

rstb.royalsocietypublishing.org



Research

Cite this article: Erisman JW, Galloway JN, Seitzinger S, Bleeker A, Dise NB, Petrescu AMR, Leach AM, de Vries W. 2013 Consequences of human modification of the global nitrogen cycle. *Phil Trans R Soc B* 368: 20130116. <http://dx.doi.org/10.1098/rstb.2013.0116>

One contribution of 15 to a Discussion Meeting Issue 'The global nitrogen cycle in the twenty-first century'.

Subject Areas:

environmental science, ecology, biochemistry

Keywords:

food security, reactive nitrogen, environmental effects, human health, climate, biodiversity

Author for correspondence:

Jan Willem Erisman

e-mail: j.erisman@louisbolck.nl

*Present address: European Commission, Joint Research Centre, Institute for Environment and Sustainability (IES) Air and Climate Unit, TP290 Via Enrico Fermi 2749, 21027 Ispra, Varese, Italy.

Consequences of human modification of the global nitrogen cycle

Jan Willem Erisman^{1,2}, James N. Galloway³, Sybil Seitzinger⁴, Albert Bleeker⁵, Nancy B. Dise⁶, A. M. Roxana Petrescu^{2,7,*}, Allison M. Leach³ and Wim de Vries⁸

¹Louis Bolk Institute, Hoofdstraat 24, 3972 LA Driebergen, The Netherlands

²VU University Amsterdam, de Boelelaan 1085, 1081 HV AV Amsterdam, The Netherlands

³University of Virginia, PO Box 400123, Charlottesville, VA, USA

⁴International Geosphere-Biosphere Programme (IGBP) Secretariat, Royal Swedish Academy of Sciences, PO Box 50005, 104 05 Stockholm, Sweden

⁵Energy research Center of the Netherlands, ECN, PO Box 1, 1755 ZG Petten, The Netherlands

⁶Department of Environmental and Geographical Sciences, Manchester Metropolitan University, John Dalton East Building, Chester Street, Manchester M15GD, UK

⁷European Commission, Joint Research Centre, Institute for Environment and Sustainability (IES) Air and Climate Unit, TP290 Via Enrico Fermi 2749, 21027 Ispra, Varese, Italy

⁸Alterra Wageningen University and Research Centre, PO Box 47, 6700 AA Wageningen, The Netherlands

The demand for more food is increasing fertilizer and land use, and the demand for more energy is increasing fossil fuel combustion, leading to enhanced losses of reactive nitrogen (N_r) to the environment. Many thresholds for human and ecosystem health have been exceeded owing to N_r pollution, including those for drinking water (nitrates), air quality (smog, particulate matter, ground-level ozone), freshwater eutrophication, biodiversity loss, stratospheric ozone depletion, climate change and coastal ecosystems (dead zones). Each of these environmental effects can be magnified by the 'nitrogen cascade': a single atom of N_r can trigger a cascade of negative environmental impacts in sequence. Here, we provide an overview of the impact of N_r on the environment and human health, including an assessment of the magnitude of different environmental problems, and the relative importance of N_r as a contributor to each problem. In some cases, N_r loss to the environment is the key driver of effects (e.g. terrestrial and coastal eutrophication, nitrous oxide emissions), whereas in some other situations nitrogen represents a key contributor exacerbating a wider problem (e.g. freshwater pollution, biodiversity loss). In this way, the central role of nitrogen can remain hidden, even though it actually underpins many trans-boundary pollution problems.

1. Introduction

Reactive nitrogen (N_r) is created from N_2 naturally by biological nitrogen fixation, biomass burning and lightning. Nitrogen is an essential nutrient for the growth and functioning of plants, animals and humans, and an essential element for food security [1,2]. However, limited amounts of natural nitrogen fixation have led to the world's ecosystems becoming adapted to low rates of N_r supply, with limited productivity but high biodiversity. Because of their limited availability, some essential N_r molecules are efficiently conserved and re-used in most natural environments. Nitrogen is commonly a limiting factor for the production of food. Humankind has sought different ways to increase crop production to provide food to sustain a growing population. This has led to the development of synthetic fertilizer production based on the Haber–Bosch process [3,4]. Nitrogen currently provides many benefits to society, in particular to agriculture and industry [5].

While the industrial fixation of N_2 is essential for food production, it is not without costs for the environment and human health. The amount of N_r used to produce food is on average about 10-fold higher than its consumption, owing to inefficiencies in the food production–processing–consumption chain [6–8]. Agricultural sources of N_r produce atmospheric emissions of ammonia (NH_3),

Table 1. Overview of N_r emission-related health impacts and a summary of limit values for concentrations in air, as set by EU policies [9,10]. AOT40, accumulated exposure over a threshold ozone concentration of 40 ppb; MAC, maximum allowable concentration.

emission	routes	health impacts	indicators	limit values/targets
NO _x	inhalation: — direct impacts of NO ₂ — impacts via O ₃ — impacts via PM visibility (PM)	asthma, respiratory disorder, inflammation of airways, reduced lung functions, bronchitis, cancers	NO _x	40 µg m ⁻³ (annual mean) 200 µg m ⁻³ (hourly mean) 400 µg m ⁻³ (threshold, 3 h) 30 µg m ⁻³ (annual mean; plant damage)
			O ₃	180–240 µg m ⁻³ (hourly mean) AOT40 120 µg m ⁻³ (hourly mean)
NH ₃	inhalation: — direct impacts (negligible) — impacts via PM odour	see NO _x modest odour contribution		18 ppm (MAC value) 1 µg m ⁻³ (annual mean, plants)
				—
N ₂ O	health impact due to global warming, often enhanced by eutrophication health impact due to loss of stratospheric ozone depletion	enhancement of vectors for infectious diseases (e.g. malaria) and frequency of infestations (e.g. algae blooms, insects)		—
				—

nitrogen oxides (NO_x) and nitrous oxide (N₂O) from agriculture to the air, and nitrate (NO₃) to groundwater [8]. At the same time, combustion processes in energy production, transport and industry have led to the formation of new N_r through the emission of NO_x as an unintentional waste product.

N_r is highly mobile. Most of it dissipates into the environment and cascades through air, waters and terrestrial ecosystems where it contributes to a multitude of effects, including adverse impacts on human health, ecosystem services, biodiversity and climate change [4,7,8]. The endpoint of the cascade is ultimately the conversion back to unreactive N₂ gas, although N_r is being produced more rapidly than it is being converted back to N₂, so in many regions N_r is accumulating in the environment.

Overall, as human fixation of nitrogen continues to rise, the direct public health benefits through food production will probably continue to rise. However, the negative health consequences on ecosystems and people may become more diverse, and might in total increase more rapidly than the benefits.

This paper presents an overview of the consequences of N_r in the global environment. In the following sections, we elaborate in more detail on the impacts of N_r on (i) air quality and human health, (ii) aquatic and terrestrial ecosystems, and (iii) climate change, including global overviews whenever available.

