# NITROGEN FROM THE ATMOSPHERE



March Constantion

## SUMMARY: NITROGEN FROM THE ATMOSPHERE

#### Nitrogen surrounds us.

Nitrogen (N) is required by all life on earth. N is also the most abundant gas in our atmosphere, existing primarily as N<sub>2</sub>, a form of N that almost all plants and animals cannot use. It is therefore termed non-reactive nitrogen (N<sub>n-r</sub>). Reactive forms of nitrogen (N<sub>r</sub>), nitrogen that can be used by organisms, is a small fraction of what's naturally found in the atmosphere. However, humans learned in the early 1900s to change N<sub>2</sub> into reactive forms of N to create N-based fertilizers to increase plant growth. Humans also began to burn fossil fuels, changing N<sub>n-r</sub> to N<sub>r</sub>. This N<sub>r</sub> is the N that is most important to us.

#### Reactive nitrogen causes a cascade of effects.

 $N_r$  can enter ecosystems from the air or through fertilizer application to soils, having unintended effects.  $N_r$  cycles through many other forms that can move from the soil into water resources or to and from the atmosphere. For example, too much  $N_r$  in streams can cause overgrowth of algae that chokes out fish. Too much  $N_r$  in soils can damage non-crop plants, such as trees, and change soil chemistry.  $N_r$  that goes back to the air contributes to air pollution such as acid rain, ozone, and visibility problems. Nitrogen can then fall back to land and water in wet deposition (rain or snow), or as dry deposition of  $N_r$  particles and gases.

#### NADP measures N<sub>r</sub> from the atmosphere.

The National Atmospheric Deposition Program (NADP) began measuring some forms of N<sub>r</sub> in 1978. Ammonia (NH<sub>3</sub>) and nitrogen oxides (NO<sub>x</sub>) react in the atmosphere and can dissolve in precipitation, falling as rain or snow in the forms of ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>). Measuring this wet atmospheric deposition is a relatively simple way to estimate how much of these N<sub>r</sub> pollutants were emitted into the air and to gauge how much N<sub>r</sub> is being added to different ecosystems. Nitrogen can also be deposited in dry form (as both gas and particles) but is more difficult to measure directly. NADP works closely with the Clean Air Status and Trends Network (CASTNET) to estimate N dry deposition.

#### Why is it important to measure Nr deposition?

Man-made processes have doubled the global amount of N<sub>r</sub> in the environment compared to pre-industrial times. The long record of data collected by NADP across the USA gives valuable information about how and where N<sub>r</sub> deposition has changed. Continuing to measure N<sub>r</sub> in deposition can help policymakers make good decisions about protecting the environment while meeting our energy and food needs. NADP gives land managers important data about agricultural inputs and outputs and emission products. Scientists can continue to use NADP data to monitor changes in ecosystems as a result of changes in N<sub>r</sub>. All of us can consider what actions we might take to limit our contribution to N<sub>r</sub> in the environment.

#### **Chemical terms**

 $N_r$  = Reactive nitrogen  $N_{n-r} = Non-reactive nitrogen$  $N_2 = Molecular nitrogen$ NH<sub>3</sub> = Ammonia  $NH_4^+ = Ammonium$ NH<sub>x</sub> = Ammonia plus ammonium  $NO_3^- = Nitrate$ NO = Nitric oxide  $N_2O = Nitrous oxide$ NO<sub>2</sub> = Nitrogen dioxide  $NO_x = Nitrogen oxides$  $NO_v = NO_x$  and other combinations of nitrogen and oxygen (except N<sub>2</sub>O)  $HNO_3 = Nitric acid$ HONO = Nitrous acid  $O_3 = Ozone$ 



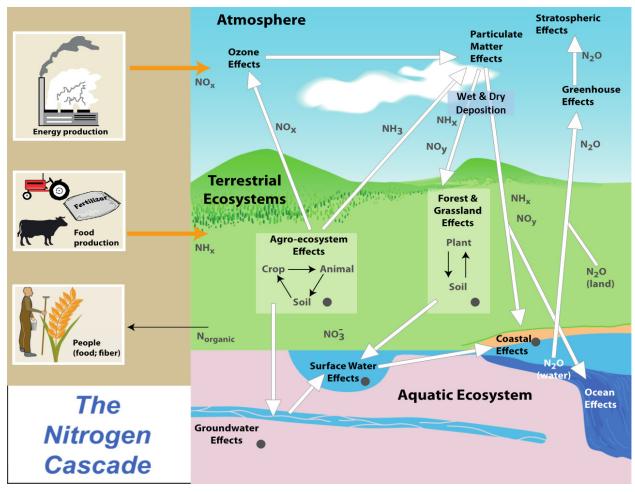


Illustration of the nitrogen cascade showing the sequential effects that a single atom of nitrogen in its various molecular forms can have in various reservoirs after it has been converted from nonreactive N<sub>2</sub> to a reactive form by energy and food production (orange arrows). Once created, the reactive nitrogen contributes to impacts until it is converted back to N<sub>2</sub>, a process called denitrification. The small black circle indicates the potential for denitrification to occur within that reservoir.
Source: adapted from Ciais et al., 2013 with permission from the GEO Yearbook 2003, and originally presented in Galloway et al., 2003.

