

Chapter 1

Environmental and Human Impacts of Reactive Nitrogen

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No longer is it tenable to consider ecosystems isolated from humans. Of course it has been recognized for decades—even made explicit in the writings of Aldo Leopold in the 1940s—that human activity has compromised ecosystem functions ... but it is also true that ecosystem degradation has compromised humans. —David J. Rapport, 2003

INTRODUCTION

Scientific literature provides overwhelming evidence of the importance of managing nitrogen (N) to protect water quality as well as the environment in general. The goal of this chapter is to address many of the questions concerning this subject. Enhanced N management is increasingly necessary to decrease the impacts that excessive amounts of N in its reactive forms (i.e., Nr) can have on ecosystems. Dinitrogen gas (N₂) is the most abundant element in the Earth's atmosphere and

accounts for about 78% of the air we breathe. N_2 is inert and not directly available for metabolism in biological systems, yet once the triple bond of the N_2 molecule is broken the single N atoms become reactive (Nr) and bonds with elements, such as oxygen (O), carbon (C), and hydrogen (H), to form some of the most mobile ionic substances found in the soil-plant-atmosphere system. The need to understand N transformations and transport and the role of Nr in the environment has been the subject of many reviews and/or books (Follett, 1989; Follett et al., 1991; Follett and Hatfield, 2001; Galloway et al. 1995; Hallberg, 1987, 1989; Hatfield and Follett, 2008; Keeney, 1982, 1989; Laegreid, et al., 1999; Mosier, et al., 1998; Power and Schepers, 1989; SCOPE 65, 2004).

Excessive Nr is directly associated with the need for food production. Prior to the development of the Haber-Bosch process, natural biological N fixation (BNF) of N_2 gas was the dominant source of Nr. The Nr made available by BNF was less than the demand for Nr in most terrestrial and aquatic ecosystems. Consequently, the amazingly diverse array of plants, animals, and microorganisms that evolved on Earth often existed under intensely N-limited conditions. Haber was a professor in Karlsruhe, Germany, where he demonstrated the feasibility of ammonia synthesis in 1909 from atmospheric N_2 gas and hydrogen from fossil fuels. Bosch, an engineer at BASF in Ludwigshafen, Germany, then overcame the engineering problems that were associated with the enormous pressure required by the process. Commercial fertilizer N production started in 1913 and since then has been critical for the production of food to meet the needs of increasing numbers of humans. The Haber-Bosch process has been called the most important invention of the 20th century, because it allowed for the production of inexpensive fertilizer N to produce food for rapidly growing populations and is said to have "detonated the population explosion," driving the World's population from ~1.8 billion in 1913 to 6.7 billion in 2009 (US Census Bureau, 2009). Nearly one century after its invention, the process is applied all over the world. In 2002, world production of nitrogenous and total fertilizer production was ~90 and ~148 million metric tons (MMt), respectively (Food and Agriculture Organization, 2004). US agriculture is directly responsible for well over 10% of all national energy consumption, with the equivalent of 1,514 liters (400 gallons) of oil required to feed each American per year; about one-third of that amount goes toward fertilizer production (Heinberg, 2005). The use of fertilizer N allows the world's farmers to feed 70 million more people each year. However, our dependence on Nr and problems associated with its management will only increase as the global population moves from the present 6.7 billion to over 9 billion people projected by 2050 (US Census Bureau, 2009).

Many ecological problems occur with increased inputs of Nr into the environment. Although the focus of this book is upon water quality, the importance of managing Nr is much broader and extends to numerous issues associated with excessive Nr in the environment in general. Numerous transformations of Nr into its various combination and

bonding with H, O, and C contribute to its transport both by water and through the air. Because of the mobility of the various forms of Nr, ecosystem boundaries are crossed and intended beneficial effects often become unintended detrimental effects for adjacent ecosystems or even within the system that the use of Nr was intended to benefit. Within the terrestrial system, when Nr is separated from C, its most common partner (Asner et al., 1977), Nr can be transformed into many mobile forms by processes that include nitrification, denitrification, and nitrous and nitric oxide formation. The transformation of Nr can result in, for example, the interaction of nitrogen oxides and ammonium with fine particulates and ozone, leaching of nitrate and nitrite in water, and/or volatilization of and aerial transport of ammonia.

This chapter describes *N-transformation*, *N-form*, and *N-transport* and includes the descriptions of the processes and the potential impacts of Nr on ecosystems. The ecosystems addressed include the terrestrial, aquatic, and atmospheric ecosystems as well as the human biological ecosystem (i.e., human health) which may also be impacted by Nr. Society is placing an increasingly higher priority upon improved management of Nr because of the concerns that they perceive exist between the management of Nr and human health.

THE NITROGEN CYCLE

Nitrogen Transformation and Form

Various transformation processes occur because of the changes in and the various number of, valence states of the N atom. N can exist in numerous forms and varied types of compounds and is found in valence states between +5 (electron-poor) and -3 (electron-rich). In its many combined forms, Nr takes part in numerous reactions and is found in many compounds. Table 1 provides a brief scheme of the valence states and N compound formulas. The following discussion of the N-cycle describes transformation processes and refers to all but two of the N forms in Table 1. The two forms of Nr shown in Table 1 not discussed as part of the N-cycle or the impacts of Nr on ecosystems are *hydroxylamine* and *hydrazine*. A very pure, ≤ 50 wt %, stabilized solution of *hydroxylamine* is considered safe. However extensive stabilizer additives and proper containment are vital for its safe storage. Safe handling and storage of hydroxylamine requires prevention of contamination with metal ions and avoiding excessive temperatures (above 35°C). Pure free base hydroxylamine is estimated to have the approximate decomposition energy of trinitrotoluene (TNT) and can be highly dangerous (Brookhaven National Laboratory, 1999). The second Nr molecule is *hydrazine*, a highly reactive base and reducing agent that can be used as a high-energy rocket propellant, as a reactant in fuel cells, an ingredient in nickel plating, to polymerize urethane, to remove halogens from wastewater, to inhibit corrosion in boilers, and in photographic development (Von Burg and Stout, 1991).

Table 1. Form of reactive nitrogen (Nr), formula, valence, and general chemical/physical state.

| Ion or molecule | Formula | Valence of Nr | General state |
|------------------|------------------------|---------------|------------------------------|
| Nitrate | NO_3^- | +5 | Ion, highly soluble in water |
| Nitrogen dioxide | NO_2 | +4 | Gaseous |
| Nitrite | NO_2^- | +3 | Ion, highly soluble in water |
| Nitric oxide | NO | +2 | Gaseous |
| Nitrous oxide | N_2O | +1 | Gaseous |
| Elemental N* | N_2 | 0 | Inert gas |
| Hydroxylamine | NH_2OH | -1 | Liquid (>8°C) |
| Hydrazine | N_2H_4 | -2 | Oily liquid / white crystal |
| Ammonia | NH_3 | -3 | Gaseous |
| Ammonium | NH_4^+ | -3 | Ion, highly soluble in water |

* N_2 is nonreactive N.

The discussion of the transformation processes within the N-cycle can begin in the upper left corner of Figure 1 with *biological nitrogen fixation (BNF)*. Symbiotic and non-symbiotic organisms can fix atmospheric N_2 gas into organic N forms. A few living organisms are able to utilize molecular N_2 gas from the atmosphere. The most well known of these organisms are the symbiotic bacteria Rhizobia (legume bacteria); nonsymbiotic free-living bacteria such as Azotobacter and Clostridium; and blue-green algae. Generally, in a symbiotic relationship one organism uses light energy and contains chlorophyll to produce carbohydrates. The other organism receives some of the carbohydrates to use as an energy source to enzymatically fix atmospheric N_2 into the ammonia (NH_3) form of N and then into amino acids and other nitrogenous compounds that are nutritionally useful to the chlorophyll containing organism. For agricultural purposes the most important type of BNF is symbiotic fixation by legumes (i.e., alfalfa, clovers, peas, beans, etc.).

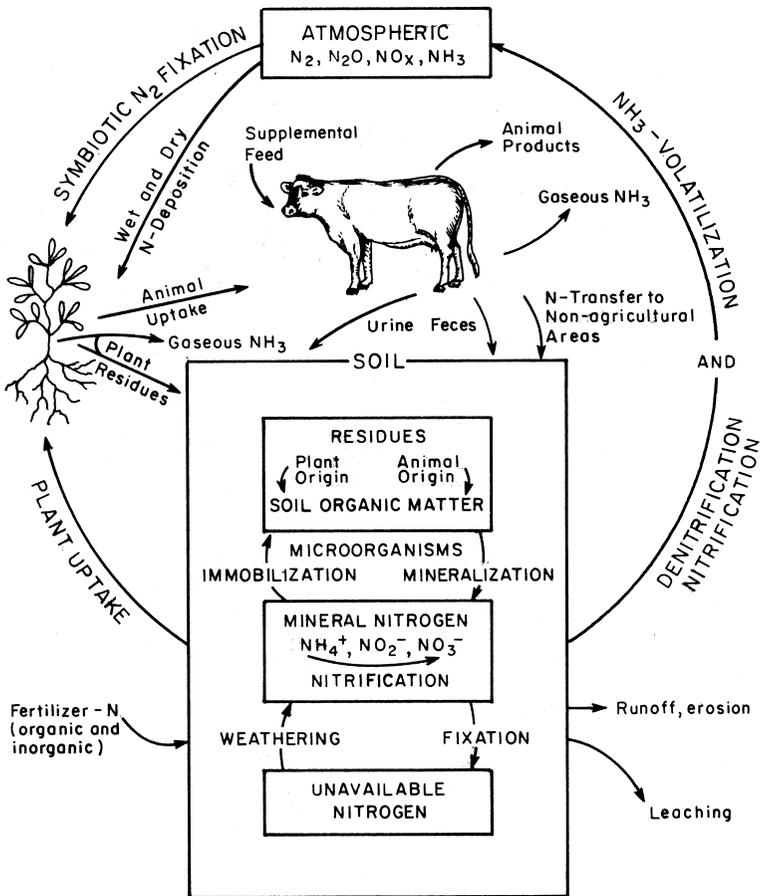


Figure 1. Agriculture and the nitrogen cycle.

