

# **Earth's Future**

## **COMMENTARY**

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#### **Key Points:**

- The rapid growth of anthropogenic reactive nitrogen production now makes it unquestionably dominant relative to the total of natural sources
- Anthropogenic production of reactive nitrogen has increased almost five-fold in the last 60 years.
- This anthropogenic activity is a massive perturbation of a global geochemical cycle in a relatively short period of time.

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# Is nitrogen the next carbon?

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**Abstract** Just as carbon fueled the Industrial Revolution, nitrogen has fueled an Agricultural Revolution. The use of synthetic nitrogen fertilizers and the cultivation of nitrogen-fixing crops both expanded exponentially during the last century, with most of the increase occurring after 1960. As a result, the current flux of reactive, or fixed, nitrogen compounds to the biosphere due to human activities is roughly equivalent to the total flux of fixed nitrogen from all natural sources, both on land masses and in the world's oceans. Natural fluxes of fixed nitrogen are subject to very large uncertainties, but anthropogenic production of reactive nitrogen has increased almost fivefold in the last 60 years, and this rapid increase in anthropogenic fixed nitrogen has removed any uncertainty on the relative importance of anthropogenic fluxes to the natural budget. The increased use of nitrogen has been critical for increased crop yields and protein production needed to keep pace with the growing world population. However, similar to carbon, the release of fixed nitrogen into the natural environment is linked to adverse consequences at local, regional, and global scales. Anthropogenic contributions of fixed nitrogen continue to grow relative to the natural budget, with uncertain consequences.

**Plain Language Summary** Almost 50 years ago, C. C. Delwiche (1970) wrote in Scientific American "Of all man's recent interventions in the cycles of nature, the industrial fixation of nitrogen far exceeds all the others in magnitude." Since then, the climate change impacts of human contributions to the carbon cycle have come under intense scrutiny and debate. Meanwhile anthropogenic production of reactive nitrogen has continued to increase with associated adverse environmental consequences. As in the case of carbon dioxide (CO<sub>2</sub>), some impacts of reactive nitrogen are difficult to measure on a short timescale. Reactive nitrogen also has a place in the agricultural revolution, which is analogous to the role of carbon from fossil fuels in the Industrial Revolution. This leads us to ask the question: is the anthropogenic augmentation of the nitrogen cycle growing to a point where it may have adverse environmental consequences on a global scale, and where the critical role of reactive nitrogen in the agricultural system will make it very difficult to mitigate these consequences? In short, "Is nitrogen the next carbon?"

## 1. Introduction

Almost 50 years ago, C. C. *Delwiche* (1970) wrote in *Scientific American* "Of all man's recent interventions in the cycles of nature, the industrial fixation of nitrogen far exceeds all the others in magnitude." Since then, the climate change impacts of human contributions to the carbon cycle have come under intense scrutiny and debate (*IPCC*, 2013). Meanwhile anthropogenic production of reactive nitrogen has continued to increase with associated adverse environmental consequences. As in the case of carbon dioxide (CO<sub>2</sub>), some impacts of reactive nitrogen are difficult to measure on a short timescale. Reactive nitrogen also has a place in the agricultural revolution, which is analogous to the role of carbon from fossil fuels in the Industrial Revolution. This leads us to ask the question: Is the anthropogenic augmentation of the nitrogen cycle growing to a point where it may have adverse environmental consequences on a global scale, and where the critical role of reactive nitrogen in the agricultural system will make it very difficult to mitigate these consequences? In short, "Is nitrogen the next carbon?" (Figure 1).

This paper combines historic data on crop cultivation and fertilizer usage with recent estimates of nitrogen-fixation rates in order to analyze trends in the anthropogenic production of biologically

available nitrogen since 1900. The paper also places these trends in context with recent estimates of natural nitrogen-fixation and removal of fixed nitrogen by denitrification in terrestrial and aquatic ecosystems.

## 2. Trends in Human Nitrogen use

Nitrogen-rich manure has been used to fertilize crops for millennia—long before the discovery of nitrogen as a distinct chemical element (*Columella*, 1954). The role of nitrogen as a crop nutrient was explored scientifically in the 1800s (*Boussingault*, 1856), and a market developed for nitrogen-rich deposits of mineralized



**Figure 1.** Is nitrogen the next carbon?

guano from South America and the South Pacific islands, reaching about 1 Tg N  $y^{-1}$  by 1900 (*Cushman*, 2013). Though small by today's standards, the trade in nitrogen fertilizer was a main object of contention in the 1879 War of the Pacific, between nascent South American nations (*Ortega*, 1984). Industrial processes for fixing nitrogen, especially the Haber-Bosch process, greatly expanded the availability of nitrogen-based fertilizers in the early 1900s (*Smil*, 2001). Nevertheless, use of synthetic fertilizers did not become routine until the mid-twentieth century. In the U.S., less than 40% of farms reported the use of any synthetic fertilizer in 1939, but more than 60% reported the use of chemical fertilizer in 1954 (*Hurley et al.*, 1959).

