

Chapter 1. Why does nitrogen matter?

This chapter explains why the nitrogen cycle is an important issue for environmental policy. It provides an overview of the main sources of nitrogen, the pathways normally used by nitrogen once released into the environment, and the health and environmental risks associated with excess nitrogen in the receiving ecosystems. The chapter introduces the concept of "nitrogen cascade", which translates an unpredictable sequence of nitrogen cycle effects.

Three elements, carbon, oxygen and hydrogen, constitute more than 90% of our bodies by weight. Carbon comes from carbon dioxide (CO₂), which plants take in by photosynthesis and turn into food. We breathe atmospheric oxygen into our blood, and hydrogen reaches us through water. But the most important element in many ways for humans is the 4th most common in our bodies – and the hardest to find in nature in forms we can use: nitrogen.¹ Every living creature requires nitrogen. For example, nitrogen is a major component of chlorophyll, the most important pigment needed for photosynthesis. It is required in all the DNA and RNA in our cells. It is also required in amino acids, the key building blocks of proteins.

The atmosphere we breathe is 78% dinitrogen.² However, if we had to rely on dinitrogen only, it would be like floating on the sea, dying of thirst (Hager, 2009). This is because dinitrogen in the atmosphere is in the form of N₂ molecules which have a very strong (triple) chemical bond and are basically useless to living creatures in that form. Conversion of dinitrogen to biologically available (“reactive”) nitrogen, a process called “fixation”, involves several processes, as part of the nitrogen cycle (Annex A).

1.1 A doubling of global nitrogen fixation since pre-industrial time

Until the end of the 19th century, limited availability of nitrogen severely constrained agricultural and industrial productivity.³ At the start of the twentieth century, several industrial processes were developed to fix dinitrogen into nitrogen. The most important process turned out to be the Haber–Bosch process.⁴ Prior to the Haber–Bosch discovery, in 1913, nitrogen fixation depended almost entirely on bacteria (see Annex A). By adding industrial clout to the efforts of the microbes that used to do the job single-handed, humans have dramatically increased the annual amount of nitrogen fixed on land (The Economist, 2011). Humans have actually doubled the annual input of nitrogen (Table 1.1).⁵ By comparison, our intervention in the carbon cycle has added roughly 10% to the natural pre-industrial land-atmosphere flux (Prentice et al., 2015).

Table 1.1. Contributions to annual global nitrogen fixation

Mechanism	Amount ¹ (million tonnes N per year)
Terrestrial pre-industrial biological fixation	58
Marine biological fixation	140
Lightning fixation of nitrogen	5
Sub-total of “natural” fixation	203
Biological fixation by croplands	60
Combustion	30
Fertiliser and industrial feedstock	120
<i>o/w fertiliser</i>	96
<i>o/w industrial feedstock²</i>	24
Sub-total of “anthropogenic” fixation	210
Total fixation	413

1. Many uncertainties remain about the stocks and flows of nitrogen within and between air, land, freshwater and oceans. For example, a “remarkably large uncertainty” remains as to the extent of biological fixation of nitrogen (Stocker et al., 2016) and recent studies show that more than a quarter of the nitrogen used by plants would come from the Earth’s bedrock (Houlton et al., 2018).

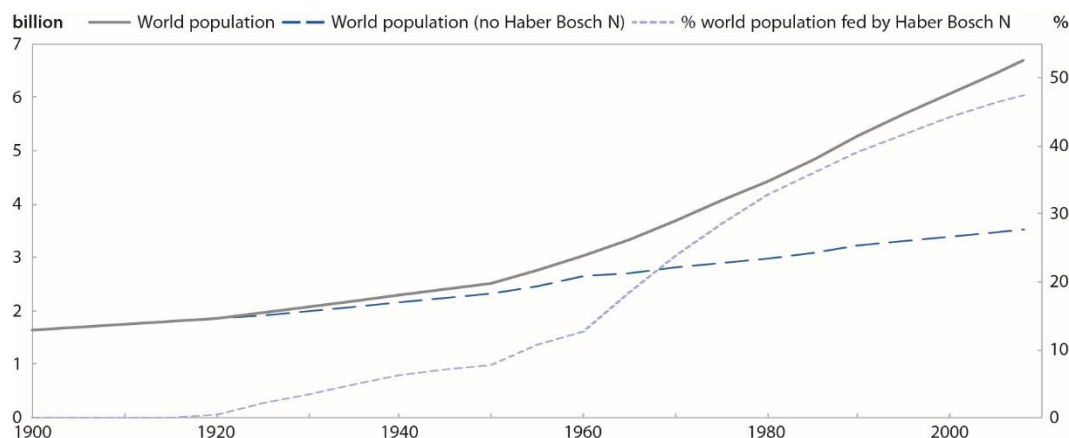
2. Including nylon, plastics, resins, glues, melamine, animal/fish/shrimp feed supplements, and explosives.

Source: Fowler et al. (2013).

1.2 An essential nutrient, but a potential pollutant

The Haber–Bosch process is the main industrial process for the production of nitrogen. Most (80%) is used to produce fertiliser; the remaining 20% is used to make explosives, dyes, household cleaners and nylon. Erisman et al., 2008 estimated that around half of the nitrogen in the protein that humans eat today got into that food by way of artificial fertiliser (Figure 1.1), illustrating the world’s increasing dependence on the use of fertiliser.

Figure 1.1. Feeding the world with artificial fertiliser



Note: The Haber–Bosch process was discovered in 1913.

Source: Erisman et al. (2008).

Today, nearly three-quarters of anthropogenic nitrogen is intentionally added to soils by cultivation of nitrogen-fixing crops and application of chemical fertiliser. An additional 10% is fixed intentionally to produce industrial feedstock and the remaining 15% is unintentionally created as nitrogen oxides (NO_x) into the air as a result of energy combustion.⁶ Despite immense benefits in terms of food and energy security, losses of nitrogen fertiliser and nitrogen from combustion in the environment have numerous and significant side effects on human health and the environment, as evidenced by various recent assessments (Sutton et al., 2011; USEPA-SAB, 2011; SRU, 2015; Tomich et al., 2016; Abrol et al., 2017; Hellsten et al., 2017). The top five threats of excessive release of nitrogen into the environment are water quality; air quality; greenhouse balance and ozone layer; ecosystems and biodiversity; and, soil quality, which Sutton et al., 2011 summarises by the acronym WAGES (Table 1.2).

Table 1.2. Key threats of excessive release of nitrogen into the environment

Environmental issue	Adverse impact on health and the environment	Main form of nitrogen involved
Water	Nitrate contamination of ground- and drinking water	Nitrate (NO ₃ ⁻)
Air	Human health effects and effects on vegetation Effects on materials and monuments	Nitrogen oxides (NO _x), ammonia (NH ₃), particulate matter (PM) ¹ , ground-level ozone (GLO) Nitric acid (HNO ₃), PM ¹ , GLO
Greenhouse balance and ozone layer	Global warming and ozone layer depletion	Nitrous oxide (N ₂ O)
Ecosystems and biodiversity	Eutrophication and acidification of terrestrial ecosystems Eutrophication of freshwater and marine ecosystems	NO ₃ ⁻ , ammonium (NH ₄ ⁺) NO ₃ ⁻ , organic nitrogen ²
Soil	Acidification	Organic nitrogen ²

1. Coarse particles (1-10 micrometres in diameter, or PM₁₀) and fine particles (1-2.5 micrometres in diameter, or PM_{2.5}).

2. Dissolved and particulate organic nitrogen.

Source: Adapted from Geupel (2015) and Sutton et al. (2011).

1.3 Nitrogen has multiple sources

Table 1.2 summarises the main reactive forms of nitrogen. Human activities often represent a significant part of their emissions (Table 1.3).

