

A reexamination of the impact of anthropogenically fixed nitrogen on atmospheric N₂O and the stratospheric O₃ layer

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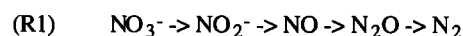
Abstract. The impact of anthropogenic nitrogen fixation on atmospheric N₂O is estimated using the approach of the 1970s, which assumed that some fraction β of anthropogenically fixed nitrogen is rapidly denitrified back to the atmosphere, with a significant fraction α of the end product as N₂O. Appropriate values for β and α are discussed and applied to current anthropogenic nitrogen fixation rates, which are dominated by synthetic fertilizer and crop production. These calculations yield an N₂O source of about 3.5 Tg N/yr associated with anthropogenic nitrogen fixation, which accounts for most of the observed atmospheric N₂O increase of 3–5 Tg N/yr. This simple nitrogen cycle-based approach toward estimating anthropogenic N₂O sources provides a useful check on the more complex approaches employed today, in which emissions from a large number of small, independent sources are estimated by extrapolating measured emissions coefficients. Such approaches can be inconsistent with considerations of the global nitrogen cycle and likely have underestimated the fertilizer N₂O source and double counted other sources. A box model of atmospheric N₂O which assumes an anthropogenic N₂O source proportional to past and projected future rates of anthropogenic nitrogen fixation can reproduce much of the historic growth in N₂O. Continued growth in the rate of anthropogenic nitrogen fixation could increase atmospheric N₂O to 400–500 ppbv by the year 2100. Two-dimensional model calculations suggest that the corresponding increase in stratospheric NO_x would cause a small loss of O₃, which would be superimposed upon a larger recovery due to the phaseout of anthropogenic halocarbons. An increase in N₂O could put more NO_x into the middle and upper stratosphere than supersonic aircraft, although the relevant time scale is considerably longer. To better understand the impact of anthropogenic nitrogen on atmospheric N₂O and the stratospheric O₃ layer, more information is needed about future anthropogenic nitrogen fixation rates, the N₂O yields of denitrification and nitrification, net storage/loss of naturally and anthropogenically fixed nitrogen, and NO_x chemistry in the stratosphere.

1. Introduction

Human disturbance of the global nitrogen cycle has increased to the point where anthropogenic nitrogen fixation now approximately equals total natural fixation on land. Nitrogen fixation is defined as the conversion of inert atmospheric N₂ to compound forms such as NO + NO₂ (NO_x), NO₃⁻, and NH₃/NH₄⁺, which are biologically available. Natural nitrogen fixation is carried out mainly by a variety of bacteria and blue-green algae, both free-living and symbiotically associated with certain plants and fungi [e.g., Paul and Clark, 1989]. NO_x formed by lightning discharges is an additional, relatively small source of naturally fixed nitrogen [e.g., Logan, 1983]. Fertilizer production, which involves the reduction of N₂ to NH₃ at high heat and pressure, supplies the main source of anthropogenically fixed nitrogen. Fossil fuel combustion, in which N₂ is thermally converted to NO_x is another source. In coal combustion, NO_x may result from organically bound N in the fuel itself, but this

can still be considered "anthropogenic" nitrogen fixation, much as CO₂ released by fossil fuel combustion is considered "anthropogenic" carbon [Kinzig and Socolow, 1994]. The increased planting of N₂-fixing crops, also may be generating "anthropogenic" biologically fixed nitrogen [Galloway *et al.*, 1995]. Table 1 shows that total natural and anthropogenic N₂ fixation today are comparable in magnitude.

Fixed nitrogen is returned to the atmosphere through denitrification, a primarily bacterial process. Denitrifying bacteria are a specialized group that can use NO₃⁻ as an electron acceptor under anaerobic or near anaerobic conditions. Denitrifiers reduce NO₃⁻ in a stepwise sequence that ends with N₂ but leaves some fraction incompletely reduced as N₂O [Bryan, 1981].



A small amount of fixed nitrogen can be denitrified to N₂O by another group of bacteria known as nitrifiers (discussed in detail in section 6). Denitrification can also occur through burning of organic N biomass, i.e., pyrodenitrification [Crutzen and Andreae, 1990]. Denitrification and nitrogen fixation eventually must balance one another to prevent the atmosphere from gaining

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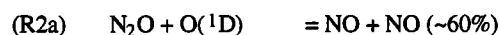
Table 1. Estimated Rates of N₂ Fixation and Denitrification, Taken From Ayers *et al.* [1994]

	Tg N/yr	
Natural N ₂ Fixation		
Land	100	
Ocean	30	(125±40)
Lightning	3	
Anthropogenic N ₂ Fixation		
Fertilizer	90	
Leguminous Crops	40	
Fossil Fuel Combustion	20	
Denitrification		
Land	80-130	
Ocean	50-70	(175±25)

Alternate values for ocean fluxes based on Gruber and Sarmiento [1997] are given in parentheses, since large uncertainties exist in the literature.

or losing N₂, which comprises 78% of the atmosphere. On a geological scale, atmospheric N₂ is regulated by a balance between burial of organic matter in sediments and release by weathering and volcanism, but these nitrogen fluxes are an order of magnitude smaller than those of N₂ fixation and denitrification and probably do not vary greatly on the decadal time scales considered in this paper [Walker, 1977; Holland, 1978].

While N₂ is chemically inert in the troposphere and stratosphere, N₂O plays an important dual role in regulating the Earth's atmosphere. In the troposphere N₂O is a greenhouse gas which has caused about 6% of the increase in trace gas radiative forcing since pre-industrial times [Schimel *et al.*, 1995]. In the stratosphere, N₂O provides the main source of stratospheric NO_x, which is an important regulator of stratospheric O₃.



Concerns were first raised in the 1970s that anthropogenic nitrogen fixation, particularly fertilizer production, could lead to a significant reduction in stratospheric O₃. These concerns were based on the reasoning that anthropogenically fixed nitrogen eventually must be denitrified, with some fraction of the end product going to N₂O [Crutzen, 1974]. Crutzen's paper prompted a lively debate which centered around the large uncertainties in the global N₂O budget, the fraction of anthropogenically fixed nitrogen rapidly denitrified, and the N₂O yield of denitrification [Crutzen, 1976; Liu *et al.*, 1976, 1977; Johnston, 1977; McElroy and Wofsy, 1976; Sze and Rice, 1976; Crutzen and Ehhalt, 1977; Pratt *et al.*, 1977]. Johnston [1977] framed the problem in terms of equation (1):

$$\Delta P_{N_2O} = \Delta N_f \alpha \beta \quad (1)$$

where ΔN_f is the rate of anthropogenic nitrogen fixation, ΔP_{N_2O} is the resulting change in the N₂O source (both in Tg N/yr), β is the fraction of ΔN_f denitrified over a short period of time (e.g., a few years), and α is the fractional N₂O yield N₂O/(N₂+N₂O) of denitrification. Crutzen and Ehhalt [1977] estimated a ΔP_{N_2O}

range of 3-11 Tg N/yr by the early 21st century. In the meantime, direct atmospheric monitoring networks and studies of gases trapped in firn and ice cores have shown that N₂O indeed is increasing in the atmosphere, at a recent rate of about 3-5 Tg N/yr (Figure 1), implying a comparable value for ΔP_{N_2O} [Weiss, 1981; Prinn *et al.*, 1990; Khalil and Rasmussen, 1992; Climate Monitoring and Diagnostics Laboratory (CMDL), 1991-1994; Prather *et al.*, 1994; Machida *et al.*, 1995; Battle *et al.*, 1996; J. Butler, personal communication, 1997].

The studies of the 1970s estimated a linear decrease in O₃ in response to increasing N₂O, based on the results of atmospheric models using the known chemistry at that time [Crutzen, 1974; Grobecker *et al.*, 1975]. The atmospheric N₂O lifetime τ was important to these estimates, since atmospheric N₂O was assumed to respond to the increased source ΔP_{N_2O} on a timescale τ . Future O₃ reductions were estimated to range from < 1% to as much as 20%, depending largely on the values adopted for ΔN_f , α , β , and τ . The discoveries that halogens and HO_x are important catalysts of O₃ destruction in the lower stratosphere and that NO_x mitigates O₃ loss by those cycles forced a dramatic re-evaluation of the impact of increasing N₂O on stratospheric O₃. Models which took the new chemistry into account predicted that increasing N₂O could actually increase stratospheric column O₃ [Turco *et al.*, 1978; Crutzen, 1981]. In the following years, the question of the impact of anthropogenic nitrogen fixation on the ozone layer largely dropped out of the scientific literature.

In the 1990s a new batch of global fertilizer N₂O emissions estimates emerged which came from a much different perspective than the papers of the 1970s and generally did not address the question of N₂O's impact on the O₃ layer. The older estimates had been based on large-scale input/output issues concerning the global nitrogen cycle, but had lacked specific information on fertilizer emission yields. In contrast, the new studies based their

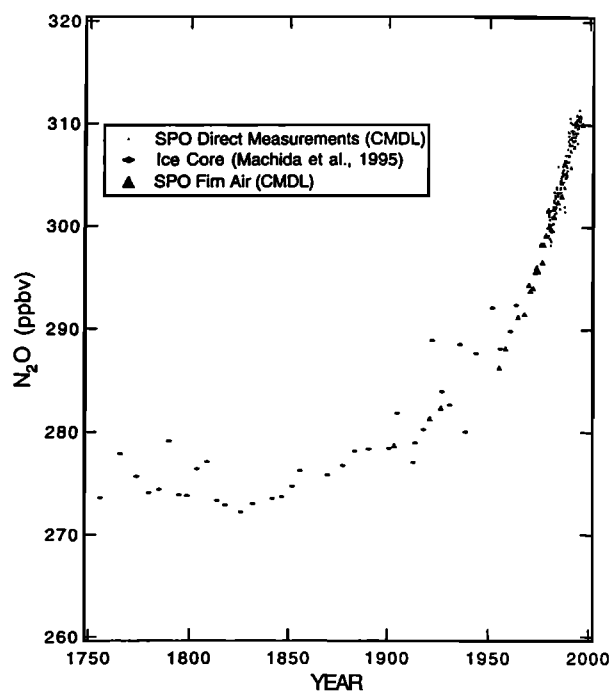


Figure 1. Growth in atmospheric N₂O from south pole ice core data, firn data and direct atmospheric measurements [Machida *et al.*, 1995; Battle *et al.*, 1996; CMDL, 1991-1994, J. Butler, personal communication, 1997].

estimates on global extrapolations of measured N_2O emissions from fertilized fields. Often, the calculations used highly resolved ($1^\circ \times 1^\circ$) geographical databases of fertilizer consumption [Mathews, 1994; Bouwman *et al.*, 1995], and distinguished between various types of fertilizers, such as ammonium nitrate and urea [Eichner, 1990; Mathews, 1994]. Because the measured emission coefficients captured mainly short term N_2O emissions directly from the field, the resulting global estimates were often relatively small, ranging from 0.01 to 2.2, with mean values generally less than 1 Tg N/yr. This was true even when the studies considered only emissions coefficients that had been measured over at least one full year [Bouwman *et al.*, 1995] or when the measured coefficients were doubled in an attempt to account for longer term fates fertilizer [Eichner, 1990; Bouwman *et al.*, 1995]. These 1990s studies suggested that fertilizer might be a modest or even relatively small source of the observed atmospheric N_2O increase. Some more recent estimates, which once again attempt to account for all short and long term fates of agricultural nitrogen, have moved toward much larger values. Mosier *et al.* [1997], for example, estimate an agricultural N_2O source of 6.3 (1.2-17.9) Tg N/yr. Notably, the mean and upper range of this estimate significantly exceed the observed atmospheric increase of 3-5 Tg N_2O -N/yr