2. Impacts on air, water quality and human health

(a) Impacts on human health: air quality

When released into the lower atmosphere, NO_x can increase tropospheric ozone (O₃) formation, smog, particulate matter (PM) and aerosols. Particulate nitrate can be formed

following the oxidation of NO₂ to nitric acid (HNO₃), which can then further react with NH₃ to form ammonium nitrate, NH₄NO₃. NO₃ and NH₄ are two of the major inorganic components in urban aerosol particles. In the atmosphere, NH₃ reacts not only with HNO₃ but also with aerosols and other acid gases such as H₂SO₄ and HCl to form ammonium-containing particles (e.g. (NH₄)₂SO₄; NH₄NO₃; NH₄Cl). NO_x can also contribute to formation of the secondary organic aerosol particles in photochemical smog.

Table 1 provides an overview of N-related health impacts. The direct impacts of NH₃ are mainly of importance within or close to N_r sources such as animal housing units or manure storage tanks. Direct impacts of NO_x exposure and indirect impacts through PM and O₃ exposure are most important for health. NO₂ is an irritant gas and can cause severe damage to the lungs if inhaled. High indoor NO₂ levels can also induce a variety of respiratory illnesses. Concentrations above 60–150 ppm can cause coughing and a burning sensation deep inside the lungs. Damage to the lungs can be visible after 2 to 24 h. These concentrations are, however, an order of magnitude higher than ambient levels and occur in special conditions. Continuous exposure to low concentrations of NO₂ can cause a cough, headache, loss of appetite and stomach problems. Environmental studies have shown that children exposed to chronically elevated NO₂ in their environment are more likely to develop respiratory diseases and reduced breathing efficiency [9].

Concentrations of NO₂ are often strongly correlated with those of other toxic pollutants with similar sources in industry and transport, and, being relatively simple to measure, NO₂ is often used as a surrogate for the pollutant mixture as a whole [10]. Achieving guideline concentrations for individual pollutants such as NO₂ may, therefore, reduce the level of many other pollutants that have the same source,

bringing public health benefits that exceed those anticipated on the basis of estimates of a single pollutant's toxicity.

O₃ is an important pollutant affecting human health, almost exclusively through inhalation [9,11]. Adverse health impacts that can be initiated and exacerbated by O₃ exposure include coughs and asthma, short-term reductions in lung function and chronic respiratory disease [9,11]. A recent overview of health risks of ozone by the World Health Organization (WHO) indicates a clear increase in mortality and respiratory morbidity rates with increasing levels of ozone in the environment [12]. An estimated 21 000 premature deaths in the EU member states are associated with ozone levels exceeding a maximum daily 8-h average of 35 ppb. Ozone is also associated with 14 000 respiratory hospital admissions annually in the EU member states [12]. A statistically significant increase in mortality risk has been observed at O₃ concentrations above 70 µg m⁻³ (35 ppb). Outdoor air pollution contributes to 5 per cent of all cardiopulmonary deaths worldwide [13]. In many countries approximately 20–40 deaths per 100 000 population are reported to be due to cardiopulmonary illness. In 2008, urban outdoor air pollution was responsible for an estimated 1.3 million annual deaths, representing 2.4 per cent of the total deaths in the world, mainly in the Eur-Asia region and in urban areas. Worldwide, urban air pollution is estimated to cause about 9 per cent of lung cancer deaths, 5 per cent of cardiopulmonary deaths and about 1 per cent of respiratory infection deaths [13].

PM is the most significant contributor to adverse health effects from air pollution [13]. It is an environmental health problem that affects people worldwide, but middle-income countries disproportionately experience this burden. According to a recent study on behalf of the European Environment Agency, pollution of fine particles is associated with more than 455 000 premature deaths every year in the EU27 member states [14]. The scattering and absorbing of light owing to particles also affects visibility in cities and scenic areas.

Apart from direct effects on humans, ozone damages crops and forests, and leads to reduced agricultural yields [15–17]. O₃ is absorbed into plants via stomatal pores on the leaf that open during the day to allow CO₂ absorption for photosynthesis and evaporation of water. O₃ damages cell walls and membranes leading to cell death and reduction in photosynthesis rates [17]. This negatively affects crop and horticultural plant yields and CO₂ uptake. Global relative yield losses owing to ozone exposure are estimated to range from 7 to 12 per cent for wheat, 3 to 4 per cent for rice, 3 to 5 per cent for maize and 6 to 16 per cent for soybeans. In Europe, the regionally aggregated yield losses for these crops are estimated to be 5 per cent, 4 per cent, 5 per cent and 27 per cent, respectively [15].

(b) Impacts on human health: nitrogen enrichment of drinking water and food

It is important to note that a healthy immune system requires adequate nutrition, thus one of the most important links between fixed nitrogen and many tropical diseases may be that better access to nutrients in undernourished regions increases the overall health and disease resistance of the population [18]. However, when in excess, different forms of N_r can cause human health problems.

Nitrate pollution of groundwater poses a recognized risk to human health. The WHO standard for drinking water is 50 mg NO₃⁻ l⁻¹ (as NO₃⁻) for short-term exposure, and 3 mg NO₃⁻ l⁻¹ for chronic effects [13]. Agriculture puts the

largest pressure on both groundwater and surface water pollution owing to reactive N [19,20]. Although nitrate concentrations have slightly decreased over the past decades in some European rivers, levels have remained high in others and, overall, nitrate levels in groundwater have remained constant. Although some improvements have been made in reducing nutrient inputs from wastewater discharge, diffuse pollution of agricultural origin remains a major threat for waters in the EU [19]. From 2000 to 2003, nearly 40 per cent of the groundwater monitoring stations in the EU exceeded average values of 25 mg NO₃⁻ l⁻¹, and almost 50 per cent of the surface water monitoring stations exceeded average values of 10 mg NO₃⁻ l⁻¹ [19]. Similar high levels occur in other parts of the world where high levels of fertilizer are used [20].

There are other impacts related to the intake of N_r through our food system. Diets in developed countries generally contain more protein than required for human health [8,21,22]. The WHO reports that current knowledge of the relationship between protein intake and health is insufficient to enable clear recommendations about either optimal intakes for long-term health or to define a safe upper limit [22]. High protein uptake can lead to high urea production and elevated blood pH, leading to an overreaction of the immune system. Furthermore, the kidneys can be overloaded causing possible kidney failure. A high blood pH can lead to loss of bone mass. Gout has also been associated with high purine foods such as meat [22].

