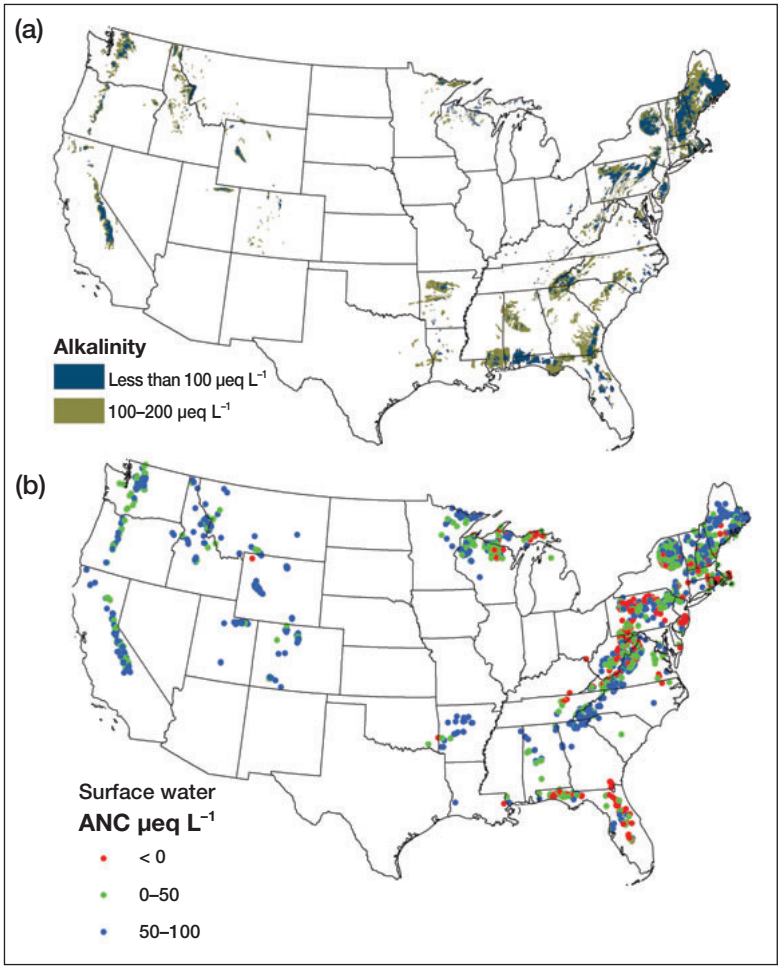

Figure 3. *A synoptic illustration of surface-water sensitivity to acid deposition in the conterminous US. Maps of (a) total alkalinity classified by Omernik and Powers (1983), which is based on available measurements of the acid-neutralizing capacity (ANC) of surface waters from data collected before 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-

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).

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).