Prevailing thoughts about the cause of the atmospheric N_2O increase have evolved over time. The papers of the 1970s, which were written when only sketchy evidence of the atmospheric increase existed, focused on fertilizer as the main potential anthropogenic N_2O source. In the 1980s, attention shifted to direct production of N_2O during fossil fuel combustion. For many years, until the discovery of artefact N_2O production in flask samples [Muzio and Kramlich, 1988], the direct fossil fuel source was overestimated by an order of magnitude, perhaps diverting attention from the need to identify other sources. The common view today is that the atmospheric N_2O increase is caused by many different small anthropogenic sources, most of which are difficult to quantify [Prather *et al.*, 1994]. The current list of proposed anthropogenic sources has expanded to include adipic acid (used for nylon) production, nitric acid production, automobiles, power plants, forest, firewood, and agricultural waste burning, trash incineration, enhanced soil emissions following grassland and savanna burning, manure, fertilizer, atmospheric deposition, land use change, biological N_2 fixation, groundwater, sewage, mineralization of organic soils, eutrophication in coastal and fresh waters, and global warming [e.g., Ronen *et al.*, 1988; Khalil and Rasmussen, 1989, 1992; Bouwman *et al.*, 1995; Mosier *et al.*, 1997]. The industrial and fossil fuel sources at the beginning of the list have been estimated somewhat accurately at 1.2 ± 0.6 Tg N/yr [Prather *et al.*, 1994]. Of this, an estimated 0.4-0.6 Tg N/yr results from emissions associated with adipic acid production, which may soon be phased out by the manufacturers. In contrast, the direct fossil fuel source may become more important in the future due to increasing energy consumption and the expanding use of catalytic converters, which increase the N_2O yield from fuel combustion [Dasch, 1992]. The remaining sources result from anthropogenic impacts on microbial activity and pyrodenitrification. Most of these sources are associated with agriculture and many reflect either short or long term fates of fertilizer. The magnitude of these sources remains highly uncertain.

The long list presented above prompts the question of whether the subdivision of anthropogenic microbial N_2O production into numerous small, independent sources actually leads to an accurate total source estimate. A useful check on this reductionist

approach involves a more holistic partitioning of the anthropogenic source into the following categories: (1) direct production from industrial processes, and (2) modified microbial (or pyrodenitrification) emissions resulting from (a) anthropogenic nitrogen fixation, and (b) changes in N_2O yields and/or rates of natural N cycling. This paper will focus on the contribution of category 2a to the increase in atmospheric N_2O . We will estimate a collective N_2O source associated with anthropogenic N_2 fixation using the nitrogen cycle-based approach of the 1970s, and will examine the potential effect of that N_2O on the stratospheric O_3 layer. Our goals are (1) to provide a check on the agricultural N_2O source estimated by extrapolating measured emission coefficients, (2) to quantify the impact of increased N_2O on the O_3 layer based on updated information, and (3) to offer an alternative perspective on the atmospheric N_2O increase by reexamining the subject in its historical context. In reapplying the 1970s approach, we take advantage of 20 years of progress in the understanding of the N_2O budget, the nitrogen cycle, and stratospheric chemistry.

2. N_2O Lifetime τ and Background N_2O Sources

Before estimating the N_2O source associated with anthropogenic nitrogen fixation, we will review the past and present understanding of the natural cycle of N_2O production and destruction. In the classical view of the N_2O cycle (Figure 2), N_2O is produced mainly at Earth's surface by microbial denitrification and nitrification. N_2O destruction is thought to occur almost entirely in the stratosphere by photolysis and oxidation, although a soil sink of unknown significance is sometimes discussed [Ryden, 1981; Cicerone, 1989; Donoso *et al.*, 1993; Bouwman and Taylor, 1996] and some regions of the ocean may also be sinks [Elkins *et al.*, 1978; Cohen and Gordon, 1979; Nevison *et al.*, 1995]. The atmospheric N_2O lifetime τ is regarded as a measure of the magnitude of the N_2O sink relative to the total atmospheric burden and is estimated today at 120 ± 30 years [Prather *et al.*, 1994]. N_2O 's long lifetime implies that the

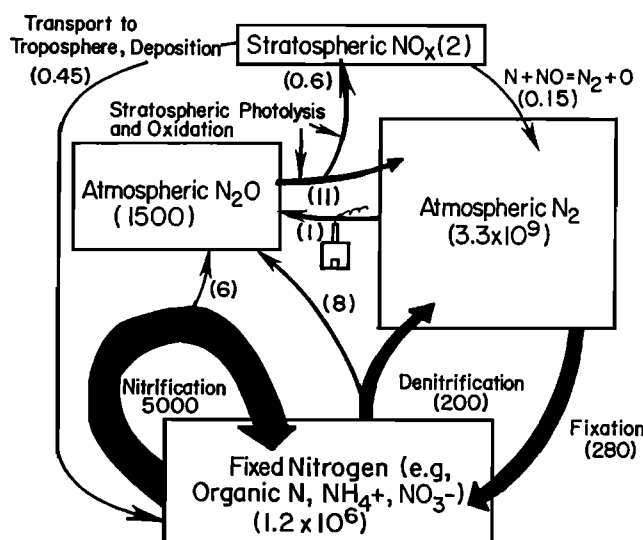


Figure 2. Cycle in which atmospheric N_2O is produced from and converted back to N_2 . Estimates of present-day pools and fluxes (in Tg N and Tg N/yr) are based on Najjar [1992] and Ayers *et al.* [1994] and the N_2O yields α and α_{nit} discussed in this paper. Note that Ayers *et al.* assume a large net uptake of anthropogenic N, in contrast to the discussion in section 4.

stratospheric sink still more or less balances the natural background source. Given the total atmospheric burden of 1500 Tg N₂O-N, a 120 ± 30 year lifetime requires a natural source of 9-16 Tg N/yr.

The efforts of the 1970s to estimate the impact of fertilizer on N₂O and O₃ were hampered by major gaps in the understanding of τ and of background N₂O sources. The papers of that time commonly assumed a lifetime of 10-20 years, which was based on N₂O's observed tropospheric variability of up to 80 ppbv [Junge, 1974]. This conflicted with the lifetime of >100 years calculated based on the known stratospheric sinks of N₂O [McElroy and Wofsy, 1976] and led to the hypothesis of an unknown tropospheric sink. Advances in the measurement of atmospheric N₂O due to improvements in calibration [Connell *et al.*, 1980] and to monitoring networks started in the late 1970s now have revealed that N₂O is very well mixed in the troposphere. Surface N₂O varies by only a few ppbv relative to a global mean concentration of 312 ppbv [Weiss, 1981; Prinn *et al.*, 1990; CMDL, 1991-1994]. Lifetime calculations today commonly involve coupling atmospheric models to satellite data to estimate N₂O loss rates or mass fluxes, with the major uncertainty revolving around the distribution of stratospheric N₂O [Minschwaner *et al.*, 1993]. Recent calculations of this sort have tended toward a longer lifetime [Gettelman *et al.*, 1997], although an independent technique based on tracer correlations gives a lifetime of just 112 ± 21 years [Volk *et al.*, 1997].

The 1970s N₂O budget was further clouded by the huge ocean source estimated at 85 Tg N/yr [Hahn, 1974]. A much smaller ocean source of 1.4-6.4 Tg N/yr, attributed to microbial production, is now estimated based on extrapolations of measured sea surface supersaturations and modeled air-sea transfer coefficients [Butler *et al.*, 1989; Watson *et al.*, 1990; Nevison *et al.*, 1995]. The natural soil N₂O source has been estimated independently at about 6 - 7 Tg N/yr (± ~50%), coming mainly from the tropics, based on various models and extrapolations of measured emissions coefficients [Prather *et al.*, 1994; Bowman *et al.*, 1995; Potter *et al.*, 1996]. The microbial soil and ocean N₂O sources of 6-7 ± ~50% and 1.4-6.4 Tg N/yr, respectively, yield a combined background source of about 10 ± 5 Tg N/yr, more or less in balance with the 9-16 Tg N/yr source inferred from the stratospheric sink, within the uncertainties.

A number of recent papers have challenged the classical view of N₂O production and destruction shown in Figure 2. These papers have hypothesized new atmospheric sources and sinks of N₂O on the basis of modeling studies, discrepancies in isotopic measurements, and in some cases, a perceived need to balance the N₂O budget. Johnston *et al.* [1995] and T. Rahn and M. Wahlen (Stable isotopes in stratospheric nitrous oxide, submitted to *Science*, 1997) have shown that the measured isotopic signatures of N₂O in the lower stratosphere appear inconsistent with the measured isotopic fractionations of the two known N₂O loss mechanisms photolysis and oxidation, suggesting an as yet undiscovered stratospheric sink for N₂O. Dentener and Crutzen, [1994], Prasad [1994], and McElroy and Jones [1996] have proposed a variety of new atmospheric sources and sinks of N₂O that may be significant relative to the known sources and sinks. Recent laboratory studies have shown that some of these proposed sources are unlikely to be important in the atmosphere [Hwang *et al.*, 1997]. In general, the new hypothesized atmospheric sources and sinks of N₂O are not well understood, making their relevance to the global N₂O budget and to the analysis presented in this paper difficult to assess at this point.

The observed increase in atmospheric N₂O (Figure 1) suggests that the N₂O source has increased by at least 30% above its

background level. As discussed earlier, direct industrial production of N₂O can only explain about 20-30% of the increase. The remainder likely has been caused by changes in microbial N₂O production or pyrodenitrification associated with disturbances to the global nitrogen cycle. These disturbances have been dominated by a large anthropogenic increase in the rate of nitrogen fixation. In the following sections, we will use equation (1) from the 1970s to estimate the increase in the N₂O source associated with anthropogenic nitrogen fixation. First, we will discuss the three inputs to equation (1) individually, beginning with ΔN_f , the rate of anthropogenic nitrogen fixation.