## WHICH HUMAN ACTIVITIES CONTRIBUTE NITROGEN?

#### **Fossil Fuel Combustion**

Combustion creates high temperatures in which atmospheric  $N_2$  is transformed to reactive  $NO_x$ . It's not surprising, then, that emissions from motor vehicles, electric utilities, and industrial processes are the largest sources of atmospheric  $NO_x$  in the United States. Human (anthropogenic) activities now account for more than 80% of USA  $NO_x$  emissions. According to the US National Emissions Inventory (NEI), anthropogenic  $NO_x$  emissions peaked around 1980 at 24.6 million metric tons and have declined, especially after 1995 when the 1990 Clean Air Act Amendments legislation took effect, to a low of 11.3 million metric tons by 2014.  $NO_x$  emissions expressed as units of N only were 7.5 million metric tons for 1980 and 3.4 million metric tons for 2014.

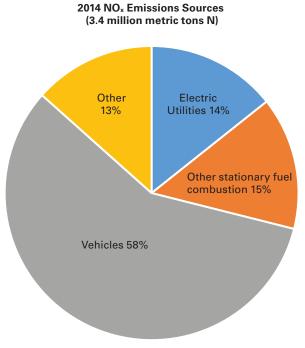
Atmospheric chemical reactions that occur when sunlight is present strongly link  $NO_x$  and other trace gases to the formation of  $O_3$ . Depending on atmospheric conditions, these reactions can occur within several hundred meters of the original  $NO_x$  source or after the pollutants have been transported several hundred to thousands of kilometers downwind-perhaps crossing state or national borders. Ultimately, some  $NO_x$  is converted to  $HNO_3$  vapor or particulate  $NO_3^-$ , both of which are efficiently removed from the atmosphere by deposition processes.

As a consequence,  $NO_3^-$  concentrations in precipitation tend to be highest where the air is most polluted with  $NO_x$ . These areas (e.g., the eastern USA) are likely to have high population densities, numerous motor vehicles (mobile sources), and many power plants or industrial boilers (stationary sources). A regional-scale study (Elliot et al., 2007) that analyzed stable nitrogen isotopes in NADP precipitation samples, shows a strong link between surrounding stationary NO<sub>x</sub> emission sources and NO<sub>3</sub><sup>-</sup> in precipitation for the Northeastern and Midwestern USA. According to emissions inventories, stationary source NO<sub>x</sub> emissions at the time were smaller than vehicle emissions in these regions, suggesting that NO<sub>x</sub> deposition end products from the transportation sector are not being fully accounted for in precipitation samples.

#### **Agricultural Sources**

Fertilizer use greatly augments the agriculture industry allowing for more production, but also increases the amount of N<sub>r</sub> cycling into the environment. Fertilizer is often applied in reduced form (NH<sub>3</sub> & NH<sub>4</sub><sup>+</sup>) and can enter ecosystems directly via volatilization during application or because of runoff into waterways. Emissions of reduced, reactive nitrogen are also a by-product of livestock production usually entering the ecosystem via the handling of animal waste. Livestock production represents the largest source of NH<sub>3</sub> emissions.

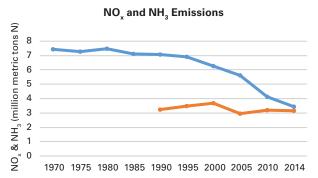
Together, livestock production and fertilizer use are the primary sources of NH<sub>3</sub> emissions and account



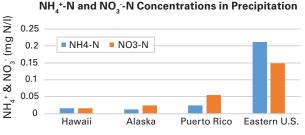
USA 2014  $\mbox{NO}_{\rm x}$  emissions by source from National Emissions Inventory (NEI).

for over 80% of total  $NH_3$  emissions in the United States. The National Emissions Inventory (http:// www3.epa.gov/ttn/chief/net/2011inventory.html) reports emissions of approximately 1 million metric tons of  $NH_3$  from fertilizer application and 2 million metric tons of  $NH_3$  from livestock production in the USA during 2011.

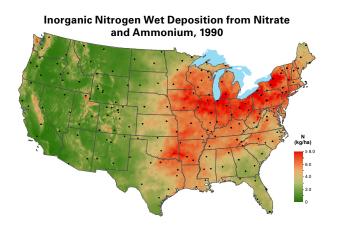
Precipitation readily removes NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> from the air. Wet deposition of these compounds (along with atmospheric NO3<sup>-</sup>) could be viewed as another source of fertilizer for agricultural crops. It can also be an unwanted input of fertilizer to sensitive ecosystems. The maps below show the inorganic nitrogen deposited in precipitation (i.e.,  $NO_3^- + NH_4^+$ ) in 1990 and 2014 in the USA. Wet inorganic nitrogen deposition is highest in the intensely cultivated upper Midwest. Parts of eight states from eastern Nebraska to western Ohio received 5 kg-N/ha (4.4 pounds/acre) or more of deposition annually. Sixty percent to 75% of the wet inorganic nitrogen deposited in this area is from NH4<sup>+</sup> deposition, which peaks in this same area. Atmospheric NH<sub>3</sub> emissions also peak in this region.



USA NO<sub>x</sub> and NH<sub>3</sub> emissions expressed as million metric tons or teragrams ( $10^{12}$  grams) of N. There have been significant declines in NO<sub>x</sub> emissions, but very little change in NH<sub>3</sub> emissions since 1990.



