

Thesis Master Environmental Biology
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The impact of a changing global N cycle on terrestrial ecosystems

Abstract

Nitrogen is an essential element of life. It is also one of the most abundant, making up approx. 78% of the Earth's atmosphere. N is largely made up of inert atmospheric N₂, less than 2% of all N is directly available for organisms. N₂ first has to be fixed and converted to reactive nitrogen (Nr) before usage. N-fixing microorganisms provide the largest natural source of Nr. In the last 50 years, this source has been exceeded by anthropogenic Nr, mainly originating from synthetic N fertilizers. This has caused an major input of Nr into the global N cycle. Input of anthropogenic Nr will continue to rise, primarily driven by the increase in the human population in Asia. Nr plays a role in environmental issues like the greenhouse effect, smog forming, stratospheric ozone depletion, acid deposition, coastal eutrophication, and reduced diversity of water bodies and terrestrial ecosystems. Although the effects are predominantly detrimental, they differ greatly between terrestrial ecosystems and depend on many factors. In both agriculture and industry, the excess in N can be reduced by several measurements. The biggest challenge for the future is increasing the efficiency of N fertilizer use while decreasing the negative effects on the environment.

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Introduction

Nitrogen is an essential element of life. It is also one of the most abundant, making up approx. 78% of the Earth's atmosphere (Galloway et al. 2004). The total amount of N present on Earth is approximately 4×10^{21} g (Mackenzie 1998). This is more than any other element on Earth (Galloway et al. 2003). Less than 2% of all N is however directly available for organisms (Mackenzie 1998). N in the atmosphere exists as inert N_2 , with the two molecular N atoms held together by a triple bond. A lot of energy is required to break this bond, and only a few species of Bacteria and Archaea have evolved the ability to do this (Galloway et al. 2004). These species are collectively called Diazotrophs (Boring et al. 1988). Archaea live freely in extreme environments, while Diazotroph bacteria can be either free-living or in symbiosis with plants. When the bond is broken the individual N atoms have to be bonded chemically to O and/or H through fixation or with C through assimilation (Galloway and Cowling 2002a). It is then a form of reactive N (Nr) that can be used by other organisms (Galloway et al. 2004).

Nr includes all biologically, photo chemically, and radioactively N compounds present on Earth. These compounds are the reduced inorganic forms of N (ammonia: NH_3 , ammonium: NH_4^+), oxidized inorganic forms (nitrogen oxides: NO_x , nitric acid: HNO_3 , nitrous oxide: N_2O , and nitrate: NO_3^-), and organic compounds (e.g. urea, amines, proteins, nucleic acids) (Bobbink et al. 2010; Galloway et al. 2003). Of all major biochemical cycles on Earth, the N cycles has changed the most due to human activity (Asner et al. 2001). Nr plays a role in environmental issues like the greenhouse effect, smog forming, stratospheric ozone destruction, acid deposition, eutrophication of marine ecosystems, and reduced diversity of water bodies and terrestrial ecosystems (Crews and Peoples 2004; Fenn et al. 1998; Galloway et al. 2004; Moomaw 2002; Vitousek et al. 1997).

N is an essential component of amino acids and nucleotides. Amino acids are the building block of proteins, and nucleotides of DNA. N is also needed for the synthesis of hormones and neurotransmitters. N cannot be stored in the body: an excess of N is excreted by metabolites rich in N. There are also small constant losses of N in the breakdown and reutilization of compounds, and excretion in the form of urine, feces, sweat or renewal of skin, hair and nails. An organism therefore needs a steady supply of N in the form of proteins in its diet (Smil 2002a). Humans require $\sim 2 \text{ kg N yr}^{-1}$ of proteins to function properly (Smil 2002).

In this thesis the impact of a changing global nitrogen cycle is discussed. The first part focuses on the production of reactive nitrogen, illustrating the role of microorganisms in the form of N-fixing bacteria associated with legumes and mycorrhiza, and humans with their agricultural and industrial practice. The middle part is dedicated to the consequences of increasing amounts of Nr in the atmosphere, divided into impact on human health and environment, and different ecosystems depending on their sensitivity. The thesis concludes with future trends and solutions regarding the nitrogen cycle in industry and agriculture.

Production of reactive nitrogen by microorganisms

Biological N-fixation rates limit and determine the productivity, composition and diversity of many ecosystems (Galloway et al. 2004; Vitousek et al. 2002b). The largest natural source of Nr is biological nitrogen fixation (BNF) by microorganisms (Figure 1). N-fixing microorganisms are widespread and divers, and their N-fixing capacity is substantial (Vitousek et al. 2002b). Their functioning therefore determines the processing rates of the N cycle in ecosystems (Craine et al. 2007). N-fixing microorganisms are responsible for the N accumulation in ecosystems, bringing the N levels to an equilibrium with other limiting factors (Vitousek et al. 2002b). A minor, additional natural source of Nr is lightning (Galloway et al. 2004).

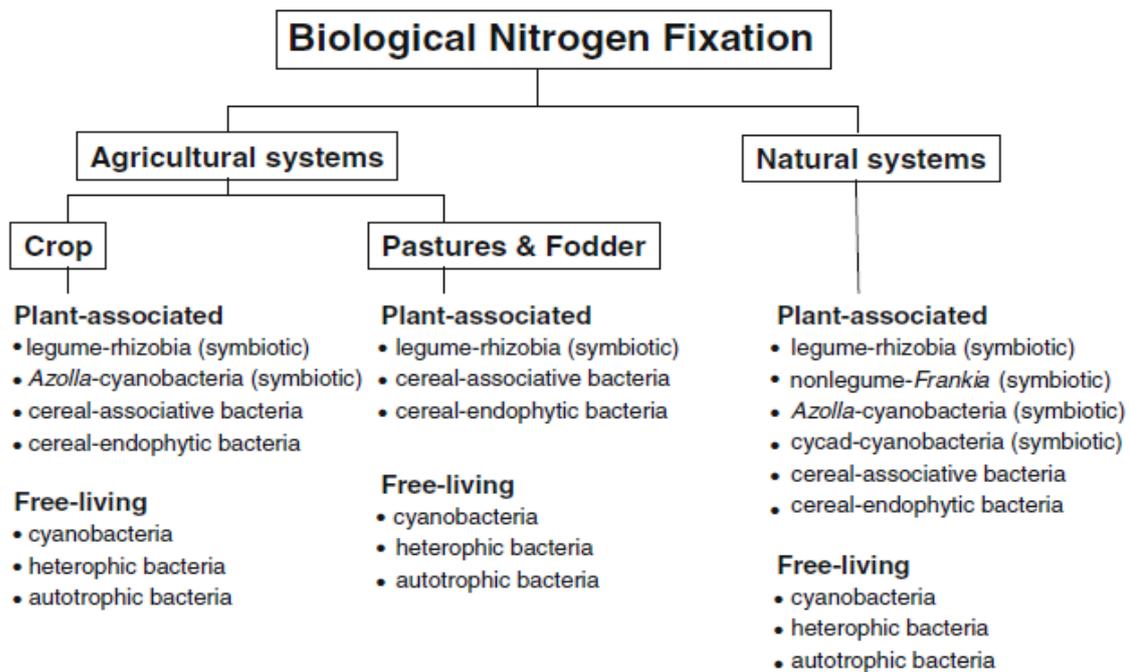


Figure 1: N-fixing microorganisms in Agricultural and terrestrial natural ecosystems (Herridge et al. 2008).

