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Chapter 1. The Nitrogen Cycle, Historical Perspective, and Current and Potential Future Concerns

D. R. Keeney
Iowa State University, Ames, IA, USA

J. L. Hatfield
USDA-ARS, jerry.hatfield@ars.usda.gov

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Chapter 1. The Nitrogen Cycle, Historical Perspective, and Current and Potential Future Concerns

D.R. Keeney[a] and J.L. Hatfield[b]

[a]Department of Agronomy, Iowa State University, Ames, IA, USA

[b]USDA-ARS-National Soil Tilth Laboratory, Ames, IA, USA

Nitrogen (N) along with carbon and oxygen is the most complex and crucial of the elements essential for life. Supplementing grain and grass forage crops with organic and inorganic N fertilizers has long been recognized as a key to improving crop yields and economic returns. Globally, N fertilizer is largely used for cereal grain production and accounts for an estimated 40% of the increase in per capita food production in the past 50 years (Mosier et al., 2001). Smil (2001) estimates that N fertilizer supplies up to 40% of the world's dietary protein and dependence on N from the Haber–Bosch process will increase in the future. Nitrogen compounds also have been recognized for their many potential adverse impacts on the environment and health (Keeney, 2002).

From 1850 to 1980, biological scientists concentrated on unraveling the biological and physical–chemical intricacies of N. We now know the paths of its comings and goings, the route it takes as it moves, at rates varying from milliseconds to centuries, through nature's compartments (atmosphere, soil, water, and living matter), and the interactions of N with various elements. We know as well its oxidation/reduction status under varying environmental conditions. But nature, in its clever way, has kept science from tracking precisely the actual ledger of this whimsical element and of predicting the impact of N on the environment when it accumulates at levels far above that for which stable ecosystems have adapted.

Many ecological problems occur when N is separated from its most common partner, carbon (Asner et al., 1997; Keeney, 2002; Townsend et al., 2003). Nitrification, denitrification, nitrous oxide formation, leaching of nitrate, and volatilization of ammonia are fates of the mobile N atom. Environmental effects vary with the N form. The atmosphere might receive more nitrous oxide than it can assimilate, resulting in stratospheric ozone destruction, while nitrous oxide and ammonia are greenhouse gases. Combined N in the atmosphere and precipitation fertilizes natural ecosystems resulting in lowered biodiversity, stress, and N leakage, while acidity from nitric oxide and ammonia oxidation depletes ecosystems of bases and results in acid lakes and streams and declining health of forests.

Lakes, coastal waters, and estuaries, overloaded with biologically available N, produce organic materials in abundance. The N atom gets connected to carbon, but the unwanted effects of excess growth and subsequent decay create anaerobic conditions. Nitrogen is widely regarded as responsible for the hypoxia (low oxygen) zone in the Gulf of Mexico that concerns ecologists and conservationists as well as those financially dependent on fish and shrimp catches. Decaying organic matter removes oxygen, changing the ecology and productivity of the bottom waters in a large area of the Gulf. Productive agricultural regions of the Central US are the major source of the nitrate to the Gulf.

Can the N cycle be managed to minimize the problems N generates? Given the world's needs for food – the great ability of annual grains to produce the needed food (and animal feed) – and the economic returns from N fertilizers, change on the larger scale will be slow and requires policy changes as well as economic assessments that include externalities. The United Kingdom and Western Europe have adopted strict manure and fertilizer application regulations with stiff fines for failing to adhere to the regulations. Other countries, including the United States and Canada, have relied on education and demonstration programs to lessen environmental effects from excess N fertilizer use. The changing economics of N use and return from commodity crops may also play a role. Iowa and some other states in the United States have had some modest success at decreasing N fertilizer use through research and education projects. However, ground and surface water quality measurements in Iowa have shown little long-term change in nitrate concentrations illustrating again the problems of second guessing the N cycle.

The solutions to the issues on environmental effects of N will involve looking beyond the edge effects to redesigning agriculture in ways that will tighten up the N cycle and that will provide for N sinks such as grasslands and wetlands. To do this, policies will need to be developed that assure the farmer and the public that such measures will not cost productivity, and that a redesigned agriculture can provide for future food needs. Turning back is not possible. The road ahead will demand a level of innovation of agricultural research and development of new agriculture systems.