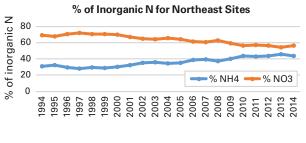
Comparison of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> content (as N) of precipitation in remote (Hawaii, Alaska, Puerto Rico) and more highly populated (eastern USA) areas of the USA. Based on NADP 2012 to 2014 annual volume-weighted mean concentrations (except Hawaii, which is based on 2002 to 2004; site closed in 2005).

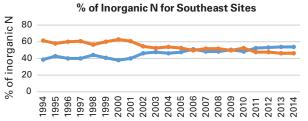


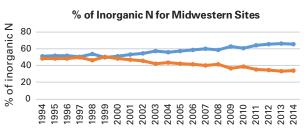
Inorganic Nitrogen Wet Deposition from Nitrate and Ammonium, 2014



Inorganic nitrogen (NO $_3^-$  and NH $_4^+$ ) wet deposition for 1990 and 2014.







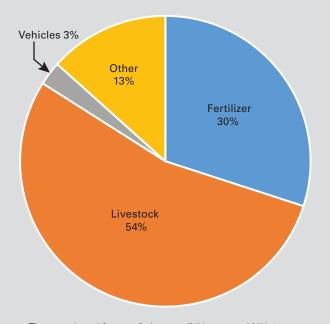
Percentage of inorganic nitrogen from NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> as measured in precipitation samples for the Northeast, Southeast, and Midwest sectors of the USA from 1994 to 2014. These data are based on five long-term NADP sites in the Northeast (VT01, MA08, NY68, PA42, and MD13), Southeast (AL10, GA41, SC06, NC36, and KY22), and Midwest (IL11, IN20, IA23, MI26, and MN27).



## NITROGEN AND AGRICULTURAL PRODUCTION

Over the past several decades, the crop and animal agriculture industries have become increasingly focused on the issue of nitrogen deposition. This focus is motivated by increasing the productivity and efficiency of farming practices, while increasing environmental sustainability.

Plant growth and crop yield are dependent on numerous factors including historical land use, crop type, soil type and condition, and availability of nutrients required for growth, especially nitrogen. Nitrogen availability in soils is influenced by the amount of N mineralized from previous crop residues, the amount of N released by organic matter, and the amount of N deposited from the atmosphere. Precipitation over the Midwest annually contributes 4 to 7 kilograms per hectare of inorganic N to the soil. This represents less than 5% of the inorganic N needs of corn and up to 15% of the N needs of wheat, depending on the target yield of the crop and on soil quality. Estimated wet and dry atmospheric N deposition for areas in the eastern United States could account for at least 10%



2014 NH<sub>3</sub> Emissions Sources (3.1 million metric tons N)

These reduced forms of nitrogen (NH<sub>3</sub> gas and NH<sub>4</sub><sup>+</sup> as a particulate or dissolved in water) are becoming relatively more important in terms of emission levels and atmospheric deposition. NH<sub>3</sub> emissions have not substantially declined over the past two decades in comparison to NO<sub>x</sub> emissions, which have declined significantly due to regulated controls on NO<sub>x</sub> emissions. of the nitrogen needs of major, non-nitrogen-fixing crops. In order to meet crop needs, application of N-based fertilizers to crop systems is generally very large compared to these sources, and has proven very effective in increasing crop yields, but excess fertilizer can result in unnecessary costs and nitrogen losses leading to unintended environmental effects. Research has focused on development of technologies and management practices that can decrease emissions of NH<sub>3</sub> and control N runoff, and especially on innovations that provide economic incentives for the farmer.

The animal agriculture industry has evolved so that most livestock and poultry produced for food in the USA are raised in large, concentrated operations. On these farms, large numbers of hogs, cattle, turkeys, and chickens as well as their feed, feces, and urine are confined to a relatively small area. Animal houses and waste lagoons are large sources of NH<sub>3</sub>. Application of manures to nearby cropland takes advantage of the nutrients contained in the manure for crop production, but is another source of N emission and potential runoff. Proper management of these significant sources can severely cut back on unintended N losses to air and water, and farmers develop animal waste management plans that are tailored to their operations. New measures are being investigated and implemented that focus on reducing water pollution and air emissions associated with animal agriculture.

Our knowledge base of N emissions from agricultural production has grown over the past 30 years and technologies have been developed that can limit those emissions. Because of the additional costs often associated with these measures, economic factors such as market demand can play a role in widespread adoption of some of these practices. Ongoing monitoring of N deposition by NADP offers a quantitative measure of the impact of changing management practices on regional deposition.

All of us benefit as science and technology continue to work together to optimize crop and animal production and safeguard terrestrial and aquatic ecosystems, as well as drinking water supplies.

## WHAT EFFECTS ARE ASSOCIATED WITH NITROGEN DEPOSITION?

Depending on the chemical form and amount in the environment, nitrogen can serve as a nutrient, enhancing growth and productivity, or as a toxin, causing ecological damage or harming human health. Scientists often refer to N as a macronutrient because plants and animals require it in relatively large proportions compared to other essential nutrients such as iron or copper.