N-fixing legumes

BNF is mediated in three different ways: (1) by N-fixing bacteria in symbiosis with vascular plants, (2) by cyanobacteria in symbiosis with fungi (lichens) or plants, or (3) by free living heterotrophic or autotrophic bacteria typically associated with soil or detritus (Sprent and Sprent 1990). The symbiosis between N-fixing bacteria and vascular plants achieves in general the highest rates of fixation per unit area (Boring et al. 1988). Symbiotic fixation rates in coniferous forests are in the range of 10-160 kg N ha⁻¹ yr⁻¹, and in tropical forests this amount is at least doubled. In contrast, non-symbiotic fixation rates do not exceed ≤ 1-5 kg N ha⁻¹ yr⁻¹ (Boring et al. 1988).

The plant family Fabaceae (Leguminosae) is the most diverse and wide-spread off all vascular plant species in symbiosis with N-fixing bacteria (Crews 1999). Not all Fabaceae species are able to form the symbiosis, but it is not known how common it is since only a few selected have been examined (Crews 1999). The N-fixing bacteria in symbiosis with Fabaceae species are either from the *Rhizobium* or the *Bradyrhizobium* genera (Sprent 1994). These soil bacteria can be free-living, only limited by organic carbon (C) amounts in the soil (Aber et al. 1998; Veresoglou et al. 2012). When a Fabaceae species is present they form a biotrophic endosymbiosis with it (Geurts et al. 2012). Upon symbiosis, the roots of the host plant start to form specialized organs called nodules to accommodate the rhizobia. Nodules originate from primordia formed in the cortex of the root. The centre of the nodules consists of infected cells filled with rhizobia. The rhizobia are separated individually or in clusters by a membrane, forming so-called symbiosomes. Separation into symbiosomes aids in facilitating the nutrient exchange between bacterium and host plant (Geurts et al. 2012).

It is energetically more costly to form a symbiosis with N-fixing bacteria than to grow roots and take up soil N directly (Vitousek and Howarth 1991). But where soil N is not readily available, N-fixing plants have an advantage to non-fixing plants and receive more N for aboveground growth (Vitousek and Howarth 1991). The symbiosis with N-fixing bacteria allowed for spreading out of the Fabaceae species to ecosystems with lower levels of N in the soil, notably semi-desert areas and the tundra (Sprent 1994). The Fabaceae probably emerged in the humid tropics (Herendeen et al. 1992), and are widespread within this ecosystem and in the drier tropics (Crews 1999). These ecosystems have high amounts of N in the soil, thus minimizing the costs of symbiotic N fixation (Vitousek et al. 2002b). Tropical savannas also have a good representation of Fabaceae, while deserts show a lower presence of Fabaceae (Crews 1999). While the tropics have a wide representation of Fabaceae species, the floras of temperate regions show a dominance of early successional legumes, with the absence of woody legumes or legumes in late seral stages (Crews 1999). In comparison to the tropics the costs of symbiotic N fixation are higher in temperate regions, but it is still a more profitable strategy than non-symbiotic N fixation (Vitousek et al. 2002b).

Where N-fixing plants dominate an ecosystem, N limitation is rare (Vitousek et al. 2002a). Fabaceae have an advantage in N-limiting ecosystems, so it is surprising that in most regions they are not the dominant type and the ecosystem is still N-limited. Vitousek and Howarth (1991) examined the mechanisms behind this occurrence and proposed three possible explanations: (1) energetic constraints on the plant to fully colonize and function in an ecosystem, (2) limitation by another essential nutrient, or (3) other physical and ecological factors. Crews (1999) however argues that the main reason for the existence of N limitation in many (temperate) terrestrial ecosystems is due to the limitation on the geographical radiation of woody members of the Fabaceae family. According to Vitousek and Field (1999), symbiotic N-fixation in late-successional forests is also limited by shade tolerance, P limitation, and grazing on N-rich plant biomass (Vitousek and Field 1999).

Mycorrhiza

In contrast to N-fixing bacteria, arbuscular mycorrhizal fungi (AMF) are able to form symbiosis with ~80% of all land plants (Fellbaum et al. 2012). Forming a symbiosis with a host plant is their only mode of survival, because they can't, unlike N-fixing bacteria, have a free-living lifestyle in the soil (Fellbaum et al. 2012). AMF exchange soil nutrients for carbon (C) fixed by the photosynthesis of the host plant. They also play a role in soil aggregation, water retention, and the stress endurance and susceptibility to diseases and insect attacks of the host plant (Veresoglou et al. 2012). Because of the multifunctional nature of the symbiosis, AMF have a direct and indirect effect on the N cycle of terrestrial ecosystems.

AMF can transfer inorganic N from the soil to the host plant directly (He et al. 2003). The N is firstly taken up by the extraradical hyphae of the AMF. N uptake is initiated by the translocation of carbon hydrates from the host plant to the AMF (Fellbaum et al. 2012). But what triggers the transport of N toward the host plant is unknown (Jin et al. 2012). The absorbed N is then incorporated into amino acids, and subsequently transported to the intraradical mycelium in the form of arginine. It is then transferred to the host plant as NH_4^+ (Jin et al. 2005). Aside from NH_4^+ , AMF are also capable to take up and assimilate NO_3^- and amino acids (Hawkins et al. 2000). NO_3^- is more mobile in soil and thus more accessible for plants, but it is also the form of N preferred by AMF for uptake (Toussaint et al. 2004). This could be explained by the energy cost for assimilation by AMF, which is higher for NH_4^+ than for NO_3^- (Jin et al. 2012).