1. THE NITROGEN CYCLE

AZOT, the German word for N, was the subject of ancient philosophers. AZOT is believed to be formed from the ancient scientific alphabets, A (the beginning of scientific Latin, Greek, and Hebrew) and zet, omega, and tov, the last letters of these alphabets. The term "saltpeter" came from the association of nitrate salts with the salt of the earth or the salt of fertility. Potassium nitrate was manufactured for gunpowder in the 14th century. By the 1650s Johannes Rudolph Glauber spoke of "nitrum as the 'soul' or 'embryo' " of saltpeter. He states, "It is like a wingless bird that flies day and night without rest; it penetrated between all the elements and carries with it the spirit of life–from nitrum are originated minerals, plants and animals. (It) never perishes; it only changes its form; it enters the bodies of animals in the form of food and then is excreted. It is thus returned to the soil, from which part of it again rises into the air with vapors, and hence it is again among the elements." The N cycle was never better described even though this was 350 years ago. [Much of the material for this paragraph originated from Vorhees and Lipman (1907); Waksman (1952); and Harmsen and Kolenbrander (1965).]

Nitrium was the subject of numerous other early scientists. In the 1780s Cavendish discovered that the inert gas of air would combine with oxygen to give oxides. The stage was set for the linkage of the lifeless AZOT and saltpeter. The French scientist, Boussingault, the founder of modern agrochemistry, did this with the sand culture research during the 1830s to 1860s. He deduced that the fertilizing properties of manures came from the ammonium formed in the soil and that ammonium was taken up by the plant root (Waksman, 1952; Burns and Hardy, 1975).

Research during 1880–1910 revealed many basic reactions of the N cycle and set the stage for five decades of vigorous and detailed N cycle studies. Denitrification was first demonstrated in the 1860–1880 period (Waksman, 1952). Gayon and Dupetite reported their research on denitrification in 1882 and coined the term at that time (Broadbent and Clark, 1965). Davy, in 1813, first attributed the beneficial effects of legumes to soil AZOT. While Boussingault quantified this benefit, Liebig was not convinced and hence the classical experiments of Lawes, Gilbert, and Pugh were established at Rothamsted in 1857. Unfortunately their sterile sand experiments destroyed the *Rhizobium* population and it was not until the late 1880s and early 1890s Hellriegel and Wilfarath did confirm that biological N fixation. Beijerinck isolated *Rhizobia* in 1888 and *Azotobacter* in 1901. Winogradsky identified *Clostridium* in 1890. Burns and Hardy (1975) reported much of this history of N research.

Nitrification received much study during the early 1900s on the belief that nitrate was the dominant form of N used by plants. King and Whitson (1902) at Wisconsin conducted some excellent research on the effects of environmental variables on the rate of nitrification. Their research also examined the effects of cropping on profile nitrate concentrations and leaching of nitrate. The use of a nitrification test to measure soil fertility was proposed, tested, and abandoned. Heterotrophic nitrification was identified and following the acceptance in 1926 of two-electron shifts during sequential oxidation, research began on determining nitrification intermediates. Allison (1927) studied the first nitrification inhibitors, the cyanamides. During this time denitrification received little attention. In 1910, Beijerinck and Minkman, and Suzuki in 1912, concluded that nitric oxide and nitrous oxide were obligatory intermediates in denitrification and that organic matter was the major electron donor (Alexander, 1965; Payne, 1981; Firestone, 1982). Waksman and Starkey (1931) dismissed denitrification as of little economic importance; Broadbent and Clark (1965), Payne (1981), and Firestone (1982) have provided comprehensive reviews of denitrification, and helped establish the key chemical and biochemical aspects of denitrification. Allison (1955) in a seminal review pointed out that nitrogen balances are never obtained in field and hypsometer experiments, and denitrification is assumed to be one of the major N sinks (Payne, 1981).

Mineralization and immobilization were recognized as important reactions, but most scientists looked at these as separate rather than coupled transformations. Much time was spent evaluating the fertilizer values of manures and compost (e.g., Blair, 1917). It was left to Jansson and Persson (1965) to couple these critical reactions of the N cycle. Ladd and Jackson (1982) reviewed the biochemistry of ammonification, including the presence and reactions of extracellular enzymes including soil urease. Soil tests to estimate N availability by the rate of ammonium formation in incubated samples were first studied at about the turn of the century. The first modern "N Cycle" was probably the one published in 1913 by Lohnis (Lohnis, 1926). The concepts he proposed are valid today. Blair, in 1917, presented a more ecosystem-oriented N cycle, including abiotic reactions. For the next 88 years agronomists and soil scientists have added important details of the N cycle in various soils and cropping systems. For more of the history of the N cycle, see reviews by Bartholomew and Clark (1965), Campbell and Lees (1967), and Stevenson et al. (1982).