People normally consume more nitrates from vegetables than from cured meat products. Spinach, beets, radishes, celery and cabbages are among the vegetables that generally contain very high concentrations of nitrates [23]. Nitrates can be reduced to nitrites by certain micro-organisms present in foods and in the gastrointestinal tract. This has resulted in nitrite toxicity in infants fed vegetables with a high nitrate level. No evidence currently exists implicating nitrite itself or nitrate as a carcinogen [24]. There are both experimental and epidemiologic studies that indicate possible chronic health effects associated with consumption of elevated levels of nitrate in drinking water, although results are inconsistent. Likewise, there are no good estimates of damage to health related to methaemoglobinemia owing to drinking water nitrate. Evidence is emerging for possible benefits of nitrate or nitrite as a potential pharmacological tool for cardiovascular health [18].

The available evidence supports a positive association between nitrite and nitrosamine intake and gastric cancer, between meat and processed meat intake and gastric and oesophageal cancer, and between preserved fish, vegetable and smoked food intake and gastric cancer, but is not conclusive [25]. A diet high in red meat is associated with the formation of nitrosamines through the additives (sodium nitrite) that increase the red colour of the meat. The natural breakdown products of proteins can combine with nitrites to form compounds such as nitrosamines. There are many different types of nitrosamines, most of which are known carcinogens in test animals. It is unknown at what levels, if any, nitrosamines are formed in humans after they eat cured meat products, or what constitutes a dangerous level in meat or in humans.

3. Impacts of N_r on natural ecosystems

N_r can both acidify and eutrophy ecosystems. The impact of N_r on a species or ecosystem depends on several factors, including the duration of exposure, total amount and form of nitrogen;

the sensitivity of the species; and intrinsic ecosystem properties such as fertility and acid neutralizing capacity [26]. High concentrations of N_r (especially reduced N) can be toxic to organisms that adsorb elements directly from the environment, such as sensitive algae, lichens or bryophytes [27]. More commonly, N_r acts indirectly on organisms through factors such as nutrient enrichment, oxygen depletion (in aquatic ecosystems), soil or water acidification, altering nutrient ratios, or intensifying the impact of other stressors such as pathogens or climate change. In this section, major impacts of N_r on aquatic and terrestrial ecosystems are presented.

(a) Aquatic ecosystems

(i) Acidification

Aquatic ecosystems with a low acid neutralizing capacity (primarily freshwater) can be acidified by atmospheric deposition of reactive N and S. With a sharp decline in sulfur emissions beginning in the mid-1980s, N_r has become the major component of acidic deposition in many areas of Europe and North America, and a growing problem in many developing countries. With persistent acidification, species composition at the base of the food chain is shifted, and often simplified, to favour acid-tolerant macrophytes and phytoplankton. Early life stages of fish and aquatic invertebrates can be especially sensitive to acidification, but direct and indirect impacts have been reported at all higher trophic levels, including zooplankton, benthic invertebrates, amphibians and birds [28,29].

(ii) Eutrophication

Nutrient enrichment of freshwater and coastal ecosystems usually originates from surface sources such as fertilizer runoff, erosion of nutrient-rich sediments or sewage discharge. In oligotrophic ecosystems, biomass or diversity may increase with increasing nutrient load [30]. However, as levels of N_r and P increase, phytoplankton capable of efficiently assimilating these nutrients are increasingly favoured over species more limited by other factors (e.g. diatoms, requiring silica, or benthic primary producers, requiring light). Low-diversity algal or cyanobacterial blooms can result, leading to surface water hypoxia and the release of toxic compounds. This in turn impacts sensitive higher trophic level organisms, such as invertebrates and fish [27,31]. Sedimentation and decomposition of biomass from phytoplankton blooms can deplete oxygen in bottom waters and surface sediments, especially in ecosystems with low rates of water turnover [31]. This further shifts the benthic community towards fewer tolerant species. Changes in the benthic community alter nutrient cycling in the sediments and overlying water, feeding back to further alter the rest of the aquatic ecosystem ([32], and references therein).

Coastal eutrophication has recently emerged as a global issue of serious concern, with a steady growth in the extent and persistence of eutrophic, hypoxic and anoxic coastal waters [31,33], and related incidences of toxic algal blooms such as red tides [34]. Coral reefs, sea grass beds, wild or farmed fish and shellfish can be particularly sensitive to eutrophication and oxygen depletion. Similar to acidification, impacts on lower trophic levels can move up the food chain to seabirds, mammals and other marine animals.

A recent estimate identifies 415 eutrophic and hypoxic coastal systems worldwide [33], with 169 documented hypoxic areas, 233 areas of concern and only 13 systems in recovery.

These numbers are very likely to be underestimates owing to low data availability in many areas, particularly Asia, Africa, Latin America and the Caribbean. The most underrepresented region is probably Asia, with relatively few documented eutrophic and hypoxic areas despite large increases in intensive farming methods, industrial development and population growth over the past 20 years.

(b) Terrestrial ecosystems

In high concentrations, N_r can cause direct foliar damage, primarily to lower plants. NH_3 , NO_x and NH_4^+ are especially phytotoxic [35]. This is a particular problem downwind of direct sources such as intensive livestock production. Whereas direct foliar damage is usually due to high local concentrations of N_r , broader ecosystem-scale changes to soil and vegetation often arise from chronically elevated regional N_r deposition. N_r is the limiting nutrient for plant growth in many natural and semi-natural terrestrial ecosystems. Over time, species composition changes, and diversity often declines, as characteristic species of oligotrophic, mesotrophic or circumneutral habitats are out-competed by more nitrophilic or acid-resistant plants. Forbs, bryophytes, lichens and nutrient-poor shrubs are the most impacted functional types; graminoids adapted to higher nutrient levels are the main beneficiaries of elevated N_r deposition.

Chronically elevated N_r deposition can also enhance susceptibility to stress, such as frost damage, herbivory or disease ([36] and references therein). Northern temperate, boreal, arctic, alpine, grassland, savannah and Mediterranean biomes are particularly sensitive to N_r deposition [37]. As with aquatic ecosystems, effects of N_r have been identified at all trophic levels, including indirect impacts on above-ground fauna such as insects and birds.

Within the soil, N_r fertilization can reduce the allocation of organic carbon from the vegetation to mycorrhizal fungi, because the increasing supply of N_r from above reduces the plant's dependence on mycorrhizae for scavenging N_r from the soil [38]. Free-living fungi and N-fixing bacteria are also sensitive to N_r . Changes in the microbial community in turn impact soil processes such as organic matter mineralization and nutrient cycling. The soil fauna—protozoa, worms, insect larvae, etc.—primarily react to N_r indirectly, through changes in the microbial community, microbial-driven processes or vegetation growth and composition [39,40]. Changes in macrobiota in turn influence the physical properties of soil, such as soil aggregation, water infiltration and organic matter turnover [41,42].

