

# A chronology of human understanding of the nitrogen cycle

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- Q1** Please check the edit made to the affiliations and inserted city name in affiliations 2 and 3.
- Q2** Please check the edit made to the sentence 'Priestley [11], an English scientist. . .' is correct.
- Q3** Please provide expansion for the acronym OSPAR, EPA and TFRN.
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- Q5** Please check the publisher details in ref. [11].
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- Q8** Please provide the editor details for the ref. [25].
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## Review

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<sup>†</sup>We dedicate this paper to Scott Nixon who provided guidance on the coastal ecosystems material but who died before he could see the fruits of his labour. Scott was a giant in biogeochemistry and was an amazing mentor to many. We are grateful for his life and contributions; we miss him.

# A chronology of human understanding of the nitrogen cycle<sup>†</sup>

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Q1

Nitrogen over the ages! It was discovered in the eighteenth century. The following century, its importance in agriculture was documented and the basic components of its cycle were elucidated. In the twentieth century, a process to provide an inexhaustible supply of reactive N (Nr; all N species except N<sub>2</sub>) for agricultural, industrial and military uses was invented. This discovery and the extensive burning of fossil fuels meant that by the beginning of the twenty-first century, anthropogenic sources of newly created Nr were two to three times that of natural terrestrial sources. This caused a fundamental change in the nitrogen cycle; for the first time, there was the potential for enough food to sustain growing populations and changing dietary patterns. However, most Nr created by humans is lost to the environment, resulting in a cascade of negative earth systems impacts—including enhanced acid rain, smog, eutrophication, greenhouse effect and stratospheric ozone depletion, with associated impacts on human and ecosystem health. The impacts continue and will be magnified, as Nr is lost to the environment at an even greater rate. Thus, the challenge for the current century is how to optimize the uses of N while minimizing the negative impacts.

## 1. Introduction

The chronology of human understanding of nitrogen is a story of curiosity, common sense, scientific advancement, and societal concern. Curiosity was the driver to generate specific questions about the world we live in that led to the accumulation of basic information about nitrogen (its species and their reactions and role in life on Earth). Common sense was the underpinning of early agricultural practices—people knew that if certain practices were followed, crops grew better. Scientific advancement provided rigor that led to the identification of nitrogen compounds, their reactions, their biological relevance, the development of the nitrogen cycle and an understanding of why specific agricultural practices worked. Societal concern grew out of the myriad of negative effects on humans and ecosystems associated with excess reactive nitrogen (Nr) in the environment.

To better understand the time course of discovery, this paper begins with the early history of nitrogen and then progresses through time, documenting societies' advances in knowledge. The paper discusses the fundamental advances in the discovery of chemicals, biological processes and plant nutrition. It then discusses the development of understanding of biogeochemical cycles and negative impacts on the environment and people. The paper concludes with a brief review of the historical development of regulations controlling nitrogen in the environment.

The paper identifies key discoveries with dates and people. Given the extensive work on nitrogen over the last 300 years, not all events can be discussed. Rather we have selected a few key discoveries (figure 1) from a larger array of studies (table 1) compiled from the extensive literature. Each study has an associated reference for the reader to further pursue the topic.

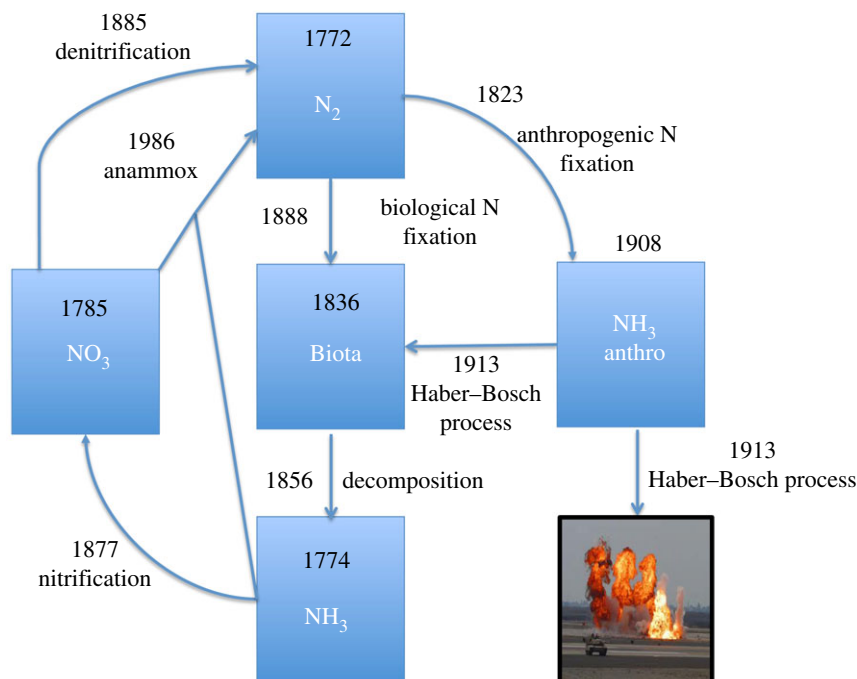


Figure 1.

