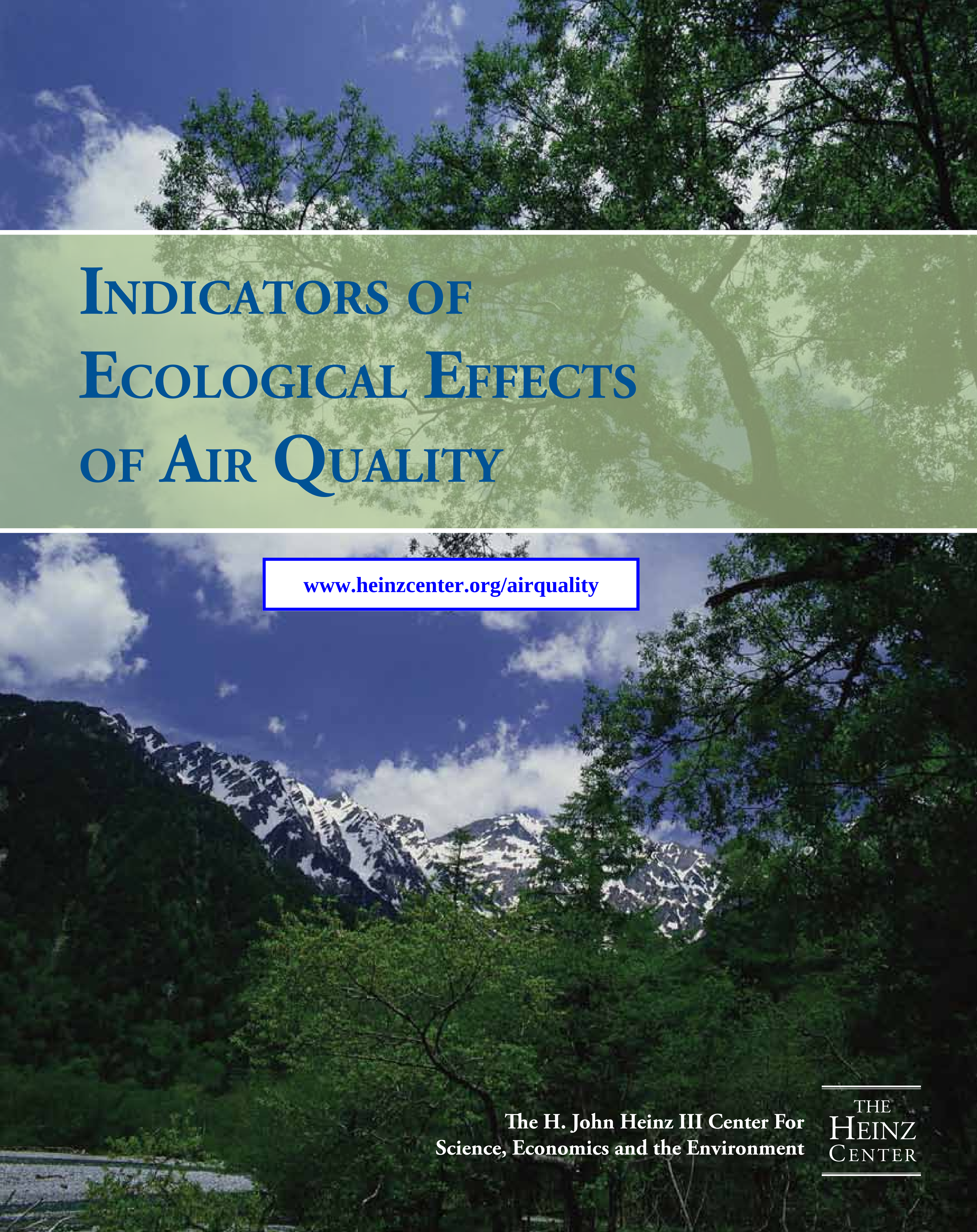

Indicators of Ecological Effects of Air Quality

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Established in 1995 to carry on the work of Senator John Heinz (1938-1991), The Heinz Center is a nonpartisan, nonprofit institution dedicated to improving the scientific and economic foundation for environmental policy. The Center fosters collaboration among industry, environmental organizations, academia, and all levels of government in each of its program areas and projects.

Project Team

Project Lead: Christine Negra

Consultants: Emilian Geczi
Sriram Gopal
Caroline Sweedo

Data Providers: BioDiversity Research Institute (David Evers and Kate Williams)
National Atmospheric Deposition Program (Bob Larson)
U.S. Department of Agriculture, National Soil Survey Characterization Database (Thomas Reinsch)
U.S. Environmental Protection Agency (Jason Lynch)
U.S. Forest Service (Gretchen Smith and John Coulston)
U.S. Geological Survey (David Krabbenhoft)

Acknowledgements

The project team greatly appreciates the contributions of the Steering Committee and technical subcommittees of this project (see Appendix A) as well as the data providers listed above. Robin O'Malley and Anne Marsh provided invaluable technical expertise and counsel. Special thanks to Stacia Van Dyne and Claire Hayes for their support. We would also like to recognize Anthony Janetos and Ian Carroll for their leadership in the initial phases of this project.

Funding

Financial support for this project has been provided by EPA's Clean Air Markets Division (http://www.epa.gov/airmarkets/progsregs/index.html) which manages a variety of cap-and-trade programs focused on sulfur dioxide, nitrogen oxides, ozone and mercury including the Acid Rain Program, the NO_x Trading Programs, the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR).

Executive Summary

Ecological indicators are needed to improve understanding and monitoring of the effects of air pollutants on ecosystems and to scientifically assess the effectiveness of air pollution control strategies. Traditionally, research and monitoring of air quality have focused on human health impacts and have been concentrated in urbanized areas, however pollution impacts on ecosystems are an equally important measure of how well our emission control policies are working.

Decision-makers need tools to help them understand whether and how their decisions are contributing to the achievement of air quality goals. Ecosystem monitoring is one such tool; chosen well, indicators of ecosystem change can help to inform policy development and implementation by documenting whether emission control policies and programs are working as intended and helping to determine if policy change is needed to achieve further ecosystem protection.

With support from the U.S. Environmental Protection Agency (EPA) Clean Air Markets Division, the Heinz Center has developed a suite of indicators to inform environmental data collection and integrated assessment of ecosystem response to changes in air quality. This report focuses on four major ecological effects of air pollution: acidification by nitrogen and sulfur, nitrogen enrichment, ozone damage to plants, and mercury bioaccumulation.

Recommended Indicators

This project identifies well-documented and widespread ecological responses to air pollutants (i.e., ecological conditions that are sensitive to changes in air quality over time) and recommends a small number of ecological indicator metrics that demonstrate the links between ecosystem exposure and response where they are strongly established.

Acidification by nitrogen and sulfur deposition:

Base Saturation. This indicator would report change in the base saturation of forest soils: the relative abundance of basic cations (such as calcium, magnesium, and potassium) compared to total exchangeable cations (i.e., base cations plus acid cations such as hydrogen and aluminum). This metric has been found to be correlated to biological availability of nutrient cations.

Acid Neutralizing Capacity. This indicator will report the percentage of freshwater systems with low, medium, and high ANC, for both chronic and episodic acidification. ANC is well correlated with pH, an important chemical variable for aquatic biota, but also reflects ecological susceptibility to changing pH.

Nitrogen enrichment:

Streamwater Nitrogen. This indicator will report change in nitrate levels in forested streams nationwide. This metric is intended to capture nitrate leaching and export resulting from nitrogen saturation in forest systems.

Organic Soil Carbon to Nitrogen Ratio. This indicator would report the ratio of organic carbon to nitrogen in the surface horizon of forested soil systems. This metric is relevant to the decomposition rate of organic materials and relates to the forests' overall vulnerability to nitrogen enrichment and leaching loss.

Ozone damage to plants:

Foliar Injury in Forests. This indicator will report an index value for ozone-induced foliar injury detected in sensitive forest plant species, stratified by two important controlling variables: ozone exposure and plant available moisture.

Change in Growth/Yield in Cropped Systems. This indicator will report the mean national annual yield of several crops that are known to be sensitive to ozone stratified by ozone exposure.

Mercury bioaccumulation:

Change in Methylmercury in Prey Fish and Piscivorous Fish and Birds. These indicators would report annual summary statistics (e.g., annual average) for methylmercury levels in biota that have been documented to bioaccumulate mercury, stratified by watershed categories of mercury sensitivity and mercury deposition. (National-scale mercury data are not yet available and watershed categories are under development.)

Research Needs

A number of other metrics of ecological response to air pollution were evaluated, however further scientific investigation is needed to support indicator development for these metrics. In the future, as research continues, it may be possible to develop additional indicators to complement the indicator metrics recommended above.

Nitrogen enrichment:

Foliar N Concentrations and Nitrogen to Nutrient Ratios. Foliar chemistry changes and nitrogen to nutrient ratios may be useful indicators of nitrogen-induced changes in terrestrial ecosystems, particularly in N-limited forests, but more research is needed to clarify issues such as sampling methods and the interaction of multiple effects.

Changes in Community Structure. Bioindicators such as lichens and diatoms are useful integrators of changing ecological conditions, and changes in nitrogen-sensitive species can signal the onset of broader pollution-induced changes in community composition, but knowledge of these relationships is still geographically limited.

Nitrogen Enrichment in Coastal Systems. Nitrogen loading to coastal systems has been shown to produce harmful effects such as algal blooms and oxygen depletion, however the relative contribution of atmospheric nitrogen deposition is not yet fully understood. In order to propose a nationally-relevant indicator metric for this ecological effect, further progress in synthesizing and/or scaling up existing watershed-level research may be needed.

Ozone damage to plants:

Changes in Species Composition. Ozone-induced changes in community composition have been detected for lichens and other organisms at the research-scale, however broad-scale or long-term decline in ozone-sensitive species is difficult to detect due to confounding factors (e.g., moisture availability). Future research holds promise for indicator development.

Remotely Sensed Changes in Plant Physiology. Emerging research in the use of remote sensing data represents an opportunity to detect patterns of ozone effects on plant chlorophyll levels and water use efficiency by factoring out effects of climate and/or ambient CO_2 concentrations. As this work matures, the scientific basis and data systems may support national-scale indicator reporting.

Mercury bioaccumulation:

Change in the Relative Abundance of Methylmercury in Streams and Coastal Systems. This metric would reflect the overall bioavailability of mercury for methylation, however, comprehensive national-scale monitoring systems are not yet in place for mercury in water and sediments. Therefore, at this time indicator development is constrained (although there is a consortium actively designing a comprehensive national mercury monitoring network).

Change in Total Mercury in Invertivores. Mercury bioaccumulation pathways have begun to be detected in terrestrial systems and, as research develops further, mercury levels in insect-eating organisms (e.g., spiders, songbirds, and bats) may represent a useful indicator of the transfer of atmospheric mercury to higher tropic level biota.

Conclusion

Scientists have learned much about the ability to track pollution effects in ecosystems, and how to tease apart the causes behind those changes. For many air pollution impacts, existing research provides a solid foundation for understanding how ecosystems are being affected. For others, research is still emerging or limited to geographic regions.

The intention of this project is to provide federal and state agencies and other natural resource managers and policy makers with quantitative tools for assessing ecosystem responses to changes in air quality. In moving towards a set of ecological indicators of air quality supported by a comprehensive system for which data will be collected and reported on a regular basis, it is important to continue to draw others into the decision-making process. Indicators are an evolving tool, a starting point to be refined and revised as necessary. With information in hand, policymakers can make informed decisions about proposed changes to legislation and associated activities. In the realm of the impacts of air quality on ecosystems, this project aims to assist in the development of a monitoring system that is comprehensive, cost-effective, and flexible enough to be adaptable to future changes.

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Chapter I. Introduction

Air Quality and Ecosystems

Over the past several decades much attention has been paid to monitoring pollutants as they affect human health. An extraordinary amount of progress has already been made: the enactment of the Clean Air and Clean Water Acts; advancements in technology for cleaner burning fuel; our increased understanding of how pollutants move through our air, land and waters. Until recently, less attention has been paid to a more subtle but increasingly pervasive set of pollution effects in ecosystems – impacts such as fish kills in northeastern streams, dead zones in the Gulf of Mexico, reduced crop production, and reproductive problems in piscivorous birds.

Compounds such as nitrogen, sulfur, ozone and mercury – the focus of this report – contribute to these problems. These (as well as many other) pollutants chart their own unique, and sometimes quite complex, pathway through ecosystems, and at times these pollutants also interact with one another. They move between air, water, soil and biota in wetlands, forests, grasslands, shrublands, fresh waters, coastal zones, and agricultural areas. When these pollutants or their precursors are emitted into the air, they may have significant local ecological impacts through deposition or elevated ambient concentrations, however some pollutant impacts may be far from their original source at regional or even global scales. The changes these pollutants generate in affected ecosystems may be cumulative over time periods ranging from growing seasons to decades or even centuries.

Drivers of air pollution-induced ecosystem changes include industrial processes and the burning of fossil fuels, but also population changes, land use dynamics, and agriculture. For example, increased suburbanization in metropolitan areas causes people to drive greater distances to get to work, shopping, and other places. As a result, more air pollution may be emitted (taking into account that cars are increasingly fuel efficient). A number of other factors influence the degree to which pollutants affect ecosystems. These factors include, but are not limited to climate (temperature, precipitation), the alteration of other components of the environment (e.g. elevated ambient CO_2 concentrations), whether the exposure is chronic or acute, and the inherent sensitivity of certain ecosystems or biota to particular pollutants. For example, plant stress can be exacerbated in drought-affected systems that also receive elevated nitrogen deposition from the atmosphere because excess nitrogen may reduce function of root systems and lead to a decreased water supply in the plant. And recent studies suggest that, in combination with drought, both ozone exposure and atmospheric nitrogen deposition may increase the susceptibility of pines to insect infestations (Jones et al., 2004).

The Need for Indicators of Ecological Effects

Ecological indicators are needed to improve understanding and monitoring of the effects of air pollutants on ecosystems and to scientifically assess the effectiveness of air pollution control strategies. Traditionally, research and monitoring of air quality have focused on human health impacts and have been concentrated in urbanized areas (e.g., most criteria

Nitrogen and Sulfur. An important nutrient for plant growth, nitrogen is found in both inert and biologically available forms. Human activities such as the production and use of synthetic fertilizers, burning of fossil fuels, and production of nitrogen-fixing crops (e.g. soybeans) have increased biologically available nitrogen to the point that it has become a problem pollutant in some ecosystems. Perhaps the most widely cited example is the transfer of nitrate from land (either via fertilizers, manure, or industrial inputs) to rivers and streams where it is eventually carried to coastal waters, contributing to algal blooms and low oxygen levels ("dead zones"). Nitrogen, along with sulfur, also contributes to acid rain. Sulfur may be found in "raw" materials such as fossil fuels and metal ores. When processed or burned, these materials release sulfur oxide gases (SO_x). In the atmosphere, SO_x interacts with water vapor, gases or particles, to form acid and other harmful products that may then precipitate onto land or water.

Ozone. Ambient ozone is formed when certain pollutants from vehicles, paints or solvents, unburned fuel, and industrial sources interact with sunlight near the surface of the earth. Human health effects include lung irritation; similarly, ozone affects respiration in animals and plants, and for plants in particular can cause long-term damage at elevated levels. Ozone enters plant tissues through the stomates—the small pores in leaves and stems where gas exchange takes place. Ozone reacts with cellular components found in plants and produces various organic compounds, oxidizers, and free radicals that can impair cell functioning.

Mercury. Although a naturally-occurring element, recent increases in atmospheric mercury are linked to industrial activities such as coal-fired power plants and waste incineration. Ecological responses to changing atmospheric mercury deposition vary in magnitude and timing. More rapid responses are likely to occur in watersheds that rapidly transfer mercury to aquatic systems and that efficiently methylate mercury (i.e., high mercury sensitivity). In its methylated form, mercury can accumulate in fish and other wildlife, where it can cause reproductive or neurological damage when it accumulates to toxic levels.

pollutant and Hazardous Air Pollutants (HAPs) monitoring). However, pollution impacts on ecosystems are an equally important measure of how well our emissions-control policies are working. Air quality managers need mechanisms for identifying ecological impairment due to air pollution. While some impacts are relatively well-documented (e.g. acidification of forest systems caused by acid rain), the ability to systematically track other ecosystem responses to airborne pollutants has been more limited. Current and future air pollution-control programs need tools for documenting improvements in ecological condition resulting from pollution reductions.

Indicators have been developed for some ecosystem effects, such as altered stream chemistry; however, indicator development is needed for other ecosystem characteristics that might be affected by air quality (e.g., coastal eutrophication, agricultural productivity). National-scale indicators of ecological condition have been produced through several high-profile environmental reporting projects such as the Heinz Center's *State of the Nation's Ecosystems* report, the Environmental Protection Agency's *Report on the Environment* and the *National Coastal Condition Report*, reports from the forest, water, and rangeland sustainable roundtables and the National Research Council's (NRC) *Ecological Indicators for the Nation*. The efforts have produced indicators of air quality and related ecological features, however a focused attempt to identify those indicators most relevant for monitoring ecological responses to changing air quality conditions has not yet been implemented.

The NRC's 2004 *Air Quality Management in the U.S.* recommends that a comprehensive suite of indicators of terrestrial and aquatic effects of air quality be thoroughly and consistently measured and reported. The NRC report calls for research

> …to determine appropriate suites of measurements, sample design, and sampling intensity to detect changes in ecosystem condition in response to pollutants. This is particularly important for terrestrial ecosystems, where little progress has been made. Biogeochemistry, habitat and biodiversity, and the linkage between diversity and productivity, are important factors for which a comprehensive suite of indicators should be developed. Indicators should include intermediate variables (for example, leaf area index and the foliar chemistry used to model productivity) as well as final variables (for example, mortality). (p. 371)

This report recommends indicators that can help natural resource managers and policy makers to monitor and assess the effects of air quality on ecosystems. Indicator selection and design was guided by the most current scientific information and focused on representing changes in ecological condition that result from air pollution. However, the effects of changing climate and other environmental conditions on the biosphere are complex (Neilson, 1993). For example, stream nutrient levels can be affected by changes in seasonality of snowfall and snowmelt that alter streamflow patterns (Mote, 2003). And a recent report by the Environmental Protection Agency concludes that changing climate is a factor that air quality managers will have to take into account when developing future air pollution control strategies for ground-level ozone (EPA, 2009). While the indicators in this report will still serve their intended function, any environmental monitoring program designed to inform these indicators must take this complexity into account.

POLICY CONTEXT

A number of governmental policies instituted over the past several decades have contributed to the reduction of pollutants in the atmosphere. In the U.S., the 1970 Clean Air Act (CAA) and its amendments of 1977 and 1990 created guidelines for both stationary and mobile sources. Primary National Ambient Air Quality Standards (NAAQS) established by the Environmental Protection Agency (EPA) under the CAA set limits for six "criteria" pollutants: particulate matter, ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead, based on human health effects. Individual states are required to complete State Implementation Plans (SIPs) which identify mobile or stationary sources of criteria pollutants unique to the state, and ways in which reduction of those sources at the state level can contribute to established national goals. Secondary NAAQS, which address the effects of pollutants on ecosystems, are also periodically reviewed. For example, an Integrated Science Assessment was recently published for nitrogen and sulfur oxides (EPA, 2008) and will form the basis of a review of the relevant secondary air quality standards.

Cap and trade programs are another very effective CAA mechanism used by EPA to reduce emissions of sulfur and nitrogen. With this type of program, a cap is set on the amount of pollution that can be emitted from power plants and other regulated entities. Each entity can choose how to meet the cap, for example by installing scrubbers, purchasing allowances from other regulated partners, or increasing the efficiency of their overall operation. Participating entities report results back to EPA. Current cap and trade programs include the Acid Rain Program, in which SO_2 emissions from power generation sources are controlled through a cap and trade program implemented under Title IV of the CAA. Preliminary data from 2008 show that SO_2 emissions from sources affected by this program have decreased by about 8.1 million tons (51 percent) from 1990 levels. Starting in 2003, EPA worked with the States in the Eastern U.S. to implement a second cap and trade program focused on reducing the regional transport of NO_x, an ozone precursor. The NO_x Budget Trading Program has reduced NO_x emissions from power generation units and large industrial sources by over 60 percent from 2000 levels, helping states in the East achieve attainment of the 1997 ozone NAAQS.

Recent rules promulgated under the CAA authority are intended to assist EPA in improving the nation's air quality. The Clean Air Interstate Rule (CAIR) was issued by EPA in 2005 and is intended to reduce sulfur dioxide and nitrogen oxide emissions from power plants through the use of a cap and trade program similar to the existing Title IV Acid Rain Program and NO_x Budget Trading Program. If fully implemented as currently written, it is projected to reduce target pollutants by 70%. A recent court decision, however, requires EPA to rewrite the rule to correct "fatal flaws," among them to increase the rigor of the rule and to move up the date by which states will be required to fully comply. The Clean Air Mercury Rule (CAMR) was issued simultaneously with CAIR, and was intended to reduce mercury emissions from coal-fired power plants, also through the use of a cap and trade system. A future system for controlling mercury emissions is under development both at the state and federal levels, and will impact national standards in the coming years. In 1999 the Regional Haze Rule was implemented by EPA to improve visibility at national parks in cooperation with the National Park Service, U.S. Fish and Wildlife Service, U.S. Forest Service, and others. State plans for reducing particulate matter and other forms of pollution that cause haze will contribute to the overall reduction goal.

Information about ecological condition is commonly inadequate to fully understand the effectiveness of air pollution control strategies and a more comprehensive approach to monitoring impacts of air pollution on ecosystems is needed. Cowling et al. (1998) present an argument for a more comprehensive approach to controlling impacts of reactive nitrogen in ecosystems, both from a policy and a management perspective. They also suggest development of guidelines for nitrogen that will balance human activities with the need for cleaner air, water and soil. In 2003, the Society for Environmental Toxicology and Chemistry collaborated with EPA to convene a national expert workshop focused on designing a national mercury monitoring network that would provide more comprehensive information about how emissions are affecting mercury in the atmosphere, in fresh and coastal waters, and in fish and wildlife (Harris et al., 2007; Mason et al., 2005). And Lovett and Tear (2008) recommend an expanded and integrated national monitoring system that would build on existing multi-pollutant monitoring programs.

International policies also affect U.S. air quality goals. The 1979 Convention on Long-Range Transboundary Air Pollution, whose parties include the U.S. and Canada as well as much of Europe and Russia, contains several protocols specific to a number of pollutants. Its leadership regularly reviews progress towards meeting global goals and revises protocols as needed. And in Europe, current air quality policies rely in part on knowledge gained in recent decades through large-scale ecosystem manipulations aimed specifically at forming policy solutions to air pollution (Wright & Rasmussen, 1998).

The concept of "critical loads" is an important emerging approach to managing pollution effects. Critical loads are defined as "a 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 & Grennfelt, 1988). A pollution limit for an ecosystem is set by linking specific levels of pollution inputs (e.g., annual deposition) to a particular ecosystem response (e.g. plant growth). Limits may be applied county-wide, or may have regional differences, and can be used for a variety of management goals (e.g., setting limits for sulfur, nitrogen, or both when addressing acid deposition; nitrogen loading to sensitive systems). Some federal agencies, like the U.S. Forest Service, already promote the use of critical loads in meeting their specific mandates for managing air pollution.[1] A number of other agencies have voiced support for the integration of critical loads at both the federal and state level (Lovett & Tear, 2008; Milford & Middleton, 2008; Porter et al., 2005). Work on critical loads in Canada and in some European countries, which have been ongoing for some time, may provide guidance for any development of national assessments in the U.S. This report, to the extent that it reviews ecological endpoints of air pollution, will contribute to the continuing conversation on critical loads.

With so many agencies, domestic and international, making policy decisions about pollution control, it is not surprising that continual refinement of goals is necessary. With every new policy that is implemented, decision-makers need

1. See http://www.nrs.fs.fed.us/clean_air_water/clean_water/critical_loads/

tools to help them understand whether and how these decisions are contributing to the achievement of air quality goals. Ecosystem monitoring is one such tool; chosen well, indicators of ecosystem change can help to inform policy development and implementation by documenting whether emission control policies and programs are working as intended and helping to determine if policy change is needed to achieve further ecosystem protection.

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Chapter II. State of the Science Assessment

Project Objectives

To scientifically assess the strength of air pollution control and environmental management strategies, federal and state agencies and other natural resource managers need improved understanding and monitoring of the effects of air pollutants on ecosystems. With support from the U.S. Environmental Protection Agency (EPA) Clean Air Markets Division, the Heinz Center has developed a suite of indicators to inform environmental data collection and integrated assessment of ecosystem response to changes in air quality. This project expands on the *State of the Nation's Ecosystems* project[2] by investigating ecosystem responses specific to changes in air quality.

A key goal of this effort was to elicit and synthesize the most important scientific ideas and information and to translate this knowledge into policy-relevant ecological indicators. This project identifies well-documented and widespread ecological responses to air pollutants (i.e., ecological conditions that are sensitive to changes in air quality over time) and recommends a small number of ecological indicator metrics that demonstrate the links between ecosystem exposure and response where they are strongly established. Pollutants of interest for this project include nitrogen, sulfur, ozone, and mercury. Ecological responses to both ambient and deposited air pollutants are included.

Project Methods

Indicator selection and design was built on the foundation of an advisor-driven, 'state-of-the-science' assessment. The project Steering Committee oversaw three technical subcommittees charged with providing guidance for indicator metric selection and development. A review of scientific work on ecosystems and air pollution included more than 150 peer-reviewed journal articles and government-sponsored reports. This review was used to catalogue common measures of ecosystem properties that respond to air pollutant exposure, to develop concepts about the multiple impacts air pollution can have on the chemical and biological condition of ecosystems, and to narrow the focus of candidate indicators. Finally, an assessment of data systems was conducted, focused on options for data sourcing for recommended indicators. Based on the combined recommendations of the three technical subcommittees, the Heinz Center performed and commissioned targeted analyses to support the resulting indicator metrics.

Advisory Committees

A nine-person Steering Committee was formed to provide overall project guidance, to help in synthesizing findings from multiple project elements, and to build linkages to other projects and emerging research. Three technical advisory subcommittees were convened to guide and inform indicator development (see Table 1), with participation by Steering Committee representatives. Each subcommittee encompassed expertise in the biogeochemical effects of nitrogen and sulfur in terrestrial and aquatic ecosystems, ozone effects on crops and other vegetation, and mercury transformations across environmental media. Appendix A provides committee membership lists; Appendix B provides guiding principles for committee discussions.

2. http://www.heinzcenter.org/ecosystems

TABLE 1 Technical Subcommittees

Ecological Change subcommittee	• Evaluated a preliminary list of over 30 ecological endpoints across 11 ecosystem types affected by air pollution for scientific maturity and relevance • Identified 9 major categories of ecological effects and, within each of these categories, potential indicator metrics that should be further investigated
Air Quality subcommittee	• Explored the linkages between exposure to air pollution (i.e., atmospheric composition, atmospheric deposition) and ecological endpoints recommended by the Ecological Change subcommittee • Discussed the potential for identifying specific ecosystem types likely to be more responsive to changes in air quality
Analysis subcommittee	• Evaluated strategies for quantitatively linking metrics of air pollution exposure and ecological response • Proposed targeted analyses to evaluate the role of air quality in changing ecosystem condition and to identify the most useful metrics

The Ecological Change subcommittee assigned each of the recommended ecological endpoints to one of three categories[3] (see Table 2):

1. *Well-studied* ecological effects for which literature synthesis can produce a viable indicator metric.
2. Ecological effects that *require further analysis* to formulate a suitable indicator metric.
3. Ecological effects for which the *science base is not yet mature enough to support indicator development* (e.g., there is an inadequate number of controlled or natural gradient experiments or a lack of relevant conceptual models for stress-response relationships).

Subsequent discussions by the Air Quality and Analysis subcommittees focused on scientifically robust linkages among:

- atmospheric nitrogen and sulfur deposition, 'primary' acidification and enrichment effects, and a suite of 'secondary' effects on organisms, species and ecosystems;
- ambient ozone concentration, foliar injury, and plant physiological responses; and
- contemporary atmospheric mercury deposition, transformations in terrestrial and aquatic systems, and bioaccumulation.

Cross-Cutting Issues in Indicator Design

In order to identify ecological indicators that are responsive to changing air quality over management-relevant timescales, project advisors encouraged consideration of several cross-cutting issues and development of clearly articulated rationales for indicator design choices such as measurement intervals.

Temporal variability in air pollutant exposure generates variable ecological responses and there may be non-trivial lag time between changes in air quality and changes in ecological endpoints. Pollutant exposure may vary seasonally or interannually and ecological effects may be acute or chronic. Pollutant transfer to aquatic systems may represent contemporary or historical air emissions.

Spatial variability in air pollutant exposure and ecological response presents challenges in defining appropriate geographic scales for indicator metrics. As a result of patterns of emissions, weather systems, land cover and other factors, ambient pollution concentrations or pollutant deposition may produce 'hotspots' of exposure. Similarly, watersheds and biological systems may exhibit highly variable sensitivity to air pollution exposure. Indicator metrics and datasets should be optimized to avoid obscuring important spatial patterns. For example, coarse-scale data may be applied more universally and produce strategic level indicators while fine-scale data may be applied more locally and produce tactical level indicators.

Form of pollutant exposure. Air pollutant speciation and form of deposition can influence bioavailability and transport within ecosystems. For example, in addition to mercury methylation impacts, the atmospheric forms of mercury (i.e., gaseous, particulate, elemental) also exhibit different patterns of deposition and accumulation by ecosystems that influence the nature of mercury's effects on biota. Similarly, the fate of nitrogen and sulfur deposited directly on water surfaces may produce different ecological effects than when it is deposited to terrestrial systems where important biochemical transformations and retention occur. Indicator design should consider the role of pollutant speciation and deposition in modifying ecosystem response.

Complexity. While air pollution exposure can result in direct ecological response (e.g., foliar injury), many responses result from more complex processes (e.g., mercury bioaccumulation) for which dose-response evaluation can be more elusive. In addition to air pollutants, many ecological components are commonly affected by a suite of other stressors, such as climate change, disturbance patterns and management activities, which can obscure or amplify signals of air pollution effects. Proposed indicators should account for these interactions and enable users to parse out ecological responses to changes in air quality.

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3. This approach was also used in Lovett et al. (2009), *Effects of Air Pollution on Ecosystems and Biological Diversity in the Eastern United States* (Annals of the New York Academy of Sciences 1162: 99-135): "In general we reserved the highest level of confidence for targets in which air pollution impacts are well established from experimental and/or gradient studies within the region… We had moderate confidence in conclusions inferred from studies on similar species or ecosystems outside the region. We had low confidence in conclusions drawn from mechanistic arguments about what species are likely to be sensitive to pollution, when those arguments were accompanied by little or no direct empirical support from either inside or outside the region."

TABLE 2 Categories of Ecological Effects

Ecological Effects		Literature review to identify best metric	Further analysis required	Expanded scientific basis needed
NITROGEN AND SULFUR DEPOSITION				
Acidification	Terrestrial	Change in base cation status in forest soils (e.g., base saturation; BC:Al ratio)		Change in relative productivity, acid-sensitive biota
		Change in forest soil pH		
	Freshwater	Change in ANC in streams, lakes, ponds		Change in relative productivity, acid-sensitive biota
		Change in sulfate in streams, lakes, ponds		
Nitrogen Enrichment	Terrestrial	Change in C:N ratio in soil organic matter	Change in community structure (lichen abundance or chemical composition; grass species dominance)	Altered chemical cycles (N uptake; N volatilization; relative net nitrification; litter decomposition/ accumulation)
		Change in foliar N:P ratio or N:productivity		Alteration of N-sensitive species/ features, seedling root:shoot ratio, ratio of nitrophilic/phobic species, mycorrhizae, etc.
		Change in streamwater nitrogen status (e.g., nitrate, total nitrogen, N:P ratio; DIN:Total P ratio, DON:DIN ratio)		Altered disturbance regimes, e.g., hydrology, fire frequency (with change in species mix); pest outbreaks; invasive species
				Change in species composition (red:sugar maple ratio; fungal:bacteria ratio; hetero:autotrophic nitrifiers)
	Freshwater		Change in community structure (diatoms)	Change in species composition, abundance (nitrophilous algae; fish)
	Coastal systems		Change in total nitrogen	
			Change in dissolved oxygen	
			Change in Chlorophyll a (abundance, timing)	
AMBIENT OZONE				
Plant Injury	Terrestrial	Foliar injury (e.g., lesions, leaf senescence) in forests, croplands and grass/shrublands	Change in plant physiology, e.g., yield (cropped systems); chlorophyll/water use efficiency in forests	
			Changes in species composition (ozone-sensitive species in forests)	
MERCURY DEPOSITION				
Methylation	Aquatic	Change in MeHg:Total Hg ratio in wetlands		Change in MeHg:Total Hg ratio in streams, coastal systems
Bioaccumulation	Terrestrial			Change in total Hg in tissues (blood/egg) of invertivores
	Aquatic	Change in MeHg in young-of-the-year fish tissues		
		Change in total Hg in tissues of piscivores (mature fish)		

Chapter III. Acidic Deposition

Background

Acidification refers to the increase in the acidity of soils and waters, particularly as a result of the atmospheric deposition of sulfuric acids, nitric acids, and ammonium. The burning of fossil fuels and certain agricultural activities release sulfur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3) into the atmosphere. These gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. They are deposited back on the ground as dissolved sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+). As a cation, ammonium is less mobile in soil until converted to nitrate, a mobile anion that, like sulfate can leach through soil and into surface waters, contributing to soil and stream acidification (Lovett et al., 2009).

Deposition of these pollutants occurs via wet and dry deposition. Wet deposition occurs when acidic compounds fall to the ground or other surfaces in the form of rain, snow, fog, or mist. Under dry conditions, acidic compounds may become incorporated into dust or smoke and accumulate on surfaces through dry deposition. Levels of dry deposition are difficult to assess because of numerous uncertainties in measurements and monitoring (Krupa, 2003). Also, available data on precursor air concentrations and deposition (wet and dry) may be limited spatially and temporally.

The U.S. Environmental Protection Agency (2008) has summarized ecological impacts of acidic deposition:

> Acidic deposition has altered major biogeochemical processes in the United States by increasing the sulfur and nitrogen content of soils, accelerating [sulfate] and [nitrate] leaching from soil to drainage water, depleting base cations (especially calcium and magnesium) from soils, and increasing the mobility of aluminum. (p. 4-7).

When acidic compounds are deposited to terrestrial systems, hydrogen ions (H^+) can displace base cations adsorbed to soil surfaces. Soils that have abundant base cations have greater capacity to buffer pH changes from acid deposition and other acidifying processes, such as plant growth. But changes brought about by acidic deposition can lead to decreases in the availability of plant nutrients and declines in the capacity of ecosystems to neutralize continuing inputs of acidic compounds. The mobilization of aluminum by loss of base cations can also have toxic effects on biota. In aquatic ecosystems, acidic deposition can also impact the species diversity and abundance of fish and other organisms—a process particularly noticeable in the eastern United States (Bulger et al., 2000; Driscoll et al., 2001).