Exceedance of critical loads for nutrient nitrogen is linked to reduced plant species richness in a broad range of ecosystems and $5\text{--}10\text{ kg N ha}^{-1}\text{ yr}^{-1}$ has been used as a threshold value for sensitive ecosystems, although effects may occur over the long-term at lower levels ([26,36] and references therein). Combining global modelled N deposition with the spatial distribution of protected areas (PAs) under the convention on biological diversity, Bleeker *et al.* [43] showed that 40 per cent of all PAs (11% by area) are projected to receive N deposition higher than $10\text{ kg N ha}^{-1}\text{ yr}^{-1}$ by 2030 (figure 1). These cover almost all of southern Asia and the eastern USA, as well as parts of Africa and South America.

(i) Ozone exposure

As with impacts on food crops (described above), O_3 also affects natural ecosystems. The most prominent effect is that

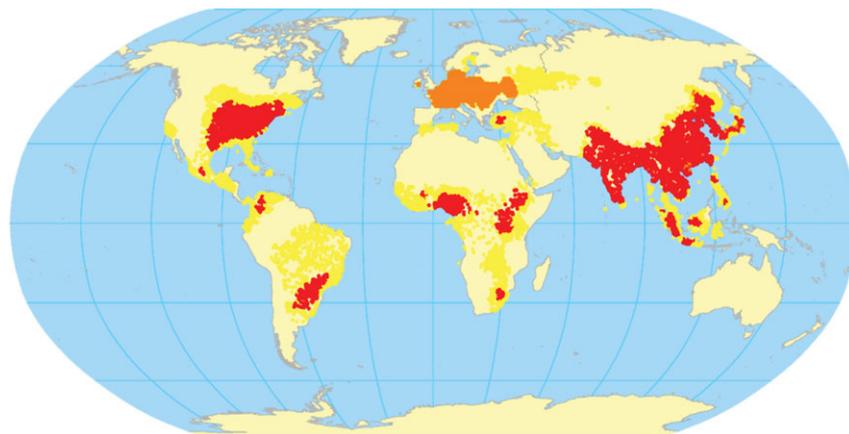


Figure 1. Distribution of N_r deposition classes and exceedance of deposition levels in the period 2000–2030 on Protected Areas (PAs) under the Convention on Biological Diversity [41]. Red PAs show an exceedance of $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and deposition in 2030 higher than 2000. Orange PAs show a current exceedance, but deposition in 2030 lower than 2000. Yellow PAs might be under threat in the near future since N_r deposition exceeds $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, but is increasing over the period 2000–2030.

it reduces forest productivity and thereby carbon sequestration. In a meta-analysis, Wittig *et al.* [44] estimated the magnitude of the impacts of current and future O_3 concentrations on the biomass, growth, physiology and biochemistry of trees representative of northern hemisphere forests. They found that current ambient O_3 concentrations (40 ppb on average) significantly reduced the total biomass of trees by 7 per cent compared with trees grown in charcoal-filtered controls, which approximates pre-industrial O_3 concentrations. Their results are in line with estimates of forest yield losses of 6 per cent for Norway spruce in Europe due to current exceedances of O_3 critical levels [16,45].

(c) Interactions

N_r also acts with other human-influenced impacts on natural ecosystems, such as land-use change, climate change, sulfur deposition, ground-level O_3 enrichment and exotic species invasion. Research on the impacts of multiple stressors is increasing, but much more understanding is needed; an in-depth review of the existing studies is beyond the scope of this paper. Effects may be additive, synergistic or antagonistic. For instance, a recent evaluation suggests that enhanced exposure of ground-level O_3 to acid grasslands in Europe may impact different plants, and in different ways, than N_r deposition, thus making N_r an additive stress [46].

4. Reactive nitrogen and climate change

N_r has many direct and indirect links to climate (summarized by Erisman *et al.* [47]). The most important warming effects of N_r on climate are:

- N_2O formation during industrial fertilizer production, incomplete combustion or microbial denitrification and nitrification—notably after fertilizer and manure application to soils. Excess N_r can also lead to hypoxia and anoxia in the ocean and surface waters, enhancing rates of denitrification and N_2O release;
- ground-level O_3 formation from NO_x . O_3 is an important greenhouse gas. It is also formed in the troposphere as a result of NO_x and volatile organic compound (VOC)

emissions. O_3 reduces plant productivity, and therefore reduces CO_2 uptake from the atmosphere; and

- changes in ecosystem CH_4 production and consumption. N_r deposition to wetlands may increase vascular plant production, thus increasing root exudation of low-molecular weight carbon compounds such as acetate, a major substrate source for some groups of methanogenic Archaea. A shift towards vascular plants such as sedges also increases the rate of release of CH_4 to the atmosphere through stems, bypassing CH_4 oxidation in the soil. N_r may also increase rates of CH_4 consumption by methanotrophic bacteria in wetlands; however, the opposite may be the case in upland soils, with the balance depending on the background levels of both CH_4 and nutrients.

The most important cooling effects of N_r on climate include:

- enhancement of the biospheric CO_2 sink owing to increased supply of N_r . Because N (often together with P) is commonly a growth-limiting element, increased N_r increases primary productivity, and thus CO_2 uptake from the atmosphere, in many terrestrial ecosystems, rivers, estuaries and areas of the open ocean. N_r may reduce productivity in very high N deposition areas; however, these are fairly rare. Increasing N_r may increase or reduce the rate of organic matter breakdown, dependent upon the background level of N_r in the environment and the type of organic matter. Estimates of the quantitative importance of N on carbon sequestration vary widely;
- N-containing aerosols. This occurs both directly via absorbing terrestrial radiation and scattering solar radiation, and indirectly, e.g. by influencing cloud formation;
- changes in CH_4 production and emission from ruminants. Increased N_r supply can be associated with more digestible diets, potentially reducing CH_4 emission from these animals. This effect is, however, small; and
- effects of O_3 on CH_4 . Elevated tropospheric O_3 increases the formation of the hydroxyl radical ($\cdot OH$), which is a major sink for atmospheric CH_4 . However, O_3 can also reduce the emission of CH_4 from wetland plants, possibly by impacting photosynthesis and reducing root exudation of carbon [42].

Table 2. Societal costs of nitrogen emissions in ranges based on the references [49–51]. Units are euro per kg N_r.

N _r flux	health	ecosystem/ coastal systems	crop decline O ₃	climate	total
NO _x -N to air	10–30	2–10	1–3		13–43
NH ₃ -N to air	1.1–20	2–10			3.1–30
N _r to water	0–4	5–50			5–54
N ₂ O-N to air	1–3			1–15	2–18

Estimating the net effect of these major interactions between N_r on climate at the global scale, Erisman *et al.* [47] calculated an overall small net cooling effect of -0.24 W m^{-2} , but with a large uncertainty range of -0.5 to $+0.2 \text{ W m}^{-2}$. This cooling effect should not be taken as indicating that N_r is not an issue for climate policies. We should conclude from this that, whatever measures are taken that affect N_r emissions, potential climate effects should be evaluated to ensure that the role of N_r does not change to make it more of a contributor to climate warming. Furthermore, it is very relevant to include the climate effect when addressing N_r reduction for environmental reasons in order to prevent trade-offs or pollutant (issue) swapping. The reason for this is that environmental policies will affect different sources and sectors, which all contribute to only a part of the nitrogen cycle.