Rhizobia are able to fix more N when the root nodules of their leguminous host plants are also colonized by AMF (Smith and Read 2008). Adding AMF together with the N-fixing legumes is thus has a stronger effect on the N-fixation rate (Garg and Chandel 2010). By influencing the aggregation of the soil, AMF could also have an effect on nitrification and denitrification, which are dependent on the oxygen concentration in the soil pores (Veresoglou et al. 2012). Nitrification and denitrification rates also depend on the moisture levels in the soil, which can also be affected by the presence AMF (Fellbaum et al. 2012). Furthermore, AMF can affect the soil pH, and in this way alter the availability of N-compounds (de Boer and Kowalchuk 2001). Lastly, AMF are able to modify the microbial community in the rhizosphere (Rillig et al. 2006). By immobilizing and transferring N to their host plant, AMF can reduce the N sources for other soil microorganisms (Veresoglou et al. 2012). However, AMF themselves are a large source of C for soil microorganisms, because of the rapid turnover of their extraradical mycelium (Veresoglou et al. 2012).

Production of reactive nitrogen by humans

Anthropogenic Nr is the creation of Nr by human activities. In the last 50 years, anthropogenic Nr creation has increased while natural terrestrial BNF has decreased due to land use change (Galloway et al. 2004). There are various sources of anthropogenic Nr.

Agricultural sources

Food production in agriculture is an activity where Nr is created deliberately to increase yields (Galloway et al. 2004). Agriculture is the major source of anthropogenic Nr (Smil 1999). The natural limitation by N in terrestrial ecosystems is a huge challenge in agricultural fields, where maximum biomass production is the highest aim. Because of increased N fixation and increased proneness to leaching, the depletion rate of Nr in agricultural systems is rapid (Vitousek et al. 2002a). Frequent additional supplies of Nr therefore needed to keep a field productive. Nr in agriculture is created by increasing the BNF, application of manure, and the use of synthetic fertilizers.

BNF and manure application

In pre-industrial times there were three ways of creating new Nr for agriculture (Smil 2001). One way is by legume-based field rotation, where for one growing season a depleted field is used to grow legumes on. This way, new Nr is added to the soil by BNF of the legumes. Legume-based rotation is still common practice in sparsely populated or resource-poor countries, or where pulses form a part of the staple diet (Evans et al. 2001). In the highly productive farming systems of North America and Europe it is rare, with the expectation of fields used for organic farming (Crews and Peoples 2004).

Another way is use of animal and human waste as manure. Manure application represents the recycling of already fixed N, rather than creation of new Nr as is the case with BNF (Vitousek et al. 1997). 50 to 90% of assimilated N on productive pastures can be consumed by livestock when intensively grazed (Thomas 1995). Although 75 to 95% of this consumed N is in the form of excreta that can be used anew as manure, large amounts are lost by leaching or gaseous emissions (People et al. 1994). These pastures are therefore in continuous need of supplementary N (Peoples et al. 1995). The last method is the plowing under of leguminous cover crops as green manures (Smil 2001). At best, these three practices could provide not more than 120-150 kg N ha⁻¹ year⁻¹ (Smil 2001). An increase in BNF because of agricultural practices is largest in crop, fodder and pasture systems (Smil 1999).

Although legume-based rotation is less used nowadays, BNF is still the most important natural source of anthropogenic Nr. This is because the leguminous crop production has increased significantly worldwide (Galloway et al. 2004; Herridge et al. 2008). Soybean (*Glycine max*) is the dominant crop legume; 50% of global crop legume area and 68% of global production is taken up this crop (Herridge et al. 2008). Rice cultivation also promotes BNF, because the paddies create an anaerobic environment suitable for cyanobacteria capable of BNF (Galloway et al. 2004). BNF of Nr induced by humans was an estimated 15 Tg ($\text{Tg} = 10^{12} \text{ g}$) N yr^{-1} in 1900 (Smil 2002). In comparison, the natural creation of Nr was $\sim 300 \text{ Tg N yr}^{-1}$ (Galloway 1995). By 1990, BNF decreased to $\sim 90 \text{ Tg N yr}^{-1}$ because of conversion of natural ecosystems to farmlands. Nr created by anthropogenic activities increased to $\sim 187 \text{ Tg N yr}^{-1}$. That is a nine-fold increase for a global human population that increased 3.5-fold (Galloway and Cowling 2002a). By 2005, N emissions from natural sources had diminished, and anthropogenic N had increased (Galloway et al. 2008). Nowadays, as little as 20% of the available Nr in farming systems has its origin in BNF, compared to 50% in the 1950s (Smil 2002b).

Synthetic fertilizers

The largest source of anthropogenic Nr globally is the use of synthetic N fertilizers (Galloway et al. 2004; Howarth et al. 2002; Figure 2). Synthetic N is the main component of almost all commercially produced N fertilizers (Fixen and West 2002). 82% N for synthetic N fertilizers is made with the Haber-Bosch process (Fixen and West 2002). This technique was developed in 1909 and involved producing NH_3 from N_2 and H_2 (Galloway et al. 2004; Smil 2001). Nr in agriculture has increased from $\sim 15 \text{ Tg N year}^{-1}$ in 1860 to $187 \text{ Tg N year}^{-1}$ in 2005. Of this 2005 amount, $\sim 165 \text{ Tg}$ is supplied by N created using the Haber-Bosch process (Galloway et al. 2004). This is almost twice as much as the N created by BNF ($\sim 90 \text{ Tg N yr}^{-1}$) (Galloway and Cowling 2002a). China is the largest producer of synthetic NH_3 with 25%. The U.S. and India account for 21% (Fixen and West 2002). Around 85% of N in food proteins comes from agriculture, and 40% of N in these proteins have their origin in the Haber-Bosch process (Smil 2002a).

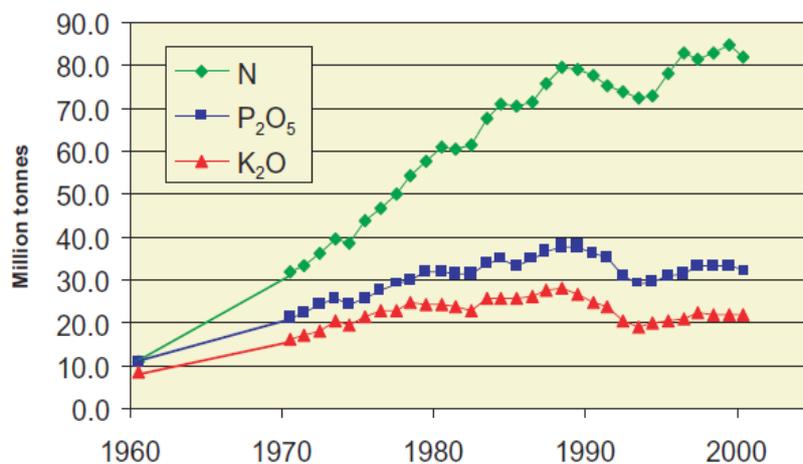


Figure 2: Global consumption of Fertilizers (Fixen and West 2002).

