The global nitrogen cycle in the twenty-first century

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Global nitrogen fixation contributes 413 Tg of reactive nitrogen (N_r) to terrestrial and marine ecosystems annually of which anthropogenic activities are responsible for half, 210 Tg N. The majority of the transformations of anthropogenic N_r are on land (240 Tg N yr^{-1}) within soils and vegetation where reduced N_r contributes most of the input through the use of fertilizer nitrogen in agriculture. Leakages from the use of fertilizer N_r contribute to nitrate (NO_3^-) in drainage waters from agricultural land and emissions of trace N_r compounds to the atmosphere. Emissions, mainly of ammonia (NH_3) from land together with combustion related emissions of nitrogen oxides (NO_x), contribute 100 Tg N yr^{-1} to the atmosphere, which are transported between countries and processed within the atmosphere, generating secondary pollutants, including ozone and other photochemical oxidants and aerosols, especially ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(NH_4)_2SO_4$). Leaching and riverine transport of NO_3 contribute 40–70 Tg N yr^{-1} to coastal waters and the open ocean, which together with the 30 Tg input to oceans from atmospheric deposition combine with marine biological nitrogen fixation (140 Tg N yr^{-1}) to double the ocean processing of N_r. Some of the marine N_r is buried in sediments, the remainder being denitrified back to the atmosphere as N_2 or N_2O. The marine processing is of a similar magnitude to that in terrestrial soils and vegetation, but has a larger fraction of natural origin. The lifetime of N_r in the atmosphere, with the exception of N_2O, is only a few weeks, while in terrestrial ecosystems, with the exception of peatlands (where it can be 10^2–10^3 years), the lifetime is a few decades. In the ocean, the lifetime of N_r is less well known but seems to be longer than in terrestrial ecosystems and may represent an important long-term source of N_2O that will respond very slowly to control measures on the sources of N_r from which it is produced.

1. Introduction

The global nitrogen cycle is central to the biogeochemistry of the Earth, with large natural flows of nitrogen from the atmosphere into terrestrial and marine ecosystems through biological nitrogen fixation (BNF), in which the largely un-reactive molecular nitrogen is reduced to ammonium compounds. The fixed nitrogen is subsequently transformed into a wide range of amino acids and oxidized compounds by micro-organisms, and finally returned to the

atmosphere as molecular nitrogen through microbial denitrification in soils, fresh and marine waters and sediments [1]. The initial fixation steps generate compounds containing reactive nitrogen (N_r, which includes NH_3, NH_4, NO, NO_2, HNO_3, N_2O, HONO, PAN and other organic N compounds) which, in addition to their role in biological and ecosystem function in terrestrial and marine ecosystems, also become widely distributed in the atmosphere and cryosphere as described in papers within this issue. The presence of N_r in these components of the Earth system provides a tracer of the biogeochemical cascade of N_r through the environment as discussed by Galloway et al. [2]. In the atmosphere, NO_x plays a key role in the photochemical production of ozone and other key oxidants and radical species [3] and is closely coupled to the oxidizing capacity of the atmosphere [4]. Similarly, the emission of N_2O following denitrification plays a key role in the radiative balance of the Earth and in the chemistry of the ozone layer in the stratosphere, where N_2O is destroyed by photolysis [3].

In the absence of human influences, BNF and the production of NO_x by lightning would be the only sources of new N_r in the environment.

The supply of N_r is essential for all life forms, and increases in nitrogen supply have been exploited in agriculture to increase the yield of crops and provide food for the growing global human population. It has been estimated that almost half of the human population at the beginning of the twenty-first century depends on fertilizer N for their food [5]. The nitrogen applied in agriculture is derived from atmospheric sources, but unlike the natural process of N fixation, most agricultural N is fixed industrially by the Haber–Bosch process [6], the remainder by nitrogen-fixing crops [7]. Nitrogen fixation by the Haber–Bosch process also provides N_r for other industrial applications, including explosives. Overall, the fixation of nitrogen through Haber–Bosch (120 Tg N yr^{-1}) in 2010 was double the natural terrestrial sources of N_r (63 Tg N yr^{-1}). Atmospheric nitrogen is also fixed unintentionally through human activities, especially during the combustion of fossil fuels by internal combustion engines, and industrial activity, including electricity production.

The overall magnitude of anthropogenic relative to natural sources of fixed nitrogen (210 Tg N yr^{-1} anthropogenic and 203 Tg N yr^{-1} natural) is so large it has doubled the global cycling of nitrogen over the last century. As nitrogen is a major nutrient, changes in its supply influence the productivity of ecosystems and change the competition between species and biological diversity, [8]. Nitrogen compounds as precursors of tropospheric ozone [9] and atmospheric particulate material [10] also degrade air quality. Their effects include increases in human mortality [11], effects on terrestrial ecosystems [12,13] and contribute to the radiative forcing of global and regional climate [4].

There are therefore important consequences of the human modification of the global nitrogen cycle, with benefits in food production and costs due to impacts on human health, biodiversity loss and climate [8].

Knowledge of the global nitrogen cycle is incomplete, but has developed rapidly over the last two decades, with many new measurements and improved instrumentation, models and process understanding. Galloway et al. [14] documents a chronology in the development of the science and shows major changes in understanding as knowledge has accumulated and the range of processes and compounds involved has expanded.

This paper describes the global nitrogen cycle at the beginning of the twenty-first century, and quantifies each of the major terms in the global budget, separating where possible the natural fluxes from those created by anthropogenic activity. In this way, the contemporary magnitudes of natural and anthropogenic contributions are identified and contrasted. The very different sources and chemical properties of reduced and oxidized forms of nitrogen are also separated, to illustrate their relative magnitudes.

The overview presents the major fluxes between terrestrial and marine ecosystems and the atmosphere. The detailed descriptions of N_r processing within the atmosphere and terrestrial and marine ecosystems are provided by companion papers in this issue. The individual papers have been written independently and where possible cross references are made to the common issues, processes and fluxes. The fluxes used in this global summary are largely those deduced within each of the sectors (terrestrial, marine, etc.) presented in the companion papers.

2. Sources of fixed nitrogen

(a) Biological fixation

(i) Terrestrial ecosystems

BNF provides an important reference when quantifying the importance of human inputs to the global nitrogen cycle, as this is the primary non-anthropogenic input of N_r [15]. The quantity from lightning, discussed later, is over an order of magnitude smaller than any of the estimates of BNF, albeit of large importance for the formation of ozone in and the maintenance of the oxidation capacity of the global atmosphere. The process of BNF was identified in the late nineteenth century and has since become a focus of ecological interest. There remain important limitations in understanding, including why, with such a widespread capability in ecosystems to fix atmospheric N_2, organisms do not fix more N, when the benefits would provide advantages over competitor organisms that lack a nitrogen-fixing capability. For many ecosystems, the availability of N_r in soils clearly down-regulates BNF, so perhaps the widespread application of N_r on farmland and deposition to semi-natural land has decreased non-agricultural BNF (as assumed in [1]). Current knowledge of processes and controls has not provided unambiguous answers to these questions. The review in this issue by Vitousek et al. [16] provides an estimate of annual pre-industrial BNF in terrestrial ecosystems of 58 Tg N, within a range of 40–100 Tg, and a discussion of current understanding and limitations. The uncertainty range is large and reflects the difficulty in estimating the component terms. The value deduced by Vitousek et al. [16] is smaller than many published estimates, especially earlier values suggesting pre-industrial BNF in the range 100–290 Tg N yr^{-1}. However, this new calculation is based on estimates of hydrological losses of nitrogen from terrestrial systems and the fraction of nitrogen denitrified in streams and rivers may be overestimated.