Synthetic nitrogen fertilizer usage grew to about 12 Tg N  $y^{-1}$  in 1960, more than a tenfold increase over mineral nitrogen fertilizer usage prior to the commercialization of the Haber-Bosch process (1911). Since 1960, synthetic nitrogen fertilizer use has grown almost another tenfold to 110 Tg N  $y^{-1}$  in 2013. Initially, this growth occurred in the U.S. and Europe. Consumption in these regions leveled off in about 1990, and the growth since then has occurred primarily in Asia (*IFA*, 2016).

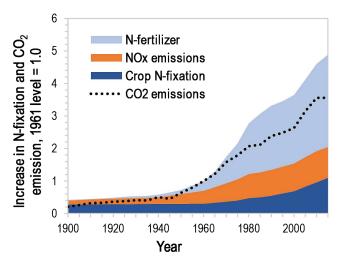
The last half of the 20th century also saw large increases in the cultivation of nitrogen-fixing crops, especially soybeans. These have been cultivated in Asia for at least 1000 years, but after the nitrogen-fixing capabilities of the crop were recognized, cultivation in other parts of the world grew rapidly. World soybean production increased by more than a factor of 3 between 1910 and 1960 (*Shurtleff and Aoyagi*, 2004); with production in the U.S. exceeding Asian production by 1955 (*FAO*, 2015). Since 1960, world production of soybeans has increased by a factor of 10, with the largest share of new production occurring in South America. Soybeans are often grown in rotation with other crops, such as corn. This crop rotation serves to increase the amount of nitrogen available and to break the cycles of crop pests.

Cultivation of other legumes (e.g., peas, beans, lentils, and peanuts) has increased by a factor of about 2.6 since 1960. Total global nitrogen fixation in croplands is estimated at about 43 Tg N  $y^{-1}$ , with a range from 30 to 51 Tg N  $y^{-1}$  based on the ranges of nitrogen fixation yields (*Herridge et al.*, 2008). This estimate includes soybeans, other beans and legumes, and inadvertent nitrogen fixation by cyanobacteria associated with the cultivation of rice and sugar. The estimate does not include legumes in pasturelands or savannas used for grazing.

A substantial portion of the nitrogen is transported and lost to the surrounding environment, through runoff, leaching to groundwater, and emissions of ammonia ( $NH_3$ ), nitrogen oxides ( $NO_X$ ), and other nitrogen compounds ( $NO_X$ ), and  $NO_X$ 002;  $NO_X$ 101. No emissions from combustion sources also constitute a source of reactive nitrogen. These emissions increased from approximately 5.8 Tg N y<sup>-1</sup> in 1910 to approximately 38 Tg N y<sup>-1</sup> in 2010. Since the 1990s,  $NO_X$ 101 emission sources have been subject to pollution controls in the U.S. and Europe, resulting in substantial emission reductions. However, emissions continue to increase in the developing world, especially China ( $NO_X$ 101).

The increased use of synthetic fertilizer, increased cultivation of nitrogen-fixing crops, and increased emissions of  $NO_X$  all contribute to increases in the overall level of reactive nitrogen in the environment. The total of these three sources for 2014 is 190 Tg N  $y^{-1}$ , with a plausible range from 160 to 210 Tg N  $y^{-1}$ . The trajectories of anthropogenic production of reactive nitrogen are shown in Figure 2, and are compared with the trajectory of  $CO_2$  (Boden et al., 2013; International Energy Agency (IEA), 2017). The  $CO_2$  curve shows a

sharp upward inflection in the mid-1940s. The nitrogen curve lags the  $CO_2$  curve by 10-15 years, showing an upward inflection about 1960. The trends for anthropogenic nitrogen and  $CO_2$  in the last half of the 20th century are similar. While reported global  $CO_2$  emissions have not shown an increase since about 2013, the



**Figure 2.** Trends in anthropogenic reactive nitrogen sources since 1900 compared with the trend in anthropogenic  $CO_2$  emissions. Fertilizer trends are adapted from *IFA* (2016), *Cushman* (2013), and *Smil* (2001).  $NO_X$  trend is adapted from *UN* (2010). Trends in nitrogen-fixing crops are computed by combining nitrogen fixation yields (*Herridge et al.*, 2008) with crop production statistics (*Shurtleff and Aoyagi*, 2004; *FAO*, 2015).  $CO_2$  trend is adapted from *Boden et al.* (2013) and *IEA* (2017).

use of nitrogen fertilizers and the cultivation of nitrogen-fixing crops are expected to continue to increase in most future scenarios (*Bouwman et al.*, 2013a; *Winiwarter et al.*, 2013, *International Energy Agency (IEA*), 2017).