Research shows that acidic deposition is associated with the decline of certain tree species—such as red spruce and sugar maple—and with adverse effects on several fish species and aquatic invertebrates in the eastern United States (Driscoll et al., 2007a; NAPAP, 2005). Acidic deposition also contributes to the corrosion of buildings, bridges, and other structures, impaired visibility, and human ailments such as asthma and bronchitis.

Chemical reactions in soils are key to understanding how acidification occurs and what conditions make certain sites more sensitive than others. One of the major sources of calcium and other nutrients needed for plant growth is weathering, i.e. the breakdown of rocks and minerals in the soil in the presence of water. Small clay and humus particles in the soil possess weak electrical charges on their surfaces, which attract the nutrients released from the mineral layer. Plant roots can then take up these positively charged nutrients—calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+), in particular—by donating hydrogen ions (H^+) in exchange (Harpstead, 1997). But acid anions, or negatively charged ions, originating in atmospheric deposition (such as SO_4^{2-} and NO_3^-) are generally highly mobile in the soil, and, when leached in drainage waters, they tend to first strip basic cations (positively charged ions such as Ca^{2+}, Mg^{2+}, and K^+) and then acid cations (such as H^+ and Al^{n+}) from soils. This process not only depletes essential nutrients from soils, but also acidifies ecosystems and mobilizes forms of aluminum that can be toxic to organisms (Driscoll et al., 2007b; NAPAP, 2005; Sullivan, 2000).

Bedrock geology determines to a great extent the availability of base cations and, therefore, the sensitivity of ecosystems to acidification. Research conducted in western Virginia showed a strong correlation between local geology and the acid-base status of streams (Bulger et al., 2000). Sullivan et al. (2007) used that finding, along with the conclusions of several other similar studies, to develop a regional landscape classification scheme for the Southern Appalachian Mountains "based in part on the relationship between lithology [the gross physical characteristics of the surrounding rock formations] and streamwater ANC [i.e. Acid Neutralizing Capacity, a measure of the difference between base cations and acid anions in an ecosystem]" (p. 58). Similarly, Berg et al. (2005) used the catchment bedrock type, categorized into classes based on

sensitivity to acidic waters, as one of the variables entered into a model for predicting the acid neutralizing capacity of lakes in California's Sierra Nevada Mountains.

Other physical factors, apart from bedrock geology, that impact the sensitivity of soils and surface waters to acidification include topography, soil chemistry, land use, and hydrologic flowpath (EPA, 2008). Sullivan (2000) lists the physical characteristics typically exhibited by aquatic ecosystems that are sensitive to acidification:

> Sensitive waters are usually found at moderate to high elevation, in areas of high relief, with flashy hydrology and minimal contact between drainage waters and soils or geologic material that may contribute weathering products to solution. Sensitive streams are generally low order. Sensitive lakes are generally small drainage systems. An additional lake type that is often sensitive to acidification is comprised of small seepage systems that derive much of their hydrologic input as direct precipitation to the lake surface. (p. 11)

Similar observations were made in western alpine regions (Clow & Sueker, 2000).

Not all regions of the United States are exposed to similar levels of acidic deposition. Electric utilities and industrial combustion are responsible for the great majority of sulfur dioxide emissions and a sizable percentage of nitrogen oxides emissions, and states along the Ohio River Valley are the largest emitters of sulfur and nitrogen oxides in the country (Driscoll et al., 2001). Legislation passed in the 1970s and the 1990s has resulted in a "dramatic decrease" of total sulfur deposition in the Eastern U.S., with the largest reductions occurring in the Northeast, downwind from the Ohio River Valley (CASTNET, 2007). But despite these encouraging trends, acidic deposition continues to pose risks to ecosystems in the U.S. (EPA, 2007). Long term ecosystem damage to terrestrial and aquatic biota may still occur (Clow

& Mast, 1999). Reductions in nitrogen deposition over the last twenty years have not been as pronounced as those for sulfur, since the major source of nitrogen oxides is the burning of fossil fuels for transportation. According to the EPA (2007), "inorganic nitrogen in wet deposition decreased commensurately in the Mid-Atlantic and Northeast." (p. 28). The diversity of sources of nitrogen oxides, sulfur oxides, and ammonia in the U.S. translates into a dynamic picture of change in acidic deposition trends. Development and population increases in the West, along with changes in the agricultural production system, constitute just two of the many socioeconomic factors that will likely impact the future distribution of acidic deposition in the U.S.

But while challenges persist for predicting future acidic deposition trends, research points to some signs of ecosystem recovery from acidification. A global-scale analysis of surface water acidification indicators, published by Stoddard et al. (1999), revealed that sulfate concentrations had declined across most of Europe and North America over the 1980s and 1990s, with the exception of Great Britain. The analysis showed large-scale increases in the ability of aquatic ecosystems to neutralize acids across Europe in the 1990s, but did not find similar signs of recovery in the U.S. Midwest and Northeast. The researchers hypothesized that the lack of recovery in these regions may have been due to depleted cation pools in watershed soils, and that after a certain "time lag" the rates of weathering would once again begin to exceed the loss rates due to leaching by acid anions, especially if sulfur deposition continued to decline. Subsequent work in the U.S. has documented ecosystem recovery with declining acidic deposition. For example, Driscoll and colleagues (2007a) found increases in ANC and pH and decreases in aluminum in Adirondack lakes.

More recent studies, focused on aquatic ecosystems in the Adirondack and Catskill Mountains of New York, confirmed that, overall, lakes and streams in the two regions are exhibiting declining trends in sulfate and, to a lesser extent, nitrate concentrations (Baldigo et al., 2009; Burns et al., 2006; EPA, 2007; Lawrence et al., 2008a; Momen et al., 2006). The studies also found that the acid neutralizing capacity of surface waters is increasing as sulfate reduction trends are beginning to exceed base cation reduction trends. Burns et al. (2006) warned, however, that "local scale processes and factors," such as climate and flow, "that affect the rates of cycling of nitrogen and base cations are significant and are likely to confound a simple cause-effect relation between S and N emission trends and the response of acid-base conditions of surface waters" (p. 1625). In general, perched seepage lakes and drainage lakes in watersheds with thin deposits of glacial till, whose water comes largely from direct precipitation or shallow flowpaths, have been the most responsive to decreases in acidic deposition (Driscoll et al., 2007a).

A key concept in understanding the impact of acidic deposition on ecosystems is *episodic acidification*, i.e. the "short-term decreases of acid neutralizing capacity (ANC) that often occur during high streamflow associated with rainstorms and snow melt" (Wigington et al., 1996, p. 374). Although episodic acidification can be brought about by natural processes, there is evidence that acidic deposition has contributed to an increase in the magnitude and frequency of these acidification events (EPA, 2008; Wigington et al., 1996). Episodic acidification can have long-term effects on aquatic fauna (NAPAP, 1990). The EPA's Episodic Response Project examined 13 small streams in the Adirondacks, Catskills, and the Appalachian Plateau and found that "streams with suitable conditions [for fish survival and reproduction] during low flow, but adverse chemical conditions during high flow, had higher fish mortality in bioassays, net downstream fish movement during events, lower brook trout density and biomass compared to non-acidic streams, and most lacked acid-sensitive species" (Baker et al., 1996, p. 431).

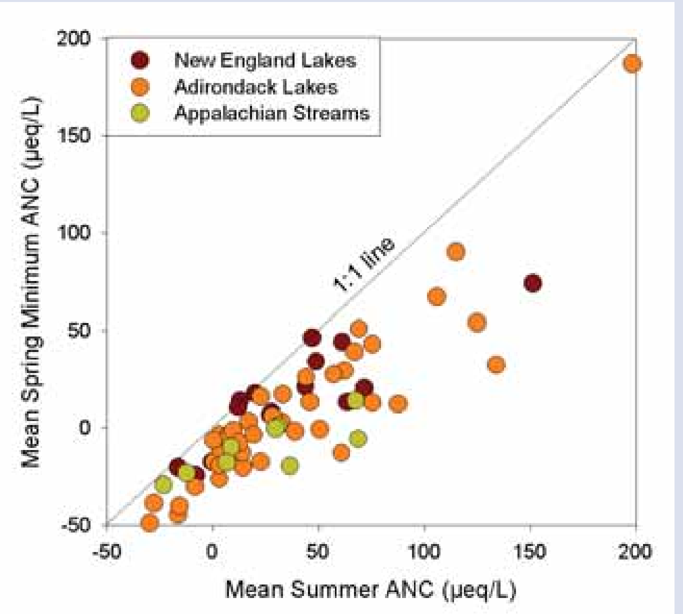
The EPA (2008) provides an example of the significance of episodic acidification in assessment of acidification:

> baseflow samples collected from 1991 to 1994 through the EPA Temporally Integrated Monitoring of Ecosystems (TIME) Program indicated that 10% of the 1,812 lakes larger than 1 ha surface area in the Adirondack region could be considered chronically acidic (ANC values less than 0 meq/L), but that an additional 31% of these lakes had baseflow ANC values less than 50 meq/L and were, therefore, estimated to be susceptible to episodic acidification. (p. 4-21)

In many parts of the U.S., spring (peak) flows are commonly associated with episodic acidification and summer (base) flows are associated with chronic acidification. Work by EPA (2003) found that, on average, spring ANC values are 30 μeq/L lower than summer values (see Figure 1).

The most important characteristic affecting the sensitivity of aquatic ecosystems to episodic acidification is hydrology—the pathways followed by snowmelt and storm-flow water through the watershed. The less contact there is between water and acid-neutralizing materials and soil layers, the lower the surface water's acid neutralizing capacity (EPA,

FIGURE 1 The relationship between spring and summer ANC values at sites in New England, the Adirondacks, and the Northern Appalachian Plateau (EPA, 2003). Values are mean summer values for each site during the period 1990-2000 and mean spring minima for each site during the same time period.



2008). Sullivan (2000) lists the types of ecosystems at risk for episodic acidification: "High-elevation watersheds with steep topography, extensive areas of exposed bedrock, deep snowpack accumulation, and shallow, base-poor soils are most sensitive. Such systems are common throughout the mountainous West and in portions of the Northeast and Appalachian Mountains." (p. 140). Notably, climate change is likely to affect watershed hydrology.

DeWalle and Davies (1997) examined seasonality of ANC in the 13 Episodic Response Project streams and found time-of-year effects in 12 of them. The mean amplitude was 10.9 meq/L, ranging from 0 meq/L in one stream to 53 meq/L in another—amplitudes consistent with seasonal ANC ranges found in other studies. These findings underscore the importance of establishing a consistent methodology for measuring the acid-base chemistry of aquatic ecosystems and for extrapolating ANC data from one time of the year to another.

Indicators of ecological effects of acidic deposition on terrestrial and aquatic systems should reflect meaningful change in chemical and biological aspects of ecological functioning. Acidification is a chemical process that produces changes in soil and surface water chemistry that, in turn, alters living conditions for plants, fish and other organisms.

TERRESTRIAL ACIDIFICATION INDICATORS

Forest soil pH

There is ample evidence that acidic deposition decreases the concentration of base cations (especially calcium and magnesium) in forest floors. A nine-year acidification experiment conducted in Maine demonstrated that the addition of nitrogen and sulfur resulted in an increase in stream concentrations of calcium, magnesium, sodium, potassium, aluminum, sulfate, and nitrate, and decreases in acid neutralizing capacity and pH level, in the treated watershed relative to a reference watershed (Fernandez et al., 2003). Although some studies do not find significant decreases in base cation forest pools over the last twenty to thirty years in natural settings (e.g. Yanai et al., 1999), Bailey and colleagues (2005) believe that most base cation depletion occurred during the 1970s, and research projects initiated subsequently may therefore have missed some of the major historical acidification-induced changes in soil chemistry. Their own study, conducted in the Allegheny Plateau in Pennsylvania, found long-term decreases at all soil depths in pH, calcium, and magnesium concentrations, and increases in aluminum concentrations, between 1967 and 1997.

Similarly, Drohan and Sharpe (1997) found significant decreases in soil pH and calcium and magnesium concentrations, accompanied in some study sites by increases in aluminum concentrations, in a study comparing soil chemistry variables between 1957 and 1993 in Pennsylvania hardwood stands. In conjunction with the decrease in pH, the investigators observed a decrease in exchangeable magnesium and calcium. These results matched with similar observations in Europe. The authors conclude that declines in calcium and magnesium accompanying the decrease in pH might have "potentially ominous" effects on the health and nutrition of forests in that area, citing several other studies documenting the effects that decreased calcium and magnesium soil concentrations have on tree health.

Ca:Al Ratio

The *ratio of calcium to aluminum* (Ca:Al) in soil solution is often employed as an indicator of the probability of stress to forest ecosystems. Once soil base cation pools are depleted, continued inputs of acid anions can mobilize inorganic forms of aluminum that are toxic to plants. Aluminum minerals found in soils are generally insoluble, but acid inputs can dissolve the minerals and release aluminum ions into the soil solution. A Ca:Al ratio of 1.0 is generally proposed as a threshold value. Cronan and Grigal (1995) reported a 50% risk of adverse impacts on tree growth or nutrition when the Ca:Al ratio is as low as 1.0, a 75% risk when the soil solution ratio is as low as 0.5, and nearly a 100% risk when ratio reaches 0.2.

There is a recognition that different tree species are sensitive to different aluminum stress levels (EPA, 2008; Pardo & Duarte, 2007; Sullivan, 2000). Kobe et al. (2002) showed that under realistic field conditions, the amount of exchangeable calcium ions estimated to have been depleted from a hardwood forest significantly influenced the growth of sugar maple seedlings. Equivalent additions of aluminum significantly increased mortality in sugar maple and red spruce seedlings. Studying the response of European chestnut trees to varying Ca:Al ratios, Zysset et al. (1996) found that the various Ca:Al ratios did not effect biomasses of roots, stems, shoots, and total plants. At a very low Ca:Al ratio of 0.1, they observed decreases in foliar growth.

Aluminum concentrations also show significant spatial and temporal variability, a trait possibly related to pulses of nitrate in soil solution (Sullivan et al., 2002). The level of this nitrate leaching is under biological control, and is therefore susceptible to seasonal variability, which in turn has a temporal effect on the Ca:Al ratio. There is an established relationship between peak concentrations of nitrate in soil solution and potentially toxic peaks in aluminum concentration. The variation in aluminum toxicity will also contribute to varying response. For example, in organically rich soil horizons, aluminum will form organic complexes that are non-toxic (Sullivan et al., 2002).

Base saturation

Soil *base saturation* is the percentage of basic cations (such as calcium, magnesium, and potassium) measured in a soil sample relative to the total quantity of exchangeable cations (i.e. base cations plus acid cations such as hydrogen and aluminum). Soil base saturation and biological availability of base cations are correlated. Therefore, soil base saturation is a commonly used indicator of acidification effects in terrestrial ecosystems that tracks changes in soil chemistry that are meaningful for biological functioning.

Cosby et al. (2006) synthesized available information related to soil base saturation to arrive at the following categories of concern for acidification in Shenandoah National Park's terrestrial systems (Table 3).

Other researchers also provide a base saturation value of 20% below which ecosystems in the U.S. are "vulnerable to" (Driscoll et al., 2007b) or "at risk with respect to" (Gbondo-Tugbawa & Driscoll, 2003; Pardo & Duarte, 2007) additional acidic deposition. The EPA's (2008) review of base saturation as an indicator of acidification similarly concluded that values below 15%-20% tend to be associated with negative ecosystem health effects. Base cation depletion, of which base saturation is a measure, contributes to soil acidification by affecting the ability of soils to neutralize acidity in future acidifying deposition. It also impacts the ability of watershed soils to support acid-sensitive vegetation. At a soil base saturation of even 20% to 25% or lower, acidifying deposition can mobilize potentially toxic inorganic aluminum, which can leach into soil waters and surface waters (EPA, 2008). One study reported that a decrease in base saturation from 30% to 20% over a period of 37 years led to decreases in diameter growth of Norway spruce in northwestern Russia (Lawrence et al., 1995). Another demonstrated that calcium depletion from soil was associated with winter injury of red spruce foliage (Hawley, 2006). Changes in soil base cation chemistry have also contributed to high mortality rates and decreasing growth trends of red spruce trees (Sullivan et al., 2002).

Rationale for Indicator Selection

Three metrics were evaluated for development as indicators to evaluate terrestrial acidification in forested systems:

- change in forest soil pH
- change in Ca:Al ratio
- change in soil base saturation

TABLE 3 Expected Effects of Acidification on Aquatic Biota at Varying Levels of Base Saturation in Forest Soils (from Cosby et al., 2006)

Level of Concern	Percent Base Saturation (BS)	Expected Effects (partial list)
Low	BS > 20%	No effects
Moderate	BS between 10% and 20%	Moderate effects probable: base cation availability reduced and forest growth probably slowed
Elevated	BS between 5% and 10%	Moderate effects certain and severe effects probable: base cation availability greatly reduced with risk of mortality from stresses
Acute	BS < 5%	Severe effects certain: high risk of forest mortality from stresses and direct acidification effects

While these three indicators reflect the same general biogeochemical process, change in base saturation provides the most continuous measure of changing acidification status and can be considered a "leading" indicator. Once changes in Ca:Al ratio and forest soil pH are observed, ecosystems may have already crossed key chemical thresholds.

RECOMMENDED METRIC

Base Saturation. Once ongoing national-scale measurements are available, this indicator will report the amount of basic cations (calcium, magnesium, and potassium) calculated in a soil sample relative to the total amount of exchangeable cations (i.e. base cations plus acid cations such as hydrogen and aluminum) (Table 4).

TABLE 4 Base Saturation Levels at Forested Sites (1955-2008) found in the USDA-NRCS National Soil Survey Characterization Database (See technical note for additional information.)

Percent Base Saturation	Percentage of Sites
Less than 5% (acute concern)	2.25
5 to 10% (elevated concern)	5.06
10 to 20% (moderate concern)	7.82
Greater than 20% (low concern)	83.66

The USDA-NRCS National Soil Survey Characterization Database contains data on basic and exchangeable cations that are collectively produced with the National Cooperative Soil Survey Program. The data used here were extracted using land cover recorded at the time of sampling, or from data extracted from the USGS National Land Cover Database. The queried data match the criteria where the land cover class was forest in either of these data sets, the mineral horizon was at the surface (and not a horizon that experiences plowing or other disturbance, e.g., Ap), and contained both base saturation and C:N ratio information. The query yielded a sampling size of over 2000 sites. In Table 4, base saturation data are grouped using categories reported by Crosby et al. (2006).

Data Limitations

The data presented show the percentage of forested sites within the database for which the measured base saturation levels fall within the specified range for the years 1955-2008. There is currently no national program, or even large scale regional program, which measures base saturation levels on an on-going basis. The USDA-NRCS program is designed for soil characterization, as opposed to continuous monitoring, therefore, the information shown in Table 4 simply illustrates how soil base saturation data could be configured. As data become available, they would be displayed as a time series for relevant geographic categories.

AQUATIC ACIDIFICATION INDICATORS

Acid Neutralizing Capacity

Acid neutralizing capacity (ANC) is a widely used indicator of acidification in aquatic ecosystems. ANC is usually well correlated with pH, and this relationship can be used to estimate impacts to various aquatic biota (NAPAP, 1990). Decreases in the ANC of stream waters have been shown to be related to decreases in the soil base saturation caused by acidic deposition (Lawrence et al., 1999).[4] ANC can be measured through titration (i.e., measuring the amount of base in solution by determining the amount of acid that must be added to neutralize it) or can be calculated as the difference between the sum of base cations and the sum of acid anions in solution. The difference between measured and calculated ANC increases as the organic acid concentration in a solution increases—a fact that carries important methodological implications for the interpretation of chemical changes in acidic or near-acidic systems (Sullivan, 2000).

Generally, lowest (i.e., episodic or acute) ANC levels in surface waters are associated with high spring streamflow, while ANC levels relevant for assessing chronic acidification are associated with the late summer/fall "base flow." The distinction between chronic and episodic acidification adds an important seasonal component to ANC measurements. Notably, stream monitoring systems do not always provide sufficient seasonal coverage to provide data for both chronic and episodic acidification. Hyer et al. (1995) also showed the short term variation in ANC that occurs during storm events. In a study of three streams located in Shenandoah National Park, ANC decreased, or even became negative, in a storm's aftermath. They also concluded that a stream's antecedent base flow ANC is the best predictor of the stream's minimum ANC.

Webb et al. (2004) have used ANC and sulfate concentration trends to ascertain the recovery of streams in western Virginia and the Shenandoah National Park from acidification. Similarly, Momen et al. (2006) employed ANC, along with pH levels, as a measure of chemical recovery from acidification in the Adirondacks. ANC thresholds values were also used by Sullivan and colleagues (2007) in a modeling study of ecosystem response to sulfur and nitrogen emission reductions in Shenandoah National Park.

4. Lawrence et al. (2008b) have also developed a novel approach to studying organic acids in aquatic systems by measuring base cation surplus, though this approach is not as widely used.

Bulger et al. (2000) used calculated ANC to define four categories of brook trout response to acidic conditions in Southern Appalachian mountain streams (see Table 5). Brook trout are a relatively acid-tolerant species. Cosby et al. (2006) took into account the impact of acidification on other fish species, macroinvertebrates, and insects, in addition to brook trout, and determined that surface waters in the Shenandoah National Park experience adverse effects at ANC values smaller than 100 meq/L. For example, at ANC values between 50 and 100 meq/L, the researchers found fish species richness to be much reduced, and the diversity and number of macroinvertebrates and insects to begin to decline. Earlier work by Bulger et al. (1995) found that ANC values in Shenandoah National Park waters were related to brook trout and blacknose dace response variables such as condition factors, densities, species richness, and annual production. Driscoll et al. (2003) reviewed similar relationships between low ANC and diminished fish species diversity and abundance in the Adirondacks. Heard et al. (1997) compared water chemistry and fish communities in 70 Pennsylvania streams with historical records to determine whether fish species richness had declined. The study concluded that many Pennsylvania streams have undergone an alarming reduction in fish diversity during the past 25–34 years, and that in many of the streams the loss of diversity is due to episodic acidification. Acidic episodes, associated with low pH, elevated inorganic aluminum concentrations, and high streamwater discharge caused rapid fish mortality under some conditions (Baker et al., 1996).

Change in sulfate concentration

Measurements of *sulfate concentration* in surface waters have been utilized extensively in analyzing the acid-base chemistry of aquatic ecosystems and its relation to atmospheric sulfur deposition. Driscoll et al. (2001) report that the concentration of sulfate in streams in the Northeast has shown a significant long-term decline between 1963 and 1994. The EPA (2007) states that sulfate concentrations in surface waters declined substantially from 1990-2006 in New England lakes, Adirondack lakes, and in northern Appalachian streams, but it increased slightly in southern Appalachian streams due to the sulfur retention characteristics of soils in the region. The EPA (2008) also summarized the available scientific evidence: the "data indicate a pattern of increasing concentrations of [sulfate] in surface waters before the year of peak sulfur emissions in 1973, followed by widespread decreasing trends in [sulfate] concentrations after the peak (with the only exception being the Blue Ridge Mountain region in Virginia)" (p. 4-39).

There can be a lag between sulfate deposition and its acidification effects on surface waters. While sulfur compounds can be assimilated by biological processes, the overall demand for sulfur is limited and so most deposited sulfur moves into the soil as SO_4^{2-}. Sulfate leaching is responsible for most of the ecological impacts of sulfur deposition because as divalent SO_4^{2-} moves through the soil profile into surface waters, base cations are effectively mobilized and leached from soil systems (EPA, 2008). Natural sources of sulfur may also contribute to observed concentrations in aquatic systems.

The EPA (2008) has summarized regional differences in the levels of sulfur retention in terrestrial systems in the United States. In the Southeast, sulfate adsorption to soil surfaces is pronounced and leaching can be delayed. Over time, delayed release of adsorbed sulfate can continue to acidify surface waters despite reduced levels of deposition. In the Northeast, a positive relationship between atmospherically deposited SO_4^{2-} and total sulfur concentrations in forest floor soils has been observed (Driscoll et al., 2001). As decreases in atmospheric deposition of sulfate have occurred, there

TABLE 5 Brook Trout Response as a Function of ANC Class and Range (from Bulger et al., 2000)

Stream Category	ANC Class and Range in microequivalents per liter (μeq/L)	Brook Trout Response
Suitable	Not acidic (ANC > 50)	No threat to brook trout
Indeterminate	Indeterminate (ANC between 20 and 50)	Possibility of lethal acidification episodes; status of brook trout contingent on various habitat characteristics
Marginal	Episodically acidic (ANC between 0 and 20)	Lower body weight, condition factor, and population density; acidic episodes are likely lethal to fry
Unsuitable	Chronically acidic (ANC < 0)	Lethal effects on brook trout

has been a net loss of sulfate from forest soils, however ongoing sulfate release to soils and surface waters has delayed their recovery from atmospheric deposition. In addition to temporal dimensions of sulfate deposition, retention, and acidification, recovery of soil and surface water systems is also influenced by the rates of mineral weathering and decomposition of organic matter. Recent research suggests that the recovery process could take decades or more (Bailey et al., 2005; Sullivan, 2000).

Rationale for Indicator Selection

Two metrics were evaluated for development as indicators to evaluate aquatic acidification in freshwater ecosystems:

- change in measured acid neutralizing capacity (ANC)
- change in sulfate concentrations of freshwater systems

While both metrics are useful for tracking the effects of freshwater acidification, ANC is recommended as a more continuous measure of general vulnerability to acid deposition that can be considered a 'leading' indicator while detection of change in sulfate concentration in streamwater may lag behind changes in patterns of atmospheric deposition. Changes in ANC demonstrate a freshwater system's susceptibility to acidification. Over time, measurements of ANC also show whether an aquatic ecosystem is subject to chronic or episodic acidity, and can therefore be used to evaluate the long-term level of acidity a system faces. There is also a correlation between ANC in freshwater systems and the base saturation levels of the surrounding soils, therefore the two indicators can be used in tandem to assess the general health of a forested ecosystem.

Recommended Metric

Acid Neutralizing Capacity. This indicator will report the percentage of freshwater systems with low, medium, and high ANC. The indicator is intended to report on both chronic and episodic acidification.

Two potential data sources were explored for this indicator. Base-flow ANC measurements made by the national-scale Wadeable Streams Assessment (WSA) provide information on chronic acidification; however, national-scale data are not available to provide information about episodic acidification (see *Data Limitations*, below). The EPA produced the WSA in 2006 to report on the ecological condition of wadeable streams in the conterminous U.S., organized into three major regions, which included a goal of identifying the relative importance of chemical and physical stressors on stream condition. The WSA's statistical design enables EPA to make conclusions about most wadeable streams in the U.S. Data reported here (see Figure 2) were collected from over 1,300 wadeable perennial stream locations in the lower 48 states over a five-year period; see technical note for more information.

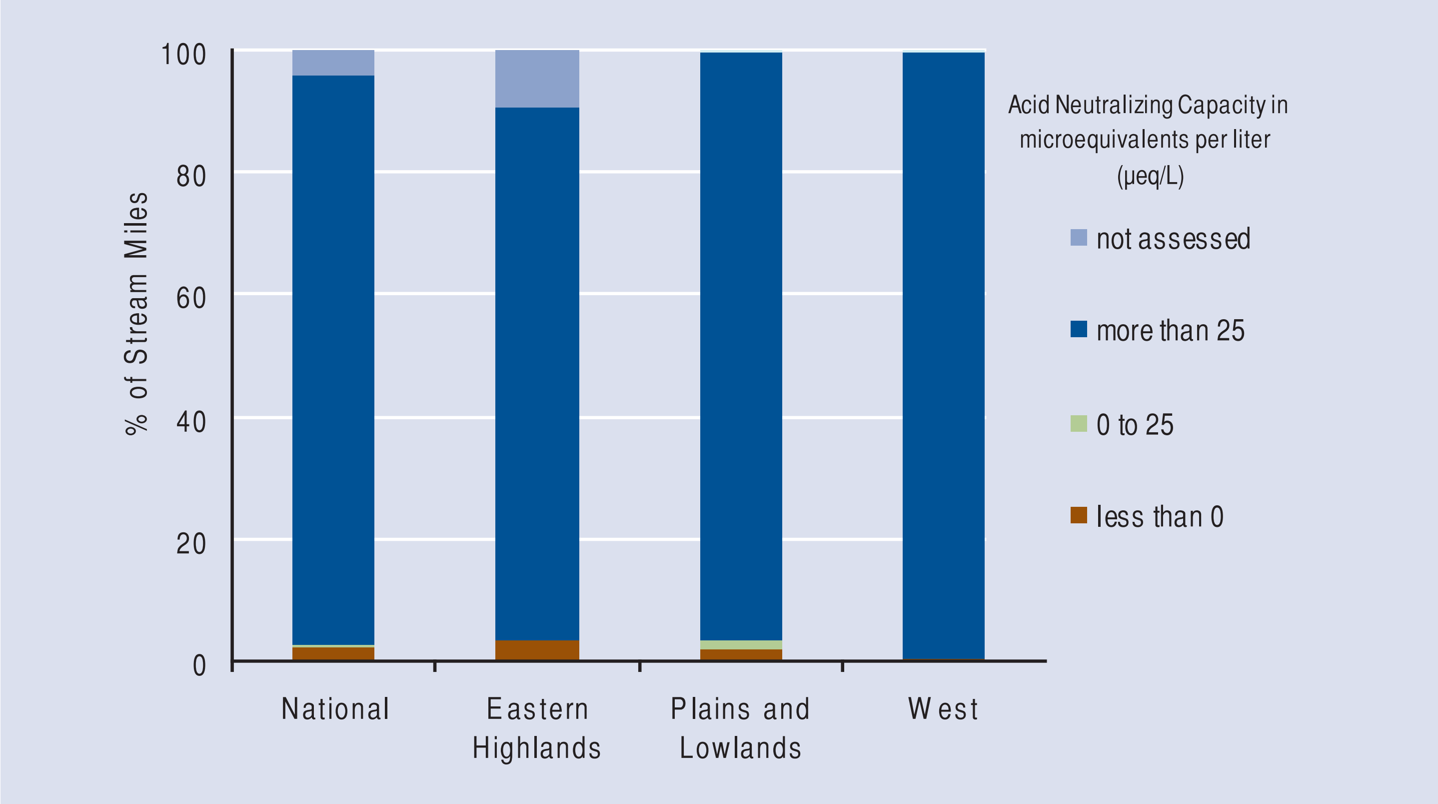
A second data source is the Environmental Protection Agency's Temporally Integrated Monitoring of Ecosystems/Long Term Monitoring (TIME/LTM) program. The primary objective of the TIME/LTM program is to detect long-term trends in acid/base status of lakes and streams across a gradient of acidic deposition. The TIME/LTM network consists of a subset lakes and streams that are particularly sensitive to acidity with most site records extending back to the early 1980s. Sites are sampled 3 to 15 times per year with a higher proportion of sampling conducted in the spring which coincides with higher rates of runoff (e.g., snow melt) and higher stream flows. This information is used to characterize how the most sensitive of aquatic systems in each region are responding to changing deposition, and provides information on seasonal chemistry and episodic acidification. Aquatic effects of acidic deposition often exhibit seasonality (e.g., causing harm in the winter or spring when the more sensitive life stages of some fish species are present). In most regions, a small number of higher ANC (e.g., Gran ANC > 100 μeq/L) sites are also sampled, and help separate temporal changes due to acidic deposition from those attributable to other disturbances (e.g., climate change, land use change).

The data presented from the TIME/LTM program show the percentage of sites from the Adirondack sampling region that have a minimum ANC value, in μeq/L, of less than zero, 0 to 25, or greater than 25 out of twelve monthly measurements (see Figure 3). In most cases, the month with the minimum value was between April and June. Minimum annual ANC values represent an estimate of episodic acidification. Figure 4 shows an average ANC level based on the average for all 12 monthly values, which represents chronic acidification. The TIME/LTM data show not only the significant impact episodic acidification can have on freshwater systems, but also show that a sizeable percentage of those systems are chronically acidic, based on average ANC values.

Data Limitations

Nationally, 4.1% of the WSA's target streams were not assessed for ANC and 9.5% of Eastern Highlands streams were not assessed (first order streams in this region were not included in the 2000-2004 sampling program) even though this region is likely to be significantly affected by acidification. While WSA data sampling is generally geographically robust, there is significant temporal variation in the data because samples are collected during a summer index period to coincide with base-flow conditions. In addition, WSA data only show chronic acidification under base-flow conditions and do not capture episodic acidification.

FIGURE 2 Percentage of stream miles, sorted by region, which had a measured ANC of less than 0 (acidic), 0 to 25 (sensitive), or greater than 25 μeq/L (not sensitive) from 2000-2004. Analysis performed by EPA Wadeable Streams Assessment program. See technical note for more information and for a map of WSA regions.



TIME/LTM data can be used to track both chronic and episodic acidification. While the TIME/LTM dataset provides a robust time series, sampling is limited to Northeastern regions and focuses on sites that exhibit greater acid sensitivity and also receive high rates of acid deposition (i.e., no coverage in the Southeast, West, or much of the Midwest). Furthermore, while TIME/LTM covers several regions in the Northeast, the Adirondacks dataset is the most thorough and continuous.

Other regional and national data systems are available, but the TIME/LTM and WSA datasets are representative of the criteria used to determine an adequately continuous, temporally and geographically robust system.

Research Needs

One promising area of research in determining an ecosystem's sensitivity to acidification is concerned with *critical loads* of air pollutants. The United Nations Convention on Long-Range Transboundary Pollution (1988) defined a critical load as "a quantitative estimate of the 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" (Article 1.7). While the use of critical loads has a longer history in Europe and Canada than in the U.S., American researchers are beginning to devise models that employ critical load data in assessing the impact of acidic deposition on ecosystem health. Citing these studies, McNulty et al. (2007) estimated the critical acid load (and the exceedance of it) of forest soils in the coterminous U.S. using a formula that takes into account base cation deposition, chloride deposition, base cation weathering, base cation uptake, nitrogen immobilization, nitrogen uptake, denitrification, and forest soil ANC. The model used a coarse scale of analysis, but found some obvious regional patterns in critical acid load exceedance:

> Much of the forest soil in New England and West Virginia is in exceedance of the CAL [i.e. critical acid load] by over 500 eq per hectare per year. These are historic areas of concern for acid loading. The model also predicted that a small portion of southeastern North Carolina had forest soil CAL exceedances greater than 500 eq per hectare per year. No areas with forest soil CAL exceedance greater than 500 eq per hectare per year were found in the western U.S., and only a few areas (e.g. southern California) showed any exceedance. (pp. 289-290)

FIGURE 3 Percentage of TIME/LTM Adirondack sites with a minimum ANC value of less than 0 (acidic), 0 to 25 (sensitive), or greater than 25 (not sensitive), 1993-2007. Analysis by the U.S. EPA Clean Air Markets Division.