N fertilizers have increased the agricultural yield in two ways. Firstly, by meeting the N demands of crops throughout the growing season the production is optimized resulting in higher yields. Secondly, the farmer doesn't have to spend a growing season on cultivation of N-fixing legumes to restore the levels of Nr in his fields (Crews and Peoples 2004). In comparison to legume-based crop rotations, N fertilizers are cheaper in both labor and land (Crews and Peoples 2004; Peoples et al. 1995). Of all the N input of global croplands, ~50% comes from N fertilizers. This input accounts for 40% of globally consumed food (Smil 2001).

Industrial sources

An activity where Nr is created as a byproduct is energy production (Galloway et al. 2004). 90% of modern day energy production involves emission of Nr as a by-product (Galloway and Cowling 2002a). Nitrogen oxides (NO_x), a mixture of NO and NO_2 , are released during combustion of fossil fuels and biomass, and during the production of certain chemicals and produces. Release of NO_x during fossil fuels combustion is either achieved by thermal production; the direct reaction between atmospheric N_2 and oxygen O_2 to produce two new units of NO, or by pyrolysis of organic compounds containing N, resulting in mobilization of sequestered NO_x (Galloway et al. 2004; Moomaw 2002).

Because natural gas doesn't contain organic N, no NO_x is released during its combustion. The amount of organic N is almost 2% in petroleum and 1-2% in coal (Moomaw 2002). Additionally, N_2O , a potent greenhouse gas, is released during production of adipic and nitric acid, and during the burning of biomass (Kroeze et al. 1999). N_2O is also released from farming systems, and soil after large N inputs in the form of fertilizers, animal waste, crop residues, and BNF (Kroeze et al. 1999). The amount of NO_x emitted from soils is similar to NO_x emissions from fossil fuel combustion (Davidson and Kinglerlee 1997).

The contribution of energy production to anthropogenic Nr creation is small compared to agriculture, but both food and energy production have increased the anthropogenic Nr creation rate over a factor of 10 in over 100 years (Galloway et al. 2004). Energy production shifted from biofuels to fossil fuels in the previous millennium (Galloway and Cowling 2002a). Nr emitted during fossil fuel combustion increased from ~0.6 Tg N yr^{-1} in 1890 to ~21 Tg N yr^{-1} in 1990 (Levy et al. 1999). From 1950 to 2000, the use of fossil fuels had increased by 4.6-fold. North America accounts for one-third of fossil fuel emissions (Moomaw 2002). Globally, Nr released from fossil fuel combustion is one-fourth of the Nr released by use of N fertilizers (Howarth et al. 2002).

Consequences of increased inputs of Nr

Before the occurrence of Nr created by human activity, Nr did not accumulate in ecosystems because microbial N fixation and denitrification were in equilibrium (Ayres et al. 1994). Without human activity, BNF in natural ecosystems amounts to $\sim 89 \text{ Tg N yr}^{-1}$. Most BNF takes place in forests and grasslands (Zheng et al. 2002). Only small portion of Nr created by natural BNF is denitrified and emitted in the form of NO or N₂O (Zheng et al. 2002). But the supply of anthropogenic Nr into the global N cycle has increased several-fold in the last 150 years, with a doubling occurring in the last 50 years (Holland et al. 1999). Nr now accumulates on all spatial scales, because denitrification rates are lower than deposition rates (Holland et al. 1999; Figure 3). Of all Nr forms, N₂O is the only one not involved in N deposition (Bobbink et al. 2010). Nr deposition is becoming the main source of N in natural ecosystems, putting BNF second (Holland et al. 1999).

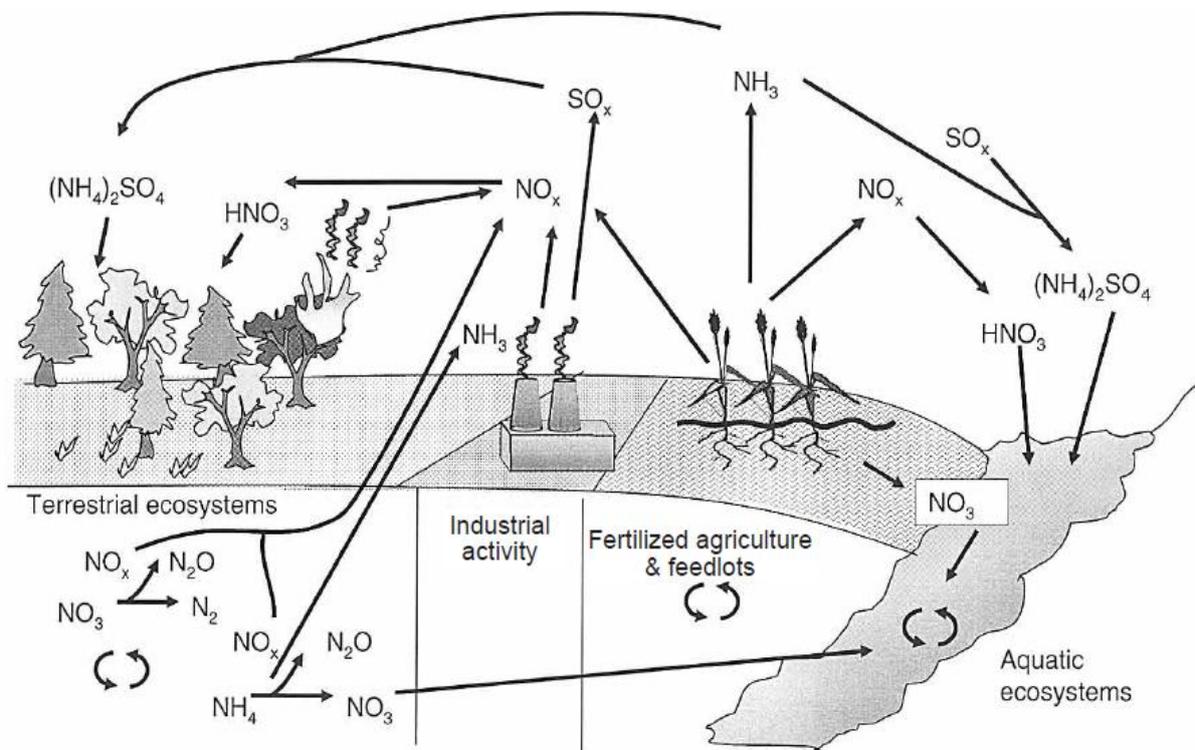


Figure 3: Global representation of the creation, transportation and deposition of Nr (Matson et al. 2002).