Climate change is, however, of central importance to the N_r budget. At a direct level, enriching the atmosphere in CO₂ can enhance net primary production rates and thus accelerate nitrogen cycling. In addition, when the climate changes, many factors such as temperature, precipitation, run-off, sea level, ocean chemistry and wind may change: these factors can strongly influence nitrogen/nutrient dynamics. For example, nitrification rates in the ocean appear to be reduced by ocean acidification resulting from increased CO₂ dissolution [48]. The consequence of this is not only reduced availability of nitrogen for phytoplankton and other micro-organisms, but also a reduction in N₂O emissions.

(a) Cost–benefit analysis for N_r

Comparing the societal costs of different effects of N_r provides a means of evaluating these different effects on the same scale. Recently cost–benefit analyses of N_r have been attempted for the Chesapeake Bay in the USA [49], for Europe [50] and as a broad overview for the USA [51]. Table 2 shows the ranges of estimated societal costs per N_r component loss and impact, based on the ‘willingness to pay’ method [50]. Based on these costs, the most important component of the N_r cycle is the emission of NO_x, owing to the health impacts of both particulates and ozone. Ammonia is also important, but the health effects are less certain. There is a large uncertainty for the cost of N_r enhancement of surface- and groundwater. Brink *et al.* [50] estimated that the agricultural benefits of N_r in Europe are €25 and €130 billion per year, whereas the total environmental costs based on the numbers in table 2 add up to €13 and €65 billion per year and are appreciable compared with the benefits.

(b) Synthesis and importance of the N_r effects

Figure 2 is a first attempt by expert judgement to describe the major consequences of human induced N_r losses to the environment as synthesized in this paper. This figure shows

two parameters: (i) the exceedance of the effects levels of N_r for ecosystems or human population and (ii) the contribution of N_r to the total effect, relative to other components or causes (e.g. natural) of the problem. For each problem an attempt is made to define the level above which effects are expected and its exceedance. The figure extends from the local scale, through the regional scale, to the global/stratospheric scale and hence represents the cascade of N_r through the environment. Overall the figure provides direct insight in where N_r is an issue and if it needs attention based on the exceedance and relative to the other stresses needing to be addressed. Note that the two parameters are not necessarily related! The following problems are included and explained:

- *Nitrate or nitrite intake by humans.* The figure describes the estimated fraction of the global population with a nitrate or nitrite intake above recommended levels. The intake comes from drinking water with excess nitrate, air pollution inhalation of nitrate particles and nitrate in food. Food and drinking water are by far the major sources for nitrate, and cured meat is the major source for nitrite [22]. We estimate that about 70 per cent of the global population has a higher intake than recommended. The human induced N_r share of the total intake of health-impacting substances through food and drinking water is large at 80 per cent, 20 per cent being of natural origin.
- *Air pollution (human health).* This is expressed as the fraction of the world’s population exposed to levels above health thresholds, such as described by WHO [9,10] (table 1). According to WHO 60 per cent of the global population in urban areas is exposed to PM, NO₂, and other toxic (N) substances (such as nitrosamines) at levels above the thresholds, and a substantial fraction of rural dwellers are exposed to O₃ and PM levels above the thresholds. Nitrogen constitutes a major source of O₃ precursor emissions: 60 per cent of the O₃ increase since 1900 is due to an increase in NO_x, with the remaining owing to an increase in emissions of CO, CH₄ and non-methane VOCs [10]. N_r globally contributes about 20 per cent to the formation of fine particles [13]. All health impact assessments (e.g. by WHO) show that particle pollution dominates total health impacts (approx. 95%).
- *Air pollution (crop loss).* Crop loss owing to air pollution is mainly caused by increased levels of surface O₃ [15,17]. The range of crop losses given in the literature is 6–11% [45]; with a NO_x contribution of 70 per cent, we set this to 4 per cent. We estimate that the N_r (as air pollution) contribution to air pollution-based crop loss, not including other stresses such as water stress, is above 50 per cent.
- *Freshwater pollution.* Fresh water eutrophication is defined as areas where the concentration of nitrate exceeds 1 mg NO₃-N l⁻¹ [20,27,52]. The Millennium Ecosystem

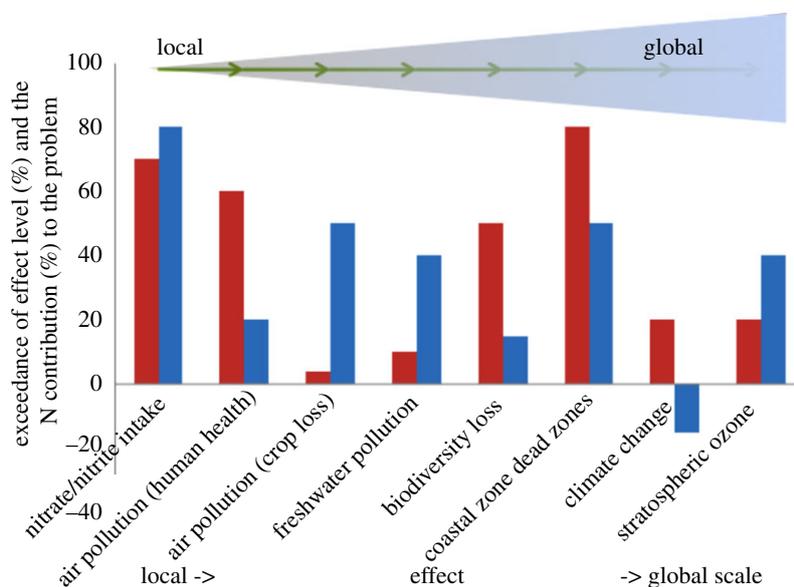


Figure 2. The exceedance (red bar) of the effects levels of N_r for ecosystems or human population, and the contribution of N_r (blue bar) to the total effect, relative to other components or causes (e.g. natural) of the problem. The figure extends from the local scale to the global/stratospheric scale and thus represents the N_r cascade (green arrow). The exceedance and contribution can be summarized as follows. Nitrate or nitrite intake: exceedance, 70% of global population exposed to above-recommended levels of either NO_3^- or NO_2^- in air, water or food; contribution of N_r , 80% (20% of the exposure to above-recommended N_r is due to natural sources). Air pollution (human health): exceedance, 60% of global population exposed to air quality above recommended safe levels; contribution of N_r , 20% of the formation of fine particles is due to human-caused N_r . Air pollution (crop loss): exceedance, 4% of global crop loss owing to air pollution; contribution of N_r , 50% of crop loss is due to human-caused N_r , primarily through tropospheric ozone enrichment. Freshwater pollution: exceedance, 10% of freshwater 'systems' area where NO_3-N exceeds 1 mg l^{-1} ; contribution of N_r , 40% relative to other freshwater pollution and natural causes. Biodiversity loss: exceedance, 50% of the total area of biodiversity hot spots in which N deposition exceeds $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$; contribution of N_r , 15% of global biodiversity loss estimated to be due to N_r . Coastal zone dead zones: exceedance, 80% of large marine ecosystems (64 in total) 'with a N_r problem'; contribution of N_r , 50% of global coastal zone pollution estimated to be due to N_r . Climate change: exceedance, 20% of the pre-industrial N_2O concentration; contribution of N_r , net cooling of 15% due to all N_r impacts on drivers of radiative forcing. Stratospheric ozone: exceedance, 20% of the pre-industrial N_2O concentration; contribution of N_r , 40% of all stratospheric ozone depletion is estimated due to N_r .

