Executive Summary

U.S. Environmental Protection Agency | Office of Research and Development | National Center for Environmental Assessment

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Introduction

This Integrated Science Assessment (ISA) is a synthesis and evaluation of the most policy-relevant science that forms the scientific foundation for the review of the secondary (welfare-based) national ambient air quality standards (NAAQS) for oxides of nitrogen (NO_X) and oxides of sulfur (SO_X). The Clean Air Act definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on man-made materials, economic values, and personal comfort and well-being. The current secondary NAAQS for SO_X, set in 1973, is a 3-hour average of 0.5 ppm[1] sulfur dioxide (SO_2), not to be exceeded more than once per year. The secondary NAAQS for NO_X is identical to the primary standard set in 1971: an annual average not to exceed 0.053 ppm nitrogen dioxide (NO_2). The current secondary NAAQS were set to protect against direct damage to vegetation by exposure to gas-phase SO_X or NO_X.

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[1] 1ppm= 1000 ppb

Scope

This ISA is focused on ecological effects resulting from current deposition of compounds containing nitrogen (N) and sulfur (S). Acidification, N nutrient enrichment and effects of sulfate (SO_4^{2-}) on methylation of mercury (Hg) are highlighted in the document. The following figure illustrates the scope of the document.
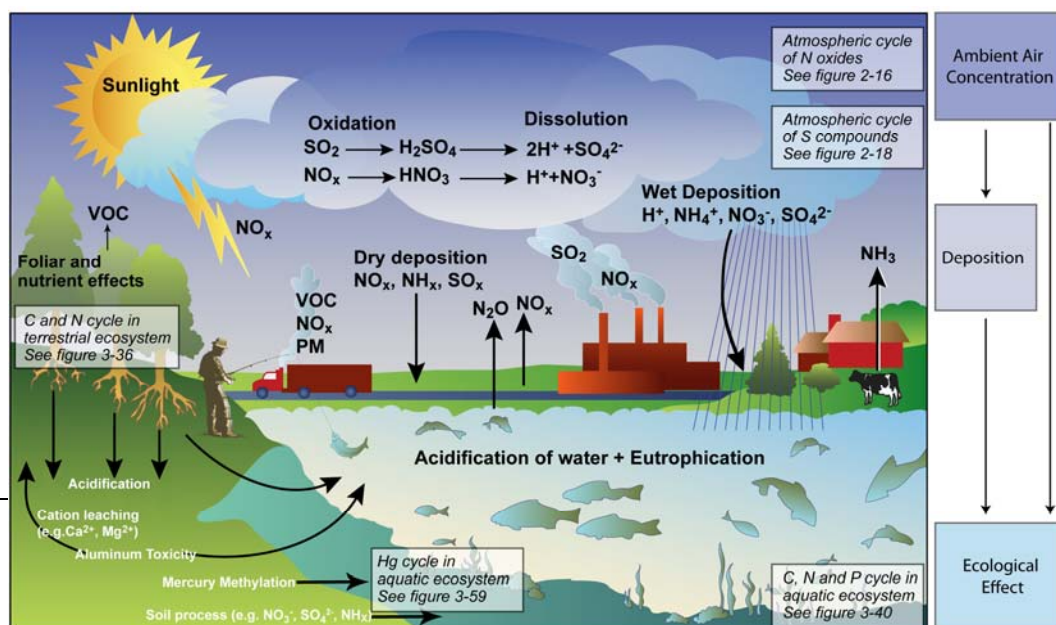
Both N and S contribute to acidification of ecosystems. This ISA considers several chemical forms that contribute to acidifying deposition, including gases and particles derived from SO_X, NO_X, and reduced nitrogen (NH_X).

Deposition of N contributes to N-nutrient enrichment and eutrophication. An assessment of the complex ecological effects of atmospheric N deposition requires consideration of many different chemical forms of reactive N (Nr). For this reason, the ISA includes evaluation of data on the most common reduced inorganic forms of N,

ammonia (NH_3) and ammonium (NH_4^+); on oxidized inorganic forms including nitric oxide (NO) and NO_2, nitrate (NO_3^-), nitric acid (HNO_3), and nitrous oxide (N_2O); and on organic N compounds including peroxyacetyl nitrate (PAN).