The N_r that is taken up by plants from the soil is generally in the form of NO_3^- or NH_4^+ ions that can remain as residual N_r in the soil or originate from indigenous organic and/or inorganic forms. Organic N is associated with organic C and occurs naturally as part of the soil's organic matter fraction; it can also be added to the soil from manure, plant residues, and other sources. Soil microorganisms and their activities are an integral part of the *immobilization and mineralization* transformation processes in soil (Figure 1); soil-organic N can be transformed to ammonium (NH_4^+) by the process of *ammonification* and subsequently to nitrate (NO_3^-) through the process of *nitrification*. Inorganic (mineral) forms of N_r include NH_4^+ or NO_3^- , both readily taken

up by crops and nitrite (NO_2^-) that occurs as an intermediate form during mineralization of NH_4^+ to NO_3^- . Even though NH_4^+ is the preferred form, microbes in soil can utilize either NH_4^+ or NO_3^- . *Immobilization* of NO_2^- and NO_3^- back to organic forms of N can also occur through enzymatic activities associated with plant or microbial N uptake and N utilization processes. Microbes and soil animals use organic matter in soil as food and excrete nutrients in excess of their own needs. When NH_4^+ is released, it is called *mineralization*. When dimolecular-oxygen (O_2) is present, microbes in the soil can readily transform NH_4^+ to NO_3^- with NO_2^- as an intermediate form, a process called *nitrification*. This is a fairly rapid process that, under aerobic conditions, can be completed in a few days. Although NO_2^- can potentially accumulate in soils under some conditions, it usually does not, because it is rapidly transformed to NO_3^- as part of the *nitrification* process or else it is *denitrified*.

Ammonium ions in the soil solution enter into an equilibrium reaction with NH_3 while in the soil solution. The NH_3 dissolved in the soil solution is, in turn, subject to gaseous loss to the atmosphere. Soil pH and concentration of NH_4^+ in the soil solution are important factors affecting the amount of NH_3 loss to the atmosphere. As soil pH increases, the fraction of soil-solution NH_4^+ plus soil-solution NH_3 in the NH_3 form, increases by an order of magnitude for every unit of pH above 6.0; thus, increasing the loss of soil-solution NH_3 to the atmosphere. The process of *NH_3 volatilization* is of most significance in calcareous soils, especially in low cation exchange capacity (CEC) soils such as sands with alkaline or even neutral pH. Losses can be high when high N organic wastes, such as manure, are permitted to decompose on the soil surface and from urea applied to grass or pasture as a result of hydrolysis of the urea to NH_3 by indigenous urease enzyme.

Anhydrous (gaseous, NH_3) is a very important direct-application N fertilizer. Gaseous NH_3 , in contact with moist soil, dissolves in and reacts with soil water to form NH_4^+ and OH^- ions. The pH is increased dramatically and immediately around the anhydrous NH_3 application-zone. Dependent upon buffering capacity of the soil and the resulting soil pH, equilibrium is approached between the soil solution NH_4^+ and NH_3 and gaseous NH_3 . If anhydrous NH_3 is placed in dry soil or at a too shallow depth, the NH_3 is subject to *volatilization*. *NH_3 volatilization* losses from livestock manure and urine can be particularly important in pasture systems. Herbage fouling by feces reduces its acceptability for grazing, thereby increasing maturity and reducing forage quality and/or consumption by grazers. Urine does not cause herbage to be unacceptable for grazing. Livestock recycle much of the N that they consume from forage back to the soil. Excretion in the forms of feces and urine both result in volatile losses of NH_3 . About 74% of the total N excreted is in the urine (Follett and Wilkinson, 1995) and a single urine spot can have an N concentration corresponding to more than 600 kg N ha^{-1} (Whitehead, 1995). Some of the N is released to the atmosphere as volatile NH_3 , while the N remaining in the excreta and its associated

plant residues return to available nutrient pools in the soil. Consumption and excretion of N by ruminants results in the gathering of N from larger areas of the pasture and deposition to smaller areas. This uneven distribution means some areas will be under fertilized and some areas will be over fertilized. Animals on range may use more of the forage near watering points. Greater density of dung and increased soil-profile NO_3^- is frequently observed in areas near watering and shade points (Haynes and Williams, 1993; Wilkinson et al., 1989).

Other inputs of Nr include those from fertilizers, wet and dry deposition from the atmosphere, and *mineralization* of soil organic matter (Figure 1). Losses may occur through harvesting of animal or plant products, transfer of N within the pasture with animal excreta, *fixation* of N in the soil, soil erosion, surface runoff, leaching, volatilization, and denitrification. The soil compartment includes a pool of available Nr (NO_3^- and NH_4^+) for plant uptake that is in equilibrium with N in residues (organic N) and for some soils with *fixed* NH_4^+ held between mineral layers of the clay. Plant uptake is from the available soil pool. The N in the herbage can be harvested and removed from the field, returned to the soil as crop residue and root material, eaten and thereby either utilized by the grazing animal or returned to the soil as feces or urine.

As organic matter in soil decomposes to release NH_4^+ or when $\text{NH}_3/\text{NH}_4^+$ forms of fertilizer are used, NO_2^- and finally NO_3^- ions are formed by *nitrification* (Figure 1 and 2). Nitrite usually does not accumulate in soil because of its rapid transformation to NO_3^- or it is *denitrified* to N_2 gas, nitrous oxide (N_2O), nitric oxide (NO), or another gaseous N oxide (NO_x) compound. Nitrate can also be lost to the atmosphere through *denitrification*. Nitrous oxide, a product of *incomplete denitrification*, is a greenhouse gas that contributes to global climate warming, and contributes to the potential thinning of the ozone layer. Not only *denitrification* (a reductive process), but also the oxidative process of *nitrification* causes emission of a small amount of N_2O (Tortoso and Hutchinson, 1990). However, *denitrification* is the route for most losses of gaseous N compounds to the atmosphere. The potential for *denitrification* is increased as O_2 levels in the soil decreases. Under favorable environmental conditions, *Nitrosomonas* spp. bacteria in the soil readily transform NH_4^+ to NO_2^- that is in turn transformed by *Nitrobacter* spp. bacteria to NO_3^- (Figure 1 and 2). The small quantity of N_2O produced in aerobic soils during *nitrification* of NH_4^+ is a direct metabolic product of chemoautotrophic NH_4^+ -oxidizing bacteria or it results from other soil processes that depend on these organisms as a source of NO_2^- (Tortoso and Hutchinson, 1990). The source of the NH_4^+ can be from ammonia containing fertilizers, the hydrolysis or mineralization of N in manure, from soil organic matter, or other organic materials.

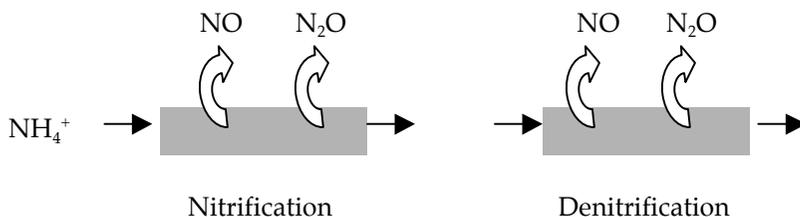


Figure 2. A conceptual model of the two levels of regulation of N trace gas production via nitrification and denitrification that includes flux of N through the process “pipes” and holes in the pipe through which N-trace gases “leak” (Firestone and Davidson, 1989).

NITROGEN EXCHANGE ACROSS ECOSYSTEM BOUNDARIES

Nitrogen Transport

The transport of N is especially important when it results in moving N_r into water bodies, across ecosystem boundaries, and into the atmosphere, which causes harmful effects to ecosystems or to a biological system. N_r , based upon its form, can move by the processes of *water and sediment associated transport* and by *atmospheric transport*. The transport of N_r can be between the atmosphere, terrestrial, and aquatic ecosystems (Figure 3). The examination of the “agro effects” (Figure 3) shows the interplay and essential link between the natural environment and humans. Agro effects relate to the human focus on production of needed animal and plant products, but can also involve environmental modifications to support the “agrosystem.” The products are consumed through human activities represented on the left hand side of the Figure 3 by the direct use of products such as food and fiber as well as indirectly through energy production and use. Humans actively assist agriculture by providing needed sustenance, or in this example, the N_r transported and applied as fertilizer-N into agricultural systems.