1.1. The Fertilizer Era

When agronomists understood the need for N fertilizers, the search was on for fertilizer sources. The first was guano, the dried bird excrement deposited on some arid offshore islands, particularly off the west coast of South America. These deposits were imported to Europe but were exhausted by 1890 (Smil, 2001). In addition, huge deposits of sodium nitrate were discovered in the arid highlands of northern Peru in the 1820s. These deposits, known as Chilean nitrates (although Chile obtained them by going to war with Peru and Bolivia), provided up to 2.7 MT of N per year, much of it to Germany. Because Chilean nitrate also was an important source of explosives, it was apparent soon that this export source could not be relied on in times of war. Industrial fixation of N became a major priority. Industrial processes were developed including recovery of ammonia from coking of coal, high temperature synthesis of cyanamide, and fixation by electrical discharge. None of these processes were able to meet the needs of the developing agriculture or the war needs of Europe and the United States.

By most measures the Haber–Bosch process for industrial synthesis of atmospheric N as ammonia ranks as one of the most important inventions of the 20th century (Smil, 2001). The lives of many billions of people benefit from the availability of nitrogen fertilizer; indeed the expansion of the world's population from 1.6 billion to over 6.5 billion presently would not have been possible without this synthesis (Smil, 2001). Smil estimates that currently synthetic fertilizers supply over half of the nutrients available to annual and permanent crops.

The industrial synthesis of ammonia was a long-sought process, involving over 100 years of experimentation, until it was finally successful on the laboratory scale in 1909. Soon Germany adapted the process to commercial scale and by 1914 a plant at Oppau was producing about 20 ton of N per day. The World War I was to intervene, and most of the ammonia produced for several years was diverted to the war effort.

Over time, the process was made about 70% more efficient, and today the best plants operate at nearly the stochiometric energy requirements but even today the production of ammonia is highly energy-intensive. Because natural gas is the feedstock for most ammonia synthesis plants, the price and availability of ammonia for industrial and agriculture use will be dependent increasingly on availability and cost of natural gas (West, 2005).

By 1921 a manufacturing plant using the Haber–Bosch process for synthesis of ammonia was operating in the United States (Smil, 2001). Synthetic ammonia plants were not widely used until the WWII munitions plants were converted to ammonium nitrate fertilizer plants. Most important was the Tennessee Valley Authority (TVA) complex at Muscle Shoals, Alabama, that was completed just as WWII was ending.

1.2. Historical and Current Trends in Nitrogen Fertilizer Use

The availability of relatively cheap ammonia-based fertilizers marked a significant change in the way N was supplied in agriculture. However, replacement of traditional N sources for crops by fertilizer N proceeded slowly until the early 1960s. The TVA began a demonstration program in the late 1940s to facilitate information on proper N fertilizer use and established a state-of-the-art research facility at its Muscle Shoals, Alabama, facility. Cooperative research programs in key U.S. agricultural colleges also helped forward the TVA research program and enabled scientists to fund research and graduate students in the areas of N fertilizer use and N cycle reactions. This cadre of soil chemists and biochemists made up the bulk of the research community in N cycle reactions during 1950–1970. The senior author was privileged to share in this particular period. It was an era never to be repeated, one full of excitement, enthusiasm, and accomplishments in understanding the N cycle. Annual cooperators' meetings at Muscle Shoals were events to be treasured because of the sharing of research ideas, results, and philosophy. This program accomplished the goal of increasing N fertilizer use. The use of N fertilizer became the mainstay of modern World agriculture.

Some now feel that the overemphasis on fertilizer to increase crop yields is at the expense of sound ecological farming approaches (Kjaergaard, 1995; Moffat, 1998; Keeney, 2002). By the 1960s, fertilizer use in agricultural regions such as the Midwest Corn Belt increased markedly. For example, in Iowa, the state with the greatest consumption of N fertilizer, consumption increased from about 1 million tons in 1960 to a stable value of about 9.8 million tons in 1996–2005. Randall and Mulla (2001) summarize the N fertilizer consumption and application in six Midwestern US states. The N rates, kg/ha, increased linearly from nil in 1945 to about 110 kg/ha in 1979, and have remained at about 100 kg/ha since. Obviously we overshot on the recommendations in the 1970s but corrections are bringing rates into an economic optimum.

During the time that N fertilizer consumption rapidly increased, N from animal manures remained steady. For example, in the United States annual production of N from all animal sources has ranged from 5.7 MT in 1982, 5.6 MT in 1987 and 1992 to 5.9 MT in 1997 (Kellogg et al., 2000). Total N from manures is relatively small compared to fertilizer sources, but the move to concentrated animal feeding operations has resulted in high N outputs in local areas and subsequent problems with water and air contamination.

Over the past 40 years there has been an eight-fold increase in fertilizer N consumption (Table 1). Until the mid-1970s the developed world had the largest share of the increase but since then the developing world has increased fertilizer use rapidly as they increase food production and use more grains for meats.

Table 1.
Nitrogen (N) fertilizer consumption (MT) in the world, developed and developing countries, 1960–2003.