## 2. Discovery: nitrogen, its species and their reactions

Food sources for humans were initially obtained by hunting and gathering. About 10 000 years ago, domestication of plants and animals began, most likely in the Fertile Crescent of Western Asia, Egypt, India and other areas [1,2]. Domestication required water. And even though there was no underpinning knowledge, it was appreciated that the use of manure and cultivation of legumes in rotation gave higher crop yields [41]. Of course, manure was first used when crop and animal domestication occurred on the same piece of land. Archaeological evidence suggests legume cultivation began over sixty-five centuries ago [2].

Two thousand years ago, the population of the world was approximately 0.2 billion people. It is now 7 billion. About 2000 years ago, human  $N_r$  creation is estimated to be approximately  $3 \text{ Tg N yr}^{-1}$  by legume cultivation. It is now approximately  $210 \text{ Tg N yr}^{-1}$  from many anthropogenic sources (legume cultivation, fossil fuel combustion, Haber–Bosch process).

The scientific connection between fertilizers and food production was first made in the mid-sixteenth century (1563) when a French craftsman, Bernard Palissy, recognized that plants use what is in the soil and that the soil, therefore, must be replenished with manure and other excreta to promote plant growth [3]. Although Palissy referred to minerals and nutrients in soil as ‘salts’, he understood that plants require some form of substance from the soil. This early acknowledgement of the needs of plants and how they use nutrients in soil has led to centuries of research into and development of fertilizers.

During the seventeenth century, little progress was made in advancing our fundamental understanding of nitrogen and its cycle, mainly because scientists such as Jean-Baptiste van Helmont and Lord Bacon concluded from their experiments that water was the only source plants needed to grow [42]. A significant finding occurred in 1675 when John Evelyn made the first notation that rainwater was not

pure but contained a beneficial material, which he termed ‘celestial nitre’ [4]. Woodward [5] proved through experimentation that there were critical compounds in Thames River other than water.

Rapid advances in our N-knowledge truly began during the eighteenth century when large strides were made by the discovery of nitrogen and the identification of its chemical forms. Nitrogen was officially discovered in 1772 by Scottish scientist Daniel Rutherford [6]. At the same time however, Carl Scheele, Henry Cavendish, Joseph Priestley and others were investigating ‘burnt or dephlogisticated air’, as air without oxygen was then called. Nitrogen makes up 78 per cent of the air’s volume and is inert. Because of this inertia, Antoine Laurent Lavoisier called it *azote*, meaning ‘no-life’. The term ‘noxious air’ came from experiments carried out by Rutherford and Priestley using mice. Mice were kept in a closed glass container and died once all the oxygen had gone. The  $\text{CO}_2$  breathed out by the mice was removed using burning potassium. The air that remained, in which nothing lived or burned, was called ‘noxious air’ and made up principally of  $\text{N}_2$  [20]. Despite these concurrent efforts, Rutherford earned the official credit for the discovery of nitrogen because he was the first to publish his results. The name ‘nitrogen’ was not actually coined until 1790 by French chemist Jean Antoine Claude Chaptal [7]. He originally named it ‘*nitrogène*’, a reference to nitre (potassium nitrate), which was known to contain nitrogen.

The identification of specific N compounds also began in the eighteenth century. Priestley [11], an English scientist and clergyman, in his book *Experiments and observations on different kinds of air* describes how he demonstrated the presence of nitrous oxide, hydrochloric acid and ammonia gases in air. The experiments he carried out in order to do this ultimately led him to discover ammonia on 1 August 1774. In 1784, C. L. Berthollet discovered that ammonia was made up of the elements nitrogen and hydrogen. Austin [8] was then one of the first to try to synthesize ammonia, which he called ‘volatile alkali’, from these elements. He studied