Populations of animals raised for food have also increased in recent decades. Animals convert only a fraction of the nitrogen in their feed to meat protein or milk protein for human consumption (U.S. Environmental Protection Agency Science Advisory Board (USEPA), 2011). Much of the balance is excreted in the form of urea and other nitrogen compounds. These nitrogen compounds in the animal waste can then produce NH<sub>3</sub> emissions to the atmosphere or increased losses to the hydrosphere by leaching and runoff. Nitrogen compounds in animal waste do not represent a new addition of

biologically available nitrogen to the environment, since this nitrogen is derived from plant proteins consumed by the animals. However, losses of N gases and runoff of animal waste components are important pathways for the release of nitrogen compounds from farms to the surrounding environment. Therefore, the increased animal populations also affect the nitrogen cycle.

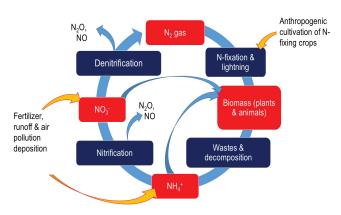
## 3. Human Impacts on the Nitrogen Cycle

Figure 3 illustrates the natural nitrogen cycle, showing how anthropogenic inputs of nitrogen compounds contribute to this cycle. Nitrogen-fixing bacteria convert nitrogen gas  $(N_2)$  to biologically available nitrogen compounds, which are in turn taken up by plants and incorporated into proteins and other essential molecules. Nitrogen compounds in decomposing plant matter and animal waste are released as ammonium  $(NH_4^+)$ , which is oxidized by bacteria, producing nitrate ion  $(NO_3^-)$ , which is consumed by other bacteria that perform denitrification. The denitrification reaction completes the cycle by producing  $N_2$  gas, but also produces some gaseous nitrous oxide  $(N_2O)$  and nitric oxide (NO).

Both the use of synthetic nitrogen fertilizer and the anthropogenic cultivation of nitrogen-fixing crops increase the overall mass of biologically available nitrogen compounds. This nitrogen is intended to remain within the farm system, ultimately for the production of food for humans or for animals raised to feed humans. However, a substantial portion of the reactive nitrogen (~70%) escapes to the surrounding environment (*Galloway and Cowling*, 2002). Fertilizers and residues from nitrogen-fixing crops, and deposited nitrates all ultimately increase the amount of nitrate processed by denitrifying bacteria, both on farmlands and in surrounding ecosystems.

The magnitudes of fluxes in the natural nitrogen cycle are subject to considerable uncertainty, as stated colorfully in the title of a paper by Burris: "The global nitrogen budget – science or séance?" (Burris, 1980). Galloway et al. (2004) gave a global estimate of 120 Tg N y $^{-1}$  for biological nitrogen fixation in terrestrial ecosystems under preindustrial conditions based on a compilation of nitrogen fixation fluxes from various ecosystems. Using nitrogen-isotope abundances, Vitousek et al. (2013) obtained a considerably lower preindustrial estimate of 58 Tg N y $^{-1}$  for terrestrial nitrogen fixation, with a possible range from 40 to 100 Tg

N y<sup>-1</sup>. This lower estimate is adopted by *Fowler et al.* (2013). *Cleveland et al.* (2013) estimate natural nitrogen fixation in terrestrial ecosystems at 127 Tg N y<sup>-1</sup>, based on biogeochemical modeling of the contributions of different terrestrial ecosystems.



**Figure 3.** The nitrogen cycle. Orange arrow depict anthropogenic additions to the natural cycle.

Estimates of nitrogen fixation in marine ecosystems range from 121 to 177 Tg N y<sup>-1</sup> (Gro $\beta$ kopf et al., 2012; Jickells et al., 2017). Lightning strikes are estimated to account for an additional 5.4 Tg N  $y^{-1}$  on a global basis (Galloway et al., 2004). Combining these estimates with the range of values for terrestrial ecosystems, we estimate the global rate for production of reactive nitrogen at 166-302 Tg N y<sup>-1</sup> under preindustrial conditions. Using central estimates for terrestrial nitrogen fixation and marine ecosystems, the overall global preindustrial nitrogen fixation rate would

be about 240 Tg N  $y^{-1}$ . Table 1 summarizes estimates of anthropogenic and natural fluxes of reactive nitrogen.