(ii) Marine ecosystems

The nitrogen cycle in the oceans including BNF and denitrification is reviewed by Voss et al. [17]. Estimates of both terms suggest either an excess of denitrification over BNF or an approximate balance of the two [18]. However, uncertainties in

the individual terms preclude a clear consensus. The underpinning control mechanism over the balance between BNF and denitrification at large scales has not been demonstrated, but phosphorus and iron availability may be important contributors. Covering three quarters of the Earth's surface, oceans clearly dominate the surface area and even relatively small fluxes per unit area have the potential to make a substantial contribution to total N fluxes between the atmospheric N_2 reservoir and marine N_r. One of the key uncertainties in the rates of marine BNF is spatial variability, since these are coupled to the supply of other nutrients required for the processes, especially phosphorus and iron whose supply is spatially variable [19]. Larger rates of BNF have been suggested for the Atlantic than the Pacific oceans due to greater nutrient supply [17].

Global marine BNF has been estimated at 125 Tg N annually [20], with a suggested range of 60–200 Tg N [21]. Other recent estimates of marine BNF include values of 140 Tg N yr^{-1} from Canfield et al. [22] and 145 Tg N yr^{-1} from Galloway et al. [1]. It is unclear from the papers how independent the estimates are and while there are substantial sets of measurements, these do not appear to be systematic in covering the spatial and temporal scales needed to provide rigorous estimates of variability.

Here, the value for marine BNF argued by Voss [17] of 140 Tg N yr^{-1} (± 50) has been adopted in the global budget.

(b) Lightning

In addition to BNF, nitrogen is also fixed naturally as NO_x by lightning, which introduces reactive N to relatively remote regions of the troposphere.

The process is has been investigated using direct measurements and supported by satellite remote sensing of lightning activity. Global production has been estimated using available data and models, but with substantial uncertainties in part due to difficulties in up-scaling, by Brasseur et al. [23], who also consider possible effects of climate change on rates of NO_x production from lightning. These authors calculate an increase in NO_x production with increasing global temperature in the range 3–12% per $^\circ$K. Estimates of the overall global source strength vary from 2 to 10 Tg N yr^{-1} [24,25], with the more recent values closer to 5 Tg N annually. For this review a value of 5 Tg N yr^{-1} has been adopted.

(c) Global natural sources of reactive nitrogen

The global natural sources of N_r total 203 Tg N (± 50 Tg N yr^{-1}), comprising approximately one-third from terrestrial ecosystems and two-thirds from marine ecosystems, with just 2.4 per cent from lightning (table 1). The uncertainty in each of the estimated components is very large, reflecting the difficulty in up-scaling from the available data and the lack of global scale measurements to constrain the values. The marine fixation is the largest contributor to BNF but the factor of two difference between marine and terrestrial is larger than many earlier estimates due to the smaller estimate of terrestrial BNF.

(d) Anthropogenic nitrogen fixation

Anthropogenic fixation of nitrogen compounds, while uncertain, is better known than natural fixation, in part because the source sectors have been subject to more extensive measurements and have also been subject to greater scientific scrutiny, with regular monitoring of some large industrial sources. The gases created are the oxidized nitrogen compounds NO and NO_2 from

Table 1. Global nitrogen fixation prior to human influence on agricultural BNF and before the industrial revolution.

pre-industrial terrestrial BNF	58 Tg N yr^{-1}
marine BNF	140 Tg N yr^{-1}
lightning fixation of nitrogen	5 Tg N yr^{-1}
total global natural annual sources of N_r	203 Tg N yr^{-1}

transport and industry, biomass combustion and reduced nitrogen as NH_3 from the Haber–Bosch process (figure 1).

Organic nitrogen compounds, for example as amines, are widely present in the environment and the quantities may be substantial, as discussed by Cape et al. [26] and Jickells et al. [27]. However, there is no evidence that these compounds represent additional N_r, which is therefore derived from the natural or anthropogenic BNF or industrial sources of NH_3 or NO_x. The compounds and processes involved in emission of organic nitrogen and their fluxes into the atmosphere are not known in sufficient detail to enable the up-scaling for regional or global estimates of their source strength. Thus an important contribution to anthropogenic emissions of N_r may be missing from the global N_r budgets constructed to date, including the one presented here, but these compounds are unlikely to represent additional primary sources of N_r.
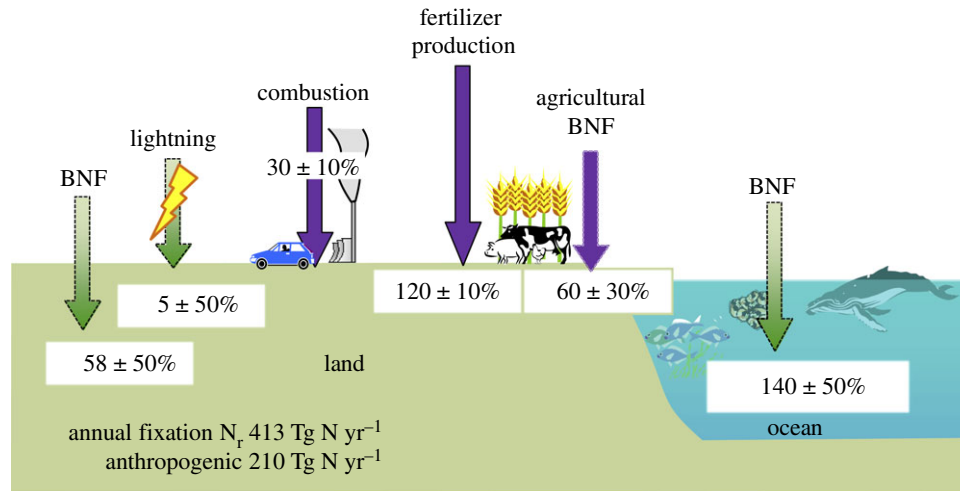
(i) Biological nitrogen fixation in cropland

Nitrogen-fixing agricultural crops also contribute substantial quantities of N_r to soils. In a recent detailed review of agricultural BNF, Herridge et al. [28] compiled data from direct measurements of BNF from a range of agricultural systems globally and up-scaled annual nitrogen fixation rates using land-use and cropping data to calculate a global total. The current global BNF from agricultural crops and grazed savannahs estimated by Herridge is 50–70 Tg N yr^{-1}. For the purpose of summarizing the data, a central value of 60 Tg N yr^{-1} as the global annual N_r flux for BNF in cropland has been used in this review. The value of BNF for cropland is very close to the pre-industrial BNF and is indistinguishable within the current range of uncertainty.