Assessment shows that in most of the continents, apart from North and South America, this level is exceeded (60% of freshwater systems). Based on the Global Environmental Outlook (GEO-4, [20]) we estimate that globally about 10 per cent of the freshwater area exceeds the 1 mg l^{-1} limit. The contribution of N_r relative to other freshwater pollution is 40 per cent; most of the other pollution results from industrial leaching of toxic substances and run-off of fertilizers, and faecal and organic pollution where apart from N_r also P and other pollutants are of concern.

- *Biodiversity loss.* Biodiversity loss owing to N_r deposition has been linked to the critical load for N_r , which, for sensitive terrestrial ecosystems, is between approximately 5 and $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ [26]. If we take the global deposition estimates by Dentener *et al.* [53] and the distribution of biodiversity hot spots or eco-regions, the global exceedance of $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ is 50 per cent [43]. Overall, biodiversity loss is primarily caused by land-use change, probably followed by climate change, with N_r deposition estimated to account for about 5–15% of current global biodiversity loss [36,37]. Food production and its associated N_r use drives land-use change, although on the other hand land change is avoided by intensified production through N_r use. These land-use change effects on biodiversity are not taken into account here.
- *Coastal dead zones.* The reported number of coastal dead zones has increased from nine in the 1960s to 460 currently [33]. There are currently 64 Large Marine Ecosystems (LMEs), defined as relatively large areas of ocean space of

approximately $200\,000 \text{ km}^2$ or greater. These LMEs are located in coastal waters adjacent to continents; primary productivity is generally higher than in open ocean areas [54]. The LMEs produce about 80 per cent of the annual world's marine fisheries catch. Globally they are centres of coastal ocean pollution, nutrient over-enrichment, habitat degradation (e.g. sea grasses, corals, mangroves), overfishing, biodiversity loss and climate change effects. According to the National Oceanic and Atmospheric Administration of the United States, most LMEs are subjected to significant eutrophication in coastal waters [54]. There is a N_r problem in about 80 per cent of the LMEs [54]. Compared with other pollution issues of coastal zones, such as phosphorus, the contribution of N_r is estimated to be about 50 per cent.

- *Climate change.* Radiative forcing due to N_r is expressed as the current N_2O concentration level (325 ppb) above the pre-industrial level (approx. 270 ppb; [55]), which is regarded as the 'safe' level because there are currently no thresholds defined [56,57]. The exceedance of the pre-industrial level is 20 per cent. The contribution of all N_r emissions to the total radiative forcing is a net cooling of 15 per cent as determined by Erisman *et al.* [47] and explained in this paper. This assumes that the short-lived cooling effect lasts for a hundred years if no emission reduction measures are taken. Additionally, the long-term N_2O effects will outweigh the other long-term effect, the additional carbon stored per kg N, which is also much more uncertain.

— *Stratospheric ozone depletion*. Contribution of N₂O to stratospheric O₃ depletion can be expressed similarly to the contribution to climate change: 20 per cent exceedance of the pre-industrial concentration. N₂O emission is currently the single most important ozone-depleting agent, and is expected to remain the largest throughout the twenty-first century [58]. The contribution of N_r has increased because of the reduction of the other stratospheric O₃-depleting substances, and it is now the dominating factor (40%).

Figure 2 shows that, for those issues where both the exceedance and the contribution of N_r are high, there is a clear need for focus in N_r policies. This holds especially for nitrate or nitrite intake, air pollution, coastal dead zones and stratospheric ozone. There is a tendency for the N_r contribution to the effect to decrease as the scale increases from local to global, suggesting that local-scale intervention will be especially effective for reducing N_r impacts. At larger scales, N_r abatement also becomes more difficult. Finally, because of the cascade of N_r, focusing on local-scale issues has a clear benefit for the larger scale.

5. Concluding remarks

Much evidence exists for N_r effects on eutrophication of coastal zones, increased concentrations of ozone and PM in the atmosphere, ozone depletion in the stratosphere and biodiversity loss in terrestrial and aquatic ecosystems. Less is known about the relationship with human health (air and water) and climate. Furthermore, although there is strong

evidence for the N_r cascade of effects, better data are needed to quantify the components of the cascade to best support policy options. This review presents as far as possible quantified impacts on the global scale. On smaller scales there are still many uncertainties owing to spatial and temporal variability, and insufficient knowledge.

Current assessments, such as the IPCC AR5, Global Environmental Assessment and regional assessments need better quantitative relationships between nitrogen levels and effects, and we also need to improve our knowledge of the impact of a shortage of nitrogen for many societies. Overall there is large spatial and temporal variability in nitrogen shortages, excesses, fluxes, sources and effects. This is made even more complex through the cascade of nitrogen through the environment and related linked effects. Coupling of the different scales is, therefore, very important, although we still lack effective tools to do so. Although local sources (air emissions or run-off of N_r) contribute primarily to local effects, they also contribute to effects on regional, national, continental and sometimes global scales. Focusing effort on reducing local N_r sources and impacts, therefore, can reap significant benefit at the larger scale.

We greatly acknowledge discussions with the participants of the 7–8 December 2011 Royal Society of London meeting on a Global N policy organized by David Fowler and Mark Sutton, in particular Tim Jickells, David Read, Nick Hewitt, Klaus Butterbach-Bahl, Markus Amann, Liu Xuejun, Sonke Zaehle, Keith Goulding, Fraser Leith and Till Spranger. Figure 2 is largely based on expert judgement by participants of the 7–8 December 2011 Royal Society of the United Kingdom meeting on a global N policy.