**Table 1.** Major events in the history of nitrogen.

year	event	refs
10 000–8000 BC	domestication of plants and animals began	[1,2]
1563	Bernard Palissy advocated for the use of fertilizers	[3]
1675	John Evelyn noted that rainwater contained ‘celestial nitre’	[4]
1699	John Woodward proved that what is dissolved in water is essential for plant growth	[5]
1772	Daniel Rutherford discovered nitrogen; he receives credit because he published first	[6]
1772	Carl Scheele, Henry Cavendish, Joseph Priestley, and others concurrently and independently discovered nitrogen	[7]
1774	Joseph Priestley discovered nitrous oxide and ammonia	[8]
1785	C. L. Berthollet determined that ammonia is made up of nitrogen and hydrogen	[9]
1785	Henry Cavendish discovered $\text{HNO}_3$	[10]
1787	William Austin was one of the first to try to synthesize ammonia	[11]
1790	Jean Antoine Claude Chaptal officially named nitrogen	[7]
1823	Johann Wolfgang Döbereiner produced ammonia using a platinum catalyst	[12]
1824	Joseph Fourier was one of the first to describe the greenhouse effect	[13]
1836	Jean-Baptiste Boussingault identified nitrogen as a nutrient for plants	[7]
1838	Jean-Baptiste Boussingault determined legumes could fix their own nitrogen, but he did not know how	[7]
1840	Justus von Liebig advocated the addition of certain nutrients to the soil for plant growth, making him the founder of the artificial fertilizer industry	[14]
1843	John Bennet Lawes and Joseph Henry Gilbert confirmed that nitrogen helps plants grow and that nitrogen comes from sources other than precipitation	[7]
1845	M. Ducros determined that hail contained nitric acid, and called it ‘pluie acide’ or acid rain	[15]
1852	Robert Angus Smith connected the presence of acid rain with human activities	[16]
1856	Jules Reiset recognized that decaying matter releases nitrogen, providing the basis for the nitrogen cycle	[17]
1877	Theophile Schloesing and Achille Müntz discover the process of nitrification	[18,19]
1880	Herman Hellriegel and Hermann Wilfarth discovered the process of biological nitrogen fixation	[20]
1886	Ulysse Gayon and Gabriel Dupetit discovered the process of denitrification	[17,18]
1896	the greenhouse effect was more fully quantified by Svante Arrhenius	[21]
1909	Fritz Haber synthesized ammonia from nitrogen and hydrogen gas	[7,22,23]
1913	Carl Bosch performed Haber’s ammonia synthesis on an industrial scale	[7]
1947	it was reported that many lakes in the US and Europe were undergoing eutrophication	[24]
1950s	through the mid-1950s, N additions to coastal ecosystems were incorrectly considered a benefit to productivity	[25]
1950s	concern about coastal eutrophication was first noted in Moriches Bay, New York	[26,27]
1953	Haagen-Smit <i>et al.</i> were one of the first to document ground-level ozone formation and the role of $\text{NO}_x$ in its formation	[28]
1960s	there existed 9 reported ‘dead zones’ in coastal areas	[29]
1968	Svante Oden was the first to link $\text{NO}_x$ emissions from one country (the UK) to freshwater acidification in another country (Sweden)	[30]
1970s	on a global scale, the rate of N <sub>r</sub> creation by the Haber–Bosch process surpassed natural N fixation	[31]
1970	Paul Crutzen quantified the role of nitrogen oxides in ozone depletion	[32]
1972	Sweden made a presentation to the UN Conference on the Human Environment, which started efforts to better understand acidification	[30]
1972	Likens <i>et al.</i> demonstrated that nitric acid formed from fossil fuel combustion leads to acid rain	[15,33]
1985	the greenhouse effect was further quantified by Ramanathan <i>et al.</i> , including the contributions of $\text{N}_2\text{O}$	[34,35]
1985	Stratospheric ozone depletion was discovered by scientists from the British Antarctic Survey	[36]
1986	Anammox (anaerobic ammonium oxidation) was first observed in a Dutch wastewater treatment facility	[37]

(Continued.)

Table 1. (Continued.)

year	event	refs
1989	John Aber <i>et al.</i> demonstrated that excess N deposition to forests not only causes damage to the forest, but it can also make forests a net source of N	[38]
2003	the concept of the nitrogen cascade was proposed.	[31]
2009	Ravishankara <i>et al.</i> discovered that N <sub>2</sub> O emissions are currently the most important ozone-depleting substance.	[39]
2011	there are 540 reported dead zones on a global basis.	[29]
2011	The European Nitrogen Assessment provides the first integrated and comprehensive look at N use in Europe	[40]

the discoveries of Berthollet and Priestley and came to the conclusion that, if ammonia is decomposed by spark, it must also be possible to form it from its original elements. Priestley describes 'nitrous air' (nitric oxide, NO) and developed a 'nitrous air test' to determine the 'goodness of air'. Using a pneumatic trough, he would mix nitrous air with a test sample, over water or mercury, and measure the decrease in volume—the principle of eudiometry. Henry Cavendish produced HNO<sub>3</sub> in 1785 by passing sparks through a jar of air confined over water. Between 1772 and 1780, Joseph Priestley isolated 10 different gases, among those were nitric oxide, nitrogen dioxide and nitrous oxide. He also invented the apparatus to create his experiments, and wrote and published to disseminate his findings.

If the eighteenth century was known for the discovery of N and its species, the nineteenth century was noted for the discovery of how nitrogen was transformed from one species to another. Most notably, and with a hint of what was to come about 80 years later, in 1823, Johann Wolfgang Döbereiner was one of the first to produce ammonia from the elements hydrogen and nitrogen using platinum as the catalyst [12]. This was a notable achievement for a number of reasons, not the least of which was that it demonstrated that NH<sub>3</sub> could be synthesized from its elements by human action. However, the process was inefficient and could not be reproduced on a large scale.

In 1836, over sixty centuries after it was noted that manure and legumes were beneficial to crop production, French chemist Jean-Baptiste Boussingault also identified nitrogen as an important substance for plants, recognizing that the effectiveness of a fertilizer depends on and is proportional to its nitrogen content [7]. The revolutionary work of von Liebig [14] entitled '*Die organische Chemie in ihre Anwendung auf Agrikultur und Physiologie*' (Organic Chemistry in its Application to Agriculture and Physiology) heavily criticized the old concepts of plant nutrition, such as the humus theory, and developed modern ideas. Von Liebig believed that plants only need a limited number of nutrients to grow. These nutrients are present in the soil and, having been used up following intensive cultivation, need to be added to the soil again in order to guarantee the next crop. He was, therefore, the founder of the artificial fertilizer industry. However, confusion about where the necessary nitrogen came from remained. Liebig's incorrect belief that all nitrogen assimilated by plants came from precipitation inspired further research, including a long-running crop experiment started by John Bennet Lawes and Joseph Henry Gilbert in 1843 at

Rothamsted, UK. In these experiments, plots of wheat received varying treatments; they learned that crops with added nitrogen (applied as ammonium sulfate) achieved substantially larger yields [7]. This finding confirmed the belief that nitrogen helps plants grow, and it also proved that nitrogen comes from sources other than precipitation.