It is helpful to separate the oxidized and reduced sources of N_r, as these are produced by very different sources and have effects and pathways through the environment which also differ.

(ii) Oxidized nitrogen

The main process creating oxidized N_r compounds is combustion within internal combustion engines and industrial power plants, especially for electricity supply. It is important to distinguish between the creation of N_r and emission to the atmosphere. The focus in this section is on the creation of N_r but the subject of most research in this field has been on emissions to the atmosphere, as this is the driver of many of the environmental issues involving NO_x. The compounds generated are mainly NO and NO_2, which arise from oxidation of atmospheric N_2, and there is an additional contribution from nitrogen compounds in the fuel, derived from sequestration at the time the organic deposits were laid down [3]. Biomass burning represents an important global contribution of N_r to the atmosphere, but this is primarily from nitrogen in the fuel and does not represent new N_r fixation. Emissions of NO_x have been extensively measured both directly from sources

Figure 1. Global nitrogen fixation, natural and anthropogenic in both oxidized and reduced forms through combustion, biological fixation, lightning and fertilizer and industrial production through the Haber–Bosch process for 2010. The arrows indicate a transfer from the atmospheric N_2 reservoir to terrestrial and marine ecosystems, regardless of the subsequent fate of the N_r. Green arrows represent natural sources, purple arrows represent anthropogenic sources.

and also derived from satellite remote sensing to estimate global biomass emissions [29].

Emissions of nitric oxide (NO) from soils also contribute significantly to atmospheric emissions, but this is not an additional source of N_r as it results from the microbial transformations of existing N_r in soil, through nitrification and denitrification [30,31]. The processes leading to soil emissions are discussed by Butterbach-Bahl et al. [32] and Pilegaard [33]; while emission rates per unit land area are small (5–50 ng NO-N $m^{-2} s^{-1}$) relative to combustion sources, the emissions occur over large areas of the global agricultural landscapes.

Recent reviews of global emissions show a surprising agreement in the overall magnitude of NO_x emissions but larger differences in specific source contributions, as discussed by Granier et al. [34] and Isaksen et al. [4]. Estimates of global NO_x production and emissions from van Vuuren et al. [35] show values for the year 2000 of approximately 40 Tg N yr^{-1} of which 30 Tg N yr^{-1} is new N_r, the remainder being N_r in fuel and in biomass. The 40 Tg N total annual emission comprises 30 Tg N from fossil fuel combustion, 5 Tg N from biomass combustion and 5 Tg N from soil NO emissions. Control measures on emissions, despite industrial development in parts of Asia and Africa are assumed to reduce emissions by the middle of the twenty-first century to approximately 30 Tg N yr^{-1}, but with large uncertainty.

(iii) Reduced nitrogen

Anthropogenic fixation of reduced nitrogen (NH_3) is through nitrogen-fixing crops and the main source through the Haber–Bosch process, where H_2 and N_2 are combined at high temperatures and pressures in the presence of catalyst [5]. The process was developed during the early years of the twentieth century and by the first decade of the twenty-first century is producing 120 Tg N as NH_3 annually, of which 80 per cent is used as agricultural fertilizer and 20 per cent as feedstock for industrial processes [36]. The fate of nitrogen used in crop production varies, with only 17 per cent consumed by humans in crops, dairy and meat products, the remainder being lost to the soils, freshwaters and the atmosphere [37]. In the longer term (decades to centuries), most of the N_r is returned to the atmosphere as N_2 following denitrification,

but the lifetime in different reservoirs en route back to the atmosphere allows opportunities for transport into freshwaters or the atmosphere in reactive form. Some of the crop N_r applied as fertilizer is emitted to the atmosphere as NH_3 depending on the relative balance between ambient NH_3 concentrations and the equilibrium concentration with the NH_4^+ concentration within intercellular fluids [38]. The annual total production through the Haber–Bosch process of 120 Tg N as NH_3 represents the largest single contribution to N_r formation through anthropogenic activity. The use of nitrogen-fixing crops in agriculture contributes an additional 60 Tg N annually [28], which enters the crop and soil cycling of N_r (figure 2). The total anthropogenic production of N_r in reduced form is therefore 180 ($\pm$20) Tg N annually.

The total fixation of atmospheric N_2 by natural and anthropogenic activities at the beginning of the twentieth century is therefore 413 Tg N of which approximately half results directly from human activity. The relative proportions of reduced and oxidized nitrogen within the anthropogenic component is 85 per cent and 15 per cent, respectively, revealing the dominant role of reduced N_r and the Haber–Bosch process in the budget of emissions. The components of global N_r production are summarized in figure 1.

3. Trends in N_r emissions during the twenty-first century

Emissions of N_r to the atmosphere are a key driver of atmospheric chemistry and composition [10]. Estimates of emissions of N_r compounds through the twenty-first century are provided by van Vuuren et al. [35] from a range of scenarios, including the IPCC-SRES and the RCP projections for the 4th IPCC assessments [39]. Emissions of approximately 40 Tg N annually of NO_x continue through the period 2000–2040, and then decline through to 30 Tg N yr^{-1} according to the RCP scenarios by the end of the century, with a gradual increase in uncertainty with time such that the envelope containing the 25th and 75th percentiles stretches from 15 Tg N yr^{-1} to 70 Tg N yr^{-1} by 2100. The future emissions of NO_x strongly depend on the assumptions on how activities, especially energy and transport use will
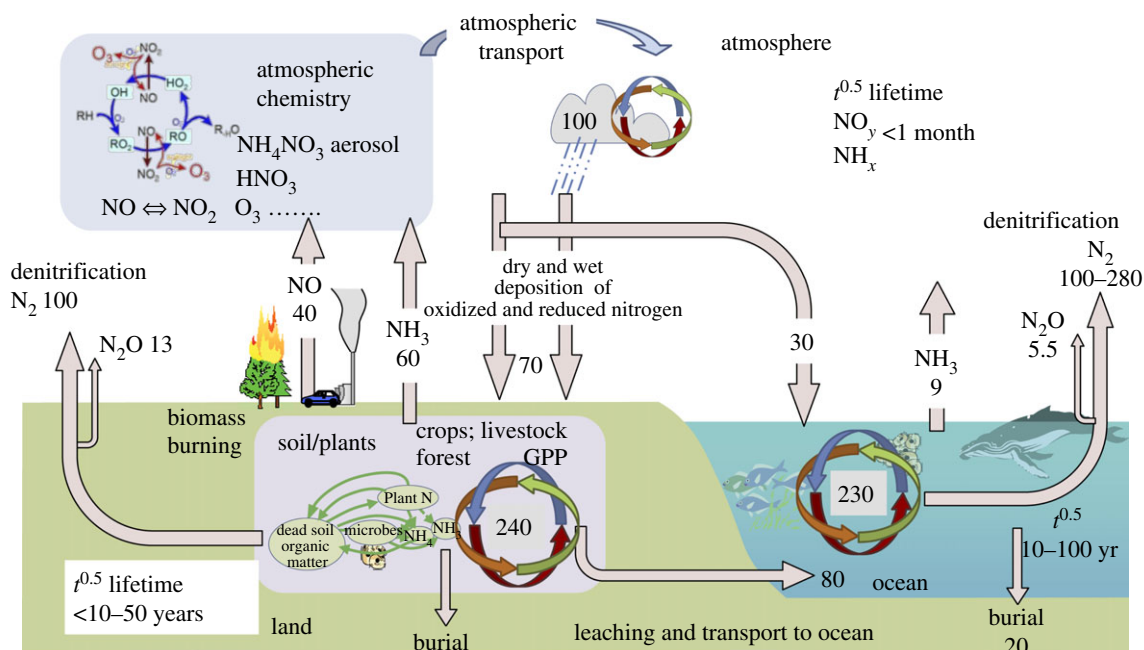
Figure 2. The processing and fluxes of reactive nitrogen in terrestrial and marine systems and in the atmosphere (Tg N yr^{-1}), showing the dominant forms of the N$_r$ in the exchanges and the magnitude of the boundary fluxes, and approximate lifetimes, integrated over global scales.