Table 1.3. Anthropogenic sources of nitrogen

Environmental impact	Share of anthropogenic emissions in total emissions	Activity
Water quality	NO ₃ ⁻ (?)	Agriculture, urban and industrial sewage, atmospheric deposition
Air quality	NO _x (~ 70%) NH ₃ (~ 90-100%) PM (?) GLO (~ 80%)	Burning fossil fuels and, to a lesser degree, biomass (the latter mainly due to slash-and-burn agriculture) Agriculture (volatilisation following spreading of livestock manure or urea fertiliser) Formed in the atmosphere from precursors NO _x and NH ₃ Formed in photochemical processes from precursor NO _x
Greenhouse balance and ozone layer	N ₂ O (~ 40%)	Agriculture and, to a lesser degree, burning fossil fuels and biomass, industrial processes, atmospheric deposition and sewage
Ecosystems and biodiversity	NH ₃ and NH ₄ ⁺ (~ 90-100%) NO ₃ ⁻ and organic nitrogen (?)	Agriculture (volatilisation following spreading of livestock manure or urea fertiliser) Agriculture, urban and industrial sewage, atmospheric deposition
Soil quality	NH ₄ ⁺ (~ 90-100%); NO ₃ ⁻ and organic nitrogen (?)	Agriculture and, to a lesser degree, atmospheric deposition

Source: OECD Secretariat.

Human activity is a major source of NO_x in the troposphere, especially the burning of fossil fuels.⁷ In such combustion processes, nitrogen from the fuel or dinitrogen from the air combines with oxygen atoms to create nitric oxide (NO). This further combines with ozone (O₃) to create nitrogen dioxide (NO₂). The initial reaction between NO and O₃ to form NO₂ occurs fairly quickly during the daytime, with reaction times on the order of minutes. Due to the close relationship

between NO and NO₂, and their ready interconversion, these species are often grouped together and referred to as NO_x. The majority of NO_x emissions are in the form of NO. For example, 90% or more of tail-pipe NO_x emissions are emitted as NO (Richmond-Bryant et al., 2016). Actually, only a small part of vehicle NO_x emissions come from the oxidation of organic nitrogen in gasoline or diesel fuel.⁸ Vehicle NO_x comes mainly from incoming air that mixes with fuel inside the vehicle's engine.⁹

Human activity is also a major source of NH₃ emissions. Global NH₃ emissions into the atmosphere are dominated by agricultural practices (e.g. in Western Europe and the United States, as much as 90–100% of NH₃ emissions result from agriculture).¹⁰ Agricultural NH₃ is emitted mainly by manure (excretion, storage and spreading) and, to a lesser extent, through volatilisation following the application of mineral fertilisers, especially when temperatures are mild and soils are moist and warm.

A range of nitrogen forms are created in the atmosphere from the oxidation of NO and NO₂.¹¹ The main pathway is oxidation to nitric acid (HNO₃).¹² HNO₃ can react with NH₃ to form ammonium nitrate (NH₄NO₃), a secondary PM known as “fine nitrate aerosol”,¹³ or be absorbed onto primary PM₁₀ (e.g. dust, sea salt) to form “coarse nitrate aerosols”. NH₄NO₃ is also formed by reaction in liquid phase (e.g. droplets) of HNO₃ with NH₄⁺ and subsequent water evaporation. In the atmosphere, NH₃ reacts not only with HNO₃ but also with other acidic gases such as sulphuric acid to form ammonium sulphate aerosol and hydrochloric acid to form ammonium chloride aerosol.

GLO is not directly emitted. It is a secondary (novel) pollutant formed by sunlight driven atmospheric chemical reactions involving carbon monoxide (CO), volatile organic compounds (VOCs), including methane (CH₄), and NO_x. Contrary to NO_x, there is substantial background GLO pollution. In the United States, background GLO — defined as stratosphere-to-troposphere transport,¹⁴ imports of GLO and GLO from natural sources¹⁵ — contributes a major portion to estimated total GLO (Lefohn et al., 2014).

Natural sources create some 60% of total N₂O emissions, in particular from microbial denitrification in soils under natural vegetation and in the oceans (Denman et al., 2007). Anthropogenic sources account for only 40% of total emissions, with agriculture accounting for about two thirds of anthropogenic emissions (ibid). Agricultural N₂O is emitted directly from fertilised agricultural soils and livestock manure (some 60%) and indirectly from runoff and leaching of nitrogen fertilisers (the remaining 40%). Other anthropogenic sources are fossil fuel combustion and industrial processes, biomass burning, atmospheric deposition and, to a lesser extent, human sewage. N₂O is a by-product of fossil fuel combustion in mobile and stationary sources. Industrial processes also emit N₂O, particularly during the production of nitric acid (an important ingredient for synthetic fertilisers) and adipic acid (primarily used for making synthetic fibres). Biomass burning (e.g. to destroy crop residues or clear land for agricultural or other uses) oxidises part of the nitrogen that is in the biomass and surrounding air, creating N₂O emissions. Atmospheric deposition provides terrestrial and aquatic ecosystems with extra nitrogen, which stimulates microbial denitrification. N₂O is also released from the bacteriological treatment (denitrification) of waste water.

In addition to agriculture and wastewater (urban and industrial), another important source of nitrogen in water is atmospheric deposition. Seitzinger et al., 2010 divides the main sources of nitrogen exports to the oceans between agriculture (50%), natural biological fixation (25%), atmospheric deposition (20%) and wastewater (5%). These data are global averages, the percentages varying according to coastal areas.

Common inorganic nitrogen forms in water are NO_3^- , nitrite (NO_2^-), NH_4^+ and NH_3 . NO_3^- is stable: it is highly soluble (dissolves easily) and is easily transported in streams and groundwater. NO_2^- is relatively short-lived and is quickly converted to NO_3^- by bacteria. NH_3 is the least stable form of nitrogen in water: it is easily transformed to NO_3^- in waters that contain oxygen and can be transformed to nitrogen gas in waters that are low in oxygen. The dominant form between NH_4^+ and NH_3 depends on the pH and temperature of the water. A significant part of the total nitrogen load in surface waters is in the form of organic nitrogen, including dissolved organic nitrogen (DON) and particulate organic nitrogen (PON), even in NO_3^- enriched rivers. There is uncertainty as to how quickly organic nitrogen (DON and PON) is being recycled through the food web. For example, DON tends to be stored for much longer periods of time (up to 200 years) in high-elevation lake ecosystems (Goldberg et al., 2015).¹⁶

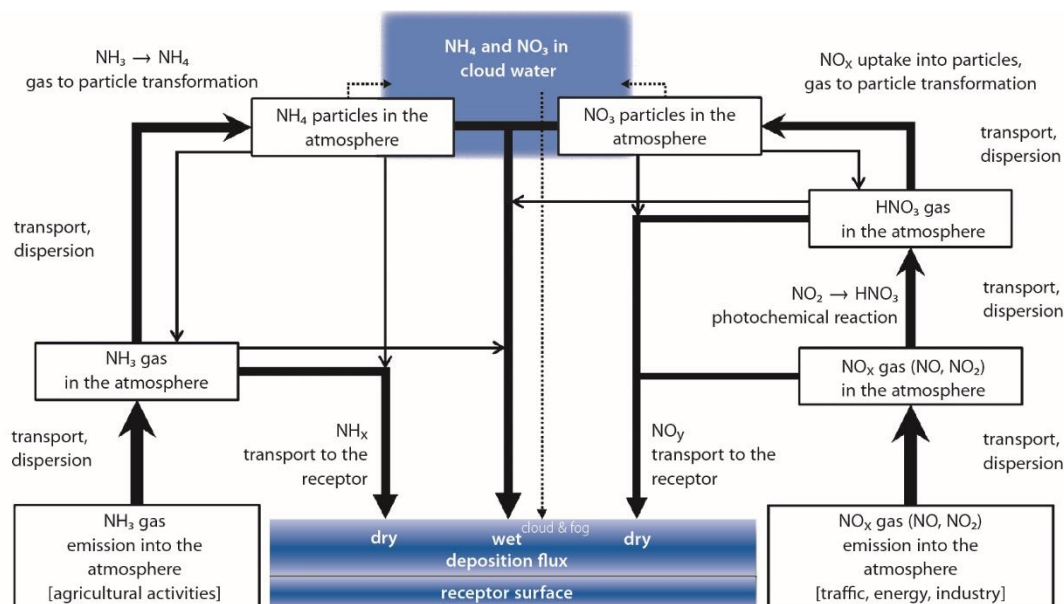
1.4 ...multiple pathways

1.4.1 Air

Apart from N_2O which is a very stable molecule in the troposphere¹⁷ where it has a greenhouse effect, other atmospheric emissions of nitrogen can undergo rapid changes and create health hazards in the troposphere. They then deposit on the earth's surface within hours or days, creating a risk to ecosystems¹⁸ (Salomon et al., 2016). They impact in part on the area near the source of emissions, but some nitrogen emissions may be transported over considerable distances before being deposited and having harmful effects. This is because both NH_3 and NO_x can react with each other or with atmospheric components, forming or attaching to aerosol particles which can be transported for thousands of kilometres before they are removed from the atmosphere in the process known as wet deposition, i.e. mainly by precipitation (Hertel et al., 2011).

