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Nitrogen Deposition in the Southern High Plains

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Nitrogen is necessary for life on earth, but getting too much of it can be harmful. Recent research in delicate alpine watersheds of the western United States has suggested that the amount of nitrogen in those watersheds is increasing and that the surrounding ecosystems are changing—some dramatically.

Although no evidence of these major ecosystem shifts has been found in the Southern High Plains, landowners in this region should be aware that all rangeland, cropland and surface water receive some supplemental nitrogen from the atmosphere. In fact, plants in native rangeland have probably evolved to subsist on nitrogen received from the atmosphere.

What's the big deal with nitrogen?

The most abundant element in the atmosphere—78 percent—is nitrogen (N), which is necessary to sustain life on this planet. Slightly more than three-quarters of a ton of nitrogen sits atop every square foot of the earth's surface; nearly 10 quintillion pounds of the element are in the earth's atmosphere. (The earth itself weighs about a million times the amount of nitrogen in the atmosphere.)

Because of its molecular structure, nitrogen can take a wide variety of forms. Despite its vital importance to nearly all forms of life on the planet, the predominant form of atmospheric nitrogen—dinitrogen gas (N_2)—is biologically and chemically inert, so it does not pose a significant threat to the environment. Dinitrogen contains two nitrogen atoms held together by one of nature's strongest chemical bonds. As a result, converting dinitrogen to other forms of nitrogen requires a lot of energy to break that bond. Some natural processes that can break dinitrogen apart include lightning and nitrogen fixation in the soil.

A lightning bolt generates high enough temperatures—approaching 18,000 degrees F—to split molecules of dinitrogen and oxygen (O_2) so the atoms can rearrange themselves as nitrogen oxides, or thermal nitrogen oxides. This is essentially the same process that generates nitrogen oxides during the combustion of fossil fuels. Temperatures as low as 3,000 degrees F are sufficient to generate thermal nitrogen oxides from the air.

Photosynthetic energy in plants and chemical energy in soil microorganisms also can convert nitrogen into other chemical forms. Legume roots sustain rhizobia, the organisms capable of nitrogen fixation, a microbial process for converting nitrogen into ammonium (NH_4).

Reactive nitrogen species (RNS) are nitrogen-bearing compounds that react with other compounds to form new nitrogen-bearing chemicals. The reactive nitrogen species classification usually does not include dinitrogen. Reactive nitrogen species may react to form either useful or harmful byproducts. Reactive nitrogen species in the environment include ammonia (NH_3) and its related compounds, amines (NH_2), nitrite (NO_2) and nitrate (NO_3), all of which are relatively soluble in water.

Much of the reactive nitrogen in the environment originated from industrial fertilizer production since the early 1900s, when the Nobel Prize-winning German scientist Fritz Haber invented what is now known as the Haber-Bosch process. This process, currently responsible for producing 500 million tons of nitrogen fertilizer each year, combines dinitrogen with naturally occurring methane gas (CH_4) at high temperatures and pressures to form ammonia gas (NH_3), one of the most reactive, ecologically significant nitrogen species.

Because reactive nitrogen species are available in many different forms and as a result of many different pathways, the global nitrogen cycle is complicated (Fig. 1).

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Conservation of mass: It's not just a good idea, it's the law

Nitrogen, along with every other element in nature, obeys certain physical laws. The first of those laws, the law of conservation of mass, states that matter entering a system will exit the system, accumulate in the system or become transformed into some other kind of matter. To understand the big picture of global nitrogen cycling, think of the ecosphere as the system, then trace the nitrogen flow as it either remains in the same chemical form or is transformed from one chemical form to another. No matter which kind of process is being considered, however, the total mass of nitrogen in the system remains constant.

The processes that change one element into another are known as nuclear reactions; these processes are not the focus of this publication. In the case of nitrogen-bearing compounds, the processes are chemical reactions that may occur spontaneously or from the actions of living organisms.

The ecosphere is a system made of the lower atmosphere, the earth's surface and a thin upper layer of the earth's crust. This habitable zone, or biosphere, contains all the main processes and resources that support life on the planet's surface.