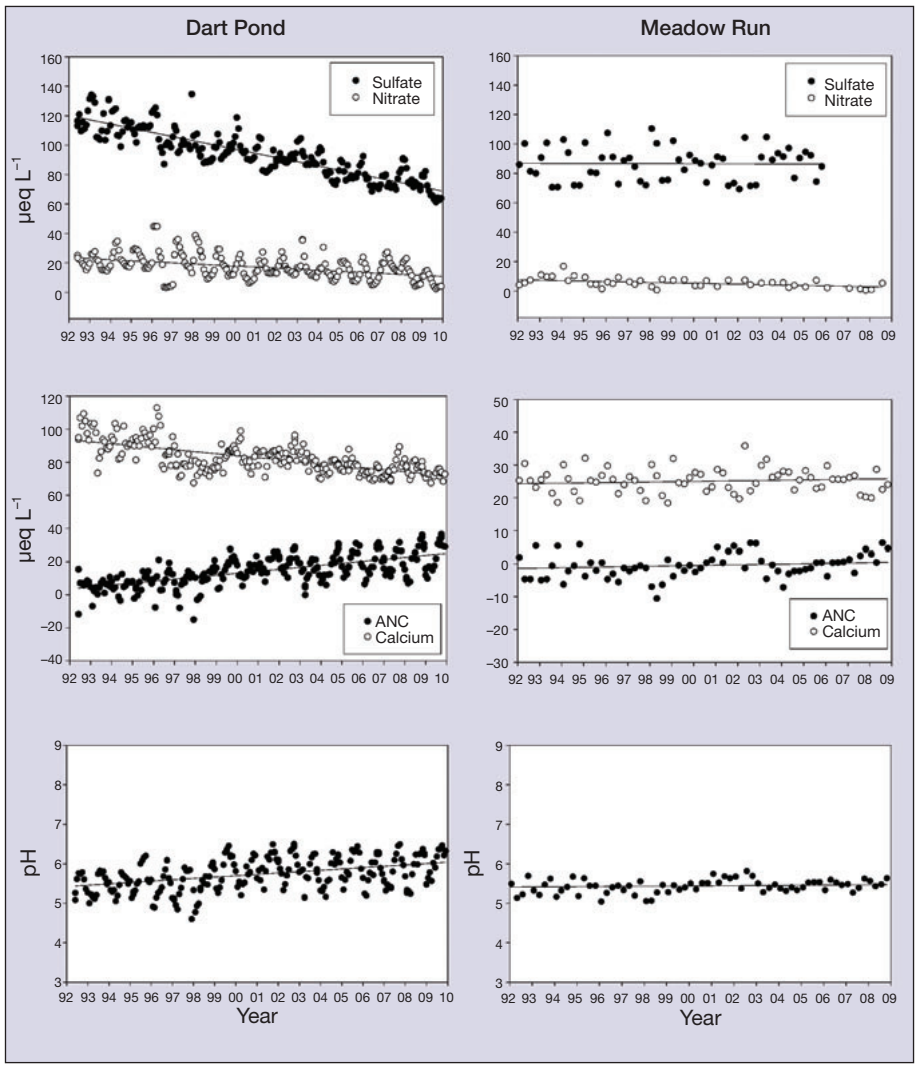

Figure 4. *Time-series data for sulfate (SO_4^{2-}), nitrate (NO_3^-), calcium ions (Ca^{2+}), Gran-acid neutralizing capacity (ANC), and pH in Dart Pond, New York (Adirondack region) and Meadow Run, Virginia (a stream in the Shenandoah region). Data collected as part of two EPA programs: the Temporally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

Nitrogen 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.