NO_x and NH_3 can undergo chemical and physical transformation as they disperse from their source, leading to different forms of deposition (Figure 1.2). For oxidised nitrogen,¹⁹ these comprise dry deposition of NO_x gases and wet deposition of NO_3^- while for reduced nitrogen, these comprise dry deposition of NH_3 gas and wet deposition of NH_4^+ . Dry deposition of particulate and aerosol nitrate and ammonium can also contribute.

Figure 1.2. Nitrogen emission and deposition pathways



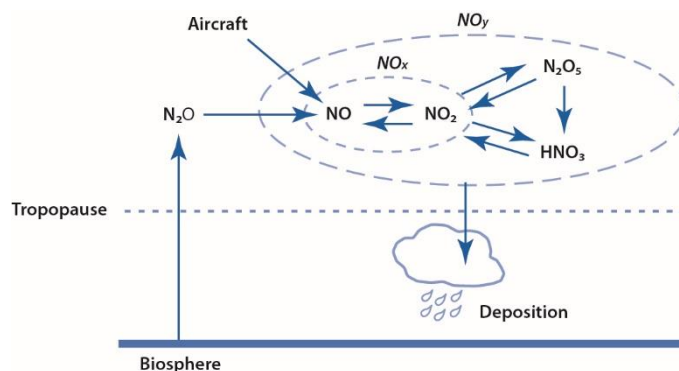
Note: N₂O is excluded as it does not play an important role in nitrogen deposition. For simplicity, reservoir compounds like HONO, HO₂NO₂, peroxyacetylnitrate (PAN) and PAN-like species have also been disregarded.

Source: Adapted by Th. Gauger from Hertel et al. (2006).

1.4.2 Greenhouse balance and ozone layer

With respect to the risk of a greenhouse effect, N₂O, CO₂ and CH₄ remain in the atmosphere long enough to become well mixed, meaning that the amount that is measured in the atmosphere is roughly the same all over the world, regardless of the source of the emissions. Dinitrogen and N₂O are the two most important end-products of the nitrogen cycle, dinitrogen usually being produced in excess of N₂O. Following Portmann et al., 2012, N₂O is relatively inert in the troposphere. It is then transported to the stratosphere where most (90%) is eventually broken down through interaction with high-energy light (i.e. photolysis) into dinitrogen passing through different oxidised nitrogen forms. N₂O is a stock pollutant in the troposphere. This is because N₂O is long-lived – with a tropospheric lifetime of over a century – and as only 7% of N₂O returns to the land surface by deposition.²⁰

N₂O provides a natural source and is the main supplier of NO_x to the stratosphere through oxidation to NO (Figure 1.3).²¹ The residence time of NO_x in the stratosphere is 1-2 years. In the stratosphere NO reacts rapidly with O₃ to produce NO₂, which releases O₃ by photolysis (“null cycle”) or reacts with O, resulting in a net loss of O₃ (“loss cycle”).²²

Figure 1.3. Sources of stratospheric nitrogen oxides (NO_x)*Notes:*

NO_y is the sum of all oxidised nitrogen forms.

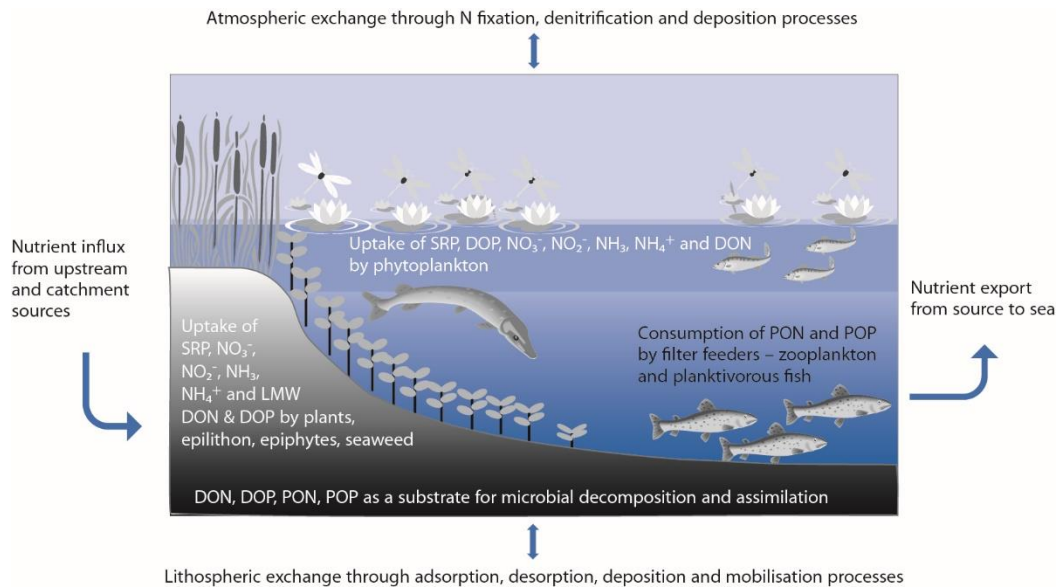
Nitric oxide (NO) is also produced by aircrafts (by oxidation of dinitrogen at the high temperatures of the aircraft engine)

The tropopause is the boundary between the troposphere and the stratosphere.

Source: Jacob (1999).

1.4.3 Water

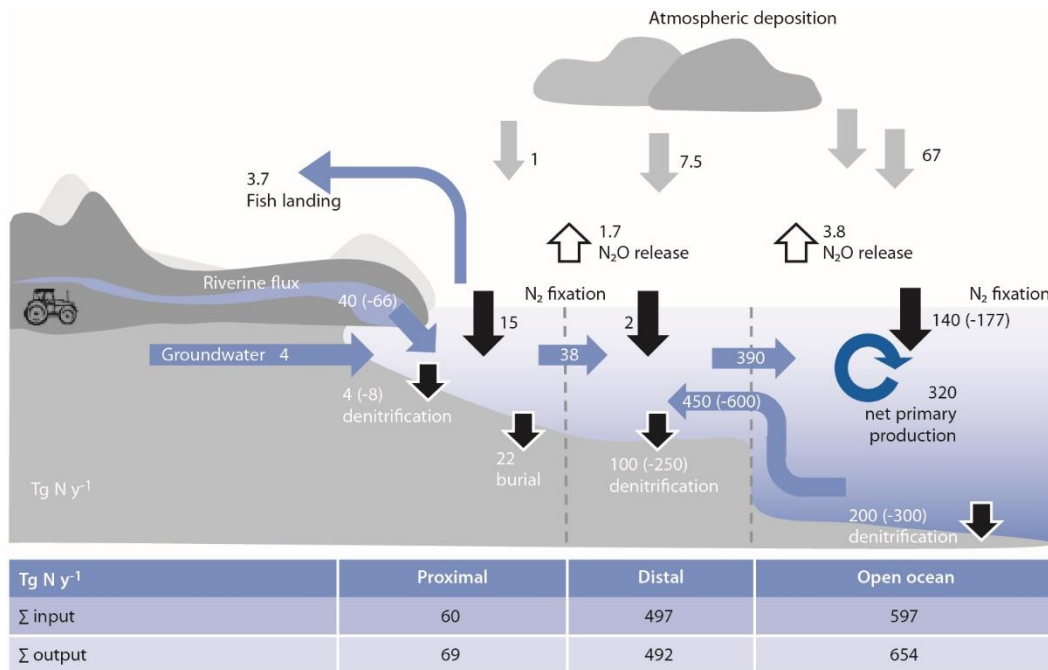
Nitrogen pathways in freshwater include dinitrogen fixation, denitrification and nitrogen deposition, exports to sea, and exchange with the sediments (Figure 1.4). In addition to direct discharges by industry and wastewater treatment plants, nitrogen finds its way into the surface waters via pathways that are mainly fed by agriculture such as groundwater, drainage water and runoff. The NO_3^- inputs into groundwater (i.e. NO_3^- not used by crops or denitrified by soil bacteria) are usually the result of leaching from the soil (Durand et al., 2011), where the leaching potential is a function of soil type, crop, climate, tillage practices, fertiliser management, and irrigation and drainage management (USEPA, 2003). The risk of leaching is higher for coarse textured soils and for crops with poor efficiency of nitrogen use (ibid). Nitrogen exports from surface water to downstream estuaries (via riverine and groundwater flow) can be expected to be watershed specific, being typically lower in less developed, highly forested watersheds than in highly developed urban watersheds. Atmospheric depositions of nitrogen into lakes, wetlands and marine waters add to the amounts carried in from rivers (Swackhamer, 2004).