3. Anthropogenic Nitrogen Fixation ΔN_f

The studies of the 1970s focused on synthetic fertilizer as the main contributor to anthropogenic N fixation. Our discussion will also focus mainly on fertilizer, although we will also consider ΔN_f associated with fossil fuel combustion and leguminous crops. Fertilizer use began on a large scale after World War II and grew rapidly thereafter (Figure 3), enabling a rapid expansion of agricultural productivity during the Green Revolution. Based on the annual 6% growth rate of fertilizer use in the 1970s, the N₂O studies of that time predicted a global fertilizer consumption rate of 200 TgN/yr by the year 2000 [Hardy and Havelka, 1975]. In reality, the growth in fertilizer consumption slowed down in the 1980s to 3.3-3.5%/yr [Mathews, 1994; Galloway *et al.*, 1995], reaching a maximum of 80 Tg N/yr in 1989, and actually dropping in recent years to a minimum of 73 Tg N/yr in 1993-1994 (Figure 3). Much of the recent global decrease occurred because of the collapse of governments in the former Soviet Union and Eastern Europe. Fertilizer consumption is still increasing rapidly in many regions,

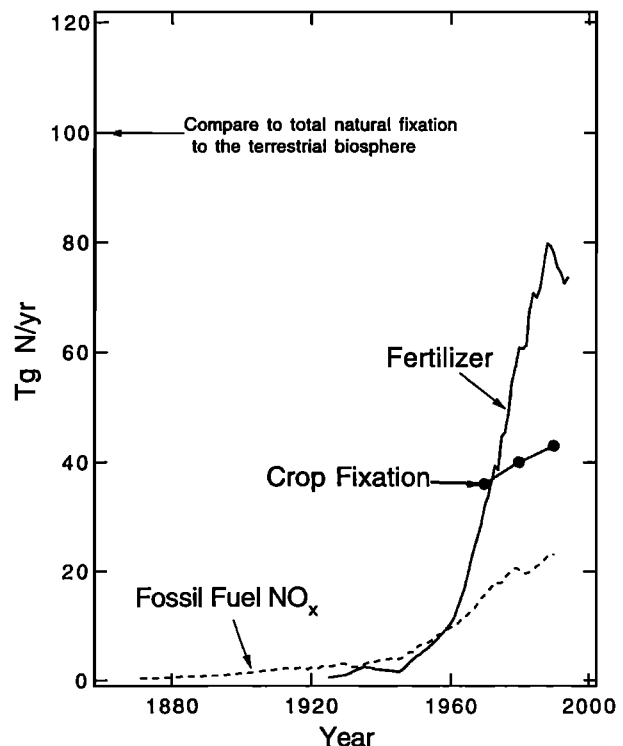


Figure 3. Growth in anthropogenic nitrogen fixation. Global fertilizer consumption is estimated from FAO [1995] and Smil [1990]. Fossil fuel NO_x production is taken from Müller [1992]. Crop N₂ fixation is based on Galloway *et al.* [1995].

particularly in developing countries in the tropics [Food and Agricultural Organization (FAO), 1995]. Over the decade from 1980 to 1990, per capita fertilizer consumption in developing countries increased from about 7 to 10 kg N/person/yr, compared to a relatively static consumption rate of 30 kg N/person/yr in developed countries [Kroeze, 1994]. The most recent FAO data from 1994-1995 show a small renewed increase in global fertilizer consumption to 74 Tg N/yr.

Predicted trends in fertilizer consumption have varied widely. Near-future growth rates (to 2020) have been estimated at 1.5-1.8%/yr, with much of the growth occurring in the tropics [Galloway et al., 1995; Matson et al., 1996]. In the year 2100, projected fertilizer consumption rates range from 164 Tg N/yr, corresponding to a growth rate of 0.14%/yr from 2050 to 2100 (inferred from Leggett et al. [1992]) to 280 Tg N/yr, corresponding to growth rates of about 0.8%/yr from 2025 to 2100 [Bouwman et al., 1992; Kroeze, 1994]. Obviously, the confidence in future scenarios decreases as the time horizon increases.

Future fertilizer consumption rates depend on a number of difficult-to-predict factors, including population growth, improvements in fertilizer use efficiency, and changes in dietary structure. According to current trend scenarios, the world population will double to 11 billion people by the year 2100, implying an inexorable rise in food demand and thus fertilizer use. However, A.R. Mosier et al. (Mitigating agricultural emissions of nitrous oxide, submitted to *Climatic Change*, 1997) estimate that improvements in efficiency could significantly reduce both fertilizer use for a given amount of food production and N₂O emissions per unit fertilizer. These improvements include better matching the nitrogen supply with fertilizer demand, retaining more crop residue and manure on the production site, using advanced fertilization techniques such as controlled release fertilizers and nitrification inhibitors, and optimizing tillage, irrigation, and drainage. (Many of these measures may also help reduce N₂O emissions associated with the erosion of naturally fixed nitrogen from cultivated land discussed later.) Improved dietary efficiency also could reduce fertilizer consumption substantially. Because of the trophic levels in the food chain, diets centered around fertilized grain-fed meat require more fertilizer per capita than diets centered around fertilized grain. The increased use of fertilized feed grains in place of traditional fodder such as grass, crop waste, and kitchen scraps has driven much of the rapid historic growth in fertilizer consumption. Currently about 30% of the total world crop is grown for livestock feed. Regionally, this percentage can be as high as about 50% in the U.S. and as low as 1-2% in India and many African countries (estimated from FAO [1992]; Durning and Brough [1992]). Similar percentages may apply to total nitrogen fertilizer consumption, although the exact numbers will depend on differential crop fertilization rates.

NO_x production during fossil fuel combustion has increased since the 19th century due to increasing population growth and energy consumption, and is currently estimated at about 20-23 Tg N/yr (Figure 3) [Müller, 1992; Holland et al., 1997]. The IS92a scenario predicts an approximate tripling in fossil fuel NO_x production to 75 Tg N/yr by 2100 [Leggett et al., 1992]. Most of the growth is expected to occur in developing countries, where current per capita production rates are about 7 times less than those in developed countries [Kroeze, 1994].

The anthropogenic nitrogen fixation associated with increased planting of leguminous crops is currently estimated at 44 (32-53) Tg N/yr [Ayers et al., 1994; Galloway et al., 1995]. The majority

of this ΔN_f term is due to soybeans and forage crops such as clover and alfalfa commonly fed to livestock [Galloway et al., 1995]. Estimates of ΔN_f associated with leguminous crops are considerably more uncertain than those associated with fertilizer and fossil fuel NO_x. These estimates also may not adequately account for reductions in natural biological N₂ fixation, due either to physical displacement and degradation, or to chemical suppression by nitrogen (particularly NH_x) deposition [Eisele et al., 1989]. The temporal trends in ΔN_f associated with leguminous crops are not well known. Galloway et al. [1995] estimate about a 20% increase from 1970 to 1990. In the future planting of legumes likely will continue to increase, especially if bio-engineered N₂-fixing crops are used in place of synthetic fertilizer.

4. Fraction β of Anthropogenic Nitrogen Quickly Denitrified

To evaluate the impact on N₂O production of the large ΔN_f terms discussed above, we need to know what fraction of anthropogenically fixed nitrogen is quickly denitrified back to the atmosphere and what fraction is stored in long term reservoirs. The studies of the 1970s examined the fate of anthropogenic nitrogen in terms of β , the fraction denitrified back to the atmosphere on a short time scale of a few years. These studies estimated β to range anywhere from 1 to nearly 0 [Crutzen, 1976; Liu et al., 1976; Sze and Rice, 1976]. According to equation (1), if β is large the increase in denitrification and thus N₂O production will be maximized. To estimate β , we begin by mapping out the probable fate of 100 units of synthetic fertilizer nitrogen (Figure 4), including rapid volatilization (10%) to N₂O, N₂, NO_x, and NH₃, and other gases, immobilization into soil organic matter (SOM) (20%), leaching (30%), and uptake into crops (40%). The fraction of fertilizer apportioned to each of

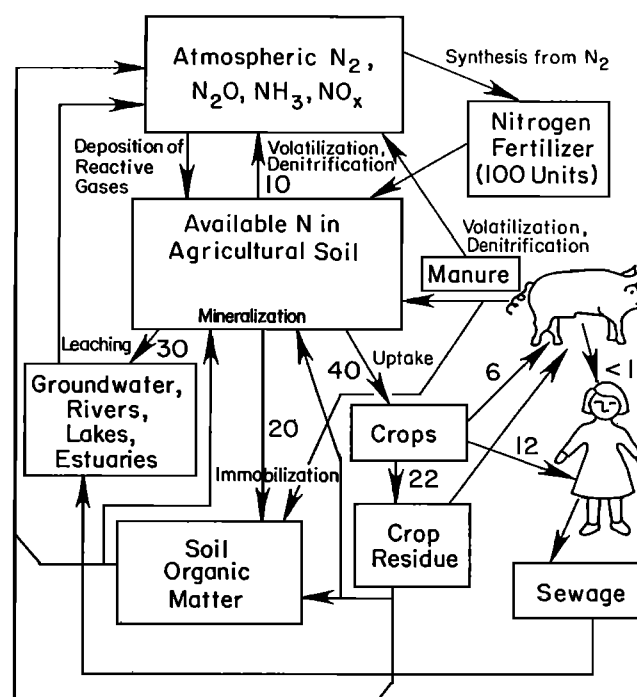


Figure 4. The probable fate of 100 units of fertilizer nitrogen. Estimates reflect best guess global average values based on FAO [1992] and Mosier et al. [1997].

these fates reflects best guess global average values, although the partitioning may vary widely in individual agricultural systems (estimated based on *Mosier et al.*, [1997]). Crops, in turn, may be consumed by livestock (15%) and humans (30%), eventually becoming manure or sewage. About 55% of crop biomass becomes residue or waste which can meet a variety of fates, including consumption by livestock, decomposition on the field, and burning. The partitioning of the fate of crop nitrogen in Figure 4 is estimated from world averages in the *FAO* [1992].

Of the 30 units of fertilizer leached into aqueous systems in Figure 4, the majority, probably at least 75% or 22 units, is denitrified relatively quickly back to the atmosphere. This assumption is based on studies showing that about 50% of nitrogen entering rivers is denitrified within the river, and another 25% is denitrified within receiving lakes and estuaries [*Seitzinger*, 1988; *S.P. Seitzinger and C. Kroeze*, Estimates of the spatial distribution of N inputs, nitrous oxide production and denitrification in freshwater and coastal marine ecosystems, submitted to *Global Biogeochem. Cycles*, 1997; hereinafter referred to as submitted paper]. The remaining 25% may be incorporated into bottom sediments or organic matter in lakes and estuaries, but much of this is likely to be quickly remineralized and denitrified [*Najjar*, 1992; *S.P. Seitzinger and C. Kroeze*, submitted paper, 1997]. Some authors have suggested that groundwater may be an important long-term reservoir for anthropogenic nitrogen, based on the elevated NO_3^- levels measured in groundwater receiving anthropogenic N inputs [*Ronen et al.*, 1988; *Galloway et al.*, 1995]. However, the fraction of nitrogen added to groundwater is probably small compared to that added to rivers [*Vitousek et al.*, 1997 and references therein].

Of the 20 units of fertilizer N immobilized into SOM in Figure 4, $\leq 25\%$ will enter fast or labile SOM pools with turnover times of a few years, $\geq 65\%$ will enter slow pools with decadal turnover times, and only about 10% or less will enter recalcitrant pools with thousand year turnover times [*Parton et al.*, 1988; *Schimel et al.*, 1994]. This suggests that about 5 units of fertilizer immobilized into SOM will be denitrified back to the atmosphere within a few years. Here, we assume that all nitrogen stored in labile SOM undergoes denitrification rather than being recycled into plant matter, on the basis of the relatively inefficient use of nitrogen in agricultural systems [*Howarth et al.*, 1996; *Holland et al.*, 1997]. We note that turnover times for SOM are generally shorter in the tropics, where much of the future growth in fertilizer use will occur [*Mathews*, 1994]. Even in temperate zones, the large fraction of anthropogenic N sequestered into the slow pool of SOM will not be indefinitely removed from the atmosphere, but will be returned on decadal time scales.

The 40 units of fertilizer taken up into crops in Figure 4 has a low potential for long term storage, since crops are generally harvested on an annual basis. If we assume that half of the 22 units of crop residue in Figure 4 plus some fraction of the manure, say 1 unit, is incorporated into SOM, with about 75% partitioned to slow and recalcitrant pools as discussed above, we roughly estimate that about 10 units of crop N has some potential for long term storage, while the remaining 30 units is likely to be denitrified quickly back to the atmosphere.