About three decades after it was discovered that living plants needed nitrogen, Jules Reiset recognized in 1856 that decaying organic matter releases nitrogen [17]. This discovery ultimately provided the basis for the nitrogen cycle because it was the first evidence of nitrogen cycling in the biological sphere.

The next advances were with respect to the role that microbes play in converting N from one species to another. In short order, the processes of nitrification, biological nitrogen fixation (BNF) and denitrification were discovered. The process of nitrification was discovered in 1877 by Theophile Schloesing and Achille Müntz through their experiments with sewage water filtered through a mixture of sand and limestone [18,19]. In 1886, Ulysse Gayon and Gabriel Dupetit officially discovered the process of denitrification after isolating two strains of denitrifiers [17,18].

The remaining process left to be discovered was arguably the most important—BNF. In the mid-nineteenth century, scientists wondered how legumes could grow and thrive without nitrogen additions. In 1838, Boussingault conducted a series of experiments in which he grew legumes in sterilized sand, which did not have any nitrogen [7]. When the legumes continued to grow, the only conclusion he could reach was that they are capable of fixing their own nitrogen, but he did not yet know how. In 1880, Hermann Hellriegel and Hermann Wilfarth answered this question through their discovery of BNF, the process by which microbes can convert unreactive diatomic nitrogen into a usable reactive form [20]. They had carried out experiments testing the response of legumes and cereals to additions of different mediums and to different treatments. They determined that the only explanation for their results was that microbes can fix nitrogen and that the nodules on the roots of legumes contain these nitrogen-fixing microbes.

So by the end of the nineteenth century, the basic building blocks of the N cycle had been discovered—the species, their reactions and how the reactions connected into a cycle that converted N<sub>2</sub> to reactive N forms, and then reconverted back to N<sub>2</sub>. Or so it was thought. One century later, a new microbially mediated process was discovered. Anaerobic ammonium oxidation (anammox) was hypothesized by the

Austrian theoretical chemist Engelbert Broda in 1977; about 10 years later in 1986 it was observed to account for the disappearance of  $\text{NH}_4^+$  and the formation of  $\text{N}_2$  in a Dutch wastewater treatment facility [37]. Anammox organisms have the ability to combine ammonium and nitrite or nitrate to form  $\text{N}_2$ . This discovery led to the realization that a substantial part of the enormous nitrogen losses that are observed in the marine environment—up to 50 per cent of the total nitrogen turnover—were due to the activity of these bacteria [37].

### 3. Focus on food

During the late nineteenth century, farmers used many natural sources of nitrogen fertilizers, including legumes for BNF, livestock manure, guano and mineral nitrate deposits. However, in 1898, British chemist Sir William Crookes recognized that the world was running out of nitrogen, and he stated that chemists must determine how to feed the growing population [7]. Around the same time, German scientist Wilhelm Ostwald realized that Germany could be destroyed in a military conflict if its nitrate imports were cut off, which were necessary for both fertilizer and munitions. He concluded that to remain a strong military power, Germany must determine how to synthetically fix nitrogen to form ammonia for chemical warfare [22].

The earliest attempt to synthesize ammonia from hydrogen and nitrogen at high temperatures occurred in 1787 [7]. Many attempts followed over the years but none could be scaled up nor could be made cost-effective on a large scale.

It was not until 1909 that German scientist Fritz Haber found the right process and conditions that made it feasible to be eventually scaled up to an industrial level. Haber's eventual success culminated in the submission of three patents: the first in October 1908 describing the circulation process, the second in March 1909 naming osmium as a successful catalyst and the third in September 1909 describing the high-pressure situation required for the process [7].

Despite his success, Haber's experimental laboratory could not produce ammonia on a large scale. Carl Bosch, a German chemist and engineer, was tasked with the challenge of extending Haber's laboratory system up to an industrial scale. He knew that he had three primary obstacles: finding nitrogen and hydrogen gas at low costs, identifying effective and stable catalysts and designing converters and equipment (vessels) that could handle the high-pressure system. After experiments at a prototype plant, Bosch oversaw the construction of the first real ammonia plant in 1913, and it was producing more than 10 tons of ammonia each day.

The combined discoveries of Haber and Bosch led to what is now known as the Haber–Bosch process. This process has allowed for the mass production of synthetic fertilizer, which now feeds about 50 per cent of the world's population [23]. Although the Haber–Bosch process has allowed billions of people to live, a major motivator for its discovery in Germany was for the development of munitions. The Haber–Bosch process was not widely used for fertilizer production in the decades after its development. It was not until the 1950s that the production of synthetic fertilizers for food production began rising rapidly. By the 1970s, on a global scale, creation of  $\text{NH}_3$  from  $\text{N}_2$  by the Haber–Bosch process became more important than terrestrial BNF in unmanaged ecosystems—i.e. humans became 'better' than nature at introducing  $\text{Nr}$  to the environment.