Figure 1.4. Nutrient pathways in freshwater

DON, PON = Dissolved Organic Nitrogen; Particulate Organic Nitrogen
 DOP, POP = Dissolved Organic Phosphorus; Particulate Organic Phosphorus
 SRP = Soluble Reactive Phosphorus
 LMW: low molecular weight
 Source: Johnes (2016).

Nitrogen pathways in marine water include nitrogen imports by river discharge and precipitation; dinitrogen fixation by cyanobacteria, bacterial remineralisation of dead particulate biomass in sediments and denitrification. The nitrogen budget of continental shelf systems is primarily governed by exchanges with the open ocean (Figure 1.5).

Figure 1.5. Nutrient pathways in marine water



Source: Voss et al. (2013).

Oceanic currents play a role in the exchange of nitrogen within the sea and the resuspension of sediment nitrogen. They may shift impacts long distances away from nutrient sources. For example, recent scientific evidence – prompted by impacts on the tourism industry – revealed that nutrients originating from the Amazonian river basin, where soils are washed away by the rains as a result of deforestation and intensive agriculture, were a major contributor to algal blooms in Caribbean coastal areas.²³ Nutrient-rich waters can also replace nutrient-poor waters in some coastal areas of the ocean and large lakes (such as the North American Great Lakes). Indeed, there is mass continuity in the ocean and large lakes (water being a continuous fluid), so that a change in distribution of water in one area is accompanied by a compensating change in water distribution in another area.

1.4.4 Ecosystems and biodiversity

Apart from acid rain, little recognition had been given to the environmental consequences of nutrients (and toxic substances) that fall from the air as wet and dry deposition onto land-based and aquatic ecosystems (Swackhamer et al, 2004). Yet, the deposition of NH_4^+ and NO_3^- on terrestrial ecosystems favours some species over others (see Annex A). It leads to the accumulation of organic nitrogen in the soil and there is strong evidence that ecological communities respond to the accumulated pool of plant-available nitrogen in the soil, even if the long-term implications are not clear. It is very likely that nitrogen deposition acts synergistically with other stressors, in particular climate change, acid deposition, and GLO; these synergies are poorly understood. The nature and rate of recovery of biodiversity from nitrogen pollution is not well understood. The point is that

even if nitrogen deposition rates were to be significantly reduced in the future, habitat recovery would be slow (Plantlife and Plant Link UK, 2017).

Acid rain is a cumulative problem for non-alkaline soils; as the acid-neutralising capacity of soils gets depleted, the ecosystems become increasingly sensitive to additional acid inputs. In contrast, acid rain falling over the oceans is rapidly neutralised by the large supply of carbonate ions. Acid rain falling over regions with alkaline soils or rocks is also quickly neutralised once the acid has deposited to the surface.

1.4.5 Soil

Most of the transformations involved in the biogeochemical nitrogen cycle are carried out by microorganisms in water and soil (in part, following Söderlund and Rosswall, 1982). In non-alkaline soils, NH_3 tends to convert into NH_4^+ . Under aerobic conditions (in the presence of oxygen), certain autotrophic bacteria – nitrifying bacteria – can use NH_4^+ oxidation as an energy-yielding process. They can oxidise NH_4^+ to NO_2^- and NO_3^- .²⁴ Because it releases hydrogen, nitrification also contributes to the acidification of soils.²⁵

Under anaerobic conditions (in the absence of oxygen), certain aerobic bacteria – denitrifying bacteria – can use NO_3^- and NO_2^- in place of oxygen, reducing it to dinitrogen. In the process, denitrification generates N_2O and NO .²⁶

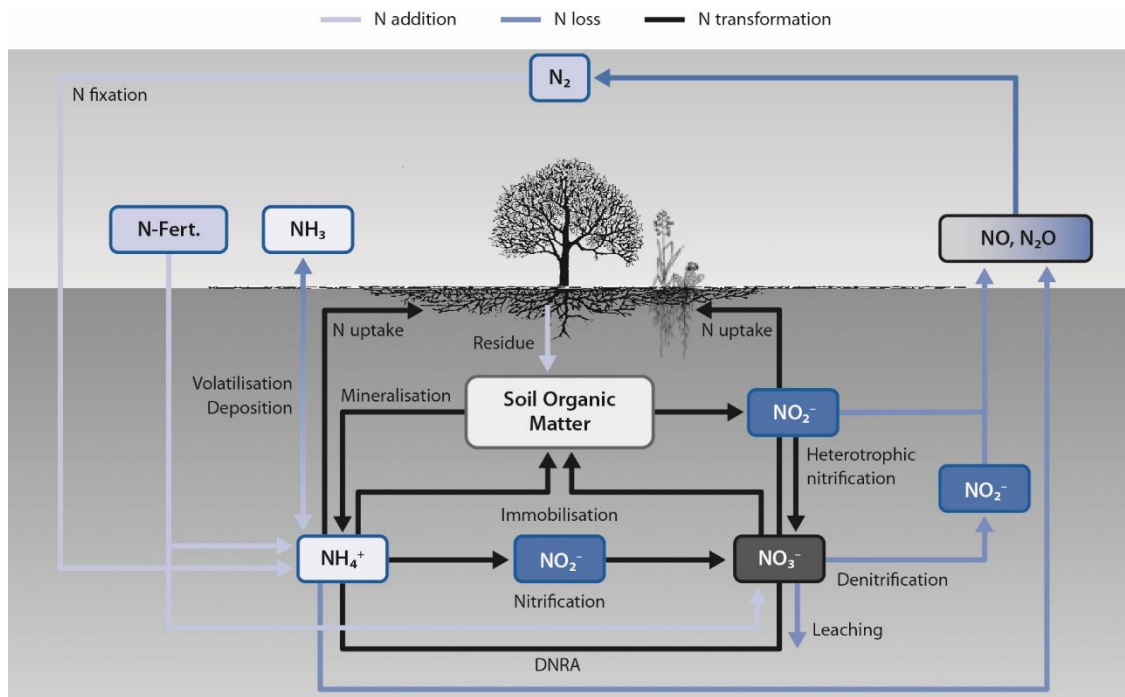
Plant-soil interactions are mainly governed by interactions between the carbon and nitrogen cycles (in part, following Müller and Clough, 2014). Microbial activity in soils is driven by “rhizodeposition”²⁷. As such, nitrogen cycling is closely associated with plant productivity. Conditions that favour plant carbon assimilation may also enhance rhizodeposition. Conversely, a higher demand for nitrogen by plants (e.g. favourable growth temperatures) increases competition for nitrogen between plants and microbes, potentially affecting microbial life. However, very few studies have examined the links between the nitrogen cycle, plant activity, and associated changes in microbial diversity.

Plants utilise mineral nitrogen (NH_4^+ or NO_3^-) and organic nitrogen that enters the soil either via rhizodeposition or microbial mineralisation (DON). DON uptake is reported to be more significant under conditions of nitrogen limitation and low pH. Despite the significance of DON in agricultural ecosystems, current knowledge of the soil DON dynamics is still limited. The role DON plays in gaseous nitrogen loss pathways is also under-researched. Evaluation of the various simultaneously occurring nitrogen transformations in plant–soil systems that lead to mineralisation and immobilisation of nitrogen in the rhizosphere is lacking.