Other welfare effects addressed in the ISA include effects of SO_4^{2-} deposition on Hg methylation, along with evidence related to direct exposure to gas-phase NO_X and SO_X. The key conclusions of the ISA follow.

Current concentrations and deposition

*A*mbient annual NO_X and SO_X concentrations as reported in the routine national networks have decreased substantially owing to controls enacted since the 1970s. NO_X decreased ~35% in the period 1990-2005, to current annual average concentrations of ~15 ppb. Emissions of SO_X have been substantially reduced in recent years: annual average ambient SO_X concentrations have decreased ~50% in the period 1990–2005 and now stand at ~4 ppb for both aggregate annual and 24-hour average concentrations nation-wide.

Emitted NO_X, SO_X, NH_X and other pollutants can be transported vertically by convection into the upper part of the mixed layer on one day, then transported overnight in a layer of high concentrations. Once pollutants are lofted to the middle and upper troposphere, they typically have a much longer lifetime and, with the generally stronger winds at these altitudes, can be transported long distances from their source regions. The length scale of this transport is highly variable owing to differing chemical and meteorological conditions encountered along the transport path.

Numerical chemical-transport models (CTMs) are the prime tools for computing emissions and interactions among pollutants like NO_X, SO_X, and NH_X, their transport and transformation including production of secondary aerosols like ammonium nitrate and ammonium sulfate, the evolution of particle size distributions, the resulting atmospheric concentrations and the deposition of these pollutants to the surface. CTMs are driven by calculated emissions for primary species such as NO_X, SO_X, NH_3, and primary particulate matter, and by the meteorological fields produced by other numerical prediction models. As such, CTMs are the chief means of relating emitted pollutants with deposited ones.

The emitted, transported, and transformed pollutants reach the surface where they can have ecological effects largely through deposition. Direct and indirect wet and dry deposition to specific locations like watersheds depend on air pollutant emissions and concentrations in the airshed above the watershed, but the shape and areal extent of the airshed is quite different from that of the watershed owing to the transport and transformation of emitted pollutants described above.

Deposition is spatially heterogeneous across the U.S. In the years 2004-2006, routine na-

tional monitoring networks reported mean S deposition in the U.S. highest east of the Mississippi River with the highest reported deposition, 21 kg S/ha/yr, in the Ohio River Valley where most recording stations reported three-year averages for this period of more than 10 kg S/ha/yr. Numerous other stations in the eastern U.S. reported S deposition greater than 5 kg S/ha/yr. Data are sparse for the central U.S. between the 100th meridian and the Mississippi River; but, where available, deposition values there were lower than in most of the eastern U.S., ranging from 4 to over 5 kg S/ha/yr. Total S deposition in the U.S. west of the 100th meridian is lower than in the East or upper Midwest, owing to lower densities of high-emitting sources in the West. In the years 2004-2006, all routine recording stations in the West reported less than 2 kg S/ha/yr and many reported less than 1 kg S/ha/yr. S was primarily deposited in the form of wet SO_4^{2-}, followed by a smaller proportion of dry SO_2, and a much smaller proportion of dry SO_4^{2-}.

Expanding urbanization, agricultural intensification, and industrial production during the previous 100 years have produced a nearly 10-fold increase in total N deposited from the atmosphere compared to pre-industrial levels. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the U.S. and comprises from 50 to 75% of current

total N atmospheric deposition. This wet and dry atmospheric N deposition is spatially heterogeneous, too, owing to the influence of meteorology, transport, precipitation patterns and land use.

For 2004–2006, routine national monitoring networks reported the highest mean N deposition totals in the U.S. in the Ohio River Valley, specifically in the states of Indiana and Ohio, with values greater than 9 kg N/ha/yr. N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central U.S., the highest N annual average deposition totals were on the order of 6 to 7 kg N/ha/yr. Measured concentrations and inferred deposition totals were dominated by wet NO_3^- and NH_4^+ species, followed by dry HNO_3, dry NH_4^+, and dry NO_3^-. NH_3 is not yet measured routinely in any national networks; however, smaller-scale intensive monitoring and numerical air quality modeling both indicate that it may account for more than 80% of the dry reduced N deposition total.