Most plants, animals, and microorganisms are adapted to efficiently use and retain small increments of additional N_r . Thus, addition or transport of additional N_r to most ecosystems first leads to increased uptake, storage, and use. Such additions to agrosystems leads to increased food and fiber production, but further additions of N_r beyond an optimal amount leads to imbalances in the N-cycle and potential leakages of different forms of N_r to the other compartments (Figure 3) and can also result in feedback effects that affect human health.

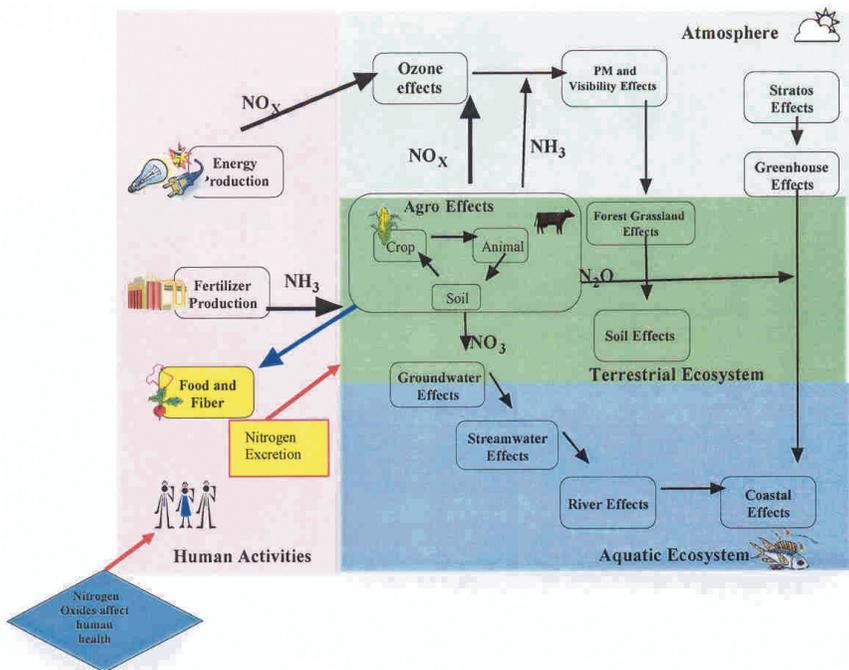


Figure 3. Ecosystems and reactive nitrogen (Nr) transport (adapted from Cowling et al., 2001; Galloway et al., 1993).

Water and Sediment Transport

Nitrogen and aquatic ecosystems. The Nr that reaches aquatic ecosystems can be from airborne, surface, underground, and in situ sources (Figure 3). Water quality impact zones for N are wells, ground water supplies, streams, and surface water bodies. Because 95% of rural inhabitants and substantial livestock populations consume ground water, NO_3^- concentration is most important and can cause both human and animal health effects (Follett and Follett, 2001, 2007). Those factors that control NO_3^- concentration in groundwater, such as dilution and well position relative to the primary source areas for NO_3^- , can greatly affect their impact on ground water quality. In contrast, stream flow tends to mix ground water discharge and surface runoff from different land uses and time periods, thus causing generally much lower and more stable NO_3^- concentrations. Although elevated concentrations of NO_3^- are most often observed at shallow water table depths, long term increases in deeper wells are possible where deep aquifers are recharged by water rich in NO_3^- . Movement of NO_3^- with percolating water through the unsaturated zone can be very slow and the time required for present-day inputs of NO_3^- to reach the ground water reservoir may take many years. Schuman et al. (1975) observed an average rate of NO_3^- movement

through loess (silt) in Iowa of about one meter per year. Where 168 kg N ha⁻¹ (the recommended N rate) was applied, N did not accumulate beneath the crop-root zone. Ground water flows from areas of high pressure toward areas of low pressure (hydraulic head). Movement is slow and little mixing of contaminated with uncontaminated ground water occurs as they flow through the saturated zone. Contaminants tend to remain concentrated in zones but because of the slow rate of movement and lack of dilution, contamination may persist for decades and centuries, even if input sources of NO₃⁻ are decreased or eliminated. Unfortunately, reclamation is generally technically and economically impossible in most cases (Keeney, 1982).

Water transport. Leaching of NH₄⁺ is generally not important, since it is strongly adsorbed by soil, except for sands and soils having low retention (cation exchange) capacities. The NO₃⁻ ion is readily leached deeper into the soil profile, below the bottom of the root zone, and may eventually enter ground water supplies. Ground water flows within permeable geologic formations called aquifers (Figure 4). Aquifers are natural zones beneath the earth's surface and often yield economically important amounts of water. The Nr often observed in streams that drain agricultural land primarily comes from ground water contributions (including tile-drainage effluent) to stream flow, rather than from overland-flow runoff of Nr. In a very simple system, water and dissolved NO₃⁻ percolate below the root zone and through the intermediate vadose zone to an aquifer. From there, these waters can recharge deeper aquifers or discharge to streams or water bodies. During discharge events, the ground water and its NO₃⁻ load will include shallow interflow (sometimes referred to as subsurface runoff). NO₃⁻ and NO₂⁻ ions are both highly soluble and susceptible to transport in water. The NO₂⁻ ion is seldom a major Nr form because it is rapidly transformed to NO₃⁻. During a majority of the time, deeper ground-water baseflow provides the major contribution of NO₃⁻ as it rejoins surface-water flows (Hallberg, 1989). Deeper aquifers can be recharged by, or discharge to, streams or water bodies. Aquifers are subdivided based upon geology. A meaningful division, from the perspective of ground water quality, is between confined and unconfined aquifers. Confined aquifers are separated from the Earth's surface by flow-impeding layers that, depending upon the degree of flow impedance, are referred to as aquicludes or aquitards (Figure 4).

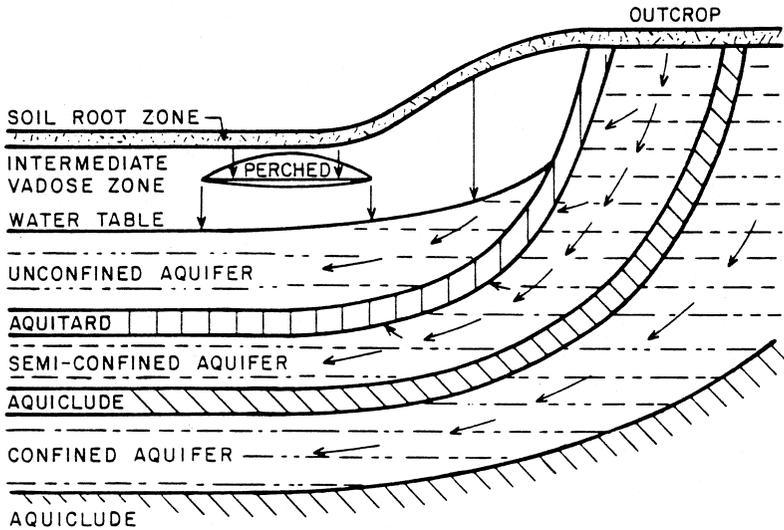


Figure 4. Schematic of vadose zone, aquifer system, and flow direction (from Pionke and Lowrance, 1991).

Unconfined aquifers are not separated from the Earth's surface by a flow-impeding layer, and are therefore in contact with the atmosphere through the unsaturated zone. Aquifer systems are often complex. To minimize the amount of NO_3^- that may enter groundwater, it is necessary to understand the aquifer system and then to identify and apply improved N management practices to the recharge area of the aquifer. Structure of the aquifer system and subsequent flow patterns affect NO_3^- dilution, transport, and removal. Groundwater can rejoin the surface water down-slope and adjacent to a perennial stream, often along a riparian zone. During storms or wet periods, the water table can rise rapidly to intersect the land surface at some distance from the stream and discharge of ground water to the soil surface results. The system can be dynamic, with water table levels, extent of the saturated zone, and flow directions changing substantially and rapidly with precipitation (Pionke and Lowrance, 1991). As the ground water and its dissolved NO_3^- move into the more biologically and chemically active soil zones, the NO_3^- becomes available for uptake by riparian vegetation. Also, if O_2 level become limited, activation of biological and chemical soil regimes denitrify the NO_3^- form of N to the gaseous N_2 form.