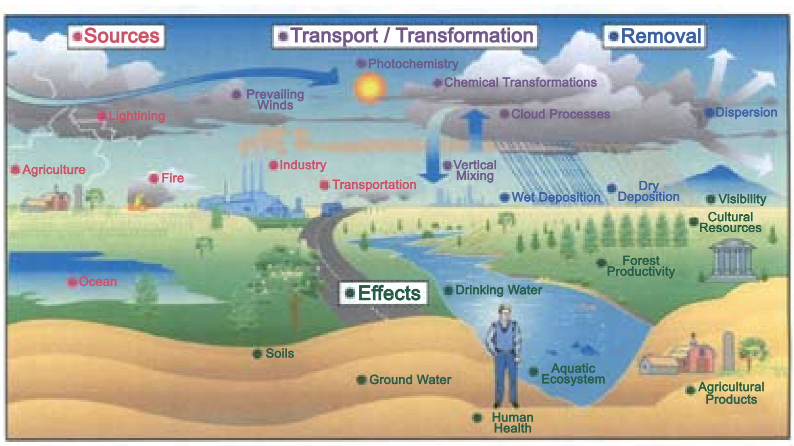

Figure 1. The global nitrogen cycle. (Source: Adapted from National Science and Technology Council Committee on Environment and Natural Resources, Air Quality Research Subcommittee, 1999)

A mass balance is the process of accounting for 100 percent of the matter in a dynamic system. This concept originates in the idea that matter can be neither created nor destroyed, only changed into different forms.

Recently, several scientists studying changes in the ecosphere's nitrogen balance since the Haber-Bosch process was invented have reached some remarkable conclusions:

- Human activities have led to major increases in global emissions of reactive nitrogen species to the atmosphere.
- More dinitrogen is converted to reactive nitrogen species by humans for energy production, fertilizer production and crop cultivation than is produced by biological processes.
- Since the start of the agricultural and industrial revolutions, the amount of global atmospheric emissions of reactive nitrogen species has almost quadrupled.

Although dinitrogen is still the dominant form of nitrogen in the atmosphere, the amount of reactive nitrogen species flowing through the environment is increasing significantly. A significant fraction of that increase is in atmospheric particles known as aerosols and gases containing reactive nitrogen.

Sources of atmospheric reactive nitrogen species

The greatest proportion of atmospheric reactive nitrogen species is in nitrogen oxides and ammonia. Nitrogen oxides are emitted to the atmosphere in exhaust from burning fossil fuels such as gasoline, diesel, coal and natural gas, and from wildfire and prescribed burning of forests and grasslands. Nitrogen releases from livestock and agriculture production are primarily in the form of ammonia. When more nitrogen is produced than is taken by plants or the soil, some of the excess nitrogen may be emitted to the atmosphere as gas.

Global atmospheric sources of ammonia are shown in Table 1. Once in the atmosphere, thermal nitrogen oxide may be transformed into secondary pollutants, such as nitric acid (HNO_3), nitrate and organic compounds such as peroxyacetyle nitrate. In the presence of atmospheric water, nitric acid gas can dissolve as the ammonium ion (NH_{4^+}), where it may react with

Table 1. Global atmospheric sources of ammonia (Source: A.F. Bouwman,1997).

Source	NH_3 Emission (10^6 tonnes N yr^{-1})	Percent
Dairy cattle	4.3	8
Non-dairy cattle	8.6	16
Buffaloes	1.2	2
Pigs	3.4	6
Poultry	1.9	4
Sheeps/ goats	1.5	3
Other animals	0.7	1
Subtotal domestic animals	*21.6*	*40*
Fertilizer	9.0	17
Agricultural crops	3.6	7
Biomass burning	4.1	8
Seas	8.2	15
Other sources	7.2	13
Total	*53.7*	*100*

a number of dissolved anions to form very small aerosol particles. Those ammonium salts are major components of both atmospheric nitrogen aerosols and wet-deposited nitrogen.

In the United States, livestock and poultry production is the largest contributor of ammonia gas emissions, followed by agricultural fertilization. In animal production, ammonia gas emissions are caused by a series of reactions that begin with the hydrolysis of urea in the waste stream. Intensive agriculture accounts for nearly 65 percent of ammonia gas emissions.

The primary nitrogen oxide sources in the United States are electric utilities, industrial boilers, and gasoline- and diesel-fueled vehicles. In 2002, the transportation sector contributed 56 percent of the nation's total nitrogen oxide emissions. The electric utility sector contributed 37 percent of the nation's nitrogen oxide emissions, with the balance coming from industrial and miscellaneous sources. Human activities account for more than 90 percent of the total nitrogen oxide emissions.

Has the human-caused increase in atmospheric reactive nitrogen species changed the way the ecosphere functions?