develop, and to what extent emissions will be abated by air pollution controls.

For reduced nitrogen, emissions to the atmosphere increase from 60 Tg N yr^{-1} in 2000 to between 70 and 80 Tg N yr^{-1} by 2100, mainly depending on the need for food and the nitrogen fertilizer required. These scenarios, while uncertain, are partly based on the assumption that as society develops, gradually emissions of NO$_x$ to the atmosphere are controlled, and while this has been the case over the last few decades, it is a simple assumption that may not be correct for the future. This is also a period in which global climate is projected to change, with substantial warming, averaging between 2 and 4 °K relative to pre-industrial times by 2100 [39]. Changes in temperature of this magnitude will directly influence the surface to atmosphere exchange of many trace gases, and NH$_3$ in particular, the emissions of which are strongly coupled to the temperature of vegetation [40]. The magnitude of increases in NH$_3$ emissions as a consequence of changes in climate is addressed by Sutton *et al.* [41], and might reach 130 Tg NH$_3$-N yr^{-1} by 2100.

Emissions to the atmosphere of N$_r$ from anthropogenic activities seem destined to increase, driven by the dominant term, the emissions of NH$_3$ from agriculture. The global fluxes of N$_r$ shown in figures 1, 2 and 3 are listed in table 2, with their author attributions.

4. Processing and distributing N$_r$ through the Earth system

The N$_r$ fixed by natural processes or anthropogenic activity is processed chemically in the atmosphere and largely by microbial and plant biochemistry in terrestrial and marine environments. The products of the chemical processing include a wide range of inorganic and organic compounds. The relative magnitudes of the quantities of N$_r$ cycling within each of these environments are shown in figure 2. This simple representation shows the terrestrial component to be responsible for processing of 240 Tg N in its different

forms, while 230 Tg N yr^{-1} is processed in the oceans and approximately 100 Tg N yr^{-1} is processed in the atmosphere, ignoring the fluxes into and out of the much larger atmospheric N$_2$ reservoir. Also shown in figure 2 is a rough estimate of the residence time of the N$_r$ in each of these environments to show that the atmospheric residence time is short relative to marine and terrestrial compartments, and that even in the case of terrestrial environments (except peatlands), the average lifetime of N$_r$ is only a few decades. Such averaging over the global terrestrial biosphere is potentially misleading as there are long-lived reservoirs, such as organic matter in peatlands and N$_r$ in ice sheets and in deserts and aquifers. The N$_r$ generated through BNF in terrestrial and marine ecosystems is processed by plant metabolism and microbial activity and converted into plant and microbial protein. The vegetation bound N$_r$ in agricultural crops is either used directly as food for human consumption or fed to livestock and converted, rather inefficiently, to protein for human consumption. The conversions and transfers from initial fixation through the food chain all present opportunities for leakages to ground water or the atmosphere.

The readily available inorganic N$_r$ in soils, if not sequestered by vegetation is transformed through nitrification or denitrification to gaseous forms (NO, N$_2$O or N$_2$) depending on soil physical conditions and oxidation state [31]. The fluxes from soil to the atmosphere, soil water and rivers transport the N$_r$ compounds over a range of distances, depending on subsequent transformations, as illustrated in figure 2 and described in greater detail in the companion papers in this issue.

(a) The nitrogen cascade

The transfer of N$_r$ from soils to atmosphere and to freshwaters has a wider application in considering the leakages of N$_r$ from transformations in soils, vegetation and water. Galloway *et al.* [2] introduced the nitrogen cascade concept to illustrate the many inter-conversions and leakages of N$_r$ occurring between the original fixation step and denitrification back to the atmosphere as N$_2$. It is helpful to take an example describing the fate
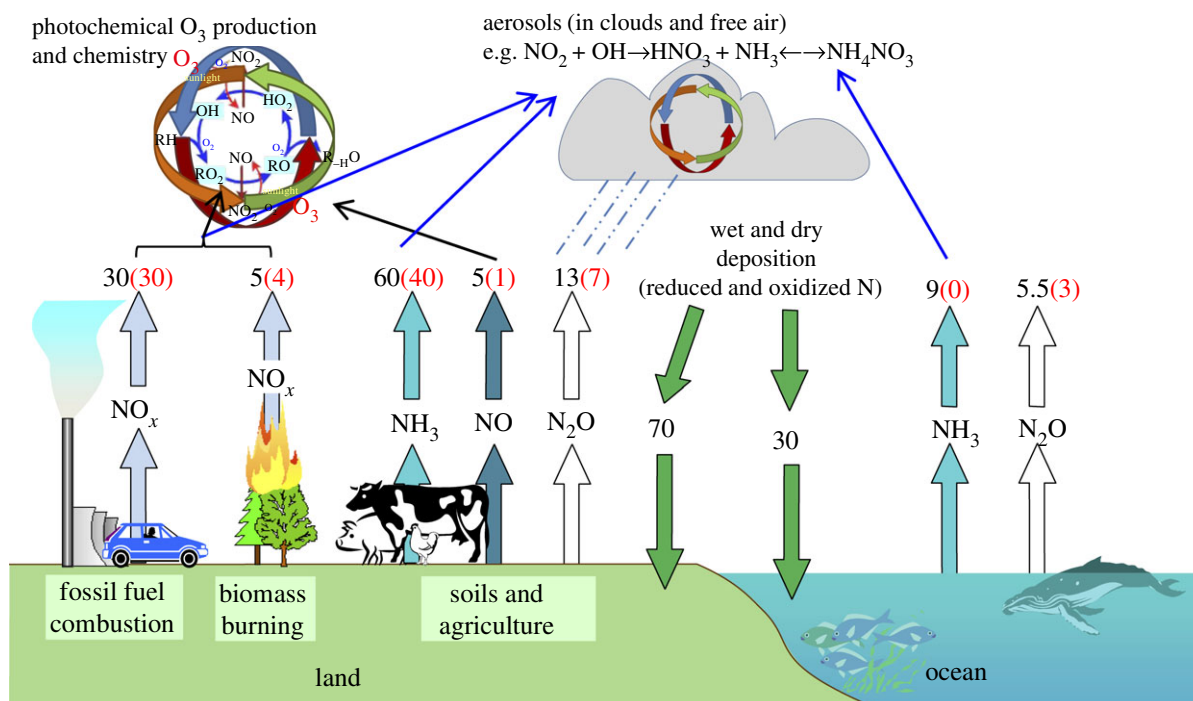
Figure 3. The global atmospheric processing of reactive nitrogen, illustrating the main sources, the main chemical pathways and products and the magnitudes of the fluxes (units Tg yr^{-1}). The emission flux values in black are the total fluxes while the red values indicate the anthropogenic contribution.