Finally, of the 10 units of fertilizer quickly volatilized in Figure 4, less than 25% is likely to be transported and deposited on natural ecosystems capable of long term N storage [*Holland et al.*, 1997; *Townsend et al.*, 1996], with the remaining ~8 units likely to be denitrified within a few years. Figure 4 illustrates why the fertilizer estimates of the 1990s discussed in section 1,

which were based on global extrapolations of the N_2O component of the direct volatilization pulse from agricultural fields, probably have underestimated the fertilizer N_2O source. Simply put, these estimates neglect most of the longer term fates of fertilizer. Figure 4 shows, furthermore, that a mere doubling of measured direct emission coefficients [*Eichner*, 1990] is unlikely to adequately account for the other fates.

To summarize our discussion of the fate of fertilizer nitrogen in Figure 4, the main opportunities for long-term N storage include retention in groundwater, immobilization into SOM, and uptake into natural ecosystems of volatilized NH_3 and NO_x which have been transported and redeposited away from agricultural land. Adding our estimates above (22 units of leached N, 5 units of N immobilized into labile SOM, 30 units of N taken up into crops, and 8 units of rapidly volatilized N) we calculate that about 65 out of 100 units of fertilizer N is returned to the atmosphere within a few years, i.e., $\beta = 0.65$. We attempt to account for the uncertainty in β by estimating an error of ± 0.15 , which yields a range of values for β from 0.5-0.8. For lack of better information, we will assume the same β range for anthropogenic nitrogen associated with N_2 -fixing crops.

The fate of anthropogenic NO_x produced during fossil fuel combustion is illustrated in Figure 5, based on the study of *Holland et al.* [1997], who reported the distribution of nitrogen deposition predicted by a variety of chemical transport models. All the models predicted that nearly half of fossil fuel NO_x is deposited on the ocean. The fate of this nitrogen is not well known. Much of it probably is quickly denitrified, but some unknown fraction may be stored in deep water in either organic or inorganic form with a very long residence time [*Galloway et al.*, 1995]. Of the remaining fossil fuel nitrogen, about half is deposited on agricultural land, which, as discussed above, has a limited potential for long-term storage, and the other half is deposited on various classes of natural land cover. Only about 5% of all fossil fuel N is deposited on natural forests, which are the most capable of sequestering nitrogen into vegetation and soil pools with long turnover times. In some natural ecosystems, deposition of excessive levels of anthropogenic nitrogen, i.e., acid

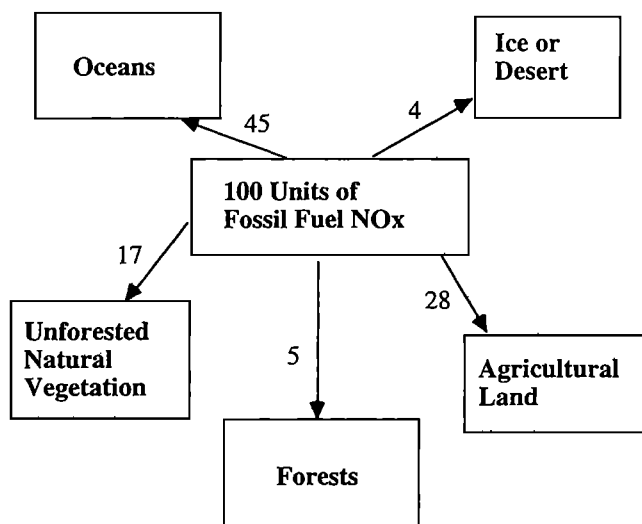


Figure 5. The probable fate of 100 units of NO_x produced by fossil fuel combustion. Estimates are based on the averaged predicted distributions of five chemical transport models [*Holland et al.*, 1997].

rain, may cause damage rather than promote growth, leading to net N loss [Aber *et al.*, 1989; Schulze, 1989]. We estimate β for fossil fuel NO_x to range from about 0.8, assuming accumulation and storage of nitrogen only in the 22 units of forested and unforested natural vegetation, to about 0.3, assuming the additional accumulation and storage of the 49 units of nitrogen deposited on ocean, deserts, and ice.

The fate of anthropogenic nitrogen is often difficult to separate from the fate of naturally fixed N that has been anthropogenically perturbed. We will digress here from our discussion of β to address the larger question of whether Earth's fixed N reservoirs are losing or gaining mass, or in other words whether the atmosphere as a whole is gaining or losing N_2 . A direct answer to this question is probably not possible, since the likely change is on the order of one part per hundred million relative to the vast atmospheric reservoir of N_2 . We must turn instead to indirect evidence for loss and gain of fixed nitrogen, borrowing largely from studies of the carbon cycle, which is closely linked to the nitrogen cycle. Some nitrogen cycle studies have estimated net storage of more than half of anthropogenically fixed nitrogen, corresponding to $\beta < 0.5$, with no concurrent loss of naturally fixed nitrogen [Ayers *et al.*, 1994; Galloway *et al.*, 1995]. We question this assumption, based on the large losses of naturally fixed nitrogen that have occurred from cultivated and deforested land. Historically, cultivated land has experienced an average loss of about 30% of its soil organic carbon, mainly occurring within the first few years of cultivation [Davidson and Ackerman, 1993]. Soil organic nitrogen levels also have been observed to decline significantly after cultivation, even with the addition of nitrogen fertilizer [Parton *et al.*, 1988], with associated enhancements in gaseous N losses. Indeed, some model studies and observations have suggested that changes in soil texture and soil moisture dynamics due to tillage of agricultural land can cause greater increases in denitrification rates and N_2O fluxes than the addition of anthropogenic fertilizer itself [Li *et al.*, 1996; W.J. Parton *et al.*, Generalized model for N_2 and N_2O production from nitrification and denitrification, submitted to *Global Biogeochemical Cycles*, 1997; hereinafter referred to as submitted paper]. Cultivation losses may be particularly high from N-rich organic soils [Mosier *et al.*, 1997; Vitousek *et al.*, 1997]. Net loss of naturally fixed nitrogen can also occur through deforestation. Deforestation of tropical ecosystems is considered to be a source of atmospheric CO_2 [Houghton, 1990; Schimel *et al.*, 1995]. Since organic carbon and nitrogen are linked by a characteristic C:N ratio, deforestation most likely also has caused nitrogen loss from these ecosystems. We roughly estimate the losses of (largely natural) N from soil cultivation and tropical deforestation at 10-15 and 15-55 Tg N/yr, respectively. (Deforestation losses are estimated from Schimel *et al.*'s [1995] estimate of 1.6 ± 1 Pg of carbon lost because of tropical land use change. Assuming 80% is lost from vegetation with an average C:N ratio of 100 [Vitousek *et al.*, 1988] gives 5-20 Tg N/yr. The 20% assumed lost from soil organic matter, at C:N = 15 [Post *et al.*, 1985], gives 10-35 Tg N/yr. Soil losses from cultivated ecosystems are estimated based on Esser [1987]. We assume a global soil organic carbon pool of 1500 Pg C, of which 6% is cultivated between 1860 and 1981, with an average loss of 30% [Davidson and Ackerman, 1993] at C:N = 15-20 [Post *et al.*, 1985], yielding an average loss of 10-15 Tg N/yr.) Compared to the 6-11 Tg N/yr of N storage in natural (mainly temperate) ecosystems estimated by the model study of Holland *et al.* [1997], these estimates suggest that uptake of anthropogenic and mobilized natural N into temperate soil and vegetation reservoirs is unlikely to compensate for the loss of

naturally fixed nitrogen from cultivated and deforested land, even if some fraction of the lost nitrogen is redistributed and taken up into other fixed N reservoirs. Quantitative estimates of uptake into additional fixed N reservoirs such as groundwater and the deep ocean are needed to fully answer the question of the net change in atmospheric N_2 . We suggest that the sign of the change is not necessarily negative.

Returning to our discussion of equation (1), we adopt values of $\beta = 0.5-0.8$ for anthropogenically fixed nitrogen associated with fertilizer and legumes, and $\beta = 0.3-0.8$ for NO_x produced by fossil fuel combustion. To better quantify β , more information is needed about anthropogenic N residence times in groundwater, ocean, and soil and vegetation reservoirs. We acknowledge that the probable net losses of nitrogen from cultivated and deforested land discussed above represent potential N_2O sources that are not represented by equation (1). Instead they fall into our proposed category 2b, i.e., microbial (and pyrodenitrification) N_2O emissions associated with changes in cycling rates and/or N_2O yields of naturally fixed N. Such emissions are discussed in more detail in section 8 from the perspective that they may represent displacements and/or temporary increases in N_2O production rather than long-term net sources.

5. N_2O Yield α of Denitrification

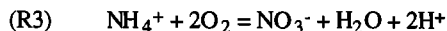
The N_2O yield of denitrification α ($= \text{N}_2\text{O}/(\text{N}_2 + \text{N}_2\text{O})$) is the final input to equation (1). Some studies of the 1970s considered N_2O yields from soils as high as 0.3-0.5. However, typical values ranged from 0.05-0.1 with a best guess of 0.06, based on the recommendation of the *Council for Agricultural Science and Technology* [1976]. The new information collected in the meantime has not dramatically narrowed down the estimate of α in soils. In fact, Weier *et al.* [1993], who measured N_2O denitrification yields ranging from $\ll 0.01$ to > 0.9 , concluded that an average yield could not be defined due to the natural variability of the soil environment. Some authors in the 1970s raised concerns that the N_2O yield from soils of anthropogenically fixed nitrogen might differ from that of naturally fixed nitrogen [Sze and Rice, 1976; McElroy and Wofsy, 1976]. N_2O yields in general are known to increase with low pH, which inhibits the conversion of N_2O to N_2 , and high ratios of NO_3^- to organic carbon [e.g., Sahrawat and Keeney, 1986; Seitzinger, 1988; Weier *et al.*, 1993]. Both of these conditions are likely to be found in fields receiving nitrate fertilizer. Very high N_2O yields also may occur in fertilized soils in the tropics, where much of future fertilizer growth is likely to occur [Keller and Matson, 1994; Matson *et al.*, 1996]. Some biogeochemical models are beginning to predict how soil moisture, agricultural practices etc. affect N_2O yields [Li *et al.*, 1992; W.J. Parton *et al.*, submitted paper, 1997].

The studies of the 1970s had little information about N_2O yields from aquatic environments, where Figures 4 and 5 suggest nearly half of anthropogenic N denitrification occurs. The available measurements today suggest N_2O denitrification yields of $\sim 0 - 0.06$, with a mean value of about 0.005 [Seitzinger, 1988]. These yields are low compared to soil yields, probably due to the relatively high degree of anaerobiosis in the aquatic environment. Decreasing anaerobiosis in general tends to increase N_2O yields from denitrification, while at the same time slowing the overall rate of denitrification [e.g., Joergensen *et al.*, 1984]. Taking N_2O denitrification yields of 0.06 and 0.005 for soil and aquatic environments, respectively, and weighting by the respective fractions of anthropogenic nitrogen subject to each process

(assumed, based on Figures 4 and 5 to be about 50% each), we estimate a global value for α of about 0.03, with a reasonable range probably lying somewhere between 0.01 and 0.06.