Even considering the uncertainty in the magnitude of fluxes in the nitrogen cycle, anthropogenic sources of reactive nitrogen represent a significant perturbation to the terrestrial nitrogen cycle and to the global nitrogen cycle as a whole. The trend for the anthropogenic nitrogen contribution includes synthetic fertilizer, cultivation of nitrogen-fixing crops, and NO<sub>X</sub> emissions from fossil fuel combustion (Figure 4). Reactive nitrogen in pasturelands may also be increased by anthropogenic activities such as the increased pasturing of food animals.

Figure 4 shows that the anthropogenic nitrogen contribution would have surpassed the lower end estimate of preindustrial nitrogen fixation in terrestrial ecosystems by 1960; and would have surpassed the upper end estimate for terrestrial ecosystems by about 1980. Based on the central estimates given in Table 1, the current anthropogenic contribution accounts for about 70% of total production of reactive nitrogen in terrestrial ecosystems. The anthropogenic contribution is close to our best estimate of overall global nitrogen fixation under preindustrial conditions (240 Tg N  $y^{-1}$ ), and is increasing across the uncertainty bar for the global estimate. This suggests that the anthropogenic inputs may now account for about half of the total reactive nitrogen flux on Earth, both terrestrial and marine.

Anthropogenic reactive nitrogen produces multiple impacts at local, regional, and global scales. Emissions of  $NH_3$  and  $NO_X$  contribute to the formation of fine particulate matter ( $PM_{2.5}$ ), which is associated with various adverse human health impacts, including premature death (*Pope et al.*, 2009; *Kwok et al.*, 2013; *Lelieveld et al.*, 2017).  $PM_{2.5}$  can also contribute to visibility impairment and regional haze (*Wang et al.*, 2012).

Reactive nitrogen fertilizes terrestrial and aquatic ecosystems, which can affect species diversity and can lead to eutrophication of aquatic ecosystems (*Jones et al.*, 2013; *Paerl*, 1988; *U.S. Environmental Protection Agency Science Advisory Board (USEPA)*, 2007). The use of synthetic nitrogen has also been associated with the depletion of other soil nutrients in agricultural systems. In India, crop yields have leveled off despite increases in the use of synthetic nitrogen fertilizer (*IPC*, 2008).

Reactive nitrogen compounds can leach into groundwater, contaminating drinking water supplies (*UNEP*, 2007; *Tomich et al.*, 2016). A portion of reactive nitrogen processed by soil and aquatic microbes is also converted to  $N_2O$ , which reenters the atmosphere.  $N_2O$  is a long-lived absorber of infrared radiation, with a climate change potential approximately 250 times that of  $CO_2$  (*IPCC*, 2013). Nitrous oxide is also associated with the depletion of stratospheric ozone (*Ravishankara et al.*, 2009).