of a freshly produced NH_3 molecule to illustrate the point: consider a nitrogen atom converted to an NH_3 molecule in the Haber−Bosch process, applied as fertilizer to soil and transformed many times before finally being returned to the atmosphere as N_2. A possible sequence of transformations is illustrated in table 3, with an indication of the environmental effects at each stage.

The wide range of issues and processes in which nitrogen is involved are very seldom integrated at a global scale. Instead, the science is described within components such as the oceans, atmosphere or terrestrial ecosystems, as in the companion papers. The issues within each and the approaches to describe and investigate them are different. The following three sections outline approaches and issues for N_r in the atmosphere and terrestrial and marine ecosystems.

(b) Atmospheric processing of N_r
(i) Application of chemistry transport models
Emissions of NO_x to the atmosphere from anthropogenic and natural processes have been a focus of interest as these compounds play a major role in atmospheric chemistry, especially of photochemical oxidants such as ozone (figure 1). The chemical processing has been simulated within chemistry transport models (CTM) to quantify transport transformation and deposition at regional and global scales. Early models of the global cycles of oxidized and reduced nitrogen (NO_y and NH_x) were treated separately [52]. Currently, while almost all global atmospheric chemistry models include a representation of NO_y chemistry, few models include reduced nitrogen (NH_x). In a recent model intercomparison [45], 23 global models included NO_y, while only seven included NH_x. However, increasingly, models now include combined aerosol and photochemistry descriptions, as reviewed by Fiore et al. [53].

The first attempts to model the global NH_x cycle were based on a simplified, empirical approach that assumed a limited uptake of NH_3 according to $(NH_x)_{1.5}H_{0.5}SO_4$.

Table 2. A summary of global fluxes of N_r and literature sources.

global nitrogen fluxes	Tg N yr^{-1}	references
industrial production (fertilizer 100, chemical industry 20)	120	[36,42]
N_2 fixation natural ecosystems	58	[16]
N_2 fixation by oceans	140	[17]
N_2 fixation by agricultural crops	60	[28]
combustion NO_x emissions	40	[35]
NO emissions from soils	5	[33,43]
N_2O emissions from soils	13	[44]
lightning	5	[24,25]
NH_3 emissions from terrestrial ecosystems into the atmosphere	60	[41]
wet and dry deposition of oxidized nitrogen to terrestrial surfaces	70	[45,21]
wet and dry deposition of oxidized to oceans	30	[45,21]
NH_3 emissions from oceans (and volcanoes) to atmosphere	9	[42,39,21]
N_2O emissions from the oceans to atmosphere	5.5	[46]
denitrification to N_2 in oceans	100 − 280	[17,47,21]
N_r burial in oceans	20	[17]

More recent models describe aerosol equilibrium using equilibrium modules.

The resolution of global models currently ranges from $0.5° \times 0.5°$ to $4° \times 5°$ latitude−longitude and is expected to increase to $0.25° \times 0.25°$ in the coming years. Also the spatial

Table 3. Illustrating the nitrogen cascade: a possible life cycle of a nitrogen atom following fixation in the Haber–Bosch process to NH_3 and its pathway through terrestrial and marine ecosystems and the atmosphere before returning to the atmospheric N_2 reservoir. The single N atom contributes en route to eutrophication and acidification of terrestrial and marine ecosystems, and to human health and climate effects.

transformation	pathway	environmental effect
N_2 fixation: Haber–Bosch process $N_2 \rightarrow NH_3$	industry	energy intensive process, production of CO_2 plus all the consequences of the N_r as it cascades through soils, the atmosphere and aqueous phases
N fertilizer on crops	agricultural lands	provision of food for human consumption
NH_4 nitrified to $\rightarrow NO_3$ NO in soil $\rightarrow$ atmosphere oxidation of $NO \rightarrow NO_2 \rightarrow HNO_3$	NO emission from soil to atmosphere and ozone production during volatile organic compound degradation	ozone effects on vegetation or human health [48,49]
aerosol formation, $HNO_3 \rightarrow NO_3$	in atmosphere	planetary albedo, human health [50]
wet + dry deposition NO_3 to soil $\rightarrow$ vegetation $NO_3 \rightarrow R\text{-}NH_2$	removal from atmosphere and transfer to plant biomass	eutrophication, acidification [51]
consumption by herbivores: excreted as urea $R\text{-}NH_2 \rightarrow CO(NH_2)_2$	plant biomass $\rightarrow$ animal protein $\rightarrow$ excreted and returned to soil	eutrophication [51]
urea converted to NH_3 in soil and released to atmosphere	soil to atmosphere flux of NH_3	eutrophication
NH_3/NH_4 uptake by vegetation	removal from atmosphere by dry deposition to vegetation	eutrophication
decomposition $R\text{-}NH_3 \rightarrow NH_4$	vegetation to soil	eutrophication
NH_4 nitrified to NO_3 transferred to river/estuary/open ocean	soil to ground water $\rightarrow$ river $\rightarrow$ ocean	eutrophication
ocean uptake in phyto/zooplankton	shelf seas to open ocean	eutrophication
denitrification in ocean sediments $NO_3 \rightarrow N_2$	returns to atmosphere as N_2 and N_2O	climate change

domain and resolution of regional models has been steadily improving typically from 36 km to 12 km grid sizes, and higher resolutions for limited periods. As we argue below high resolution is important to accurately describe deposition, especially over complex terrain.

(ii) Dry and wet removal

Realistic descriptions of wet and dry deposition and thorough evaluation with high-quality measurements remain a major weakness of global modelling of the atmospheric N_r cycle. Rain formation, as a part of the hydrological cycle, is one of the more difficult parameters in global weather forecasting, and the removal of pollutants by rain formation in clouds and scavenging below clouds is even more uncertain. Wet removal is especially uncertain in tropical regions, where rainfall often occurs on sub-grid model scales in convective storms and in the mid-latitudes over mountains where orographic wet scavenging processes operate at sub-grid scales for these models [54]. The description of dry deposition often follows simplistic deposition velocity schemes [55], coupled to a land-use database and model generated meteorology. Such approaches are some decades behind current understanding of processes for trace gases generally and nitrogen compounds in particular [56]. In practice, some components of N_r are both emitted and deposited onto terrestrial surfaces, a process referred to as bidirectional exchange. The direction of the flux

is determined by the relative concentrations in the vegetation and above canopy air according to a compensation point [38]. At present, global CTMs do not consider interactive exchange with nitrogen pools in vegetation and soils. Moreover, the lack of routine flux measurements of reactive nitrogen compounds precludes validation of modelled dry deposition with field data at any more than three or four locations.