6. Nitrification as a Source of N₂O

A twist on the topic of anthropogenic N₂O which generally was not incorporated into the studies of the 1970s, and which equation (1) neglects, is that N₂O may be produced by nitrifying bacteria as well as denitrifying bacteria [Bremner and Blackmer, 1981 and references therein]. Rather than returning fixed nitrogen to the atmosphere, nitrifying bacteria oxidize NH₄⁺ released from the mineralization of organic matter to NO₃⁻:



NO₃⁻ can then be recycled back through plants and organic matter in a loop that may repeat itself 15 times or more in soil and over 100 times in the ocean before NO₃⁻ is finally lost to the atmosphere through denitrification [Ayers *et al.*, 1994]. Generally, NO₃⁻ is recycled much more efficiently in natural ecosystems than in anthropogenically perturbed systems, where the loop may only repeat about 5 times [Ayers *et al.*, 1994]. During nitrification, in what has been described as a "leaky pipe," a small amount of N₂O may be produced [Firestone and Davidson, 1989; Davidson, 1991]. The global nitrification flux is an order of magnitude greater than the denitrification flux, but the N₂O yield of nitrification α_{nit} in soils is generally only about 0.001-0.002 of the NH₄⁺ substrate [Lipschultz *et al.*, 1981; Joergensen *et al.*, 1984; Sahrawat and Keeney, 1986]. In the oceans α_{nit} is about 0.001 [Najjar, 1992; Nevison *et al.*, 1995]. In ocean depth profiles, N₂O is commonly anticorrelated to oxygen and positively correlated to NO₃⁻ [Yoshinari, 1976], suggesting that N₂O production is associated mainly with the mineralization and nitrification of fixed nitrogen in organic matter, although uncertainties about the importance of denitrification remain [Yoshinari *et al.*, 1997]. In rivers and estuaries receiving high levels of anthropogenic N runoff, α_{nit} may be as high as 0.005, i.e., essentially equal to the α for denitrification in aquatic environments [S.P. Seitzinger and C. Kroeze, submitted paper, 1997; S. Seitzinger, personal communication, 1996].

The error in equation (1) due to the neglect of N₂O produced during nitrification is probably relatively small. We demonstrate this in Table 2 by multiplying estimated nitrification and denitrification fluxes by the respective N₂O yields α and α_{nit} discussed above. The nitrification and denitrification rates in Table 2 are taken mainly from Ayers *et al.* [1994], who estimated natural base rates and anthropogenic additions to those rates. These rates have a high uncertainty and are presented here mainly for illustrative purposes. Ayers *et al.* do not predict any erosion of the natural rates in response to land use changes, in disagreement with our discussion in section 4. Despite its large uncertainties, Table 2 conveys the point that anthropogenic nitrogen affects denitrification considerably more than nitrification. Anthropogenic nitrogen additions increase nitrification by only ~10% on land and by < 1% in the ocean because the pools of naturally fixed N involved in this process are large compared to the added N. In contrast, anthropogenic additions increase denitrification by ~60% on land and ~40% in the ocean, since anthropogenic nitrogen fixation (and thus denitrification) is comparable in magnitude to natural fixation, as we have emphasized in this paper.

Table 2. Estimate of Natural and Anthropogenic N₂O production from Nitrification and Denitrification

	Flux, Tg N/yr	N ₂ O Yield	N ₂ O Source, Tg N/yr
Land			
Nitrification	1300 + (100)	0.0015	2 + (0.15)
Denitrification	80 + (50)	0.06	5 + (3)
Ocean			
Nitrification	4000* + (20)	0.001	4 + (0.02)
Denitrification [†]	50+(20)	0.005	0.25 + (0.1)

Values in parentheses are estimated additional anthropogenic fluxes. Flux estimates are taken from Ayers *et al.* [1994].

*from Najjar [1992].

[†]The tendency of recent studies [e.g., Codispoti, 1995; Gruber and Sarmiento, 1997] to revise the global ocean denitrification flux upward to 200 Tg N/yr or more suggests a more significant associated N₂O source of ~ 1 Tg N/yr. However, since denitrifying bacteria can also consume dissolved N₂O [Elkins *et al.*, 1978; Cohen and Gordon, 1979], which originates in large part from equilibration with the atmospheric reservoir, the magnitude and even the sign of marine denitrification's contribution to the N₂O budget are highly uncertain.

The importance of N₂O production from nitrification may be greater than Table 2 suggests if the N₂O yield α_{nit} of anthropogenic N is significantly higher than that of natural N, such as in the polluted rivers and estuaries discussed by S.P. Seitzinger and C. Kroeze, (submitted paper, 1977). Increases in nitrification due to anthropogenic nitrogen additions also might be important in the future on a long timescale if these additions were to cause a significant buildup in the stores of soil and ocean fixed nitrogen [Liu *et al.*, 1976]. To account for nitrification, equation (1) can be adjusted by augmenting the α due to denitrification by α_{nit} multiplied by an assumed recycling efficiency ϵ . The ϵ accounts for the fact that anthropogenic nitrogen may be nitrified, assimilated into plants or organic matter, mineralized and nitrified again multiple times, with N₂O yield α_{nit} each time the loop repeats. If we assume for simplicity that the same fraction β is nitrified as well as denitrified within a few years, equation (1) becomes

$$\Delta P_{\text{N}_2\text{O}} = \Delta N_f \beta (\alpha + \epsilon \alpha_{\text{nit}}) = \Delta N_f \beta \alpha' \quad (2)$$

where α_{nit} = g N₂O-N produced per g NH₄⁺-N nitrified, and ϵ is the recycling efficiency of anthropogenic nitrogen.

Assuming $\epsilon = 5$ and $\alpha_{\text{nit}} = 0.001-0.005$, nitrification may provide an additional fractional yield of ~ 0.01 g N₂O-N per g anthropogenic N. Adding the denitrification yield $\alpha=0.01-0.06$ discussed in section 5 gives an α' range of 0.02- 0.07, which we will assume in subsequent calculations.

7. Application of Equation (2) and Estimation of N₂O Emissions

We are now ready to use equation (2) to estimate both present day and future (year 2100) N₂O production associated with anthropogenically fixed nitrogen. Our calculations are summarized in Table 3 using the inputs ΔN_f , β , and α' to equation (2) discussed in the previous sections. Our present-day estimate of 3.5 (1-8.5) Tg N/yr suggests that much of the currently

Table 3. Estimates of N₂O Production Associated With Anthropogenic Nitrogen Fixation Based on Equation (2)

Process	ΔN_f , Tg N/yr	Fraction β Denitrified Within a Few Years	N ₂ O Yield α'	N ₂ O Source, Tg N/yr
<i>1990</i>				
Fertilizer	80	0.65 (0.5-0.8)	0.04 (0.02-0.07)	2 (0.8-4.5)
Fossil Fuel NO _x	22	0.55 (0.3-0.8)	0.04 (0.02-0.07)	0.5 (0.1-1)
Crop N ₂ Fixation	44 (32-53)	0.65 (0.5-0.8)	0.04 (0.02-0.07)	1 (0.3-3)
Total				3.5 (1-8.5)
<i>2100</i>				
Fertilizer	160-280	0.65 (0.5-0.8)	0.04 (0.02-0.07)	6 (2-16)
Fossil Fuel NO _x	75	0.55 (0.3-0.8)	0.04 (0.02-0.07)	2 (0.5-4)

observed atmospheric N₂O increase of 3-5 Tg N/yr has been caused by anthropogenic nitrogen fixation. Our estimate in the year 2100 implies a future total N₂O source that may be double or even triple its preindustrial value. We have not attempted to estimate year 2100 N₂O emissions associated with crop N₂ fixation in Table 3 because of the especially large uncertainty in ΔN_f .

Our present-day upper bound of 8.5 Tg N/yr appears unrealistically high compared to the observed atmospheric increase, which imposes its own constraint on how large the anthropogenic source can be (assuming no significant increase in sinks). Again we note that other global estimates of the agricultural N₂O source which attempt to account for both immediate and longer term fates of fertilizer [e.g., Mosier *et al.*, 1997], share this tendency to exceed the atmospheric increase in their upper bounds. Part of this problem may result from overestimates of "anthropogenic" biological N₂ fixation, which may not adequately account for possible reductions in natural N₂ fixation. Another part may simply reflect uncertainty in the estimates.

Although the equation (2) approach to estimating N₂O sources involves large uncertainties, it provides a useful consistency test for N₂O budget estimates that are calculated independently from considerations of the nitrogen cycle, e.g., estimates based on extrapolations of measured N₂O emission coefficients from fertilized fields or extrapolations of N₂O supersaturation anomalies measured in the surface ocean. Equation (2) type approaches provide approximate answers and can help identify unreasonably large or small sources estimated by these extrapolation approaches. Our lower bound of 0.8 Tg N₂O-N/yr associated with fertilizer, estimated from equation 2 in Table 3, suggests that the very small fertilizer sources of $\ll 1$ Tg N/yr estimated in the early 1990s [Eichner, 1990; Watson *et al.*, 1990, 1992; Matthews, 1994] are inconsistent with considerations of the nitrogen cycle. By similar logic, we can argue that the 85 Tg N/yr ocean source estimated by Hahn [1974] is inconsistent with nitrogen cycle-based estimates of ocean denitrification and nitrification and their respective N₂O fractional yields (Table 2). Indeed some studies of the 1970s questioned the 85 Tg N/yr ocean source on these grounds [Pratt *et al.*, 1977]. As a final example of how an equation (2) type consistency test might be applied, we consider the hypothesis that N₂O production in the subsurface ocean could be isotopically lightening some 200 Tg N₂O-N/yr by -2 ‰ in $\delta^{15}\text{N}$ relative to atmospheric N₂O [Kim

and Craig, 1993]. Ocean production of N₂O estimated based on nitrogen cycle considerations is only about 4 Tg N/yr (Table 2) [Najjar, 1992; Nevison *et al.*, 1995]. Much of this occurs in deeper ocean regions where isotopic enrichment of N₂O is observed [Kim and Craig, 1990]. Even if as much as 2 Tg N/yr of near-surface N₂O production were to occur, an unreasonably large isotopic fractionation during N₂O production of -100 per mil would be required to lighten 200 Tg N₂O-N/yr, considering the 2/200 dilution factor involved. The Kim and Craig [1993] hypothesis therefore appears inconsistent with the current (admittedly uncertain) understanding of the marine nitrogen cycle.

8. Modified N₂O Emissions Associated With Naturally Fixed Nitrogen

A potentially important source of N₂O ignored by equation (2) is our proposed category 2b, i.e., modified microbial/pyrodenitrification emissions associated with naturally fixed N. As suggested by Figure 2, changes in N₂O release from fixed N reservoirs can be generated by forcings that either change the rate of nitrification or denitrification in a system or that change the N₂O yield. Such forcings can increase N₂O emissions without any necessary additional anthropogenic nitrogen fixation. They can also decrease N₂O emissions, which is a less commonly noted point. Land use changes are examples of forcings that can lead to modifications of N₂O emissions from naturally fixed N. Four land use change-related anthropogenic forcings that are commonly regarded as N₂O sources include livestock manure, forest clearing, sewage, and biomass burning. Below we examine how current estimation methodologies may be double counting these "sources" of N₂O by failing to acknowledge their long-term effects on naturally-fixed nitrogen.

