nature geoscience

ARTICLES

PUBLISHED ONLINE: 30 AUGUST 2009 | DOI: 10.1038/NGEO608

The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860

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Atmospheric nitrous oxide concentrations have been increasing since the industrial revolution and currently account for 6% of total anthropogenic radiative forcing. Microbial production in soils is the dominant nitrous oxide source; this has increased with increasing use of nitrogen fertilizers. However, fertilizer use alone cannot account for the historical trends of atmospheric concentrations of nitrous oxide. Here, I analyse atmospheric concentrations, industrial sources of nitrous oxide, and fertilizer and manure production since 1860. Before 1960, agricultural expansion, including livestock production, may have caused globally significant mining of soil nitrogen, fuelling a steady increase in atmospheric nitrous oxide. After 1960, the rate of the increase rose, due to accelerating use of synthetic nitrogen fertilizers. Using a regression model, I show that 2.0% of manure nitrogen and 2.5% of fertilizer nitrogen was converted to nitrous oxide between 1860 and 2005; these percentage contributions explain the entire pattern of increasing nitrous oxide concentrations over this period. Consideration of processes that re-concentrate soil nitrogen, such as manure production by livestock, improved 'hind-casting' of nitrous oxide emissions. As animal protein consumption in human diets increases globally, management of manure will be an important component of future efforts to reduce anthropogenic nitrous oxide sources.

Following carbon dioxide (CO_2), methane (CH_4) and chlorofluorocarbon-12, nitrous oxide (N_2O) is the fourth most important anthropogenic greenhouse gas[1] and it is also a reactant in the destruction of stratospheric ozone[2]. Atmospheric N_2O increased from pre-industrial concentrations of 270 parts per billion (ppb) to 319 ppb in 2005, increasing linearly during the past few decades (at the time of writing) at a rate of about 0.26% per year[1]. With an atmospheric lifetime of 114 years[1], the legacy of increasing N_2O concentrations will remain long after mitigation strategies become effective. The dominant source of both anthropogenic and natural N_2O is microbial production by means of nitrification and denitrification, which has been stimulated by the use of synthetic nitrogen fertilizers for food production[2–4]. The use of synthetic fertilizers is projected to increase in response to growing human population, per capita meat consumption and crop-based biofuel production[5], which may accelerate the rate of increase of atmospheric N_2O content (ref. 7). Although there is little doubt that increasing human food production is the dominant cause of increasing atmospheric N_2O (refs 1–9), the fraction of fertilizer-N that is emitted as N_2O is uncertain. Improved quantitative estimates of the amounts of N_2O coming from the various sources are needed to prioritize effective mitigation strategies.

Numerous approaches have been used to identify and quantify the globally important sources of N_2O since its role in stratospheric ozone depletion was recognized[8]. Bottom-up methods of estimating global budgets of N_2O, such as the IPCC (Intergovernmental Panel on Climate Change) methodology[3,6], require uncertain extrapolations of mean emission rates and emission factors across broad regions, leading to large ranges bracketing each source estimate (Table 1; ref. 3). According to the IPCC methodology, about 1% of fertilizer-N added to soils is directly emitted to the atmosphere as N_2O, and about another 1% is emitted indirectly from downwind and downstream ecosystems (including disposal of human sewage), which receive forms of N that are transported away from the agricultural fields by wind, water and commerce. A top-down method recently published by Crutzen *et al.* (ref. 7), indicates that the IPCC estimates may be too low by about a factor of two. These authors used global N budgets at two points in time—the pre-industrial period and the 1990s—to derive the fraction of newly fixed N introduced into the biosphere annually (through lightning, biological N fixation, production of synthetic fertilizers, industrial and transportation sources) that must be converted to N_2O to make the global N_2O budget balance. Estimates of the stratospheric sink of N_2O are reasonably well constrained[2,7], so the global source strength can be inferred from knowledge of the sink and the rate of N_2O accumulation in the atmosphere. For the period before the industrial revolution, when primarily natural N_2O sources and sinks were approximately in balance, each at about 10.2 Tg N_2O–N yr^{-1}, N_2O production from natural terrestrial and coastal ecosystem sources was 4–5% of the estimated natural rate of N fixation by lightning and biological N fixation[7]. Similarly, in the 1990s, after adjusting the growth of atmospheric N_2O for estimated industrial sources, the annual increase was equal to 3–5% of the sum of estimated anthropogenic sources of new N fixation[7]. Crutzen *et al.* concluded that a reasonable approximation of N_2O production, both before and after the industrial revolution, from terrestrial and coastal systems is about 4% ($\pm$1%) of annual new N fixation (natural and anthropogenic) in the biosphere[7].