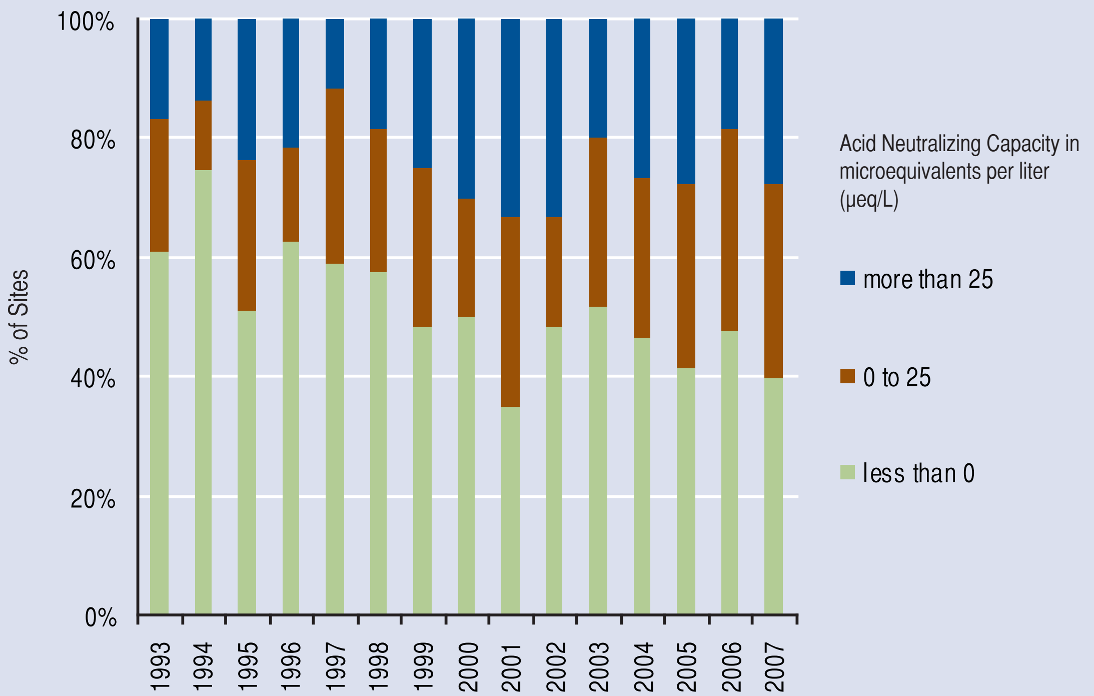
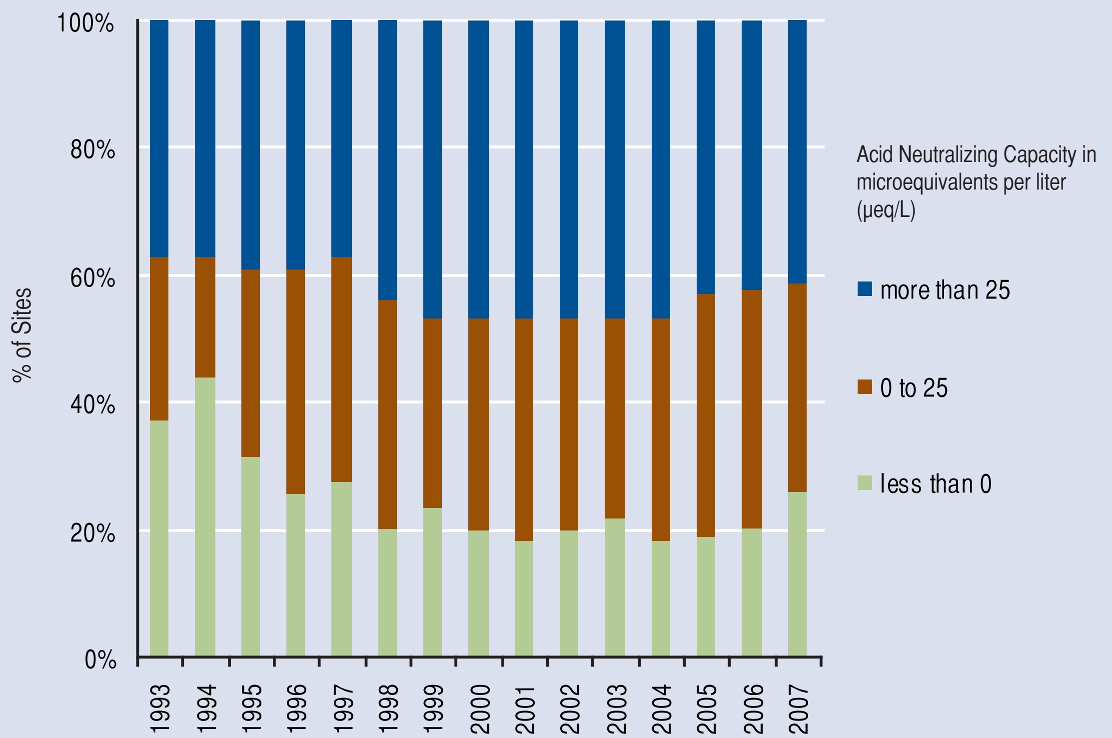


FIGURE 4 Percentage of TIME/LTM Adirondack sites with an average ANC value of less than 0 (acidic), 0 to 25 (sensitive), or greater than 25 (not sensitive), 1993-2007. Analysis by the U.S. EPA Clean Air Markets Division.



Sullivan's et al. (2007) research in Shenandoah National Park demonstrates the utility of critical load modeling for estimating the response of ecosystems to future sulfur and nitrogen deposition trends. There are many critical models for either aquatic or terrestrial acidification, and different critical loads will result depending on selection of type of model, the ecosystem indicators used, and thresholds for these indicators (Pardo & Duarte, 2007). The researchers also point out some of the key decisions that policymakers and scientists need to make when employing critical loads in research: "What is/are the selected critical endpoint criterion value(s) for the response indicator? What constitutes 'recovery' in the context of this indicator? What is the time period of evaluation of the critical load?" (p. 97). Porter et al. (2005) makes the case for increased coordination and communication between land managers and scientists to arrive at policy-relevant and research-supported answers to these types of questions.

Technical Notes

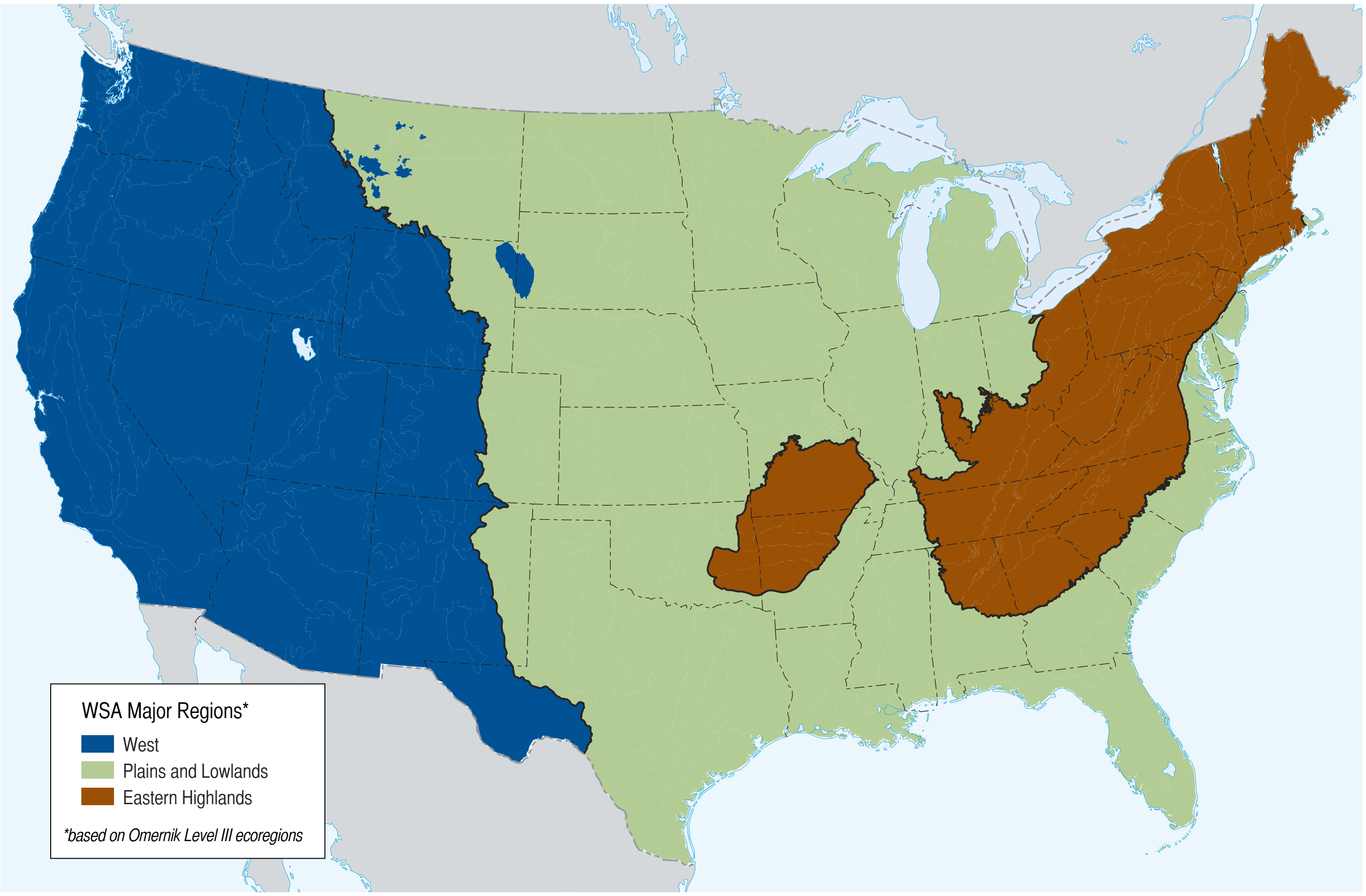
Base Saturation

The data sources highlighted in this indicator include:

National Soil Survey Characterization Database, National Soil Survey Center, USDA Natural Resources Conservation Service Soil Survey Laboratory. Sites for the database were generally selected and sampled by soil survey personnel in respective states. Pedons were sampled and analyzed by horizons. Pedons represent either the central concept of a soil series, the central concept of a map unit, or unspecified sites on a project specific basis. These data include both sites that are contaminated and non-contaminated. The database contains more than 30,000 pedons, 80 percent with profile descriptions, and more than 200,000 samples; the query for this analysis yielded a sampling size of 2136 sites. These data are categorized in four geographic layers: Site Info, Major Elements, Trace Elements, and Selected Characterization Data (which includes base saturation). The samples were analyzed using standardized procedures (found at ftp://ftp-fc.sc.egov.usda.gov/NSSC/Lab_Methods_Manual/SSIR42_2004_view.pdf).

The land use or cover type was derived by extracting the raster data from the Enhanced Historical Land-Use and Land-Cover Data Sets of the U.S. Geological Survey. See http://pubs.usgs.gov/ds/2006/240/ for more detail. The land use was derived by extracting the raster data from the National Land Cover Database (NLCD) from 2001. See http://www.mrlc.gov/about.php for more detail.

FIGURE 5 Map of Regions Used by the WSA. The regional definitions presented here are based on the Omernik's Level III ecoregions (see http://nationalatlas.gov/mld/ecoomrp.html). These regions are consistent with those used by the U.S. Environmental Protection Agency, Wadeable Streams Assessment.



Note: These data are also proposed for the C:N ratio indicator.

Data Availability: See the National Resource Conservation Service web site at http://ssldata.nrcs.usda.gov/default.htm for data access information and program contacts.

Acid Neutralizing Capacity

The data sources highlighted in this indicator include:

Wadeable Streams Assessment (WSA), Environmental Protection Agency. Data on Acid Neutralizing Capacity were collected by EPA, states, tribes and other federal agencies from over 1,392 wadeable perennial stream locations in the lower 48 states over a five-year period (Figure 5). The statistical sampling design allows for representative coverage of wadeable streams in three major climatic and landform regions and nine ecological regions during base-flow conditions.

Stream sites were sampled through EPA's Wadeable Streams Assessment between 2000 and 2004 during a summer index period. Values for ANC are based on the quantity of inorganic base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and inorganic acid anions (SO_4^{2-}, NO_3^{-}, Cl^{-}), but do not account for naturally-occurring organic acids.

Notably, seasonal variation in ANC values is not captured by the WSA program. (In general, spring high flow is associated with lower ANC values and late summer/fall "base flow" is associated with higher ANC values.) However summer "base flow" measurements offer interannual consistency in assessing trends over time. It has been noted that the WSA sampling program was not designed explicitly for the purpose of characterizing stream acidity and that chemical sampling was intended to support the primary focus on stream biological condition. The WSA dataset was highlighted because ANC measurements were collected through a nationally representative stream survey which is scheduled for repetition on a 5-year cycle.

Data Availability: See http://www.epa.gov/owow/streamsurvey/web_data.html for data access information and program contacts.

Temporally Integrated Monitoring of Ecosystems/Long-Term Monitoring (TIME/LTM), U.S. Environmental Protection Agency. For this analysis, 50 sites were included and the data were categorized in a manner consistent with the corresponding categories of the Wadeable Streams Assessment.

To evaluate the acidity of surface waters in sensitive ecosystems the following regions have long-term data: The Adirondack Mountains, New England, the Northern Appalachian Plateau, the Ridge/Blue Ridge provinces, and the Upper Midwest (sampling has been discontinued). Trends are available from these sites for the chemical constituents as measured in surface water.

While these monitoring programs were specifically designed to measure the trends in acidity of freshwater aquatic systems, they were implemented only in northeastern regions primarily affected by acidification (i.e., sampling was concentrated on waters likely to be at the greatest risk of acidification, but did not include all geographic areas with acid-sensitive lakes and streams). Also, within the sampled regions, there was substantial variation in the sampling frames used. The absence of sampling in the Southeast, West and much of the Midwest make these datasets inappropriate for national-scale reporting.

Data Availability: See http://www.epa.gov/airmarkets/assessments/TIMELTM.html for data access information and program contacts.

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Chapter IV. Nitrogen Enrichment

Background

Nitrogen (N) is necessary for life. But the form of nitrogen found most abundantly in nature (N_2) is unusable by plants and animals. N_2 needs to be transformed, or *fixed*, into reactive forms of nitrogen (Nr) before living organisms can assimilate it. Reactive forms of nitrogen include ammonia (NH_3), ammonium (NH_4^+), nitrogen oxides (NO_x), nitric acid (HNO_3), nitrous oxide (N_2O), nitrate (NO_3^-), and organic compounds such as urea and proteins (Galloway et al., 2002, 2003).

The major natural sources of Nr are nitrogen-fixing bacteria, cyanobacteria, and, to a lesser extent, lightning. Nitrogen-fixing bacteria often work in symbiotic relationships with plants such as legumes. With the help of an enzyme that they manufacture, the bacteria convert N_2 into plant-usable forms of nitrogen. Another specialized group of microorganisms can transform Nr back into N_2 – a process known as *denitrification*. In pre-industrial times, nitrogen fixation and denitrification rates were approximately equal, and nitrogen was one of the major limiting factors on ecosystem processes and functions (Galloway et al., 2002; UNEP, 2007; Vitousek et al., 1997).

Humans began to significantly alter the nitrogen cycle at the beginning of the twentieth century. Anthropogenic sources of Nr include:

> (1) widespread cultivation of legumes, rice, and other crops that promote conversion of N_2 to organic N through BNF [biological nitrogen fixation]; (2) combustion of fossil fuels, which converts both atmospheric N_2 and fossil N to reactive NO_X; and (3) the Haber-Bosch process, which converts nonreactive N_2 to reactive NH_3 to sustain food production and some industrial activities. (Galloway et al., 2003, p. 341)

Human activities mobilized about 70 Tg (grams x 10^{12}) of nitrogen per year in 1970. By the mid-1990s, they mobilized about 140 Tg N per year (Galloway, 1998). In 2005, that number increased to 187 Tg N per year (Galloway et al., 2008). Vitousek et al. (1997) argue that human activities introduce about twice as much reactive nitrogen into ecosystems as natural sources do. While some areas of the globe receive more of this extra Nr than others, the entire planet is affected by the increased availability of nitrogen.

Almost half of today's world population can find sustenance thanks to the increases in agricultural yields made possible by the Haber-Bosch process (UNEP, 2007). At the same time, reactive nitrogen emissions contribute to climate change and the thinning of the stratospheric ozone layer, and lead to the formation of smog, acid precipitation, aquatic eutrophication, terrestrial over-fertilization, and ground-level ozone. While all of these positive and negative effects are important, this review will focus only on the environmental impacts of Nr from atmospheric deposition.

A discussion of the *nitrogen cascade* phenomenon is useful for understanding the potential impacts of Nr on the environment. Galloway et al. (2003) define the N cascade as "the sequential transfer of Nr through environmental systems which results in environmental changes as Nr moves through or is temporarily stored within each system" (p. 343). For example, an atom of nitrogen released into the atmosphere as NO_x can contribute to increased ozone levels, atmospheric haze, and acid rain. Once deposited on the ground, the same nitrogen atom can increase soil acidity and affect biodiversity and ecosystem productivity. Nitrogen can then increase water acidity, if released into the aquatic ecosystem, or decrease stratospheric ozone, if released into the atmosphere as nitrous oxide. A key characteristic of the N cascade "is that once it starts, the source of the Nr (e.g. fossil fuel combustion or fertilizer production) becomes irrelevant. Nr species can be rapidly interconverted from one Nr form to another" (Galloway et al., 2003, p. 343).

Aber and colleagues (1989, 1998) developed a set of hypotheses to predict ecosystem responses to long-term chronic additions of nitrogen. Based on studies of nitrogen deposition in temperate forest ecosystems, the hypotheses attempt to explain the *nitrogen saturation* process, that is, "the long-term removal of nitrogen limitations on biotic activity, accompanied by a decrease in N retention capacity" (Fenn et al., 1998, p. 707). The hypotheses predict – and research has borne out the prediction – that foliar nitrogen concentrations increase with Nr additions to the ecosystem (Aber et al., 1998). There is some disagreement as to the effect that nitrogen deposition has on forested systems. Magnani et al. (2007) found that net carbon accumulation in temperate and boreal forests is driven by nitrogen deposition, a finding they believe casts "doubts on the risk of widespread ecosystem nitrogen saturation under natural conditions." (p. 848). This finding is in dispute, and its opponents argue that this group ignores "the effect of N deposition and saturation on soil acidification, groundwater and surface water quality, biodiversity, and ecosystem services other than C sequestration" (De Schrijver et al., 2008).

Other ecosystem processes show non-linear responses to N inputs: nitrogen mineralization rates (the conversion of organic nitrogen compounds into ammonium and nitrate) and forest productivity increase initially, but eventually decline, with continued nitrogen additions. The nitrogen saturation hypotheses indicate that, in predicting ecosystem response to nitrogen additions, researchers need to be aware of (1) differences in the relative degree of nitrogen saturation in different study sites *prior to increased N deposition*, and (2) differences in the rate at which different sites move toward saturation. Aber et al. (1998) suggest that prior land-use history, in particular, can play a major role in preconditioning ecosystem response to nitrogen additions: "essentially, the greater the previous extraction of nitrogen from a site by agricultural conversion, fires, or harvesting, the greater the nitrogen limitation on net photosynthesis and forest growth and the larger the amount of nitrogen deposition needed to move toward saturation" (p. 927).

A meta-analysis of studies with respect to the effects of air pollution on ecosystems in the Eastern United States attempted to characterize how different air pollutants affect various terrestrial and aquatic ecosystems. The investigators concluded that of eight target system groups, introduction of nitrogen has either a likely or known effect on all of them (Lovett et al., 2009). Studies have documented impacts on high gradient headwater streams, as well as lakes and ponds. Based on studies in other regions of the world, nitrogen enrichment also has a likely impact on alpine and subalpine ecosystems, forests, bogs and fens, grasslands, low gradient rivers, as well as estuaries, bays, and saltmarshes. These impacts may be subtle, but important because they can propagate through an ecosystem's food web. For example, increasing the nitrogen content of a tree may not be fatal in and of itself, but it may make a tree more susceptible to pests and pathogens.

Fenn and Poth (1998) suggest several scientific and practical criteria for selecting indicators of forest nitrogen status, and conclude that "a complementary set of nonredundant indicators" is likely needed to establish an ecosystem's "relative degree of N limitation, sufficiency, or saturation (excess)" (p. 124).

Nitrogen Enrichment Indicators

Nitrate leaching / export

Excessive nitrate loss has been called a "cardinal" (Fenn & Poth, 1998; Fenn et al., 1998) and a "primary" (Magill et al., 2000) indicator of an N-saturated ecosystem. Specialized bacteria produce nitrate (NO_3^-) through the oxidation of ammonia and ammonium. Once the capacity of ecosystems to retain nitrate through consumption and soil chemical fixation mechanisms is exceeded, the nitrogen compound is exported through the soil profile and in streamwaters. Ecosystems do manifest seasonal fluctuations in streamwater nitrate loss—for example, temperate forest watersheds experience significant nitrate losses during the spring water flow, when plant and microbial nitrogen demand are low and the amounts of nitrogen leached from the main rooting zone are high. But it is possible to identify sampling windows when nitrate levels are "indicative of above-normal N losses or N saturation" in a given ecosystem (Fenn & Poth, 1998, p. 126). Geographic variability in nitrogen movement emerges from heterogeneity in the underlying geology, substrate type and age.

Fenn et al. (1998) reviewed several North American case studies of nitrogen enrichment and found that nitrate exports and concentrations increased rapidly after fertilization at sites in the East and were also coincident with ambient nitrogen deposition in the Los Angeles Air Basin and the Colorado Front Range. A synthesis of data collected at 354 upland forested catchments across the Northeast showed close parallels between nitrogen deposition and surface waters nitrate concentrations (Aber et al., 2003). Nitrate concentrations were relatively low in watersheds receiving low amounts of nitrogen, and "the only lakes and streams with relatively high NO_3^- concentrations were those receiving relatively high N inputs, although responses to increased N deposition varied greatly" (Aber et al., 2003, p. 385). The study's authors were also able to conclude that nitrate

concentration data were free from potential covariation between nitrogen deposition, elevation, and climate factors: "relationships between N deposition and NO_3^- concentrations were far stronger than between elevation and spring or summer NO_3^- concentrations" (Aber et al., 2003, p. 385). Clear patterns also emerged between nitrate exports and N deposition: NO_3^- losses increased steeply above a 7 kg per hectare per year nitrogen deposition threshold, measured at the base of the watershed.

Driscoll et al. (2003) point out that the usefulness of nitrate leaching and export as indicators of nitrogen enrichment has been proven experimentally at sites in the Northeast and in Europe. Fertilization of a watershed in Maine "resulted in long-term increases of NO_3^- in streamwater and high annual exports of NO_3^-" (Driscoll et al., 2003, p. 363). Nine years of chronic nitrogen amendments at the Harvard Forest in central Massachusetts revealed that the addition of high levels of nitrogen to pine stands led to immediate increases in nitrate concentrations and fluxes below the rooting zone (Magill et al., 2000). However, hardwood stands showed a considerable time delay (approximately seven years) in the onset of nitrate losses, leading the researchers to underscore the importance of initial, pre-deposition conditions to a stand's progression toward saturation. Subsequent work by Magill et al. (2004) confirmed the differences between the pine and the hardwood stands: measurable Dissolved Inorganic Nitrogen (i.e. ammonium + nitrate; DIN) concentrations were detected in most years in the high- and low-N addition pine plots, but DIN was not detected in any of the hardwood plots until seven years after the onset of fertilization, and has continued to remain undetectable in low-N addition hardwood plots. Nitrate and ammonium concentrations did not exhibit any consistent increases over time in either the hardwood or the pine plots, but they exhibited a statistically significant relationship with fertilization levels and season of the year (McDowell et al., 2004).

A 20-year-long fertilization study conducted in Sweden confirmed that "concentrations and leaching of nitrate were higher where N had been added and were also positively related to the dose" (Nohrstedt, 2001, p. 566). And a summary of nitrogen deposition experiments conducted at four European sites concluded that losses of inorganic nitrogen by drainage were low at low N inputs and high at high N inputs (Tietema et al., 1998). The study's authors argue that drainage losses, along with microbial populations in the soil organic layer, are "the first ecosystem compartments to be affected" by N input manipulations.

A recent review of the ecological effects of nitrogen deposition in the western United States concluded that high nitrate concentrations in streamwater "are the most obvious symptom of ecosystem N overload in the Colorado Front Range, in montane watersheds in southern California, and in parts of the southwestern low-elevation Sierra Nevada" (Fenn et al., 2003, p. 405). The authors go on to assert that levels of nitrate in streamwater are particularly elevated in watersheds downwind of Los Angeles. Nitrate concentrations in southern Californian springs "correspond to N deposition levels, with relatively constant concentrations year round, … indicating that N deposition is affecting NO_3^- levels in groundwater" (Fenn et al., 2003, p. 410).

The authors of a broad review of ecosystem responses to nitrogen deposition state that "nitrate leaching has been identified as a primary sign of N saturation in N-limited temperate forests if it occurs at a significantly higher rate than 'background' levels, immediately after N additions without a significant temporal lag period, or aseasonally in a naturally seasonal ecosystem" (Matson et al., 2002, p. 113). The authors also point out, however, that ecosystems exhibit large differences in the onset and rates of leaching, and that the "greatest leaching losses occur when inputs are high or sustained, when the ecosystems are strongly limited by some other nutrient, or when soils are shallow or coarse-textured" (Matson et al., 2002, p. 118).

In summary, nitrate leaching and export are well-documented indicators of terrestrial ecosystems' N-saturated status. Their coincidence with nitrogen deposition levels has been documented at many European and North American sites. Generally speaking, atmospheric nitrogen deposition of 8-10 kg per hectare per year results in nitrate leaching in eastern U.S. forests. In the West, even lower deposition levels (less than 5 kg per hectare per year) may lead to nitrate leaching, especially in high elevation/low biomass systems (EPA, 2008). However, nitrate leaching and export metrics also possess some important limitations: First, nitrate leaching and export occur when an ecosystem has reached the nitrogen saturation stage. They tell us little about the initial ecosystem responses to nitrogen additions, when net primary productivity and, in some cases, species composition can already be affected by N inputs.[5]

And second, at many sites, previous land use histories going back as far as one hundred years are better predictors of nitrate leaching and export than nitrogen deposition data are. This is an important limitation if the goal is to identify quantifiable indicators of exposure-response relationships. Nitrate leaching/export indicate that an ecosystem has reached nitrogen saturation. High levels of nitrate in forest streams can indicate that forest ecosystems are no longer able to store additional nitrogen. As excess nitrate leaks from soils into streams, it can carry other important plant nutrients with it, acidifying forest soils. Under such nitrogen-saturated conditions, forests may show decreased growth and increased susceptibility to disturbance and disease. At high levels, nitrate leached from terrestrial systems can be toxic to aquatic biota in receiving surface waters.

Organic Soil Carbon to Nitrogen Ratio

The balance of carbon and nitrogen (C:N ratio) in forest soils is an important factor in determining the rate of decomposition of organic materials. The C:N ratio can inform our knowledge of C and N stocks and cycling processes, as well as of ecosystem responses to nitrogen input manipulations (Snowdon et al., 2005). Dise et al. (1998) argue that the C:N ratio in the organic soil layer, when combined with nitrogen input data, can help to assess an ecosystem's general "risk" of nitrate leaching. Dise and colleagues (1998) analyzed data from 33 sites in 11 European countries, selected to span a wide geographical and nitrogen deposition range, and found that the risk of nitrate leaching was enhanced as the C:N ratio decreased, while the amount of nitrate leaching at any C:N value depended on N input levels. In their conclusion, they recommended that,

> leaching risk be considered a sliding scale related to both the overall level of N-input and the organic horizon C:N ratio. Thus, different sites receiving the same level of nitrate deposition may leach different levels of nitrate, depending on their C:N ratio. Conversely, changes in the deposition of nitrate may have rapid effects on the quality of runoff and seepage water, without immediately changing the C:N ratio (Dise et al., 1998, p. 456).

Gundersen and colleagues (1998) performed a similar analysis on three independent datasets from European sites and confirmed that nitrate leaching is strongly related to the forest floor C:N ratio and is influenced by N inputs. The data indicate that considerable leaching occurs at C:N ratios below 24 or 25, leading the authors to argue that improving the ability to predict the rate of changes in the forest-floor C:N ratio would help to predict changes in nitrate leaching. Additional research conducted in Europe (Gundersen et al., 1998) and the United States (Aber et al., 2003; Lovett &

5. Interestingly, Fenn et al. (2008) calculated a critical load for nitrate leaching in mixed conifer forests in California by pinpointing the peak NO_3 leaching threshold during winter runoff at which the incipient stages of elevated NO_3 leaching occur.

Rueth, 1999) also concluded that net nitrification rates (i.e. the microorganism-driven conversion of ammonia to nitrate) increase significantly below the 24 or 25 C:N organic soil ratio threshold.

A study of ecosystem response to N deposition in New Hampshire's White Mountains (Goodale & Aber, 2001) revealed that nitrification rates were much higher at old-growth sites (which had low C:N ratios) than they were at historically disturbed sites (which had high C:N ratios). The study's authors argue that the C:N ratio integrates the carbon and nitrogen accumulation histories of a site: old-growth forests are characterized by declining litter inputs, net primary productivity, and soil organic matter levels (i.e., declining carbon content). At the same time, old-growth vegetation has less demand for nitrogen, allowing for increased nitrogen accumulation (i.e. increasing nitrogen content), nitrate production, and nitrate losses. Fenn and Poth (1998) referred to this long-term integrative function of C:N when they declared that the ratio is "less temporally and environmentally sensitive" than other nitrogen enrichment indicators, including streamwater nitrate concentrations. However, forest fires and species distribution can impact soil characteristics—including C and N pools—over very short spatial scales, leading researchers to express some reservations about the use of the C:N ratio as a nitrogen status indicator (Aber et al., 2003; Fenn & Poth, 1998). The effects of elevated ambient CO_2 concentration on C:N ratio are just beginning to be understood, however elevated CO_2-induced increases in carbon sequestration are likely to limited by nitrogen supply (Reich et al., 2006).

Lower C:N ratios have been found to be correlated with higher N inputs in relatively undisturbed ecosystems under ambient soil as well as experimental conditions. Baron et al. (2000) studied high-elevation ecosystem response to nitrogen deposition east and west of the Colorado Front Range. The study found that ambient NO_3 and NH_4 concentrations were significantly higher at sites east of the Continental Divide. Also, east site soils had significantly greater organic soil nitrogen percentage and lower C:N ratios. After controlling for soil physical characteristics and species composition, the researchers concluded that atmospheric nitrogen deposition accounted for 75% of the observed difference in soil organic matter nitrogen pools between the east and west sites (also see Rueth & Baron, 2002). Hogberg et al. (2006), reporting on a long-term nitrogen loading experiment conducted in a Swedish boreal forest, state that the organic horizon C:N ratio decreased from 41 ± 0.6 in control plots to 25.9 ± 0.6 in high-N addition plots ($P<0.001$).

Fertilization experiments conducted at some of the Colorado Front Range sites discussed above revealed that C:N ratio responded to nitrogen inputs only at sites on the west side of the Divide (Rueth et al., 2003). This finding allowed the researchers to surmise that nitrogen pools increase with fertilization in N-limited forests up to the point when the forest floor C:N ratio reaches a critical threshold level of 24 or 25. Below that critical ratio, further nitrogen additions result in nitrogen mineralization and nitrate and ammonium losses. The study's authors conclude that,

> A relationship exists between the forest floor C:N ratio and the initiation of changes in biogeochemical processes following elevated N inputs. When the ratio approaches 24, changes in N cycling and leaching losses occur. … With further fertilization at Fraser [a site on the west side of the Divide] we expect the soil N pool to increase, continually narrowing the C:N ratio and subsequently initiating elevated N cycling rates and leaching losses. (Rueth et al., 2003, p. 670)

Lovett and Rueth (1999) found that beech stands in the northeastern U.S. may show no net nitrification even at low (18-22) organic horizon C:N ratios. However, the C:N ratio remains a well-documented indicator of potential alterations to the nitrogen biogeochemical cycle (EPA, 2008).

Rationale for Indicator Selection

Two metrics were evaluated for development as indicators of nitrogen enrichment in terrestrial systems:

- streamwater nitrogen status
- C:N ratio in soil organic matter

Indicators were chosen because they are applicable across a wide geographic and temporal range and because they are strongly linked to atmospheric nitrogen deposition. Soil C:N ratio can serve as a leading indicator of the overall vulnerability of a system to nitrogen enrichment. Streamwater nitrogen status is a useful indicator of nitrate leaching and export although it may be affected by time lags between change in atmospheric deposition and change in observed stream water concentrations.

Recommended Metrics

Streamwater Nitrogen. This indicator will report nitrate levels in forested streams nationwide over time.

Two datasets have been identified to be used together for population of this indicator: data on nitrate in streams from the U.S. Geological Survey, and wet atmospheric deposition data from the National Atmospheric Deposition Program. Atmospheric deposition is useful for examining where elevated deposition levels correspond to elevated streamwater nitrogen levels.

The U.S. Geological Survey's National Water Quality Assessment (NAWQA) program provided data from sites with upstream land cover that was primarily forested (generally less than or equal to 25% agricultural and less than 5% urban), and where the total area of forested land was greater than that of grassland or shrubland. Each study unit assessment adhered to a nationally consistent sampling and analytical methodology, so that water-quality conditions in a specific locality or watershed can be compared to those in other geographic regions. NAWQA data also includes controls for upstream transport of aquatic loading from point or nonpoint sources. Figure 6 covers 51 major river basins.

The National Atmospheric Deposition program collects data on wet deposition of atmospheric nitrogen. Deposition at each NADP site (see Figure 7) was computed by calculating the precipitation-weighted means N concentration for a 10 year period (1992-2001). These values were multiplied by the annual average precipitation for the same period at each site, yielding the annual average N deposition for the period. Only sites that meet a 75 percent data completeness criteria for period are included. Color contours on the maps were created using site values to compute an array of regularly spaced grid-point values covering the country. (See technical note for additional details.)

Data Limitations
The NAWQA study units are representative of a wide range of stream sizes and types. However, NAWQA sites were not selected to be a statistically representative sample of the nation's aquatic resources. Furthermore, while NAWQA provides national-scale data, the program's sampling design does not represent the most sensitive systems or sites.

With respect to NADP, the data are not collected on a national scale for dry deposition. Dry deposition is an important component of atmospheric deposition that is generally under-characterized.

Organic Soil Carbon to Nitrogen Ratio. This indicator will report the ratio of organic carbon to nitrogen in the surface horizon of forested soil systems. There is no national system tracking this metric, so the data presented come from the USDA-NRCS National Soil Survey Characterization Database, which is designed primarily as a soil characterization system, as opposed to a soil monitoring system.

The USDA-NRCS National Soil Survey Characterization Database contains data on basic and exchangeable cations produced collectively with the National Cooperative Soil Survey Program. The data discussed here were extracted using land cover recorded at the time of sampling, or from data extracted from the USGS National Land Cover Database, for the period between 1955 and 2008. The queried data matches the criteria where the land cover class was forest in either of these data sets, the mineral horizon was at the surface (and not a horizon that experiences plowing or other disturbance, e.g., Ap), and contained both base saturation and C:N ratio information. The query yielded a sampling size of over 2000 sites (see technical note for more information). Among those sites, which are spread out across the country, 85.8% of the sites had a C:N ratio of less than 25, while the remainder had a ratio greater than 25.