(iii) Uncertainties and constraints on global atmospheric budgets

The missing processes in the formulation of global atmospheric transport models include: sub-grid deposition; incomplete mixing on sub-grid scales (consider, e.g., farm scale NH_3 emissions and regional sulfate plumes), and emissions from canopy and oceans. To what extent, then, can we trust the outputs of global models for global deposition? Some constraints are offered by recent satellite observations. For example, NO_2 observations from Sciamachy instruments [57] provide constraints on NOx emissions, and thus to some extent also on deposition. Underestimates of NO_x emissions over China were reported by Van Noije et al. [58]. Very recent NH_3 satellite observations indicate in some cases missing hot spots of NH_3 emissions [59] but have not so far been used to constrain the global NH_3 cycle.

The global models cannot provide much of the regional deposition detail; nevertheless, there was a recent comparison by Dentener et al. [45] of 21 global models with

wet deposition measurements in North America and Europe. They demonstrate reasonable performance in southeast Asia, but problems in Africa, South Asia and South America. A lack of high-quality data in the latter regions still precludes clear conclusions on model performance with regard to deposition. Mass conservation requires that global emissions equal global deposition; until higher accuracy measurements with sufficient spatial coverage become available, the global atmospheric nitrogen cycle will be associated with uncertainties in the order of 30–50%.

The reactive gases are processed rapidly and lead to the formation of O_3 and other photochemical oxidants and secondary inorganic and organic aerosols [9] during the photochemical degradation of volatile organic compounds. The NH_3 is either dry deposited back to the surface or incorporated in aerosol, either as NH_4NO_3 or, if SO_2 is present in significant quantities, as $(NH_4)_2SO_4$. The lifetime of these short-lived compounds is typically a day or two, being longer as aerosol, which relies on wet scavenging for the majority of the removal process. The models are able to capture the global distribution of ozone in the troposphere at the surface quite well [9]. However, at regional scales there remain considerable problems reproducing the trends in surface concentration changes through the last few decades [60].

The atmospheric processing of reduced nitrogen compounds has received much less attention than oxidized nitrogen, but is now incorporated in many regional [61,62] and global models [45]. Projected trends in emissions of NH_3 make this the dominant component of emissions through this century, and one which is likely to increase with temperature, owing to the coupling between temperature and the gas and liquid phase partitioning [63].

Emissions of N_2O from soil during denitrification [64,65] have a longer atmospheric lifetime at approximately 100 years, relying on photolysis in the stratosphere for its removal.

The net flow of N_r from the land into the oceans and the atmosphere is unsurprising given the mobility of N_r in soil water and transfer to the oceans by rivers [66] and the advection of the atmospheric N_r by wind over coastlines. There is also transfer within the terrestrial landscape from the N_r hot spots to areas with small N_r inputs from farming and industry. These include large areas of semi-natural land (e.g. heathlands, forest and mountains) but also include small areas embedded within intensively used parts of the landscape such as nature reserves or unmanaged land surrounded by industrial areas or farmland. These are the components of the landscape showing some of the largest effects of N_r deposition, including widespread changes in flora or the emission of trace N_r species [67,68].

(c) Terrestrial processing of N_r

Most of the anthropogenic perturbation of the nitrogen cycle is driven by activity on land, both through the use of N_r in agriculture and through industry, electricity generation and transport. Although the initial steps in much of the industrial and transport N_r production lead directly to emissions to the atmosphere, the relatively short residence times of oxidized N_r compounds lead to rapid return of NO_y and NH_x to the Earth's surface as deposition. The geographical distribution of N_r source areas leads to two-thirds of global atmospheric

N_r inputs to terrestrial surfaces and one-third onto marine surfaces [1] (figure 2).

To date, the most detailed assessment of terrestrial processing and fluxes of N_r on a regional basis has been provided within the European Nitrogen Assessment (ENA) [69]. Assessments for other regions and the global scale have yet to be completed. Earlier analyses by Galloway *et al.* [1] provide estimates of the global transformations and flow of N_r through terrestrial ecosystems and into the atmosphere and oceans. These two syntheses are broadly consistent in showing the dominant role of terrestrial processing of N_r (figure 4).

The analysis within the ENA allows the relative scales of the different activities to be compared. The cycling of N_r within agriculture through fertilizer inputs to cropland and the flow of N_r through livestock and back into soils reveals the central role of processes, with soils as the principle location of N_r transformations and ultimately the main site of denitrification back to N_2. If we fully understood these processes globally and knew the magnitude of the fluxes and their spatial distribution globally, the uncertainties in global budgets would be greatly reduced. Simply ranking the magnitudes of the fluxes in the European N cycle by size shows that of the 35 fluxes quantified in figure 4, fluxes from or to soils comprise the top 15 and compromise most of the N_r processing within Europe. The processing and leaching of N_r in catchments and the export to coastal seas are described by Howarth *et al.* [70] and Billen *et al.* [66]. The long-term trends in nitrate in the Thames in the UK (between 1868 and 2008) reveal the magnitude of the change in countries that industrialized early [71].

(d) Processing N_r in the oceans

The cycling and processing of N_r within the oceans has received much less attention, but recent reviews have identified the major components and issues [17,21,72]. BNF in oceans is a very large component at 140 Tg N annually, among the largest in the global budget (figure 2), and is subject to more uncertainty than most of the terrestrial terms owing to the lack of measurements. The net transfer of N_r to oceans from terrestrial systems is processed (figure 5) and some is buried in organic sediments while the remainder is denitrified and returned to the atmosphere as either N_2 or N_2O. The fraction of the N_r returned to the atmosphere as N_2O is spatially very variable, and quantifying the global N_2O source from ocean sources, while subject to considerable uncertainty, is a substantial term, estimated by Duce *et al.* [21] to be 5.5 Tg N yr^{-1} as N_2O, and represents approximately 30 per cent of the emission flux of N_2O, from the ocean [17]. A source strength of this magnitude may offset as much as two-thirds of the enhancement of the ocean sink for CO_2 owing to nitrogen fertilization of the oceans [21].