Although S and N deposition in most areas of the U.S. occurred as wet deposition, there were some exceptions, including parts of California where N deposition was primarily dry.

The thin coverage of monitoring sites in many locations, especially in the rural West, means that limited data exist on deposition totals in a large number of potentially sensitive places. Numerical modeling experiments can help fill in these data gaps and suggest that local and even regional areas of high ambient concentration and deposition exist where measured data are unavailable. Model-predicted values for N deposition in some regions of the Adirondacks in New York are greater than 20 kg N/ha/yr; other model estimates as high as 32 kg N/ha/yr have been made for a region of southern California, where more than half of that total was predicted to come from NO and NO_2.

The ISA concludes that the national-scale networks routinely monitoring N deposition are inadequate to characterize both the full range of reduced and oxidized forms of N deposition and the substantial regional heterogeneity across the landscape of the U.S.

Ecological effects of acidification

The effects of acidifying deposition on ecosystems have been well studied over the past several decades and vulnerable areas have been identified in the U.S. The wealth of data has led to the development of widely used ecological models for predicting soil and surface water acidification. Regional and ecosystem vulnerability to acidification results from inherent sensitivity and exposure to acidifying deposition.

Sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition is regional and predominantly governed by surficial geology. Other factors contributing to the sensitivity of soils and surface waters to acidifying deposition include topography, vegetation, soil chemistry, land use, and hydrologic flowpath.

Soil acidification is a natural process, but is often accelerated by acidifying deposition, which can decrease concentrations of exchangeable base cations in soils. Biological effects of acidification on terrestrial ecosystems are generally attributable to Al toxicity and decreased ability of plant roots to take up base cations. Areas

most sensitive to terrestrial effects from acidifying deposition include forests in the Adirondack Mountains of New York, 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 Appalachians. While studies show some recovery of surface waters, there are widespread areas of ongoing depletion of exchangeable base cations in forest soils in the northeastern U.S., despite recent decreases in acidifying deposition.

In aquatic systems, consistent and coherent evidence from multiple studies of many species shows that acidification can cause the loss of acid-sensitive species, and that more species are lost with greater acidification. These effects are linked to changes in

The evidence is sufficient to infer a causal relationship between acidifying deposition and effects on:

(1) biogeochemistry related to terrestrial and aquatic ecosystems;

(2) biota in terrestrial and aquatic ecosystems.

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surface water chemistry, including concentrations of SO_4^{2-}, NO_3^-, inorganic Al, and calcium (Ca^{2+}), surface water pH, sum of base cations, acid neutralizing capacity (ANC),

Examples of biogeochemical indicators of effects from acidifying deposition on ecosystems	
Ecosystem	Biogeochemical Indicator
Terrestrial	• Soil base saturation • Inorganic Aluminum concentration in soil water • Soil carbon-to-nitrogen ratio
Aquatic	• Sulfate • Nitrate • Base cations • Acid neutralizing capacity • Surface water inorganic Aluminum • pH

| Examples of biological indicators of effects from acidifying deposition on ecosystems	
Indicator	Measure
Terrestrial Ecosystems	
Red Spruce	• Percent dieback of canopy trees
Sugar Maple	• Dead basal area, crown vigor index, fine twig dieback
Aquatic Ecosystems	
Fishes, zooplankton, crustaceans, rotifers	• Presence/absence • Fish condition factor • Biodiversity

and base cation surplus. These effects are also influenced by historical inputs to these systems. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in zooplankton, macroin-

vertebrates, and fish species richness. These effects on species richness may also affect ecosystem services, such as biodiversity and cultural services such as fishing and tourism.

Although both N and S deposition can cause terrestrial and aquatic acidification, S deposition is generally the primary cause of chronic acidification, with secondary contributions from N deposition. Following decreases in S deposition in the 1980s and 1990s, one quarter to one third of the chronically acidic lakes and streams in the U.S. were no longer acidic during baseflow in the year 2000. A number of lakes and streams, however, remain acidic even though wet SO_4^{2-} deposition has decreased by as much as 30% since 1989. N deposition, which has also decreased in the years since 1990 in most places in the U.S. with routine monitoring, is the primary cause of episodic acidification which, despite its short duration, has been shown to cause long-term biological effects.