Data Limitations
The data described here show the percentage of forested sites within the database for which the measured carbon to nitrogen ratio falls within the specified range, sampled between 1955 and 2008. There is currently no national program, or even large scale regional program, which measures the C:N ratio on an on-going basis. The USDA-NRCS program is designed for soil characterization, as opposed to continuous monitoring. Therefore, this information is simply a snapshot and does not account for temporal and geographic fluctuations that would occur if the data were more complete.

Research Needs

The following were considered as possible indicators for nitrogen saturation and enrichment in terrestrial and aquatic ecosystems. Due to limitations in scientific understanding they were not reported as such. Future research could lead to these indicators being used in addition to, or in replacement of, those suggested above.

Foliar N Concentrations and Nitrogen to Nutrient Ratios
One of the predictions of the nitrogen saturation hypothesis is that foliar nitrogen concentrations increase with elevated N inputs in terrestrial ecosystems (Aber et al., 1998; Galloway et al., 2003). Research has not proven this prediction wrong, although a large-scale analysis of data collected in northeastern states showed that foliar N concentrations had a stronger relationship with elevation and with climatic variables that vary with elevation than with nitrogen deposition (Aber et al., 2003). Given the small number of species sampled, the study's authors could not disentangle the individual effects on foliar chemistry of nitrogen deposition and climatic gradients (which covary in the study region).

FIGURE 6 Nitrate in Forest Streams (1992-2001). Analysis by the U.S. Geological Survey, National Water Quality Assessment program.

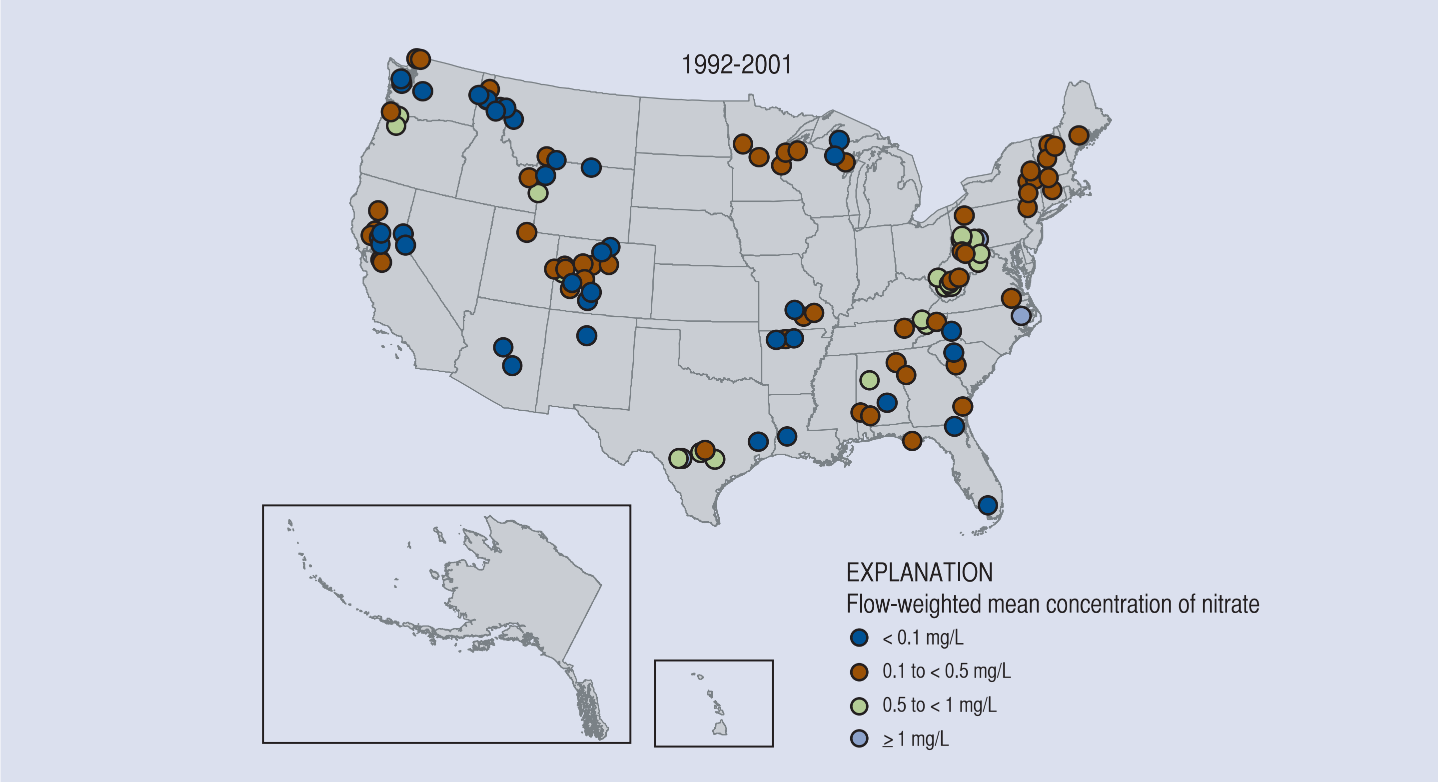
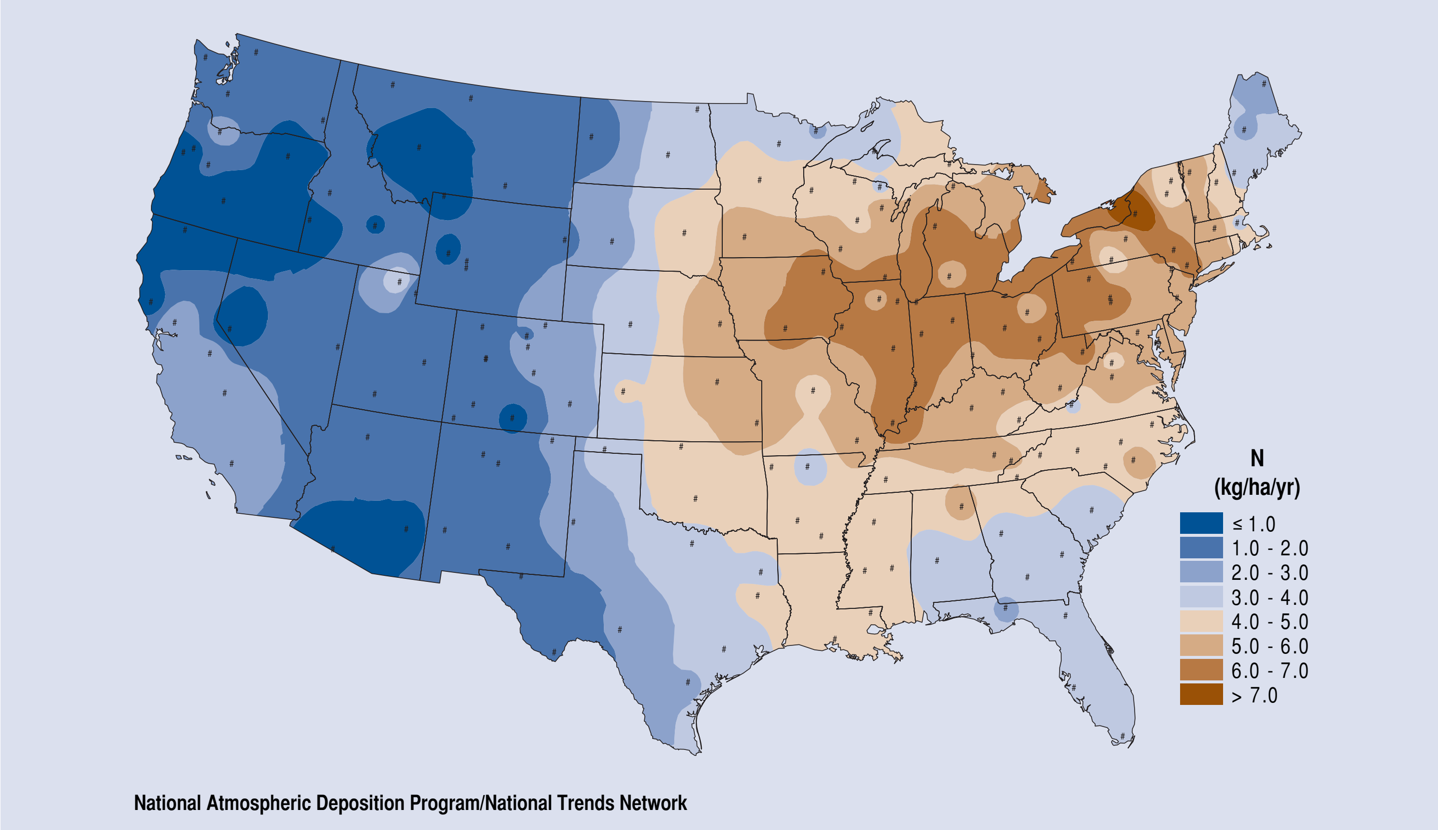


FIGURE 7 Average Atmospheric Nitrogen Deposition, 1992-2001. Analysis by the National Atmospheric Deposition Program.



A synthesis of 15 years of research at experimental forest stands in Massachusetts by Magill et al. (2000) showed that nitrogen concentrations in red pine foliage increased by 100% and 50% in high N input and low N input plots, respectively, when compared with control plot foliage. N concentrations in hardwood stands increased by smaller, but still significant, amounts (33% and 15% increases in high and low N plots, respectively). A meta-review of nitrogen excess in North American ecosystems led Fenn et al. (1998) to conclude that "increased foliar N and N:nutrient ratios are nearly universal phenomena in N-saturated forests" (p. 719). Nutrient addition experiments conducted in Sweden also showed consistent increases with N inputs in N concentrations and N:nutrient ratios in needles (Nohrstedt, 2001).

Research in Colorado by Baron et al. (2000) showed that even low, chronic nitrogen inputs are correlated with significantly greater foliar N percentage, N:magnesium, N:calcium, and N:phosphorus ratios. However, research reported by Rueth et al. (2003) suggests that, as forests approach nitrogen saturation status, their foliar nitrogen percentage and the N:magnesium and N:potassium ratios increase more slowly, with additional N inputs, than in N-limited forests.

Foliar chemistry changes may be useful indicators of nitrogen-induced changes in terrestrial ecosystems, particularly in N-limited forests. However, their relatively small geographical and temporal integrative function can subject them to significant climatic variation, leading Aber et al. (2003) to declare that, "synoptic, broad-scale, repeatable sampling, like that becoming possible for foliage through imaging spectroscopy … may be the only method by which foliar chemistry could be a valuable broad-scale spatial predictor of forest N status" (p. 387).

Changes in Community Structure

Nitrogen enrichment can have major effects on an ecosystem's biota by inducing potential changes in productivity and competitive interactions. Species that are best able to take advantage of the increased N supply are likely to out-compete nitrogen-sensitive species (e.g., nitrogen addition has been linked to shifts in the balance of N-fixing and non-N-fixing microbes).

In terrestrial ecosystems, plant species in grasslands have suffered negative impacts from chronic low level nitrogen enrichment (Clark & Tilman, 2008; Wedin & Tilman, 1996). Epiphytic lichens (i.e. lichens that grow on other plants) have been shown to be particularly sensitive to nitrogen enrichment. EPA's (2008) review of the biological effects of nitrogen deposition revealed that, in parts of Southern California, "up to 50% of lichen species that occurred in the region in the early 1900s have disappeared, with a disproportionate number of locally extinct species being epiphytic cyanolichens" (p. 4-130). The review also found well-documented cases of decline of nitrogen-sensitive lichens in Europe and the Pacific Northwest.

Fenn et al. (2003) summarized eight years' worth of surveys of epiphytic lichens in the Pacific Northwest (carried out by the USDA Forest Service Pacific Northwest Air Resource Program and the national Forest Inventory and Analysis Program) and concluded that, in nitrogen-enriched areas, nitrophilous (i.e. nitrogen-loving) lichens out-competed pollution-sensitive species. This pattern was particularly pronounced in urban areas, intensive agricultural regions, and downwind of major urban and industrial centers. Geiser and Neitlich (2007) analyzed Forest Inventory and Analysis data collected in western Oregon and Washington between 1994 and 2001 and found a positive correlation between nitrogen deposition and lichen communities dominated by nitrogen-loving species. Jovan's and McCune's (2005) research in California's Central Valley also revealed a positive association between nitrogen deposition (in the form of ammonia) and the abundance and diversity of nitrophilous lichens. The same researchers used FIA lichen data to develop a gradient model of ammonia deposition in the greater Sierra Nevada that attempted to circumvent the confounding effects of elevation on the biological impact of air pollution (Jovan & McCune, 2006). Fenn et al. (2008) developed critical loads from changes in epiphytic lichen communities, elevated nitrate leaching in streamwater, and reduced fine root biomass in ponderosa pine at sites with varying N deposition. It is hoped that such modeling studies will eventually yield more quantitative estimates of nitrogen deposition than are currently possible, but it should be noted that biomonitoring research employing lichens has been largely concentrated in the West so far.

In aquatic environments, the biovolume, species composition, and diversity of diatoms (i.e. a group of simple algae that serve as food for many animals) have been shown to be impacted by nitrogen enrichment. Baron et al.'s (2000) analysis of lake sediment records in the Colorado Front Range revealed that changes in isotopic nitrogen values over the last 100 years were "nearly coincident" with changes in diatom flora, and neither the algae nor the nitrogen values corresponded "with other signals of anthropogenic influence recorded in the lake sediments over this period, such as increases in atmospherically deposited lead" (p. 358). The researchers also concluded that the introduction of non-native fish and the aerial transport of phosphorus to the alpine lakes are unlikely to explain the "dramatic change" in the diatom communities. In another project report, Wolfe and colleagues (2001) stated that, although the rate of reactive nitrogen deposition in the

Front Range "is currently less than half of maximum values measured in the eastern USA, it is nonetheless sufficient to induce substantial changes in the structure of algal communities, and shift sediment nitrogen isotopic signatures to reflect augmented anthropogenic contributions" (p. 4).

Bioindicators such as lichens and diatoms are useful integrators of ecological conditions, and changes in nitrogen-sensitive species can signal the onset of broader pollution-induced community reorganizations. It is likely that shifts in diatom and lichen communities occur in many parts of the U.S., but our knowledge of nitrogen-driven changes in community structures is still geographically limited (EPA, 2008). There is good evidence that N deposition also impacts the species richness of grasslands by favoring the growth of N-demanding species at the expense of less competitive species (Stevens et al., 2004), but this type of research is also geographically limited in the U.S.

Nitrogen Enrichment in Coastal Systems

The role anthropogenic nutrient inputs play in aquatic ecosystems has been widely recognized, and nitrogen enrichment may be the largest pollution problem facing coastal waters of the United States (Diaz & Rosenberg, 2008). Eutrophication can lead to harmful algal blooms (HABs) in coastal systems,[6] and cyanobacteria blooms in lakes (Conley et al., 2009). Increased nutrient loading to coastal waters is now considered to be one of the major reasons why HABs are occurring with increasing frequency and duration. The dynamics of HAB development are complex, as they are affected by chronic and episodic nutrient delivery. Not all nutrient rich waters support HABs, and not all HABs occur in nutrient rich waters (Glibert et al., 2008). There is a general consensus that further research and characterization is required (Heisler et al., 2008).

These events, along interannual and interdecadal ocean-atmosphere oscillations, or regime shifts, can disrupt food webs, lead to hypoxia, and eventually lead to "dead zones" (Pew, 2007). There is a synergistic relationship between N and phosphorus (P) supply and demand, and therefore the nutrients are in close balance (Davidson & Howarth, 2007). Over time, P reduction programs reduced supply of the nutrient and improved water quality in many lake systems, but there was not a parallel improvement in estuaries and coastal systems. This led to recognition of the need to control N inputs to coastal waters (Conley et al., 2009). Atmospheric nitrogen deposition resulting from fossil-fuel combustion has been estimated to contribute up to 30% of the total nitrogen inputs to coastal marine ecosystems; another 10% of these inputs come from ammonia volatized into the atmosphere from agricultural sources (Howarth, 2008; Paerl et al., 2007).

Wet and dry deposition of nitrogen to estuaries and coastal ecosystems can either be direct or indirect. Spatial coverage of networks measuring wet and dry deposition is inadequate to produce robust predictions for direct N deposition to coastal areas, but general estimates are that direct deposition to surface waters contributes between 1% and 40% of the total nitrogen inputs to coastal ecosystems, with the direct deposition being most significant in very large systems or in coastal systems which have relatively small watersheds in comparison to the area of their surface waters. The indirect pathway refers to nitrogen deposited to terrestrial surfaces that is transported via surface runoff or subsurface flow to freshwater systems and subsequently released to coastal waters primarily via river systems. In most coastal systems, this is the major route by which atmospheric deposition contributes nitrogen (Howarth, 2008).

There are several possible indicators that might be used to measure the ecological effects of nitrogen enrichment in coastal systems. Federal agencies and numerous researchers, using a variety of quantitative approaches, have developed estimates of the relative contribution of atmospheric nitrogen to coastal eutrophication (confounding factors include non-atmospheric nitrogen sources, watershed properties, climate, land use, etc.) In order to propose a nationally-relevant indicator metric for this ecological effect of atmospheric nitrogen deposition (e.g., change in nitrogen levels in coastal waters, change in dissolved oxygen, change in chlorophyll *a*) further progress in synthesizing and/or scaling up existing watershed-level work may be needed. It may be possible to develop an indicator that is more sensitive to changes in pollutant exposure by focusing on smaller, 'reference' estuaries that are not substantially influenced by other factors such as major agricultural and point sources.

Technical Notes

USGS National Water Quality Assessment (NAWQA), U.S. Geological Survey (USGS). The NAWQA program provides nationally consistent monitoring of the physical, chemical and biological condition of streams (water, sediment, fish) and groundwater in 51 major hydrologic systems (referred to as study units) in the conterminous U.S., Alaska, and Hawaii, as well as the High Plains Regional Ground Water Study. In each study unit, land use and human activities were characterized so that water quality could be compared across different land use and land cover types. Between 2001 and 2012, NAWQA monitoring will continue in 42 of the 51 study units completed in the first decade.

6. Note that addition of oxidized, reduced and organic species of nitrogen may produce different ecological responses (e.g., stimulating particular types of algae).

All water samples were collected and analyzed by USGS according to the overall NAWQA design. Typically, streamwater samples were collected using depth and width integrating techniques so that the sample is representative of the water flowing past the sampling point. Basic sampling frequency at stream and river sites was monthly with several additional high-flow samples collected during high-intensity sampling years and during time periods when concentrations of certain constituents were expected to be high. To compute flow-weighted means, mean-annual loads were estimated by relating individual sample concentrations to the corresponding stream flow for the date and time each sample was collected for each site where samples could be fit into a regression model. The flow-weighted mean concentration was then calculated by dividing the total load by the total flow.

Data Availability: See http://water.usgs.gov/nawqa for data access information and program contacts.

Streamwater Nitrogen

The data sources highlighted in this indicator include: *National Atmospheric Deposition Program (NADP).* The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) is a nationwide network of precipitation monitoring sites. The network is a cooperative effort between many different groups, including the State Agricultural Experiment Stations, U.S. Geological Survey, U.S. Department of Agriculture, and numerous other governmental and private entities. The NADP/NTN has grown from 22 stations at the end of 1978 to over 250 sites spanning the continental United States, Alaska, and Puerto Rico, and the Virgin Islands.

For the map presented in the indicator description, an inverse weighted distance method was utilized for the spatial interpolation. Sites within 500 kilometers of each grid point were used in the computations. Color contours were drawn on this array of grid-point values. Each contour represents the class of deposition indicated in the legend.

Data Availability: See http://nadp.sws.uiuc.edu/ for data access information and program contacts.

Organic Soil Carbon to Nitrogen Ratio

The data sources highlighted in this indicator include: *National Soil Survey Characterization Database, National Soil Survey Center, USDA Natural Resources Conservation Service Soil Survey Laboratory.* Pedons were sampled and analyzed by horizons. Pedons represent either the central concept of a soil series, the central concept of a map unit, or unspecified sites on a project specific basis. These data include both sites that are contaminated and non-contaminated. The database contains more than 30,000 pedons, 80 percent with profile descriptions, and more than 200,000 samples; the query for this analysis yielded a sampling size of 2136 sites. These data are displayed in four geographic layers: Site Info, Major Elements, Trace Elements, and Selected Characterization Data (which includes base saturation). The samples were analyzed using standardized procedures (found at ftp://ftp-fc.sc.egov.usda.gov/NSSC/Lab_Methods_Manual/SSIR42_2004_view.pdf).

The land use or cover type was derived by extracting the raster data from the Enhanced Historical Land-Use and Land-Cover Data Sets of the U.S. Geological Survey. See http://pubs.usgs.gov/ds/2006/240/ for more detail. The land use was derived by extracting the raster data from the National Land Cover Database (NLCD 2001). See http://www.mrlc.gov/about.php for more detail.

Note that the C:N ratio was computed from two procedures for measuring the level of carbon. Organic carbon was measured using the Walkley-Black method and total carbon using combustion. Inorganic carbon in the form of $CaCO_3$ was subtracted from the total carbon before computation.

Note: This data source is also proposed for the base saturation indicator.

Data Availability: See the National Resource Conservation Service web site at http://ssldata.nrcs.usda.gov/default.htm for data access information and program contacts.

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Chapter V. Ozone

Background

Ozone (O_3) is a gas that occurs throughout the atmosphere, in both populated and remote areas of the globe. In the stratosphere—the atmospheric layer situated between 6 and 30 miles above the earth's surface—ozone is produced naturally and it protects the earth from the sun's ultraviolet rays. But ozone that occurs in the troposphere—the layer that extends from the earth's surface to the stratosphere—is a harmful pollutant and the primary component of smog. Tropospheric ozone results from the sunlight-driven reactions of volatile organic compounds (VOCs) or hydrocarbons and nitrogen oxides (NO_x). These precursor classes of chemicals are pollutants in their own rights, and are emitted primarily by motor vehicles, industrial facilities, electrical utilities, and other human activities. Natural processes such as lightning during thunderstorms also produce tropospheric ozone, although in relatively smaller amounts. While tropospheric ozone is commonly concentrated near urban areas, wind can easily carry it to distant places (EPA, 2003, 2006). In fact, air quality monitoring efforts have ascertained that tropospheric ozone often occurs at higher concentrations in rural areas downwind from cities than in the cities themselves (Samuelson & Kelly, 2001).[7] In the remainder of this section, the term "ozone" will refer exclusively to tropospheric ozone.

Ozone can cause a variety of respiratory problems in humans and animals, but this document is concerned with the impact of ozone on vegetation. It is difficult to estimate the overall percentage of U.S. plant species that are affected by ozone. The U.S. Forest Service has published a list of ozone-sensitive tree and shrub species (Smith et al., 2008); about half of the 100+ eastern species and all 28 western species reported are at least moderately sensitive to ozone. However, many species remain to be tested, and many sensitivity tests were conducted in greenhouses rather than in the natural environment. In cropped systems, there are thousands of cultivars that encompass all major and minor agricultural and horticultural crop species for which there is no assessment of ozone sensitivity, and new cultivars are being released constantly. While there are recognized crops that are considered to be more sensitive than others (e.g., soybean), it would be challenging at best to test all cultivars.

Ozone has a direct toxic effect on plants. The combined effects on individual organisms range in character from tissue damage to changes in competitive ability with respect to other species. Harmful effects on individual organisms, if widespread, can lead to declines of whole populations and replacement of one species by another that is either unaffected by air quality or whose competitive ability is enhanced. Ozone can lead

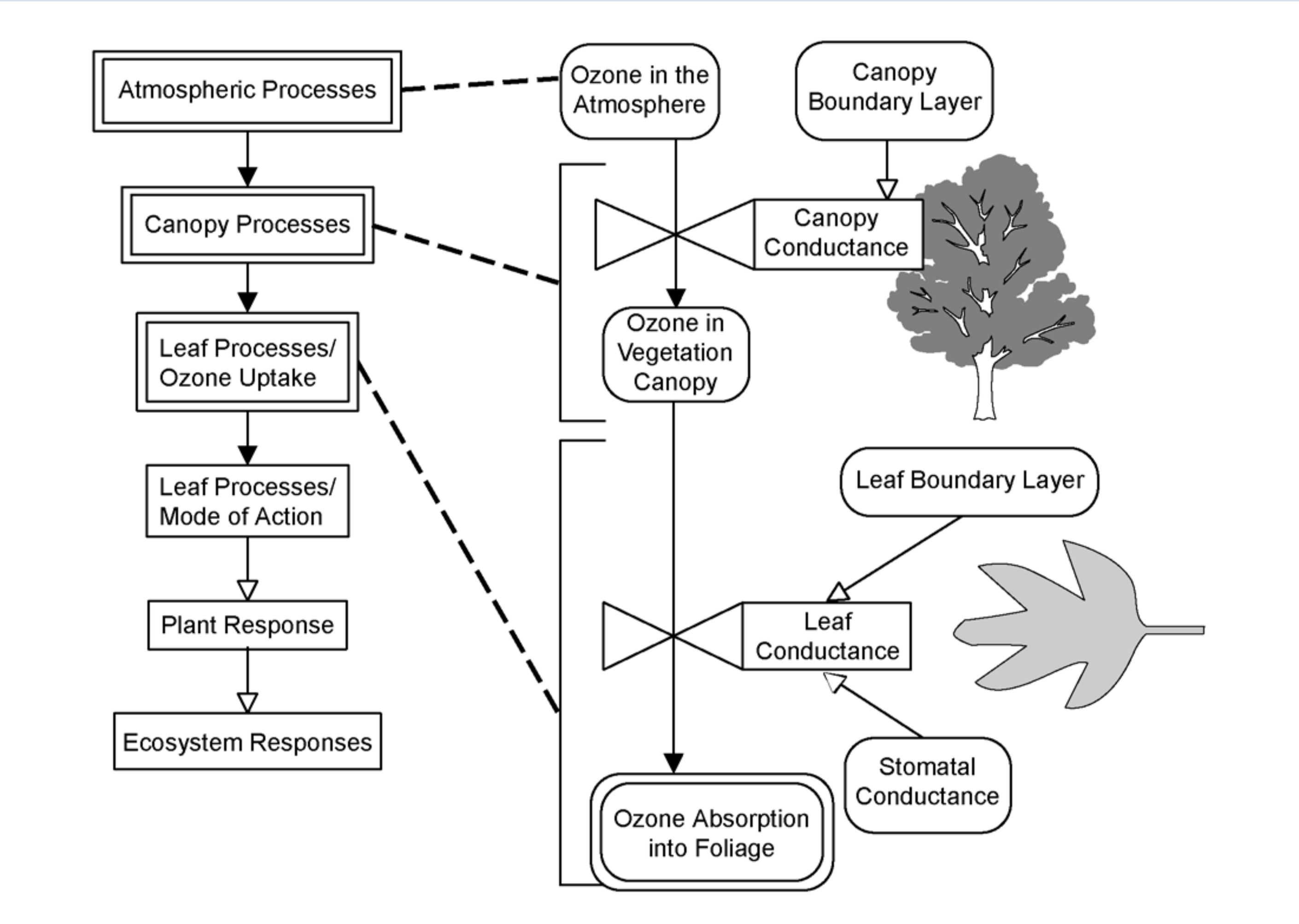
> …to reduced agricultural crop and commercial forest yields, reduced growth and survivability of tree seedlings, and increased susceptibility to diseases, pests and other stresses such as harsh weather. In the United States alone, ground-level ozone is responsible for an estimated $500 million in reduced crop production each year. Ground-level ozone also damages the foliage of trees and other plants, affecting the landscape of cities, national parks and forests, and recreation areas. (EPA, 2003, p. 3)

Citing a variety of scientific sources, Schaub et al. (2005) declare that ozone poses a more "serious threat to the health and productivity of vegetation" (p. 553) in certain regions of the U.S. than any other pollutant. And a review of 50 years of research on the impacts of ozone on forests reveals that the gas can induce visible leaf injuries, decrease chlorophyll content in leaves, accelerate leaf deterioration, decrease photosynthesis, alter the allocation of carbon, decrease fitness, and produce a variety of other physiological effects in plants (Karnosky et al., 2007). One can now point to an extensive literature on the mechanics of ozone intake and on potential exposure-response relationships.

Ozone exposure causes injury to vegetation through one or more of the following mechanisms: (1) membrane damage within the leaf interior; (2) reduced photosynthetic capacity from effects on RUBISCO, a crucial leaf enzyme; (3) limited allocation of carbohydrates to developing plant organs; (4) production of signals simulating pathogen attacks or wounding-type responses; and (5) accelerated leaf senescence (Fuhrer & Booker, 2003). Ozone enters plant tissue primarily through the stomates—the small pores in leaves and stems that allow the plants to exchange gases with their environment. Ozone also reduces the modulation ability of the stomates, that is, their ability to open and close. Once inside the plant, ozone reacts with cellular components found

7. Elevation and rural-urban gradients have been identified as factors of ozone exposure. Boundary layer effects at higher elevation can considerably reduce diurnal variability in ozone exposure (notably, commercial forestry and crop production occur at lower elevation). Diurnal variability may also be lower in rural and high elevation areas due to the absence of NO_x scavenging (i.e., urban areas have lower nighttime ozone levels because NO_x production continues overnight and ozone is consumed by reacting with NO).

FIGURE 8 Ozone uptake from the atmosphere. From EPA, 2006.



in plants and produces various organic compounds, oxidizers, and free radicals. These products can destroy cell proteins and membranes and lead to impaired cell functioning and death. Certain antioxidant compounds in plants (such as ascorbic acid) can protect cells from ozone-induced oxidative damage, although the exact biochemical processes involved are not yet completely understood (Fuhrer & Booker, 2003; Krupa et al., 2000).

Ozone naturally occurs at low concentrations due to trace gases and VOCs generated by ecosystem processes (April-May maximum is ~40 parts per billion or ppb), and plants are capable of detoxifying small amounts of ozone.[8] When exposure to elevated concentrations of ozone triggers plant detoxification mechanisms, plants redirect resources to ozone detoxification (away from other plant processes); if detoxification is overwhelmed plants may experience chlorosis or early senescence (Winner, 1994). At the individual level, ozone injury translates into reduced growth (of primary concern in agroecosystems) and competitive ability.

A long history of ozone research in California has demonstrated that some species are resistant to ozone injury, that water availability is an important factor affecting whether ozone injury induces growth reductions, and that enhanced growth from nitrogen deposition may be offsetting ozone responses (Takemoto et al., 2001). A recent review on ozone effects on trees and crops (Felzer et al., 2007) drew similar conclusions for forests, but found less of a compensation effect for managed ecosystems with significant nitrogen fertilization. Further, models developed by Ollinger and colleagues (2002) suggest that, over the last several decades, higher productivity caused by increases in carbon dioxide and nitrogen in forests of the northeastern U.S. is offset by ozone effects. At the species or community levels, ozone

8. Project advisors noted that when plants allocate energy to ozone detoxification, more energy is used to protect above-ground plant material, resulting in less root growth than shoot growth. Work by McLaughlin et al. (2007) highlights decreased growth and increased water use of mature forest trees under episodically high ambient ozone concentrations.

exposure (as well as other factors) can also affect species fitness or reproduction, and consequently plant community structure and biodiversity. Long term trends at sites in the San Bernardino Mountains show that tree species' differential responses to ozone exposure and nitrogen deposition may lead to shifts in forest species composition. Ozone tolerant white fir and incense cedar are replacing ponderosa pines and leading to overall increases in stand density at highly polluted sites, while low pollution sites appear undisturbed (Arbaugh et al., 2003).

Kohut (2007) proposes a "triad concept of injury" for describing how ozone impacts vegetation. He argues that, first, the species must be "genetically predisposed to be sensitive to ozone" (p. 3). Genetic differences between and within species can lead to different ozone flux rates (i.e., the rate of entry of the pollutant into the plant) and detoxification capacities. Studies of ozone impacts using different clones or cultivars of the same species (e.g. Burkey et al., 2005; Heagle et al., 2003; Morgan et al., 2006) have shown that genetic variation indeed plays a key role in ozone sensitivity, and a recent analysis of foliar injury in soybean cultivars highlights priority candidates for additional genetic screening in order to identify those cultivars that are most likely to be resistant to foliar injury (Burkey & Carter, 2009).

The second element of Kohut's (2007) "triad of injury" is the level of exposure to ozone, that is, the concentration of ozone multiplied by the length of time the plant is exposed to it.[9] Vegetation is subjected to both *acute* and *chronic* levels of exposure. Acute exposure refers to relatively high concentrations of ozone over a short period, while chronic exposure denotes relatively low concentrations over the lifetime of the plant. Acute and chronic exposures may lead to different injury manifestations in vegetation (Krupa et al., 2000). In fact, at low concentrations of ozone, only species that retain their leaves or needles for several growth seasons may exhibit visible signs of injury (Campbell et al., 2000). Ozone concentration also varies with the season and the time of day—an important consideration in devising ozone injury studies (Grulke, 2003).

Finally, Kohut's (2007) model points to the *environmental conditions* that influence ozone uptake. For example, temperature, light, and humidity conditions that favor photosynthesis also lead to increased gas exchange rates and therefore to increased ozone intake. The relationship between ozone uptake and stomatal aperture has been demonstrated both under controlled conditions and in field studies and has yielded conflicting results (e.g., Mansfield et al., 1993; Reich, 1987; Tjoelker et al, 1995). Available light (Chappelka et al., 2003; Schaub et al., 2005) and soil moisture (Musselman et al., 2006; Samuelson & Kelly, 2001) have been shown to influence the amount and severity of ozone injury, as have been wind speed and various other environmental conditions (Chappelka & Samuelson, 1998; Percy et al., 2007). The EPA (2006) has concluded that "many biotic and abiotic factors, including insects, pathogens, root microbes and fungi, temperature, water and nutrient availability, and other air pollutants, as well as elevated CO_2, influence or alter the plant's response to ozone," (p. E-25) although the current state of knowledge does not allow quantification of these influences. A recent study by Booker et al. (2009) suggests that future climate change will require that plant breeding incorporate ozone sensitivity into selection strategies.

It is important to consider some concerns in ozone research design that may affect the design of indicators for assessing the response of vegetation to ozone. Broadly speaking, ozone impact research has progressed over the last fifty years from laboratory-based studies using seedlings and young plants to field-based studies of mature specimens grown under ambient conditions. While exceptions to this rule abound, and laboratory-based studies continue to offer insights into exposure-response relationships, reviews of ozone metrics development underscore that early studies relied almost exclusively on "different forms of chambers inside growth rooms, laboratories, or greenhouses" (Karnosky et al., 2007, p. 495). The EPA (2006) declares that, "in spite of providing little resemblance to real-world conditions," these types of studies "yielded much of the basic information on the visible and physiological effects" of ozone on plants (p. AX9-3).