### 4. Evolution of nitrogen budgets

Given the critical role that N plays in food production, it is not surprising that the first nitrogen budgets were for agricultural systems. A few years after Jean-Baptiste Boussingault identified nitrogen as a nutrient for plants, he became the first to use an N balance sheet for field plots on his farm in France [43]. Other soil N budgets followed, most notably those of John B. Lawes and Joseph H. Gilbert in the UK with their work at Rothamsted [44]. Then as a better understanding of how to manage N in agricultural systems developed, numerous other studies added to fundamental understanding. This progress in knowledge-attainment has been documented by several reviews of the historical development of soil nitrogen budgets—Allison [45,46], and most recently Meisinger *et al.* [44] and Groffman [47].

N budgets at global scales did not appear until the mid-twentieth century. The earliest focused on specific reservoirs (e.g. atmospheric; Eriksson [48]) and specific N species (e.g.  $\text{N}_2\text{O}$ ; McElroy *et al.* [49]). Multi-reservoir budgets appeared in the 1970s (e.g. Delwiche, 1970 [50]; Soderlund & Svensson [50,51]) and with time, they became more complete with respect to the fluxes considered ([52–54]; table 2). The work of Soderlund & Svensson [51] was arguably the beginning of the complete assessment of N budgets on the global scale. They differentiated between the land and the oceans, and they developed detailed sub-budgets for individual N species.

It is worth comparing how fluxes changed over this period of development to track how our collective understanding has matured with time the mid-1950s to the mid-1990s and beyond (table 2). For some fluxes, our understanding has been relatively complete and differences over this time period have either been minimal or understood, for example,  $\text{NH}_3$  created from the Haber–Bosch process was zero in 1900, and is now about  $120 \text{ Tg N yr}^{-1}$ . The change with time is simply owing to increased creation from  $\text{N}_2$  and  $\text{H}_2$ . For other fluxes, our knowledge is poor (e.g. organic N cycling in the atmosphere). A recent analysis suggests that the flux of organic nitrogen is about 25 per cent of the total nitrogen deposition flux [57]. And in some cases, there has been a tremendous temporal variability owing to an incomplete understanding of the key controls on the fluxes. For example, estimates of terrestrial BNF have varied, in a non-linear fashion, from approximately  $100$  to  $210 \text{ Tg N yr}^{-1}$  over the period mid-1950s to mid-1990s. The most recent estimate,  $58 \text{ Tg N yr}^{-1}$ , is significantly lower, although its range ( $50$ – $100 \text{ Tg N yr}^{-1}$ ) overlaps the range of the earlier studies [58]. Similarly, estimates of terrestrial denitrification have varied from  $43$  to  $290 \text{ Tg N yr}^{-1}$  over the same period (table 2). Given that these are two of the most important N fluxes to understand (the former tells how much  $\text{Nr}$  is created from  $\text{N}_2$ ; the latter how much is converted back to  $\text{N}_2$ ), it is easy to understand why in some cases our ignorance of the N cycle is especially profound.

### 5. Discovery: human impact on the nitrogen cycle and resulting impacts

As noted in the introduction, one of the historical aspects of understanding the human alteration of the N cycle was the growing awareness of the negative impacts of excess N on people and ecosystems. This section briefly reviews the time

Table 2. Compilation of global nitrogen budgets.

	Eriksson [48]	Robinson & Robbins [55]	Delwiche [50]	Burns & Hardy [56]	Soderlund & Svensson [51]	McElroy et al. [49]	Galloway et al. [52]	Galloway et al. [53]	Fowler et al. [54]
<i>Nr creation</i>									
lightning	—	—	7.6	—	—	10	3	5.4	5
fossil fuel combustion	15	19	—	—	19	—	21	24	30
<i>BNF</i>									
terrestrial	104	118							
natural	—	—	30	50	50	170	90–130	98	58
cultivation	—	—	14	89	89	40	43	32	60
marine	—	12	10	—	30–130	10	40–200	121	140
Haber–Bosch	15	20	30	30	36	40	78	100	120
<i>Nr losses to atmosphere</i>									
NH <sub>3</sub> emissions	99	957	—	165	133–244	150	64	58	69 <sup>a</sup>
NO <sub>x</sub> emissions	15	234	—	20	21–89	—	36	41	20
N <sub>2</sub> O emissions	—	353	—	—	36–150	50	11	15	18 <sup>a</sup>
<i>Nr losses to coastal systems</i>									
(DIN + Norg, unless as noted)	21 (DIN)	13	—	—	13–24	20	42	48	80
<i>storage</i>									
terrestrial	—	—	—	—	—	—	—	60	75
marine sediments	—	—	0.2	—	—	—	—	16	22
<i>denitrification</i>									
terrestrial	65	—	43	—	91	243	130–290	115	109
marine	87	—	49	—	5–99	106	150–180	270	100–280

Q12Terrestrial and marine emissions.

course of understanding of these impacts. Erisman *et al.* [59] provides more extensive information about each impact.

Anthropogenic activities have dramatically increased the amount of Nr present in the environment [54,60]. The most dominant is agriculture, which creates new Nr through cultivation-induced BNF when legumes are planted and also uses  $\text{NH}_3$  produced by the Haber–Bosch process. The burning of fossil fuels for energy production has also increased the amount of Nr in the environment, as  $\text{NO}_x$  is formed as a by-product during combustion. Of equal magnitude globally with respect to Nr creation by fossil fuel combustion,  $\text{NH}_3$  produced by the Haber–Bosch process is used as a feedstock for a variety of industrial products (e.g. nylon, explosives). Through these activities, humans are now dominating the introduction of Nr to the terrestrial environment. This significant imbalance has led to a number of environmental and human health impacts, which have been discovered and regulated throughout the twentieth century.