This top-down budgeting model seems to work for 1860 and 1995, which Crutzen *et al.* chose for calibrating their 4% estimate[7], but it does not hold up for the period between those two dates (Fig. 1a). On the basis of 4% of newly fixed N, the prediction from this model is that atmospheric N_2O should have started to rise sharply only after about 1960, because significant increases in newly fixed N started with the use of synthetic N fertilizers and with the expansion of NO_x production by industry and transportation sectors after the Second World War (Fig. 1b). However, the atmospheric record shows that N_2O concentrations were increasing steadily from 1860 to 1960, although the rate of growth did increase after 1960 (Fig. 1a). The discrepancy between this application of the top-down model[7]

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Table 1 | Estimates of anthropogenic emissions of nitrous oxide (Tg N_2O–N yr^{-1}).

Source	Mosier *et al.* 1998 (ref. 3)	EPA 2006 (ref. 14)	Crutzen *et al.* 2007 (ref. 7)	This study
Direct emissions from fertilizer on soils	1.5 (0.2–2.7)	4.4	4.3–5.8	2.2 (1.5–2.4)
Indirect fertilizer emissions: atmospheric deposition	0.3 (0.06–0.6)			
Indirect fertilizer emissions: leaching	1.6 (0.1–7.7)			
Indirect emissions: human sewage	0.2 (0.04–2.6)	0.2		Included with fertilizer & manure estimates
Manure: soil applications	0.6 (0.1–1.1)	Included with fertilizer emissions		2.8 (2.2–3.3)
Manure: livestock management systems	2.1 (0.6–3.1)	0.4		
Biomass burning	0.5 (0.2–1.0)	0.6		0.5
Industrial & transport	1.3 (0.7–1.8)	0.8	0.7–1.3	0.8
Total anthropogenic	8.1 (2.1–20.6)	6.3	5.6–6.5	6.3

1 Tg = 10^{12} g. The base year was 1994 for the Mosier *et al.* study and was 2000 for each of the other three studies. The ranges of uncertainty for fertilizer and manure sources in this study (shown in parentheses) are derived from the sensitivity analyses presented in the Supplementary Information.

and the observed atmospheric record suggests that a constant percentage of newly fixed N may be too simplistic, and that another source of N_2O was important during the late nineteenth and early twentieth centuries.

Estimating sources of nitrous oxide

Although N enters and moves through ecosystems in many diffuse forms, the most concentrated forms of anthropogenic N inputs are synthetic fertilizers, animal manures and human sewage. Nitrifying and denitrifying bacteria are most active and produce the most N_2O when N is abundant relative to assimilatory demands by other microorganisms or by plants[10]. Pulses of N_2O emissions from soils following fertilizer applications have been widely described[11]. Livestock concentrate N from their feed into protein for human consumption as well as N-rich wastes. High rates of N_2O emissions have been measured from animal urine patches and manure[3,12]. In addition to animals in feedlots, grazers concentrate N from grasses and other plants, rendering it more likely to be converted to N_2O when excreted in concentrated forms onto rangelands. Humans also concentrate N, releasing sewage into the environment in numerous forms and ways, including in field applications (often called 'night soil'), in discharge of raw sewage into waterways, and to sewage treatment facilities. Of course, N_2O production continues as inputs of fertilizer-N, manure-N and sewage-N cascade in more diffuse forms through various downstream and downwind ecosystems[13], but the highest rates of N_2O emissions are likely to occur where N availability to microorganisms exceeds carbon availability[10], as is often the case when fertilizers and manures are applied to the soil.