Nitrogen needs vary, depending on the ecosystem and the plant or animal species. Different life forms within the same ecosystem do not have the same N requirements. Many ecosystems and crops are limited by the availability of nitrogen. That's why the advent of synthetic fertilizers via the Haber-Bosch process early in the 20th century has been such a boon to agricultural productivity. That is also why atmospheric deposition of nitrogen in some ecosystems may stimulate unhealthy growth or cause growth of some plants at the expense of others.

Air quality and atmospheric deposition are closely linked.  $NO_x$  contributes to the formation of  $O_3$ , a serious lung irritant. Many studies have shown that elevated  $O_3$  levels also damage plant leaves and reduce crop yields. Near urban or industrial air pollution sources, high concentrations of particulate  $NH_4^+$  and  $NO_3^-$  and  $NO_x$  gas can irritate human lung tissues and lower resistance to influenza or other respiratory infections.

Visibility degradation and acidic deposition are also linked to nitrogen. Too many fine particles in the air create the unsightly haze that reduces visibility in many USA cities and even occasionally shrouds the beautiful vistas in national park and wilderness areas. These fine particles contain nitrogen compounds ( $NO_3^-$ ,  $NH_4^+$ , or both) and other pollutants (sulfate [ $SO_4^{2-}$ ] and carbon compounds).





Stream acidification in Shenandoah National Park has had effects on some native species, such as this brook trout. Stream-water nitrogen often reaches a peak during the spring when snowmelt or rainstorms can flush NO<sub>3</sub><sup>-</sup> from the soils. Photo courtesy of U.S. National Park Service.

SO<sub>4</sub><sup>2-</sup> is often more important than nitrogen compounds in degrading visibility, especially in the eastern United States. When sunlight is present, NO<sub>x</sub> gas may also contribute to degradation of visibility. Although precipitation cleans the air, rain and snow can contain acidic NO3<sup>-</sup> and SO4<sup>2-</sup>. Statues, monuments, and the exteriors of buildings are all subject to acid rain damage. Acidic precipitation also affects sensitive streams, lakes, and soils, which are easily altered by chemical inputs. Acidic precipitation can disturb the delicate balance in these sensitive ecosystems. The good news is that because of large reductions of NO<sub>x</sub> and SO<sub>2</sub>, NADP data show acid deposition in large parts of the United States has been significantly decreasing in the past three decades. The same is true in much of Europe.

#### **Effects on Freshwaters and Forests**

Freshwater streams, ponds, and lakes respond to the water and chemical inputs from rain storms and snowmelt. On occasions when the ground is frozen, some headwater streams carry a surge of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and acidity provided directly by rain or melting snow. This also occurs in urban environments where the ground is covered with hard surfaces such as concrete or asphalt. More typically, precipitation soaks into the ground adding NO3<sup>-</sup> and NH<sub>4</sub><sup>+</sup> to the nitrogen cycle, which also involves soils, decaying plant and animal matter, microbes, and living plant roots. Many factors control the rate at which nitrogen enters and leaves this complex cycle, including soil type, temperature, microbial activity, and plant needs. Precipitation is just one source of the nitrogen in soils.

How a rain of fertilizer caused a reign of fire Nitrogen deposition is like fertilizer raining down out of the sky. Just as the fertilizer that people put on their lawns causes them to be lush and grow quickly, atmospheric deposition of excess nitrogen can cause invasive grasses biomass to increase exponentially in natural areas, where they don't belong. In Joshua Tree National Park, a desert area in southern California, nitrogen deposition has caused non-native grasses to increase so much that they can now carry fire across some parts of the landscape. Park managers are now preparing for increased fire in the park, and it is unknown what will happen next, as large, intense fires have never been observed there since the establishment of Joshua Tree National Monument in 1936.



Scientists have found that the cumulative effect of years of nitrogen deposition does increase the amount of nitrogen carried by streamflow from some watersheds. Rain storms and snowmelt can flush accumulated  $NO_3^-$  from soils into these streams. Nitrogen deposition, especially in combination with  $SO_4^{2-}$ , can contribute to episodic acidification of streams. Not all aquatic organisms have the same tolerance for these episodes, which can cause a decline in populations of acid-sensitive fish, amphibians, and invertebrates.

Nitrogen deposition to forest and alpine soils can affect plant populations and overall forest health. Decades of acidic  $NO_3^-$  and  $SO_4^{2-}$  deposition have depleted the supply of calcium (Ca<sup>2+</sup>) and mobilized aluminum (Al<sup>3+</sup>) in some forest soils. Ca<sup>2+</sup> is essential for tree growth, but Al<sup>3+</sup> interferes with the uptake of this nutrient by tree roots. Low soil Ca<sup>2+</sup> has been linked to the dieback of sugar maples

in some northeastern forests. Researchers have studied nitrogen-saturated, high-elevation spruce/fir forests in the Great Smoky Mountains National Park. They have found that as  $AI^{3+}$  in soil water increases, the  $Ca^{2+}$  in spruce trees decreases, possibly making trees more vulnerable to drought and insect infestations. Further, experiments have shown that adding nitrogen to alpine forest and grass communities alters the species mix. Those plants that can store and use the added nitrogen become more dominant, while those that cannot decline in number.