Livestock, particularly when raised in modern feedlots, produce vast amounts of nitrogen-rich manure, which provides substrate for nitrification and denitrification. Measurements inside feedlots suggest relatively high yields of N₂O [Khalil and Rasmussen, 1992]. Enhanced N₂O emissions also have been measured in a variety of other animal management systems and from cultivated land fertilized by manure [Mosier *et al.*, 1997]. The huge mass of manure produced by the world's livestock (Figure 6) has led to manure N₂O source estimates as high as 2.1 (0.6-3.1) Tg N/yr [Mosier *et al.*, 1997]. Such estimates commonly have treated manure as an external input of nitrogen

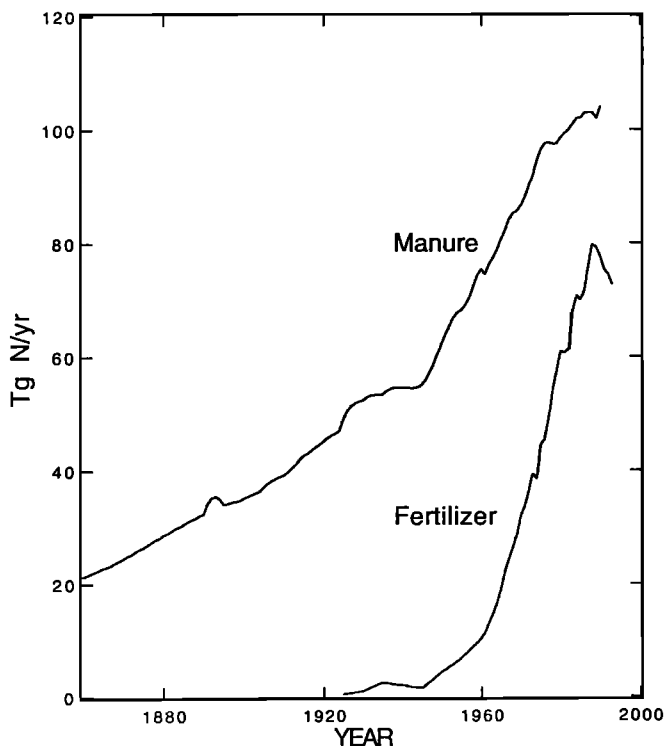


Figure 6. Growth in manure production estimates from livestock populations [Nevison *et al.*, 1996]. Global fertilizer consumption described in Figure 3 is included for reference.

and have not addressed the question of where manure N is derived from. The origin of manure N is not obvious, since agricultural databases generally do not keep track of essential details such as the amount of nitrogen fertilizer used on livestock feed crops [FAO, 1992, 1995]. However, a few back of the envelope calculations, guided by Figure 4, suggest that only about 5 Tg N/yr in fertilized crops is directly fed to livestock. Even if we generously assume that half of all fertilizer in crop residue (9 Tg N/yr) and two thirds of all legume crops (29 Tg N/yr) are consumed by livestock, this yields about 40 Tg N/yr of manure derived from anthropogenically fixed nitrogen out of a total of >100 Tg N/yr. Thus we conclude that the majority of manure N is still probably derived from naturally fixed nitrogen reservoirs in cultivated or grazed soils. Grazing acts to accelerate the nitrogen cycle, mobilizing nitrogen and ultimately mining an ecosystem of its nitrogen and other resources, particularly when nutrients in the form of animal products are permanently removed from the system. Continuously overgrazed ecosystems commonly experience a decline in soil organic matter, N mineralization, nitrification and denitrification, and a reduction in N_2O emissions [Bauer *et al.*, 1987; Holland *et al.*, 1992; Seagle *et al.*, 1992; Milchunas and Lauenroth, 1993; Belsky and Blumenthal, 1997]. Methodologies that treat manure as a source of N_2O therefore should probably offset the estimated source by the decline in natural microbial N_2O production due to the livestock grazing from which much of manure N is derived.

Two other N_2O sources that also may involve double counting of nitrogen are forest clearing and biomass burning. Conversion of tropical forests to pastures liberates a large amount of forest-derived organic matter for mineralization, nitrification, and denitrification and alters the microclimate of the soil. N_2O

production may accelerate for a few years immediately after forest conversion [Luizão *et al.*, 1989], but in subsequent years, as the organic matter decomposes away, production has been observed to decline to below preconversion levels [Keller *et al.*, 1993]. Biomass burning, which is commonly associated with forest clearing and agriculture, may produce N_2O directly during combustion and indirectly through the stimulation of microbial N_2O emissions following burning. However, considered in the context of the natural litterfall and decomposition it replaces, direct combustion of biomass has a relatively low N_2O yield of only ~0.7% of N biomass [Crutzen and Andreae; 1990]. (Unlike microbial denitrification, pyrodenitrification yields many end products other than N_2 and N_2O , such that a meaningful yield α is difficult to define.) Biomass burning may stimulate N_2O emissions in the short term [Anderson *et al.*, 1988; Levine *et al.*, 1988], but long-term studies in tall-grass prairie have shown that repeated burning ultimately reduces soil organic nitrogen, available mineral nitrogen, microbial biomass, and litter quality [Ojima *et al.*, 1994]. Thus forest conversion, repeated biomass burning, and livestock grazing have a similar effect: a temporary acceleration of the N cycle resulting in increased N_2O emissions followed by a decline as the ecosystem's nitrogen resources are depleted.

N-rich human sewage is similar to livestock manure in that a large fraction of its associated N_2O production can be derived from anthropogenically fixed nitrogen [Mosier *et al.*, 1997]. Although high N_2O emissions have been observed from rivers receiving sewage effluent [Kaplan *et al.*, 1978], the nitrification and denitrification of sewage in rivers and estuaries, assuming a relatively low denitrification α of 0.005 and a low recycling efficiency of nitrogen, may simply replace natural mineralization of organic matter which could yield a higher fraction of N_2O per unit nitrogen. The anthropogenic fraction of sewage N most likely does lead to a net increase in N_2O emissions above natural levels, but these emissions are already accounted for by equation (2). Similarly, equation (2) accounts for the fraction of manure N that is derived from anthropogenically fixed nitrogen.

The above discussion suggests that the net N_2O production resulting from many types of land use change which is not already incorporated into equation (2) may be only marginally greater than the natural N_2O production it replaces. Indeed in some cases land use change may result in lower net N_2O production, especially in the long term. Because of the risk of double accounting of N, explicit estimates of separate N_2O emissions from sources such as forest clearing, manure, biomass burning, and human sewage and waste processing may be misleading when these anthropogenic sources are considered in isolation from natural sources.

Climate change is a final type of forcing that can lead to modifications of N_2O emissions from naturally fixed N. The effects of climate change induced by greenhouse warming on natural N cycling and N_2O yields are difficult to predict due to uncertainties in future temperature and precipitation patterns and in how these interacting influences will alter future microbial behavior and plant productivity. Although warmer temperatures generally increase microbial activity and plant productivity, the effect of temperature is not always clear for processes like N_2O production that involve multiple microbial pathways. A study of Hawaiian soils, for example, found no consistent response of N_2O production to temperature [Holland *et al.*, 1995]. Changes in soil moisture due to shifts in rainfall and evapotranspiration patterns also may have nonlinear effects on microbial N_2O production [W.J. Parton *et al.*, submitted paper, 1997]. Considering

increased atmospheric CO₂ under the heading of "climate change," the exact influence of CO₂ fertilization on the global (or local) nitrogen cycle is unclear [Koch and Mooney, 1996]. The observed increases in the C:N ratio of plant material resulting from CO₂ fertilization may slow the rate of decomposition and nitrogen cycling, which could offset any increase in plant productivity that might provide more litter for soil microbes [Rastetter et al., 1992]. The prediction of future changes in microbial N₂O production resulting from climate change is a complex problem which probably requires a biogeochemical model to account for the many nonlinear responses of plants and microbes.

9. Temporal Trends in Atmospheric N₂O

Historic trends in atmospheric N₂O are known from ice core and firn data and direct atmospheric measurements (Figure 1). A number of studies have shown that the growth in atmospheric N₂O can be represented by an exponential source that became significant around the middle of the 20th century [Weiss, 1981; Khalil and Rasmussen, 1988]. Such a source is consistent with historic trends in anthropogenic nitrogen fixation [Nevison et al., 1996]. Recent high precision measurements of N₂O trapped in south pole ice and firn air suggest that a slow increase in N₂O began prior to the mid-1900s [Machida et al., 1995; Battle et al., 1996].

Predictions of future atmospheric N₂O have been hampered by the perceived large uncertainty in the present day budget. A simple projection of present day atmospheric growth rates yields a mixing ratio of about 400 ppbv by the year 2100. However, no obvious likelihood exists that atmospheric growth will continue indefinitely at its current rate. The IPCC IS92 scenarios yield an N₂O mixing ratio in 2100 ranging from 391 to 433 ppbv [Leggett et al., 1992]. In these scenarios, fertilizer is the major component of the projected future anthropogenic source and growth in the source is assumed to be largely proportional to growth in fertilizer consumption. The focus on fertilizer seems to belie the 1992 IPCC budget estimate of 0.03-3 Tg N/yr [Watson et al., 1992], which suggests a huge uncertainty in the fertilizer N₂O source and a lack of a clear sense of the cause of the observed atmospheric increase.

We use the following numerical box model to investigate the past and future growth of atmospheric N₂O:

$$\frac{d[\text{N}_2\text{O}]}{dt} = S(t) - \frac{[\text{N}_2\text{O}]}{\tau}, \quad (3)$$

where [N₂O] is in Tg N, S(t) is the N₂O source in Tg N/yr, and τ is the atmospheric N₂O lifetime in years.

For simplicity, we assume an anthropogenic N₂O source that is driven solely by anthropogenic N fixation. Admittedly this approach neglects the direct industrial emissions described earlier. This approach also neglects emissions associated with changes in N₂O yields and/or rates of cycling of naturally fixed N, which, as we noted in the previous section, could cause either a net increase or decrease in the total N₂O source. Our source can be expressed as,

$$S(t) = S_{\text{bkgd}} + \left\{ [\text{fert}(t) + \text{foss}(t) + \text{cropfix}(t)] \beta + \frac{R}{\tau_{\text{res}}} \right\} \alpha', \quad (4)$$

where fert is fertilizer consumption, foss is fossil fuel NO_x production, cropfix is crop N₂ fixation, and S_{bkgd} is a constant background source, all in Tg N/yr. R is an accumulating reservoir of anthropogenically fixed nitrogen (Tg N), governed by

$$\frac{dR}{dt} = [\text{fert}(t) + \text{foss}(t) + \text{cropfix}(t)] * (1 - \text{perm} - \beta) - \frac{R}{\tau_{\text{res}}}$$

where τ_{res} is the assumed turnover time for R (years), and perm is the fraction of anthropogenic nitrogen that is "permanently" removed from the atmosphere, i.e., sequestered into pools with thousand year turnover timescales. β here is effectively defined as the fraction of anthropogenic nitrogen denitrified within 1 year.

Prior to 1994, actual values for fert are taken from FAO Fertilizer Yearbooks and prior to 1990, actual values of foss are taken from Müller [1992]. Future values are projected using exponential growth rates μ, assumed to be 1.8%/yr from 1991 or 1994-2020 and to range from 0.2 to 1%/yr from 2020 to 2100. For lack of better information, cropfix is assumed to increase linearly by 0.4 Tg N/yr based on Galloway et al. [1995]. Default values of perm = 0.05 and τ_{res} = 40 years are assumed, based largely on the assumed partitioning and turnover of slow and recalcitrant soil organic matter pools [Schimel et al., 1994]. The background source S_{bkgd} is assumed to be 11 Tg N/yr, corresponding to a steady state atmospheric lifetime τ of 120 years. The treatment of S_{bkgd} assumes (perhaps incorrectly) that increases and decreases in X(t) associated with changes in natural N cycling rates and N₂O yields will roughly balance one another. The box model results show different degrees of sensitivity to various input parameters. Results are highly sensitive to α', β, and μ (Figure 7), and moderately sensitive to S_{bkgd}, τ, τ_{res}, and perm, within reasonable ranges of uncertainty.