Year	World	Developed	Developing
1960/1961	10.80	8.55	2.28
1970/1971	31.75	23.13	8.61
1975/1976	43.90	30.79	13.11
1980/1981	60.78	35.79	24.90
1985/1986	70.37	38.86	31.51
1990/1991	77.56	33.07	42.39
1995/1996	78.07	29.88	49.18
2000/2001	81.19	29.07	52.12
2002/2003	85.11	28.71	56.40

Adapted from IFIA (2004).

2. MODERN NITROGEN CYCLE RESEARCH

The period between 1945 and 1980 was marked by a spectacular increase in research activity on all facets of N in agriculture. The mass spectrometer developed for the Manhattan project was subsequently used for innovative ^{15}N research. The application of ^{15}N isotope methods by Bremner, Burris, Broadbent, and Norman in the late 1940s and 1950s demonstrated the tremendous power of stable isotope research. The National Fertilizer Development Center at TVA was established in the mid-1950s. This center aided greatly in development and application of ^{15}N methods in agricultural research. Many other analytical methods were improved, some were automated and others were developed. Sensitive gas chromatographic methods for identification of gaseous intermediates of nitrification and denitrification facilitated research on these reactions. Computer technology was sufficient by the early 1970s to permit construction of sophisticated, mathematical models of the N cycle.

The use of ^{15}N permitted renewed emphasis on mineralization-immobilization research. Researchers included Bartholomew, Broadbent, Bremner, Harmeson, Hauck, Jansson, Jenkinson, Paul, Persson, and Van Schreven. Bremner clarified the denitrification process, and developed many methods for analysis of ^{15}N. Jansson (1958) identified the central role of ammonium in mineralization-immobilization. Major reviews by Harmesen and Van Schreven (1955), Bartholomew and Clark (1965), Jansson and Persson (1965), and Stevenson et al. (1982) set the stage for current concepts of mineralization-immobilization. The review of Jansson and Persson (1965) solidified the concepts of the universal N cycle. Major advances in nitrification pathway research were the establishment of nitrous oxide as a byproduct of ammonium oxidation and the development of commercial nitrification and urease inhibitors. Denitrification research was expanded with discovery that acetylene blocked nitrification as well as nitrous oxide reduction. The interest in nitrous oxide in ozone destruction and as a greenhouse gas gave impetus to studies to quantify its output from various agricultural and natural ecosystems.

By the early 1980s, breakthrough research on N was largely complete. Nitrogen research moved out of the public eye. Nitrogen fertility research continued on a site and crop-specific basis, but less attention was paid to environmental issues. In a recycling of issues, N is now gaining new attention as emerging environmental and health problems come to the forefront and old issues resurface. And world food pressures continue as population grows and the agricultural land resources base declines.

3. THE ISSUES

Nitrogen from anthropogenic sources, including fertilizers, biological N fixation, ammonia volatilization, combustion, and activities that bring N from long-term storage pools such as forests have been estimated by several groups to be close to the same order of magnitude as the N from natural (pre-industrial) sources (Jordan and Weller, 1996; Vitousek et al., 1997; Smil, 2001) (Table 2). The doubling of the available N pool worldwide has many implications. While most N issues are local and thus the global N cycle would not seem applicable, many issues have regional or global implications. Examples include air quality (ammonia emissions, acid rain, etc.), ecosystem stability, and land and ocean productivity.

Table 2.
Estimates of global nitrogen fixation (MMT of N).

Source	1960	1990
Legume crops	30	40
Fossil fuel emissions	10	15
Fertilizer	20	80
Total	60	145
Natural N fixation	80–130	80–130

Adapted from Vitousek et al. (1997).

Excess N in rivers, lakes, and groundwater can be toxic to humans and causes water quality problems in natural water systems (Hallberg and Keeney, 1993; Dinnes et al., 2002; Keeney, 2002; Townsend et al., 2003; Foley et al., 2005). Excess N in the estuaries of the oceans enhances growth of aquatic organisms to the point that they affect water quality and lower dissolved oxygen levels (Turner and Rabalais, 1991; Rabalais et al., 1996; Downing et al., 1999; Howarth, 2000). This affects the metabolism and growth of oxygen requiring species, causing a condition referred to as hypoxia (Rabalais et al., 1996, 2001, 2002; Downing et al., 1999). Nitrogen in the atmosphere comes from emission of ammonia from human activities such as feedlots (Jackson et al., 2000) and from combustion sources. This N contributes, as nitric acid, to acid rain, damaging lakes, rivers, and forests. In land ecosystems, excess atmospheric N may enhance growth of exotic species or accelerate growth of trees, causing disruption of ecosystem functions (Jordan and Weller, 1996; Vitousek et al., 1997) such as over-fertilizing natural grasslands and lakes (Keeney, 1997).