To estimate the contributions of various sources of N_2O since 1860, I used a combination of top-down analyses of the historic atmospheric accumulation of N_2O, further constrained by bottom-up historical estimates of industrial and transportation sources (Fig. 1c), to derive a time-course of estimated annual anthropogenic biological sources of N_2O (Methods and Supplementary Information). The most parsimonious way of analysing anthropogenic biological sources of N_2O is to focus on the introduction of concentrated forms of N to ecosystems. The fractions of N_2O emissions attributable to the two dominant inputs of concentrated N can be inferred from the fitted parameters of the following multiple linear regression for the years 1860–2005:

$$\text{anthropogenic biological } N_2O \text{ source} = 0.0203^{*}\text{manure-N} + 0.0254^{*}\text{fertilizer-N}$$

The regression is highly significant ($p < 0.0001$ for each coefficient; adjusted $R^2 = 0.975$). The regression coefficients suggest that roughly 2.0% of annual manure-N production and 2.5% of fertilizer-N production have been converted to N_2O. These values are in reasonable agreement with the direct and indirect emission factor estimates of the bottom-up IPCC methodology[6], and the estimates for 2000 are within the error terms of previous budgets[2,3], with manure as the single largest source (Table 1). The sources attributed to fertilizers and manures include indirect emissions from downwind and downstream ecosystems, including human sewage. Whereas fertilizer-N and manure-N follow very different historical patterns (Fig. 1b), human sewage-N covaries strongly with the sum of fertilizer-N and manure-N ($R^2 = 0.98$; Supplementary Information), which means that adding sewage-N as a third 'independent' form of concentrated N in the regression analysis provides little new information and increases the R^2 of the regression from 0.975 to only 0.976. Human sewage is estimated to contribute about 3% of total anthropogenic N_2O emissions[14], and this regression approach does not permit distinguishing this contribution from other direct or indirect effects of historical patterns of fertilizer-N and manure-N usage.

The narrow 95% confidence intervals of the regression coefficients (0.0196–0.0210 for manure-N and 0.0237–0.0270 for fertilizer-N) do not reflect uncertainties in the input data. For example, the regression coefficient for the fraction of manure that is converted to N_2O is also sensitive to uncertainties in estimates of manure production. Smil[15] argued that global manure production had been overestimated, but estimates from a more recent Food and Agriculture Organization of the United Nations report[16] are in good agreement with the database used in this analysis. An analysis of sensitivity of the regression parameters to

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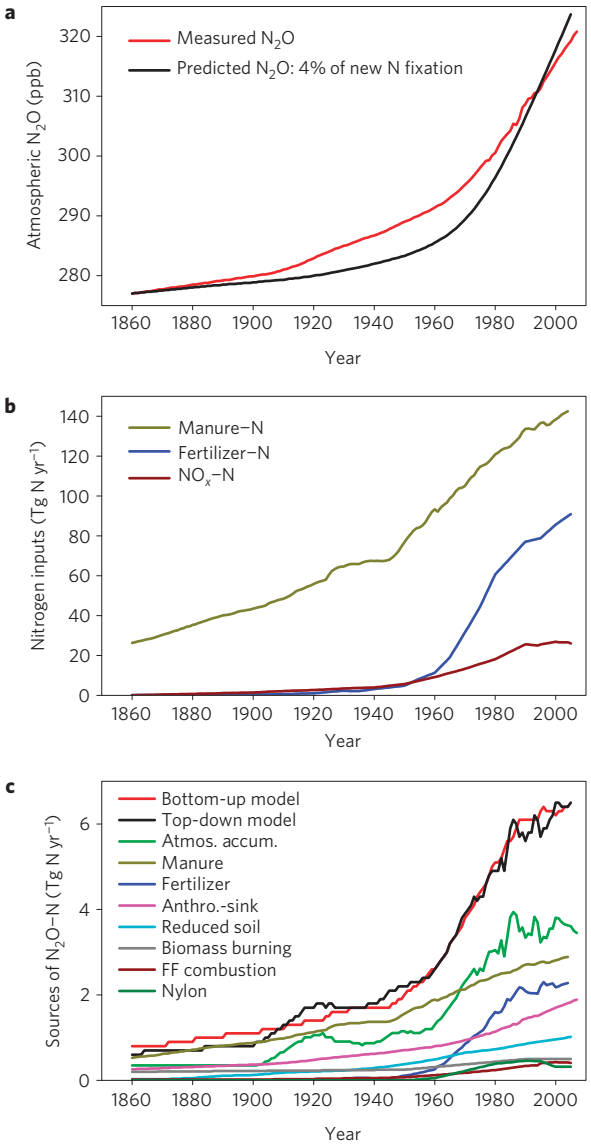