Currently, most chamber-based studies employ open-top designs set in the field (Open Top Chambers, or OTCs). Many variations of the OTC method exist, but a typical enclosure measures nine feet in both diameter and height. Many OTCs include mechanisms for controlling the amounts of ozone, humidity, or carbon dioxide present in the enclosure. OTCs have been "extremely valuable in studies of ozone effects on physiological processes and on growth and productivity," (Karnosky et al., 2007, p. 496). However, OTCs create microclimates that are often different from what is found under ambient conditions. These "chamber-effects" can lead not only to "unrealistic exposure" dynamics (EPA, 2006, p.AX9-5), but also to distorted flux rates in mixed-plant studies, due to unintended effects on inter-species competition (Nussbaum & Fuhrer, 2000).

The last twenty years have witnessed major advances in devising research designs that deliver reliable concentrations

9. Note that other factors such as plant growth stage, length of seasonal exposure where stress is greater than repair, and plant growth conditions (e.g. wet versus dry) complicate the second element of Kohut's model.

of ozone to plants grown under ambient conditions. Modeled after free-air carbon dioxide exposure (FACE) systems that disperse gases in the air surrounding the plants based on meteorological conditions, these studies seek to overcome the limitations of chamber-based research and reach biologically-relevant conclusions about the impact of ozone. Two U.S. FACE sites that collect information on ozone exposure include AspenFACE in Rhinelander, WI, and SoyFACE in Illinois. Assessing the merits of OTC and FACE-derived research, the EPA (2006) concluded that,

> There is still little experimental evidence that allows a direct comparison of OTCs to the free-air plume systems or a determination of the degree to which chamber effects alter plant response to ozone. The evidence that is available suggests that chamber effects do not fundamentally alter the response of plants to ozone; therefore, chambers remain a useful tool for testing species sensitivity and developing ozone-response relationships. (p. AX9-12)

While FACE experiments are useful, they do not perfectly mimic processes in natural settings. Generally speaking, the more one moves away from controlled settings to ambient conditions, the less one is able to establish cause-effect relationships (NRC, 2004). There remains a need to explore new methods for more ecologically-relevant studies of ozone effects under ambient conditions.

Apart from physical setting, ecophysiological research on the impact of ozone has also varied with the reliance on seedlings versus mature plant specimens. Most ozone impact studies have employed seedlings, but the use of mature trees has gained increased traction over the last twenty years.[10] The distinction is important because the existing literature suggests that ozone uptake and ozone effects are not necessarily equivalent in seedlings and mature trees (EPA, 2006; Samuelson & Kelly, 2001). For example, a meta-study of ozone impact studies found that "stomatal aperture limits ozone uptake into leaves more for mature than juvenile trees because of greater resistance to water transport in larger trees" (Kolb & Matyssek, 2001, p. 378). While the use of seedlings allows one to examine exposure-response relationships more easily than by using mature individuals, Schaub et al. (2005) cautions against a ready reliance on data collected in this manner for modeling the effects of ozone at the forest level: "To assess the sensitivity of canopy trees to ozone and to validate the principles found from seedling studies, it is important to take into account the diverse microclimatic conditions as they occur in a natural heterogeneous forest stand" (p. 565).

Few studies have incorporated both seedlings and mature specimens in their designs. Samuelson and Kelly's (2001) comparative study of 30-year-old and 2-year-old trees of the same species provides a welcome exception. Their conclusion, that "studies of potted seedlings may underestimate ozone uptake by large hardwood trees and overestimate ozone uptake by large coniferous species" (p. 36) provides further evidence of the importance of the limitations and trade-offs between various ozone metrics development designs. Large-scale studies (above the plot/FACE scale) may have been conducted but were not assessed in this project. Further evaluation of such studies would provide information on the utility of the indicators recommended below.

Foliar Injury Indicators

Often, plants respond to ozone by developing typical foliar injury symptoms. Ozone-caused injury can manifest itself in various ways that are visible to the naked eye. Some of the most common types of injury in broadleaf plants are:

- Upper leaf surface interveinal stipple – discoloration that occurs between the leaf veins; it usually appears as red or brown spots;
- Chlorosis – loss of chlorophyll that manifests itself as non-green pigmentation in discrete patches on the leaf;
- Flecking – tan, brown, or black areas on the upper surface of the leaf that result from the death of certain cells in the plant;
- Bifacial necrosis – dead areas on both sides of the leaf; and
- Accelerated senescence – premature loss of leaves, flowers, or fruit.

In conifers, one can observe:

- Tipburn – dead tissue (usually red or brown) spreading from the tip of needles downwards;
- Chlorotic mottle – discrete patches of yellow tissue on needles; and
- Accelerated senescence.

10. The distinction between "seedling" and "mature" trees can vary depending on the species of interest, but is generally based on response to their environment, biological properties, influence on soil and microclimate, and participation in total yield for a set of individuals, as opposed to a plant's chronological age; see Rabotnov (1969) for further information.

Assessing the extent and severity of ozone-induced foliar injury does not allow one to quantify the levels of ozone in the atmosphere, but it can help in determining how significant those levels are to the plants themselves (Smith et al., 2003). *Biomonitoring*—the use of indicator plants to establish the air quality in a given environment—addresses "the complexities of exposure-plant response relationships as influenced by exposure characteristics (e.g., turbulence), plant properties (e.g., stage of development), and external growth conditions," (Coulston et al., 2004, p. 71). Biomonitoring relies on the plants themselves to integrate the various factors that influence the impact of ozone. Therefore, this methodology can lead to biologically- and ecologically-relevant findings (Manning, 2003).

Not all plants that experience foliar injury will experience growth or yield reductions (Felzer et al., 2007). Indicator plants employed in biomonitoring efforts need to meet certain requirements: they have to occur across a variety of sites, they need to be easily identifiable in the field, they need to be proven ozone-sensitive species (based on previous field and laboratory research), they need to respond to ozone in manner that is readily diagnosed, and they need to exhibit genetic stability (Chappelka & Samuelson, 1998; Kohut, 2007; Smith et al., 2003; Smith et al., 2007). There is, by now, an extensive literature on species suitable for use as bioindicators. Both broadleaf species (e.g. blackberry, black cherry, common milkweed, trembling aspen, yellow poplar) and conifers (e.g. Ponderosa and Jeffery pines) are represented in this literature. Other potential bioindicators continue to be identified (e.g. swamp milkweed in Orendovici et al., 2003).

There are several biotic and abiotic stressors, apart from ozone, that produce the same kinds of injuries.[11] Therefore, researchers conducting biomonitoring studies in the field need to be aware of other factors—such as drought or pests—potentially impacting the bioindicator species. Addressing these potentially confounding factors, Kohut (2007) concludes that,

> Diagnosis of foliar injury is to a great extent an art that reflects the scientific, analytical, and deductive abilities of the individual conducting the assessment, as well as their inherent philosophy toward decision making. The approach each individual adopts in making a diagnosis reflects their willingness or reluctance to identify markings as being caused by ozone. These differences among individuals speak to the importance of having consistency in the evaluator(s) for a field program. (p. 10)

Quality control protocols such as field audits and remeasurement activities can help strengthen the validity and reliability of biomonitoring studies.

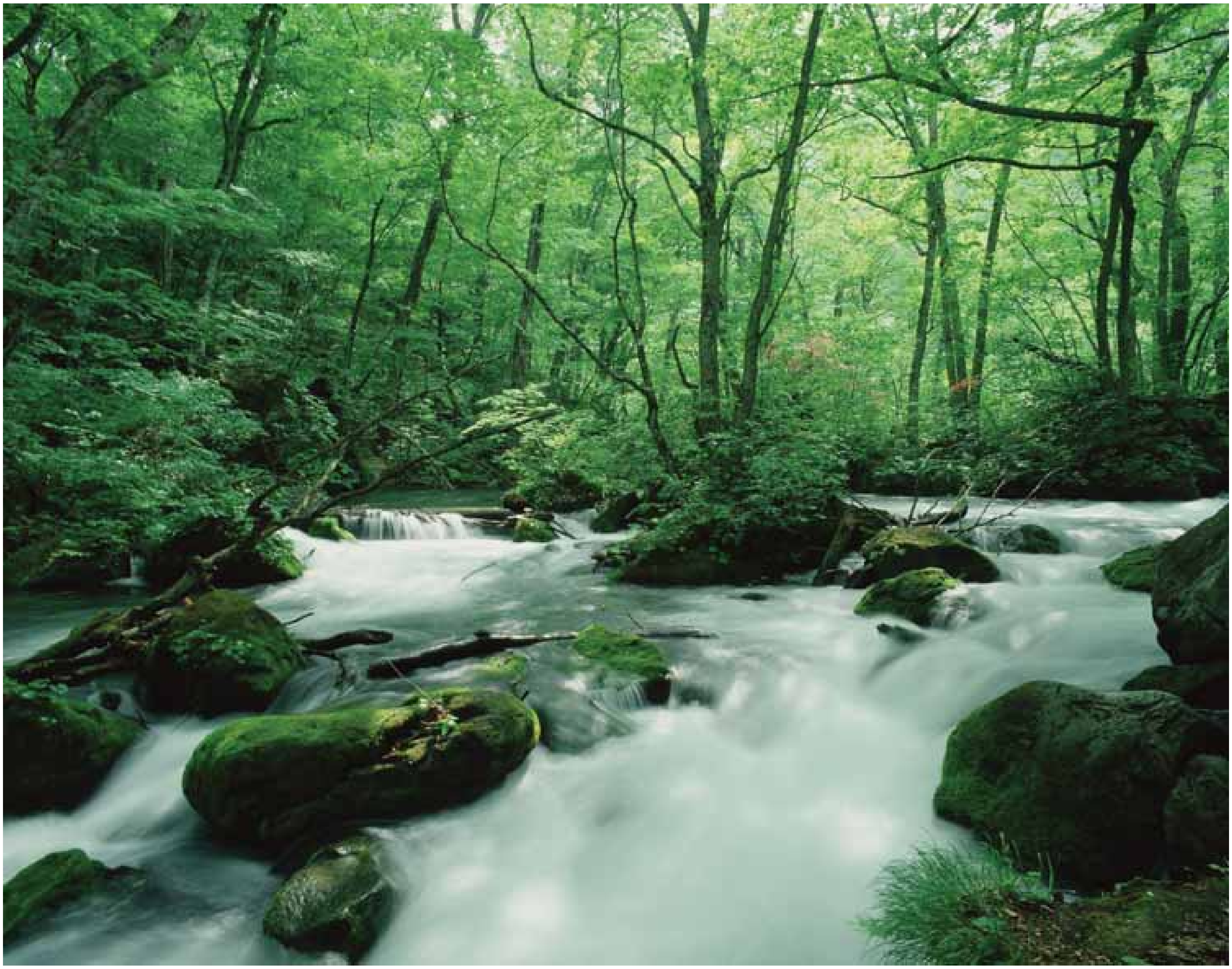
Ozone *exposure* refers to ambient concentrations of tropospheric ozone, and ozone *dose* refers to the amount of ozone that actually affects vegetation. The primary National Ambient Air Quality Standards (NAAQS), outlined by the Environmental Protection Agency, track exposure based on *peak concentrations* of ozone. While the primary NAAQS are focused on human health, some researchers have documented correlations between peak ozone concentrations and ecological effects. For example, Percy et al. (2007) found that growth of trembling aspen was related to the fourth-highest daily maximum 8-hour average O_3 concentration during the growing season. *Cumulative exposure* indicators report the sum of ambient concentrations occurring over time. In their evaluation of exposure- and flux-based ozone indices, Musselman et al. (2006) concluded that, while exposure indices do not fully account for the range of processes controlling ozone uptake by and reactions within leaves, they are preferable to flux-based indices which are challenged by uncertainty in quantifying plant defense mechanisms.

A single preferred indicator metric for ozone exposure has not come into wide use,[12] but the pool of potential indicators is small. The SUM06, W126 and AOT40 cumulative exposure indices use different methods for weighting the duration of exposure and concentration of ozone, but are constructed to return higher index values for ozone concentrations more likely to damage vegetation (Mauzerall & Wang, 2001). The SUM06 cumulative index ignores concentrations below the threshold of 60 parts per billion (ppb) under the assumption that little or no plant damage is expected at those concentrations, however this will vary by plant type and other factors. Similarly, the AOT40 relies on a threshold of 40 ppb. The W126 cumulative index does not exclude low concentrations entirely, but does reduce their impact on the index value through use of a sigmoidal weighting scheme. (See technical notes for additional description.)

Even under constant ambient concentrations, the amount of ozone actually affecting vegetation is variable, in part due to plants' ability to avoid uptake by the closing of leaf stomates.

11. Project advisors noted that in addition to a number of biotic and abiotic factors, ozone and other air pollutants have been shown to stress southern pine trees and increase susceptibility to bark beetles and also to root rot in California.

12. Notably, the Federal Land Managers' Air Quality Related Values Workgroup (FLAG) has recommended using W126 and the number of hours with ≥100 ppb ozone, based on a 24-hour, seasonal period of measurement, to describe ozone exposure (FLAG, 2000).



The CFO index is an ozone dose index that reports the total amount of ozone moving through stomates into a leaf's interior over time (Mauzerall & Wang, 2001). Ozone dose quantifications combine ambient concentration data with other factors controlling ozone impacts on plants, but the models used to estimate ozone doses require improvement (Musselman et al., 2006).[13]

In order to provide an indication of the impacts from ambient ozone exposure, some biomonitoring studies have employed a *biosite index* based on site-specific values for the proportion of leaves with ozone injury symptoms and the severity of those symptoms (e.g. Coulston et al., 2003; Coulston et al., 2004; Smith et al., 2003). Biosite index values are often grouped into four categories—little or no foliar injury, low foliar injury, moderate foliar injury, and severe foliar injury—to indicate the potential site-level risk associated with ozone exposure. Relationships between biosite indices and exposure-based metrics can be documented in some regions of the country, as Smith et al. (2003) suggest.

Dose-response relationships using foliar injury metrics were also explored by Arbaugh et al. (1998) in their examination of cumulative ozone exposure and Forest Pest Management Index data (based on assessment of ozone injury to conifers' most recent whorl of needles) as well as Ozone Injury Index data (based on assessments of visible injury, senescence, crown reduction, and needle lengths). And Yuska et al. (2003) found a significant correlation between injury to common milkweed and black cherry, on the one hand, and cumulative ozone concentrations, on the other hand, in Pennsylvania, although adding soil moisture levels data to the equation complicated the picture. (To address the influence of such confounding factors, Brace et al. (1999) recommend that researchers 1) design multi-year studies; 2) catalog the potentially

13. Project advisors noted that the ability of plants to recover from ozone impacts is reduced by multiple sequential high ozone years.

confounding factors; and 3) reproduce the observed injury symptoms under controlled conditions.)

Ozone-induced foliar symptoms in wild plants have also been documented in controlled experiments. For example, Orendovici et al. (2003) exposed several North American and European species (herbaceous and non-herbaceous) to various ozone concentrations in fumigation chambers, and found "clear exposure-response relationships between increasing ozone exposure and an increasing evidence and severity of foliar symptoms" (p. 34-35). In field specimens, Bergmann et al. (1999) argue that foliar injury remains the most reliable way of determining phytotoxic ozone levels, even while recognizing difficulties associated with the presence of confounding factors (on this last point, also see Davison and Barnes, 1998). Similarly, Chappelka et al. (2003) recognize the potential of foliar injury metrics for ozone-related research using wild plants in the field, while pointing out the vast differences in symptom development due to "elevation, microclimate, and/or genetic variability" (p. 58). Davis and Chappelka (2006) found a significant relationship between ozone-induced symptoms, moisture, wild plant species in the field, and various ozone indices.

Foliar injury metrics have also been employed extensively in crop research. Crops respond to ozone exposure by developing many of the same symptoms as trees: stipple, flecking, mottle, necrosis. While most ozone-related crop research has focused on growth and yield impacts, studies on both sides of the Atlantic have looked at the foliar injury symptoms (quantified in terms of severity and extent) triggered by ozone, in both OTC and ambient air conditions. For example, Heagle and colleagues have examined relationships between controlled ozone and carbon dioxide doses and foliar injury (as well as growth and yield effects) in potato (2003), snap bean (2002), and winter wheat (2000). In Europe, a United Nations program on the effects of air pollution on non-woody plants found ozone injury signs on a range of crops, throughout the continent and in both experimental and field settings (Benton et al., 2000; see Vandermeiren et al., 2005, for a more recent, but equally expansive, study of the effects of ozone on potato).

Rationale for Indicator Selection

Several confounding factors influence the extent and degree of foliar injury that results from ozone exposure:

- Genetics. Presence of ozone-sensitive plant species.
- Ozone exposure. Acute and/or chronic exposure to elevated ambient ozone levels. (Note: the most rapid responses to changes in ambient ozone concentration may be anticipated in ecosystems with high or continuous exposure levels.)
- Environmental conditions. Factors of ozone uptake including temperature, light, humidity, soil moisture, and nutrient availability (especially nitrogen). Presence of other constituents of ambient air such as CO_2 and SO_2. Presence of insects/pathogens.
- Plant age. Pre-dominance of seedlings vs. mature plants.

Assessing the extent and severity of ozone-induced foliar injury can help to determine how significant those levels are to the plants themselves, leading to more ecologically-relevant findings. To produce a foliar injury metric that is sensitive to changes in ozone levels over management-relevant timeframes, yet also relates to the majority of affected ecosystems, this report recommends stratification by site characteristics relevant to vegetation response. Project advisors identified level of ozone exposure and plant-available moisture as the two most important factors for ozone-induced foliar injury in U.S. forest systems. Plants that experience significant water limitations may be expected to exhibit lower productivity due to water stress, but possibly lower ozone effects because plant stomata will restrict ozone uptake. Plot-level data for foliar injury will be stratified by relevant and available measurements for ozone exposure and plant-available moisture to parse out ozone-induced plant responses and control for the confounding factor of water availability. It is important that foliar injury data be screened for other confounding factors including other air contaminants and the presence of insects or pathogens.

Recommended Metric

Foliar Injury in Forests. This indicator will report biosite index values (BI) stratified by two parameters: ozone exposure and plant available moisture.

One of the largest initiatives to employ biomonitoring techniques using established protocols is the U.S. Forest Service's Ozone Biomonitoring Program within the National Forest Inventory and Analysis Program (FIA). One measure of ozone stress to plants used by the U.S. Forest Service is biosite index values (BI). Foliar injury is evaluated under ambient exposure in forests at sites where ozone-sensitive species are present. Some of the program's field observation variables are standardized nationally (e.g. scoring methodologies and number of species and plants included in the analysis) while others (e.g. site and plant selection) are tailored to specific regions of the country. Field data are verified by regional experts who screen samples for plant injury characteristics other than those typically caused by ozone (e.g., damage due to insects, pathogens, and weather); those data are discarded. See technical note for additional information.

A customized analysis was conducted for this project by the U.S. Forest Service to evaluate the sensitivity of alternative metrics and reporting category schemes to changes in ambient ozone for forest systems. Mean annual BI data from 1997 to 2007 were obtained and partitioned by year. Ozone exposure indices (SUM06, W126, and N100) were then appended to the raw data tables of foliar injury. County-level Palmer drought data were used to assign an average growing season drought statistic to each foliar injury biosite for each year of the study. Each biomonitoring site was assigned a 3-month seasonal (June, July, August) Palmer Z drought index to demonstrate the controlling effect that soil moisture stress during the growing season often has on the foliar injury response of ozone sensitive plants in natural systems. Traditional classification schemes for seasonal drought and air quality indices were used in this study along with specific published thresholds (see technical note, Table 6). To identify the best possible metrics, a variety of combinations of the listed drought and ozone exposure values were tested. Ninety-five percent confidence intervals were calculated, and groups of data within a given year were tested for significant differences by comparison of confidence intervals. The results were used to identify and chart the most responsive ozone indicator metric for foliar injury over the 1997 to 2007 time period, which was determined to be SUM06 (see Figure 9).

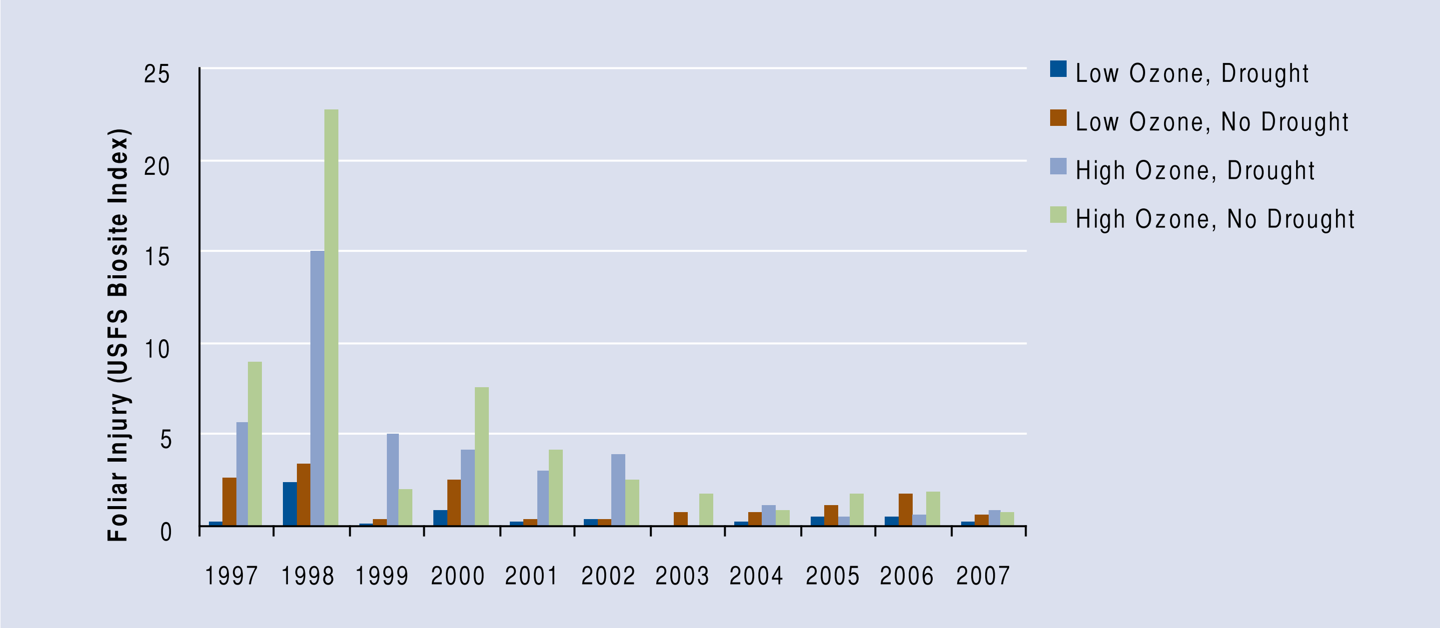
Data Limitations

There are several factors to consider when evaluating the utility of the datasets presented for this indicator.

Changes in sampling methodology have been made for the U.S. Forest Service's ozone biomonitoring program, although these changes have improved available data overall. From 1994 to 2001, BI data were collected on the same grid as the FIA tree plot data. In 2002, a new sampling grid designed specifically for ozone biomonitoring was implemented, thus improving flexibility in site selection and the quality of the BI sample (since ozone-sensitive species tend to be relatively small plants in open areas). Over the time period of this study (1997 to 2007) the number of sites generally increased every year as new states were added to the program. In 2005, full national coverage was lost as the Intermountain West dropped out of the biomonitoring program after seven consecutive years of finding no injury. In addition, evaluation of foliar injury is a subjective task, although the data collection methodology builds in a secondary evaluation of ozone injury reports (see technical note). Also, plant available moisture is quite variable among different plant types. Finally, it should be noted that ozone effects on plants may occur prior to the observation of injury.

The Palmer indices were developed for cropped systems, and therefore it may be appropriate to develop and test different moisture indices that better define moisture conditions specifically for natural systems. Ongoing work by the U.S. Forest Service may yield a more fine-scale index that could be used in the future.

FIGURE 9 Foliar Injury (Biosite Index). Analysis performed by the U.S. Forest Service. Low ozone = SUM06 ≤12 ppm hr; high ozone = SUM06 >12 ppm hr. Drought = Palmer Z ≤-0.8; no drought = Palmer Z >-0.8. BI values: 0 to <5 = little or no foliar injury; 5 to <15 = light to moderate foliar injury; 15 to <25 = moderate to severe foliar injury; ≥25: severe foliar injury



As the data above suggest, foliar injury was significantly increased by high ozone exposure conditions (seasonal mean SUM06 >12 ppm-hr), less so when drought conditions prevailed. These results were remarkably consistent over time (1997, 1998, 2000, 2001, 2003, 2005, 2006) although high ozone exposures sometimes masked the drought effect (1999, 2002, 2004, 2007). Similar results were obtained with W126 threshold values of 15 ppm-hr and N100 <1. However, there was little flexibility around these metrics suggesting a certain lack of stability in the response indicator. Injury conditions in 1998, for example, are clearly different than in any other year and are followed by a persistent downward trend in foliar injury such that the majority of BI values are at, or near zero. This is attributed to a combination of declining ozone exposures and persistent drought in certain high ozone regions of the U.S. The index formulation averages a range of response from a variety of ozone-sensitive plants, therefore tending to average out and possibly mask the more severe injury responses of individual plants or species for any given site or year. In addition, there is considerable variability in natural systems, such as differences in genotype, sensitivity to drought, and site microconditions. For the purpose of this indicator development project, and the policy directive to protect the most sensitive population from ozone exposure, it may be necessary to magnify the foliar injury signal by using the biosite index associated with the most injured species at each biomonitoring site. These data are available from the USFS biomonitoring data base and should be tested. Evaluating a more complex ozone exposure statistic that combines SUM06 and N100, or W126 and N100 is also recommended.

Indicators of Change in Plant Growth and Yield

Agricultural and natural resource managers are often more interested in the effects of ozone on plant growth and/or yield rather than foliar injury in itself. However, it is worth noting that "there is no consistent relationship" between ozone-induced visible injury and growth impacts; "a tree species ranked as ozone sensitive based on foliar response may exhibit no measurable adverse effect on growth-related processes," (Coulston et al., 2003, p. 125). However, certain species do exhibit clear relations between visible injury and growth (e.g. eastern white pine, cf. Chappelka & Samuelson, 1998) or injury and yield (e.g. white clover and snap bean, cf. Burkey et al., 2005). In addition, plants may use strategies to overcome ozone stress, such as compensation of growth by increased energy assimilation and allocation among organs, or self repair.

Due to their economic importance, crops are by far the most widely used plant species in research on the growth and yield impacts of ozone. Common growth metrics include: plant height and basal diameter, leaf number per plant, leaf area, and dry weight of seed pods, stems, leaves, or roots. Commonly used yield metrics include number and weight of tubers or seeds (total or individual). As Davison and Barnes (1998) argue, "the choice of measure can influence both the apparent magnitude of the ozone response and the relative ranking" of ozone-sensitive species (p. 137). And research has shown that, when exposed to increased ozone levels, some crop cultivars are able to maintain yield levels at the cost of leaf growth (Christ et al., 2006), further underscoring the importance of clarifying management goals prior to selecting the ozone impact metric of interest.

In order to estimate the effects of ozone exposure on crop production, the EPA-funded National Crop Loss Assessment Network (NCLAN) coordinated a relatively large number of chamber-based studies of growth/yield effects of ozone during the 1980s. Ozone-induced reductions in yield of major U.S. crops that impacted the national economy were found through NCLAN studies (Adams et al., 1986; Heck et al., 1998; Westenbarger & Frisvold, 1995). An often-cited meta-study of the NCLAN program revealed "a large disparity in the number of successful experiments for different crops and a wide range of estimated losses for different crops. A rather wide range of estimated losses often occurred for a given crop when more than one experiment was performed," (Heagle, 1989, p. 411).

Data from NCLAN and additional experiments (e.g., Heck et al., 1998) are still widely used to estimate reductions in primary productivity and carbon storage. In most assessments, empirical exposure-response curves for ozone effects on crops are still predominately based on NCLAN data, now two decades old (NRC, 2004). There is no indication that ozone impacts have become less important since the NCLAN assessment, although bioengineering of ozone tolerant crops may provide protection against yield reductions or changes in quality in the future (Fuhrer & Booker, 2003).

A more recent meta-study of the impacts of ozone on soybean, conducted for the purpose of quantifying the crop's response to the pollutant, concluded that "even a mild, chronic elevation of ozone (40-60 parts per billion) is sufficient to produce significant losses of photosynthesis, biomass and seed yield of approximately 10% in soybean" (Morgan et al., 2003, p. 1324), although response did vary "widely" between studies. There is some evidence, originating from recent studies using Free Air CO_2 Enrichment (FACE) technologies, that yield losses may be even greater under ambient conditions than predicted by previous chamber-based studies (Morgan et al., 2006). FACE-based research using trembling aspen has also concluded that an increase in ozone levels leads to negative growth effects, and has attempted to sort out the interactive effects of ozone and carbon dioxide (Isebrands et al., 2001) and ozone and meteorological conditions (Percy et al., 2007).

As with foliar injury studies, the literature suggests that soil moisture should be controlled when examining growth and productivity effects under forest conditions (Schaub et al., 2003). Using two models, TREGRO and ZELIG, Weinstein et al. (2005) predicted long-term effects of high ozone concentrations on individual tree physiology and competitive interactions within forest communities. Model outcomes suggested decline of ponderosa pine relative to white fir, although effects varied across simulated sites (based on differences in current exposure levels) and were predicted to decline in magnitude under conditions of chronic reduced moisture availability.

An analysis of ozone impacts on ecosystem function at a national scale, including agricultural and non-agricultural ecosystems, estimated a 2.6 to 6.8% reduction in annual net primary productivity (NPP) between 1950 and 1995, depending on agricultural management and land use assumptions (Felzer et al., 2004). Recent work by Sitch et al. (2007) finds that ozone-induced reduction of plant productivity may offset the carbon dioxide 'fertilization effect' leading to net reduction in terrestrial carbon storage. Indicators of ozone effects that relate to whole ecosystem functioning (e.g. biomass, NPP, carbon storage) necessarily integrate multiple stresses and can be challenging to interpret[14], although models predicting functional responses to specific stresses may be advanced enough to report whole

14. For example, elevated carbon dioxide can directly stimulate production and increase in water use efficiency in plants (Huang et al., 2007; McCarthy et al, 2007),

ecosystem level indicators of air quality. Karnosky et al. (2007) point to the challenge of characterizing landscape- and regional-scale ozone effects. The level of uncertainty associated with ozone-induced reductions in growth for forest tree species can be constrained by focusing on individual species with well established exposure-response curves generated from field exposure experiments (Hogsett et al., 1997). However, these empirical data are only available for seedlings.

RATIONALE FOR INDICATOR SELECTION

The metric evaluated for development as an indicator of the impacts of ozone on plant yield and growth was change in crop yield. As the literature cited above suggests, extensive research has been conducted on changes in yield in cropped systems, however several confounding factors influence the extent and degree of physiological impacts that result from ozone exposure:

- Ozone exposure. Acute and/or chronic exposure to elevated ambient ozone levels. The most rapid responses to changes in ambient ozone concentration would be anticipated in crop systems with high or continuous exposure levels.
- Environmental conditions. Factors of ozone uptake including temperature, light, humidity, soil moisture, and nutrient availability (especially nitrogen). Presence of other constituents of ambient air such as CO_2 and SO_2. Presence of insects/pathogens.
- Crop cultivar. Change in crop genetics over time may favor ozone-insensitive plants, inhibiting detection of ozone-related trends.

To produce a metric for physiological change that is sensitive to changes in ozone levels over management-relevant timeframes, yet also relates to the majority of affected systems, this report recommends stratification by site characteristics relevant to vegetation response. Project advisors identified level of ozone exposure and plant-available moisture as the two most important factors for ozone-induced change in crop systems in the U.S. Crops that experience significant water limitations may be expected to exhibit lower productivity due to water stress, but possibly lower ozone effects due to limited ozone uptake with drought-induced closure of stomates. Plot-level data for crop yield will be stratified by relevant and available measurements for ozone exposure to parse out ozone-induced crop responses and also will be screened for drought conditions (only for non-irrigated crops) to control for the confounding factor of water availability. Also, data should be screened for influences on crop growth such as pathogen or insect presence. Finally, data should be reported by crop type since some crops are more sensitive to ozone than others and have different growing seasons. Note that detection of interannual trends may be confounded by changes in crop plant cultivars that may affect sensitivity to ozone.

RECOMMENDED METRIC

Change in Growth/Yield in Cropped Systems. This indicator reports the mean national annual yield of crops (soybean, Upland cotton) that are known to be sensitive to ozone, stratified by ozone exposure. The indicator does not stratify by plant available moisture as crop irrigation practice was not found to influence ozone effect on yield for these crops.

The U.S. Forest Service was asked to evaluate the mean national annual yield of several ozone-sensitive crops (e.g., Durham wheat, Spring wheat, soybeans, Upland cotton, American Pima cotton, peanuts, or an orchard crop) under a range of cumulative ozone exposure index values (SUM06, W126, and AOT40) and irrigation conditions. Yield data were obtained from the National Agricultural Statistics Service, and are based on sample surveys from farmers (see technical note for additional detail). Only data for soybeans and Upland cotton were ultimately tested due to concerns regarding adequate sample size, although ideally other known ozone-sensitive crops would be reported. The national data for each of these two crops were partitioned by year and by irrigation practice. Because drought conditions were expected to decrease ozone impacts on non-irrigated crops, each county level yield statistic was assigned a 2-month seasonal (July, August) Palmer Z drought index to allow non-irrigated yield data from drought stressed sites (e.g., Palmer Z <-1.25) to be excluded from the analysis.

Once yield data were partitioned by irrigation practice (irrigated, non-irrigated with drought, non-irrigated without drought), ozone exposure data from three metrics (SUM06, W126, and AOT40) were applied. To identify the best possible ozone metric, multiple combinations of the drought and ozone values were tested based on published thresholds (see technical note for Foliar Injury in Forests, Table 6); intermediate values were also tested. When this stratification was performed, an ozone effect was noted for all three irrigation practices (with a few exceptions, e.g., data for the year 2004). Therefore, data from all irrigation practices (including yield data from non-irrigated, drought-stressed areas) were included in the final analysis.

For the final determination of the ozone metric for crop systems, irrigated and non-irrigated yields were combined for each year, and mean national annual yield values were computed in the three ozone categories (i.e., high, moderate,

FIGURE 10 Soybean yield at various ozone levels (irrigated, non-irrigated with drought, non-irrigated without drought). Analysis by the U.S. Forest Service. High ozone = SUM06 >20 ppm hr; moderate ozone = SUM06 >10 and ≤20 ppm hr; low ozone = SUM06 ≤10 ppm hr. Also see data table in technical note.