The global flow of N in oceans is coupled to the wider circulation patterns, and especially the ocean conveyor system transporting solutes southwards at the ocean floor in the Atlantic ocean towards the Antarctic circumpolar current and from there northwards into the Indian and Pacific oceans. The timescales of transport are long relative to other timescales of N_r processing, with Atlantic water residence times of approximately 180 years, exceeding the time since industrial contributions to the global nitrogen cycle began. Thus, the ocean transport timescales are long relative to the processing times in the ocean and much longer than atmospheric transport
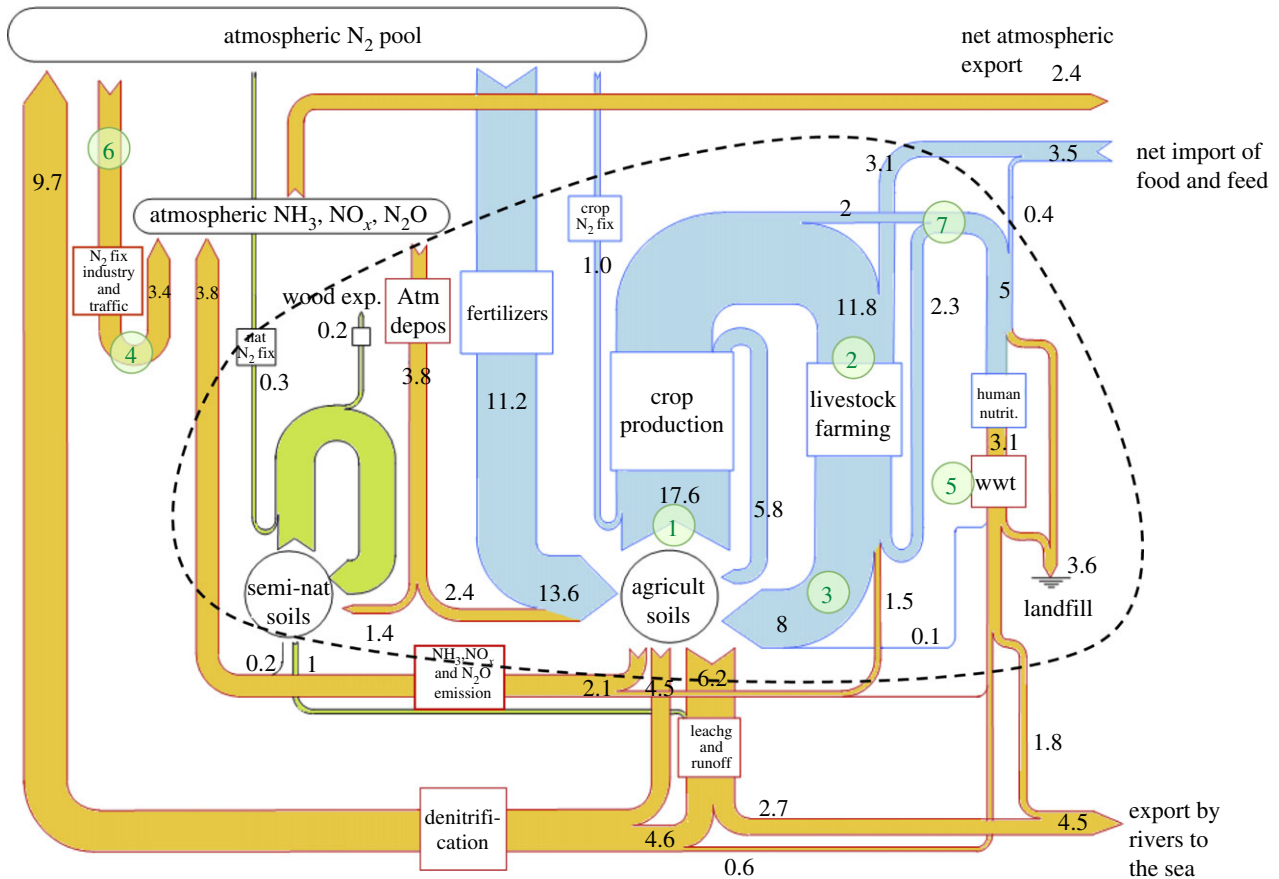
Figure 4. The nitrogen cycle within the EU-27 showing natural fluxes (Tg N) in green, (intentional) anthropogenic fluxes as blue and (unintentional) as orange adapted from the ENA [69]. The terrestrial component of the cycle is delineated by the dotted ellipse.

or land to ocean transport timescales, by several orders of magnitude. A consequence of these timescales is large regional and vertical variability in concentrations of N_r in oceans. Peak values occur in the coastal zones, which are strongly influenced by terrestrial outflow, and at the larger scale the peak values occur in polar and bottom water and minimum values occur in tropical surface waters, where available N_r is quickly assimilated. A consequence of the large spatial variability, including the coastal zones, is that hot spots of accumulation and processing are an important feature, resulting in substantial emissions of N_2O from relatively small areas of the ocean, which have not been measured.

(e) Fate and residence time of N_r in the atmosphere, and terrestrial and marine ecosystems

The ultimate fate of N_r fixed naturally and from human activity is as N_2 returned to the atmosphere. However, during the pathway from production of N_r to its ultimate fate, it presents the potential for effects on terrestrial ecosystems, human health and climate [8], as illustrated in table 2. The effects occur in part through sequestration in biomass, the largest storage term in the global processing of N_r. There are also much smaller but potentially significant stores of N_r in inorganic form in aquifers, ice sheets and peatland, all of which have residence times of century to millennia. In this section, these residence times are briefly discussed to indicate probable timescales for recovery from effects of human modification of the global nitrogen cycle.

(i) Atmosphere

The highly reactive compounds (NO, NO_2, HNO_3, NH_3 and aerosol NH_4 and NO_3) have atmospheric lifetimes ranging from a few hours (NH_3 and HNO_3) to aerosols, which have lifetimes owing to removal by precipitation of a few days to a week. The greenhouse gas N_2O has an atmospheric lifetime of approximately 100 years and relies on photolysis in the stratosphere for oxidation to NO before it can be scavenged from the atmosphere by wet and dry deposition. Thus, except for effects of N_2O, reduction in emissions of N_r to the atmosphere would lead to a rapid reduction in most compounds in air and effects on climate and human health would cease after a period of a few weeks.