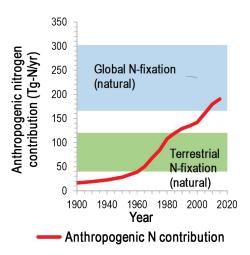
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Sources	<b>Table 1.</b> Fluxes of Reactive Nitroger	١				
Sources         Anthropogenic         Cushman (2013), IFA (2016), Smil (2001)           Synthetic or mined fertilizers         1         12         110         Cushman (2013), IFA (2016), Smil (2001)           N-fixing crops         Soybeans         0.4         1.5         25         Shurtleff and Aoyagi (2004), FAO (2015), Herridge et al. (2008)           Other beans and legumes         2.9         7.5         FAO (2015), Herridge et al. (2008)           Other         7.4         10         FAO (2015), Herridge et al. (2008)           Other         7.4         10         FAO (2015), Herridge et al. (2008)           Other         7.4         10         FAO (2015), Herridge et al. (2008)           Other         7.4         10         FAO (2015), Herridge et al. (2008)           Other         7.4         10         FAO (2015), Herridge et al. (2008)           Other Sinks         UN (2010)         UN (2010)           Interpretation         84         40-127         Galloway et al. (2004), Vitousek et al. (2013), Cleveland et al. (2013)           Interpretation         5.4         Galloway et al. (2004)         Galloway et al. (2004)           Interpretation         430         150         121-177         Galloway et al. (2004), Großkopt et al. (2012)           Interpretation         22-87<		Soi	Sources (Tg N y <sup>-1</sup> )		Range (for	
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Total natural sources 240 166–310  Total sources 430  Sinks  Denitrification  Agricultural soils 22–87 Hofstra and Bouwman (2005)  Total terrestrial 130 58–175 Seitzinger et al. (2006), Eugster and Gruber (2012)  Freshwater and groundwater 120 39–216 Eugster and Gruber (2012)  Marine 150 107–331 Seitzinger et al. (2006), Eugster and Gruber (2012)  Total denitrification 400 210–720  Other sinks  Terrestrial biomass change 9 9 9 Schlesinger (2009)  Marine sediments 13 10–16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Lightning			5.4		Galloway et al. (2004)
Total sources 430  Sinks  Denitrification  Agricultural soils 22-87 Hofstra and Bouwman (2005)  Total terrestrial 130 58-175 Seitzinger et al. (2006), Eugster and Gruber (2012)  Freshwater and groundwater 120 39-216 Eugster and Gruber (2012)  Marine 150 107-331 Seitzinger et al. (2006), Eugster and Gruber (2012)  Total denitrification 400 210-720  Other sinks  Terrestrial biomass change 9 9 Schlesinger (2009)  Marine sediments 13 10-16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Marine N-fixation			150	121-177	
Sinks  Denitrification  Agricultural soils  Total terrestrial  130  58-175  Seitzinger et al. (2006), Eugster and Gruber (2012)  Freshwater and groundwater  120  39-216  Eugster and Gruber (2012)  Marine  150  107-331  Seitzinger et al. (2006), Eugster and Gruber (2012)  Marine  150  107-331  Seitzinger et al. (2006), Eugster and Gruber (2012)  Other sinks  Terrestrial biomass change  9  9  9  Schlesinger (2009)  Marine sediments  13  10-16  Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Total natural sources			240	166-310	
Denitrification Agricultural soils Total terrestrial 130 58-175 Seitzinger et al. (2006), Eugster and Gruber (2012) Freshwater and groundwater 120 39-216 Eugster and Gruber (2012) Marine 150 107-331 Seitzinger et al. (2006), Eugster and Gruber (2012)  Total denitrification 400 210-720 Other sinks Terrestrial biomass change 9 9 Schlesinger (2009) Marine sediments 13 10-16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Total sources			430		
Agricultural soils  Total terrestrial  130  58–175  Seitzinger et al. (2006), Eugster and Gruber (2012)  Freshwater and groundwater  120  39–216  Eugster and Gruber (2012)  Marine  150  107–331  Seitzinger et al. (2006), Eugster and Gruber (2012)  Seitzinger et al. (2006), Eugster and Gruber (2012)  Notal denitrification  400  210–720  Other sinks  Terrestrial biomass change  9  9  Schlesinger (2009)  Marine sediments  13  10–16  Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Sinks					
Total terrestrial  130  58–175  Seitzinger et al. (2006), Eugster and Gruber (2012)  Freshwater and groundwater  120  39–216  Eugster and Gruber (2012)  Marine  150  107–331  Seitzinger et al. (2006), Eugster and Gruber (2012)  Marine  150  107–331  Seitzinger et al. (2006), Eugster and Gruber (2012)  Leave and Gruber (2012), DeVries et al. (2013a)  Total denitrification  400  210–720  Other sinks  Terrestrial biomass change  9  9  Schlesinger (2009)  Marine sediments  13  10–16  Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Denitrification					
Freshwater and groundwater  Marine  120  39–216  Eugster and Gruber (2012)  Eugster and Gruber (2012)  Seitzinger et al. (2006), Eugster and Gruber (2012), DeVries et al. (2013a)  Total denitrification  400  210–720  Other sinks  Terrestrial biomass change  9  9  Schlesinger (2009)  Marine sediments  13  10–16  Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Agricultural soils				22-87	Hofstra and Bouwman (2005)
Marine 150 107 – 331 Seitzinger et al. (2006), Eugster and Gruber (2012), DeVries et al. (2013a)  Total denitrification 400 210 – 720  Other sinks  Terrestrial biomass change 9 9 Schlesinger (2009)  Marine sediments 13 10 – 16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Total terrestrial			130	58-175	
and Gruber (2012), DeVries et al. (2013a)  Total denitrification 400 210–720  Other sinks  Terrestrial biomass change 9 9 Schlesinger (2009)  Marine sediments 13 10–16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Freshwater and groundwater			120	39–216	Eugster and Gruber (2012)
Other sinks  Terrestrial biomass change 9 9 Schlesinger (2009)  Marine sediments 13 10–16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Marine			150	107-331	and Gruber (2012), DeVries et al.
Terrestrial biomass change 9 9 Schlesinger (2009)  Marine sediments 13 10–16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Total denitrification			400	210-720	
Marine sediments  13 10–16 Galloway et al. (2004), Schlesinger and Bernhardt (2013)	Other sinks					
Schlesinger and Bernhardt (2013)	Terrestrial biomass change			9	9	Schlesinger (2009)
Total sinks 420 220–745	Marine sediments			13	10-16	
	Total sinks			420	220-745	

The impacts of reactive nitrogen on the environment have different time scales. Elevated levels of  $PM_{2.5}$  may persist for only a few days, but may also be chronic. Impacts on groundwater, the oceans, and climate have much longer timescales. The lifetime of  $N_2O$  in the atmosphere is estimated at 121 years (*IPCC*, 2013).