#### **Effects on Estuarine Systems**

The numerous estuaries (where fresh and salt water mix) along the USA coastline have great economic, aesthetic, and ecological value. Watershed landscape characteristics, land use (e.g., agriculture vs. forest), and atmospheric deposition all play a part in the delivery of nitrogen to estuaries and coastal systems. Nitrogen from many sources enters an estuary; only a portion is from atmospheric deposition (see section on Chesapeake Bay).

Soils, plants, and animals retain much of the nitrogen deposited in estuarine watersheds. Much of the remainder leaves these watersheds in runoff to streams and rivers. Some  $N_r$  is removed as  $N_2$  gas (and sometimes as gaseous  $N_2O$ ) by microbial denitrification processes within the watershed or the estuary itself. Subsurface water carrying nitrogen can also enter these waterways, which feed into estuaries.

Nitrogen has unique effects on individual estuaries. Along the East and Gulf Coasts, nitrogen provides a fertilizer effect and promotes algae blooms, causing coastal eutrophication. These microscopic waterborne plants cloud water and block sunlight, which can interfere with other estuarine plant and animal productivity, and affect water temperature and currents. For example, algae can inhibit growth of sea grasses that offer habitat for fish and shellfish.

Although living algae can degrade habitat, decaying algae can also have effects as they complete their life cycle, sink to the bottom, and decompose. Decomposition of algae and other dead matter removes oxygen from bottom waters and can lead to hypoxia, a low-oxygen condition. Hypoxia has negative impacts on populations of bottom dwellers such as crabs, oysters, mussels, and clams.

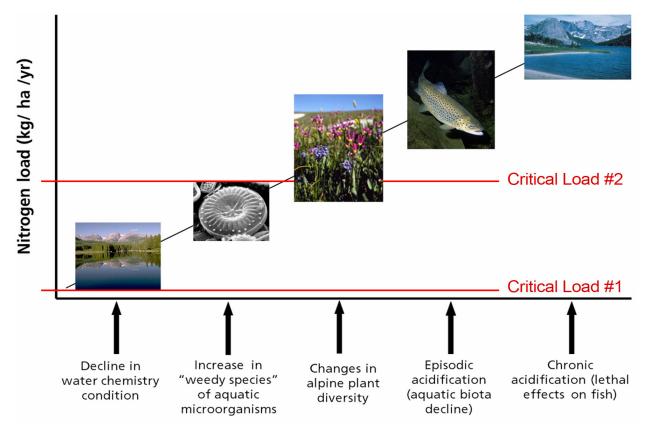
## CRITICAL LOADS: HOW MUCH N DEPOSITION IS TOO MUCH?

The term critical load is used to describe the threshold of atmospheric deposition that causes harm to sensitive resources in an ecosystem. Critical loads are typically expressed in terms of kilograms per hectare per year (kg/ha/yr) of wet or total (wet + dry) deposition. Critical loads can be developed for a variety of ecosystem responses, including shifts in microscopic aquatic species, increases in invasive grass species, changes in soil chemistry affecting tree growth, and lake and stream acidification to levels that can no longer support fish. When critical loads are exceeded, the environmental effects can extend over great distances. For example, excess nitrogen can change soil and surface water chemistry, which in turn can cause eutrophication of downstream estuaries. The long-term, spatially extensive wet deposition data provided by NADP are instrumental in developing critical loads in the USA, thereby helping to quantify the impacts of

air pollution on ecosystems. NADP also provides a format for critical loads development through the CLAD (Critical Loads and Atmospheric Deposition) Science Committee (http://nadp.isws.illinois.edu/ committees/clad/).

Critical loads are being developed in the USA for nitrogen and sulfur compounds, which are emitted by vehicles, power plants, industry, agriculture, and other sources.

As nitrogen deposition increases, impacts to sensitive ecosystem components also increase. Because pollutants accumulate in soils and lakes over time, it can take decades to reverse ecosystem degradation once it occurs. Prevention of the accumulation of pollutants in an ecosystem prior to any observable degradation is preferable. Both the US National Park Service and Forest Service are developing nitrogen critical loads for protection of the landscapes under their jurisdiction.



Schematic graph of the impact of increasing nitrogen deposition on different ecosystem health indicators. Establishment of a critical load value can depend on that which regulators want to protect. In this example, a lower critical loading value (#1) is necessary to maintain present water chemistry. A higher critical loading value (#2) is necessary if the goal is to maintain alpine plant diversity. (From http://www.nature.nps.gov/air/Studies/criticalloads/)

## HOW IS NITROGEN DEPOSITION MEASURED?

Nitrogen deposition occurs as both wet and dry deposition. The NADP National Trends Network (NTN) measures  $NO_3^-$  and  $NH_4^+$  in one-week rain and snow samples at over 250 regionally representative sites in 47 states plus Canada, the Virgin Islands, and Puerto Rico.  $NO_3^-$  and  $NH_4^+$  are measured in daily samples at another six sites in NADP's Atmospheric Integrated Research Monitoring Network (AIRMoN). These two NADP networks measure the wet deposition of inorganic nitrogen.