Figure 1 | Historical reconstructions of atmospheric N_2O and its inferred anthropogenic sources. a Atmospheric N_2O concentrations[22] are compared to predictions assuming that 4% of newly fixed N is annually converted to N_2O (ref. 7). **b** Historical records for manure-N (ref. 22), fertilizer-N (ref. 23), and NO_x-N (ref. 22). **c** Historical sources of N_2O estimated from this analysis. The 'bottom-up' model sums the sources from manure, fertilizer, biomass burning, fossil-fuel (FF) combustion, and nylon production. The 'top-down' model sums atmospheric accumulation, the anthropogenic sink and the decreased tropical forest soil source (reduced soil).

uncertainties in the input data (see Supplementary Information) indicates that the N_2O emission factors are likely to fall between 1.6 and 2.7% for manure-N production and between 1.7 and 2.7% for fertilizer-N production.

The estimated contributions of N_2O from manure and fertilizer since 1860, as well as other sources, and their sum are shown in Fig. 1c. The manure source has been important throughout this period, whereas the fertilizer, nylon and transport sources became important only during the last half of the twentieth century. The combined bottom-up source model agrees well with the newly combined top-down constraints of atmospheric accumulation and the anthropogenic sink throughout the entire 145-year period (Fig. 1c).

New nitrogen fixation versus mining of soil nitrogen

The fertilizer and manure emission factors derived from this regression analysis should not be summed to compare with the Crutzen *et al.* estimate that $4 \pm 1\%$ of newly fixed N is converted to N_2O (ref. 7), because the manure-N is not newly fixed N. Some manure is derived from recently fixed N, especially in modern animal-production systems, where livestock are fed grains recently grown from fertilized croplands. Before the widespread use of synthetic fertilizer-N, however, livestock were supported by grazing or by feed grown on unfertilized croplands[9,17]. Some of the N consumed by livestock would have been derived from contemporary natural N fixation, but depletion of stocks of soil organic N was probably also common as native soils were ploughed[4,17] and as some areas were overgrazed, mobilizing N stored in soil organic matter that had originally been fixed in previous decades or centuries[8,17]. Mining of soil nutrients has been common since the invention of agriculture[18]. Historical mass-balance analyses for the state of Illinois show that ploughing of the native prairie released on the order of 30 kg N ha^{-1} yr^{-1}, and that >85% of the grain produced on Illinois farms from the mid-1800s into the early 1900s was fed to livestock, resulting in meat, manure, riverine export and denitrification as the main fates of the mined soil N (ref. 17). The N that was mined from the soil does not represent new annual N inputs to the biosphere, so it is not included in a model of N_2O production based on 4% of annual new N fixation[7]. Nevertheless, soil mining of N was a likely source of increasing N_2O from 1860 to 1960, causing atmospheric N_2O to increase faster than predictions based only on new annual N fixation (Fig. 1a). Direct soil emissions of N_2O may also have been stimulated by tilling native soils, but pulses of N_2O production following initial tillage of native soils are probably short-lived compared with the effects of continuous manure inputs from an expanding livestock herd.

It is also possible that emissions factors could have changed as agricultural technologies changed. However, the fraction of new annual N fixation emitted as N_2O would have to have been 10% in 1950 to fit the historical pattern of increasing atmospheric N_2O (Supplementary Information). It is unlikely that N_2O emission factors would have temporarily risen so high during this period, whereas agricultural expansion, including livestock expansion, that mobilized and depleted soil N fixed in previous decades and centuries is entirely plausible.

Implications for future emissions and mitigation strategies

This analysis demonstrates that any process in the past, present or future that causes either accumulation or depletion of N reservoirs in soils or sediments could alter the ratio of current N_2O emissions to current annual N fixation rates. The importance of current mining of soil N or accumulation of N in sediments in rivers and estuaries is unknown, but it could be affecting sources of N_2O. Given these uncertainties, the sum of N-concentrating processes, primarily fertilizer-N and manure-N production involved in the global human food chain, seems to be a more effective basis for estimating historical and future production of N_2O than basing emission estimates on total global N fixation alone[19]. An improved understanding of downwind and downstream indirect sources of N_2O is also needed, but these cannot be distinguished from direct N_2O sources, obtained using top-down analyses or hybrid analyses such as the one presented here.