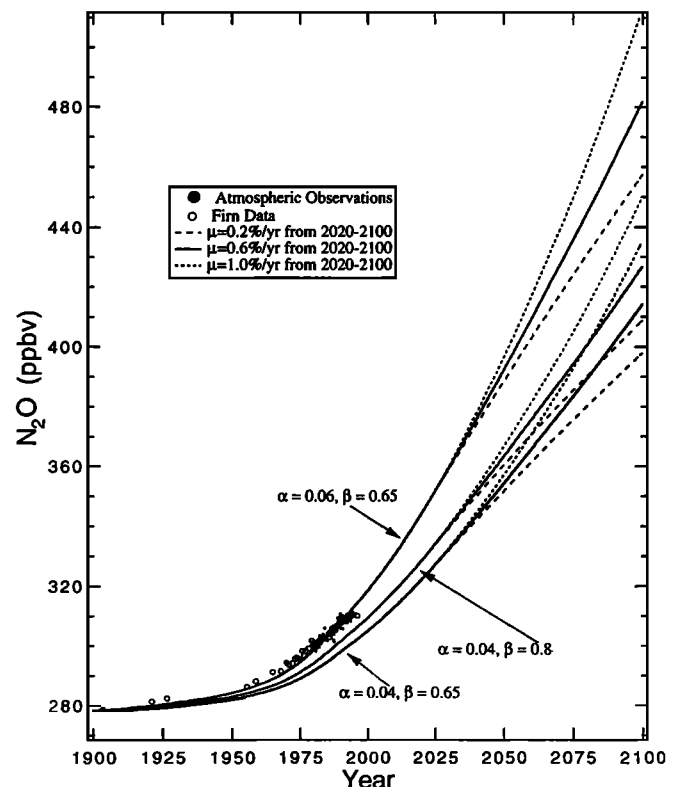


Figure 7. Trends in atmospheric N₂O predicted by the box model described in the text. In all the scenarios shown, τ = 120 years, τ_{res} = 40 years, perm = 0.05, and μ = 1.8%/year from 1990-1994 to 2020. Results are shown for α' = 0.04 - 0.06, β = 0.65-0.8, and μ = 0.2-1.0%/yr from 2020-2100. South Pole firn data and direct atmospheric measurements are superimposed [Battle et al., 1996; CMDL, 1991-1994, J. Butler, personal communication, 1997].

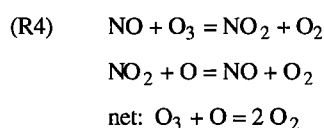
Atmospheric N₂O measurements from air and firm samples [Battle *et al.*, 1996; CMDL 1991-1994, J. Butler, personal communication, 1997] are plotted in Figure 7 to examine how well the simple box model described above reproduces the historic growth in N₂O. Box model results using $\alpha' = 0.04$ and $\beta = 0.65$, the best guess estimates discussed in this paper, somewhat underestimate the historic growth. Since the box model neglects sources associated with industry and with short-term releases of naturally fixed N from cultivated and deforested land, these results are not unexpected and suggest that the model may underestimate future N₂O. However, using $\alpha' = 0.06$, certainly within the range of uncertainty, the model can more or less reproduce the observations, lending confidence to the use of anthropogenic nitrogen fixation as an indicator of future growth in N₂O. Various combinations of input parameters yield a wide range of atmospheric N₂O concentrations by the year 2100. Estimates of 400 to 500 ppbv represent a reasonable range of possible mixing ratios, although these are not absolute lower and upper bounds.

10. Impact of Increased N₂O on Stratospheric Ozone

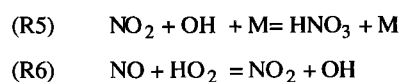
Most studies of N₂O emissions today include an introductory statement asserting that N₂O is the main source of stratospheric NO_x, which is an important catalyst of stratospheric O₃ destruction. These statements are based largely on the papers of the 1970s, which discussed anthropogenic nitrogen fixation and its effects on N₂O and O₃. Since many revisions in the understanding of stratospheric chemistry have occurred since that time, we have performed an updated calculation with a two-dimensional model to better quantify the impact of increased N₂O on O₃.

The effects of NO_x on stratospheric O₃ are more complicated than believed 20 years ago. Today NO_x is thought to be the dominant catalyst of O₃ loss between about 25 and 40 km, while catalytic cycles involving HO_x and halogens (Cl and Br) dominate at lower and higher altitudes [Garcia and Solomon, 1994; Wennberg *et al.*, 1994]. NO_x plays a mitigating role in these latter cycles. In the lower stratosphere, where NO_x is largely sequestered into longer-lived species like HNO₃ and ClONO₂, the ratio of NO_x to total reactive nitrogen NO_y is an important quantity. Low values of the NO_x/NO_y ratio occur in the presence of high aerosol surface area and limit the ability of NO_x to participate in O₃ loss reactions [Fahey *et al.*, 1993].

The early modeling studies of the 1970s considered the catalytic cycle of reactions (R4) to dominate O₃ destruction throughout the stratosphere. Hence an increase in stratospheric NO_x at any altitude, due to either increased N₂O or injection by the proposed high speed civil transport (HSCT) fleet, caused a linear decrease in O₃.



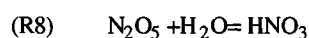
In the late 1970s attention shifted to HO_x-catalyzed O₃ destruction, in which NO_x plays a mitigating role through reactions (R5)-(R6).



Following the reevaluation of certain HO_x rate constants, HO_x was identified as the dominant catalyst of O₃ destruction below about 25 km, where more than half of the O₃ column resides. Atmospheric models incorporating the new HO_x chemistry predicted that increased stratospheric NO_x would actually increase total column O₃ by ~ 0 to +9% [Turco *et al.*, 1978; Crutzen, 1981]. A literature search shows that most of the papers specifically focused on anthropogenic nitrogen fixation and its impact on atmospheric N₂O and stratospheric O₃ were written at or before this point. However, a second dramatic change in the understanding of stratospheric chemistry occurred soon afterward when the rate constant for reaction (R7) was revised upward, effectively reducing HO_x and hence its dominance of O₃ loss in the lower stratosphere.

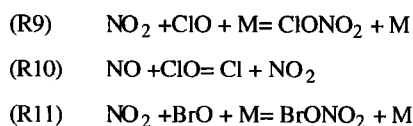


Models examining the impact of NO_x emitted by proposed HSCTs once again predicted a net decrease in stratospheric O₃ [Wine *et al.*, 1981]. The subsequent incorporation of HO₂NO₂ chemistry into models further reduced HO_x, leading to an even more negative modeled effect of NO_x on O₃ [Barnes *et al.*, 1981; Sze and Ko, 1981]. A third dramatic revision occurred with the discovery of reaction (R8), which occurs on aerosol surfaces. Reaction (R8) locks up NO_x in the relatively long lived reservoir species HNO₃, thus reducing the NO_x/NO_y ratio and promoting the role of HO_x [Hofmann and Solomon, 1989; McElroy *et al.*, 1992]:



The inclusion of (R8) reduces the predicted impact of HSCT NO_x on O₃ from clearly negative to near zero [NASA, 1995]. However, a number of recent papers have hypothesized that additional heterogeneous reactions on soot or sulfuric acid aerosols may convert HNO₃ back to NO_x in the lower stratosphere [Lary *et al.*, 1997; Iraci and Tolbert, 1997]. Because of these continuing unknowns in stratospheric chemistry, further significant revisions in the predicted effect of increased NO_x on O₃ may yet occur in the future.

In addition to NO_x and HO_x, halogens, which are released to the stratosphere mainly from anthropogenic compounds, also catalyze O₃ destruction. Early studies of halogens focused on gas-phase Cl reactions, which are most important in the upper stratosphere [Molina and Rowland, 1974; Stolarski and Cicerone, 1974]. Later, attention shifted to heterogeneous reactions on aerosol and cloud particles in the lower stratosphere, which can lead to rapid, dramatic O₃ losses, especially in the Antarctic polar region [Solomon *et al.*, 1986]. In both cases, NO_x mitigates halogen-catalyzed O₃ loss through reactions (R9)-(R11).



Several studies in the 1980s examined the effect of increasing Cl and N₂O on gas-phase O₃ chemistry and described the mitigating effect of NO_x on halogen-catalyzed O₃ loss [Isaksen and Stordal, 1986; Cicerone, 1987]. We are not aware of further studies which have examined the impact of increased N₂O in the reduced-halogen stratosphere now likely in the wake of the Montreal Protocol and its amendments [Montzka *et al.*, 1996].

The concern over stratospheric NO_x emissions from the proposed HSCT fleet (i.e., supersonic aircraft) provides the

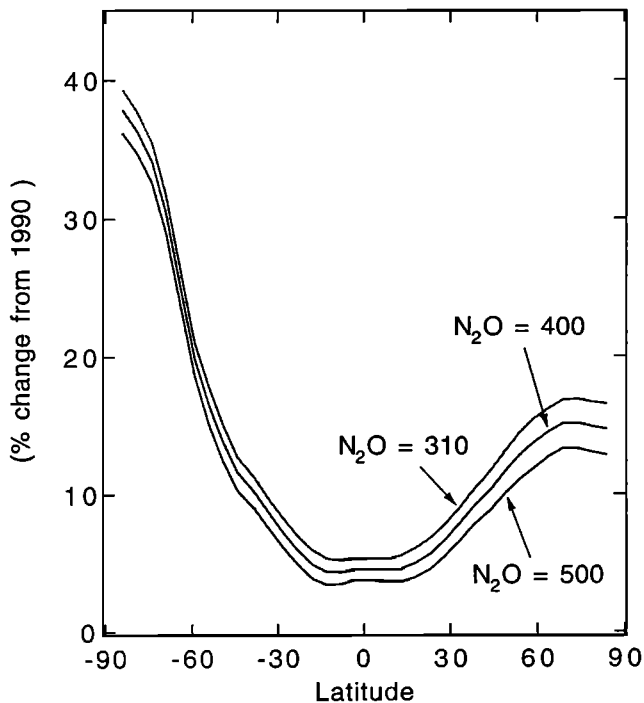


Figure 8. Percent change in global column O_3 relative to 1990 for $N_2O = 310, 400,$ and 500 ppbv. All three curves are from a future (\sim year 2100) scenario with $Cl_y = 1.3$ ppbv, $CH_4 = 3000$ ppbv, and $CO_2 = 600$ ppbv.

closest available analog to the increasing N_2O question. While N_2O today receives little attention with respect to stratospheric O_3 , an active effort is still ongoing to assess the effects of HSCTs. Most of the current information about the impact of increased stratospheric NO_x stems from this effort. As described above, predictions of the impact on total O_3 have undergone several changes in sign with the evolution of knowledge about stratospheric chemistry [NASA, 1991]. The most recent assessment predicts a net effect hovering around zero, due to the inclusion of (R8) in models [NASA, 1995]. The predicted O_3 changes are sensitive to aerosol, Cl , and water vapor levels, altitude of NO_x injection, and amount of NO_x emitted. Notably, the predicted impact of aircraft NO_x becomes more negative as the level of stratospheric Cl decreases.