3.1. Water Quality

Numerous studies, summarized by Hallberg (1989) and Keeney (1989) have documented the large increase in nitrate in ground waters in the United States relative to pre-industrial levels. Natural background levels commonly are less than 2 mg nitrate-N/L, while streams draining agricultural areas often exhibit seasonal concentrations greater than 10 mg/L especially in tile-drained regions (Randall and Mulla, 2001). The numerous sources and sinks of nitrate make evaluation and control of sources difficult and hence establishment of policies and groundwater protection goals are controversial and often unproductive. Hallberg's (1989) review points out the interaction of ground and surface water systems, particularly those that impact shallow ground waters. Keeney and DeLuca (1993) documented the influence of land use over fertilizer N use *per se* in influencing nitrate concentrations in the Des Moines River. Vitousek et al. (1997) summarized accumulation of N in surface waters, particularly riverine systems, but also estuaries. For example, Howarth (2000) estimated that riverine fluxes from lands surrounding the North Atlantic Ocean have increased from pre-industrial times by 2- to 20-fold.

3.2. Health Issues

Methemoglobinemia was first recognized by Comley (1945) who related infant illnesses to nitrate-contaminated private wells in Iowa. Nitrate can be reduced to nitrite in the digestive tract and the nitrite interferes with oxygen transport in the blood. The main health effect is with infants. The US health standard (maximum contaminant level, MCL) of 10 mg/L of nitrate-N was established by the United States Environmental Protection Agency (US EPA) in 1977 as a safeguard against infantile methemoglobinemia (Kross et al., 1992). Ground water is the primary water source of concern and many potable ground water supplies, especially those in rural areas of productive agriculture, are above the MCL (Hallberg and Keeney, 1993). For example, a recent study showed that in the early 1990s 18% of Iowa private water supply wells had nitrate-N levels above 10 mg/L (Kross et al., 1992).

Several infant illnesses and deaths from consumption of high-nitrate waters have been documented and while the numbers are small, there is also concern about subclinical exposure and under reporting of deaths and illnesses because the problems often occur in rural areas (Kross et al., 1992). Often rural water supplies are also high in bacterial pathogens and the ensuing gastric illnesses may complicate the effects of nitrate. Few government agencies enforce remedial actions for private water supplies, but most European countries and the US EPA require actions if municipal supplies are above the MCL. This has caused some municipalities such as Des Moines, Iowa, to install expensive nitrate-removal plants that operate only when the MCL gets close to the maximum concentration. New health-risk policies set by the US EPA in 1995 that evaluate risk to infants and children separately from adults may raise new concerns about the health risks of nitrate in potable water (Meyer, 1996).

Recently a spokesperson for the National Institutes of Health (Avery, 1999) suggested that nitrate toxicity was not a problem because no cases of methemoglobinemia had occurred recently. Avery also suggested that nitrate was beneficial to human health because of internal formation of nitrous oxide. He proposed increasing the MCL to 20 mg/L. Knobeloch et al. (2000) reported occurrence of blue baby syndrome in two Wisconsin households served by private water wells. They stated that their findings could not support Avery's conclusions. A review of risks of nitrate to humans (Williams et al., 1999) points out that nitrate exposure could cause not only methemoglobinemia but also diabetes and cancer. Addiscott (1999) provided additional support for Avery's view that nitrite in the stomach would be beneficial for control of pathogens and may be a natural defense mechanism in humans. Nevertheless, the overwhelming scientific literature does not support the "health benefits" of nitrate and continues rather to show that there are significant health issues associated with high levels of nitrate in drinking water (Ward et al., 2005).

4. ENVIRONMENTAL ISSUES

4.1. Surface Water Quality and Ecology

Phytoplankton and vascular plant growth in surface waters is limited by numerous factors, just as is growth of land-based plants (Downing et al., 1999). However, complications in assessing limiting factors, especially nutrients, arise because of the dynamic nature of surface waters relative to inputs, seasonal changes, turbidity that limits light penetration and differing nutrient and environmental requirements of phytoplankton and algae. In most instances, a moderate amount of growth will support a healthy food chain including fish, shrimp, and so on. Undesirable effects of excessive growth, most often a result of the decay of the excessive plant growth that consumes oxygen at a higher rate than it is replenished, will result in low to zero oxygen levels, especially in bottom waters of lakes and estuaries. High levels of algae or aquatic plants also impair use of water for recreational or industrial purposes.

Fresh water bodies differ from estuaries in their requirements for N and P relative to excessive growth. Fresh waters almost always are limited by P (Correll, 1998) while coastal zones and estuaries, which have the bulk of the biological activity in the oceans, usually are N and perhaps Si (for diatom growth) limited

(Rabalais et al., 1996; Downing et al., 1999). Hence, much attention has been paid to N management to improve water quality in important estuaries such as the Gulf of Mexico and the Chesapeake Bay on the Atlantic coast of United States.