Nitrogen may be lost from soils as NO_3^- , via leaching, or in gaseous forms such as NH_3 , NO , N_2O or dinitrogen (Figure 1.6). Denitrification is a key pathway in the soil nitrogen cycle, but a pathway that is still poorly understood. For example, there is uncertainty about soil NO emissions, which will likely increase with increasing anthropogenic sources of nitrogen but with much variability. Research is also needed to better understand the importance of “dissimilatory NO_3^- reduction to NH_4^+ ” or DNRA. While the available organic carbon and oxygen have a major impact on total denitrification, the soil pH mainly influences the

N_2O /dinitrogen ratio (the ratio tends to increase with decreasing pH). However, there is a lack of field methods to quantify the N_2O /dinitrogen ratio in situ.

Figure 1.6. Nitrogen pathways in soil



N-Fert = nitrogen fertiliser

DNRA= dissimilatory nitrate (NO_3^-) reduction to ammonium (NH_4^+)

Source: Müller and Clough (2014).

The N_2O /dinitrogen ratio of denitrification is most likely governed by the existing microbial communities. In turn soil microbial communities are influenced by environmental conditions (oxygen, temperature, pH), the availability of carbon substrates and the potential for reduction–oxidation reactions.²⁸ But the interactions between these factors are not fully understood. In fertilised soils, carbon rather than NO_3^- availability limits total denitrification. The carbon substrate determines the efficiency with which nitrogen oxides (NO_3^- , NO_2^-) are reduced.

1.5 ...and multiple impacts

1.5.1 Air quality

In the atmosphere, NO_2 is directly harmful to human health (it increases likelihood of respiratory problems) (see Annex A). Nitrogen also contributes to the most serious air pollution problems for human health, namely airborne PM and, to a lesser extent, GLO (OECD, 2012). Nitrogen is a precursor of both: $\text{NH}_3/\text{NH}_4^+$ and NO_x for secondary PM;²⁹ NO_x for GLO.³⁰ The effects of PM can range from eye and respiratory irritation to cardiovascular disease, lung cancer³¹ and consequent premature death. The PM of most concern are small (PM_{10}) and especially fine ($\text{PM}_{2.5}$) particles, as these are small enough to be able to penetrate

deeply into the lungs. Globally, 8% of lung cancer deaths, 5% of cardiopulmonary deaths and around 3% of respiratory infection deaths can be attributed to exposure to PM_{2.5} alone (WHO, 2009). Huang et al., 2017 estimated that NO₃⁻ and NH₄⁺ aerosols accounted for 30% of PM_{2.5} emissions measured in Beijing from June 2014 to April 2015. Exposure to high levels of GLO increases the risk of premature death from lung disease; GLO also affects vegetation by damaging leaves and reducing growth: exposure during the growing season, including at low levels, can have ecosystem-wide impacts as well as economic costs for cultivated land.³²

1.5.2 Greenhouse balance and ozone layer

As a greenhouse gas (GHG), N₂O produces a positive climate forcing, or global warming effect. N₂O is more effective at warming Earth than CO₂. The two most important characteristics of a GHG in terms of climate impact are how well the gas absorbs energy from light (either directly or after reflection from the earth's surface), and how long the gas stays in the atmosphere.³³ The Global Warming Potential (GWP) is a measure of the total energy that a unit mass of a gas absorbs over a particular period of time (usually a 100 year period is used). The larger the GWP, the more warming the gas causes. CO₂ has a GWP of 1 and serves as a baseline for other GWP values. N₂O is a more powerful GHG than CO₂ and, with a GWP 265 times higher over a 100-year time scale, is responsible for about 6% of the worldwide anthropogenic greenhouse effect. However, the GWP metric is not a perfect measure of climatic impacts. N₂O persists in the atmosphere for about a century, compared to thousands of years for CO₂, whereas the average lifetime of CH₄ is around 12 years (Allen et al., 2016). For long-lived GHGs, it is the cumulative GHG emissions that largely determine the extent of future climate change, not just the emissions rate in a given year. So the continually rising concentration of N₂O in the atmosphere is of concern in relation to the stringent climate goals in the Paris Agreement.

Nitrogen-containing aerosols have an offsetting greenhouse effect (see Annex A). However, N₂O remains much longer in the atmosphere than aerosols (over 120 years compared to weeks or months), so if such aerosols are reduced but N₂O remains at the same concentration or increases, the net effect would change from marginally negative to more strongly positive. The N₂O greenhouse effect is also partially offset by increased CO₂ uptake in terrestrial ecosystems due to atmospheric nitrogen deposition (see Annex A).

N₂O also contributes significantly to the depletion of the stratospheric ozone layer (O₃) that protects life on Earth by absorbing some of the ultraviolet rays from the sun. Indeed, N₂O provides a natural source of NO_x to the stratosphere and, with the phasing-out of chlorofluorocarbons (CFCs), NO_x has become a major depleting threat for O₃ in the stratosphere (Ravishankara et al., 2009) and is currently unregulated by the Montreal Protocol on Substances that Deplete the Ozone Layer (a protocol to the Vienna Convention for the Protection of the Ozone Layer).

1.5.3 Water quality

In water, nitrate (NO₃⁻) is directly harmful for human health (high concentrations in drinking water can cause blood disorder in infants) (see Annex A). NO₃⁻ in

drinking water may also increase risk of colorectal cancer due to endogenous transformation into carcinogenic N-nitrosocompounds (Jörg Schullehner et al., 2018).

High concentrations of nutrients (i.e. NO_3^- and phosphorus) in fresh and marine waters result in phytoplankton (microscopic algae) growth, a process called "eutrophication". A high density of phytoplankton reduces the water transparency and the reduced penetration of sunlight limits the depth to which macrophytes and sea grasses can grow. One of the most striking effects of excessive levels of nutrients is the formation of low oxygen (hypoxic) or oxygen-free (anoxic) zones in deep water layers where the higher organisms are unable to survive, the so-called "dead zones" (Breitburg et al., 2018; see also Chapter 3). A distinction must be made between marine waters and fresh waters. Phosphorus is often the driver of eutrophication in freshwater while it is NO_3^- in marine waters.

1.5.4 Ecosystems and biodiversity

Excess nitrogen from air-based and land-based sources is one of the major drivers of biodiversity loss in Europe (Sutton et al., 2011). Nitrogen impacts vegetation diversity through direct foliar damage, eutrophication, acidification, and susceptibility to secondary stress. The accumulation of extra nutrients, as well as reduction in soil pH, is negatively affecting natural and semi-natural habitats whose important biodiversity developed in direct response to low nutrient levels (Plantlife and Plant Link UK, 2017). Nitrogen deposition therefore contributes to biodiversity loss (nitrogen-loving species outcompete other species). While there is a wealth of evidence on the magnitude, components and effects of nitrogen deposition on floral biodiversity in Europe and North America, there is an obvious lack of information on impacts on above- and below-ground fauna, and all impacts in other parts of the world, with no clear overview of how the different strands of evidence fit together (Sutton et al., 2014).

It is not yet clear if different wet-deposited forms of nitrogen (e.g. NO_3^- versus NH_4^+) have different effects on biodiversity. However, NH_3 can be particularly harmful to vegetation, especially lower plants, through direct foliar damage (Sutton et al., 2011). For example, a long-term controlled field experiment showed that, for the same overall nitrogen load, NH_3 deposition was more damaging to bog vegetation than deposition of ammonium aerosol, which was more damaging than deposition of nitrate aerosol (Phoenix et al., 2012). However, responses to the form of nitrogen are complex and habitat dependent, with conversion between nitrogen forms resulting from the activities of soil microbes (Plantlife and Plant Link UK, 2017).

The deposition of NO_2 , NH_3 and sulphur dioxide (SO_2) acidifies terrestrial and freshwater ecosystems ("acid rain").³⁴ Acid rain remains an issue (including in the OECD area) mainly because the decrease in NO_x emissions has not been commensurate with the decrease of SO_2 emissions. Eutrophication is a consequence of excess input of nitrogen nutrients (NH_3 , NO_x); the atmospheric input of other nutrients is negligible.