Moving reactive nitrogen species from the atmosphere to the earth's surface

When a gas or an aerosol moves from the atmosphere to the earth's surface, the process is called deposition. Dry deposition is the passive migration of aerosol particles or gas molecules to a surface such as a grass blade, a tree leaf, a soil particle or a body of water. Dry deposition flux—or the amount of matter deposited per unit area in a given period—is related to the probability that the surface will intercept particles or molecules carried along by air currents. In general, that probability increases as the concentration of particles or molecules in the air increases.

Gases that are heavier than air also are more likely to undergo dry deposition than are gases lighter than air.

In contrast, wet deposition occurs when a particle or gas molecule is collected from the air and carried to the earth's surface by precipitation. Like dry deposition, wet deposition increases with the concentration of gases or particles in the air. In addition, water-soluble gases have a greater wet-deposition potential than do gases with low water solubility. Wet deposition can collect particles and gases from high altitudes.

Nitrate and ammonia, the major components within the reactive nitrogen species pool, are relatively soluble in water and may be subject to both wet and dry deposition.

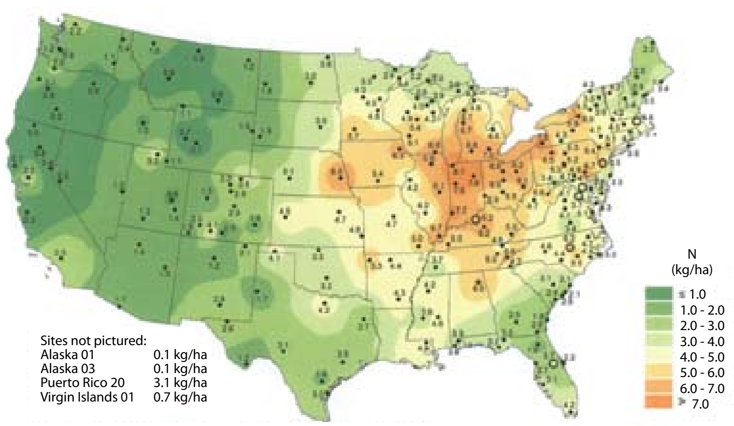

Figure 2. Inorganic nitrogen wet deposition from nitrate and ammonium, 2006 (Source: National Atmospheric Deposition Program/National Trends Network, 2007).

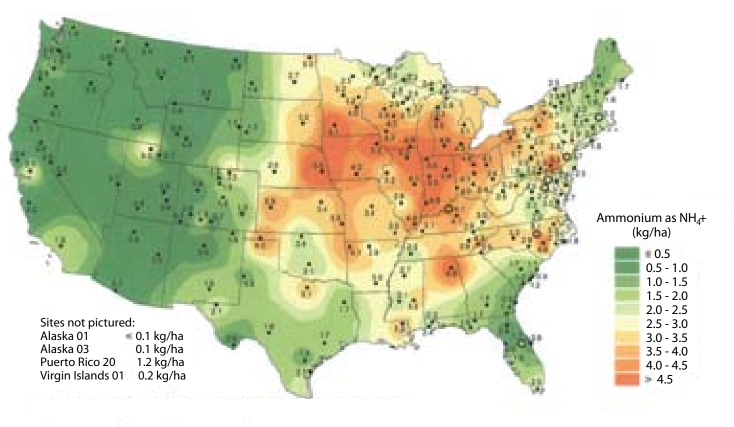

Figure 3. Wet deposition of ammonium, 2006 (Source: National Atmospheric Deposition Program/National Trends Network, 2007).

Because the amount of reactive nitrogen species in the atmosphere is increasing, reactive nitrogen species deposition is also increasing. Recent research has found that:

- In some areas of Northern Europe and North America, the rates of nitrogen deposition are significantly greater than in pre-industrial times.
- If current trends continue, the total deposition of reactive nitrogen species will be nearly twice as high in 2050 than it was in the early 1990s.

Nitrogen deposition patterns in the U.S.

In the United States, two national monitoring networks provide estimates of deposition fluxes across the country. The primary network of wet-deposition monitors is the National Atmospheric Deposition Program/National Trends Network (http://nadp.sws.uiuc.edu/), which was founded in 1978 by a consortium of federal agencies and the state Agricultural Experiment Stations.

The agency's monitoring sites provide weekly estimates of the wet deposition of nine inorganic chemicals: calcium, magnesium, potassium, sodium, ammonia, nitrate, chloride, sulfate and phosphate.