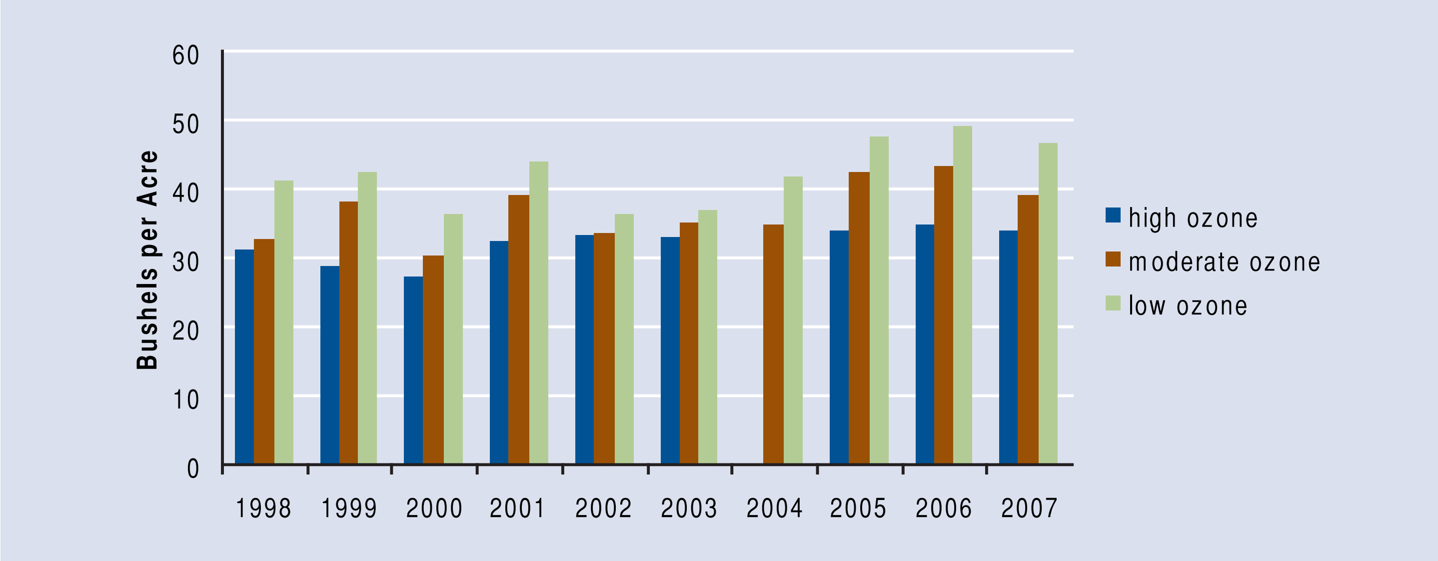
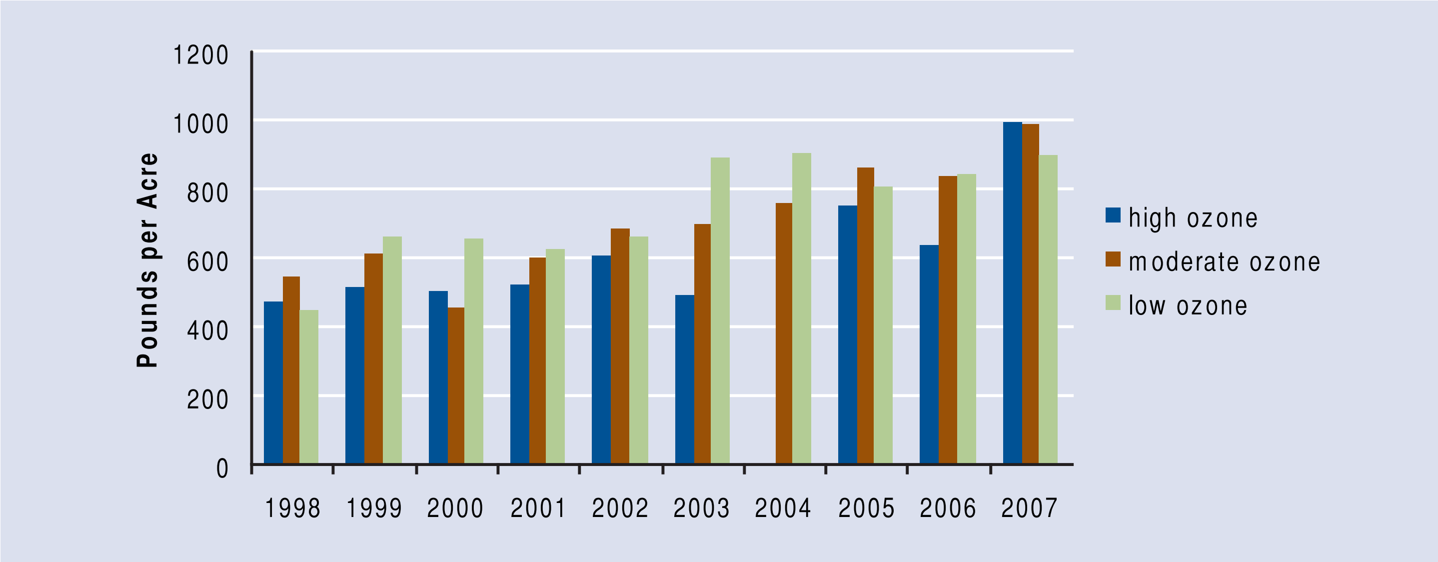


FIGURE 11 Upland cotton yield at various ozone levels (irrigated, non-irrigated with drought, non-irrigated without drought). Analysis by the U.S. Forest Service. High ozone = SUM06 >20 ppm hr; moderate ozone = SUM06 >10 and ≤20 ppm hr; low ozone = SUM06 ≤10 ppm hr. Also see data table in technical note.



and low ozone) and significance between categories was tested using a one-tailed t-test (see Table 7). The results were used to identify and chart the most responsive of the three ozone indicator metrics applied to crop yield over the 1998 to 2007 time period, which was determined to be SUM06 (see Figures 10 and 11).

Data Limitations

Figures 10 and 11 show ozone impacts on crop yield for both soybean and cotton. Over the time series shown, significantly greater yield was observed for crops that experienced ozone exposure of SUM06 ≤10 ppm-hr. A lower level of yield protection was also realized at SUM06 ≤20 ppm-hr. These results are in general agreement with previously reported ozone exposure thresholds (EPA, 2007), although they tend to support the need for a more stringent standard if a high level of crop yield protection is the policy goal.

For the purposes of testing the interactive effects of ozone exposure and plant available moisture, a limited set of data for only two ozone sensitive crops were evaluated and reported here. As irrigation practice did not demonstrate influence on the ozone effect on soybean and cotton yield, indicator reporting could be expanded to include yield data from all states reporting on these crops (see technical note).

The Palmer indices generally have several limitations. Values do not take into account other water sources besides precipitation (e.g., snow packs), so the index doesn't reflect drought conditions as effectively in mountainous areas. Also, the index may lag emerging droughts by several months. Finally, the Palmer indices are "physical" in that they rely on temperature and precipitation values, and do not account for drought as an ecosystem property.

A number of temporal and geographical limitations may have caused the unexpectedly significant response of drought-affected, non-irrigated crop yields to ozone. High ozone exposure may have occurred during wet periods, or may not have been captured by the cumulative ozone index. As well, interpolation of county-level ozone data may be based on monitors that are too far from a site. Yield data at the county level should be excluded if the ozone interpolation is questionable.

In addition, other considerations include sample size (which caused data from a number of ozone-sensitive crops to be excluded from the analysis) and the additive nature of ozone effects over time. And ideally, other indices of drought could be tested (e.g. weekly data may be more useful than the Palmer Z index, which is a monthly index value).

Research Needs

The following ecological effects of ozone were considered for indicator development, however it was determined that further scientific investigation is needed, based on literature review and consultation with project advisors. In the future, as research continues, it may be possible to develop a population and community-level indicator of ozone's ecological effects as well as a plant physiology metric based on remote sensing data to complement the indicator metrics recommended above.

Changes in Species Composition

Biotic indicators at the population and community level are rarely employed as air quality indicators. Ozone exposure-response curves have been developed for some forest plant species and models have predicted relative decline in ozone-sensitive species in forests with high ozone exposure. However, confounding factors (e.g., moisture availability) inhibit detection of plant species shift in response to ozone.

Forest tree species composition. Project advisors recommended scanning Forest Inventory and Analysis (FIA) data for long-term patterns of decline of ozone-sensitive tree species (e.g., black cherry, white ash) and investigating corroborating evidence of effects of chronic elevated background ozone levels on plant communities. This approach would look for correlation between spatial patterns of peak or cumulative ozone exposure and spatial patterns of decline in ozone-sensitive species (based on established databases of species sensitivity). Note that it would be necessary to parse out confounding factors such as temperature, moisture, fire and pest outbreaks. The U.S. Forest Service is exploring the spatial correlation between ozone exposure and decline in ozone-sensitive species, and these data may be available in the future. Spatial change analysis for ozone-sensitive tree species will be conducted for two time points (approximately 1991 and 2003) to be qualitatively compared to a spatially-interpolated cumulative ozone exposure metric, W126 (for 2000-2005), to detect correspondence between areas with elevated ozone exposure and reduced tree growth. Some challenges for this work include: (1) The W126 data layer represents interpolated estimates and the spatial resolution of tree and ozone datasets are offset; (2) FIA reporting dates vary by state and have to be interpolated; and (3) FIA data are not screened for confounding factors of tree mortality (e.g. harvest, pest/pathogens, or drought).

Lichen community composition. Epiphytic lichen community composition is an example of a potential indicator that does respond predictably to air pollution. Epiphytic lichens are particularly sensitive to air quality effects because they obtain all their nutrients directly from the air and lack the protective cuticle covering plant leaves. Lichen species richness has been shown to be depressed by ozone exposure as well as nitrogen and sulfur deposition in the southeast, the northeast, the Colorado front range, southern California and the Pacific Northwest (Fenn et al., 2003; McCune, 2000; Nash & Sigal, 1999). Jovan and McCune (2005) found gradients in lichen community data corresponding to ambient levels of ozone and other air pollutants, but were unable to determine whether primary stressors were climate, air pollution or both. Ozone-induced effects on lichen have been primarily documented areas with high peak ozone exposure (NPS, 2003). Lichens, apart from their own conservation value, play a role in mineral cycling and soil fertility and also provide forage for insects, birds and some mammals. The degree to which pollution-tolerant species are replacing pollution sensitive species, preventing an overall decline of lichen abundance, is not documented, although current research by the U.S. Forest Service Forest Inventory and Analysis Program should provide these data.

Remotely Sensed Changes in Plant Physiology

The use of remote sensing data to detect patterns of ozone effects on plant chlorophyll levels and water use efficiency (an organism-level phenomenon that can be amplified to larger scale) has considerable potential for tracking the ecological effects of chronic elevated ozone levels. There is a growing body of research in this area, however, at this time, it appears that the technical measurement capability and data systems are not yet mature enough to support on-going, national-scale indicator reporting. For example, it has not been demonstrated that under ambient conditions the measured signals are specific to ozone and not other forms of stress. When fully developed, this approach represents a possible opportunity to factor out climatic effects (i.e., effect of moisture/temperature on stomata and gas exchange) and/or ambient CO_2 concentrations from ozone exposure effects.

Remote measurements of fluorescence and reflectance signatures (by airborne and satellite sensors) have been associated with changes in plant physiology (e.g., photosynthesis efficiency, foliar chlorophyll). Ecosystem responses to increasing CO_2 concentrations can manifest in many different ways, depending on the current status of the ecosystem, from young to mature, open to closed canopy, or nutrient and water limitations. However, CO_2 impacts can be expressed via changes in energy-use-efficiency (EUE), water-use-efficiency (WUE) and nutrient use efficiency (NUE), all of which might find levels of co-limitation. Minor adjustments can occur through shifts in carbon allocation, height growth, root growth and leaf area among others. This is a property of complex systems (Buckley, 2008; Franklin, 2007). In recent years, studies have investigated the potential of remote sensing to synoptically detect vegetation stress, based on spectral signatures associated with altered foliar chemistry and structure (Meroni et al., 2007, 2008). Fluorescence emissions have been used to measure change in photosynthetic efficiency and broadband R has been used to measure change in foliar chlorophyll at the top of the canopy (but is of limited use for early detection of vegetation stress or estimation of vegetation changes unrelated to chlorophyll). In comparing spectral reflectance (R) and fluorescence (F) foliar measurement approaches, Campbell et al. (2007) concluded that hyperspectral (5-10 nm) R indices—thought to be better correlated with canopy green leaf area—were significantly better than F or broadband R at distinguishing among treatment levels, although unstressed vegetation conditions could not be identified. Meroni et al. (2007) demonstrated the utility of the Photochemical Reflectance Index (PRI) for detecting plant stress from ozone exposure. Another emerging technology with promise for remote detection of ozone injury signatures, FIREMAPPER, would use components of the visible spectrum and long-wave radiation to detect specific pigments modified by ozone exposure (Grulke, 2007).

Technical Notes

Foliar Injury in Forests

The data sources highlighted in this indicator include:

Biosite Index values (BI) from the U.S. Forest Service's Ozone Biomonitoring Program, National Forest Inventory and Analysis Program (FIA). Under the FIA Program's Phase 3 sampling, an assessment of visible foliar injury is made for known ozone-sensitive species (e.g. black cherry). BI values represent site-level composite assessments of the amount and severity of foliar injury for ozone-sensitive species found on the biomonitoring site. There are over 1130 sites across 45 states. Although they are considered part of the FIA Phase 3 program, the biomonitoring sites are on a different grid because they are selected for specific attributes (accessibility; optimal plant sampling conditions such as plant size, population size, and species). Each site is evaluated annually, between late July and early August (to maximize detection of injury, and for consistency). A total of 40-60 plants are assessed at each site, 30 plants of two selected bioindicator species, and another 10-30 plants from other bioindicator species. Injury symptoms observed in the field are validated by plant pathology experts via leaf samples collected by the field crew. Injury amount (proportion of leaves) and mean severity are used to calculate an index value, based on a modified Horsfall-Barratt scale with break points at 0, 6, 25, 50, 75 and 100. Values are split into four foliar injury categories, which are subjective but based on expert opinion:

Biosite Index value 0 to <5: little or no foliar injury
Biosite Index value 5 to <15: light to moderate foliar injury
Biosite Index value 15 to <25: moderate to severe foliar injury
Biosite Index value ≥25: severe foliar injury

For more information see Smith et al., 2007 and 2008.

The USFS ozone biomonitoring data were used to test and develop reporting categories for the foliar injury metric. In the national data set, the injury data are derived from a variety of plant types (woody and non-woody) over a range of natural site conditions that vary considerably in elevation, terrain, and aspect. Data from 1997 to 2007 were downloaded and BI values from 2003 to 2007 weighted by the area of the corresponding sampling polygon. Weighted and unweighted BI data were partitioned by year and then evaluated for mean annual BI at low and high ozone exposures and wet and dry conditions of soil moisture. Analyzing the data by region did not appreciably affect the results, nor did dropping large numbers of sites from the Interior region where zero injury values are the norm. Earlier work with the biomonitoring data has demonstrated that ozone-induced foliar injury is dependent not just on cumulative ozone exposures, but also on environmental factors that condition native plants to be more or less susceptible to injury and/or more or less able to repair injury once it has occurred. At the regional level, annual fluctuations in ozone exposure and soil moisture can be used to explain changes in foliar injury over time. In high ozone areas especially, foliar injury is significantly reduced under drought conditions (Smith et al., 2008).

Data Availability: See http://nrs.fs.fed.us/fia/topics/ozone for data access information and program contacts. Data may be downloaded at http://fiatools.fs.fed.us/fiadb-downloads/fiadb3.html.

Other Potential Resources: EPIC, an environmental indicator project at the California Environmental Protection Agency, uses an ozone indicator based on the percent of needle whorl loss for pine species—notably, data aggregation for this indicator was complicated by the use of two different indices, the Ozone Injury index and a Forest Pest Management index, to quantify ozone damage during surveys (see http://oehha.ca.gov/multimedia/epic/index.html for more information).

Palmer Z Index, National Climatic Data Center (NCDC), National Oceanic and Atmospheric Administration. This index is a measurement of short-term variance (monthly) between measured moisture conditions and normal values, factoring in temperature and rainfall amounts for a given location. Some indices are even shorter term (weekly) and others are longer (annual or multi-year) depending on the use of the index (for example, weekly information that reflect short-term changes in weather patterns may be more useful to farmers than monthly data). Values are calculated by formula, and are identified by the NCDC as:

- ≥3.50 = extremely wet
- 2.50 to 3.49 = very moist
- 1.00 to 2.49 = moderately moist
- -1.24 to 0.99 = mid-range
- -1.25 to -1.99 = moderate drought
- -2.00 to -2.74 = severe drought
- ≤-2.75 = extreme drought

Because rainfall and temperature data are collected in many locations across the U.S., the index can be applied widely. However, since the calculations do not reflect other sources of water, like snow packs, the index does not reflect drought conditions as effectively in mountainous areas. It is also best used for longer-term forecasts (see http://www.drought.noaa.gov/palmer.html/ for more information).
For the purposes of this analysis, all values describing a progression from dry to near normal to wet conditions were tested. As a result, "drought" conditions were categorized as ≤-0.8 on the Palmer Z index; "no drought" conditions were categorized as >-0.8 on the Palmer Z index.

Data Availability: See http://www.ncdc.noaa.gov/oa/climate/monitoring/drought/mw/ for data access information and program contacts.

SUM06, W126, and N100 Indices, U.S. Environmental Protection Agency. National data on ozone indices were obtained from the EPA Aerometric Information Retrieval System (AIRS). These indices reflect ambient ozone in the atmosphere, each calculated in a slightly different manner based on time of exposure and specific exposure thresholds. Hourly ozone data were used to interpolate an ozone exposure surface across the landscape and assign an average growing season (June, July, and August), 12-hr (0800 to 2000) ozone exposure statistic to each foliar injury biosite (and crop-yield county, see "Change in growth/yield in cropped systems," below) for each year of the study. It should be noted that monitoring sites for ozone previously considered as ex-urban or rural no longer fit that definition, as many urban centers have grown significantly in size over the last decade. Also, by choosing to parameterize exposure metrics as 12-hour rather than 24-hour, nighttime ozone effects are excluded.

SUM06 is defined as the sum of all hourly average concentrations ≥ 0.06 parts per million (ppm) in a given year. For this analysis, SUM06 is based on 12-hour days and 3-month growing seasons (June-August). It is therefore not optimized for ozone effects on sensitive plants specifically, nor for those that exhibit nighttime gas exchange. For the purposes of this analysis, low ozone = SUM06 ≤12 ppm-hr, high ozone = >12 ppm-hr.

W126 provides a sigmoidally weighted sum of all hourly average ozone concentrations, has no minimum ozone concentration threshold, and only lightly weights the lower ozone concentrations The W126 index tends to be highly correlated with the SUM06 index.

N100 equals the number of hourly average concentrations equal to or greater than 0.100 ppm.

The SUM06 and W126 exposure indices tend to describe chronic ozone exposure conditions while the N100 ozone exposure index tends to emphasize peak values that may play a large role in foliar injury development. Although each

TABLE 6 Threshold values used in this study to evaluate and identify useful reporting categories for foliar injury and crop yield data according to ozone exposure.

Ozone Exposure Thresholds:
All values describing a progression from relatively low to relatively high ozone concentrations were tested.

SUM06 ppm-hr		Key Reference:
≤10	8-12 ppm-hr protects natural ecosystems from foliar injury	*Heck and Cowling (1997)*
≤15	High level of crop yield loss protection	*EPA-452/R-07-003. January 2007: OAQPS Staff Paper.*
≤20	15-20 ppm-hr protects crops	*Heck and Cowling (1997)*
≤25	Low level of crop yield loss protection	*EPA-452/R-07-003. January 2007: OAQPS Staff Paper.*
W126 ppm-hr		**Key Reference:**
≤12	protects natural ecosystems from foliar injury	*Smith, March, 2009*
≤13	High level of crop yield loss protection	*EPA-452/R-07-003. January 2007: OAQPS Staff Paper.*
≤15	protects highly sensitive vegetation	*A.S.L. & Associates, Feb., 2009*
≤21	Low level of crop yield loss protection	*EPA-452/R-07-003. January 2007: OAQPS Staff Paper.*
N100 ppm-hr		**Key Reference:**
<1	protects highly sensitive vegetation	*A.S.L. & Associates, Feb., 2009*
<4	protects moderately sensitive vegetation	*A.S.L. & Associates, Feb., 2009*
<5	protects natural ecosystems from foliar injury	*Smith, March, 2009*
AOT40 ppm-hr		**Key Reference:**
≤3	European Union: to protect agricultural crops	*Paoletti and Manning (2007) Environmental Pollution 150: 85-95*
≤5	European Union: to protect forest trees	*Paoletti and Manning (2007) Environmental Pollution 150: 85-95*
≤9	European Union: to protect all types of vegetation	*Paoletti and Manning (2007) Environmental Pollution 150: 85-95*

exposure statistic may be used alone to describe an ozone season, it is generally true that a combination of SUM06, W126 (or AOT40 for "Change in growth/yield in cropped systems," see below) with the N100 statistic provides a more accurate characterization of the ambient ozone exposure environment for a given area or ground location. It is reasonable to assume that the greater the seasonal ozone exposure index, whether acute or chronic, the greater the ozone stress on ozone sensitive crops, trees, and native plants provided growing conditions are favorable for ozone flux, i.e., that the plant stomates are open. Injury thresholds for each of these exposure indices have been proposed in the peer-reviewed literature (Table 6).

Data Availability: See the EPA Aerometric Information Retrieval System (AIRS) (http://www.epa.gov/oar/data/) for data access information and program contacts.

The most responsive ozone indicator metric for foliar injury was detected when the national annual BI values were grouped into SUM06 ozone exposure and Palmer Z drought categories defined as follows:

- SUM06 ≤12 ppm-hr and Palmer Z >-0.8 = low ozone, no drought;
- SUM06 ≤12 ppm-hr and Palmer Z ≤-0.8 = low ozone, drought;
- SUM06 >12 ppm-hr and Palmer Z >-0.8 = high ozone, no drought;
- SUM06 >12 ppm-hr and Palmer Z ≤-0.8 = high ozone, no drought;

An analysis of foliar injury data from the North region (Smith, 2009) highlighted a complex relationship among injury, ozone exposure, and moisture conditions in natural systems. Examination of seasonal mean values for ozone exposure, foliar injury, and drought demonstrated a significant downward trend in ambient ozone exposures and foliar injury over the 10-year period from 1997 to 2006 most notably in high ozone areas such as the Mid-Atlantic and East North Central states. Foliar injury values were highest in 1997 and 1998, years when ambient ozone exposures were relatively high and soil moisture conditions were near normal to wet. In 1999, and again in 2002, foliar injury dropped significantly despite relatively high ozone exposures, a response that was clearly linked to widespread moisture deficits on the majority of biomonitoring sites in moderate and high ozone areas. Analysis of thresholds values for injury, ozone exposure, and drought over the 10 years, indicated that foliar injury was relatively high only if all of the following conditions were met: W126 >12 ppm-hr, N100 >5 hrs, and PDSI > -0.5 (PDSI = -0.5 is the soil moisture value that indicates an incipient dry spell). This information confirms the importance of the relationship among injury, ozone exposure, and drought for forest species and validates the similar threshold values used to identify the national ozone indicator metric for foliar injury in this study.

Change in Growth/Yield in Cropped Systems

The data sources highlighted in this indicator include:

Crop Yields from the National Agricultural Statistics Service, U.S. Department of Agriculture. National data on crop yield were obtained from the United States Department of Agriculture (USDA) National Agricultural Statistics Service (NASS). State offices collect and estimate crop yield data from sample surveys of farmers and their business associates (e.g. farm service agencies). NASS obtains the yield estimates, which are verified and analyzed on a national level but are also available by county or agricultural statistics districts (groups of counties within a state). Data are supplemented by information from the Census of Agriculture, which is carried out every five years.

Yield data can be partitioned by agricultural practice, thus the data are available for irrigated and non-irrigated crops, however country-level yield data reported by irrigation practice represent only a subset of the total yield data for each crop. As a result, data for apples, peaches, soybeans, Durham wheat, Other Spring wheat, Upland cotton, American Pima cotton, and Peanuts for nuts were excluded due to limited sample size. The two crops reporting the most data for irrigated and non-irrigated yields over the 10-year time period from 1998 to 2007 were soybean and Upland cotton. These data were used to test whether irrigation influenced ozone effects on crop yield. For soybean, 31 states report yield data, but only 4 report by irrigation practice (3 of these are among the top 10 soybean producing states). For Upland cotton, 17 states report yield data, but only 6 states report by irrigation practice (all 6 states are leaders in cotton production).

Data Availability: Data were downloaded from “Quick Stats” available on the NASS website (http://www.nass.usda.gov/index.asp).

Palmer Z Index, National Climatic Data Center, National Oceanic and Atmospheric Administration. See “Foliar Injury in Forests,” above, for information on the Palmer Z index.

For the purpose of factoring out crop yield data from areas where non-irrigated crops were drought-affected, all values describing a progression from dry to near normal to wet conditions were tested. As a result, “drought” conditions were categorized as < -1.25 on the Palmer Z index (but ultimately these data were not excluded from the analysis; see *Recommended Metrics*, above).

SUM06, W126 and AOT40 Indices, U.S. Environmental Protection Agency. National data on ozone indices were obtained from the EPA Aerometric Information Retrieval System (AIRS). These indices reflect ambient ozone in the atmosphere, each calculated in a slightly different manner based on time of exposure and specific exposure thresholds.

See “Foliar Injury in Forests,” above, for information on SUM06 and W126.

The AOT40 index sums all hourly average ozone concentrations ≥0.04 ppm O_3. The indices SUM06, W126, and N100 are often used in the United States to define ozone exposure regimes, while AOT40 is more commonly used in the European Union. The AOT40 exposure index tends to describe chronic ozone exposure conditions.

All three indices were tested to determine the most responsive ozone indicator metric, using thresholds proposed in peer-reviewed literature (see Table 6), as well as other intermediate values. Although certain similarities could be detected using comparable thresholds for SUM06, W126 and AOT40, the SUM06 statistic provided the most consistent results over the 10 year period.

Data Availability: See the EPA Aerometric Information Retrieval System (AIRS) (http://www.epa.gov/oar/data/) for data access information and program contacts.

For the final determination of the ozone metric for crop systems, irrigated and non-irrigated yields were combined for each year, and mean national annual yield values were computed using the three cumulative ozone exposure indices as described previously.

The most responsive ozone indicator metric for crop yield was detected when mean national annual yields were grouped into SUM06 ozone exposure categories defined as follows:

- SUM06 ≤10 ppm-hr = low ozone exposure;
- SUM06 >10 ppm-hr and ≤20 ppm-hr = moderate ozone exposure;
- SUM06 >20 ppm-hr = high ozone exposure.

This held true for both soybean and Upland cotton yield data.

TABLE 7 Soybean Yield at Various Ozone Levels (bushels per acre)

Soybean	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
high ozone	31.1 a	28.9 a	27.4 a	32.5 a	33.3 a	33.1 a	-	33.8 a	34.9 a	33.9 a
moderate ozone	32.8 a	38.2 b	30.3 a	39.1 b	33.6 a	35.3 a b	34.7 a	42.3 b	43.2 b	39.2 b
low ozone	41.3 b	42.3 c	36.3 b	43.8 c	36.3 a	36.9 b	41.9 b	47.7 c	49.1 c	46.6 c

TABLE 8 Upland Cotton Yield at Various Ozone Levels (pounds per acre)

Upland Cotton	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
high ozone	472.3 a	513.3 a	500.7 a	521.5 a	603.3 a	490.8 a	-	749.4 a	636.8 a	992.8 a
moderate ozone	545.4 b	612.6 b	456.2 a	599.0 b	685.2 b	696.3 b	756.1 a	857.7 b	837.7 b	989.6 a
low ozone	449.6 a	661.9 b	656.1 b	625.2 b	662.2 a b	889.6 c	903.8 b	806.0 a b	841.3 b	897.7 b

For nine of the ten years of the study period, mean national soybean yields were significantly improved under conditions of low ozone exposure. Mean yields increased significantly as ozone exposure decreased from high to moderate to low ozone exposures in 5 of the 10 years (1999, 2001, 2005, 2006, 2007) and tended to follow this same trend in 3 additional years (1998, 2000, 2003). Year 2004 was relatively clean throughout the crop growing region such that no high ozone exposure soybean yield data were reported. See Table 7.

Yield results for Upland cotton were not as consistent as those for soybean. This may have to do with the relative sensitivity of these two species to ozone, or to the fact that cotton yield data come from a wider variety of agricultural systems in six different states compared to four reporting states for soybean. Mean national cotton yields were significantly improved under conditions of low ozone exposure in 1999, 2000, 2001, 2003, 2004, and 2006. The absence of high ozone crop yields in 2004 noted for soybean were similarly absent from the Upland cotton yield data. See Table 8.

When non-irrigated yields were evaluated separately, a significant ozone response was also noted for 2002 and 2005. Because all crop yield data were included regardless of irrigation practice, it is important to note that the amount of water available to these crops (regardless of irrigation or climate conditions) has a significant effect on yield. Therefore the number of samples assessed in any given year varies in the proportion affected by irrigation or drought, and this variability in yield among years should be assessed.

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Chapter VI. Mercury

Background

Mercury (Hg) is a highly toxic chemical element that can accumulate in the tissues of organisms. Lethal effects have been documented in fish, birds, and mammals, including humans. The toxicity of mercury varies with an organism's individual characteristics (such as size, age, or life stage) and environmental factors (such as temperature and the presence of other chemicals). But even at relatively low concentrations, mercury "adversely affects reproduction, growth and development, behavior, blood and serum chemistry, motor coordination, vision, hearing, histology, and metabolism" in many organisms (Eisler, 1987, p. 42).

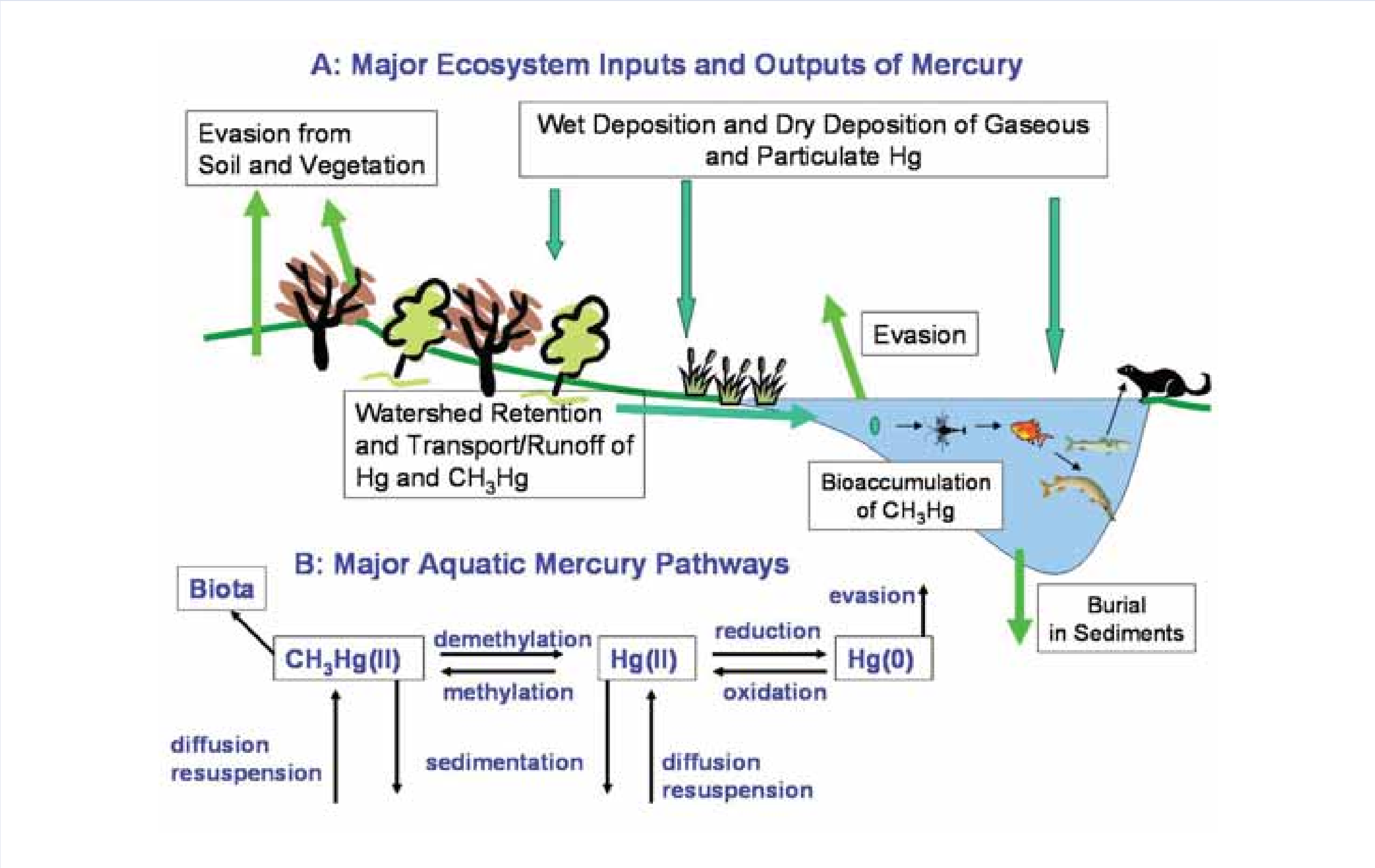
Population-level mercury impacts have been observed, especially in piscivore species such as the common loon, eagles, egrets, mink, and otters (Burgess & Meyer, 2008; EPA, 1997; Evers et al., 2008; Scheuhammer et al., 2008). Mercury toxicity often manifests itself as damage to the central nervous system (Wolfe et al., 1998) while sub-lethal and population effects often involve reduced reproductive success (Scheuhammer et al., 2007). Mercury can also diminish some of the services performed by impacted ecosystems. For example, mercury "can impair the water-treatment function and degrade the biological resources" of certain wetlands (Wiener et al., 2003, p. 439). The production of toxic forms of mercury in wetlands, their accumulation in biota, and transport to downstream reaches can continue well past the time that Hg is released from its primary source (e.g., >50 years). Modest decreases in mercury deposition may be associated with lower mercury concentrations in biota (Harris et al; 2007b).

Mercury is released naturally into the biosphere by volcanic activity and weathering of geological materials. Some estimates (Mason & Sheu, 2002; Seingeur, 2004) have attributed about one third of total mercury emissions to the atmosphere to natural sources. Human activities such as combustion of waste and fossil fuels, mining and processing of various metals, and industrial production of chlorine products have released significant amounts of mercury into the atmosphere, waters, and soils, particularly since the beginning of the Industrial Revolution. It is estimated that roughly two-thirds of the mercury currently present in the biosphere were liberated from geological stocks by human activities (Mason et al., 2005). The EPA (1997) determined that roughly 87% of the anthropogenic mercury emissions in the U.S. over the 1994-1995 period originated from combustion sources, and 10% originated from manufacturing processes.

A more recent study of anthropogenic mercury emissions, limited to the northeastern U.S., concluded that 59% of the emissions came from combustion sources (e.g., municipal waste combustors, electric utility boilers, and other large-scale operations in specific locales), 14% from manufacturing sources (e.g., cement manufacturing, petroleum refining), and 27% from "area" sources such as residential heating and electric lamp breakage (e.g. smaller-scale but geographically widespread) (NESCAUM, 2005). Most of the mercury emitted by human activities is released into the atmosphere, although some manufacturing facilities, landfills, and wastewater treatment plants release significant quantities of mercury directly into aquatic systems. It should be pointed out that the NESCAUM (2005) study also found evidence of progress made toward limiting mercury emissions in the Northeast: municipal waste combustors, electric utility boilers, residential heating, and sewage sludge incinerators have all substantially lowered their emissions over the 1998-2002 period. During that time period, a relatively rapid biotic response was documented in southeastern New Hampshire where bird blood mercury levels significantly declined when over 6,000 pounds of locally-emitted mercury was removed (Evers et al., 2007).