Many of the surface waters most sensitive to acidification in the U.S. are found in the

Northeast, the Southeast, and the mountainous West. In the West, acidic surface waters are rare and the extent of chronic surface water acidification that has occurred to date has been limited. However, episodic acidification does occur. In both the mountainous West and the Northeast, the most severe acidification of surface waters generally occurs during spring snowmelt. The ISA highlights evidence from two well-studied areas to provide more detail on how acidification affects ecosystems: The Adirondacks (NY) and Shenandoah National Park (VA). In the Adirondacks, the current rates of N and S deposition exceed the amount that would allow recovery of the most acid sensitive lakes. In the Shenandoah, past SO_4^{2-} has accumulated in the soil and is slowly released from the soil into stream water where it causes acidification, making parts of this region sensitive to even the current lower deposition loadings. Numerical models specifically calibrated to these locations and conditions suggest that the number of acidic streams will increase even under current deposition loads.
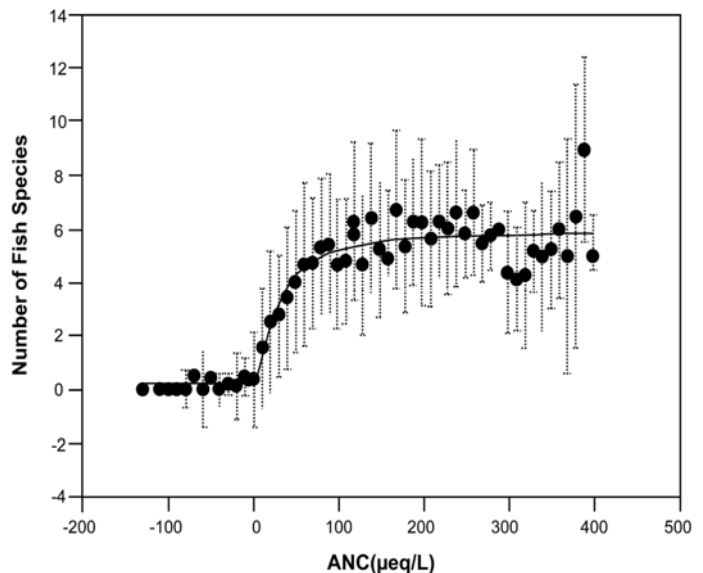
Number of fish species per lake vs. acidity status, expressed as acid neutralizing capacity (ANC), for Adirondack lakes.

Source: Sullivan et al., 2006b

Regions of the northern and eastern U.S. that contain appreciable numbers of lakes and streams sensitive to deleterious effects from acidifying deposition.

Source: Stoddard et al., 2003

Ecological effects of nitrogen deposition

There are many well-studied effects of N deposition on ecosystems and some vulnerable areas have been identified in the U.S. However, the full extent of ecosystem vulnerability is still unknown. Substantial empirical information from specific ecosystems and for specific endpoints is available, but 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. Though the sensitivity of ecosystems to N deposition across the U.S. varies, a large body of evidence clearly demonstrates a relationship between N deposition and a broad range of ecological effects.

The contribution of N deposition to total N load varies among ecosystems. Atmospheric N deposition is the main source of new N to most headwater streams, high elevation lakes, and low-order streams. Atmospheric N deposition contributes to the total N load in terrestrial, wetland, freshwater, and estuarine ecosystems that receive N through multiple pathways (i.e. biological N-fixation, agricultural land runoff and waste water effluent). There are multiple biogeochemical indicators of N deposition effects.

The evidence is sufficient to infer a causal relationship between N deposition, to which NO_X and NH_X contribute, and the alteration of the following:

(1) biogeochemical cycling of N and carbon (C) in terrestrial, wetland, freshwater aquatic, and coastal marine ecosystems;

(2) biogenic flux of methane (CH_4), and N_2O in terrestrial and wetland ecosystems;

(3) species richness, species composition, and biodiversity in terrestrial, wetland, freshwater aquatic and coastal marine ecosystems.