The amounts of N losses to natural ecosystems exceed the critical amounts that have a negative impact on the environment (Galloway et al. 2008). There is a growing concern that the excess in Nr has a profound impact on the environment, ecosystem functioning and human health (Smil 1999). A single atom of Nr can cause multiple effects as it moves through the environment. This is called the nitrogen cascade. The speed in which it cascades differs between ecosystems. The cascade is only stopped when Nr is converted back to N₂ (Galloway et al. 2003).

Environmental hazards

There is growing evidence that excess N input can lead to acidification and eutrophication of water bodies (Vitousek et al. 1997), global warming, groundwater contamination and stratospheric ozone destruction (Crews and Peoples 2004). Eutrophication causes overgrowth of algae, which in turn causes oxygen deprivation, loss of biodiversity and fish death (Moomaw 2002; Wolfe and Patz 2002). N_r is lost primarily by transport and deposition via the atmosphere (Galloway et al. 2008). Under the right circumstances, atmospheric N can be transported tens of thousands of kilometers (Bobbink et al. 2010).

NO_x plays a complex role in the atmosphere; its effects can be both beneficial as detrimental. It has a short life-span; as does NH₃, it lasts up to a day in polluted urban atmospheres, and 5 to 10 days in the upper troposphere (Moomaw 2002) before it is deposited onto the Earth's surface by wet or dry deposition (Zheng et al. 2002). It is therefore mostly a determinant in local effects (Davidson and Kinglerlee 1997). NO_x is involved in the catalytic conversion of CO to CO₂, aided by the hydroxyl radical. NO_x increases the concentration of this radical, thereby shortening the lifespan of CO₂, CH₄ and HFCs. This improves air quality and reduces the contributions to global warming (Moomaw 2002).

There are however more detrimental effects; NO₂ absorbs light and in doing so it provides the necessary energy for photochemical smog formation. NO₂ can also, by itself or in presence of volatile organic compounds, form ozone. Ozone absorbs infrared radiation, warming the atmosphere and creating a suitable environment for the formation of even more ozone (Moomaw 2002). In contrast to NO_x, N₂O can survive up to 100 years (Zheng et al. 2002) in the troposphere before it is converted to NO_x in the stratosphere (Zheng et al. 2002). NO_x forms nitric acid and related particles when combined with NH₃, moisture and other compounds (van Egmond et al. 2002), thus becoming the second largest contributor to acid rain formation (Moomaw 2002). In addition, NO₃⁻ aerosols diminish the atmospheric visibility. N₂O is a powerful greenhouse gas and depletes the stratospheric ozone layer, affecting the global climate (Moomaw 2002).

Effects on human health

N_r has an indirect effect on human health because of its role in acid rain formation, global warming and eutrophication of water bodies, amongst others (Fenn et al. 1998; Melillo and Cowling 2002). For example, water polluted by N results in a reduction of drinking water quality (Fenn et al. 1998), and can cause methemoglobinemia by indigestion of NO₂⁻, and increased exposure to toxic algae *Pfiesteria piscicida* (Wolfe and Patz 2002). In addition, NO_x is a strong oxidant and can form fine particulate matters, which can lead to respiratory and cardiac diseases in humans (Wolfe and Patz 2002). Ozone, acid rain and other oxidants can damage buildings and cultural artifacts (Galloway et al. 2002b).

Consequences to ecosystem functioning

Since the industrial and green revolution, atmospheric N deposition has grown from an insignificant flux to a dominant source of foreign N in a ecosystem (Galloway et al. 2008). N cycling in ecosystems originally had three main sources; (1) BNF that introduces new Nr into a system, (2) mineralization converting organic Nr to inorganic Nr within a system, and (3) atmospheric deposition adding Nr from one system to the other (Bobbink et al. 2010). Input of Nr from human activities had now become the fourth, major source.

N deposition into ecosystems consists of NO_x (mainly NO_3^-), originating from primarily fossil fuel combustion, and of NH_x (NH_3 and NH_4^+), which has its origin in the use N fertilizers in agriculture. In a large part of Asia and some parts of Europe, the contribution of NH_4^+ exceeds that of NO_3^- (Galloway 1995). Nr deposition is often measured in NO_3^- and NH_4^+ in precipitation (wet deposition). NO_3^- in precipitation is commonly the dissolution product of nitric acid (HNO_3), but may also come from dissolution of salts as well as organic nitrates (Holland et al. 1999).

The largest part of emitted Nr is deposited onto land, the rest into water bodies (Howarth et al. 2002). N applied to the soil can be either taken up by the plant or immobilized in either soil organic N pools consisting of microbial biomass and organic matter or soil inorganic pools. Plants can store N, but soil type may be more important than plant composition in N retention (Nadelhoffer et al. 1999a). Most N fixed by natural processes remain in terrestrial ecosystems and is denitrified in soil, sediment or groundwater (Galloway et al. 1995 in Galloway 1998). Access N that isn't stored is likely to be lost from the field by either leaching or denitrification (Cassman et al. 2002). A large part of Nr originating from N fertilizers is immobilized in the soil by microbes and only becomes available in the next year through mineralization (Howarth et al. 2002). For example, two thirds of Nr input in the U.S. in 1997 were denitrified or stored in soil/biota, while one-third was exported to other ecosystems (Howarth et al. 2002).

Atmospheric N bonds to organic matter in the soil. Accounting for 80% of total N, it is the largest N pool in forest ecosystems, but unavailable to most plants. N pools in these ecosystems are however not nearly large enough to meet N demand by plants and have to turnover several times a year (Fenn et al. 1998). By adding N to an N-limited ecosystem, the production of the plant and microbial community would increase (Aber et al. 1998; Matson et al. 2002). Temperate forests in North America and Europe are shown to grow faster now in comparison to the beginning of the previous century, and at least part of it can be attributed to increased input of N (Binkley and Högberg 1997).

But when N saturation continues, detrimental effects arise and begin to affect the plant productivity (Aber et al. 1998; Matson et al. 2002). Saturation of N occurs when N_r accumulates with a rate that's faster than the rate of denitrification (Bobbink et al. 2010). N saturation of ecosystems can be detected in heightened levels of nitrification, N mineralization and assimilation, leaching, and plant tissue concentrations (Fenn et al. 1998; Matson et al. 2002; Pardo et al. 2011). Leaching of NO_3^- is most common in forest ecosystems and can cause acidification of water bodies and the soil, nutrient imbalances in trees, and forest decline (Aber et al. 1989; Fenn et al. 1998). Besides leaching of N, gas emissions of NO, N_2O and N_2 are also a effect of N saturation (Matson et al. 2002). High inputs also cause nutrient imbalance and acidification of the soil, and increased plant susceptibility to ozone, frost, and drought (Matson et al. 2002; van Egmond et al. 2002). Increase of NO_x in the troposphere can result in ozone-induced damage to agricultural and natural ecosystems, and predisposition to attack by pathogens and insects (Galloway et al. 2002b; Matson et al. 2002).