There is need to establish water quality standards for freshwaters, especially for N and P. The Iowa Department of Natural Resources, for example, is considering adopting the tentative ESEPA total N standard of 2.18 mg/L (range 1.16–3.26 mg/L). This is below the N level of almost all of Iowa streams, showing the difficulty of achieving nutrient standards in agricultural regions.

Addressing control of nitrate sources at the estuary level is much more difficult than smaller watersheds because of the large geographical area involved (although experience indicates that reducing nitrate transport has had little success at any watershed scale). The number of point and nonpoint sources of nitrate is many, control of nonpoint sources apparently cannot be done through regulations, and N, being so pervasive, is very hard to manage. An example of the difficulty is an evaluation of nitrate concentrations in the Des Moines River from 1945, before N fertilizers were used in the highly productive agriculture watershed, through 1980s, when the watershed was predominantly row crops (corn and soybeans) and N fertilizer use was high (Keeney and DeLuca, 1993). The results indicated that the yearly flow-weighted average nitrate-N (about 7 mg/L) changed insignificantly over the 40 years of monitoring in spite of large increases in fertilizer N use and in row crops. Nitrate concentrations did relate directly to yearly precipitation; however, being highest during years of high flow. These results indicate that highly productive, tile-drained watersheds such as the Des Moines River have large reservoirs of N in the soil organic matter and that the mineralization-immobilization processes dominate the output. Denitrification, the most likely control mechanism for nitrate removal, has been minimized by tile drainage (that shunts the nitrate directly to drainage ditches rather than allowing it to flow overland) and by removal of almost all of the wetlands, the primary N sink aside from the annual corn crop.

4.2. Hypoxia in the Gulf of Mexico

Many papers and opinion pieces have discussed the current state of agriculture in the Corn Belt. Mollisols (soils formed under prairie in till and loess and high in organic matter and clay but with poor internal drainage) dominate but there are also Alfisols (soils formed under mixed prairie and forest) that have high clay subhorizons and lower amounts of organic matter and clay in the surface horizons. These soils are highly productive but have poor internal drainage. Subsurface tile drainage of soils in this region is necessary for crop production. Corn and soybean require a well-drained warm soil for optimum growth. But water moves so slowly downward to the water table that soils in the spring are often too wet and cold to be planted to corn or soybean in a timely manner. If a porous tile (farmers now use perforated plastic pipe) is placed below the seasonal water table, water flows to the tile by the force of gravity. Tiles are placed so that water flows to larger collector tile and finally to open ditches. Tile drainage short-circuits the natural drainage pattern and effectively flushes nitrate out of the soil before it is either denitrified or leached to the water table. The tile drainage systems thus become a major source of nitrate to surface water (Randall and Mulla, 2001; Dinnes et al., 2002; Keeney, 2002). Before habitation, this nitrate would have been denitrified in wetlands and ponds, or taken up by native vegetation. Effectively, human intervention has allowed nitrate transport and transformations to change markedly from pre-settlement.

Five states (Illinois, Indiana, Iowa, Ohio, and Minnesota) comprise the heart of the Corn Belt and are often referred to as the Upper Mississippi River Basin (UMRB) (the drainage above Cairo, IL: refer to Brezonik et al., 1999 for a more complete description). These states have the greatest amount of artificially drained soil, the highest percentage of total land in agriculture (corn and soybean), and the highest use of N fertilizers in the nation. The region has abundant precipitation most years for crop growth and only rarely suffers from major yield declines because of drought.

Data analyzed by Goolsby et al. (2001) showed that the UMRB generates about 19% of the flow but 43% of the nitrate load to the Mississippi River basin. Two states, Iowa and Illinois, provide 16 and 19% of the nitrate, respectively. These two states have the most intensive corn–soybean cropping systems, the most productive soils, and the highest total N fertilizer use. In 2001, Goolsby and Battaglin (2001) put together long-term nitrate changes in the Mississippi River. The nitrate concentrations and flux increased significantly in 1970–1980, with the largest changes occurring since 1970. They identified southern Minnesota, Iowa, Illinois, Indiana, and the Ohio River Basin as the predominant sources.

The UMRB basin is the most productive agricultural regions in the world. Total N output to the Gulf of Mexico has increased three- to sevenfold compared to outputs before settlement (Downing et al., 1999; Goolsby and Battaglin, 2001). The tributary rivers have been straightened and dams installed on the Mississippi River and many of its major tributaries. Industrialization at the mouth of the river has diminished wetlands and added to the pollutant load.