The most beneficial impact of the human alteration of the N cycle is that it supports food production for approximately 50 per cent of the world's population [23,60]. The negative impacts are numerous and are magnified with time as Nr moves along its biogeochemical pathway. The same atom of Nr can cause multiple effects in the atmosphere, in terrestrial ecosystems, in freshwater and marine systems, and on human health. This sequence of effects is referred to as the nitrogen cascade. As the cascade progresses, the origin of Nr becomes unimportant. The only way to eliminate Nr accumulation and stop the cascade is to stop producing Nr or convert Nr back to the nonreactive  $\text{N}_2$  form [31]. For this current paper, we examine the historical development of understanding nitrogen's role in acid rain, smog, eutrophication of coastal waters, greenhouse effect, stratospheric ozone depletion and human consumption of nitrate/nitrite.

### (a) Acid rain and nitrogen deposition

The first attribution of human impacts on the acidity of precipitation was in 1852 by Robert Angus Smith. As he noted in his 600-page book, *As a rule rain is not acid far from towns. If it is acid, artificial circumstances must be suspected* [16].

Although sulfuric acid is the primary cause for acid rain, nitric acid is also important. Likens *et al.* [33] demonstrated that  $\text{NO}_x$  formed during fossil fuel combustion leads to nitric acid in precipitation. Galloway & Likens [61] illustrated that the contributions of nitric acid to acid rain were steadily rising due to increased fossil fuel combustion. Currently the proportion of acidity contributed by nitric acid is increasing relative to sulfuric acid, owing to controls on sulfur dioxide.

When deposited to the land surface, Nr in the form of ammonia/ammonium contributes to soil acidification and forest dieback [62]. Additionally, when excess nitrogen upsets the nutrient balance in an ecosystem, it also can cause biodiversity loss owing to competition between nitrogen-philic and nitrogen-phobic species [63]. Aber *et al.* [38] established that excess nitrogen deposition in forest ecosystems not only causes damage to the forest itself (forest decline, reduced productivity), but also could cause forests to be a net source of nitrogen. After reaching nitrogen saturation levels, forests could become net sources nitrates to waterways. Once in waterways, Nr can contribute to lake acidification, algal blooms, eutrophication, climate change

and stratospheric ozone depletion either in the waterway or further down the nitrogen cascade.

### (b) Smog

Haagen-Smit *et al.* [28] were the first to document ozone formation owing to photochemical oxidation of volatile organic compounds in the atmosphere and the role that  $\text{NO}_x$  played in its formation. Over the past 60 years since that discovery, the issue of tropospheric ozone has expanded from an urban to a rural and indeed a hemispheric issue. In addition, biomass burning releases  $\text{NO}_x$  that contributes to increased tropospheric ozone [64].

### (c) Coastal eutrophication

Up to the mid-twentieth century, the injection of Nr to coastal ecosystems was considered to be a potential benefit to fisheries because it could make estuaries more productive [25]. In the same vein, Wulff [65] noted that the concept of eutrophication was relatively unheard of until 'about 20 years ago'. As cited in Nixon [26], concern about coastal eutrophication was first noted in the 1950s with respect to the impact of algal blooms on shellfish populations in Moriches Bay, NY [27].

Since that time, the extent of over-enrichment of coastal zones has grown. In the mid-1960s, there were nine reported 'dead zones' in coastal areas. The number is now 540 and growing [29]. But even today, there are coastal systems and fisheries that benefit from nutrient enrichment (e.g. Nile River [66]), and it is important to view nutrients as a potentially valuable resource for coastal systems, which needs to be well managed as any other resource [67].

### (d) Greenhouse effect and climate

One of the first mentions of the greenhouse effect was by Joseph Fourier in 1824. The concept was more fully quantified by Tyndall [68] and by Arrhenius [21]. The potential contribution of  $\text{N}_2\text{O}$  and  $\text{O}_3$  to the enhanced greenhouse effect (together with  $\text{CH}_4$  and CFCs) is estimated to be as much as 40 per cent by Ramanathan [34]. This was further quantified by Ramanathan *et al.* [35]. More recently, indirect contributions of N to the greenhouse effect and to climate change has gathered more attention, especially through the fertilization effects of Nr that lead to additional  $\text{CO}_2$  uptake from the atmosphere [69]. Nr has both substantial warming and cooling effects on climate. The net effect on climate is probably cooling, but highly uncertain. The cooling aspects of N mainly represent short-term effects, whereas the warming effect from  $\text{N}_2\text{O}$  is long term [70,71].

### (e) Stratospheric ozone depletion

The role of nitrogen oxides in ozone depletion was quantified by Crutzen [32] and Johnston [72]. In 1985, scientists from the British Antarctic Survey discovered the phenomenon of stratospheric ozone depletion [36]. Most recently Ravishankara *et al.* [39] discovered that  $\text{N}_2\text{O}$  emissions currently are the single most important ozone-depleting emission and are expected to remain the largest throughout the twenty-first century. They also note that the Montreal Protocol does not cover  $\text{N}_2\text{O}$ , although a recent paper makes a strong case for its inclusion [73].