Nitrification and denitrification are pathways for NO, N_2O and N_2 losses from soils (Matson et al. 2002). Nitrification (oxidation of NH_4^+ to NO_3^- by aerobic nitrifying bacteria) occurs in excess of N assimilation. NO_3^- is more mobile in the soil, thus a increase in nitrification results in a increase in N leaching (Matson et al. 2002). Nitrification benefits from low C:N ratios and a high temperature, pH and moisture level of the soil (Dise and Wright 1995). Continuous inputs of N increase rates of N mineralization because the additional N is incorporated into soil organic matter. This reduces the C:N ratios of the matter and increases the rate of release during decomposition (20,35 in Matson et al. 2002). Thus when mineralization increases, more N can be nitrified (Matson et al. 2002). But N saturation may in the long term lower the rate of N mineralization (Matson et al. 2002).

Denitrification (conversion of N_r to N_2) is a important N sink. More than 80% of denitrification takes place in soils and freshwater bodies. By increasing the denitrification rate of the soil, leaching of N can be reduced (Galloway et al. 2002b). Temperate forests show no N leaching at deposition levels lower than $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$. Deposition levels of $10\text{-}25 \text{ kg N ha}^{-1} \text{ year}^{-1}$ results in leaching at some sites. Above $25 \text{ kg N ha}^{-1} \text{ year}^{-1}$, leaching occurs at all sites (Dise and Wright 1995).

A change in soil N levels can make the area unsuitable for some species and alter the competitive interactions between species (Bobbink et al. 2010). A majority of ecosystem communities have evolved in presence of N-limitation (Galloway and Cowling 2002a), which has resulted in a high species diversity (Bobbink et al. 2010). An increase in N assimilation in terrestrial ecosystems influences the plant, lichen, AMF, and diatom species composition (Matson et al. 2002; Pardo et al. 2011), and supports the introduction of new nitrophylic species (Bobbink et al. 1998). Effects such as acidification, that promotes the settlement of acid-tolerant species, and N toxicity can play a supporting role (Bobbink et al. 2010; van Egmond et al. 2002). This can result in biodiversity loss, especially concerning species already

endangered (Pardo et al. 2011). Diatoms can handle only small loads on N. Lichens and bryophytes, AMF, herbaceous plants and shrubs, and trees can take up increasingly larger loads of N (Pardo et al. 2011). Ecosystems with a loss of biodiversity have a decreased N uptake (Bessler et al. 2012), and this can lead to greater N losses.

The mechanisms that control the N limitation in ecosystems determine the consequences of increased N deposition, by for instance, human activity. Ecosystems with N limitation could show more apparent consequences in comparison to ecosystems with high amounts N, like lowland tropical forests (Vitousek et al. 2002b). The duration, amount and form of N input determines if the effect on ecosystems is beneficial or detrimental (Bobbink et al. 2010). Small amounts of added N_r often have beneficial effects (Galloway et al. 2002b). But because effects do not occur immediately after N input (Matson et al. 1999) and are non-linear (Fenn et al. 1998), and because every ecosystem has a different sensitivity to N deposition (Bobbink et al. 2010), it is difficult to predict what input of N will cause to an ecosystem. In addition, the response to input of N depends on factors like the state of succession, ecosystem type, N demand and retention capacity, land-use history, soil type, topography, and climate of the area (Matson et al. 2002).

Differences of N input sensitivity between ecosystems

In pre-industrial times, N_r deposition was greatest in tropical ecosystems (Holland et al. 1999). Nowadays, N_r deposition in temperate ecosystems of the Northern Hemisphere is on average four times greater than the N_r deposition rate in pre-industrial times, and exceeds the modern N_r deposition in tropical ecosystems by far (Holland et al. 1999).

European grasslands are compared to other parts of the world much more intensively used and fertilized, and the major source of N_r in European grasslands is due to use of N fertilizers on pastures (van Egmond et al. 2002). While the total emission of NO_x are significantly higher in North America than in Europe, the emission per unit area in Europe is two times higher compared to North America and three times higher than the world average. The emissions are much more concentrated in Europe (van Egmond et al. 2002).

In temperate forest ecosystems, the decay process of soil organic matter is the rate-limiting step in the N cycle. This is because plants use N to produce carbon compounds to form plant tissue, and decomposing this plant tissue back to N is difficult. Adding inorganic N to these ecosystems can result initially in increased N uptake and growth by plants, although Nadelhoffer et al. 1999b could not find a significant increase in C uptake after N input. Upon saturation, the N retention efficiency decreases, nitrification increases and N is more prone to be lost by leaching. This ultimately leads to a decline in plant growth. This process could be sped up by removing AMF, which play an important role in N immobilization in the soil (Aber et al. 1998). Deposition of N_r into European forests has increased due to NO_x from fossil fuel combustion and NH_4^+ from N fertilizer use in agriculture. In some forests, this

input has exceeded retention capacity of the ecosystem, leading to N leaching (mostly in the form of NO_3^-) (Dise and Wright 1995).

In Europe, soil acidification caused by N saturation is most prominent in acidic coniferous and deciduous forests, with heathlands and neutral to acidic grasslands coming second (van Egmond et al. 2002).

Tropical forests have more N available than temperate forests (Martinelli et al. 1999), and are usually not limited by N in production. But there is a difference between tropical ecosystems; while most lowland tropical forests have an excess of N, montane forests and forests on sandy soils have relatively low numbers of N and are more prone to N depletion (Martinelli et al. 1999). In tropical ecosystems, the age, development, and weathering of the soil may influence the production response to N additions (Matson et al. 2002).

Although temperate forests receive the most anthropogenic N, semi-arid and tropical ecosystems receive increasing N depositions (Holland et al. 1999; Matson et al. 1999). For example, inputs anthropogenic N into Brazilian ecosystems have doubled between 1995 and 2002. Other than in North American and European systems, the main source of anthropogenic N is legume-based N fixation (Filoso et al. 2006), but use of N fertilizers is becoming a major factor too (Filoso et al. 2006). 40% of N fertilizer applications occur in the tropics and subtropics (Matson et al. 1999), and nearly two-thirds of N input will occur in the tropics by 2020 (Galloway et al. 1994).

Because tropical forests are naturally not limited by N, N deposition lead faster to N leaching, and subsequent reduction of plant growth and productivity (Asner et al. 2001; Matson et al. 1999). Many tropical forests soils are acidic, N saturation would further promote the acidity and cause losses of cations and decreased availability of P and other nutrients. This would also reduce plant productivity (Matson et al. 1999). Bobbink et al. 2010 thinks that tropical ecosystems may therefore be even more vulnerable in their regeneration phase than temperate forests (Bobbink et al. 2010).