Mercury can be emitted as elemental Hg (Hg^0), reactive gaseous mercury (RGM), and particulate Hg (PHg). Hg^0 resides for a relatively long period in the atmosphere (0.5-2 years) and can be transported over long distances (tens of thousands of kilometers). Atmospheric concentrations of Hg^0 vary from 1.4 – 1.6 ng/m^3 (away from its original source). In some cases, Hg^0 can be oxidized and deposited locally (Lindberg et al., 2002; Weiss-Penzias et al., 2003) or taken in by plants through stomatal gas exchange (Rea et al., 2002). Reactive gaseous forms of mercury are highly soluble in water and reside in the atmosphere for relatively short periods (0.5-2 days); concentrations in the atmosphere are generally below 0.05 ng/m^3 (away from its original source). RGM is usually deposited to surfaces within tens to a few hundred kilometers of the emission source. Similarly, PHg is short-lived and can be found at concentrations below 0.05 ng/m^3 in the atmosphere. As a result, any given location may receive mercury from a combination of local, regional, and global sources (Driscoll et al., 2007); depending on the location, one or more sources may dominate or drive the deposition (Cohen et al., 2004). Deposited mercury can be reemitted to the atmosphere from terrestrial, freshwater and marine systems. See Figure 12.

FIGURE 12 Major ecosystem inputs and outputs of mercury. From Mason et al., 2005.



Concentrations in wet deposition in urban environments can be three to five times greater than those in regions surrounding urban areas, and impacted regions have concentrations that are a factor of two to three times greater than background levels in remote regions. The differences are less for Hg^0 given its relatively long residence time, and greater for RGM and PHg which are more rapidly removed from the atmosphere. Therefore total deposition fluxes can be up to 10 times greater in the immediate vicinity of a local source and up to five times greater than background levels in regions surrounding large-source urban areas (Pirrone & Mason, in press).

The Mercury Deposition Network, a monitoring subnetwork of the National Atmospheric Deposition Program, has been measuring mercury in wet deposition (i.e., rain and snow) since 1996. Data from 2007 show that mercury wet deposition is highest in the Southeast and lowest in the Northwest (NADP, 2005) although a recent analysis of trends from 1998-2005 shows no significant trend (increase or decrease) in mercury concentration for the Southeast, and significant declines in the Northeastern and Midwestern regions of the U.S. (Butler et al., 2007). On the other hand, modeled dry deposition of mercury (i.e. in the form of RGM, PHg, and stomatal uptake of Hg^0) appears to be highest in the Northeast (Driscoll et al., 2007). (Note that technical challenges prevent direct measurement of dry deposition.) Grigal (2002) estimates that the total transfer of atmospheric mercury to terrestrial systems in temperate and boreal zones in the Northern hemisphere is, on average, four times higher than the amount deposited by precipitation, due to the washoff of dry deposition and litterfall – dropping of leaves that accumulated Hg^0 from the atmosphere. Grigal (2002) also states that, "atmospheric deposition of Hg to lakes is only about one-fourth that to forests in the same geographic area because the lakes lack the forest canopy and hence surfaces for both dry deposition and foliar accumulation" (p. 9). However, mercury in wet deposition is highly bioavailable while mercury in runoff is less so, and deposition to watersheds is strongly retained, as shown by the results of the METAALICUS lake and watershed isotope addition study in Canada, where mercury added directly to the lake was methylated within months while mercury deposited to the watershed has not yet appeared within the aquatic system (Harris et al., 2007b). In forested ecosystems, measurement of *throughfall* may serve as a potential integrator for total wet and dry deposition (Grigal, 2002; Weathers et al., 2006).

Mercury Methylation Indicators

Inorganic mercury is converted to MeHg by methylating bacteria, and the methylation rate is dependent on both Hg inputs and conditions favorable to MeHg production. Wiener et al. (2003) point out that the one common attribute of ecosystems at greatest risk from mercury is that they all efficiently convert reactive gaseous mercury ions to *methylmercury*, or MeHg (chemical formula: CH_3Hg^+), a highly toxic form that is easily taken up and accumulated by living organisms. A meta-study of methylmercury production by Benoit et al. (2003) concludes that there is a significant relationship between total Hg and MeHg in near-surface sediments (i.e. the primary site of methylation), but that the relationship has no predictive power, given the importance of other parameters in influencing methylation rates. Similarly, Krabbenhoft et al. (2007) state that the total mercury present in an ecosystem, taken alone, "does not give an indication of the bioaccessibility of Hg in an aquatic ecosystem" (p. 74). Coupled with other environmental data, however, total Hg can constitute a critical factor of mercury levels in biota. The central importance of MeHg to the effects of mercury on biota has led researchers to pay considerable attention to the mercury methylation process and the factors that limit it. Methylating bacteria require sulfate for their metabolic activities, and increased sulfate loads to wetlands have been shown to result in increased methylation rates[15] (Galloway & Branfireun, 2004; ICF International, 2006; Jeremiason et al., 2006), although the sulfide by-product can bind to inorganic mercury making it unavailable for methylation (Benoit et al., 2003). Amendment experiments conducted on sediment cores in the Florida Everglades suggest that methylation rates "may be controlled by either sulfate or sulfide depending on site and season," (Gilmour et al., 1998, p. 339).

It can be difficult to determine when mercury in freshwaters was originally deposited due to variability in the factors that control mercury movement through a watershed (e.g., hydrologic flow path). Mercury binds readily to organic matter, making dissolved organic carbon another key factor in Hg bioavailability and transport. Drawing on a number of mercury studies, Grigal (2002) concludes that Hg is closely related to dissolved organic carbon (DOC) in solution; in the Northern hemisphere, relationships between Hg and DOC are similar across study sites although there are important regional and local differences.

In addition to sulfate and DOC, MeHg production is also influenced by nutrient concentrations, bacterial community structure, and acid-base status (Benoit et al., 2003; Bonzongo & Lyons, 2004; Gilmour et al., 1998; Harris et al., 2007a; Miskimmin et al., 1992; Wiener et al., 2006). One indicator of methylation that integrates these factors is the *percentage of MeHg of the total Hg present in lake sediments* (Mason et al., 2005). The %MeHg indicator normalizes (or factors out) the effect of total Hg abundance in sediment on MeHg production. Additionally, as MeHg is continually formed and degraded, the measured %MeHg provides a measure of the steady state condition that reflects the overall bioavailability of mercury for methylation. Compared across sites, higher %MeHg values represent locations "where the pool of mercury in sediment is the most bioavailable to the methylation process" (Krabbenhoft et al., 2007, p. 63).

Wetlands are often sensitive to mercury inputs and act as sources of MeHg in their watershed, likely due to an abundance of dissolved organic matter and anaerobic sediments—both conducive to Hg methylation (Wiener et al., 2003). Grigal (2002) finds that there is a strong positive relationship between the percentage of wetland area in Northern hemisphere temperate watersheds and MeHg flux, and a weak positive relationship between the wetland percentage and MeHg concentration.

Rationale for Indicator Selection

Total mercury is a weak indicator of Hg bioavailability in aquatic systems because it integrates the signal of atmospheric Hg deposition over long timeframes. Percent MeHg, however, can be used to characterize the bioavailability of mercury in sediments.

The relative abundance of methylated mercury may be helpful in identifying areas that will respond quickly to deposited mercury, however this parameter is significantly influenced by native geological conditions and, depending on local watershed conditions, may not vary substantially in response to changes in mercury deposition in management-relevant timeframes. Therefore, although change in %MeHg in wetland sediments was initially recommended by project advisors as a potential indicator metric (see Table 2), this metric may be better used as a variable for developing stratified watershed reporting categories for mercury bioaccumulation indicators (described below). This approach may enable distinct tracking of changes across slow and fast responding systems.

15. This increase in methylation rates may not be applicable to coastal wetlands.

Mercury Bioaccumulation Indicators

Mercury deposited to a watershed can be transported to lakes or streams, where it can enter the food chain and accumulate, in turn, in algae, plankton, fish, piscivorous animals, and humans. Mercury can also enter terrestrial food chains and eventually be taken up by insectivorous birds (Brasso & Cristol, 2008; Evers et al., 2005). Mercury becomes available for uptake by living organisms primarily if it is converted first to MeHg which is readily absorbed by organisms and moves freely in their bodies, including across the placenta. The term *bioaccumulation* is used to describe the mechanism by which tissues of living organisms become contaminated by mercury. Bioaccumulation "refers to the net uptake of a contaminant from all possible pathways and includes the accumulation that may occur by direct exposure to contaminated media as well as uptake from food" (EPA, 1997, p. 2-12). MeHg also increases in concentration as one moves higher up on a trophic level—a process known as *biomagnification*.

Initially, many scientists believed that fish accumulated mercury in their bodies primarily through direct absorption from the water. However, the literature published over the last twenty years indicates that the dominant pathway of mercury uptake by fish is the food web. An experiment conducted by Hall et al. (1997) elegantly demonstrates this finding: researchers placed fish into one of four holding pens: low MeHg water and low MeHg food; low MeHg water and high MeHg food; high MeHg water and low MeHg food; and, high MeHg water and food (using an environmentally relevant range of MeHg concentrations). The study found a significant increase in fish Hg concentrations only in those fish that were fed high MeHg zooplankton. Direct absorption of MeHg from water was estimated to be responsible for only about 15% of the MeHg uptake. When it occurs, direct absorption of MeHg from water is dependent upon the size and trophic position of the fish, and will be least important for higher trophic level fish.

Fish not only take in mercury when they feed, but their trophic position greatly determines the mercury concentration in their bodies. Cabana et al. (1994) found that "Hg concentrations in top predators such as lake trout and northern pike is greatly influenced by the presence or absence of certain species representing important trophic links between these species and zooplankton" (p. 387). The researchers found that Hg concentrations in fish species that are not connected to the pelagic food web, such as smallmouth bass, were not related to the length of the food chain. Biomagnification patterns are similar in aquatic systems that differ in the type of water body, mercury source, and pollution intensity (Wiener et al., 2007). Research conducted by Bowles et al. (2001) in tropical ecosystems found that the "biomagnification power of the food web is similar to that of temperate-lake and Arctic-marine systems" (p. 892).

There are some exceptions in the literature that relates trophic position with mercury concentrations in fish (e.g. Greenfield et al., 2001), but all of the meta-studies reviewed for this report found that MeHg concentration increases up the food web, as does the percent of mercury present in fish as MeHg (Watras & Bloom, 1992; Watras et al., 1998; Wiener et al., 2003). Interestingly, only the methylated form of mercury biomagnifies in fish; inorganic forms do not (and become only a minuscule fraction of the total mercury present in top predators). In the muscle tissue of fish used for human consumption— regardless of whether they represent freshwater or saltwater species, free swimmers, or bottom feeders—MeHg represents greater than 90% of the total mercury burden in piscivorous fish (Bloom, 1992; Wiener et al., 2003, 2007).

As in the case of other persistent toxic substances—such as DDT and PCBs—there is a strong relationship between mercury concentrations in fish and their age and size (Exponent, 2003; Wiener et al., 2003, 2007). This relationship is likely due to a number of factors, including the tendency of foods of larger fish to be more contaminated than the foods of smaller fish and the slower rate of mercury elimination relative to the rate of uptake.

For fish of similar length and weight, and situated at similar trophic positions, variations in mercury concentrations are influenced by the factors and processes that control the abundance of methylmercury in the ecosystem and the trophic transfer of MeHg. Mercury concentrations in fish have been shown to vary positively with lake or watershed area, and negatively with pH, acid neutralizing capacity, sulfate, nutrient concentrations, conductivity, zooplankton density, and land use (Brumbaugh et al., 2001; Chen et al., 2005; Driscoll et al., 2007). Chen et al. (2005) reviewed several multi-lake studies conducted in the northeastern U.S. and determined that the "lake types associated with the greatest amount of Hg bioaccumulation are poorly buffered, low pH, low productivity lakes having forested watersheds and minimal human land use" (p. 145). Evers' (2005) summary of 21 papers on the effects of mercury pollution in the Northeast identifies the following attributes of mercury sensitive surface waters:

Chemical:

- High acidity;
- Low acid neutralizing capacity;
- High sulfate;

Physical:

- Abundant wetlands (particularly along the shore);
- Small lake with a large watershed area;
- Summer water level fluctuations greater than 6 feet;

Biological:

- Low zooplankton abundance;
- Low nutrient levels;
- Numerous trophic levels in the food chain. (p. 7)

While there is variability in watershed methylation capacity, there is evidence that even modest decreases in mercury deposition can be associated with lower mercury concentrations in fish. Hrabik and Watras (2002) analyzed the impact of deposition on fish contamination in a Wisconsin seepage lake and found that mercury levels in fish decreased by roughly 30% between 1994 and 2000 due to decreased atmospheric Hg loading (de-acidification also lowered the Hg levels), with a background decrease in atmospheric Hg deposition of about 10% per year between 1995 and 1999 (Watras et al., 2000). Harris et al. (2007b) discuss the recovery of fish from mercury contamination:

> Typically, lakes that receive all of their mercury from the atmosphere (such as perched seepage lakes) could be expected to respond [to decreased mercury loading] in approximately a decade. For all other lakes, which receive at least some of their mercury load from the watershed, as well as a portion directly from the atmosphere, we would expect multiphased responses to a reduction in input: (*i*) an initial rapid decline in the mercury content of fish as a result of reduced direct deposition to the lake, followed by (*ii*) responses from the wetland and the upland, which will be prolonged declines (taking up to centuries) driven by reequilibration of the wetland peat and upland soils. (p. 16590)

Fish are the primary pathway for methylmercury contamination in humans and they are also an important, but not the only, pathway for contributing methylmercury loads to wildlife. Therefore, fish play a pivotal role in assessing and modeling the potential impacts of changing environmental

Hg loads. There are many federal and state monitoring programs that track Hg concentrations in fish; most of these programs emphasize gamefish.

Two groups of fish are usually recommended as candidates for monitoring changes in MeHg: one-year-old prey fish and older piscivorous fish. While most mercury monitoring studies focus on large fish species that are typically consumed by humans, small prey fish often have a wider geographical distribution (judged by their presence in kilometers of streams in a certain region) and can yield greater regional estimates of contamination (Lazorchak et al., 2003). Wiener et al. (2007) summarizes the utility of prey fish in MeHg monitoring: "prey fish are present in most surface waters, require moderate sampling effort, are important in the trophic transfer of MeHg in aquatic food webs, and probably indicate annual changes in exposure to MeHg" (p. 94). Prey fish exhibit substantial seasonal variation in growth rates and, subsequently, mercury concentrations (i.e. in temperate climates, Hg concentrations increase substantially during the summer). For this reason, prey fish should be sampled in the same season every year, preferably in the early spring or fall, when temporal variation in Hg concentrations is smaller than during the summer (Mason et al., 2005; Wiener et al., 2007).

Piscivorous fish respond more gradually (often, over 3 to 5 years) to MeHg bioavailability than prey fish do, and therefore can be more susceptible to the confounding impact of age, size, nutrient input, land use change, changes in food chain structure, or variations in species competition (Mason et al., 2005). However, due to the importance of piscivorous fish to humans, there now exists extensive historic information on mercury levels in this group of fish. Targeting monitoring programs at both mid-trophic-level omnivorous species as well as high-trophic-level predatory species would also better capture "the full range of fish Hg concentrations likely to be found in any given waterbody," (Kamman et al., 2005, p. 170).

Several wildlife species that are at risk from mercury contamination have also been employed as Hg bioindicators. Fish-eating or piscivorous birds are a well-established group of organisms that provide a strong approach for examining how environmental Hg loading, combined with hydrological and biogeochemical landscape attributes, can manifest in long-lived, high trophic level organisms (Wolfe et al., 2007). Loon species, such as the Common Loon (*Gavia immer*), the Bald Eagle (*Haliaeetus leucocephalus*), and other piscivores are some of the preferred indicator species for monitoring Hg. The common loon, for example, has the highest position in the aquatic food web, is long-lived, and is generally limited to a single territory during the relatively long (4-6 months) breeding season, making young and mature individuals good indicators of lake-specific MeHg availability and long-term mercury risk to wildlife, respectively (Evers, 2006). There is a fairly substantial amount of information on mercury exposure and bioaccumulation in common loon populations. Increased mercury body burdens in loons have been linked to behavioral, physiological, survival, and reproductive impacts and adverse effect thresholds have been proposed (Burgess & Meyer, 2008; Evers et al., 2008). Variability across piscivore species in susceptibility to MeHg toxicity has been observed (Heinz et al., 2008; Scheuhammer et al., 2008).

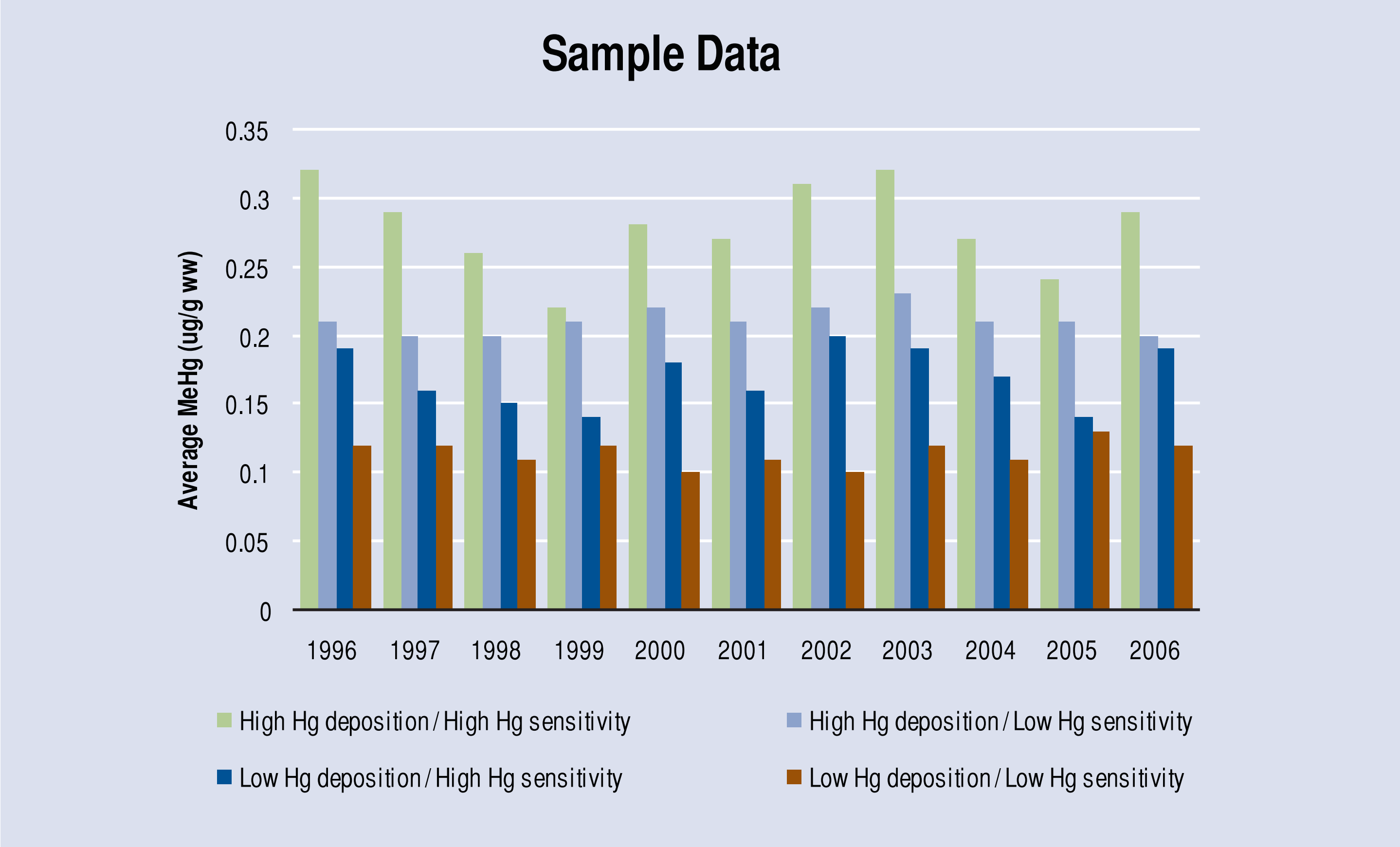
Although long thought to affect only aquatic systems, Hg has recently been shown to also have the ability to move into terrestrial ecosystems and bioaccumulate in upper trophic level terrestrial organisms, such as bats and songbirds. Though mercury is widely studied in aquatic systems, little work has been conducted in terrestrial ecosystems. Future research will improve the ability to evaluate the availability of methylmercury in ecosystems sensitive to environmental Hg loadings (such as wetlands), and to evaluate the exposure of upper trophic level biota most vulnerable to mercury contamination.

Rationale for Indicator Selection

To produce mercury bioaccumulation indicator metrics that are sensitive to changes in mercury deposition over management-relevant timeframes, yet also relate to the majority of affected ecosystems, the approach recommended by this report is to stratify spatially-resolved mercury bioaccumulation data by watershed sensitivity measures (see discussion below). This approach enables distinct tracking of changes across slow and fast responding systems. For example, slow responding systems include some lakes that experience prolonged declines on the order of centuries due to direct deposition, while fast responding systems may include watersheds that efficiently produce MeHg, or lakes that receive inputs from the atmosphere (e.g., perched seepage lakes). Indicators of mercury bioaccumulation should account for temporal trends and spatial gradients in the availability of methylmercury in aquatic ecosystems.

Mercury bioaccumulation indicator metrics would ideally represent prey fish, piscivorous fish and piscivorous birds and include measurements that are nationally-consistent and ongoing. At this point, national-scale datasets are not yet available. The utility of using threshold and subthreshold values for human health (e.g., percent of gamefish fillet Hg) and for ecological health (e.g., percent of individual population of piscivore blood Hg; egg Hg; feather Hg) should also be explored.

FIGURE 13 Sample Indicator for Methylmercury in Young-of-Year (YOY) Fish. Average methylmercury levels for young-of-the-year fish, reported as µg/g wet weight, by categories of mercury deposition and watershed mercury sensitivity.



Recommended Metric

Change in Methylmercury in Prey Fish and Piscivorous Fish and Birds. Once national-scale data are available and watershed categories of mercury sensitivity are further refined, these indicators would provide summary statistics (e.g. annual average mercury concentration) for mercury bioaccumulation data in fish and piscivorous birds, grouped by categories of watershed sensitivity and amount of mercury deposition. Figure 13 illustrates how mercury bioaccumulation data would be presented.

Numerous data sets of varying parameters already exist for mercury bioaccumulation (see technical note). A body of existing work on factors that allow some watersheds to methylate mercury more efficiently than others, as well as on mercury accumulation in biota, should provide potential data sources to populate this indicator in the near future.

Significant research exists to support the development of watershed categories that exhibit different mercury transfer rates and methylation capacity, but additional work may be needed to refine categories. Some factors are more important in certain locations of the country than others. Potential factors for watershed category definition include:

- Physical conditions: abundance of forest cover, wetlands, perched/seepage/drainage lakes, reservoirs, streams, and estuaries; watershed-to-lake area ratio; lake surface-to-volume ratio; lake stratification; soil type; depth of hydrologic flow path; land use; water level fluctuations; temperature; drying and rewetting patterns (soils, sediments)
- Chemical conditions: acid-base status (pH, ANC); sulfate/sulfide; dissolved organic carbon; nutrient concentrations
- Biological conditions: food web structure (length of food chain, benthic vs. pelagic); zooplankton abundance; bacterial community structure.

The U.S. Geological Survey (USGS) is currently revising a watershed sensitivity map (Figure 14). The goal of their project is to understand the physical and chemical characteristics of a watershed that cause it to methylate mercury at a higher rate than other watersheds, and to produce a map that reflects that sensitivity by use of a sensitivity score. This map was presented in the U.S. Geological Survey's Strategic Plan for 2007-2017 (2007), and is in the process of being updated with new, more comprehensive statistical analyses. The analyses weight data for each of a number of key factors (sulfate, pH, total organic carbon, and wetland abundance) to create a single value that accounts for the relative contribution of each factor to the overall sensitivity of the system. Although the end product is expected to look similar to the first draft of the map, the analyses will have benefited from a much more rigorous process. See technical note for more information.

Part of the verification stage for the watershed sensitivity map is to compare the geospatial patterns of sensitive watersheds to mercury contamination in biota. One such tool for this effort is the National Descriptive Model of Mercury in Fish. Through a collaborative effort between the U.S. Geological Survey and the Environmental Protection Agency, a national fish-mercury exposure map was recently developed to assess geographic and temporal distribution trends for mercury concentrations in fish. Over 30,000 samples from the National Listing of Fish and Wildlife Advisories (NLFWA) database were incorporated into the analysis. Within the NLFWA database, sampling characteristics vary widely; and thus the major work of the analysis was to standardize the data so that comparisons among the samples could be made. The variation in sampling characteristics was attributed to two main causes: the physical sample tested (e.g. whole fish vs. skin-off fillet; age and size of fish; species' location in food chain), and lack of consistent sampling across the diverse geographic range of the U.S. through time (Wente, 2004). The statistical model developed by Wente (regression method, covariance model) accounted for these variations in the data so that they could be reported on a national scale (Figure 15).

Another potential source of national-scale data on mercury bioaccumulation in biota comes from data compilations and analyses performed by the BioDiversity Research Institute (BRI). The BRI produced national maps of mercury sampling sites for perch and avian piscivores using databases available through BRI. A map (Figure 16) of fish sample sites indicates a well-distributed sampling effort across the United States since the late 1960s (n > 250,000). Areas with concentrated sampling include the Northeast, Great Lakes Region, Atlantic Coast states and other parts of the southern U.S. and the West Coast states. Table 9 (see technical note) showcases

FIGURE 14 Nationwide Mercury Sensitivity Map for Aquatic Ecosystems. Watersheds particularly sensitive to mercury are more commonly found in the eastern and southern U.S., Great Lakes, and isolated areas in the western U.S. The higher the number, the more sensitive the system. From Myers et al., 2007.

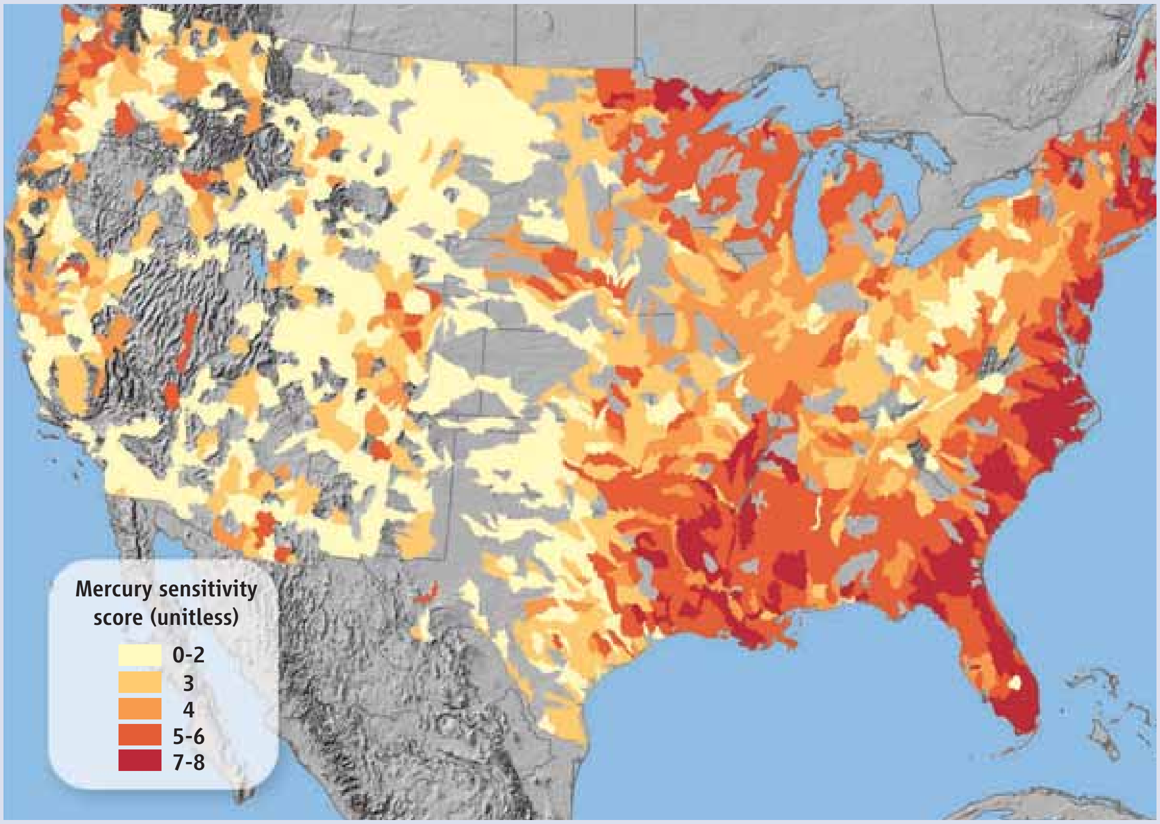
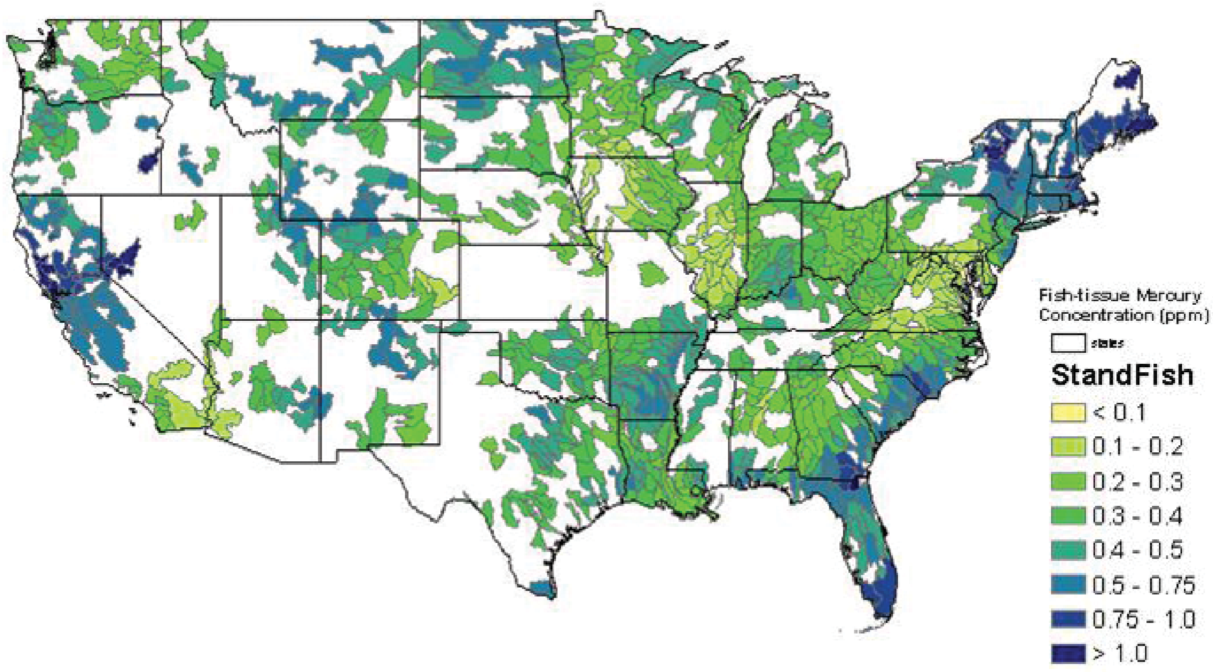


FIGURE 15 Fish Tissue Mercury Concentration (ppm). All data standardized to 14-inch largemouth bass, skin-off fillets. From Krabbenhoft and Booth, 2007.



the distribution of Great Lakes Hg concentrations in both gamefish and a selected species of fish depicting ecological health – the yellow perch (*Perca flavescens*).

Loon species are present across North America. They are well-studied, sensitive to negative impacts from current environmental mercury loads, and therefore provide a good monitoring tool for evaluating temporal trends and spatial gradients for a species at high risk. As such, long-term monitoring of Hg levels in loon tissues provides an opportunity for landscape-level standardized assessments over time. A map of the sampling sites included in the BRI database (Figure 17) indicates widespread sampling efforts for piscivores (loons, bald eagles, and other species) with an emphasis in the Northeast, upper Great Lakes Region, Chesapeake Bay, and south-central Florida. Based on common loon data, documented biological mercury hotspots are known in the Northeast (Evers et al., 2007) and there is a current effort to determine such hotspots in the Great Lakes Region. See technical note for a table showing percent of samples above and below wildlife standards.

Data Limitations
The watershed sensitivity map is still being revised, but should be available from the U.S. Geological Survey in the near future.

Work by Steve Wente has concluded although new data points are added and are available through the EMMMA website (see technical note for more information). In addition, some of these data are available through the BioDiversity Research Institute. Data compiled by BRI are from a variety of sources (federal, state, private and NGO) and cover a wide range of sampling dates and locations across the U.S. A comprehensive monitoring program is not yet in place that would allow robust data analysis of trends in mercury bioaccumulation in all wildlife in all parts of the country. However, a framework for indicator organisms and sampling methodologies has been developed (Wolfe et al., 2007) and is being implemented through developing bird mercury networks (see Table 11 for MercNet and BioDiversity Research Institute networks).

Ideally, a national, integrated monitoring network would provide consistent, long-term national-scale data for this indicator. Until that time, the proposed mercury indicator concept can be tested by combining these (or similar) datasets. When tested, further consideration should also be given to:

- Comparability of mercury bioaccumulation data across different sampling programs
- Geographic representativeness of the data

FIGURE 16 Fish Sample Locations (1967-2008). From the BioDiversity Research Institute.
[Note that data points do not constitute a nationally consistent monitoring system or dataset.]