The amount of nitrogen deposited by precipitation can be calculated for locations without NTN or AIRMoN sites. One approach uses NADP rainfall,  $NO_3^{-}$  and  $NH_4^+$  concentration data, and digital terrain maps. These maps make it possible to generate plots that account for terrain effects on wet deposition. Maps generated using this technique include important information for planners, policymakers, and the scientific community about the complex relationship between the atmosphere and the ecological health of the nation's estuarine systems. In order to further understand N in the atmosphere and its impacts on landscapes, NADP is also measuring gaseous NH<sub>3</sub>. A relatively new NADP network, begun in 2007, is the Ammonia Monitoring Network (AMoN). Atmospheric NH<sub>3</sub> concentrations are measured over a two-week period with passive samplers. There are currently 97 sites in the network.

The US Environmental Protection Agency Clean Air Status and Trends Network (CASTNET) operates 94 sites that measure weekly atmospheric concentrations of gaseous HNO<sub>3</sub> and particulate  $NH_4^+$  and  $NO_3^-$  (as well as other non-nitrogen species) at rural locations nationwide. These measurements are used in atmospheric deposition models to calculate estimates of dry deposition of gases and particles. The model uses meteorological measurements and information on land use, vegetation, and surface conditions, in addition to the atmospheric concentrations, to calculate dry deposition of  $N_r$ .



NADP site at Canyonlands National Park

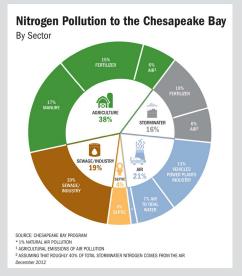
## THE CHESAPEAKE BAY: A CASE STUDY

The Chesapeake Bay is the largest of 130 estuaries in the nation and is located in coastal Maryland and Virginia. Its watershed covers 64,000 square miles over six states and the District of Columbia. The population within the Chesapeake Bay watershed is approximately 17 million and growing.

One of the largest problems facing the environmental health of the Bay is an overabundance of nutrients, especially N. This often leads to increased algal production and organic matter, a process known as eutrophication. Nitrogen is introduced into the Chesapeake Bay as runoff or wastewater from agricultural operations, storm water drainage, sewage and industry, and deposition from the air. An estimated 40.3 million kg of N (approximately one-third of the Bay's total annual load) is from atmospheric deposition as calculated by the Chesapeake Bay Program.

Most nitrogen pollutants introduced into the ecosystem are quickly converted into  $NO_3^-$ . This  $NO_3^-$  typically accumulates in the Bay during winter and spring and promotes excessive algal growth as temperatures rise. By mid-summer the decay of algae and other dead matter leads to hypoxia in the bottom waters of the Bay.

The Chesapeake Bay Program seeks ways to reduce the amount of N entering the Bay, which include programs to encourage farming conservation practices to curb drainage and runoff of fertilizers and animal

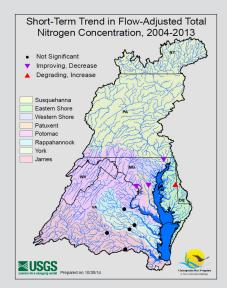


Pie Chart of Nitrogen Pollution to the Chesapeake Bay highlighting responsible sectors and sources of nitrogen pollution accumulating in the Bay. Source: Chesapeake Bay Foundation waste. Typical methods include installing streamside buffers and fences, the use of conservation tillage, and planting cover crops. Between 2004 and 2013, three of nine sites have shown improving flow-adjusted trends in nitrogen concentrations. Five have not significantly changed, but only one of the nine sites has shown a degrading trend.

Researchers are using NADP data to compute the amount of N deposited by precipitation in Chesapeake Bay and its watershed. Scientists are using computer modeling to simulate the complex cycling of nitrogen through the terrestrial watershed. High-quality data from NADP measurements give cooperating scientists and policymakers the information they need to meet this goal.



Aerial view of algal blooms in the Elizabeth, Lafayette, and James Rivers, VA. N in the water is causing the explosive growth of algae, which later die, depleting the water of oxygen and leading to hypoxic zones. Source: Chesapeake Bay Foundation.



Trends in Total Nitrogen Concentration between 2004 and 2013 in the Chesapeake Bay Watershed. Although most sites have not seen significant changes, three have had improving trends, and one has had a degraded trend. Source: U.S. Geological Survey and Chesapeake Bay Program.

## **MEASURING TOTAL DEPOSITION**

NADP has also attempted to better understand total wet and dry nitrogen deposition through the Total Deposition (TDEP) Science Committee (http:// nadp.isws.illinois.edu/committees/tdep/). Using a "hybrid" approach of combining measured data (e.g., precipitation NO3<sup>-</sup> and NH4<sup>+</sup>, dry deposition of particulate NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, and gaseous NH<sub>3</sub>) with modeled deposition data of other known, but not measured, nitrogen species (e.g., wet and dry organic N, HONO, NO<sub>2</sub>, etc.), estimates of total N deposition are obtained. The average annual total deposition for 2000 to 2002 and for 2013 to 2015 are shown below. These maps show dramatic improvements in decreasing total nitrogen deposition over large areas of the USA, a result of decreased emissions due to federal and state regulations during this period.

Such work aids another NADP science committee, the Critical Loads and Atmospheric Deposition (CLAD) Committee (http://nadp.isws.illinois.edu/ committees/clad/) in evaluating whether sensitive areas are experiencing too much N deposition.