In summary, the first potential environmental consequence of excess N in the environment was acid rain

(1860s). This discovery was followed by NO<sub>x</sub>-induced ozone contributing to smog (1950s), the fresh and coastal water quality aspects (1970s), and N<sub>2</sub>O-induced impacts on stratospheric ozone (1980s). Then in the early 2000s, it was proposed that all of the effects were linked by the nitrogen cascade, which is essentially driven by the fact that once N<sub>2</sub> is converted to Nr, that nitrogen will continue to be active in the environment with the potential to contribute to all effects in sequence until it is converted back to N<sub>2</sub> [31].

## 6. Regulating nitrogen in the environment

In the mid-1900s, governments in the United States and Europe began to pass legislation recognizing and attempting to limit the detrimental impacts of nitrogen to water quality, air quality and human health.

### (a) United States

One of the first pieces of legislation passed to protect the environment was the Federal Water Pollution Control Act in the United States, which was established in 1948 to reduce water pollution and to improve the sanitation of waterways [74]. This act was extensively revised in 1972 to form what became known as the Clean Water Act (CWA) in 1977; it has since been expanded with many amendments. Under the CWA, water quality standards have been set for water contaminants, and wastewater standards have been set for industry. Nitrogen pollution has been managed through these laws as it is a major component of municipal wastewater, stormwater and agricultural run-off. In 1998, the Harmful Algal Bloom and Hypoxia Research and Control Act provided funding for the research of hypoxia, of which nitrogen is a major cause [75].

The Safe Drinking Water Act, which was established in 1974, set drinking water quality standards [76]. Excess nitrate and nitrite in drinking water can cause methaemoglobinemia (blue baby syndrome), which can be fatal for infants. Under the Safe Drinking Water Act, the US EPA established Maximum Contaminant Levels of 10 mg N L<sup>-1</sup> for nitrates and 1 mg N L<sup>-1</sup> for nitrites in drinking water.

The Air Pollution Control Act was passed in the US in 1955 to provide funds for air pollution research [77]. In 1963, the Clean Air Act (CAA) was passed to set standards for air pollution. After many updates and amendments, the CAA now includes National Ambient Air Quality Standards (NAAQS), New Source Performance Standards for new and modified stationary sources, Acid Deposition Control, and more. Nitrogen oxides are one of the six common air pollutants regulated through NAAQS. Other efforts to improve air quality have focused on improving vehicle fuel economy, which not only conserves fuel but also reduces emissions. For example, the EPA Corporate Average Fuel Economy standards of 1975 set fuel economy standards, and the EPA Gas Guzzler Tax of 1978 taxes manufacturers for the fuel-inefficient vehicles they produce.

### (b) Europe

The United Nations Conference on the Human Environment in Stockholm in 1972 is generally seen as having been a key step for increased political awareness in Europe about environmental problems created in part by N [78] and

subsequently for the establishment of environmental policies by governments. The 1972 Conference ultimately led to the establishment, in 1979, of the UNECE Convention on Long-range Trans-boundary Air Pollution (CLRTAP) [79], which has been ratified by most countries in Europe.

International treaties and conferences also played major roles in the establishment of water-related environmental policies [80], started by the Soil Protection Act initiated to reduce over-fertilization in 1971 in the Netherlands [20].

The first Convention on the Protection of the Marine Environment of the Baltic Sea was signed in Helsinki in 1974 [81]. In 1992, a new convention was signed, aimed at protecting the Baltic Sea from all sources of pollution derived from land, shipping and atmospheric deposition [81]. The OSPAR Convention on the Protection of the Marine Environment of the North-East Atlantic was also signed in 1992 [82]. One of the recommendations was the 'substantial reduction (about 50%) of inputs of N and P into marine areas of the North-East Atlantic where these inputs are likely, directly or indirectly, to cause pollution', between 1985 and 1995, using N (and P) balances as monitoring tools.

In 1991, the European Union Urban Waste Water Directive was issued to protect the environment from pollution, including storm water run-off and municipal waste water [83]. This directive set specific standards for urban waste water discharges for nitrogen. The European Commission also adopted the Nitrates Directive in 1991, whose goal was specifically to improve water quality by limiting nitrate pollution from agricultural sources [84]. In 1999, the Gothenburg Protocol set emission ceilings for NO<sub>x</sub> and NH<sub>3</sub> in Ireland, Italy, the Netherlands, Spain, Sweden and Portugal [85].

One of the major achievements on moving towards nitrogen policies was the recent initiation of the Taskforce on Reactive Nitrogen under the aforementioned CLRTAP. The TFRN will be the policy framework for dealing with the nitrogen cascade in Europe. It is the first official body that will engage with other policy areas related to nitrogen. The TFRN will develop technical and scientific information and options, which can be used for strategy development across the UNECE, catalyzing a more integrated approach of mitigating nitrogen.

Much progress has been made developing integrated assessments of the human impacts on the N cycle and how to reverse them. The *European Nitrogen Assessment* provides an integrated and comprehensive look at the use of nitrogen in Europe and its impacts on the environment [40]. Another example of an integrated assessment of nitrogen use is the 2011 EPA Science Advisory Board report on Nr in the United States [86]. This report assesses the current situation and provides specific management strategies through which the US can reduce its impact on the environment through nitrogen. In addition to these top-down assessments, tools such as the Nitrogen Footprint Calculator [87] have become available to enable broader public education on nitrogen-related issues and what the consumer can do to lessen the loss of Nr to the environment.