## 4. Fate of Anthropogenic Nitrogen

Most of anthropogenic augmentation of reactive nitrogen is believed to be removed ultimately by denitrification, producing nitrogen gas ( $N_2$ ) and  $N_2$ O. Some of this denitrification occurs in agricultural soils, with estimates of global flux ranging from 22 to 87 Tg N y<sup>-1</sup> (*Hofstra and Bouwman*, 2005). Denitrification in agricultural soils has the effect of reducing the release of reactive nitrogen to surrounding ecosystems. However, this is indicative of an inefficiency of nitrogen use, and also results in the production of  $N_2$ O.



**Figure 4.** Trend in the anthropogenic contribution of new fixed nitrogen relative to the estimated ranges of global nitrogen fixation under preindustrial conditions.

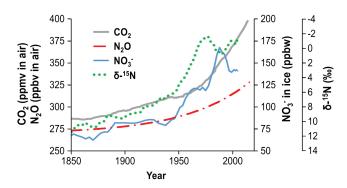
Estimates of the sinks for reactive nitrogen are also subject to considerable uncertainty. Recent estimates of global denitrification flux are from 58 to 175 Tg N y<sup>-1</sup> for terrestrial ecosystems (Seitzinger et al., 2006; Bouwman et al., 2013b), 39 to 216 Tg N y<sup>-1</sup> for freshwater and groundwater, and 107 to 331 Tg N y<sup>-1</sup> for marine ecosystems (Eugster and Gruber, 2012; DeVries et al., 2013a; Jickells et al., 2017). Combining these estimates gives a total global flux of 210-720 Tg N  $y^{-1}$ . If we combine the estimates for natural and anthropogenic nitrogen fixation, the range of estimates for total nitrogen fixation extends from 326 (160 anthropogenic +166 natural) to 520 Tg N  $y^{-1}$  (210 anthropogenic +310 natural). The range of estimates for the denitrification flux extends from below the lower-end estimate for total global nitrogen fixation to above the upper-end estimate. Thus, the global denitrification flux may or may not be large enough to balance global nitrogen fixation (Table 1).

Seitzinger et al. (2006) estimate that about 40% of land-based reactive nitrogen is denitrified in soils, while 35% is denitrified in freshwater or groundwater, and 25% is denitrified in estuaries and oceans. The total global denitrification flux is estimated at 600 Tg N  $y^{-1}$ , 58% from the oceans, 20% from freshwater and groundwater, and 22% from soils. This global denitrification flux would be sufficient to balance the rate of nitrogen fixation, including the anthropogenic increment. However, both nitrogen fixation and denitrification fluxes are subject to large uncertainties. Even if the sources and sinks of reactive nitrogen are in balance on a global basis, there are imbalances on local and regional scales which lead to adverse environmental impacts.

Sgouridis and Ullah (2015) found that natural and seminatural terrestrial ecosystems denitrified about half of the reactive nitrogen deposited to them. Similarly, Houlton and Bai (2009) estimate that denitrification accounts for about one-third of the flux of reactive nitrogen from natural terrestrial ecosystems. This finding is compatible with the estimates of Seitzinger et al. (2006), which indicate a residual flux of fixed nitrogen from terrestrial to marine ecosystems. Jickells et al. (2017) estimate the flux of fixed nitrogen from terrestrial systems to the oceans at 73 Tg N y<sup>-1</sup>. Some of the anthropogenic increment of reactive nitrogen may be accumulating in terrestrial biomass and soils. This increment has been estimated at 9 Tg N y<sup>-1</sup> (Schlesinger, 2009). Sgouridis and Ullah (2015) further suggest that this should alert us to the threat of chronic nitrogen saturation within terrestrial systems receiving nitrogen deposition.

Eugster and Gruber (2012) carried out inverse modeling of both nitrogen fixation and denitrification rates in the oceans, and estimated that the overall nitrogen cycle in the ocean is balanced to within 3 Tg N  $y^{-1}$ , with a possible range from -38 to +40 Tg N  $y^{-1}$ . In addition to nitrogen fixation and denitrification, this balance calculation includes loss to sediments, where an additional 10-16 Tg N  $y^{-1}$  may be sequestered (Galloway et al., 2004; Schlesinger and Bernhardt, 2013). Based on the ranges of reactive nitrogen inputs to the oceans (Table 1 and Seitzinger et al., 2006), between 18% and 45% of this sequestered nitrogen would derive from anthropogenic sources. The rates of accumulation of nitrogen in ocean sediments and in soils are subject to large uncertainties. Nor can these be corroborated by mass balance, because of the large uncertainties in global flux terms. It is not known whether these sinks might represent a significant build-up of reactive nitrogen over time, which could result in increased emissions of  $N_2O$  in the future.