Sediment transport. The transport of N in association with eroding sediments contributes much of the Nr that enters lakes and rivers. The Nr species transported with sediment primarily includes the NH_4^+ ion, because it is sorbed to the CEC of the surfaces of clay and finer sediments, and the Nr that is dissolved in surface runoff (primarily

NO_3^-). Also, when the C-N bonds within the soil organic matter (SOM) associated with sediments are broken both NH_4^+ and NO_3^- ions are formed. The water that runs over the soil surface during a rainfall or snowmelt event, by rill or sheet flow, or even high-order channelized flow, may have a relatively high concentration of SOM and organic N that is attached to suspended particulate matter, but the concentration of NO_3^- is typically quite low. Soil erosion is important to the movement of N into surface water, which primarily occurs in association with water-borne sediments rather than by wind. Some of the sediment may travel only a few millimeters, while other sediments may be transported long distances before either being deposited or reaching a surface water resource (e.g., lake, reservoir, or stream). The NO_3^- form is completely water soluble and thus not sorbed to the CEC and moves with the water until it re-enters the available soil pool, is utilized by microbes or plants, becomes denitrified, is possibly deposited and buried, or enters and possibly degrades surface and/or ground waters. A major source of N that degrades surface water is transported in soil organic matter. A large part of the SOM and soil organic N (SON) are concentrated near the soil surface and are, therefore, vulnerable to erosive and oxidative (mineralization/nitrification) processes. When sediments and associated nutrients are detached from the parent soil, the process is selective for soluble nutrients (such as NO_3^-) and fine soil fractions that are associated with nutrients (for example NH_4^+ and the SON). Therefore, N contained in runoff and/or associated with sediments is present in higher concentrations than in the parent soil. This difference is termed the enrichment ratio. Enrichment of sediment loads is a two-step process: enrichment during particle suspension and enrichment due to redeposition of coarser particles during overland and channel flows. Soil erosion by water produces and transports sediment-associated N. Management practices to decrease the effect of sediment transport on aquatic ecosystems must protect against the processes of detachment and transport of the soil particles by raindrops or surface flow and enhance the process of deposition of sediments and particulates within the landscape rather than allowing their movement into surface water (Foster et al., 1985).

Dredging. Dredging is used to maintain and establish waterways and harbors within the US and moves about 300 million m^3 of sediment each year (Dickerson and Dickerson, 2002). Loss of topsoil and the SON contained in dredged sediments is a primary environmental impact of accelerated soil erosion. Two independent methods of estimating the amount of eroded SON are to utilize information about river sediment loads or to use estimates of amounts of eroded sediments themselves. Data by Leeden et al. (1991) showed that the suspended sediment load was 336,000 Gg y^{-1} in 12 major US rivers during 1991. Assuming that 75% of the suspended load (mostly due to soil erosion) was contributed by cropland, the sediment transport attributed to cropland is $\sim 250 \text{ MMt y}^{-1}$. If a delivery ratio of 10% and a SON content in eroded sediment of 0.25%

is estimated (Lal, 1995; Follett et al. 1987), the total SON displaced by soil erosion from cropland would be about 6.25 MMt y^{-1} . Alternatively, Lal et al., (1998) used an estimate of the amount of eroded sediments to calculate soil organic carbon (SOC) losses. By assuming a SOC:SON ratio of 110:9 in sediment (Follett et al. 1987), the total SON displaced by soil erosion would be about 9.6 MMt y^{-1} . Thus considering only the US, soil erosion serves as an environmental source of 6 to 9 MMt N y^{-1} of SON. These amounts can be compared to the US consumption of manufactured N fertilizer, which was 10.9 MMt in 2002 (FAO, 2004).

A lot still needs to be learned about managing cropland soil erosion. For example, Follett et al. (1987) assessed effects of tillage practices and slope on amount of organic N in eroded sediments from cultivated land surfaces in Minnesota, US, for major land resource areas (MLRAs) 102, 103, 104, and 105. Their estimates, using the Universal Soil Loss Equation (USLE), average organic matter in topsoil by slope category, and dominating slope gradient and soil series, indicates that conservation tillage compared to conventional tillage decreases the amount of organic N associated with eroded sediments by about half with some additional decrease resulting from the use of no-tillage. One can assume that added fertilizer N responds similarly to organic N when sorbed to clay surfaces, finer sediments, or to soil organic matter.

Atmospheric Transport

The forms of N_r that are most subject to atmospheric transport (Table 1) include NH_x (NH₃ + NH₄⁺), NO_x (NO + N₂O), and NO₂. With the exception of NO₂ (to be discussed below) transformation processes that form these compounds are discussed above. Their importance is that the emission of NH₃ and NO_x (both biologically and chemically active) into the atmosphere serves to redistribute fixed N to local and regional aquatic and terrestrial ecosystems that otherwise may be disconnected from the sources of the N gases. In addition, the emissions of NO_x can contribute to local elevated ozone concentrations, while N₂O emission contributes to global warming and stratospheric ozone depletion (Mosier 2001a, 2001b; Oenema et al., 2001).

NH_x emissions to the atmosphere include those from ammonium fertilizers, livestock feces and urine, and possibly from various organic materials. The transport of volatilized NH₃ into the atmosphere results in its subsequent airborne transport (Figures 1 and 3). On a global scale, livestock farming is a major source of the total NH_x that is emitted into the atmosphere (Table 2). From 1961 to 1994 the NH₃ from animal production increased 54% from 14.2 to 22.1 Tg N y^{-1} and NH₃ emissions from use of synthetic fertilizer increased from 1.4 to a maximum of ~9 Tg N y^{-1} (Mosier 2001a). Most of NH₃ evolved from terrestrial systems, such as confined animal operations, is redeposited within 20 km of the point of emission, thus NH_x deposition near cattle production operations can be substantial. For example, when collected in acid traps located 2 km from the feedlot NH_x from a 90,000 head cattle feedlot was 30 kg N ha⁻¹

y⁻¹ greater than that collected 15 km from the feedlot (Hutchinson and Viets, 1969). Therefore feedlots or major livestock operations need to be considered in fertilization budgets for nearby crops.

Table 2. Total global NH₃ emission estimates adapted from Bouwman et al. (1997) for 1990 (Mosier 2001a, 2001b).

| Source | NH ₃ -N emission | |
|--------------------------------|-----------------------------|--------------------------------|
| | Estimate (Tg N) | Uncertainty of estimate (Tg N) |
| Excreta from domestic animals | 21.6 | 10–30 |
| Excreta of wild animals | 0.1 | 0–1 |
| Synthetic fertilizers | 9.0 | 4.5–13.5 |
| Biomass burning | 5.9 | 3–7 |
| Soils under natural vegetation | 2.4 | 0–10 |
| Oceans | 8.2 | 3–16 |
| Fossil fuel combustion | 0.1 | 0–0.2 |
| Industrial processes | 0.2 | 0.1–0.3 |
| Human excreta and pets | 2.6 | 1.3–3.9 |
| Crops and crop decomposition | 3.6 | 1.4–5.0 |
| Total emission | 54.0 | 40–70 |

When NH₃ is dissolved in water, ammonium ions (NH₄⁺) and hydroxyl ions (OH⁻) form as the dominant basic compound in the atmosphere and readily react with acidic gases and particulates to form hygroscopic salts of ammonium sulfate and ammonium nitrate. The reactions occur very rapidly (a few hours to a few days in the troposphere), so NH₃ is rapidly removed from the atmosphere through deposition as NH₃ and NH₄⁺ in precipitation particulates (Ferm, 1998) or through foliar absorption of NH₃ (Schjoerring and Mattsson, 2001). NH_x and other highly water soluble compounds are mainly dispersed in the so-called “mixing layer” of the lower troposphere. Transport distances within the mixing layer depend upon wind speed and the deposition rate. Model estimates indicate that ~50% of emitted NH₃ is redeposited to the Earth’s surface within 50 km of the emission source (Ferm, 1998). When gaseous NH_x reaches the top of the mixing layer (500 to 1500 m), the NH_x can be transported long distances. When clouds within the mixing layer contain water, the NH_x concentration is halved every 10 km from the source (or every 30 min.). If there is no precipitation, the NH_x concentration is halved every 1400 km (or every third day) (Ferm, 1998). Ferm (1998) also estimated that in Europe, the half-life of NH_x is 3 to 6 hours over a distance of 65-130 km. Atmospheric residence times and transport distances of NH_x are sufficiently long for significant interaction with terrestrial and aquatic systems far removed from the source of the NH_x (Nadelhoffer, 2001).

NO_x and NO₂ are two forms of N that are readily transported from the terrestrial ecosystem into the atmosphere. NO_x (NO plus N₂O) from

agricultural systems is the direct product of *nitrification* and *denitrification* through microbial transformation (Figure 2). The major source of NO_x globally is from fossil fuel burning (~58%), biomass burning (~21%), and emissions from soil (~15%) (Holland et al., 1997; Delmas et al., 1997; Wuebbles et al., 2003). The importance of N_2O is as a greenhouse gas (GHG). Over 100-yr the global warming potential of 1 kg N_2O is 296 times higher than that of 1 kg CO_2 gas (Energy Information Administration, 2005). Biological N_2O formation is enhanced by increases in available mineral N that increases nitrification, denitrification, and N_2O production. N-fertilization results in N_2O formation in the field in which the N-fertilizer is applied. The *Intergovernmental Panel on Climate Change Guidelines for National Greenhouse Gas Inventories* (Intergovernmental Panel on Climate Change, 1997; Mosier et al., 1998) refers to N_2O emissions directly from agricultural fields as direct emissions. These N inputs may also lead to 'indirect N_2O emission' after the original N inputs are leached from or run off of the fields surface and result in additional gaseous losses and deposition of NO_x and NH_3 , follow animal and human consumption of agricultural products and deposition of waste or processing in sewage systems (Intergovernmental Panel on Climate Change, 1997). Some part of the animal manure N, crop residue and sewage may have come from previous application of synthetic fertilizer. The re-entry of this N back into the soil system renders it again susceptible to microbial processes that produce N_2O .