Examples of biogeochemical indicators of effects from reactive N deposition on ecosystems	
Ecosystem	**Biogeochemical Indicator**
Terrestrial and Wetland	• NO_3^- leaching • Nitrification • Denitrification • N_2O emissions • CH_4 emissions • Soil C:N ratio • Foliar / plant tissue [N], C:N, N:magnesium, N:phosphorus • Soil water $[NO_3^-]$ and $[NH_4^+]$
Freshwater and Estuarine	• Chlorophyll *a* • Water $[NO_3^-]$ • Dissolved inorganic N • Dissolved oxygen • N:P

In terrestrial ecosystems, the onset of NO_3^- leaching is one of the best documented biogeochemical indicators that an ecosystem receives more N than it uses and is able to retain. N removal by ecosystems is a valuable ecosystem service 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 and the degradation of water quality can occur. The onset of leaching was calculated to occur with deposition levels between 5.5 and 10 kg N/ha/yr for sensitive eastern forests. In the mixed conifer forests of the Sierra Nevada and San Bernardino mountains, the onset of increased NO_3^- leaching was calculated to be 17 kg N/ha/yr. Several studies in the Rocky Mountains indicate that the capacity of alpine catchments to retain N was exceeded at levels greater than 5-10 kg N/ha/yr.

N deposition alters the biogenic sources and sinks of two greenhouse gases (GHGs), CH_4 and N_2O, in terrestrial and wetland ecosystems, resulting in increased emissions to the atmosphere. Non-flooded upland soil is the largest biological sink and takes up about 6% of atmospheric CH_4. N addition decreases CH_4 uptake in coniferous and deciduous forests, and N addition increases

CH_4 production in wetlands. Soil is the largest source of N_2O, accounting for 60% of global emissions. N deposition increases the biogenic emission of N_2O in coniferous forest, deciduous forests, grasslands, and wetlands. Although N addition can cause a general stimulation of biogenic CH_4 and N_2O emissions from soils, it is difficult to generalize a dose-response relationship between the amount of N addition and the changes in GHG flux on a large heterogeneous landscape. This is because GHG production is influenced by multiple environmental factors (e.g., soil, vegetation and climate), which vary greatly over small spatial and temporal scales.

N is often the most limiting nutrient to growth in ecosystems. N deposition thus often increases primary productivity, thereby altering the biogeochemical cycling of C. N

Examples of biological indicators of effects from N deposition on ecosystems	
Ecosystem	**Biological Indicators**
Terrestrial and Wetlands	• Altered community composition, biodiversity and/or population decline. Taxa affected include: diatoms, lichen, mycorrhizae, moss, grasses and other herbaceous plants • Plant root: shoot ratio • Terrestrial plant biomass/production
Freshwater and Estuarine	• Phytoplankton biomass/production • Toxic or nuisance algae blooms • Submerged aquatic vegetation • Fauna from higher trophic levels

deposition can cause changes in ecosystem C budgets. However, whether N deposition increases or decreases ecosystem C-sequestration remains unclear. A limited number of studies suggest that N deposition may increase C-sequestration in some forests, but has no apparent effect on C-sequestration in non-forest ecosystems.

In terrestrial ecosystems, N deposition can accelerate plant growth and change C allocation patterns (e.g. shoot:root ratio), which can increase susceptibility to severe fires, drought, and wind damage. These effects have been shown in studies conducted in the western U.S. and Europe. The alteration of primary productivity can also alter competitive interactions among plant species. The increase in growth is greater for some species than others, leading to possible shifts in population dynamics, species composition, community structure, and in few instances, ecosystem type.

There are numerous sensitive terrestrial biota and ecosystems that are affected by N deposition. Acidophytic lichens are among the most sensitive terrestrial taxa to N deposition, with adverse effects occurring with exposures as low as 3 kg N/ha/yr in the Pacific Northwest and southern California. The onset of declining biodiversity in grass-lands has been estimated to be 5 kg N/ha/yr in Minnesota and the European Union. Altered community composition of alpine ecosystems in the Rocky Mountains and forest encroachment into temperate grasslands in Southern Canada is estimated to be 10 kg N/ha/yr.

The productivity of many freshwater ecosystems is N-limited. N deposition can alter species assemblages and cause eutrophication of aquatic ecosystems to the extent that N is the growth-limiting nutrient. In the Rocky Mountains, deposition loads of approximately 1.5-2 kg N/ha/yr are reported to alter species composition in the diatom communities in some freshwater lakes, an indicator of impaired water quality.