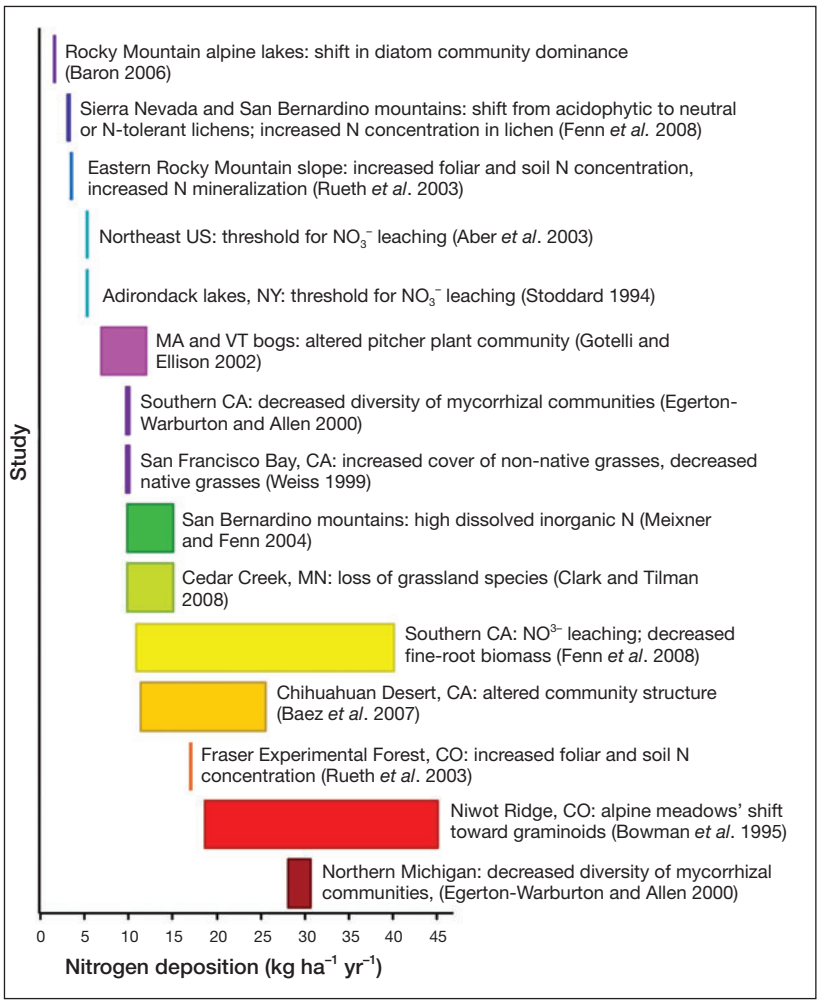

Figure 5. *The continuum of ecological sensitivity to N deposition. Bibliographic information for citations mentioned in this figure can be found in the References and WebReferences.*

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

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.

References

Aber JD, Goodale CL, Ollinger SV, *et al.* 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *BioScience* **53**: 375–89.

Bailey SW, Horsley SB, and Long RP. 2005. Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. *Soil Sci Soc Am J* **69**: 681–90.

Baker LA, Herlihy AT, Kaufmann PR, and Eilers JM. 1991. Acidic lakes and streams in the United States: the role of acidic deposition. *Science* **252**: 1151–54.

Baker LA, Kauffman PR, Herlihy AT, and Eilers JM. 1990. Current status of surface water acid–base chemistry. Washington, DC: National Acid Precipitation Assessment Program. State of Science/Technology Report 9.

Baron JS. 2006. Hindcasting nitrogen deposition to determine ecological critical load. *Ecol Appl* **16**: 433–39.

Baron JS, Driscoll CT, Stoddard JL, and Richer EE. 2011. Critical loads of atmospheric nitrogen deposition for nutrient enrichment and acidification of US freshwaters. *BioScience* **61**: 602–13.

Baumgardner Jr RE, Lavery TF, Rogers CM, and Isil SS. 2002. Estimates of the atmospheric deposition of sulfur and nitrogen species: clean air status and trends network 1990–2000. *Environ Sci Technol* **36**: 2614–29.

Bergström A and Jansson M. 2006. Atmospheric nitrogen deposition has caused nitrogen enrichment and eutrophication of lakes in the northern hemisphere. *Glob Change Biol* **12**: 635–43.

Bobbink R, Hicks K, Galloway J, *et al.* 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol Appl* **20**: 30–59.

Bowman WD, Gartner JR, Holland K, and Wiedermann M. 2006. Nitrogen critical loads for alpine vegetation and terrestrial ecosystem response: are we there yet? *Ecol Appl* **16**: 1183–93.

Braun S, Schindler C, Volz R, and Fluckiger W. 2003. Forest damages by the storm "Lothar" in permanent observation plots in Switzerland: the significance of soil acidification and nitrogen deposition. *Water Air Soil Poll* **142**: 327–40.

Bricker SB, Longstaf B, Dennison W, *et al.* 2008. Effects of nutrient

enrichment in the nation's estuaries: a decade of change. *Harmful Algae* **8**: 21–32.

Burns DA, Blett T, Haeuber R, and Pardo LH. 2008. Critical loads as a policy tool for protecting ecosystems from the effects of air pollutants. *Front Ecol Environ* **6**: 156–59.

Butterbach-Bahl K, Nemitz E, and Zaehle S. 2011. Nitrogen as a threat to European greenhouse balance. In: Sutton MA, Howard CM, and Erisman JW (Eds). The European nitrogen assessment. Cambridge, UK: Cambridge University Press.

Byun D and Schere KL. 2006. Review of the governing equations, computational algorithms, and other components of the models-3 community multiscale air quality (CMAQ) modeling system. *Appl Mech Rev* **59**: 51–77.

Cape JN. 2003. Effects of airborne volatile organic compounds on plants. *Environ Pollut* **122**: 145–57.

Castro M, Driscoll C, Jordan T, *et al.* 2003. Sources of nitrogen to estuaries in the United States. *Estuar Coast* **26**: 803–14.

Clark CM and Tilman D. 2008. Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands. *Nature* **451**: 712–15.

Compton JE, Harrision JA, Dennis RL, *et al.* 2011. Ecosystem services altered by changes in reactive nitrogen: an approach to inform decision-making. *Ecol Lett* **14**: 804–15.