Gaseous N in the troposphere. The reaction of NO_x with ground-level ozone is important, because once in the atmosphere, NO_x generally remains in the lower troposphere, where it interacts with volatile compounds. N_2O stays in the atmosphere and acts a greenhouse gas. NO and NO_2 play a role as important regulators for ground level (tropospheric) ozone production. Ground level ozone is formed when NO_x (mainly NO and NO_2) and reactive organic gas (ROG) react in the presence of sunlight (ozone formation is highly dependent on intensity of sunlight). ROG sources are from motor vehicles, solvents in paints, consumer and industrial products, natural emissions from plants and petroleum seeps, and processes in the petroleum industry. Since ozone is not directly emitted into the atmosphere but is formed as a result of the interaction of other compounds, it is classified as a secondary pollutant and is considered 'regional' because it occurs in a larger area than from which the original pollutants were emitted.

Because ozone-forming reactions take time, peak concentrations of ozone are often several miles downwind of major source areas, especially during single direction and persistent winds. Once there is a release of NO_x and ROGs, sunlight stimulates a series of chemical reactions occurring over a period of several hours. Thus, there is much less ozone production in the winter and no production of ozone during the night. The photochemistry of ozone production is complicated by several competing reactions that involve free radicals. A simplified

explanation of the series of reactions is provided below. For the purpose of this report, there are four main reactions that determine net production and decomposition of ground level ozone.

The reaction begins when the emissions of NO₂ (increasingly from internal combustion engines) are exposed to sunlight (Equation 1). This step, also called photolysis of NO₂, releases NO and a reactive single oxygen atom (O) that binds itself to molecular O₂ to form ozone (O₃) (Equation 2).



The photolysis of nitrogen dioxide (NO₂) will not give any net production of ozone, since ozone and nitric oxide (NO) react to form NO₂, which completes the chain reaction (Equation 3).



For the net formation of ozone, there must be a competing reaction that oxidizes NO back to NO₂. This competing reaction is driven by oxygen rich hydro or organic peroxy (RO₂) radicals (Equation 4). Organic compounds (ROGs) and carbon monoxide (CO) are the main sources of the peroxy radicals.



The main sink for ozone is surface deposition. Vegetation is a major recipient of ozone, which enters the stomata of plants where it destroys organic molecules in tissues. The main sink for ozone in polluted areas is decomposition through nitric acid formation (Equation 5), which contributes to acid deposition.



The relative roles of ROGs and NO_x can be summarized as follows. The downwind areas that receive ROGs produce ozone in an area determined by the availability of NO_x. The availability of NO_x determines the spatial extent of ozone production, while the availability of ROGs determine the rate of ozone formation.

Gaseous N in the stratosphere. The relationship of NO_x to ozone destruction has rather profound implications because of its interruption of the formation of ozone. In the presence of sunlight there is an equilibrium formation of ozone (O₃) from mono- and di-molecular O₂ (Equation 6) with the O₃ serving to shield against incoming ultraviolet (UV) radiation (National Atmospheric and Space Administration, 2010).



Ozone (O_3) is a very small part of our atmosphere, but its presence is nevertheless vital to human wellbeing. Most O_3 resides in the upper part of the atmosphere. This region, called the stratosphere, is more than 10 kilometers (6 miles) above Earth's surface. Approximately 90% of atmospheric O_3 is contained in the "ozone layer," which shields us from harmful UV light from the Sun. However, some human-produced chemicals (US Environmental Protection Agency, 2006) destroy and deplete the O_3 layer. The resulting increase in UV radiation at Earth's surface can increase the incidences of skin cancer and eye cataracts. Among the chemicals that destroy O_3 are NO and NO_2 , as well as chlorofluorocarbons (CFCs) for refrigeration and air conditioning, foam blowing, and industrial cleaning. The NO and NO_2 react with the O_3 to breakdown the ozone and tie it up. The destruction of O_3 involves two separate reactions. The cycle can be considered to begin with either NO or NO_2 ; the first reaction is when NO reacts with atomic O to form NO_2 (Equation 7).



The atomic O is formed when UV sunlight reacts with ozone and oxygen molecules. The NO_2 then reacts with (and thereby destroys) ozone and reforms NO (Equation 8). The cycle then begins again with another reaction of NO with O. Because NO_2 and NO are reformed each time an ozone molecule is destroyed, the NO_2 is considered as a catalyst for ozone destruction.

AGRICULTURAL PRODUCTION AND HEALTH

Crops

Because N is the most limiting nutrient for plant growth, its application is a benefit to humans and their livestock in terms of higher biomass and protein yield and N concentration in plant tissue is commonly increased. As discussed by Blumenthal, et al. (2001), N affects amino acid composition of protein and the nutritional quality of crops grown for human and animal food. Increasing the N supply generally improves kernel integrity and strength in grains, and thus the milling quality. However, too much N tends to decrease the relative proportions of lysine and threonine, which can reduce the feed and or food value of the protein. Fertilization of oil seed crops improves protein levels but may decrease oil concentration and the effects of N on oil composition and quality can be inconsistent. In root crops such as sugarbeets, N fertilization increases yields, but can reduce sucrose concentration per

unit of fresh matter and decrease the efficiency of sucrose extraction because of increased impurities (alpha-amino-nitrogen, invert sugars, and lime salts). Nitrogen supply to potatoes is managed according to market classes (table stock, French fries, and potato chips), which require different quality parameters and primarily influences tuber size, dry matter, and sugar contents.

Livestock and Forage

About 60% of the agricultural land in the United States is kept in grassland pasture and cropland used only for pasture (USDA, 2005). Nitrogen is the most limiting factor for grassland productivity. Hence, application of N fertilizers profoundly affects grassland systems in many ways. At low rates, N fertilization increases forage yield with little effect on forage N. It stimulates tiller development, increases leaf size, and lengthens the period of green leaves (Rhykerd and Noller, 1974). At a higher level of N fertilization, yield and N concentration in the forage are increased. Increased water content and decreased soluble carbohydrates are commonly observed after N fertilization of grasses (Messman et al., 1991; Brink and Fairbrother, 1992). Nitrogen fertilization of forages may at times affect forage digestibility. Van Soest (1982) reported that as N fertilization increased lignin, production and digestibility were reduced, but Messman et al. (1991) and Puoli et al. (1991) found that rate of neutral detergent fiber digestion and with it animal feed intake were increased. Nitrogen fertilization of forages was more likely to increase digestibility of warm season grasses because of their lower N content as compared to cool season grasses (George and Hall, 1983). The main beneficial effect of N fertilization of forages and on meat production per unit of land, is increased yield resulting in increased carrying capacity (Wedin, 1974). In warm season grasses, many studies found that increased N fertilization resulted in greater animal weight gain (Rhem et al., 1975; Perry and Baltensperger, 1979).

Most of the N taken up by the forages is incorporated into protein, however 10% to 30% exists in the plant as non-protein N, mainly amino acids, nitrate, and secondary plant metabolites (Dougherty and Rhykerd, 1985). Accumulation of NO_3^- within forages can be a problem under conditions of high N supply and impaired photosynthesis, e.g. low level of solar radiation or drought stress (Stritzke and McMurphy, 1982). Nitrogen fertilization also impacts the mineral composition of forage. For example, if N is supplied in NH_4^+ form then the uptake of cations (Ca^{++} , Mg^{++} , and K^+) is lowered (George and Thill, 1979). Grass tetany, a ruminant nutrient imbalance, may be induced by lower Mg^{++} concentration. Nitrogen application is reported to increase the concentration of total organic acids in forage (Follett et al., 1977). Wedin (1974) and Odom et al. (1980) suggested that increased alkaloid concentration in reed canary grass (*Phalaris arundinacea* L.) and tall fescue (*Festuca arundinacea* Scherb.) may be responsible for lower forage palatability, resulting in lower forage intake. Bush et al. (1979) observed

that accumulation of perfolone in tall fescue was a contributing factor to summer toxicosis syndrome.

Human Health

Humans impact the environment through their use of N, but N in the environment also has an impact on humans. The need by humans to produce and consume food and other agricultural products is increasing human demands for N. This need is directly related to increasing world population, demands for goods and services, and expectations. Nitrogen is contained in all of the amino acids and proteins in the foods consumed by humans and animals. Proteins are essential components in the human diet because, unlike plants, humans are unable to utilize more simple forms of N and thus rely on food sources, which can then be broken down into amino acids and used for protein synthesis in the body. Estimation of protein requirements for humans depends both on the content of essential amino acids and the protein digestibility (Fowden, 1981).

Humans participate in altering the cycling of N through daily activities. Figure 3 reflects how humans act as an external modifier of the N cycle through production and use of fertilizer, consumption of N in the form of protein, and emission of atmospheric pollutants. However, Figure 3 also demonstrates two other components to be considered for inclusion of humans in the nitrogen cycle. First, humans, like other animals, consume N as protein and then excrete N back into the cycle. Secondly, compounds produced through natural processes in the nitrogen cycle and various forms of N produced through human activities can directly affect human health when the compound enters their bodies. Similar to terrestrial, atmospheric, and aquatic ecosystems, *the concept proposed here is that the human body and other biological organisms can also be treated as 'smaller-scale' ecosystems* which have various forms of N transported into them, and therefore, can be impacted favorably (protein consumption) or harmfully (i.e., by toxic N compounds).