Acid rain has negative effects on freshwater ecosystems. Elevated acidity in a lake or river is directly harmful to fish because it corrodes the organic gill material and attacks the calcium carbonate skeleton. In addition, the acidity dissolves toxic metals such as aluminium from the sediments. Acid rain is also

harmful to terrestrial vegetation with little acid-neutralising capacity,³⁵ mostly because it leaches nutrients such as potassium and allows them to exit the ecosystem by runoff. Beyond the input of acidity, the deposition of NH_4^+ and NO_3^- is an important contributor in the eutrophication of aquatic ecosystems (by providing ecosystems with a source of directly assimilable nitrogen in addition to land-based sources). Acidifying deposition may also damage building structures and monuments.

1.5.5 Soil quality

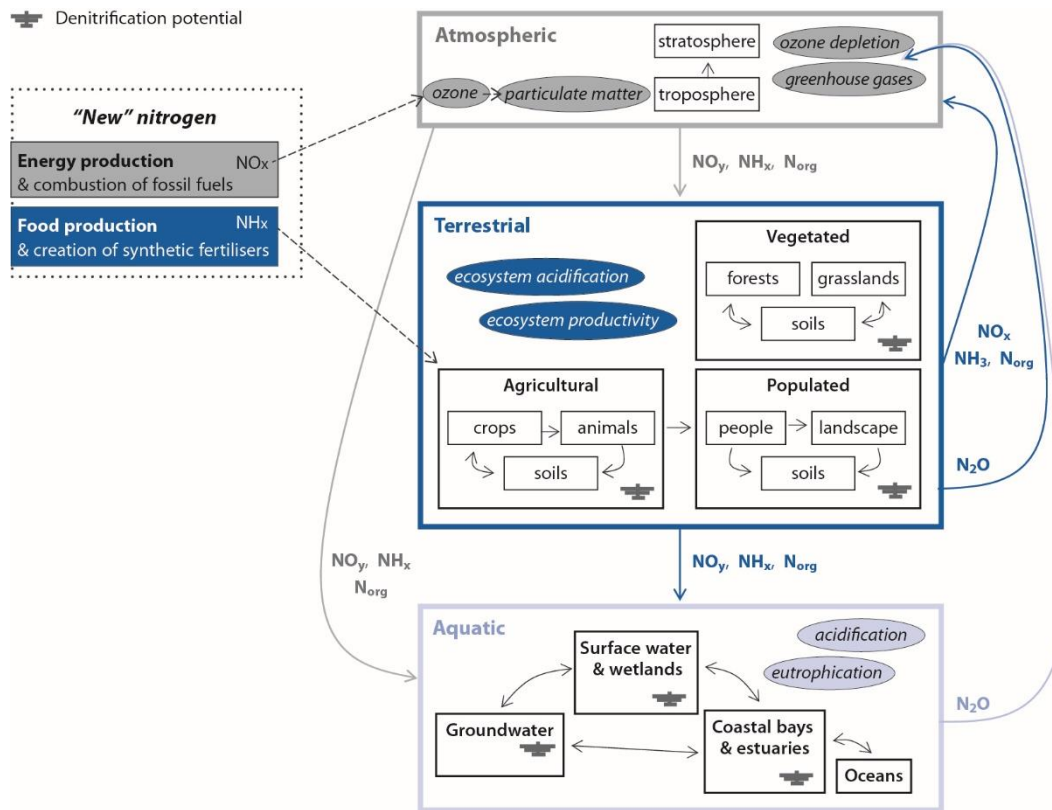
The major nitrogen threats on soil quality for both agricultural and natural soils are related to changes in soil acidification, and loss of soil diversity (Sutton et al., 2011). Soil acidification may lead to a decrease in crop and forest growth and leaching of components negatively affecting water quality, including heavy metals.

The effect of nitrogen on soil organic matter content is uncertain. The effect of nitrogen on diversity of soil (micro) organisms and the effects of changes of soil biodiversity on soil fertility, crop production and nitrogen emissions towards the environment are not fully understood.

1.6 The “nitrogen cascade”

In addition to the doubling of production since preindustrial time, nitrogen has another feature that distinguishes it from other pollutants - it can go a long way once released into the environment. Once created, the same nitrogen atom can cause multiple effects in the atmosphere, in terrestrial ecosystems, in freshwater and marine systems, and on the climate, as it moves through the biogeochemical pathways. Galloway et al., 2003 call this sequence of effects the “nitrogen cascade” (Figure 1.7).

Figure 1.7. The nitrogen cascade



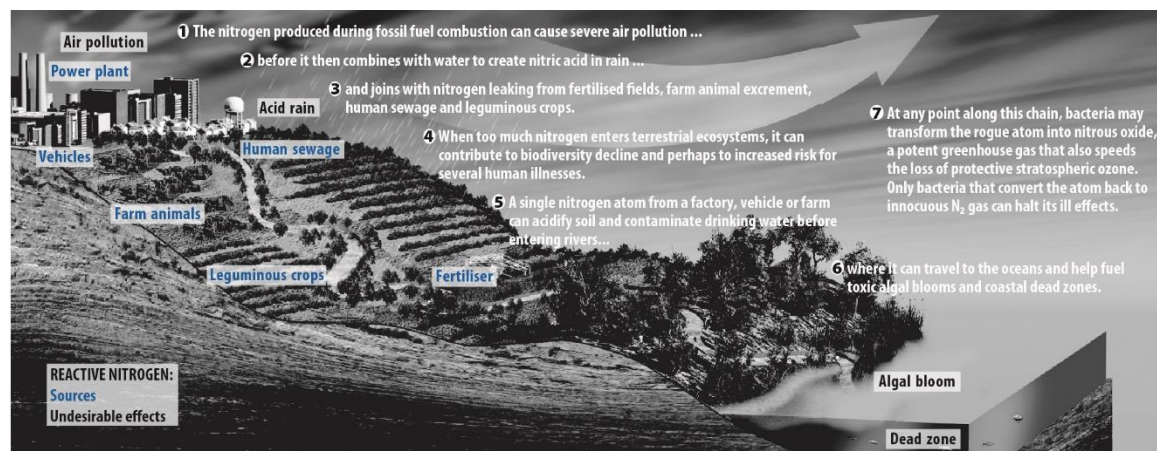
Note: Conceptual diagram illustrating the cascade of nitrogen from point of origin along its biogeochemical pathways, with the associated negative impacts.

Source: USEPA Science Advisory Board (undated),

nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs143_008785.pdf.

For example, the biogeochemical journey of an atom of nitrogen from its point of formation could be as follows. NO_x formation during fossil fuel combustion first has the potential to contribute to the creation of GLO, a component of smog,³⁶ then can be converted to HNO_3 which is a major component of acid deposition, or in the atmosphere it can be converted to an aerosol which will decrease light scattering³⁷ and promote formation of cloud drops. Once removed from the atmosphere, HNO_3 and nitrate aerosols can cause both fertilisation and acidification of soils which in turn (via NO_3^- leaching) will result in acidification of low alkalinity freshwaters and fertilisation of those same waters. Upon transport to coastal regions and lakes, the same nitrogen atom (as it cascades) can contribute to eutrophication with resulting loss of freshwater and marine biodiversity. As a final step, the nitrogen atom in soil and water can be converted to N_2O , which contributes to the greenhouse effect in the troposphere and ozone destruction in the stratosphere. Figure 1.8 illustrates another series of possible cascading nitrogen effects from one environmental media to another.

Figure 1.8. Example of serial impacts on health and the environment of a single nitrogen atom



Source: Townsend and Howarth (2010).

Notes

¹ “Nitrogen” refers to the reactive forms of nitrogen (as opposed to “dinitrogen” – N_2 - which refers to the inert form).

² Dinitrogen accounts for 78% of air on a molar (i.e. number of molecules) basis (Holloway and Wayne, 2015).

³ Until one century ago, Chilean saltpetre (and before it Peruvian guano) was the main source of nitrogen for world agriculture and industry.

⁴ Named after its inventors, the German chemists Fritz Haber and Carl Bosch. The process converts dinitrogen to ammonia (NH_3) by a reaction with hydrogen (H_2) -- $N_2 + 3 H_2 \rightarrow 2 NH_3$ -- using a metal catalyst under high temperatures and pressures.