Cronan CS and Grigal DF. 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. *J Environ Qual* **24**: 209–26.

Driscoll CT, Lawrence GB, Bulger AJ, *et al.* 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. *BioScience* **51**: 180–98.

Elliott EM, Kendall C, Wankel S, *et al.* 2007. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the midwestern and northeastern United States. *Environ Sci Technol* **41**: 7661–67.

Elser JJ, Andersen T, Baron JS, *et al.* 2009. Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. *Science* **326**: 835–37.

Elser JJ, Bracken MES, Cleland EE, *et al.* 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine, and terrestrial ecosystems. *Ecol Lett* **10**: 1135–42.

Evers DC, Han Y, Driscoll CT, *et al.* 2007. Biological mercury hotspots in the northeastern United States and southeastern Canada. *BioScience* **57**: 29–43.

Fenn ME, Haeuber R, Tonnesen GS, *et al.* 2003. Nitrogen emissions, deposition, and monitoring in the western United States. *BioScience* **53**: 391–403.

Fenn ME, Jovan S, Yuan F, *et al.* 2008. Empirical and simulated critical loads for nitrogen deposition in California mixed conifer forests. *Environ Pollut* **155**: 492–511.

Harris HH, Pickering IJ, and George GN. 2003. The chemical form of mercury in fish. *Science* **301**: 1203.

Ito M, Mitchell MJ, and Driscoll CT. 2002. Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. *Atmos Environ* **36**: 1051–62.

Kahl JS, Stoddard JL, Haeuber R, *et al.* 2004. Have US surface waters responded to the 1990 Clean Air Act Amendments? *Environ Sci Technol* **38**: 484a–90a.

Lawrence GB, David MM, Lovett GM, *et al.* 1999. Soil calcium status and the response of stream chemistry to changing acidic deposition rates. *Ecol Appl* **9**: 1059–72.

Lawrence GB, Roy KM, Baldigo BP, *et al.* 2008. Chronic and episodic acidification of Adirondack streams from acid rain in 2003–2005. *J Environ Qual* **37**: 2264–74.

Lawrence GB, Sutherland JW, Boylen CW, *et al.* 2007. Acid rain effects on aluminum mobilization clarified by inclusion of strong organic acids. *Environ Sci Technol* **41**: 93–98.

LeBauer DS and Treseder KK. 2008. Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. *Ecology* **89**: 371–79.

Liu LL and Greaver TL. 2009. A review of nitrogen enrichment effects on three biogenic GHGs: the CO_2 sink may be largely offset by stimulated N_2O and CH_4 emission. *Ecol Lett* **12**: 1103–17.

Lovett GM and Goodale CL. 2011. A new conceptual model of nitrogen saturation based on experimental nitrogen addition to an oak forest. *Ecosystems* **14**: 615–31.

McNulty SG, Cohen EC, Myers JAM, *et al.* 2007. Estimates of critical acid loads and exceedances for forest soils across the conterminous United States. *Environ Pollut* **149**: 281–92.

Munthe J, Bodaly RA, Branfireun BA, *et al.* 2007. Recovery of mercury-contaminated fisheries. *Ambio* **36**: 33–44.

Nanus L, Williams MW, Campbell DH, *et al.* 2009. Assessment of lake sensitivity to acidic deposition in national parks of the Rocky Mountains. *Ecol Appl* **19**: 961–73.

Nash THI and Sigal LL. 1999. Epiphytic lichens in the San Bernardino Mountains in relation to oxidant gradients. In: Miller PR and McBride JR (Eds). Oxidant air pollution impacts in the montane forests of southern California: a case study of the San Bernardino Mountains. New York, NY: Springer-Verlag.

Nilsson J, and Grennfelt P (Eds). 1988. Critical loads for sulphur and nitrogen. Report from a workshop held at Skokloster, Sweden, 19–24 Mar 1988. NORD Miljørapport 1988: 15. Copenhagen, Denmark: Nordic Council of Ministers.

Omernik JM and Powers MD. 1983. Total alkalinity of surface waters – a national map. *Ann Assoc Am Geogr* **73**: 133–36.

Pardo LH, Fenn ME, Goodale CL, *et al.* 2011. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecol Appl* **21**: 3049–82.

Rago PJ and Wiener JG. 1986. Does pH affect fish species richness when lake area is considered? *T Am Fish Soc* **115**: 438–47.