Exposure

A toxic compound or pollutant in the environment cannot affect an ecosystem (in this case the plant or human organism) unless exposed to it. In other words, the toxic compound must enter the organism and interfere through some mechanism of action with normal homeostasis (Landis and Yu, 2003; Burken, 2003). A common measure used in human health to determine the effects of a compound is exposure, uptake, transport, storage, metabolism, and excretion. A similar method may also apply to components within the ecosystem.

The effect of air pollution on plants offers an example of exposure (Figure 5). Exposure is dependent on how accessible the entrance and uptake are to the plant. One way in which airborne toxins enter is through the stoma which regulates entry of ambient air into the intercellular space. "Stomal resistance" is a mechanism the plant uses to

minimize uptake of air pollutants (Landis and Yu, 2003). The stomatal opening is regulated by levels of internal CO₂ and nutrient status of potassium (K). Temperature, water, and light are also involved in the regulation.

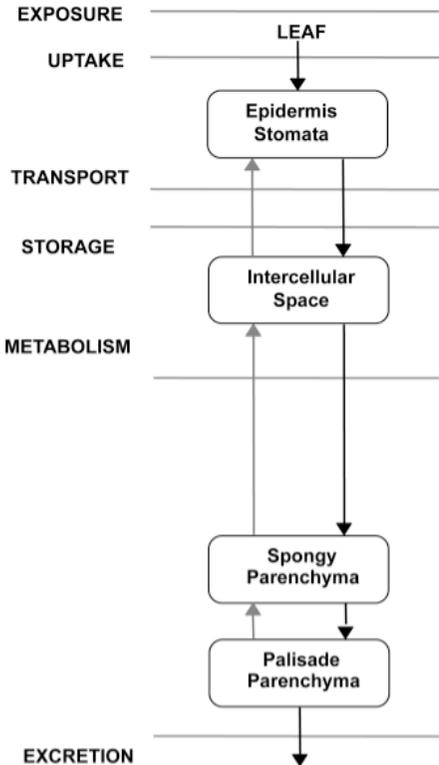


Figure 5. Exposure of plants to air pollution.

Human health can be defined as the interactions that occur between the internal biological system and the external environmental system. Routes for exposure of humans to toxins in the environment are similar to what was observed for the plant. In the human there are three major routes for introduction: the gut, skin and lungs (Figure 6). The source of entry can have a major impact on the severity and long-term effects (Landis and Yu, 2003). Once inside the body the toxin is likely be transported via the blood or lymphatic system. The storage site also depends on type of chemical. The liver plays a major role in the metabolism of toxins for secretion usually in urine. The last step is excretion of the compound.

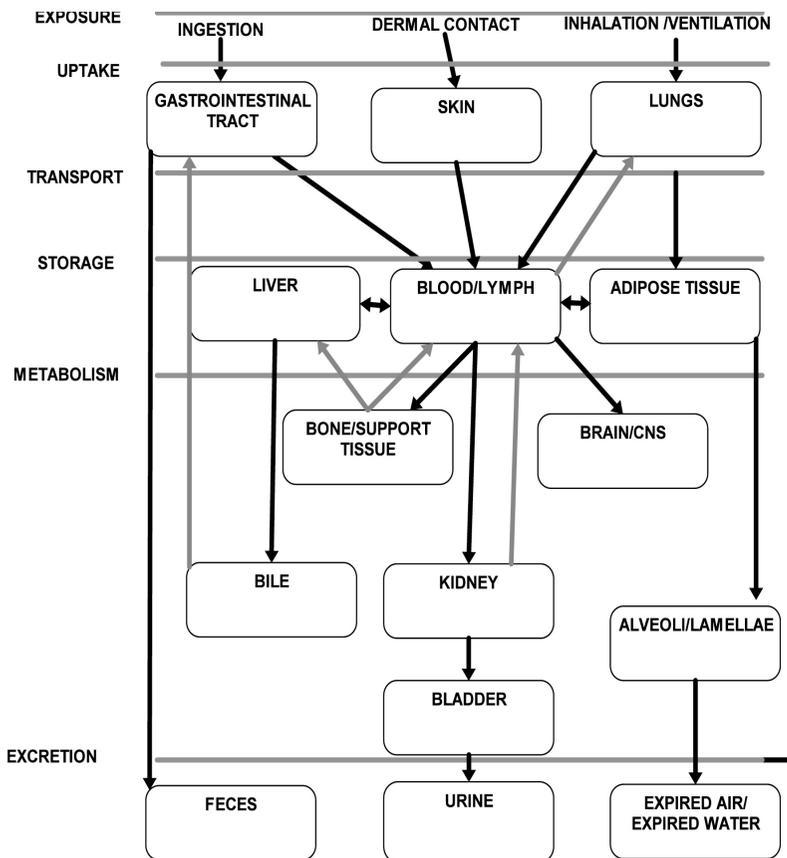


Figure 6. Pathways of human exposure to reactive forms of nitrogen (Nr).

Mechanism of Action

Toxic Nr-compounds. The manifestation of a toxic compound will affect the health of the organism. For example, NO_2 is taken in through the stoma and dissolves quickly in the internal plant water causing injury through acidifying the atmosphere or through a photo-oxidation process. A positive aspect to plant uptake of toxins is the concept of phyto-remediation in which the plant as opposed to excretion may modify and sequester the compound within the vacuole or cell wall. This is known as the Green-Liver model where plants excrete compounds by storing them in non-metabolic tissues (Burken, 2003). This method of 'storage excretion' uses similar enzymes and conjugation methods to those found in humans with the exception of humans excreting the conjugated compounds into urine.

Understanding mechanisms by which toxins act on humans is a key to health research. The four mechanisms that can be used to describe the basic action of the toxin are defined below.

1. **Disruption or destruction of cellular structure causing direct damage to the tissue:** An example is exposure to airborne NO_2 acting on the lungs. Another example is the formation of nasopharyngeal cancer-causing N-compounds during digestion, although rare in most countries, is high in areas of China, Greenland, and Tunisia (Mirvish, 1995). Dietary causes are thought to be associated with consumption of salted, dried products such as fish, which contain volatile nitrosamines such as dimethylnitrosamine, clearly shown to induce nasopharyngeal cancer in rats (Mirvish, 1995; Eichholzer and Gutzwiller, 1998). The salted and dried fish also contains amines that might participate in endogenous nitrosation (Magee, 1989).
2. **Direct chemical combination with a cell constituent:** NO_3^- consumption (specifically from water sources) by humans, especially infants and young ruminant livestock, can result in development of methemoglobinemia due to formation of NO_2^- derived from NO_3^- . The iron contained within hemoglobin in red blood cells is normally in the ferrous (reduced) state. Through oxidation, ferrous iron can be converted to ferric iron and this conversion to the oxidized state prevents transport of O_2 throughout the body. When ferrous iron in heme is converted to ferric iron the resulting hemoglobin is referred to as methemoglobin (MHb). Methemoglobin cannot transport adequate amounts of O_2 to supply the cells.
3. **Influence on enzymes through competition with a cofactor:** Nitrate appears to inhibit both uptake and retention of iodine by the thyroid. Nitrate is similar in size and charge to the iodide ion and appears to compete for the iodide binding site in the thyroid (Eskiocak et al. 2005). The effect on the thyroid is similar to that seen with the administration of thiocyanate and perchlorate anions, which also inhibit accumulation of iodide in the thyroid (Jahreis, et al., 1986). Human populations exposed to high NO_3^- levels in drinking water show a similar increase in thyroid volume and decreased levels of thyroid stimulating hormone. The effect is dose dependent with differences in thyroid volume occurring above 50 mg NO_3^-/L (van Maanen et al., 1994).
4. **Initiation of a secondary action upon ingestion:** A group of N-containing substances, the N-Nitroso Compounds (NOC), which include nitrosamines and nitrosamides are important when entering the human diet because of their ability to participate in DNA alkylation and they are identified among the most potent and broad acting carcinogens. Synthesis in the body is thought to take place through acid catalyzed and bacterial nitrosation in the

stomach and by NO formation that involves the presence of NOC precursors (Mirvish, 1995). Nitrite, participating in acid catalyzed nitrosation in the stomach, can be supplied through food, water and salivary re-secretion (Bruning-Fann and Kaneene, 1993a). It has been suggested that approximately 80% of NO_2^- found in the stomach is due to the reduction of ingested or endogenous NO_2^- re-secreted in saliva and 20% can be due to ingested NO_2^- from preserved meats, other foods, and drinking water (Mirvish, 1995). To participate in nitrosation NO_2^- must first be converted to nitrous acid (HNO_2) through acidification in the stomach (Mirvish, 1995), which is thought to then be protonated to form H_2NO_2 . The H_2NO_2 may then interact with amines and amides from food to form NOC (Mirvish, 1995; McKnight et al, 1999). Alteration in thyroid metabolism must be seriously evaluated in both the monogastric and ruminant animal in that it may partially explain some other effects seen from NO_3^- consumption including immune function, reproduction, and fetal developmental problems.