Duce et al. (2008) highlight the importance of atmospheric deposition of fixed nitrogen in the oceans. Although isotopic studies in the Atlantic have found that the importance of the anthropogenic contribution may be less than that of ocean sources (Altieri et al., 2016), studies in the Pacific have suggested that atmospheric deposition has caused an increase in nitrogen concentration there (Kim et al., 2011, 2014).



**Figure 5.** Trends in  $CO_2$ ,  $N_2O$ ,  $NO_3^-$ , and isotopic composition of  $NO_3^-$  as reflected in ice cores. Trend lines are smoothed by averaging over 5 years. Trend in  $CO_2$  is adapted from *Etheridge et al.* (1996) and *WMO* (2016).  $N_2O$  is adapted from *Bullister* (2015).  $NO_3^-$  and  $\delta^{15}N$  are adapted from *Hastings et al.* (2009) and *Felix and Eliott* (2013).

terrestrial, freshwater, marine ecosystems are historically nitrogen limited (Elser et al., 2007). Thus, export of fixed nitrogen from farmlands to these ecosystems can adversely affect biodiversity (Zaehle et al., 2011; DeVries et al., 2013b). It is possible that the deposition of reactive nitrogen to forested ecosystems may increase the sequestration of carbon in soils and biomass (Pinder et al., 2013). However, the deposition of reactive nitrogen in natural ecosystems also enhances production of N2O as a byproduct of microbial denitrification reactions. The climate change impacts of the increased N2O may offset the

impacts of carbon sequestration (Butterbach-Bahl et al., 2011; Zaehle et al., 2011).

Ice-core analyses provide a record of the increase in the atmospheric concentration of  $N_2O$  (*Bullister*, 2015), and in the long-range transport of reactive nitrogen in the form of  $NO_3^-$  (*Hastings et al.*, 2009). Figure 5 compares trends for  $N_2O$  and  $NO_3^-$  with trends measured for  $CO_2$  (*Etheridge et al.*, 1996; *WMO*, 2016). The increases in ice-core concentrations of  $CO_2$  and  $CO_2$  are believed to reflect trends in the global concentrations of these gases, since they are well-mixed in the atmosphere. The ice-core measurements of  $CO_3^-$  (in Greenland) are believed to be related to an increase in regional transport of  $CO_3^-$ . This increase corresponds with a change in the isotopic composition of nitrate-N in the ice cores, reflected by a reduction in the abundance of nitrogen-15 relative to nitrogen-14 [ $CO_3^-$ ]. The change in isotopic composition may be indicative of an increased contribution of agricultural sources (*Felix and Eliott*, 2013). However, the fractionation of nitrogen isotopes is complex, and the samples from Greenland ice cores may be open to different interpretations (*Hastings et al.*, 2009).

There is growing recognition of the impact of anthropogenically produced nitrogen compounds on the nitrogen cycle (*Gruber and Galloway*, 2008; *Sutton et al.*, 2011; *U.S. Environmental Protection Agency Science Advisory Board (USEPA)*, 2011; *Fowler et al.*, 2015). Researchers have used the concept of planetary boundaries to evaluate the magnitudes of human impacts consistent with the sustainable maintenance and development of human society (*Rockstrom et al.*, 2009; *DeVries et al.*, 2013b). Within this construct, the planetary boundary for the anthropogenic contribution to total reactive nitrogen is estimated at 62–82 Tg N y<sup>-1</sup>, based on the risk of eutrophication of terrestrial and aquatic ecosystems (*Steffen et al.*, 2015). This threshold was exceeded in the 1970s, and the current anthropogenic contribution is approximately 153 Tg N y<sup>-1</sup>.

## 5. Discussion

Regulatory and voluntary measures have been adopted to address some components of the nitrogen stream. In the U.S., livestock production facilities are required to obtain permits under the Clean Water Act in order to ensure that the surface waters surrounding the operations are not negatively impacted by animal waste. In implementing this permit system, states have identified Best Management Practices (BMPs) for the management of animal waste and for the use of synthetic nitrogen fertilizers.

Nitrogen-use efficiency has increased in the U.S. and Europe in recent years. Although the trend in nitrogen fertilizer usage in developed nations has been flat since the 1990s, agricultural production continues to increase. This suggests that increases in nitrogen-use efficiency can abate or perhaps reverse the worldwide increase in nitrogen fertilizer use (*Zhang et al.*, 2015). Changes in dietary habits and food wastage can also help reduce the need for synthetic nitrogen fertilizers.