Riddell J, Nash THI, and Padgett P. 2008. The effect of HNO_3 gas on the lichen *Ramalina menziesii*. *Flora* **203**: 47–54.

Scheuhammer AM, Meyer MW, Sandheinrich MB, and Murray MW. 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. *Ambio* **36**: 12–18.

Shanley JB, Mast MA, Campbell DH, *et al.* 2008. Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach. *Environ Pollut* **154**: 143–54.

Sullivan TJ, Cosby BJ, Herlihy AT, *et al.* 2007a. Assessment of the extent to which intensively-studied lakes are representative of the Adirondack region and response to future changes in acidic deposition. *Water Air Soil Poll* **185**: 279–91.

Sullivan TJ, Webb JR, Snyder KU, *et al.* 2007b. Spatial distribution of acid-sensitive and acid-impacted streams in relation to watershed features in the southern Appalachian mountains. *Water Air Soil Poll* **182**: 57–71.

Thomas RQ, Canham CD, Weathers KC, and Goodale CL. 2010. Increased tree carbon storage in response to nitrogen deposition in the US. *Nat Geosci* **3**: 13–17.

US EPA (US Environmental Protection Agency). 1995. Acid deposition standard feasibility study: report to Congress. Washington, DC: EPA.

US EPA (US Environmental Protection Agency). 2008. Integrated Science Assessment (ISA) for oxides of nitrogen and sulfur – ecological criteria (final report). Washington, DC: EPA.

Warby RAF, Johnson CE, and Driscoll CT. 2009. Chemical recovery of surface waters across the northeastern US from reduced inputs of acidic deposition: 1984–2001. *Soil Sci Soc Am J* **73**: 274–84.

Winner W, Mooney H, Williams K, and Von Caemmerer S. 1985. Measuring and assessing SO_2 effects on photosynthesis and plant growth. In: Winner WE, Mooney HA, and Goldstein RA (Eds). Sulfur dioxide and vegetation: physiology, ecology, and policy issues. Stanford, CA: Stanford University Press.

ever non-native species, through the simultaneous addition of species in high and low trophic positions into recipient ecosystems, may be promoting greater trophic variability and mitigating trophic downgrading caused by native species loss. Therefore, the process of trophic downgrading highlighted by Estes *et al.* (2011) may not be a general rule but is likely the exception in a world increasingly being threatened by non-native species.

Julien Cucherousset[1,2*], Simon Blanchet[1,3], and Julian D Olden[4]
[1]CNRS, UPS, ENFA, UMR 5174 EDB (Laboratoire Évolution et Diversité Biologique), Toulouse, France [*](julien.cucherousset@univ-tlse3.fr); [2]Université de Toulouse, UPS, UMR 5174 EDB, Toulouse, France; [3]Station d'Ecologie Expérimentale du CNRS à Moulis, Moulis, France; [4]School of Aquatic and Fishery Sciences, University of Washington, Seattle, WA

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement number PERG08-GA-2010-276969.

Blanchet S, Grenouillet G, Beauchard O, *et al.* 2010. Non-native species disrupt the worldwide patterns of freshwater fish body size: implications for Bergmann's rule. *Ecol Lett* **13**: 421–31.

Byrnes JE, Reynolds PL, and Stachowicz JJ. 2007. Invasions and extinctions reshape coastal marine food webs. *PLoS ONE* **2**: e295.

Clavero M and García-Berthou E. 2005. Invasive species are a leading cause of animal extinctions. *Trends Ecol Evol* **20**: 110.

Courchamp F, Chapuis JL, and Pascal M. 2003. Mammal invaders on islands: impact, control and control impact. *Biol Rev* **78**: 347–83.

Cucherousset J and Olden JD. 2011. Ecological impacts of non-native freshwater fishes. *Fisheries* **36**: 215–30.

Eby LA, Roach WJ, Crowder LB, and Stanford JA. 2006. Effects of stocking-up freshwater food webs. *Trends Ecol Evol* **21**: 576–84.

Estes JA, Terborgh J, Brashares JS, *et al.* 2011. Trophic downgrading of planet Earth. *Science* **333**: 301–06.

Gido KB and Franssen NR. 2007. Invasion of stream fishes into low trophic positions. *Ecol Freshw Fish* **16**: 457–64.