Beneficial Nr-compounds. The role of beneficial Nr compound forms to the human system requires mention of endogenous synthesis of nitric oxide (NO). NO is a free radical gas that functions as a messenger molecule important to normal physiological function for the regulation of several systems including blood vessel dilation, hormonal, and neurotransmission functions. It is a small lipophilic molecule that allows for rapid diffusion through cell membranes for interaction with intracellular target compounds (Ignarro et al., 1999). Although the primary synthesis of NO in the body occurs through arginine metabolism, it has been suggested that dietary NO_3^- and NO_2^- can be converted to NO to contribute to endogenous NO synthesis (Gruetter et al., 1981). Nitrate compounds, such as nitroglycerin (glyceryl trinitrate), are among the oldest and most utilized compounds in vasodilator therapy to decrease intramyocardial pressure leading to improved perfusion of the heart and for management of congestive heart failure. Although NO_3^- is generally considered an inorganic molecule within the medical field, it is common to refer to a number of compounds, including nitroglycerin, as “organic nitrates.”

NO has a biological half-life of approximately 5 seconds allowing it to act exceptionally well as a local mediator of physiological function (Moncada and Higgs, 1991). NO reacts in the body with water to form NO_2^- , which is an unstable compound in blood and quickly converts to NO_3^- (Ellis et al., 1998). Both NO_3^- and NO_2^- can then be excreted in the urine. The five main molecular targets for NO in the body are heme proteins, enzymes, DNA, thiols, and superoxide (Radomski, 1995).

- a. **Heme proteins:** One of the most important heme proteins that NO binds with is guanylate cyclase (GC). The binding of NO

results in the activation of GC which leads to increased synthesis of cyclic guanosine monophosphate (cGMP) (a compound involved in the mediation of ion flux), modulation of cyclic adenosine monophosphate (cAMP)-mediated responses, and increases in protein kinase phosphorylation reactions (Radomski, 1995). One of the best documented functions of NO in the body is its action as a relaxing factor on smooth muscle of blood vessel walls leading to vasodilatation and a decrease in blood pressure (Ellis et al., 1998). The interaction of NO_3^- with hemoglobin allows for an understanding of the role of NO in vasodilatation. NO first diffuses out of the cell in which it was synthesized and acts on neighboring cells. The intracellular enzyme guanyl cyclase contains a heme prosthetic group to which the NO can bind resulting in a conformational change causing activation of the enzyme. This results in the production of cGMP and causes vessel wall relaxation and leads to vasodilatation and hypotension or a decrease in blood pressure. Endothelial cell release of NO not only results in vaso-relaxation but also is a potent inhibitor of platelet adhesion and aggregation thus interfering with binding of platelets to endothelial cells (Radomski et al. 1993). In the heart, cGMP will act to relax the muscle and decrease the force of the contractions by stimulating ion pumps that maintain low cytosolic Ca^{2+} concentrations.

- b. **Other enzymes:** NO can also act on enzymes such as complex I and II of the mitochondrial electron transport chain and aconitase in the TCA cycle resulting in some of the cytotoxic effect of NO (Radomski, 1995). The anti-microbial action of NO is varied. Nitric oxide can inhibit and form complexes with heme, iron-sulfur, and copper proteins thus impairing function as well as interfering with incorporation into key enzymes. The inhibition of clostridia appears to be due in part to the interaction of NO with pyruvate-ferredoxin oxidoreductase an iron-sulfur enzyme involved in regeneration of adenosine triphosphate (ATP) (Cornforth, 1996). Inactivation of enzymes containing no redox metals such as glyceraldehyde-3-phosphate dehydrogenase, part of the glycolytic pathway, can occur as well.
- c. **Inhibition of DNA synthesis:** NO can inhibit ribonucleotide reductase (Lepoivre et al., 1991), a crucial enzyme for formation of DNA by quenching of a tyrosine radical. Interference with DNA also occurs through NO by promotion of deamination of N-terminal and other amino groups of proteins and through this process can be mutagenic (as seen in *Salmonella typhimurium* and *P. stutzeri*) where mutations in the nucleotide sequence that prove lethal to the bacteria occur. The common practice of addition of ascorbate accelerates the formation of NO and decreases formation of nitrosamines thus aiding in the antibacterial effects of NO_3^- and NO_2^- salts (Cornforth, 1996).

- d. **Interaction with thiols:** The nitrosylation of sulfhydryl groups may offer a storage mechanism for readily available NO (Stamler et al., 1992; Radomski, 1995).
- e. **Superoxide and NO:** The formation of peroxynitrite (ONOO⁻), a highly reactive molecule which can participate in the oxidation of many compounds may relate to some of the more detrimental effects of NO. The cytotoxic activity of macrophage is partially due to the endogenous production of NO from arginine which is catalyzed by cytokine inducible nitric oxide synthase. A macrophage is a type of white blood cell that ingests (takes in) foreign material. Macrophages are key players in the immune response to foreign invaders such as infectious microorganisms. Cytotoxicity is due to at least a 100-fold increase in local NO concentrations in comparison to levels generated by other cells in the body such as endothelial cells. If macrophages are arginine deficient or if inhibition of the enzyme is induced by administration of arginine analogs there is a decrease in bactericidal effectiveness. NO production relates to their cytotoxic effect and has been shown to act on bacteria, tumor cells, viruses, fungi, protozoans and helminths (Moilan and Vapaatalo, 1995). Although NO is the main oxide produced, synthesis of ONOO⁻ occurs in macrophage due to the spontaneous reactions of NO with O₂⁻ and H₂O₂ also produced by the macrophage. This more reactive oxide leads to formation of a highly reactive hydroxide radical OH⁻ and NO₂ which kill bacteria through oxidative damage. NO production is not always beneficial in free radical production because it can act as a cytotoxic molecule in autoimmune diseases as seen in diabetes. Increased NO synthesis from an autoimmune response results in decreased insulin secretion and damage to the islet cells. Similarly tissue damage during arthritis has been linked to toxic levels of NO due to an autoimmune response (Moilan and Vapaatalo, 1995). NO₃⁻ concentrations are higher in the synovial fluid, the main function of synovial fluid is to serve as a lubricant in a joint, tendon sheath, or bursa, of patients with rheumatoid arthritis and levels are increased in urine suggesting increased endogenous formation of NO (Moilan and Vapaatalo, 1995). The origin of NO in the joints is not completely known but stimulation of chondrocytes by IL-2 appears to increase NO production by the chondrocytes (Moilan and Vapaatalo, 1995). Nitric oxide plays more of a harmful effect in arthritis and appears to contribute to inflammation and destruction of tissue.

Although this review touches upon only a few established roles of NO, research continues to expand as the significance of NO in many other physiological functions becomes more apparent and more in depth

reviews of the literature are available (McKnight et al., 1999; Radomski, 1995; Moilanen and Vapaatalo, 1995).

MANAGING NITROGEN IN AGRICULTURAL SYSTEMS

Accounting for all Nitrogen Sources

Nitrogen budgets provide a valuable framework to quantify and examine N inputs and losses for agricultural production systems (also see Figure 1). Accounting for the major sources of N to cropping systems and into the environment, in general, is especially important. The following are some of the sources that should be considered:

1. Fertilizer N inputs and amounts are easily determined and can be managed.
2. Organic wastes are an important N source. Organic wastes available for use on cropland in the US include livestock wastes, crop residues, sewage sludge and septage, food processing wastes, industrial organic wastes, logging and wood manufacturing wastes, and municipal refuse. Animal manures and crop residues account for the majority of organic wastes applied to agricultural land.
3. Manure N inputs are uncertain because the N content is related not only to livestock type, age, and health, but also to variations in dietary N content. Once excreted, the N content can change considerably depending on type and amount of bedding, type and time of manure storage, and manure management and placement when being applied. The best way to overcome these uncertainties is through the use of manure analysis and calibration of application equipment. Manure credits are often used to try to account for N that becomes available from applied manure.
4. Biological N fixation (BNF), especially by legumes, can be an important source of N. Although the importance of BNF has been known for centuries, there are few quantitative methods for the estimation of BNF. Currently, the method most used is that of recognizing BNF by legumes with legume credits.
5. Nitrate contained in irrigation water is available to the crop and should be considered when making fertilizer recommendations. Crop utilization of NO_3^- from irrigation water is greatest when plant-N requirement is greatest and other N sources are not excessive.
6. Atmospheric additions, including volatilized NH_3 from livestock operations, are another source of N to agricultural systems and to the environment. The mechanisms of additions that are identified include N dissolved in precipitation, dry deposition, and direct plant absorption of gaseous NH_3 .

7. Contributions of residual soil N require soil testing for NO_3^- and NH_4^+ within the root zone and will be discussed below.
8. Nitrogen mineralization is the term given to biological decomposition of organic materials in soils and their conversion and contribution to inorganic forms are significant.

Soil nitrogen availability tests. Available soil N represents residual N in the soil profile, plus N mineralized from the soil organic matter during the growing season. While residual N has proven to be a useful index in certain regions of the US, a generally accepted index does not exist for N mineralization. Obviously, such a development would represent a major advance for avoidance of excessive fertilizer N applications. A complement to a soil N test may be a plant tissue N test. An attractive feature of tissue tests is that the plant root system tends to integrate spatial variability of soil N supplying power over a relatively large field volume.

Soil organic nitrogen availability. A significant portion of plant-N requirements are supplied by mineralization of soil organic matter during the growing season. Various N availability indexes exist, but they typically provide qualitative rather than quantitative measures of SON availability. Early concepts of an N availability index have been modified but no soil organic N availability procedure has received general acceptance from a soil test standpoint. Ultimately, a systems-type, mass balance N approach may be the best alternative. The present recommendation is to follow pertinent N fertilizer guides, which have been developed locally for specific crop needs and soil areas.