⁵ This is consistent with the estimates of Vitousek et al., 2013 and Erisman and Larsen, 2013, for which current human nitrogen production is about the same as total natural production (terrestrial and oceanic).

⁶ Percentages are rounded figures based on data in Table 1.1. They are broadly consistent with Sutton et al, 2011 who estimated that during the 2000s, food production (use of fertilisers, manure and leguminous crops) accounted for three quarters of the nitrogen produced by humans, the combustion of fossil fuels and industrial processes accounting equally for the remainder.

⁷ Jacob, 1999 estimates that natural sources generate 28% of total NO_x emissions. This includes microbial denitrification in soils (13%), oxidation of NH_3 emitted by the biosphere (7%), lightning (7%) and transport from the stratosphere (1%).

⁸ Nitrogen-enriched fuel, as paradoxical as it may seem, can reduce NO_x emissions per kilometre driven. It can slightly increase NO_x emissions per litre of fuel burned, but it helps to increase fuel efficiency because nitrogen breaks down carbon deposits on moving parts of the engine (less fuel is burned).

⁹ NO_x is produced when dinitrogen reacts with oxygen under high temperature and pressure conditions in the combustion chamber of the vehicle. However, understanding the chemical processes that govern the formation and destruction of NO_x during combustion continues to be a challenge (Glarborg et al., 2018).

¹⁰ Other sources of NH_3 comprise industries, landfills, household products, biomass burning, motor vehicles, and manure from wild animals.

¹¹ These include nitrate radicals (NO_3), nitrous acid (HONO), nitric acid (HNO_3), dinitrogen pentoxide (N_2O_5), nitryl chloride ($ClNO_2$), peroxyntiric acid (HNO_4), peroxyacetyl nitrate and its homologues (PANs), other organic nitrates, such as alkyl nitrates (including isoprene nitrates).

¹² HNO_3 is produced by atmospheric oxidation of NO_x in the daytime and via O_3 at night.

¹³ An aerosol is a suspension of a solid or liquid PM in the air.

¹⁴ Globally, more than 80% of GLO results from chemical production within the troposphere and less than 20% are supplied to the troposphere by transport from the stratosphere.

¹⁵ For example, isoprene emissions from natural vegetation (isoprene is a by-product of photosynthesis).

¹⁶ Perhaps because phosphorus limitation prevents aquatic life from developing.

¹⁷ N₂O is a relatively inert gas and thus is able to float through the troposphere without being destroyed by other atmospheric gases.

¹⁸ HNO₃ deposition (acid rain) may also affect buildings (by dissolving the calcite in marble and limestone).

¹⁹ Most of the atmospheric nitrogen falls into two broad categories: oxidised nitrogen and reduced nitrogen. The oxidised form of nitrogen is mainly dominated by nitrogen oxides (NO_x) and the reduced form by ammonia species (NH₃ and NH₄⁺, denoted NH_x).

²⁰ Around 10% is oxidised in the stratosphere to produce NO_x, 30% of which is then converted into dinitrogen and 70% deposited to the land surface (Portmann et al., 2012). Thus only 7% of N₂O eventually returns to the land surface by deposition.

²¹ In the stratosphere, N₂O encounters high concentrations of O, allowing oxidation to NO.

²² $NO_2 + h\nu \xrightarrow{O_2} NO + O_3$ (O₃ null cycle) or $NO_2 + O \rightarrow NO + O_2$ (O₃ loss cycle).

²³ The same phenomenon of accumulation of Sargassum (also known as Gulfweed) is occurring off Benin and Sierra Leone, some distance from the mouth of the Congo River.

²⁴ Since the first description of nitrifying bacteria more than 100 years ago, it was thought that nitrification was achieved by the joint activity of two groups of microorganisms - ammonia- and nitrite-oxidisers. Daims et al., 2015 discovered that complete nitrifiers exist that can oxidise as single microorganisms NH₄⁺ to NO₃⁻.

²⁵ The adsorption of NH₄⁺ on the clay-humic complex in place of hydrogen causes the acidification of the soil by the hydrogen thus released.

²⁶ The main steps in denitrification are as follows: NO₃⁻ > NO₂⁻ > NO > N₂O > N₂.

²⁷ During their life, plant roots release organic carbon and organic nitrogen (e.g. amino acids) into their surrounding environment; this process is named "rhizodeposition".

²⁸ Or "redox" (i.e. the availability of electron receptors such as nitrogen oxides).

²⁹ PM can be divided into two types: primary PM emitted directly to the atmosphere, such as black carbon; and secondary PM formed in the atmosphere from precursor gases.

³⁰ Other precursors of GLO are VOCs, including CH₄, and to a lesser extent, CO.

³¹ Toxic and carcinogenic pollutants like heavy metals or polycyclic aromatic hydrocarbon are frequently bound to PM.

³² GLO is toxic to humans and vegetation because it oxidises biological tissue.

³³ In part, following [epa.gov/climateleadership/atmospheric-lifetime-and-global-warming-potential-defined](https://www.epa.gov/climateleadership/atmospheric-lifetime-and-global-warming-potential-defined), accessed 2 February 2018.

³⁴ HNO₃ also contributes to the formation of acid rain by dissociating in rainwater to release H⁺.

³⁵ For example, areas sensitive to acid rain over North America include New England, eastern Canada, and mountainous regions, which have granitic bedrock and thin soils.

³⁶ The term "smog" was first used around 1950 to describe the combination of smoke and fog in London. Today, it refers to a mixture of pollutants made up mostly of GLO (<https://www.epa.gov/air-pollution-transportation/smog-soot-and-local-air-pollution>, accessed 17 March 2018).

³⁷ And can also reflect some sunlight back into space, offsetting some of the warming due to GHGs.

References

- Abrol, Y.P. et al. (2017), *The Indian Nitrogen Assessment, Sources of Reactive Nitrogen, Environmental and Climate Effects, Management Options, and Policies*, Elsevier.
- Allen, M.R. et al. (2016), “New Use of Global Warming Potentials to Compare Cumulative and Short-lived Climate Pollutants”, *Nature Climate Change*, 6(8).
- Breitburg, D. et al. (2018), “Declining Oxygen in the Global Ocean and Coastal Waters”, *Science*, 359 (6371).
- Daims, H. et al. (2015), “Complete Nitrification by Nitrospira Bacteria”, *Nature*, 528.
- Denman, K.L. et al. (2007), “Couplings Between Changes in the Climate System and Biogeochemistry”, in *Climate Change 2007: The Physical Science Basis*, contribution of Working Group I to the 4th Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), Cambridge University Press.
- Durand, P. et al. (2011), “Nitrogen Processes in Aquatic Ecosystems”, In: Sutton M.A. et al (Eds.), *The European Nitrogen Assessment. Sources, Effects and Policy Perspectives*, Cambridge University Press.
- Erisman, J.W. et al. (2008), “How a Century of Ammonia Synthesis Changed the World”, *Nature Geoscience*, 1, October 2008.
- Erisman, J.W. and T.A. Larsen (2013), “Nitrogen Economy of the 21st Century”, in *Source Separation and Decentralisation for Wastewater Management*, T.A. Larsen et al. (eds), IWA Publishing, London.
- Fowler, D. et al. (2013), “The Global Nitrogen Cycle in the Twenty-first Century”, *Phil. Trans. R. Soc. B*, 368(1621).
- Galloway, J.N. et al. (2003), “The Nitrogen Cascade”, *BioScience*, 53 (4).
- Gauger, Th. (2018), “Modelling and Mapping Air Concentration and Atmospheric Deposition of Reactive Nitrogen Species in Baden-Württemberg for 2012 to 2016”, Institute of Navigation, University of Stuttgart.
- Geupel, M. (2015), “Towards a National Nitrogen Strategy for Germany”, presentation to the OECD Environment Policy Committee (EPOC), 6-8 October 2015, Federal Environment Agency Germany, Section II 4.3 Air Quality Control and Terrestrial Ecosystems.
- Glarborg, P. et al. (2018), “Modeling Nitrogen Chemistry in Combustion”, *Progress in Energy and Combustion Science*, 67.
- Goldberg, S.J. et al. (2015), « Refractory Dissolved Organic Nitrogen Accumulation in High-elevation Lakes”, *Nature Communications*, 6:6347.
- Hager, T. (2009), *The Alchemy of Air*, Broadway Books.
- Hellsten, S. et al. (2017), *Nordic Nitrogen and Agriculture, Policy, Measures and Recommendations to Reduce Environmental Impact*, Nordic Council of Ministers, TemaNord 2017:547, doi.org/10.6027/TN2017-547.
- Hertel, O. et al. (2011), “Nitrogen Processes in the Atmosphere”, In: Sutton M.A. et al (Eds.), *The European Nitrogen Assessment. Sources, Effects and Policy Perspectives*, Cambridge University Press.