The apparent result of the dramatic increase in N input to the Gulf of Mexico has been a major change in the ecology of the Gulf (Rabalais et al., 1996; Downing et al., 1999). Higher productivity of phytoplankton because of increased nutrient input has provided more organic residue from dead cells. This has led to increased oxygen consumption during decomposition of the material. The result has been the development of an extensive region of oxygen deficiency (less than 2 mg/L of dissolved oxygen, commonly referred to as hypoxia). This level of dissolved oxygen is below the threshold for the survival of most aquatic organisms, hence the popular term, "dead zone." The zone runs roughly directly west from Louisiana to Texas and is the third largest hypoxia zone in the world (Downing et al., 1999). The area varies between 12,000 and 18,000 km^2 in mid-summer during normal rainfall to high years, but is smaller during drought years (Downing et al., 1999). For example, it was only about 5,000 km^2 in June of 2000 because of low rainfall in the basin (Rabalais et al., 2001).

Goolsby et al. (2001) recently examined the nitrate loads to the Gulf of Mexico from the Mississippi and Atchafalaya Rivers. Their results indicated that since 1985, the amount of N released to the Gulf has been more or less constant, varying directly in proportion to the streamflow. Streamflow is related to land drainage. In normal and wet years, much of the excess nitrate (i.e., nitrate that has not been denitrified or used by plants) is leached from the soil profile. In dry years, it is retained, but in wet years profile drainage leaches nitrate to the tile systems before it can be used by the corn crop (Brezonik et al., 1999; Randall and Mulla, 2001).

Nitrogen fertilizer use and manure production have been approximately constant in the basin over the last 15 years. The increasing yields of corn and soybean without additional N fertilizer imply a more efficient N use by the cropping system. Frequently the soil system is sufficiently high in available N that nitrogen-fixing legumes are not active. Quantification of N cycling at the basin level is not a simple balance sheet process (Keeney and DeLuca, 1993; Keeney, 2002). And the sources depend on other factors including weather changes and alterations in hydrology.

5. ECOLOGICAL ISSUES

The large increase in mobile N worldwide has had many other significant ecological effects; many so subtle that they are not noticed at the public or policy maker level (Vitousek et al., 1997). Modern day activities ranging from industry to agriculture to land clearing has increased the rate of release of several N gases in trace amounts, including nitrous oxide, nitric oxide, and ammonia. Fossil fuel combustion is the major source of nitric oxide, which is a causative effect of photochemical smog and high levels of troposphere ozone. Further oxidation of nitric oxide gives rise to nitric acid, a major component of acid rain now that sulfur emissions have been lowered. Nitrous oxide has been implicated in stratospheric ozone destruction, leading to increased ultraviolet light at the Earth's surface, and as a major contributor to greenhouse gases. Ammonia has a fairly short retention time in the lower atmosphere, but will cause significant fertilization effects on N-limited ecosystems such as prairies, forests, and waters, increasing biological productivity and lowering biodiversity (Vitousek et al., 1996).

The concept of N saturation (Aber, 1992) has been introduced to explain ecosystem changes that occur in forests. A fully N saturated system will be one that has a net zero retention of N, that is, carbon storage through primary productivity is nil. These systems leak N to the environment rather than being net sinks as they were in unaltered ecosystems. The same concept can be applied to other natural ecosystems.

Nitrogen contributes significantly to ecosystem acidity by direct deposition of nitric acid, by oxidation of ammonium, and by leaching of cations, especially calcium, from soils. Landscapes that are poorly buffered, that is, with soils that are already acidic or have low exchange capacities, and whose ecosystems are N saturated will lose cations rapidly. Plant growth, species diversity, and water quality are adversely affected.

6. NITROGEN AND SUSTAINABLE HUMAN ACTIVITY

By 2020, the world will have added another 2.3 billion people (equivalent to another China) (Rosegrant and Livernash, 1996; Smil, 2000). Population control can do little to stop this trend, only slow its steady rise, to a predicted peak of 11 billion sometime between 2050 and early in the next century. Food production, particularly in Asia but also in Africa, must intensify (Smil, 2000). Green revolution strategies which worked well to offset earlier food stresses likely will be hard to repeat for several reasons: (1) They work well in countries with an established infrastructure, for example, roads, educated workers, and credit, and these countries are among the list of those now largely self sufficient in food; (2) The international research centers no longer have the funding available or the political support to help develop and transfer new technologies; and (3) New germplasm to take advantage of current technologies, including fertilizer and pesticides, is difficult to obtain. Grain consumption by animals for meat and milk production continues to take precedence over that grown for direct consumption. A related issue is the declining land under irrigation due to urbanization, salinization, and other demands for water (Smil, 2000).