Agricultural Practices

Nitrification inhibitors. The NH_4^+ ion is sorbed to the CEC of the soil whereas NO_3^- ion is not and can be readily leached or denitrified. Both forms can be readily used by crops. Nitrification inhibitors include chemicals added to soils to stabilize fertilizer applied as NH_3 or in the NH_4^+ form by inhibiting the activity of the *Nitrosomonas* bacteria in the first step of the nitrification process.

Control/slow release fertilizer. Methods of altering the release of N from soluble materials has been to coat water-soluble N fertilizer with less water-soluble materials in order to retard entry of water into the particle and the movement of N out. Coatings applied to soluble N materials generally have been of three types: (1) impermeable coatings with small pores that allow slow entrance of water and slow passage of solubilized N out of the encapsulated area; (2) impermeable coatings that require breakage by physical, chemical, or biological action before the N is dissolved; and (3) semi-permeable coatings through which water diffuses and creates internal pressures sufficient to disrupt the coating. Sulfur-coated urea has been developed for a number of years as a product with characteristics of slow-N release (SNR) fertilizer. Newer control-release N (CRN) fertilizer materials are also being developed and

marketed (Shoji and Gandeza, 1992). These newer materials have polyolefin resin coatings. The coatings can be tailored to provide a range of N release rates that are suitable for a variety of cropping systems. Traditional CNR and SNR fertilizers have commonly been used for high-value crops, such as horticultural crops, but have not been economical for use in major grain crops because of low crop price and high cost. However, new economical CNR fertilizers are becoming available for use on field crops such as corn (*Zea mays* L.) and wheat (*Triticum aestivum* L.) (Blaylock and Tindall, 2006). Zvomuya, et al. (2003) observed less NO_3^- leaching, greater fertilizer N recovery, and greater marketable yield with CNR for potato (*Solanum tuberosum* L.) than with conventional application of urea at planting and equal applications of diammonium phosphate at emergence and hilling. Among the more economical CNR materials are those where N is released from polymer-coated fertilizers by diffusion in response to soil temperature. Coupling N release with soil temperature, a primary factor in crop growth rate and N demand, allows N release to be programmed to better match crop needs.

Agriculture contributes approximately 78% of the total N_2O emissions in the US (US Environmental Protection Agency, 2007). Nitrous oxide is a greenhouse gas emitted from soils and is produced through nitrification and denitrification processes in the soil (Figure 2). Minami (1992), Bronson et al. (1992), and Mosier et al. (1998) reported that nitrification inhibitors are useful tools in mitigating N_2O emissions in agricultural systems. Controlled release fertilizers were also proven to be useful tools for the mitigation of N_2O emissions from agricultural systems (Minami, 1992; Delgado and Mosier 1996). Delgado and Mosier (1996) reported a reduction in N_2O emissions with the application of urea plus a nitrification inhibitor and with application of a polyolefin-coated urea when compared to urea in an irrigated barley study in Colorado. Blaylock et al. (2006) reported reduced N_2O emissions from application of a polymer-coated urea (ESN) when compared to UAN and urea N sources. In a recent literature review by Snyder et al. (2009) controlled-release and stabilized N sources were reported to be effective in reducing N_2O emissions resulting from inorganic N fertilizer applications. They concluded that use of enhanced-efficiency fertilizers (controlled-release N fertilizers, nitrification inhibitors, and urease inhibitors) reduced losses of N. Halvorson et al. (2010) recently monitored N_2O emissions from N-fertilized corn-based rotations that included: conventional-till continuous corn (CT-CC); no-till continuous corn (NT-CC); NT corn-dry bean (NT-CDb); and NT corn-barley (NT-CB). A controlled-release, polymer-coated urea (ESN) and dry granular urea were compared in the NT-CC and CT-CC systems. In the NT-CDb and NT-CB rotations, a stabilized urea source (SuperU) was compared with urea. Nitrous oxide fluxes were measured during two growing seasons using static, vented chambers and a gas chromatograph analyzer. Cumulative growing season N_2O emissions from urea and ESN application were not different under CT-CC, but ESN reduced N_2O

emissions 49% compared to urea under NT-CC. Compared to urea, SuperU reduced N₂O emissions by 27% in dry bean and 54% in corn in the NT-CDb rotation and by 19% in barley and 51% in corn in the NT-CB rotation. This work shows that use of no-till and enhanced-efficiency N fertilizers can potentially reduce N₂O emissions under irrigated agricultural systems, but that further field research is needed to insure the utility of these newer materials for cropping systems and to understand their potentials to decrease N losses through either leaching or gaseous emission.

Conservation tillage. Use of conservation or reduced tillage (including no-till) continues to increase as an alternative for nearly all forms of crop production. Management systems which maintain crop residues at or near the soil surface have several attractive features, including less on-farm fuel use and its associated carbon dioxide emissions (Follett, 2001), more available soil water, and reduced soil erosion.

There is no question that conservation tillage is effective in decreasing particulate N losses associated with soil erosion and surface water runoff as discussed above. However, effects of conservation tillage on leachable N are not as well delineated as are surface losses. Generally, conservation tillage provides a wetter, cooler, more acidic, and less oxidative soil environment. Under such conditions, processes of ammonification and denitrification may be favored over nitrification. Conversely, for NO₃⁻ that is already present, the leaching potential may be greater under conservation tillage. This is because more undisturbed soil-macropores exist for NO₃⁻ and water movement. Increased water flow, into and through the root zone, has been observed under no-till compared to conventional-tillage soils and is indicative of improved microstructure under no-till conditions (Endale, et al. 2002; Bakhsh et al. 2002, Buczko, et al. 2003). This higher flow has been attributed to decreased water evaporation because of surface residues and increased numbers of undisturbed channels (e.g., earthworm and old roots) continuous to the soil surface. The surface mulch enhances the environment for earthworms and the lack of tillage preserves existing channels for several years.

Rotations, cover crops, and nitrogen-scavenging crops. Rotations and cover crops are used to conserve soil and/or provide an organic N source and aid in avoiding excessive N losses to the environment. Whereas monocultures of grain crops (e.g., corn and wheat) require high inputs of fertilizer N, such inputs can decrease with crop rotations that include crops that fix atmospheric N. Because less excess profile N or greater N utilization may be expected with a rotation, there should be less potential for N leaching. An exception may be under certain rotation-fallow conditions designed to conserve water in drier areas.

Winter cover crops can be effective for absorbing both NO₃⁻ and available water during the fall, winter, and spring, thereby decreasing the N leaching potential. When the cover crop is returned to the soil,

some of the absorbed N is then available to the following crop (Delgado et. al., 2004). Both legumes and non-legumes are used from a strictly N leaching standpoint. While an annual crop such as rye can be effective in scavenging excess available N from within crop rooting zones deep-rooted perennials should be considered for NO_3^- accumulation below normal rooting depths. Alfalfa, with a potential rooting depth in excess of 15 feet, is a crop that merits particular attention.

Filter strips. Vegetative filter strips, also referred to as buffer strips and riparian zones, remove sediment, organic matter, and other pollutants from runoff and waste waters. Under field conditions, excess runoff from terraces is frequently diverted to a strip. Upon entering the strip, both the flow velocity and transport capacity of the runoff are reduced. The sediment and its associated pollutants are then removed from the runoff by filtration, deposition, infiltration sorption, decomposition, and volatilization processes. The effectiveness of filter strips in removing sediment and particulate N is well established (Lee et al. 1999). Less certain is the effectiveness of filter strips for removing soluble N in runoff. Uptake by filter strip vegetation of mineral N transported by runoff water may occur during times of active growth but less during other times of the year. Also, some denitrification may be occurring. Scavenging of N from underground water and the vertical horizon by riparian vegetation, especially by deeper rooted plants, also may be important for removing dissolved N in surface and subsurface flows before the N is transported into streams and lakes.

SUMMARY

Nitrogen is ubiquitous in the environment. It is also one of the most important plant nutrients and is central to the growth of all crops and other plants. Because of humans' needs for agricultural products, humans impact on the environment through their use of N. This chapter has considered practices and concepts that lessen the opportunity for loss processes to occur and that help decrease the amount of Nr that may be lost to the environment while also achieving positive impacts from N use. When N is in its reactive form (Nr), it can combine with other elements that are among the most mobile compounds in the soil-plant-atmosphere system and there is mounting concern about agriculture's role in Nr delivery into the environment. Nitrogen is the mineral fertilizer most applied to agricultural land. This is because available soil-N supplies are often inadequate for optimum crop production. This manuscript reviews the fate and transport of N from the various sources used to supply the N-requirements of crops in the context of the N cycle. Use of N budgets or a mass balance approach is needed to understand the options for improving management of N in farming and livestock systems and for mitigating the environmental impacts of N. Fertilizing crops for crop N uptake that will be near the point of maximum yield generally is an economically and environmentally acceptable practice.

The objectives of improved management are to: achieve the beneficial effects on N on food and fiber production, achieve livestock and human health goals, lower the rate and duration of N-loss processes, decrease potential negative impacts of Nr within the ecosystem to which it is applied, minimize undesirable transport of Nr into other ecosystems, and to prevent negative impacts of Nr upon human health.

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