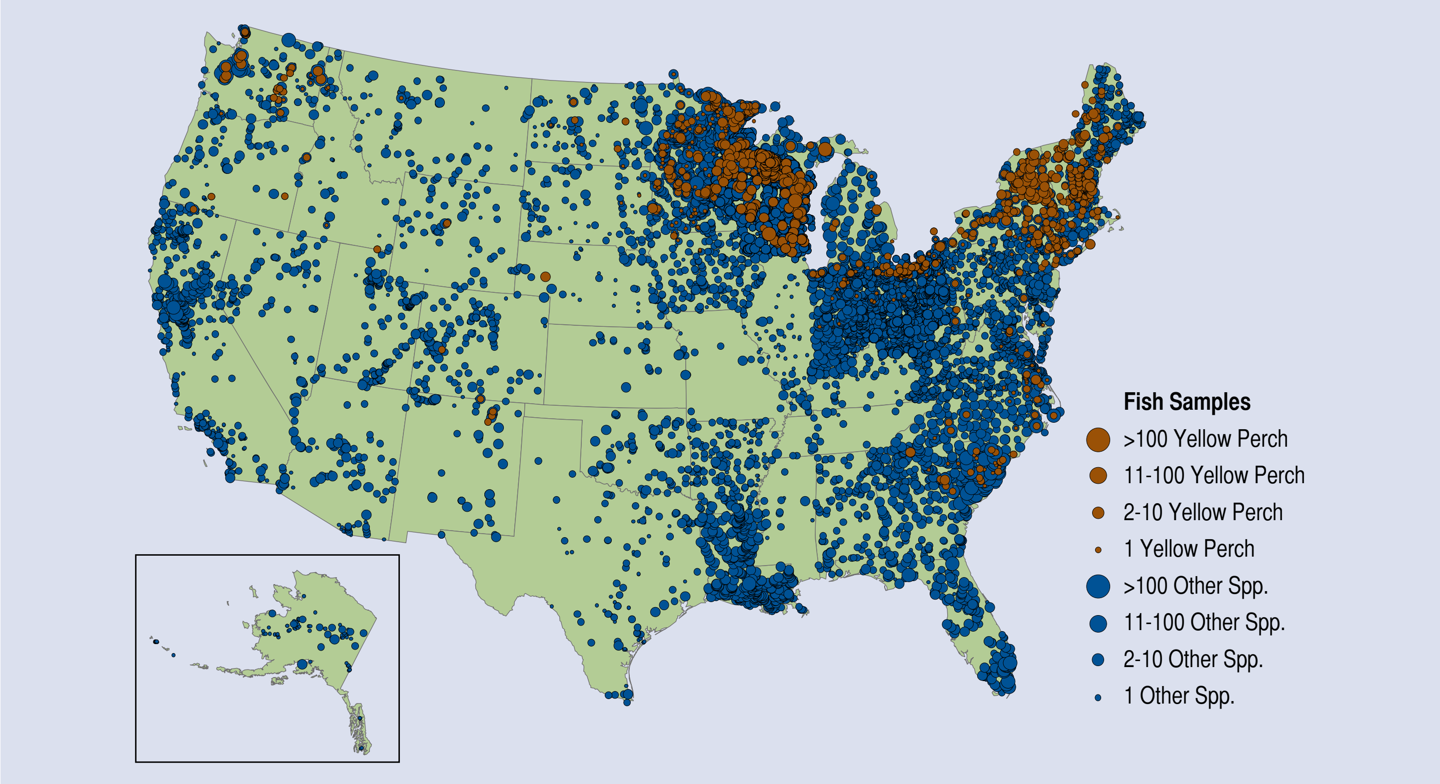
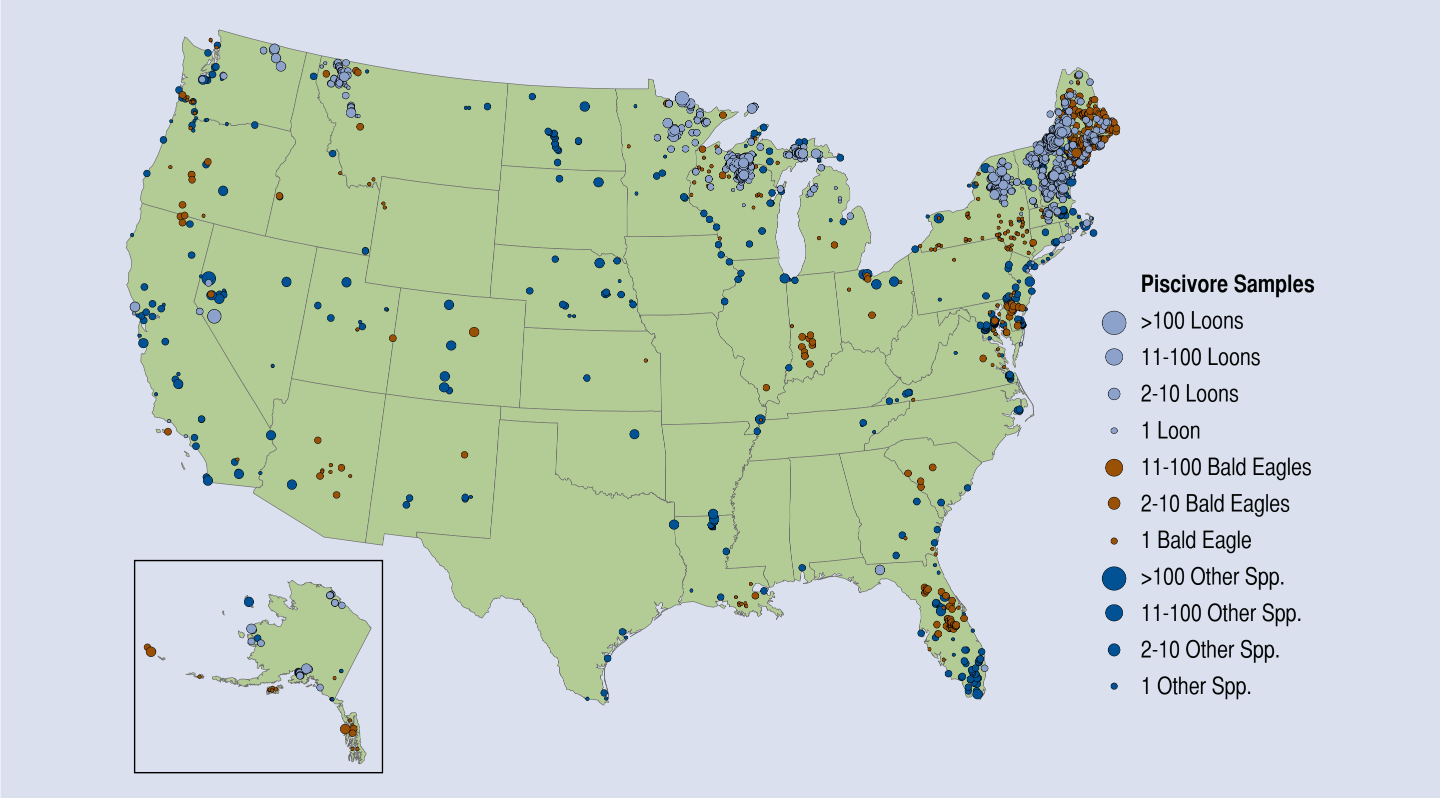


FIGURE 17 Avian Piscivore Sample Locations (1964-2008). From the BioDiversity Research Institute.
[Note that data points do not constitute a nationally consistent monitoring system or dataset.]



Research Needs

The following metrics of mercury methylation and bioaccumulation were considered for indicator development, however it was determined that further scientific investigation is needed, based on literature review and consultation with project advisors. In the future, as research continues, it may be possible to develop additional indicators of mercury's ecological effects to complement the indicator metrics recommended above.

Change in the Relative Abundance of Methylmercury in Streams and Coastal Systems

Comprehensive, national-scale monitoring systems are not yet in place for mercury in water and sediments, so at this time, it is not possible to fully populate this indicator with data. (There is a consortium actively designing a comprehensive national mercury monitoring network.[16]) Recent work by the U.S. Geological Survey has focused on mercury cycling in stream ecosystems, benthic methylmercury production, and trophic dynamics (see Brigham et al., 2009; Chasar et al., 2009; and Marvin-DiPasquale et al., 2009). One cited result of these studies was that wetlands play an important role in mercury transfer between systems. This work will contribute to increased understanding of how best to establish monitoring systems that account for the spatial variation in the transfer and transformation of mercury. Eventually, a metric measuring the change in %MeHg in streams and coastal systems could be combined with a similar metric for wetlands to provide a more robust picture of methylation in aquatic ecosystems. Spatial and temporal aspects of these processes should be taken into account.

Change in Total Mercury in Invertivores

Though mercury is widely studied in aquatic systems, little work has been conducted in terrestrial ecosystems. It is essential that Hg researchers evaluate the availability of methylmercury in ecosystems sensitive to environmental Hg loadings (such as wetlands), and to evaluate the exposure of upper trophic level biota that are thought to be most vulnerable to mercury contamination. Interestingly, terrestrial Hg studies may also provide new opportunities to understand how atmospheric mercury becomes bioavailable and moves through the food web. Efforts to model fate and transfer in aquatic systems have on the whole been inconclusive. By examining this process in simpler terrestrial systems, through concurrent measurements of Hg levels in atmospheric deposition, soil, and different biotic endpoints (e.g., spiders, songbirds and bats), it may be possible to link deposition with a biotic response (taking into account spatial and temporal issues).

The BioDiversity Research Institute has overlaid sampling locations for data on invertivorous bats and birds with mercury deposition monitoring stations, to explore the percentage of these records that are within 50 miles of a mercury deposition station. (Impacts from atmospherically deposited mercury are generally considered local if within 100 miles of an emission source.) More information regarding their efforts may be found in Table 11. By examining Hg in bats and birds near Hg deposition monitoring stations, it may be possible to more directly determine the relationship among emission point sources, levels of deposited mercury, and the response from local biota.

Technical Notes

Change in Methylmercury in Prey Fish and Piscivorous Fish and Birds

The data sources highlighted in this indicator include:

Mercury Sensitivity Map for Aquatic Ecosystems, U.S. Geological Survey, Wisconsin Water Science Center, Mercury Studies Team (MST). The mercury sensitivity map is a nationwide look at the mercury sensitivity of watersheds. A number of key factors (sulfate, pH, total organic carbon, and wetland abundance) are weighted to create a sensitivity value (ranging from 0 to 8). The methods used to weight each factor are currently being revised and will be published in the near future. For more information, see http://wi.water.usgs.gov/mercury/.

National Descriptive Model of Mercury in Fish, U.S. Geological Survey, Environmental Mercury Mapping, Modeling, & Analysis (EMMMA). The goal of the National Descriptive Model of Mercury in Fish was to separate spatio-temporal effects (differences in sampling across programs and geographical regions over time) from sample characteristic effects (size of fish, cut of fish tested, and species). The vision for this model was as a tool for evaluating trends in fish-mercury concentrations, and for developing fish-consumption advisories. The model incorporates methods from an analysis of covariance and multiple-linear regression. Several assumptions were made in designing the model, including a linear relationship between the size of the fish and fish-mercury concentration, and that variation within each set of parameters was assumed to be small. Observation data were taken from the National Listing of Fish and Wildlife Advisories data set. After removing samples that were not able to be utilized (missing information such as species name or sampling date), 31,183 samples from 28 states were incorporated into the model. Samples represent primarily freshwater fish species from U.S. inland waters. Seven different types of fish cuts were represented (whole fish, skin-on fillet, skin-off fillet, carcass, eggs, liver and viscera). Data points that were not adequately geo-referenced for mapping (~22%) were used as a calibration set for the model.

16. For additional information, see http://nadp.sws.uiuc.edu/mercnet/.

For additional information about the model, see Wente (2004).

Data Availability: The data tested for this model, plus some additional data, are available through the EMMMA website (http://emmma.usgs.gov). Some of the data are also included in the BioDiversity Research Institute's collection.

Sample locations for fish and avian piscivores, BioDiversity Research Institute (BRI). The BRI maintains a collection of mercury datasets that cover multiple taxa over several decades.

Fish. Over 43,000 gamefish, including bass, salmonids, pike, muskellunge, catfish and other species of interest for human consumption from one region – the Great Lakes – indicate between 41 to 64% of the individuals sampled exceeded U.S. Environmental Protection Agency human health advisory standards. Gamefish Hg levels for the last 40 years in the Great Lakes region indicate a downward trend from the late 1960s to 1999 and an increasing trend in the past decade. A smaller dataset of 503 yellow perch samples was used to evaluate ecological health over time. Yellow perch that are 10-15 cm in total length generate a negative reproductive response from avian piscivores, such as the Common Loon, when reaching Hg concentrations of at least 0.16 ppm (ww, whole body analysis) (Evers et al., 2008). Time trends are difficult to assess with small dataset over a shorter period of time, but about 7 to 12% of the individuals analyzed exceeded levels of concern. See Table 9.

Piscivores. The Global Loon Mercury and Monitoring Research (GLMMR) cooperative is a program directed by BioDiversity Research Institute. GLMMR contributes information to national and global regulatory interests through ongoing monitoring of all loon species in North America and elsewhere. For example, Environment Canada is using the Common Loon as the endpoint indicator for monitoring environmental Hg loads related to changes in mercury emissions driven by new regulations. Table 10 of piscivore Hg concentrations (n = 9,270) represents

TABLE 9 Percent of gamefish fillet Hg concentrations, and Perch whole body samples, above and below human health advisory standards (parts per million, ppm; wet weight, ww) in the Great Lakes region (1967-2008). Note these data are a regional subset of the data presented in Figure 16 and are similar, but not an exact match, due to lack of georeferencing for some samples.

Gamefish fillet Hg

Time Period	n	%<0.3 ppm ww	%>0.3 ppm ww
pre-1980	2009	36%	64%
1980-1984	1067	44%	56%
1985-1989	5210	40%	60%
1990-1994	6849	53%	47%
1995-1999	9502	59%	41%
2000-2004	11539	55%	45%
2005-2009	7435	54%	46%
Total	**43611**		

Yellow Perch whole body Hg (10-15cm)

Time Period	n	%< 0.16 ppm ww	%> 0.16 ppm ww
pre-1990	7	100%	0%
1990-1994	11	91%	9%
1995-1999	137	88%	12%
2000-2004	165	91%	9%
2005-2009	183	93%	7%
Total	**503**		

TABLE 10 Percent of samples (adult blood, adult feathers, and eggs) above and below wildlife standards (1964-2008). Note that data presented here are similar to, but not an exact match of, the data presented in Figure 17, due to lack of georeferencing for some samples.

	Adult blood			Adult feathers			Eggs		
Time Period	n	% < 3.0 ppm ww	% > 3.0 ppm ww	n	% < 40 ppm fw	% > 40 ppm fw	n	% < 1.3 ppm ww	% > 1.3 ppm ww
pre-1990	21	90%	10%	65	100%	0%	512	98%	2%
1990-1994	442	81%	19%	719	99%	1%	1275	97%	3%
1995-1999	885	82%	18%	923	99%	1%	742	91%	9%
2000-2004	939	86%	14%	621	98%	2%	1022	92%	8%
2005-2009	288	86%	14%	261	96%	4%	555	96%	4%

widespread sampling efforts with an emphasis in the Northeast, upper Great Lakes Region, Chesapeake Bay, and south-central Florida. While loons (n = 5,192) and eagles (n = 939) dominate the sampling effort, many other avian piscivores are represented (n = 60 species). A simple analysis of the temporal trends of Hg in avian piscivores indicates a tendency for declining Hg body burdens from 1990 to 2009 in adult blood and eggs (both tissues represent recent dietary uptake of methylmercury). Adult feathers, which more likely represent lifetime body burdens of Hg, indicate a slight increase.

Other Potential Resources: A number of mercury monitoring programs exist within federal and state government agencies, tribal governments, and private and non-profit organizations. Table 11 outlines existing or emerging programs.

TABLE 11 Mercury and Ancillary Monitoring Programs. From the 2008 National Mercury Monitoring Workshop report, with additional input from the BioDiversity Research Institute.

Agency/Program	Mercury monitoring activity
National Atmospheric Deposition Program (NADP), Mercury Deposition Network (MDN)	NADP currently monitors mercury in wet deposition at 90 MDN sites. A new Atmospheric Mercury Initiative measures air concentrations of mercury in its gaseous and particulate forms, event-based mercury wet deposition, and meteorological and land-cover variables needed for estimating dry deposition fluxes. Fifteen sites are already participating, with several more due to come on line. A standard operating procedures (SOP) document for mercury sampling and analysis (developed to facilitate site data comparisons over time) is in its first version and a second version of the field SOP has been produced.
U.S. Geological Survey (USGS) National Water Quality Assessment Program (NAWQA)	Detailed mercury cycling studies in streams in Oregon, Wisconsin, Florida, coastal plain of South Carolina, and the Adirondacks monitor food web, water quality, sediment geochemistry, and wet deposition. Currently developing models of mercury transport and cycling in South Carolina and New York studies, in collaboration with EPA. Large-scale synoptic studies use one-time sampling of mercury in the water column, sediments, and fish tissue at several hundred stream sites across the United States. Selected other USGS mercury studies have been done for Lake Champlain tributaries, California streams and rivers, high-elevation lakes located in the West, and lakes in northern Minnesota (Voyageurs National Park).
National Oceanographic and Atmospheric Administration (NOAA)	Monitoring and modeling of mercury in air, water, sediments, and biota in U.S. coastal regions and the Great Lakes focuses on understanding the fate and cycling of mercury. Atmospheric measurements are gathered at several long-term sites and via aircraft. Several NOAA programs gather data on mercury in biota. Mussel Watch provides a long-term, nationwide dataset for mercury in bivalves. Fish and dolphin monitoring data have been gathered for regional and national surveys. Additional work looks at mercury in seafood, as well as integrated ecological assessments.
National Park Service (NPS)	NPS hosts 14 MDN sites at different parks across the United States. Extensive studies on the ecological effects of mercury have been completed or are in progress at several national parks. The recently completed, 5-year Western Airborne Contaminants Assessment Project (WACAP) examined mercury and other contaminants in air, snow, water, sediments, lichen, conifer needles, and fish at eight parks in the western United States, including Denali, Gates of the Arctic, Glacier, Mount Rainier, Noatak, Rocky Mountain, Olympic, and Sequoia National Parks. The final report is available at http://www.nature.nps.gov/air/Studies/air_toxics/wacap.cfm.
U.S. Environmental Protection Agency (EPA)	EPA supports several collaborative monitoring programs: • The EPA Office of Air and Radiation (OAR) collaborates with the National Atmospheric Deposition Program (NADP) and other organizations to establish a new, national, standardized network to monitor mercury in the atmosphere (see above). Related to NADP, EPA-OAR administers the Clean Air Status and Trends Network (CASTNET), a long-term network of over 80 atmospheric monitoring sites that provide ancillary measurements useful for mercury monitoring and model development. • The EPA Office of Water (OW) recently initiated the National Rivers and Streams Assessment, which will include fish tissue sampling for mercury. Field collection will occur over 2 years (2008-2009) at approximately 2,000 sites including both wadeable and non-wadeable water bodies. EPA-OW has also been working with states to standardize protocols for monitoring mercury in water. • The EPA Office of Research and Development (ORD) is conducting an ongoing investigation of mercury fish tissue concentrations. In 2005, ORD re-sampled 42 sites from the original Mid-Atlantic Highlands Assessment (MAHA), where fish tissue Hg samples were collected in 1993-1994. Additionally in 2005, ORD sampled 60 Temporally Integrated Monitoring of Ecosystems (TIME) sites in the mid-Atlantic region for the first time for fish tissue mercury. ORD intends to re-sample these sites for fish tissue mercury every 2-3 years, as funds allow.

Agency/Program	Mercury monitoring activity
States	States have expended more than $50 million on mercury research and monitoring over the past 15 years. Primary focus has been on studies of mercury in fish and other biota, mercury emission inventories, lake sediment core analyses, atmospheric deposition modeling and monitoring, and research on mercury attributable to consumer products. Of 47 states, two tribal agencies and one Canadian province responded to a recent survey (percentages refer to proportion of respondents for each question): ● All have fish consumption advisories because of mercury in fish. ● 94 percent have ongoing fish contaminant monitoring programs (FCMPs). ● In 67 percent, the FCMP is intended only for fish consumption advisories. ● 63 percent use FCMP data for trend analysis. ● 65 percent use trend monitoring at fixed stations (x-sites every y-years); all but two of these fixed station FCMPs have a 1 to 5 year sample cycle. ● Average period of record for monitoring is 14 years. ● 54 percent have prepared monitoring reports. ● 60 percent use largemouth bass as the indicator fish species, 37 percent use walleye, and 33 percent use trout species. [Based on 2008 surveys of states by C. Mark Smith, Massachusetts Department of Environmental Protection, and Bruce Monson, Minnesota Pollution Control Agency]
Tribes	<u>Tribes with MDN Sites</u>: Potawatomi Nation, WI; Menominee Indian Tribe of Wisconsin; Cherokee Nation (Stillwell, OK; Newkirk, OK); Yurok Tribe, CA; Makah Nation, WA; Cheyenne River Sioux Tribe, SD; Grand Traverse Band of Ottawa and Chippewa Indians, MI; Micmac Tribe, ME; Sac and Fox Nation, KS. <u>Pending MDN sites</u>: Penobscot Nation, ME. <u>Possible MDN sites</u>: Mille Lacs Band of Ojibwe, MN (might start again); Zuni Nation, NM. <u>Inactive MDN sites</u>: Mille Lacs Band of Ojibwe, MN; Passamaquaddy, ME. Several tribes have begun to measure mercury in fish within their tribal waters.
BioDiversity Research Institute (BRI)'s Global Loon Mercury Monitoring Research Cooperative (GLMMR) and Terrestrial Ecosystems Research and Assessment (TERRA) Mercury Network	BRI monitors mercury in wildlife at sites across North and Central America, and coordinates two major collaborative monitoring and research programs: ● GLMMR: Loons are long-lived piscivorous species present across North America that are well-studied, are sensitive to environmental mercury loads, and therefore provide a good monitoring tool for evaluating temporal trends and spatial gradients. As such, long-term monitoring of mercury levels in loon tissues provides an opportunity for landscape-level standardized risk assessments over time. The GLMMR cooperative is contributing information to national and global regulatory interests through ongoing monitoring of all loon species in North America and elsewhere. ● TERRA: Mercury has recently been shown to have the ability to move into terrestrial systems and bioaccumulate in upper trophic level terrestrial organisms such as bats and songbirds. TERRA's goals are to 1) Link atmospheric deposition of mercury to a biotic response, through concurrent measurements of mercury in multiple media (atmospheric deposition, soil, litterfall, invertebrates, songbirds, and bats); 2) Evaluate the exposure of biota in locations and ecosystems thought to be most affected by long-distance mercury transport; and 3) Evaluate the exposure of upper trophic level biota that are thought to be most vulnerable to mercury contamination. TERRA's standard operating procedures document (SOP) is available on the BRI website.
MercNet	MercNet is a collaborative partnership. A broad cross-section of agencies and institutions are working to coordinate mercury monitoring and data collection activities. A May 2008 National Mercury Monitoring Workshop included federal agencies (U.S. Environmental Protection Agency, U.S. Fish and Wildlife Service, U.S. Geological Survey, National Oceanic and Atmospheric Administration, National Park Service), the National Atmospheric Deposition Program, state and tribal agency representatives, industry, and scientists from academic and private research institutions. The workshop was part of an ongoing effort to enhance mercury monitoring in the United States through coordination of existing monitoring efforts and implementation of new monitoring, if funding resources were available. To facilitate the design of a national network workshop, scientists and agencies developed the "MercNet" meta-database. This database includes major environmental monitoring databases from the U.S. Environmental Protection Agency, U.S. Fish and Wildlife Service, U.S. Geological Survey, the National Oceanic and Atmospheric Administration, the National Atmospheric Deposition Program, and the BioDiversity Research Institute, and seeks to answer the who, what, where, when, and why of mercury monitoring. The database provides a valuable tool to identify potential monitoring network sites and inform gap analysis. Work continues to populate this database.

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Chapter VII. The Future of Ecological Indicators of Air Quality

Importance of the Project

The intention of this project is to provide federal and state agencies and other natural resource managers and policy makers with quantitative tools for assessing ecosystem responses to changes in air quality. Indicators can help people to understand the outcomes of management and policy decisions on ecosystems. By drawing upon a rich body of scientific work and guidance from expert advisors, this project has produced a set of ecosystem indicators that can assist decision-makers as they develop and evaluate appropriate policy and management strategies for air pollution.

This report focuses on four major ecological effects of air pollution: acidification by nitrogen and sulfur; nitrogen enrichment, ozone damage to plants, and mercury bioaccumulation. Scientists have learned much about the ability to track pollution effects in ecosystems, and how to tease apart the causes behind those changes. For many air pollution impacts, existing research provides a solid foundation for understanding how ecosystems are being affected. For others, research is still emerging or limited to geographic regions.

In the face of human health issues, ecosystem "health" can seem less important, but ultimately it supports human existence through ecosystem services (from fishing, swimming and food production to nutrient transport and filtration). Growing stressors on the environment, especially those due to climate change, will accelerate the need for understanding and maintaining ecosystems, which at times may be sentinels for greater impacts to society.

Next Steps

There is a mounting call for improved environmental monitoring systems, both within and among federal agencies and their partners. The National Research Council's *Ecological Indicators for the Nation* (2000), which was commissioned by EPA, recommended the development of procedures to maintain, monitor, and archive environmental data. In its 2004 report on environmental indicators, the U.S. Government Accountability Office cited the difficulties that EPA had in its attempts to create an agency-wide set of environmental indicators that would link environmental management actions and program activities to ecosystem changes over time. In its results summary, the report noted that EPA is hindered in its attempts by

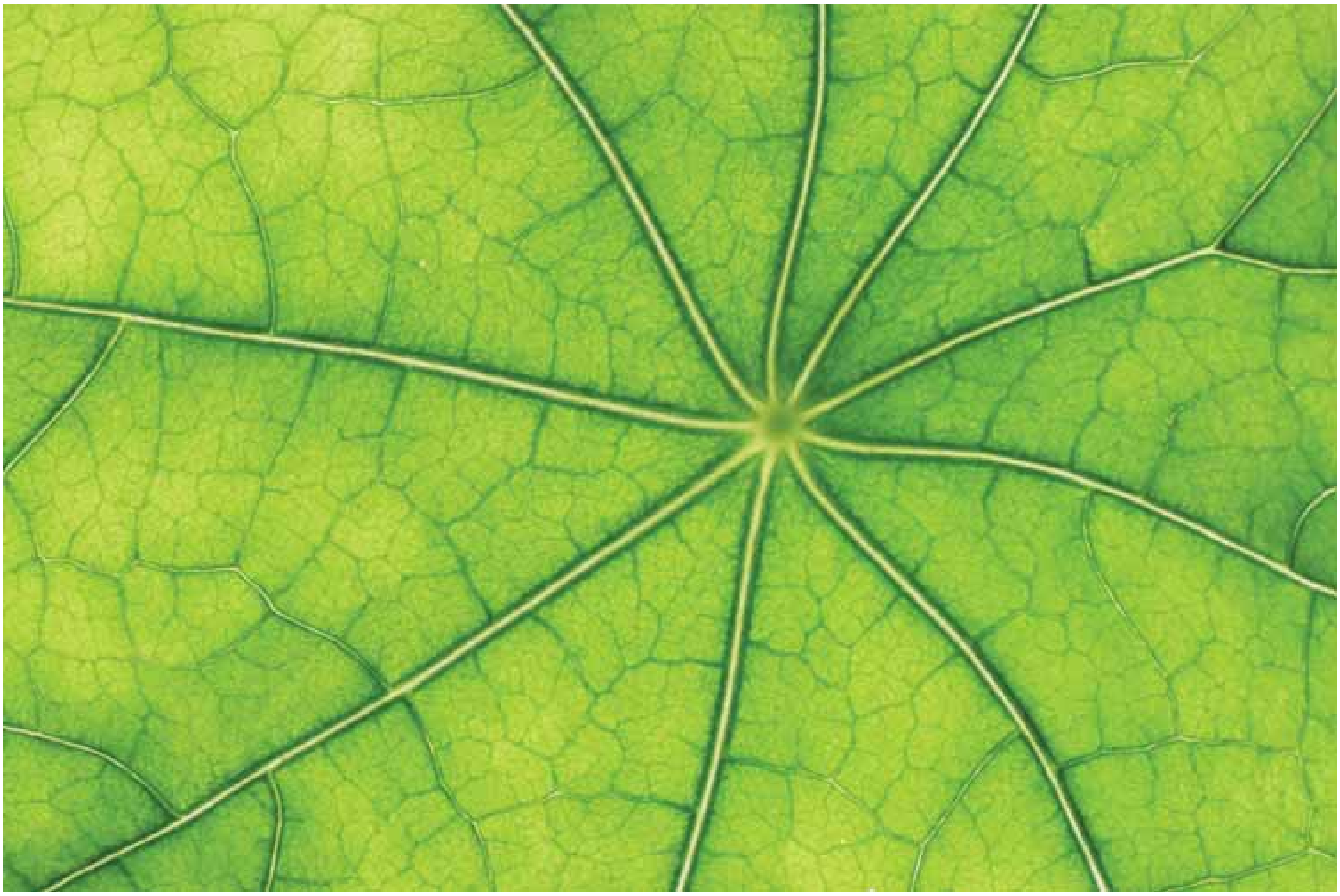
> …technical difficulties in establishing linkages between program activities and changes in the environment, but also by changes in leadership within the agency and the lack of needed resources for monitoring the natural resources and the environment. (p. 7)

The Heinz Center has published two reports specifically addressing the need for a comprehensive, national environmental monitoring system. *Environmental Information* (2008) proposed the establishment of a set of national environmental indicators, and that the process of creating that set of indicators be used to drive improvements in environmental monitoring by all involved stakeholders (federal, state, local and nongovernmental parties). In *Filling the Gaps* (2004), the Center proposed that more attention be paid to the nation's environmental monitoring system, which spans multiple federal agencies as well as other organizations that collect data based on unique missions and interests. Without a central organizing entity, the report notes that

> …there are few mechanisms by which overall priorities can be assessed—whether to identify areas for new investment, to allocate or reallocate existing resources, or to foster and encourage integration of methods so that data are comparable across agencies and geographic areas." (p. 33)

And with regard to monitoring systems for ecosystem responses to air pollutant exposure in particular, the NRC's 2004 *Air Quality Management in the U.S.* points to inadequate coordination among agencies and programs and the lack of "a cohesive long-term program on monitoring terrestrial and aquatic ecosystem conditions," (p. 371).

In moving towards a set of ecological indicators of air quality supported by a comprehensive system for which data will be collected and reported on a regular basis, it is important to continue to draw others into the decision-making process. Indicators are an evolving tool, a starting point to be refined and revised as necessary. With information in hand, policymakers can make informed decisions about proposed changes to legislation and associated activities. In the realm of the impacts of air quality on ecosystems, this project aims to assist in the development of a monitoring system that is comprehensive, cost-effective, and flexible enough to be adaptable to future changes.



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APPENDIX A.
PROJECT ADVISORY COMMITTEE MEMBERS

We are deeply grateful for the many contributions of all the advisors for this project, which benefited from the guidance of the project Steering Committee and the rich intellectual input of three technical subcommittees.

Steering Committee

Jill Baron
US Geological Survey/Natural Resource Ecology Laboratory

Ellis Cowling
North Carolina State University

Dave Evers
BioDiversity Research Institute

Ben Felzer
Lehigh University

Tom Jorling
International Paper/NEON

Manuel Lerdau
University of Virginia

Robert Howarth
Cornell University

Steve McNulty
USDA-Forest Service

Ronald P. Neilson
USDA Forest Service

Ecological Change Subcommittee

Jill S. Baron
US Geological Survey/Natural Resource Ecology Laboratory

Tamara Blett
National Park Service

Kent Burkey
USDA-ARS

Emily M. Elliott
University of Pittsburgh

Dave Evers
BioDiversity Research Institute

Mark Fenn
USFS Pacific Southwest Research Station - Forest Fire Laboratory

Patricia M. Glibert
University of Maryland Center for Environmental Science

Sagar Krupa
University of Minnesota

Robert Mason
University of Connecticut

Mark Southerland
Versar, Inc. ESM

Jill Webster
U.S. Fish and Wildlife Service

Air Quality Subcommittee

Praveen Amar
NESCAUM

Richard Artz
NOAA - Air Resources Laboratory

Richard Ayres
Ayres Law Group

Kevin Civerolo
New York State DEC

Ellis Cowling
North Carolina State University

Marion Deerhake
RTI International

Robert P. Mason
University of Connecticut

Joe Rudek
Environmental Defense

Analysis Subcommittee

Ben Felzer
Lehigh University

Mark Garrison
ERM

Robert Goldstein
Electric Power Research Institute

Reed Harris
Tetra Tech Inc.

Christopher D. Knightes
US EPA National Exposure Research Laboratory - Ecosystems Research Division

Manuel Lerdau
University of Virginia

Steve McNulty
USDA-Forest Service

Ronald P. Neilson
USDA Forest Service

Richard Smith
U. S. Geological Survey

Agency Liaisons

Colleen Mason
Environmental Protection Agency

Jason Lynch
Environmental Protection Agency

Appendix B. Guiding Principles for Committee Discussions

A set of general principles was provided to each subcommittee as a guide for its discussions and recommendations. These principles were informed by over a decade of experience in developing and implementing *The State of the Nation's Ecosystems*, the Heinz Center's effort to report on unbiased, policy-relevant and scientifically credible indicators of the use and condition of U.S. ecosystems. In addition, several guidance documents from EPA were useful resources in developing the principles (*Generic Ecological Assessment Endpoints (GEAEs) for Ecological Risk Assessment; A Framework for Assessing and Reporting on Ecological Condition: An SAB Report; Ecological Benefits Assessment Strategic Plan*).

Focus on Ecological Condition. A key objective of this project is to identify metrics that indicate ecological responses to air pollutant exposure. Therefore, indicator metrics should characterize ecological condition or processes rather than stressors or management practices. Whether these metrics relate to biological, chemical or physical properties will depend on their power to detect changes in ecosystem condition or function.

Scope of Ecological Effects. We are interested to begin the workshop by assessing the full range of potential ecological endpoints of air pollution, including those in forests, croplands, grasslands, shrublands, fresh waters, coasts, oceans and urban ecosystems. There may be important differences in the magnitude of research that has been focused on these ecosystem types or on particular geographic regions, however, in its initial discussions, we recommend that the subcommittee take a broad view in assessing the scientific foundation for air pollution impacts on ecosystems. By the end of the first day, we hope to focus in on a small number of candidate endpoints.

Stressor-Effect Links. While air pollution exposure can result in direct ecological response (e.g., foliar injury), many responses result from more complex processes (e.g., mercury bioaccumulation) for which dose-response evaluation can be more elusive. The subcommittee may wish to clarify those metrics for which dose-response analysis may be possible and those for which directional responses are more likely.

Scale. Indicator metrics should be sensitive enough to capture changes (but not so sensitive that 'noise' outweighs signal) at relevant geographic and temporal scales. For any ecological feature of interest, it is important to understand the relevant geographic and temporal variability and associated vulnerability to air pollutant stressors. While providing an aggregated view of ecological trends is valuable, indicators that report national or regional averages may not provide an appropriate level of geographic resolution. In cases where air pollution impacts are concentrated in 'hotspots', it may be appropriate to use metrics that track the distribution of conditions across space or monitoring sites. Similarly, annual averaging of ecological metrics may obscure the impact of peak exposures.

Data Sources. Indicator metrics should be anchored in current or potential monitoring programs that can consistently produce data with statistical confidence. Acquiring high-quality data is central to the utility of ecological indicators and a clear understanding of the relative merits of potential data sources can be quite useful. In recommending metrics for tracking ecological effects, the subcommittee may wish to evaluate whether likely data sources would be based on field measurements or modeled estimates. While most measured datasets incorporate some element of statistical modeling (e.g., relating sampling sites to larger geographic areas), some estimation models build in assumptions that may not be widely accepted in the relevant technical community.