What contributes most to the changing N cycle however is conversion of the Amazon to pastures (Filoso et al. 2006). When Amazon forests are converted to pastures, rates of N mineralization and nitrification tend to decrease. This reduces the N availability in soils and N leaching (Mellilo et al. 2001). This is in contrast to conversion of land in temperate ecosystems to agriculture, which results in a large net release of N_r due to mineralization in excess of immobilization (Howarth et al. 2002). But in the long-term the intensely grazed pastures in the tropics will need additional N supplies, promoting further use of N fertilizers and reoccurrence of N leaching. There is a lot more research needed to understand the effect of N inputs into tropical ecosystems. Vulnerable ecosystems with little data are large parts of Asia and Africa, and tropical regions in the Americas (Bobbink et al. 2010).

A number of ecosystems have low NO emissions and are not heavily affected by N deposition. These ecosystems are: montane and temperate forests, swamps and marshes, and tundras. The largest NO emissions were observed in tropical savannas and woodlands, chaparral and agricultural ecosystems. Emissions within these ecosystems differ greatly amongst each other, but it is not clear whether low and high emissions differ significantly (Davidson and Kinglerlee 1997).

Future trends and possible solutions

In the last 40 years, the world population has increased by 78%, and reactive N (Nr) in the global N cycle has increased by 120% (Galloway et al. 2008). Nr pollution is now considered to be the main problem in coastal ecosystems of the U.S. (Howarth et al. 2002), and N deposition into ecosystems will increase in 2030 (Dentener et al. 2006 in Bobbink et al. 1998). Input of Nr has an undeniable effect on all aspects of the Earth's systems, so it is essential to control the increase of anthropogenic N. In both agriculture and industry, the excess in N can be reduced by several measurements. The biggest challenge for the future is increasing the efficiency of N fertilizer use while decreasing the effects on the environment (Galloway et al. 2008).

Industry

By decreasing the temperature of combustion or by converting NO_x back to N₂ before emission, the amount of released NO_x can be reduced (Galloway et al. 2002b). NO_x released during fossil fuel combustion can also convert back to N₂ (Galloway et al. 2002b). Use of N released during fossil fuel combustion is still unusual (Galloway et al. 2002b), but may provide a solution. Removal of waste gasses containing Nr produced during fossil fuel combustion or from sewage can also reduce N emissions (Townsend and Palm 2009). Lastly, emission of NO_x can be restricted by add-on emission control technology (Moomaw 2002).

Biofuel combustion may release less NO_x than burning of fossil fuels, recent studies show that ethanol used as biofuel and produced from corn has a larger impact on global warming than gasoline (Howarth et al. 2009). This is because fields designed for biofuel production demand high levels of N fertilizer use (Howarth et al. 2009). Most biofuel is created from corn produced in the U.S. or sugar cane from Brazil (Galloway et al. 2008). In the U.S., 29 million ha of corn is grown with an N fertilizer input of 160 kg N ha⁻¹ yr⁻¹. Brazil has ~7 million ha of sugar cane, with 100 kg N ha⁻¹ yr⁻¹. The area is expected to double by 2016. In Brazil, the fertilizer efficiency is very low: only ~30% of added N ends up in the plant tissue (Galloway et al. 2008). The rest is lost via leaching or gas emissions. N release from fossil fuel and biomass combustion is increasing, but is still dominated by the agricultural sector (Galloway et al. 2008). Increasing the efficiency of N fertilizer use in agriculture is therefore of main concern.

Agriculture

Agricultural practices are an important source of NO emission (Davidson and Kinglerlee 1997). In the past 30 years, the amount of newly converted farmland has leveled off, showing discrepancy with the growth of the global human population (Galloway 1998). Food demand for 2030 is estimated to be around 2800 Tg year⁻¹ (Roy et al. 2002). But should the human population and its increasing consumption continue to be equally demanding, the impact on agriculture will result in 10⁹ hectares of land being converted from natural ecosystems to cropland by 2050 (Tilman et al. 2001). But another possibility is that food production will increase because of higher yield from existing fields, and not from expansion of the croplands (Roy et al. 2002). Global N losses to the environment from fertilizers was 36 Tg year⁻¹ in 2002 (Roy et al. 2002). Should leaking of nutrients from ecosystems follow the trend, eutrophication of water bodies by N and P will increase by 2.4 to 2.7 fold by 2050 (Tilman et al. 2001).

While Nr production in North America and Europe might decrease, the production will increase in Asia due to growth of the economy and human population (Fixen and West 2002; Figure 4 and 5). Anthropogenic Nr in Asia has increased from ~14.4 Tg N yr⁻¹ in 1961 to ~67.7 Tg N yr⁻¹ in 2000. According to various predictions this amount will increase to 105.3 Tg N yr⁻¹ by 2030. Deposition of Nr occurs almost entirely in natural ecosystems; ~82% of emitted NO_x and NH₃ in Asia is deposited back on land in Asia. The rest is deposited into water bodies (Zheng et al. 2002).

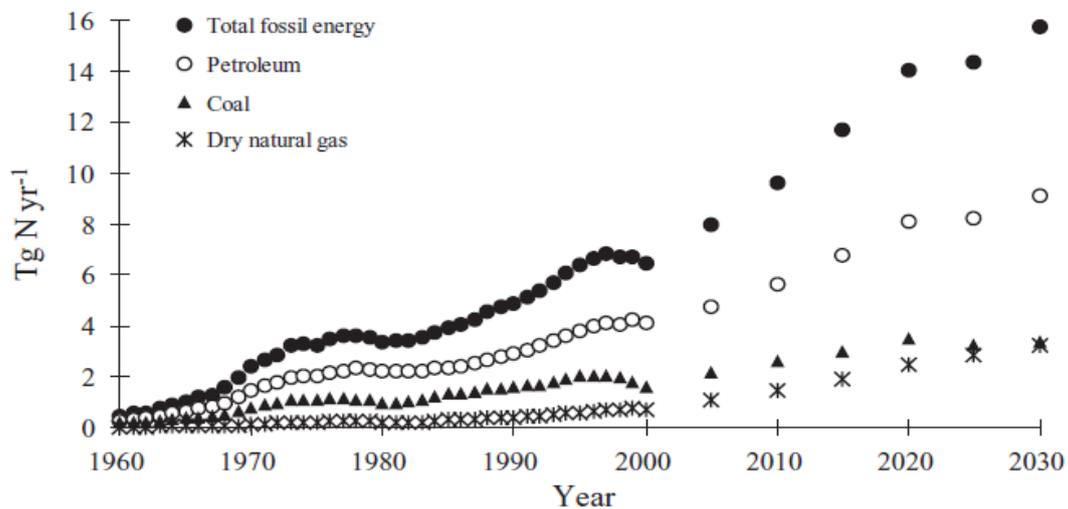


Figure 4: Nr creation by fossil fuel combustion in Asia over 1960-2030 (Zheng et al. 2002).