References

- Marschner H. 1995 *Mineral nutrition of higher plants*, 889 pp., 2nd edn. London, UK: Academic Press.
- Hatfield JL, Follett RF (eds.) 2008 *Nitrogen in the environment: sources, problems, and management*, 702 pp. Amsterdam, The Netherlands: Elsevier.
- Smil V. 2001 *Enriching the Earth*, 338 pp. Cambridge, USA: The MIT Press.
- Erismann JW, Galloway JA, Sutton MS, Klimont Z, Winiwater W. 2008 How a century of ammonia synthesis changed the world. *Nat. Geosci.* **1**, 636–639. (doi:10.1038/ngeo325)
- Stoumann JL *et al.* 2011 Benefits of nitrogen for food, fibre and industrial production. In *The European nitrogen assessment: sources, effects and policy perspectives* (eds MA Sutton, CM Howard, JW Erismann, G Billen, A Bleeker, P Grennfelt, H van GrinsvenB Grizzetti), pp. 32–62. Cambridge, UK: Cambridge University Press.
- Sutton MA, Oenema O, Erismann JW, Leip A, van Grinsven H, Winiwater W. 2011 Too much of a good thing. *Nature* **472**, 159–161. (doi:10.1038/472159a)
- Galloway JN, Aber JD, Erismann JW, Seitzinger SP, Howarth RW, Cowling EB, Cosby BJ. 2003 The nitrogen cascade. *BioScience* **53**, 341–356. (doi:10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2)
- Galloway JN, Townsend AR, Erismann JW, Bekunda M, Cai Z, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA. 2008 Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. *Science* **320**, 889–892. (doi:10.1126/science.1136674)
- WHO. 2003 Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide. Report on a WHO Working Group; Bonn, Germany, 13–15 January 2003. Copenhagen, Denmark: WHO Regional Office for Europe.
- WHO. 2006 *WHO air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulphur dioxide, global update 2005: summary of risk assessment*. Geneva, Switzerland: World Health Organization.
- Von Mutius E. 2000 The environmental predictors of allergic disease. *J. Allergy Clin. Immunol.* **105**, 9–19. (doi:10.1016/S0091-6749(00)90171-4)
- WHO. 2008 Health risks of ozone from long-range transboundary air pollution. Report of World Health Organisation. Copenhagen, Denmark; WHO Regional Office for Europe.
- WHO. 2011 Global health observatory map gallery. See <http://www.who.int>.
- De Leeuw F, Horálek J. 2009 Assessment of the health impacts of exposure to PM_{2.5} at a European level. ETC/ACC technical paper2009/1. See <http://air-climate.eionet.europa.eu/reports/#tp>.
- Van Dingenen R, Dentener FJ, Raes F, Krol MC, Emberson L, Cofal J. 2009 The global impact of ozone on agricultural crop yields under current and future air quality legislation. *Atmos. Environ.* **43**, 604–618. (doi:10.1016/j.atmosenv.2008.10.033)
- Skarby L, Ottosson S, Karlsson PE, Wallin G, Sellden G, Medin EL, Plejleil H. 2004 Growth of Norway spruce (*Picea abies*) in relation to different ozone exposure indices: a synthesis. *Atmos. Environ.* **38**, 2225–2236. (doi:10.1016/j.atmosenv.2003.10.059)
- Mills G, Harmens H. 2011 *Ozone pollution: a hidden threat to food security*. Edinburgh, UK: CEH, IGBP Vegetation.
- Wink DA, Paolucci N. 2008 Mother was right; eat your vegetables and do not spit! When oral nitrate helps with high blood pressure. *Hypertension* **51**, 1–3. (doi:10.1161/HYPERTENSIONAHA.107.106617)
- European Environment Agency (EEA). 2005 *The European environment: State and outlook 2005*, 576 pp. Copenhagen, Denmark: European Environment Agency.
- United Nations Environment Programme (UNEP). 2007 *Global Environmental Outlook-4 (GEO-4)*. Nairobi, Kenya: UNEP.
- Leach AM, Galloway JN, Bleeker A, Erismann JW, Kohn R, Kitzes J. 2012 A nitrogen footprint model to help consumers understand their role in nitrogen losses to the environment. *Environ. Dev.* **1**, 40–66. (doi:10.1016/j.envdev.2011.12.005)