There are at least three distinct schools of thought on how to meet world food needs in the next century. One is to press for high yield, high input agriculture (Avery, 1995). Rosegrant and Livernash (1996) echo the opinions of others that agricultural intensification has imposed heavy environmental costs in many developing countries. Lester Brown and the WorldWatch Institute (Brown, 1995) present a pessimistic scenario, somewhat like that of Kendall and Pimentel (1994). These groups feel that rapidly expanding populations, poor land use decisions, environmental degradation, and demands for a changing lifestyle will move the world to a bidding war for available food within the next 2–3 decades. Somewhere in the middle are calls for moderation in our views of the future policies and practices. The challenges for equitable production and availability of food for even the next 25 years will require concentrated large-scale efforts in both developed and developing countries and to remain committed to further improvements in agricultural technologies (Smil, 2000).

7. FOOD PRODUCTION AND NITROGEN FERTILIZERS

The above discussion on world food needs perhaps digresses from the main topic of this chapter, but yet is critical to our decisions as a society and as scientists regarding where N fits in the overall scheme of world food production, global environmental issues, and our collective futures. Fertilizer N use in the developed world is stable or declining on a per hectare basis (Table 1). This is not reflected in yields of most grains (except possibly rice), showing clearly that earlier inefficiencies in fertilizer N use can be overcome by management and especially by plant breeding, even without clear economic or political pressures. Some of our efforts must continue to concentrate on increasing fertilizer N efficiency (e.g., use of nitrification inhibitors, precision farming, and other efficiency technologies). Even more bold approaches involving plant as well as management alternatives are needed. But it is critically important to spend more of our intellectual capital developing new systems and redesigning the ones we have. What are the "more sustainable technologies?" It is up to us to ask these questions and to find the answers. Foremost in the questions to be addressed regards minimizing the ecological and health effects of excess nitrogen. New sustainable technologies surely will be aimed at using less N fertilizer per unit of yield.

Market forces will dominate land use and agricultural management decisions in developed countries in the foreseeable future barring unforeseen catastrophes. Grain will continue to be the major farm commodity, and N fertilizers will be essential. Nitrogen fertilizer efficiency improvements will be widely heralded, particularly if the price of N fertilizers rises as might be expected in an energy-short future.

The recent increases in the cost of energy brought on by many forces, including US hurricanes and general political instability worldwide will certainly change the cost/benefit ratio for N fertilizers. Natural gas accounts for 70–90% of the cost of N fertilizers (West, 2005).

Further plant breeding efforts should be applied to developing highly efficient grains and perennial crops. System science can be applied even in grain growing regions of the world to develop approaches that tighten up the N cycle through combinations of legumes, perennials, and annuals. More efficient use of animal manures will be required. Land use that provides N sinks, such as including wetlands and overflow regions for runoff rather than short-circuiting the hydrologic cycle through tile drainage, will be major policy decisions of the future. There is need for more perennials that provide economic returns. Property rights issues will need to be solved to advance land use planning to minimize N pollution. The increasing use of biomass for energy will require more efficient crops to maximize energy output relative to energy required to grow the crop.

8. REGULATORY AND EDUCATIONAL APPROACHES

The use of regulatory approaches to modify human behavior can have some success, particularly when the activities being regulated are outside the bounds of society's desires. Europe for example has had some success using rules and stiff fines to modify fertilizer and animal waste use. Educational programs are important to change the way farmers manage N in their farms. A concerted effort by Iowa educators has helped lower N fertilizer use by about 20% over the last 20 years (Hallberg, 1996), although recent yield trends indicate that Iowa farmers were over-applying N fertilizer and the educational programs mainly aided in bringing rates in line with crop needs.

9. OTHER HUMAN ACTIVITIES

The effect of anthropogenic activities on the N cycle has been addressed to some extent earlier. It is critical to realize that more than just agriculture is involved in solving the recurring issues of N in the environment. Point emissions from sewage treatment plants and industrial operations must be recognized. Emissions from autos and industry must be addressed as part of the ozone, smog, and acid rain issue. Land use is critical. Development now takes our best agricultural lands as well as lands critical to environmental stability. The way we build and populate landscapes must be reassessed.

10. ARE THERE SOLUTIONS THAT MEET ECONOMIC, ECOLOGICAL, AND SOCIOLOGICAL NEEDS AND ARE SUSTAINABLE?

This review attempts to broaden the perspective on N in the environment beyond that of agriculture and crop production. The issues are major, and are recurring. Some are recycled and some are new, brought on by advances in science and monitoring that increased our awareness (e.g., hypoxia) and some are new because ecosystems are now showing stress that they were able to overcome earlier (global climate change, acid rain, ecosystem degradation). The issues may ebb and flow, but they will not go away. Society-wide spread dissemination of knowledge, open and informed discussion at world forums, and consensus on appropriate actions is called for. Technical solutions are the domain of the scientist, but such solutions must fit the world needs for a sustainable future.

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