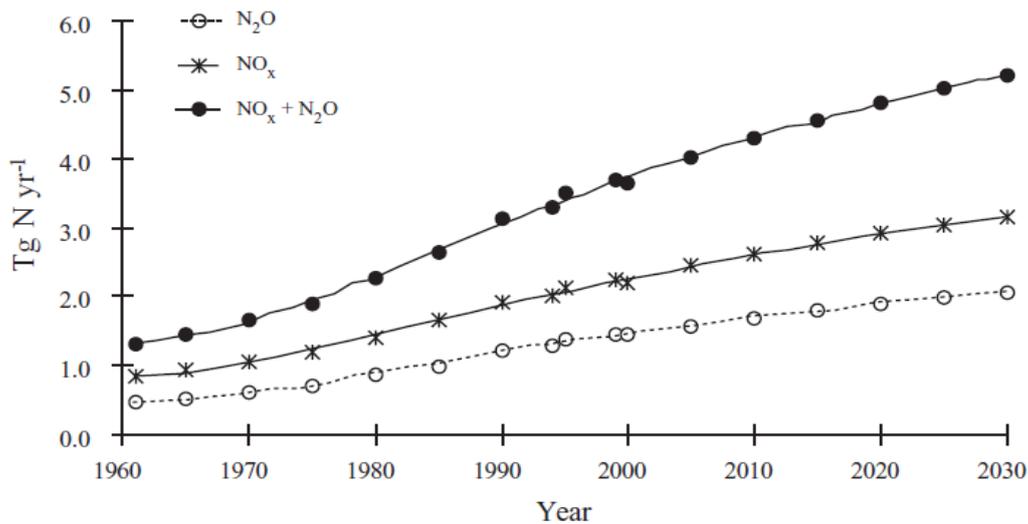


Figure 5: Biological emission rates of NO_x and N₂O from anthropogenic Nr created in Asia over 1960-2030 (Zheng et al. 2002).

Cereals represent 50% of global food consumption (Roy et al. 2002). N fertilizers are the largest source of N input and loss in cereal cropping systems, accounting for 46% of total N input (Smil 1999). BNF, atmospheric deposition, manure and crop residues make up 20%, 12%, 11% and 7% respectively (Smil 1999). But even well-managed cereal crop fields still lose 40 to 60% of N from N fertilizer inputs (Galloway et al. 2002b). Excess of N input is lost from crop fields to the atmosphere by gas emissions or denitrification, or to other ecosystems by leaching and erosion (Smil 1999).

Crop yield is determined by climate and management practices. The N demand of crop depends on the biomass yield and the physiological requirements for tissue N, and is determined by the efficiency of the plant to turn N into biomass and grain yield (Cassman et al. 2002). It is essential to adjust the supplement of N fertilizer to the demands for maximum crop yield, without meeting deficiency or excess (Cassman et al. 2002; Fixen and West 2002). By increasing the uptake efficiency of plants, or by limitation of N losses from soil N pools, N losses from agricultural fields can be reduced (Cassman et al. 2002).

Improved agricultural management practices in developed countries have already reduced N losses while maintaining an increase in yield (Roy et al. 2002). Economic and environmental incentives will improve fertilizer efficiency in especially these countries (Roy et al. 2002). Use of N fertilizers in livestock systems can be reduced by higher feeding efficiencies and changing the human diet towards a less demanding one (Smil 2002a). In an ideal situation all added N would be taken up and used by the grow for growing plant tissue. This is difficult to achieve because of the strong focus on increasing crop yields that, aided by the accessibility and low price, stimulates excessive use of N fertilizers (Cassman et al. 2002).

Organic farming, where N is supplied by N-fixing legumes and animal manure, is considered by some to be a more sustainable alternative to the N-demanding practices in conventional farming (Crews and Peoples 2004). However, organic farming produces less yield per area of

land, even when practiced in the most efficient way. This could lead to more natural ecosystems being converted to farmland (Cassman et al. 2002). Furthermore, organic farming depends on livestock for managing and/or foraging, expanding the size of livestock beyond the demand for animal products. Lastly, as a additional source of N-rich organic materials are often imported from other areas, depleting these areas from their N and decreasing their productivity (Fixen and West 2002). So although the land for organic farming has increased in the EU over the years, rather than eliminating the use of N fertilizers, crop yield should be increased by synchronizing the crop demand and the application of N (Crews and Peoples 2004).

A major problematic aspect that drives the demand for ever-increasing crop yields is in the trend for an unhealthy and unnecessary protein-rich diet in developed countries, and increasingly in developing countries (Roy et al. 2002). Especially the consumption of a disproportionate amount of meat proteins, which demands a high crop yield, drives the use of N fertilizers up in the agricultural sector (Howarth et al. 2002). Low-income countries are meanwhile still unable to provide a diet with enough proteins for their human population, despite the fact that 65% of all N fertilizer use is accounted for these countries (Smil 2002a). In the developed world, N fertilizers are not used to overcome insufficient crop yields, but to create a surplus of food allowing for protein-rich diets (Smil 2002a). A significant amount of food is also exported to other countries (Smil 2002a). Changing the diet of the developed world and distributing food more evenly would have an immense impact on the agricultural sector.

Atmospheric concentrations of N_r vary greatly between regions. The highest values are found in and downwind of urban areas like the northeast of the U.S., western and central Europe and east Asia (Holland et al. 1999). Smog and acid rain are limited to urban regions and to areas downwind from these regions (Moomaw 2002). Elevation of anthropogenic N in a region is not solely due to agricultural practices but can also have a secondary source, like atmospheric deposition and net import of food. Reducing the use of N fertilizer in this region will therefore have little consequences. Removing N by wastewater treatment results in larger reduction of estuarine N (Driscoll et al. 2003).

Conclusion

The global N cycle is one of the most important biochemical cycles on Earth. In recent decades, human activity has caused a new major source of N_r , influencing the natural N cycle. The effects of excessive N_r are as of yet not fully understood. It is however undeniable that there are many detrimental consequences to all aspects of life, affecting productivity of ecosystems, human health and global climate. Most anthropogenic N_r is created in the agricultural sector, with the use of synthetic N fertilizers accounting for the major part. By increasing the efficiency of N fertilizer use and changing the demanding diet in the developed world, the production of N_r could be significantly reduced.

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