22. WHO. 2007 Protein and amino acid requirements in human nutrition: report of a joint FAO/WHO/UNU expert consultation. WHO technical report series no. 935. Geneva, Switzerland: WHO.
23. Schuster B, Lee K. 1987 Nitrate and nitrite methods of analysis and levels in vegetables. *J. Food Sci.* **52**, 1632–1641. (doi:10.1111/j.1365-2621.1987.tb05893.x)
24. Van Grinsven HJM, Ward MH, Benjamin N, de Kok TM. 2006 Does the evidence about health risks associated with nitrate ingestion warrant an increase of the nitrate standard for drinking water? *Environ. Health Glob. Access Sci. Sour.* **5**, 26. (doi:10.1186/1476-069X-5-26)
25. Jakszyn P, González CA. 2006 Nitrosamine and related food intake and gastric and oesophageal cancer risk: a systematic review of the epidemiological evidence. *World J. Gastroenterol.* **12**, 4296–4303.
26. Bobbink R *et al.* 2010 Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol. Appl.* **20**, 30–59. (doi:10.1890/08-1140.1)
27. Camargo JA, Alonso A. 2006 Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. *Environ. Int.* **32**, 831–849. (doi:10.1016/j.envint.2006.05.002)
28. Durand P *et al.* 2011 Nitrogen processes in aquatic ecosystems. In *The European nitrogen assessment: sources, effects and policy perspectives* (eds M Sutton, CM Howard, JW Erisman, G Billen, A Bleeker, P Grennfelt, H van Grinsven, B Grizzetti), pp. 126–146. Cambridge, UK: Cambridge University Press.
29. Ormerod SJ, Durance I. 2009 Restoration and recovery from acidification in upland Welsh streams over 25 years. *J. Ecol.* **46**, 164–174. (doi:10.1111/j.1365-2664.2008.01587.x)
30. Oczkowski A, Nixon S. 2008 Increasing nutrient concentrations and the rise and fall of a coastal fishery: a review of data from the Nile Delta, Egypt. *Estuar. Coast. Shelf Sci.* **77**, 309–319. (doi:10.1016/j.ecss.2007.11.028)
31. Rabalais NN, Turner RE, Scavia D. 2002 Beyond science into policy: Gulf of Mexico hypoxia and the Mississippi River. *BioScience* **52**, 129–142. (doi:10.1641/0006-3568(2002)052[0129:BSIPGO]2.0.CO;2)
32. Grizzetti B *et al.* 2011 Nitrogen as a threat to European water quality. In *The European nitrogen assessment: sources, effects and policy perspectives* (eds MA Sutton, CM Howard, JW Erisman, G Billen, A Bleeker, P Grennfelt, H van Grinsven, B Grizzetti), pp. 379–404. Cambridge, UK: Cambridge University Press.
33. Selman M, Sugg Z, Greenhalgh S, Diaz R. 2008 Eutrophication and hypoxia in coastal areas: a global assessment of the state of knowledge. WRI Report (<http://www.wri.org/publication/eutrophication-and-hypoxia-in-coastal-areas>).
34. Rabalais NN. 2002 Nitrogen in aquatic ecosystems. *Ambio* **31**, 102–112.
35. Van Herk CM, Mathijssen-Spiekman EAM, de Zwart D. 2003 Long distance nitrogen air pollution effects on lichens in Europe. *Lichenologist* **35**, 347–359. (doi:10.1016/S0024-2829(03)00036-7)
36. Dise NB *et al.* 2011 Nitrogen as a threat to European terrestrial biodiversity. In *The European nitrogen assessment: sources, effects and policy perspectives* (eds MA Sutton, CM Howard, JW Erisman, G Billen, A Bleeker, P Grennfelt, H van Grinsven, B Grizzetti), pp. 463–494. Cambridge, UK: Cambridge University Press.
37. Sala OE *et al.* 2000 Global biodiversity scenarios for the year 2100. *Science* **287**, 1770–1774. (doi:10.1126/science.287.5459.1770)
38. Treseder LK. 2004 A meta-analysis of mycorrhizal responses to nitrogen, phosphorus, and atmospheric CO₂ in field studies. *New Phytol.* **164**, 347–355. (doi:10.1111/j.1469-8137.2004.01159.x)
39. Payne RJ, Thompson AM, Standen V, Field CD, Caporn SJM. 2012 Impact of simulated nitrogen pollution on heathland microfauna, mesofauna and plants. *Eur. J. Soil Biol.* **49**, 73–79. (doi:10.1016/j.ejsobi.2011.08.003)
40. Bardgett R. 2005 *The biology of soil: a community and ecosystem approach*. Oxford, UK: Oxford University Press.
41. Velthof G, Barot S, Bloem J, Butterbach-Bahl K, DeVries W, Kros J, Lavelle P, Oleson JE, Oenema O. 2011 Nitrogen as a threat to European soil quality. In *The European nitrogen assessment: sources, effects and policy perspectives* (eds M Sutton, CM Howard, JW Erisman, G Billen, A Bleeker, P Grennfelt, H van Grinsven, B Grizzetti), pp. 495–512. Cambridge, UK: Cambridge University Press.
42. Toet S, Ineson P, Peacock S, Ashmore M. 2011 Elevated ozone reduces methane emissions from peatland mesocosms. *Glob. Change Biol.* **17**, 288–296. (doi:10.1111/j.1365-2486.2010.02267.x)
43. Bleeker A, Hicks WK, Dentener F, Galloway J, Erisman JW. 2011 N deposition as a threat to the World's protected areas under the Convention on Biological Diversity. *Environ. Pollut.* **159**, 2280–2288. (doi:10.1016/j.envpol.2010.10.036)
44. Wittig VE, Ainsworth EA, Naidu SL, Karnosky DF, Long SP. 2009 Quantifying the impact of current and future tropospheric ozone on tree biomass, growth, physiology and biochemistry: a quantitative meta-analysis. *Glob. Change Biol.* **15**, 396–424. (doi:10.1111/j.1365-2486.2008.01774.x)
45. Sitch S, Cox PM, Collins WJ, Huntingford C. 2007 Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. *Nature* **448**, 791–794. (doi:10.1038/nature06059)
46. Payne RJ, Stevens CJ, Dise NB, Gowing DJ, Pilkington MG, Phoenix GK, Emmett B, Ashmore M. 2011 Impacts of atmospheric pollution on the plant communities of British acid grasslands. *Environ. Pollut.* **159**, 2602–2608. (doi:10.1016/j.envpol.2011.06.009)
47. Erisman JW, Galloway JN, Seitzinger S, Bleeker A, Butterbach-Bahl K. 2011 Reactive nitrogen in the environment and its effect on climate change. *Curr. Opin. Environ. Sustain.* **3**, 281–290. (doi:10.1016/j.cosust.2011.08.012)
48. Beman JM, Sachdeva R, Fuhrman JA. 2010 Population ecology of nitrifying Archaea and Bacteria in the Southern California Bight. *Environ. Microbiol.* **12**, 1282–1292. (doi:10.1111/j.1462-2920.2010.02172.x)
49. Birch MBL, Gramig BM, Moomaw WR, Doering III OC, Reeling CJ. 2011 Why metrics matter: evaluating policy choices for reactive nitrogen in the Chesapeake Bay Watershed. *Environ. Sci. Technol.* **45**, 168–174. (doi:10.1021/es101472z)
50. Brink C *et al.* 2011 Costs and benefits of nitrogen in the environment. In *The European nitrogen assessment: sources, effects and policy perspectives* (eds MA Sutton, CM Howard, JW Erisman, G Billen, A Bleeker, P Grennfelt, H van Grinsven, B Grizzetti), pp. 513–540. Cambridge, UK: Cambridge University Press.
51. Compton JE, Harrison JA, Dennis RL, Greaver TL, Hill BH, Jordan SJ, Walker H, Campbell HV. 2011 Ecosystem services altered by human changes in the nitrogen cycle: a new perspective for US decision making. *Ecol. Lett.* **14**, 804–815. (doi:10.1111/j.1461-0248.2011.01631.x)
52. Vörösmarty M *et al.* 2005 Fresh water. In *Ecosystems and human well-being. Synthesis. A Report of the Millennium Ecosystem Assessment* (eds WV Reid *et al.*). Washington, DC: Island Press. (<http://www.millenniumassessment.org/documents/document.356.aspx.pdf>)
53. Dentener F *et al.* 2006 Nitrogen and sulphur deposition on regional and global scales: a multimodel evaluation. *Glob. Biogeochem. Cycles* **20**, GB4003. (doi:10.1029/2005GB002672)
54. Sherman K, Aquarone M, Adams S. 2007 Global applications of the Large Marine Ecosystem concept 2007–2010. NOAA Technical Memorandum NMFS-NE-208. Narragansett, RI, USA: National Marine Fisheries Service.
55. IPCC. 2007 *Climate Change 2007: impacts, adaptation and vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (eds ML Parry, OF Canziani, JP Palutikof, PJ van der Linden, CE Hanson), 976 pp. Cambridge, UK: Cambridge University Press.
56. Davidson EA. 2009 The contribution of manure and fertiliser nitrogen to atmospheric nitrous oxide since 1860. *Nat. Geosci.* **2**, 659–662. (doi:10.1038/ngeo608)
57. Syakila A, Kroeze C. 2011 The global nitrous oxide budget revisited. *Greenhouse Gas Meas. Manage.* **1**, 17–26. (doi:10.3763/ghgmm.2010.0007)
58. Ravishankara AR, Daniel JS, Portmann RW. 2009 Nitrous oxide (N₂O): the dominant ozone-depleting substance emitted in the 21st century. *Science* **326**, 123–125. (doi:10.1126/science.1176985)