In estuarine ecosystems, N from atmospheric and non-atmospheric sources contributes to increased phytoplankton and algal productivity, leading to eutrophication. Estuary eutrophication is an ecological problem indicated by water quality deterioration, resulting in numerous adverse effects including hypoxic zones, species mortality, and harmful algal blooms. The calculated contribution of atmospheric deposition to total N loads can be as high as 72% in estuaries. The Chesapeake Bay is an example of a large, well-studied, and severely eutrophic estuary that is calculated to receive as much as 30% of its total N load from the atmosphere.

Examples of quantified relationships between deposition levels and ecological effects	
Kg N/ha/yr	Ecological effect
~1.5	Altered diatom communities in high elevation freshwater lakes and elevated N in tree leaf tissue high elevation forests in the western U.S.
3.1	Decline of some lichen species in the western U.S.
4	Altered growth and coverage of alpine plant species in the western U.S.
5	Onset of decline of species richness in grasslands of the U.S. and U.K.
5.5 - 10	Onset of nitrate leaching in Eastern forests of the U.S.
5-10	Multiple effects in tundra, bogs and freshwater lakes in Europe
5-15	Multiple effects in arctic, alpine, subalpine and scrub habitats in Europe

Other welfare effects: Mercury methylation

Hg is highly neurotoxic and once methylated, principally by S-reducing bacteria, it can be taken up by microorganisms, zooplankton and macroinvertebrates, and concentrated in higher trophic levels, including fish eaten by humans. In 2006, 3,080 fish consumption advisories were issued because of methylmercury (MeHg), and as of July 2007, 23 states had issued statewide advisories. The production of meaningful amounts of MeHg requires the presence of SO_4^{2-} and Hg, and where Hg is present, increased availability of SO_4^{2-} results in increased production of MeHg. The amount of MeHg produced varies with

The evidence is sufficient to infer a causal relationship between S deposition and increased Hg methylation in wetlands and aquatic environments.

oxygen content, temperature, pH, and supply of labile organic C. Watersheds with conditions known to be conducive to Hg methylation can be found in the northeastern U.S. and southeastern Canada, but biotic Hg accumulation has been widely observed in other regions that have not been studied as extensively, and where a different set of conditions may exist.

Other welfare effects: Direct phytotoxic

Acute and chronic exposures to SO_2 have phytotoxic effects on vegetation which include foliar injury, decreased photosynthesis, and decreased growth. Acute exposures to NO_2, NO, PAN, and HNO_3 cause plant foliar injury and decreased growth. However, the majority of studies have been performed at concentrations of these gas-phase species above current ambient conditions observed in the U.S. Consequently, there is little evidence that current concentrations of gas-phase S or N oxides are high enough to cause phytotoxic effects. One exception is that some studies indicate that current HNO_3 concentrations may be contributing to the decline in lichen species in the Los Angeles basin.

The evidence is sufficient to infer a causal relationship between exposure to SO_2, NO, NO_2, PAN, and HNO_3 and injury to vegetation.

Conclusion

The main effects of N and S pollution assessed in the ISA are acidification, N enrichment, and Hg methylation. Acidification of ecosystems is driven primarily by deposition resulting from SO_X, NO_X, and NH_X pollution. Acidification from the deposition resulting from current emission levels causes a cascade of effects that harm susceptible aquatic and terrestrial ecosystems, including slower growth and injury to forests and localized extinction of fishes and other aquatic species. In addition to acidification, atmospheric deposition of reactive N resulting from current NO_X and NH_X emissions along with other non-atmospheric sources (e.g., fertilizers and wastewater), causes a suite of ecological changes within sensitive ecosystems. These include increased primary productivity in most N-limited ecosystems, biodiversity losses, changes in C cycling, and eutrophication and harmful algal blooms in freshwater, estuarine, and ocean ecosystems. In some watersheds, additional SO_4^{2-} from atmospheric deposition increases Hg methylation rates by increasing both the number and activity of S-reducing bacteria. Methylmercury is a powerful toxin that can bioaccumulate to toxic amounts in food webs at higher trophic levels (e.g. bass, perch, otters, or kingfishers).