(ii) Terrestrial ecosystems

In terrestrial ecosystems, the additional N_r leads to enhanced quantities of N_r cycling between vegetation and the soil, with the main removal process being leaching as NO_3 to ground water and denitrification as N_2 back to the atmosphere. Plant and soil communities have evolved to sequester and recycle N_r as it is an essential and often limiting nutrient [73]. In tropical ecosystems, N_r is rapidly cycled, maintaining small pools of inorganic N_r in soil. Except for peatlands that store carbon and nitrogen for millennia, the majority of temperate and tropical ecosystems cycle the organic matter and nitrogen sufficiently quickly and a pulse of additional N_r is lost through denitrification and fire over a few decades. Thus, it appears that terrestrial ecosystems would recover from excess N_r inputs over a period of less than a century, and probably a few decades, following a reduction in N_r input. The species composition of the post-
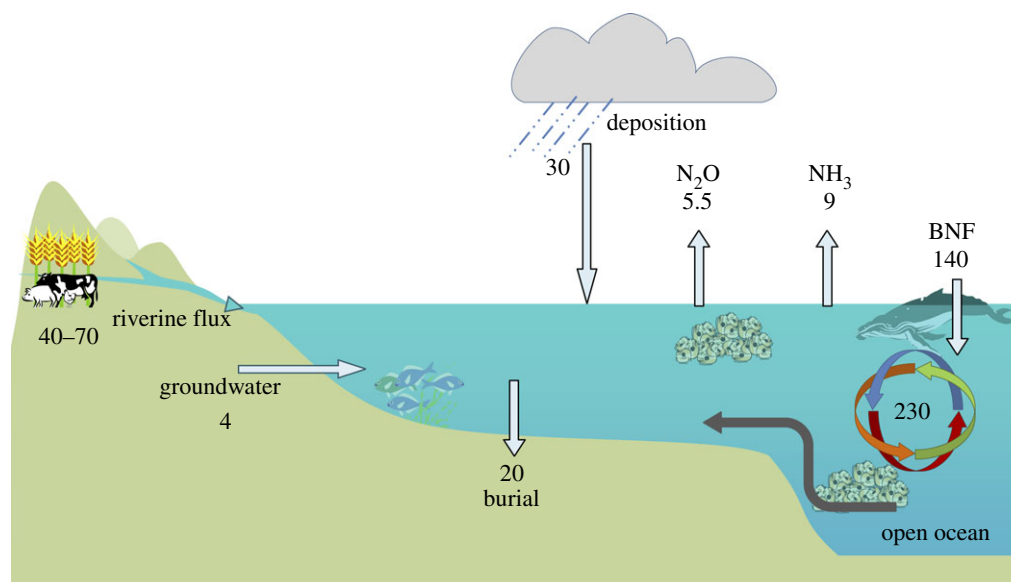
Figure 5. A simplified schematic of nitrogen cycling in the global oceans (adapted and simplified from [17]). The fluxes are as detailed in the text to be consistent with figure 2.

recovery ecosystems, however, may differ substantially from the composition prior to enhanced nitrogen deposition. In some semi-natural ecosystems, active management has been used to remove N_r from top soils, to restore low fertility plant communities and accelerate the recovery process [74].

Regional changes in biodiversity as a consequence of N_r deposition have been observed across Europe [12,51], and it is likely that the other major regions of enhanced N_r deposition will show similar trends. The primary productivity of these ecosystems may also be changing as many semi-natural ecosystems are nitrogen limited. The additional biomass sequestered as a consequence of the N_r deposition has been estimated for forests [75,76]. These studies consistently show that forests in areas of enhanced N_r deposition have been growing more rapidly in recent decades, an effect that has been shown to be a consequence of N_r deposition rather than changes in climate or forestry practice [76]. To date, the data from long-term N_r addition field experiments show increases in productivity and nitrogen enrichment of vegetation and surface soils [73]. In contrast to the networks of flux monitoring stations for terrestrial carbon exchange, there are no systematic measurements of nitrogen sequestration in terrestrial ecosystems, even though the sequestration of N_r is one of the driving variables for carbon sequestration [76]. Carbon sequestration in terrestrial ecosystems is clearly coupled to nutrient supply, especially of nitrogen and phosphorus [73,77].

(iii) Marine ecosystems

As with terrestrial ecosystems, there are no systematic measurements of nitrogen sequestration in the oceans and, again, carbon sequestration is clearly coupled to nutrient supply. The timescales of transport and N_r sequestration in the ocean are substantially longer than those in the atmosphere and in the majority of terrestrial ecosystems. Furthermore, the anoxic bottom waters are accumulating N_r, estimated by Galloway et al. [1] to be approximately $4 \, \text{Tg N yr}^{-1}$ and from which N_2O is generated, which may represent an important long-term global problem. Thus, marine N_r reservoirs may prove to be more important in the longer term, as terrestrial and atmospheric reservoirs appear to recover more rapidly.

(f) Nitrogen sequestration

The global sequestration of N_r has been quantified using ecosystem models as described by Zaehle [78], who estimated terrestrial N_r sequestion of $27 \, \text{Tg N yr}^{-1}$ between 2001 and 2012. This may be compared with a rough estimate made using the annual terrestrial global C sequestration [79] and Churkina et al. [80], assuming a C/N ratio. Adopting this very simplistic approach for a C/N ratio of 30, terrestrial N sequestration would be $75 \, \text{Tg N yr}^{-1}$ and would vary between 50 and 100 Tg N for C/N ratios between 25 and 50, effectively spanning the range of observed C/N values, and similar to the value of 60 Tg N estimated by Galloway et al. [1] and significantly larger than the estimate by Zaehle [78].

The quantity of N_r sequestered in ice is discussed by Wolff [81] and estimated at 260 Tg N. Although this quantity may seem large, it represents accumulation over a very long time and the annual inputs are small.

5. Closing remarks

The global nitrogen cycle has been greatly modified by human activity, and among the key biogeochemical cycles on which ecosystems depend for their sustainability the nitrogen cycle is the most perturbed on the planet. Many components of the global budget have been quantified over the last 20 years, and the contrast between knowledge of the major fluxes in 1982 [82] and the descriptions of N_r cycling in ocean and terrestrial ecosystems and the atmosphere presented in this issue are striking. However, many fluxes are subject to large uncertainties and require extensive measurements to constrain the current range of values, a conclusion similar to that reached by Stewart [83] following the discussion meeting on the nitrogen cycle in 1981.

The consequences of human intervention in the nitrogen cycle include the obvious benefits for food security with approximately half of the global human population dependent on the increased yields of agricultural crops owing to fertilizer nitrogen usage, and substantially enhanced carbon sequestration resulting from N_r deposition to forests and other semi-natural terrestrial ecosystems [76]. The negative

consequences of human fixation of nitrogen are also substantial and include the N_r contribution to effects of aerosols and ozone on human health [84], terrestrial ecosystem losses in biodiversity owing to N_r deposition at regional scales [85] and effects of N_r on climate described by Erisman *et al.* [8]. The effects on terrestrial ecosystems and the atmosphere have been subject to much more control than effects in marine ecosystems, which are the destination for a substantial fraction of N_r applied to terrestrial ecosystems. The transfer of 80–100 Tg N_r from land to oceans annually represents approximately half of anthropogenic emissions and comprises 50–70 Tg N leached from land to the ocean in freshwaters and the deposition of an additional 30 Tg N from the atmosphere on oceans. There are very few control measures in place to reduce the transfer of N_r to oceans and no international measures to regulate the overall effects of perturbation of the nitrogen cycle by human activity.

The Malthusian concept of food security being compromised by population growth has an interesting resonance in the context of the human influence on the nitrogen cycle. The problem of growing sufficient food to date has been largely solved by agricultural science, and the supply of nitrogen as fertilizer from the Haber–Bosch process has been a substantial contributor to increased productivity. However, the amounts of nitrogen applied have not been sufficiently constrained to prevent widespread leakage to freshwaters and the atmosphere, with consequent effects on human health, biodiversity and climate. The N_r injected into the environment from industry and transport, largely combustion sources, further increases the scale and range of effects. The irony here is that the societal needs for use of N_r for food have been satisfied by inefficient nitrogen use in agriculture, compromising other ecosystem services. To date, there has been much more effective regulation of N_r from combustion and transport sectors than N_r use in agriculture. Many of the accumulated effects of N_r are not attributable to any specific country or region, and the oceans may represent an important long-term problem as the marine N_r store gradually releases N_2O to the atmosphere.

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