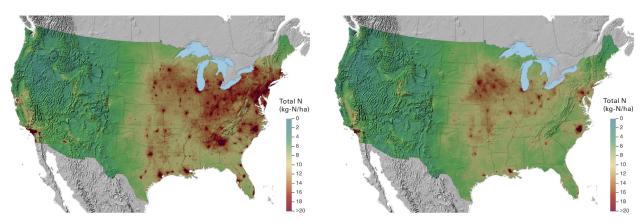


CASTNET monitoring station, Gothic, CO

#### Whooooooo cares about lichens?

Some types of lichens are very sensitive to air pollution, and have disappeared from forests in the Pacific NW in areas where air pollution has increased just a small amount. Many of these same lichen species serve as critical food and nesting material for mammals and birds. For example, the northern flying squirrel relies exclusively on forage lichens as a winter time food source. In turn, the flying squirrel is almost the exclusive food source of spotted owl. The spotted owl is an endangered species and its recovery plan has been controversial, because of the associated estimated \$3.6 billion in economic losses from logging and related industries that must be reduced for better habitat protection. Despite that investment, owl populations are continuing to decline because of many factors. Air pollution may be one of these factors, as decreases in sensitive lichen species and flying squirrels have also been documented. So when excess air pollution causes declines in sensitive lichen species, the whole food chain may be impacted, all the way up to the endangered spotted owl!





Total annual N deposition estimates for the continental USA for the average of 2000 to 2002 and the average for 2013 to 2015. These values are based on a "hybrid" approach of combining measured and, where measured values are not available, modeled nitrogen species data, and then summing all nitrogen species. More details are provided in http://nadp.isws.illinois.edu/committees/tdep/.

## ABOUT THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

Evaluating nitrogen deposition, as well as deposition of other chemical species from the atmosphere, is a major role of the National Atmospheric Deposition Program (NADP)—a partnership of State Agricultural Experiment Stations, federal, state, and local government agencies, universities, public institutions, Native American organizations, and industries. Continued commitments by these organizations make it possible for NADP to provide the only long-term record of precipitation chemistry in the United States. This information is used by scientists, policymakers, and the public in addressing the health, environmental, and agricultural issues facing the nation, including policy decisions related to the Clean Air Act amendments. NADP was initiated in 1977 to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters, and other natural resources. NADP coordinates over 250 sites in the National Trends Network, which collects weekly precipitation samples for chemical analysis. Samples are analyzed at the program's Central Analytical Laboratory in Champaign, Illinois, to determine the amounts of certain chemicals, including NO3- and NH₄+.

Two additional networks joined NADP in the 1990s: the Atmospheric Integrated Research Monitoring Network (AIRMoN) in 1992 (which includes a data record for some sites starting in 1976) and the Mercury Deposition Network (MDN) in 1996. The AIRMoN wet deposition program, presently consisting of six sites, evaluates the effect of emission changes on precipitation chemistry, combining measurements with atmospheric models. MDN is investigating the importance of atmospheric deposition as a source of mercury in terrestrial ecosystems, lakes, and streams, and includes 110 sites.

Further expansion of NADP after 2000 includes the start of the Atmospheric Mercury Network (AMNet) and the Ammonia Monitoring Network (AMoN). AMNet began in 2009 to measure atmospheric concentrations of gaseous oxidized, particulate-bound, and elemental mercury using consistent method-ologies. There are currently 24 sites. Additionally, estimates related to mercury deposition in forested landscapes are being complimented by the NADP Litterfall Mercury Monitoring Initiative. AMoN began operation in 2007 and currently operates 98 sites, making integrated bi-weekly measurements of atmospheric NH<sub>3</sub> concentrations using passive samplers.

A number of federal agencies support NADP, including the US Department of Agriculture (National Institute of Food and Agriculture and Forest Service); US Department of Commerce (National Oceanic and Atmospheric Administration); US Department of Interior (Bureau of Land Management, National Park Service, US Fish & Wildlife Service, and US Geological Survey); and US Environmental Protection Agency.

Additional support comes from various other federal agencies, State Agricultural Experiment Stations, state and local government agencies, universities, tribal organizations, and public and private research organizations.

#### How acidification ruined Christmas (trees) and Easter (bunnies)

Balsam fir are an important tree species in cold high elevation areas of the eastern US. They represent a \$17,000,000 business in Christmas trees and aromatic oils in the U.S. They also serve as valuable habitat for small mammals and birds. However balsam fir trees are vulnerable to acid rain, because chemical changes in the soils deplete essential nutrients which many types

of tree species need to thrive. Acidification of soils in the eastern US has decreased the growth of balsam fir and made them susceptible to damage by ice storms, insects and disease. In the Southern Appalachians only small relic populations of these tree species remain. Snowshoe hare population declines (through decreased reproduction and increased predation) in the Appalachians have been associated with decreases in balsam fir tree health because hares require dense forests which they use for both





food and shelter. Acidification of forest soils in the eastern US has consequences throughout these ecosystems, impacting both the economic benefits of forest products, such as Christmas trees, and the societal desire to protect locally endangered species, such as the snowshoe hare.

## **GLOSSARY OF TERMS**

#### Ammonia/Ammonium (NH<sub>3</sub>/NH<sub>4</sub>+)

Compounds of nitrogen and hydrogen that readily dissolve in water. In oxygen-rich water,  $NH_4^+$  is microbially transformed to  $NO_3^-$  and in oxygen-poor water to molecular nitrogen.  $NH_4^+$  and nitrate comprise most of the inorganic nitrogen in precipitation.