The Clean Air Status and Trends Network (http://www.epa.gov/castnet/), founded in 1987 by the U.S. Environmental Protection Agency (EPA), is the nation's primary source for data on dry deposition and rural, ground-level ozone. The agency's monitoring sites are administered by the EPA or the National Park Service. Some sites are located with either the deposition program's wet-deposition monitors or with visibility-monitoring sites under the Interagency Monitoring of Protected Visual Environments program.

Figure 2 shows the 2006 distribution of wet deposition of total inorganic nitrogen, which includes the nitrogen from nitrate and ammonium. Wet deposition of inorganic nitrogen was highest in the upper Midwest, with parts of eight states from eastern Nebraska to western Ohio receiving 7 kilograms per hectare or more. Fifty percent to 75 percent of the total inorganic nitrogen deposited in this area was from ammonium deposition, which peaks in this same area. Ammonium-nitrogen dominates the total inorganic nitrogen deposition in the upper Midwest (Fig. 3), whereas nitrate-nitrogen generally predominates in the Northeast (Fig. 4).

Areas with the highest nitrogen emissions do not necessarily see the greatest deposition fluxes, nor are the relative deposition fluxes of nitrate and ammonium uniform across the country (Figs. 5 and 6). These maps show that in the Midwest and Northeast, wet deposition is more prevalent than is dry. In the West, low deposition fluxes cover vast areas, with "hot spots" downwind of metropolitan centers or areas of intensive agriculture.

Ecological effects of nitrogen deposition

Increases in total nitrogen flux into the ecosystem can shift the plant, animal and microbial populations toward species that can use more nitrogen than the original, native species. Native ecosystems tend to develop in response to the nutrition provided by soil, water and air. In nitrogen deposition, the microbial, animal and plant life native to an ecosystem self-selects to use maximum benefit from the nitrogen available from all sources, including the atmosphere.

In self-selection, those species best adapted to use the available resources have a competitive advantage over species that are not as well adapted. For example, in the Southern High Plains, native turfgrasses such as buffalograss (*Buchloe dactyloides*) tend to be drought-tolerant, while imported grasses such as Kentucky bluegrass (*Poa pratensis*) wither and fade without supplemental irrigation.

Population shifts have been documented in a wide range of species in high alpine watersheds in the Rocky Mountains. Baseline nitrogen deposition in Rocky Mountain National Park has been estimated at less than 1.5 kilograms per hectare per year; over the past several years nitrogen deposition in the national park's Loch Vale watershed has reached as high as 7 kilograms per hectare per year. Some scientists associate the increased nitrogen deposition in these ecosystems with dramatic changes in vegetation, water chemistry, soil alkalinity and populations of aquatic species.

Summary

Nitrogen is an important limiting nutrient in sensitive ecosystems, and atmospheric nitrogen deposition is a significant component of the ecosystems' balance. When excessive nitrogen deposition distorts that balance by enriching

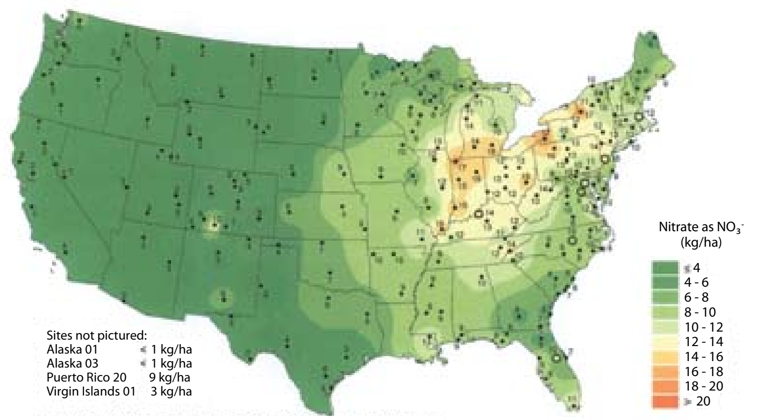

Figure 4. Wet deposition of nitrate, 2006 (Source: National Atmospheric Deposition Program/National Trends Network, 2007).

Figure 5. Wet and dry deposition of nitrogen, 2006 (Source: Clean Air Status and Trends Network/CASTNET, 2007).

Figure 6. Wet and dry deposition of inorganic nitrogen components, 2006 (Source: Clean Air Status and Trends Network/CASTNET, 2007).

soils and surface water beyond the native species' capacity to adapt, long-term changes in species distribution and water soil quality are likely. Either native plants adapt to use the excess nitrogen or nonnative species that use more nitrogen take over the ecosystem. Long-term monitoring of both dry and wet deposition of reactive nitrogen species may help predict or diagnose these ecosystem shifts.

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