 $NO_X$  emissions from combustion sources have been the target of pollution controls in order to mitigate acid rain and smog in the U.S. These controls have produced a 50% reduction in nationwide  $NO_X$  emissions since 1996 (U.S. Environmental Protection Agency (USEPA), 2017). Total deposition of inorganic nitrogen has

declined by 19 to 32% since the 1980s (*Burns et al.*, 2011). This demonstrates that  $NO_{\chi}$  emissions can be reduced without preventing economic growth.

Unfortunately, there is no integrated regulatory approach for control of reactive nitrogen compounds (*Aneja et al.*, 2008, 2009). In particular, agricultural emissions of reactive nitrogen compounds to the atmosphere are not regulated in the U.S. Because of its contribution to the formation of  $PM_{2.5}$ , individual states can regulate  $NH_3$  as part of their approaches to meeting  $PM_{2.5}$  standards. However, the U.S. has not adopted a national program for  $NH_3$  emissions.  $NH_3$  is the largest volume air pollutant for which no national or regional control program has been developed. Thus, wet deposition of  $NH_4^+$  has increased in much of the U.S. by ~22% in the last 20 years (*Li et al.*, 2016). Some European nations have adopted control measures for  $NH_3$ , which have produced significant reductions in emissions from agriculture (*Erisman et al.*, 2008). A combination of BMPs and engineered solutions for the management of animal waste and for the use of synthetic nitrogen fertilizers can reduce releases of  $NH_3$  and other reactive nitrogen compounds to the natural environment (*Galloway et al.*, 2008; *Erisman et al.*, 2015).

Human-induced changes to the global nitrogen cycle bear a number of similarities to our changes in the global carbon cycle. Fixed N and fossil C have provided great benefits to the human standard of living. The increased use of nitrogen has been critical for increased crop yields and protein production to keep pace with the growing world population. Like the burning of fossil carbon, increased fixation of nitrogen can have adverse environmental consequences at local, regional, and global scales. In addition, our use of both fossil carbon and synthetically fixed nitrogen has grown exponentially in the past 150 years. Anthropogenic production of fixed nitrogen has grown in relation to natural sources, so that the anthropogenic increment is nearly as large as the best estimate of the total natural nitrogen fixation in terrestrial and marine environments.

Some measures for reducing  $CO_2$  emissions will reduce releases of fixed nitrogen, and vice versa. For instance, renewable energy sources generally will reduce fuel consumption, thereby reducing  $NO_X$  emissions. Switching from coal to natural gas also reduces both  $CO_2$  and  $NO_X$  emissions. In addition, the production of synthetic nitrogen fertilizer requires significant fuel consumption, with associated  $CO_2$  emissions. Thus, improvements in nitrogen-use efficiency would reduce  $CO_2$  emissions as well as releases of fixed nitrogen.

There are also important differences pertaining to human impacts on the carbon and nitrogen cycles. A significant fraction of anthropogenic  $CO_2$  emissions has been taken up by the oceans. In contrast, most anthropogenic fixed nitrogen is believed to be converted to  $N_2$ . Although some fixed nitrogen may be accumulating in soils and in ocean sediments, the fraction is much smaller than the fraction of carbon taken up by the oceans. This could mean that the nitrogen cycle could possibly recover more quickly from anthropogenic perturbation than the carbon cycle if releases of fixed nitrogen are mitigated. However, demands for increased nitrogen usage will continue as world population and agricultural production continue to rise. Thus, reducing the demands for fixed nitrogen may prove to be more difficult than reducing emissions of  $CO_2$ .

The impacts of anthropogenic perturbations on the reactive nitrogen cycle are local, regional and global scale. Current estimates indicate that global nitrification fixation is balanced by denitrification, although these budget calculations are subject to large uncertainties. Thus, the large increase in anthropogenic production may be balanced by increased denitrification, and there is no apparent "missing sink" for reactive nitrogen. Nevertheless, if anthropogenic production continues to increase, denitrification processes may not be able to offset the increased production. Continued increases in reactive nitrogen production may accelerate species diversity impacts and N<sub>2</sub>O production.

Public awareness of the impact of reactive nitrogen is also increasing. We anticipate that reactive nitrogen may be similar to the situation with carbon in another respect. The environmental impacts of anthropogenic reactive nitrogen may become more difficult to rectify as time passes. In the case of carbon, we are accumulating a burden of  $CO_2$  that will impact the atmosphere far into the future (*IPCC*, 2013). In the case of reactive nitrogen, anthropogenic contributions continue to grow in relation to the natural budget, with uncertain consequences. "Is nitrogen the next carbon?" is a thought provoking question. Mitigating both carbon and nitrogen is a grand challenge.

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