These findings have important implications for mitigation strategies, which include increasing efficiency of N use in crop production[20] and improved manure management in animal-production systems[12]. Projected increased use of N fertilizers to support the demands of human food production, including higher per capita meat consumption, is likely to increase N_2O emissions generally, but fertilizer use to support animal-production is likely

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to generate nearly twice as much N_2O as would its use for crops destined for direct human consumption or for biofuels. This is because N_2O is first produced when the fertilizer is applied to the cropland for growing the animal feed grain and then is produced a second time when the manure-N, which has been re-concentrated by livestock consuming the feed, is recycled onto the soil or otherwise treated or disposed of. In contrast, this analysis suggests that fertilizer-N used to grow crops for direct human consumption or for biofuel production, while being a significant increasing source of N_2O that warrants mitigation efforts, will not generate as much N_2O as inferred from the model based on 4% of all newly fixed N (ref. 7). Indeed, although the latter model underestimates the N_2O values for sources needed to match the atmospheric N_2O burden in 1950 and correctly estimates them in 1995, it seems to start overestimating emissions and atmospheric N_2O concentrations after about 2000 (Fig. 1a). Life-cycle analyses demonstrate that human dietary preferences affect the fate of N in food production systems, including the magnitude of direct and indirect N losses to the environment[21]. Hence, knowing the fate of fertilizer-N (crops for livestock feed, direct human consumption or biofuel) may be key to estimating changing N_2O sources, which is also necessary for identifying effective mitigation opportunities.

Methods

I supplemented a previously compiled database[22] of atmospheric N_2O, manure production, fertilizer-N use, legume cultivation and NO_x emissions with new estimates of N_2O production from nylon production, biomass burning and tropical deforestation, and temporal estimates of the stratospheric sink for N_2O, to derive a time-course analysis of sources and sinks of atmospheric N_2O since 1860 (Supplementary Information). To estimate an anthropogenic biological source of N_2O (that is, nitrification and denitrification supported primarily by fertilizer and manure), estimates of industrial and transportation sources must be subtracted from the annual growth of the atmospheric burden of N_2O. Nitrous oxide is a by-product of the production of adipic acid used in making nylon, which began in 1939 and remains a relatively minor contributor to global N_2O production[14] (Fig. 3c). Stationary fossil fuel combustion is also a minor source, as are catalytic converters of automobiles[14] (Fig. 3c). It was also necessary to calculate the change in the atmospheric sink of N_2O, which I refer to as the 'anthropogenic sink'. The stratospheric sink of N_2O has increased from 10.2 Tg N_2O–N per year in pre-industrial times to 11.9 Tg N_2O–N in 2000 (ref. 7). Assuming that this sink is concentration dependent, I scaled this change in the sink to atmospheric N_2O concentrations since 1860. Finally, the anthropogenic source must also have increased by an amount equivalent to the decrease in the natural source of soil emissions due to tropical deforestation[7] (Supplementary Information). For each year, the anthropogenic biological source ('anthro.-bio source') was calculated as follows:

$$\text{anthro.-bio source} = \text{atmospheric growth} - \text{industrial \& transport sources} + \text{anthropogenic sink} + \text{reduced natural tropical forest soil source} \quad (1)$$

The fractions of annual manure-N production (F_m) and annual synthetic fertilizer-N production (F_f) that are released as N_2O were estimated by multiple linear regression, using historical data for manure-N and fertilizer-N production:

$$\text{anthro.-bio source} = F_m{}^* \text{ manure-N} + F_f{}^* \text{ fertilizer-N} \quad (2)$$

The annual estimates for all terms in equations (1) and (2) are provided in Supplementary Table S1.

Received 2 January 2009; accepted 21 July 2009; published online 30 August 2009

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Acknowledgements

I thank the Henry Luce Foundation and the National Science Foundation (Award no. 0443439) for financial support.

Additional information

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