## 7. Conclusion

The chronology of human understanding of the nitrogen cycle is a story of curiosity, common sense, scientific advancement and societal concern that spans 300+ years. In that time

**Table 3.** Advances in understanding, by half-century, on nitrogen, its reactions and its impacts.

species	reactions	impacts
1700–1750		
1750–1800	N named; N <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , N <sub>2</sub> O discovered	NH <sub>3</sub> produced;
1800–1850		N is nutrient, discovered; acid rain discovered; Greenhouse effect described
1850–1900	discovered: —nitrification, —denitrification, —biological fixation —decomposition releases N	acid rain described as caused by humans
1900–1950	Haber–Bosch process invented	smog defined and described
1950–2000	anammox process discovered	coastal N impacts realized; ground-level O <sub>3</sub> chemistry determined stratospheric O <sub>3</sub> hole discovered; N management actions accelerate
2000–present		INI formed; N-cascade described; European Nitrogen Assessment completed.

period, nitrogen science has advanced markedly in 50-year time steps in the identification of N, and its compounds, reactions and impacts (table 3). By definition, the historical part of the story ends now, and curiosity, common sense, scientific advancement and societal concern will continue to drive future advances in the interaction between humans and the nitrogen cycle as we try to reap nitrogen's benefits, while minimizing its negative impacts on people and ecosystems.

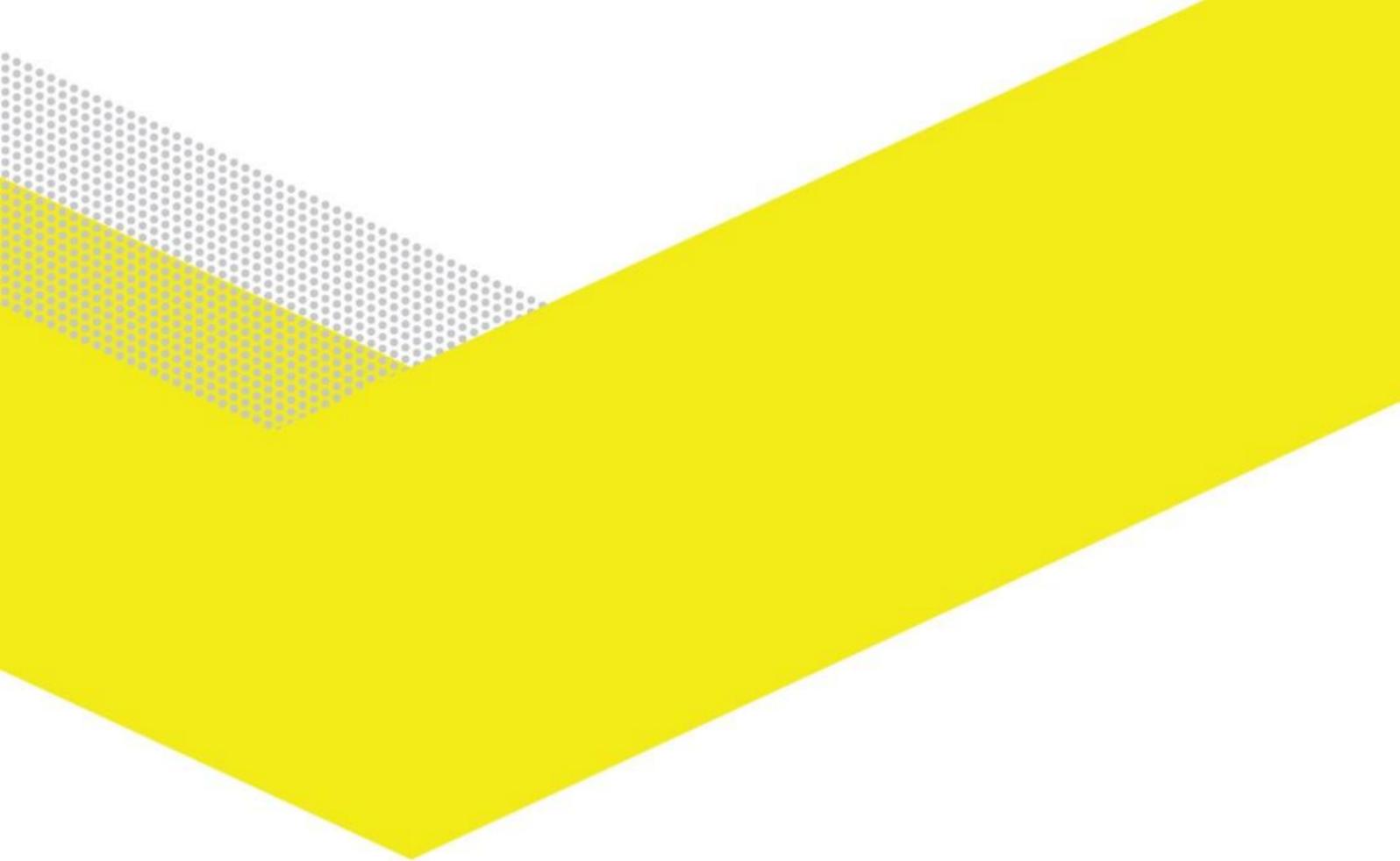
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