Gozlan RE. 2008. Introduction of non-native freshwater fish: is it all bad? *Fish Fish* **9**: 106–15.

Griffiths CJ, Jones CG, Hansen DM, *et al.* 2010. The use of extant non-indigenous tortoises as a restoration tool to replace extinct ecosystem engineers. *Restor Ecol* **18**: 1–7.

Leprieur F, Beauchard O, Blanchet S, *et al.* 2008. Fish invasion in the world's river systems: when natural processes are blurred by human activity. *PLoS Biol* **6**: e28.

Maron JL, Estes JA, Croll DA, *et al.* 2006. An introduced predator alters Aleutian Island plant communities by thwarting nutrient subsidies. *Ecol Monogr* **76**: 3–24.

Sax DF, Gaines SD, and Brown JH. 2002. Species invasions exceed extinctions on islands worldwide: a comparative study of plants and birds. *Am Nat* **160**: 766–83.

Schlaepfer MA, Sax DF, and Olden JD. 2011. The potential conservation value of non-native species. *Conserv Biol* **25**: 428–37.

Strayer DL. 2010. Alien species in fresh waters: ecological effects, interactions with other stressors, and prospects for the future. *Freshwater Biol* **55**: 152–74.

Wardle DA, Bardgett RD, Callaway RM, and Van der Putten WH. 2011. Terrestrial ecosystem responses to species gains and losses. *Science* **332**: 1273–77.

doi:10.1890/12.WB.018

Reply to Cucherousset *et al.*

We agree that non-native predators have strongly influenced the structure and function of nature in many places. We are skeptical, however, of the authors' implication that these non-native predators are functional equivalents of those that have been lost. The fundamental problem is that mean trophic level and food chain length do not reflect the complex ways in which the influences of predators spread through food webs, nutrient cycles, and other ecosystem processes.

James A Estes[1*], John Terborgh[2], Mary E Power[3], and Stephen R Carpenter[4]
[1]University of California, Santa Cruz, CA [*](jestes@ucsc.edu); [2]Duke University, Durham, NC; [3]University of California, Berkeley, CA; [4]University of Wisconsin, Madison, WI

doi:10.1890/12.WB.019

Erratum

In Greaver *et al.* (2012; 10[7]: 365–72), panel headings and selected y-axis labels in Figure 2 on page 367 were incorrectly matched with their respective panels. A corrected version of the figure appears below.

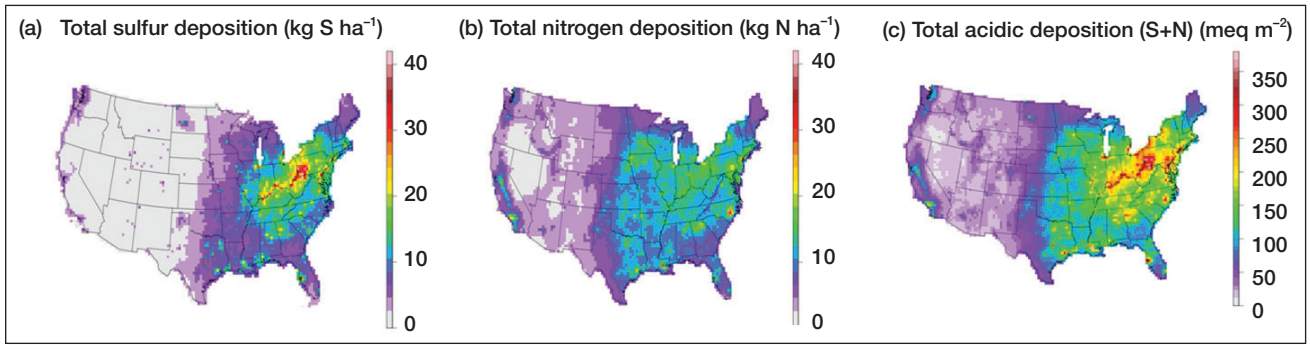

Figure 2. *Maps of CMAQv4.7.1 estimates of annual (a) sulfur, (b) inorganic nitrogen, and (c) acidic deposition for 2002 for a 12-km grid over the continental US, where wet deposition is adjusted by the ratio of observed to modeled precipitation and then regionally corrected for wet deposition bias,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