- Hertel, O. et al. (2006), “Modelling Nitrogen Deposition on a Local Scale: a Review of the Current State of the Art”, *Environmental Chemistry*, 3(5).
- Holloway, A.M. and R.P. Wayne (2015), *Atmospheric Chemistry*, Royal Society of Chemistry.
- Houlton, et al. (2018), “Convergent Evidence for Widespread Rock Nitrogen Sources in Earth’s Surface Environment”, *Science*, 360(6384).
- Huang, X. et al. (2017), “Chemical Characterization and Synergetic Source Apportionment of PM_{2.5} at Multiple Sites in the Beijing–Tianjin–Hebei Region, China”, *Atmos. Chem. Phys. Discuss.*, 17.
- Jacob, D.J. (1999), *Introduction to Atmospheric Chemistry*, Princeton University Press.
- Johnes, P. (2016), “Nitrogen Pollution of Inland and Coastal Waters: Sources, Impacts and Opportunities”, presentation to the Joint OECD/TFRN Workshop on *The Nitrogen Cascade and Policy – Towards Integrated Solutions*, OECD, Paris, 9-10 May 2016.
- Lefohn, A.S. et al. (2014), « Estimates of Background Surface Ozone Concentrations in the United States Based on Model-derived Source Apportionment”, *Atmospheric Environment*, 84.
- Müller, C and T. J. Clough (2014), “Advances in Understanding Nitrogen Flows and Transformations: Gaps and Research Pathways”, *Journal of Agricultural Science*, Special Issue from the 17th International Nitrogen Workshop, 152 (S1).
- OECD (2012), *OECD Environmental Outlook to 2050: The Consequences of Inaction*, OECD Publishing, Paris, doi.org/10.1787/9789264122246-en.
- Phoenix, G.K. et al. (2012), “Impacts of Atmospheric Nitrogen Deposition: Responses of Multiple Plant and Soil Parameters Across Contrasting Ecosystems in Long-term Field Experiments”, *Global Change Biology*, 18.
- Plantlife and Plant Link UK (2017), “We Need to Talk About Nitrogen, The Impact of Atmospheric Nitrogen Deposition on the UK’s Wild Flora and Fungi”, January 2017.
- Portmann, R.W. et al. (2012), “Stratospheric Ozone Depletion due to Nitrous Oxide: Influences of Other Gases”, *Philos Trans R Soc Lond B Biol Sci.*, 367(1593).
- Prentice, I.C. et al. (2015), “Biosphere Feedbacks and Climate Change”, Grantham Institute, Briefing Paper 12, Imperial College London.
- Ravishankara, A.R. et al. (2009), « Nitrous Oxide (N₂O): the Dominant Ozone-depleting Substance Emitted in the 21st Century”, *Science*, 326(5949).
- Richmond-Bryant, J. et al. (2016), “Estimation of On-road NO₂ Concentrations, NO₂/NO_x Ratios, and Related Roadway Gradients from Near-road Monitoring Data”, submitted to *Air Quality, Atm and Health*.
- Schullehner, J. et al. (2018), « Nitrate in Drinking Water and Colorectal Cancer Risk: A Nationwide Population-based Cohort Study”, *International Journal of Cancer*, 23 February (Epub ahead of print).
- Seitzinger, S.P. et al. (2010), “Global River Nutrient Export: A Scenario Analysis of Past and Future Trends”, *Global Biogeochemical Cycles*, 24(4), doi.org/10.1029/2009GB003587.
- Söderlund, R. and T. Rosswall (1982), “The Nitrogen Cycles”, in Hutzinger, O. (edit), *The Handbook of Environmental Chemistry*, Vol. 1 Part B (The Natural Environment and the Biogeochemical Cycles), Springer-Verlag, Berlin Heidelberg GmbH.

- SRU (2015), *Nitrogen: Strategies for Resolving an Urgent Environmental Problem*, German Advisory Council on the Environment, Berlin.
- Stocker, B.D. et al. (2016), “Terrestrial Nitrogen Cycling in Earth System Models Revisited”, *New Phytologist*, 210(4), doi.org/10.1111/nph.13997.
- Sutton, M.A. et al. (2011), *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives*, Cambridge University Press.
- Sutton, M. et al. (2014), *Nitrogen Deposition, Critical Loads and Biodiversity*, Springer.
- Swackhamer, D.L. et al. (2004), “Impacts of Atmospheric Pollutants on Aquatic Ecosystems”, *Issues in Ecology* (12).
- The Economist (2011), “The Anthropocene, a Man-made World”, *The Economist*, May 26th 2011.
- Tomich, Th. P. et al. (2016), *The California Nitrogen Assessment: Challenges and Solutions for People, Agriculture, and the Environment*, University of California Press.
- Townsend, A.R. and R. W. Howarth (2010), “Fixing the Global Nitrogen Problem”, *Scientific American*, February 2010.
- USEPA (2003), *National Management Measures to Control Nonpoint Source Pollution from Agriculture*, U.S. Environmental Protection Agency, Office of Water, EPA 841-B-03-004.
- USEPA-SAB (2011), *Reactive Nitrogen in the United States: An Analysis of Inputs, Flows, Consequences and Management Options*, U.S. Environmental Protection Agency’s Science Advisory Board, EPA-SAB-11-013, USEPA, Washington D.C., [yosemite.epa.gov/sab/sabproduct.nsf/WebBOARD/INCFullReport/\\$File/Final%20INC%20Report_8_19_11\(without%20signatures\).pdf](http://yosemite.epa.gov/sab/sabproduct.nsf/WebBOARD/INCFullReport/$File/Final%20INC%20Report_8_19_11(without%20signatures).pdf).
- Vitousek, P.M et al. (2013), “Biological Nitrogen Fixation: Rates, Patterns and Ecological Controls in Terrestrial Ecosystems”, *Phil Trans R Soc B*, 368.
- Voss, M. et al. (2013), “The Marine Nitrogen Cycle: Recent Discoveries, Uncertainties and the Potential Relevance of Climate Change”, *Phil. Trans. R. Soc. B*, 368.
- WHO (2009), *Global Health Risks: Mortality and Burden of Disease Attributable to Selected Major Risks*, World Health Organization, Geneva, who.int/healthinfo/global_burden_disease/GlobalHealthRisks_report_full.pdf.



From:
Human Acceleration of the Nitrogen Cycle
Managing Risks and Uncertainty

Access the complete publication at:
<https://doi.org/10.1787/9789264307438-en>

Please cite this chapter as:

OECD (2018), "Why does nitrogen matter?", in *Human Acceleration of the Nitrogen Cycle: Managing Risks and Uncertainty*, OECD Publishing, Paris.

DOI: <https://doi.org/10.1787/9789264307438-4-en>

This work is published under the responsibility of the Secretary-General of the OECD. The opinions expressed and arguments employed herein do not necessarily reflect the official views of OECD member countries.

This document and any map included herein are without prejudice to the status of or sovereignty over any territory, to the delimitation of international frontiers and boundaries and to the name of any territory, city or area.

You can copy, download or print OECD content for your own use, and you can include excerpts from OECD publications, databases and multimedia products in your own documents, presentations, blogs, websites and teaching materials, provided that suitable acknowledgment of OECD as source and copyright owner is given. All requests for public or commercial use and translation rights should be submitted to rights@oecd.org. Requests for permission to photocopy portions of this material for public or commercial use shall be addressed directly to the Copyright Clearance Center (CCC) at info@copyright.com or the Centre français d'exploitation du droit de copie (CFC) at contact@cfcopies.com.