#### **Atmospheric Deposition**

The process whereby airborne particles and gases are deposited on the earth's surface by wet deposition (precipitation) or by dry deposition (processes such as settling, impaction, and adsorption).

#### **Critical Load**

The threshold of air pollution deposition that causes harm to sensitive resources in an ecosystem.

#### Denitrification

The microbial process of converting  $NO_3^-$  through a series of intermediate steps to  $N_2$  gas, which occurs under very low oxygen conditions, such as in lake sediments.

#### **Dry Deposition**

Atmospheric deposition that occurs when particles settle to a surface, collide with and attach to a surface, or when gases stick to a surface (adsorption) or are absorbed.

#### Estuary

An arm of the sea at the mouth of a stream or river where freshwater and salt water meet.

#### Eutrophication

A process in which nutrients degrade water quality due to excessive growth of microscopic plants and animals. As this matter dies and decays, it sometimes removes so much dissolved oxygen from the water that fish and other organisms cannot survive.

#### Haber-Bosch process

Industrial process to convert inert, atmospheric  $N_2$  into  $NH_3$  using high pressures and temperatures and an iron catalyst.

#### Hypoxia

A low-oxygen condition whereby decaying microscopic plants and animals in estuarine waters remove oxygen to a level below which most aquatic animals can survive. Although fish and shrimp can migrate from hypoxic zones, less mobile bottom dwellers cannot.

#### Molecular nitrogen (N<sub>2</sub>)

An extremely stable gas, comprises 78% of the atmosphere. Converting this gas to other chemical

compounds requires lots of energy. Also referred to as Nonreactive Nitrogen (Nn-r).

#### Nitrate (NO<sub>3</sub>-)

A compound of nitrogen and oxygen that is highly soluble in water. Nitrate is stable over a wide range of environmental conditions and is readily transported in surface water and groundwater.

#### Non-reactive Nitrogen (Nn-r)

A nitrogen compound that is not ecologically or biologically active.

#### Reactive Nitrogen (N<sub>r</sub>)

Nitrogen compounds that are ecologically and biologically active.  $N_r$  can be in a reduced form as in ammonia (NH<sub>3</sub>), ammonium (NH<sub>4</sub><sup>+</sup>), and organic compounds such as urea, amines, proteins, and nucleic acids. Nr can also be oxidized as in nitric acid (HNO<sub>3</sub>), nitrous acid (HONO), nitrous oxide (N<sub>2</sub>O), nitrogen dioxide (NO<sub>2</sub>), nitric oxide (NO<sub>2</sub>), and nitrate (NO<sub>3</sub><sup>-</sup>).

#### **Total Deposition**

The amount of a chemical compound that is deposited to earth's surface via wet and dry deposition processes.

#### Watershed

A land surface from which water drains to a lake, stream, river, estuary, or bay.

#### Wet Deposition

Atmospheric deposition that occurs when rain, snow, or fog carry gases, particles and dissolved materials to the earth's surface.



## **RESOURCES**

Data products are available from the National Atmospheric Deposition Program (NADP) free of charge. The easiest way to obtain data is by visiting our Internet site at http://nadp.isws.illinois.edu.

NADP products include:

- Weekly (NTN) and daily (AIRMoN) precipitation chemistry data (e.g., ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>, among many other elements);
- Monthly, seasonal, and annual precipitation-weighted mean concentrations (NTN);
- Annual and seasonal deposition totals;
- Total nitrogen deposition data and maps (TDEP);
- Daily precipitation totals;
- Color isopleth maps of precipitation concentrations and wet deposition;
- Mercury precipitation concentration and wet deposition data (MDN);
- Mercury air concentration data (AMNet);
- NH<sub>3</sub> air concentration data (AMoN);
- Site photos and information; and
- Quality assurance data and other information.

For further information, contact: NADP Program Office Illinois State Water Survey 2204 Griffith Drive Champaign, Illinois 61820 E-mail: nadp@isws.illinois.edu

#### **Other Website Resources**

Chesapeake Bay Program: www.chesapeakebay.net

Chesapeake Bay Foundation: www.cbf.org

National Atmospheric Deposition Program: nadp. isws.illinois.edu

National Oceanic and Atmospheric Administration AIRMoN Dry Deposition Program: http://www.atdd. noaa.gov/

National Park Service Air Resources Division: https:// www.nps.gov/orgs/1971/index.htm

US Environmental Protection Agency Clean Air Status and Trends Network: www.epa.gov/castnet

US Environmental Protection Agency National Emissions Inventory http://www3.epa.gov/ttn/chief/ net/2011inventory.html

National Estuary Program: www.epa.gov/nep

Office of Air & Radiation: www.epa.gov/oar

US Geological Survey Acid Rain, Atmospheric Deposition, and Precipitation Chemistry: https://bqs. usgs.gov/acidrain/

US Forest Service Critical Loads: http://srs.fs.usda.gov/ airqualityportal/critical\_loads/cls\_background.php

National Park Service Critical Loads: http://www. nature.nps.gov/air/Studies/criticalLoads/index.cfm

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