We have performed our own study of the impact of increased N_2O on stratospheric O_3 using the Garcia-Solomon two-dimensional model [Garcia and Solomon, 1994]. We chose the year 2100 as an appropriate context for this study, when, as discussed in section 9, atmospheric N_2O likely will have increased to somewhere between 400 and 500 ppbv. Updated IS92a scenarios suggest that stratospheric halogens will have dropped toward preindustrial levels and CO_2 and CH_4 levels will have increased substantially [Schimel et al., 1995]. Under these conditions, steady state model results, with "background" sulfate aerosol and Cl_y set to 1.3 ppbv (about one third of current levels), suggest that global column O_3 would be about 1 and 2-2.5% less for $N_2O = 400$ and 500 ppbv, respectively, relative to what it would be if N_2O were to remain at its 1990 level of 310 ppbv (Figure 8). In all cases a net increase of $\sim 10\%$ occurs in global column O_3 relative to 1990 because of the phaseout of anthropogenic halogens and CO_2 -induced cooling of the stratosphere, which tends to slow O_3 loss rates. The increased

N_2O results are sensitive to aerosol, CH_4 concentration, and extent of sedimentation of ice particles containing HNO_3 . The latter occurs mainly in the model southern hemisphere in polar winter and reduces NO_y at midlatitudes following the breakdown of the polar vortex [Nevison et al., 1997]. The general result of the model runs is a small decrease in stratospheric O_3 due to increased N_2O , superimposed upon a larger recovery of O_3 due to the phase-out of anthropogenic halogens and to stratospheric temperature changes.

Figure 9 shows the heterogeneity of the modeled impact of increased N_2O on O_3 . Maximum O_3 losses of up to 11% (for $N_2O = 500$ versus 310 ppbv) occur in the middle stratosphere, where NO_x dominates O_3 loss. The reduction in O_3 tapers off to zero in the upper and lower stratosphere, where the reductions in HO_x and halogen-catalyzed O_3 loss due to mitigating effects of NO_x begin to compete with the direct increases in NO_x -catalyzed O_3 loss. The net O_3 increase of about +3% in the lower tropical stratosphere stems mainly from a self-healing effect in which O_3 depletion above permits more UV penetration, leading to increased O_3 production by O_2 photolysis.

11. Comparison of Climatic Impact of HSCTs Versus N_2O

The discussion above raises the question of how the climatic impact of increasing N_2O compares to that of HSCTs, considering that the latter receives considerably more attention. Table 4 compares various climatic effects of the proposed fleet of 500 HSCTs in the year 2015 to increased N_2O around the year 2100 for both $N_2O = 400$ and 500 ppbv. Concern about HSCTs first arose in the 1970s, with the recognition that supersonic aircraft could emit an amount of NO_x into the stratosphere comparable to that produced naturally by the oxidation of N_2O [Johnston, 1971; Crutzen, 1972]. Today, one can make the opposite point that an increase in N_2O could add an amount of stratospheric NO_x comparable to that injected by HSCTs. The

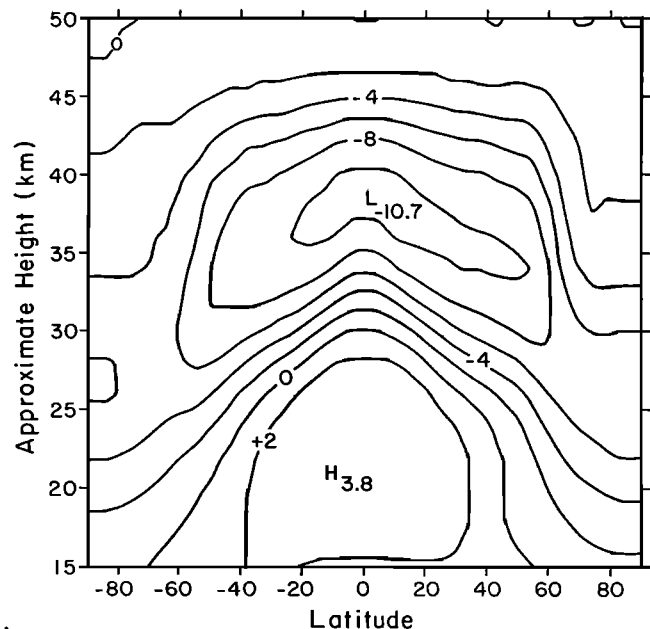


Figure 9. Percent change in O_3 for future the scenario described in Figure 8, showing the effect of a change in N_2O from 310 to 500 ppbv.

Table 4. Comparison of Climatic Impacts of High Speed Civil Transport (HSCT) and N₂O

	HSCT Aircraft ^a	N ₂ O=400 ppbv	N ₂ O=500 ppbv
Amount of NO _x	0.1-0.4 Tg N/yr	0.2 Tg N/yr ^b	0.4-0.5 Tg N/yr ^b
Altitude/latitude of introduced NO _x	50-60% 18-20 km 40-50% ≤ 17 km mainly in NH mid to high latitudes ^c	produced from N ₂ O+O(¹ D) mainly in tropics from 25 to 40 km	produced from N ₂ O+O(¹ D) mainly in tropics from 25 to 40 km
Time frame	2015	~2100	~2100
Associated emissions	S, soot, CO ₂ , H ₂ O, HCs, CO; large uncertainties in effects on O ₃	none	none
Radiative forcing relative to pre-industrial era	Current best estimates are relatively negligible, although large uncertainties remain as to indirect effects on cirrus clouds and tropospheric O ₃	+ 0.3 W/m ² ^d	+ 0.6 W/m ² ^d
Total column O ₃ change, %	~ 0 ^e	-1 ^f	-2 to -2.5 ^f

^a Fleet of 500 HSCTs flying at Mach 2.4 burning 8.2×10^{10} kg fuel with NO_x emission index of 5-15 gNO₂/kg fuel [NASA, 1995].

^b Relative to 1990 NO_x production at N₂O = 310 ppbv.

^c NASA [1993].

^d Relative to N₂O = 310 ppbv, from Shine et al., p.52 [1990] formula using CH₄ = 1714 ppbv. Does not account for indirect forcing due to changes in O₃.

^e With respect to same future scenario but without HSCT emissions. Range of models [NASA, 1995].

^f With respect to same future scenario but with N₂O = 310 ppbv. Garcia-Solomon two-dimensional model.

proposed fleet of HSCTs burning 8.2×10^{10} kg fuel/yr at an emissions index of 5-15 g NO₂/kg fuel would inject about 0.1-0.4 Tg N/yr into the atmosphere, of which about 50-60% would be above 17 km [NASA, 1993; 1995]. In comparison, an increase in atmospheric N₂O from its 1990 level of 310 ppbv would produce an additional 0.2-0.5 Tg NO_x-N/yr according to the two-dimensional model. NO_x production from N₂O oxidation occurs mainly in the tropics between 25-40 km, in the region where the NO_x catalytic cycle (R4) dominates O₃ destruction. In contrast, NO_x from HSCTs would be injected into northern middle to high-latitude flight corridors, at lower altitudes where the mitigating effects of NO_x on O₃ destruction by HO_x and halogens are important. A fraction of HSCT-NO_x would settle out of the stratosphere before ever reaching the altitudes where (R4) dominates O₃ destruction. This fraction would depend on uncertain dynamical processes including the rate of stratosphere-troposphere exchange and the rate of mixing between northern hemisphere midlatitudes and the tropics, where trace species are lofted into the middle and upper stratosphere. These dynamical uncertainties generally are not important to N₂O-NO_x, which essentially all reaches the middle and upper stratosphere. While the factors discussed above imply that increased N₂O could cause more O₃ loss than HSCTs, time scale considerations lessen the immediacy of the N₂O effect. Whereas NO_x from HSCTs would be injected into the lower stratosphere instantaneously and circulated within about 5 years or less, production of NO_x from N₂O would be delayed by the relatively gradual increase in N₂O sources and the long N₂O lifetime τ . In addition, unlike NO_x from N₂O, sulfur, water vapor, soot, and other emissions associated with HSCT-NO_x may also have significant impacts on O₃ which are not well understood [Fahey et al., 1995; NASA, 1995].

A final comparison of N₂O and HSCTs involves the consideration of radiative forcing. HSCTs may affect the Earth's radiative balance both directly through emissions of CO₂, H₂O, soot, and sulfur aerosol, and indirectly by increasing cirrus cloud and tropospheric O₃ formation. Currently, a fairly negligible effect is calculated, although large uncertainties remain [NASA, 1995]. In comparison, the direct radiative forcing due to an increase N₂O from 310 to 400-500 ppbv would cause an additional radiative forcing of 0.3-0.6 W/m² [Shine et al., 1990, p. 52]. We have not evaluated the indirect radiative effect due to N₂O-induced changes in stratospheric O₃, although qualitatively these would be positive, based on the O₃ depletion in the middle stratosphere and increase in the lower stratosphere shown in Figure 9 [World Meteorological Organization, 1994].

12. Conclusions

Anthropogenic nitrogen fixation is dominated by synthetic fertilizer production and also includes crop N₂ fixation and NO_x produced during fossil fuel combustion. Today anthropogenic nitrogen fixation approximately equals total natural nitrogen fixation on land. Because it is closely linked to crop production, anthropogenic nitrogen fixation will likely continue to increase in the future, given the predicted growth in the human population. Livestock production is a major driving force behind crop production, implying that human dietary structure may play an important role in determining future rates of anthropogenic nitrogen fixation.

Logic first articulated in the 1970s suggests that some fraction β of anthropogenically fixed nitrogen ΔN_f is denitrified back to the atmosphere on a short time scale, with a significant fraction α of the end product as N₂O, i.e., N₂O production = $\Delta N_f \alpha \beta$. We

have extended the $\Delta N_f \alpha \beta$ approach from its original conception in the 1970s to include N_2O produced during the nitrification of anthropogenic nitrogen and have adjusted α accordingly to define a new total N_2O yield α' . We have estimated N_2O emissions from this simple equation, assuming that $\alpha' \sim 0.02-0.07$ and that $\beta \sim 0.5-0.8$ for fertilizer and crop N_2 fixation and $\sim 0.3-0.8$ for fossil fuel NO_x . This calculation yields a current N_2O source associated with anthropogenic nitrogen fixation of about 3.5 (1-8.5) Tg N/yr, which accounts for most of the observed increase in atmospheric N_2O .

Many estimates of fertilizer N_2O emissions in the 1990s, which were based on extrapolations of measured N_2O emission coefficients, became narrowly focused on direct short term emissions from fertilized fields, leading to the misleading conclusion that fertilizer is not necessarily an important source of the observed atmospheric increase. Our simple $\Delta N_f \alpha \beta$ approach to estimating N_2O production provides a useful consistency check on such extrapolation approaches and can be used to show that fertilizer N_2O estimates of $\ll 1$ Tg N/yr are unrealistically low.

The $\Delta N_f \alpha \beta$ approach toward estimating anthropogenic N_2O production avoids the double counting associated with more complex approaches which define a large array of small anthropogenic sources that are often considered in isolation from the global nitrogen cycle. These multiple-source approaches generally ignore the negative impact of anthropogenic activities such as forest clearing, biomass burning, and livestock grazing on natural N_2O production and thus may be double counting nitrogen. Viewed in the context of the overall nitrogen cycle, many of these activities may not cause a net long-term increase in N_2O emissions, especially if the nitrogen involved is derived from naturally fixed sources. The $\Delta N_f \alpha \beta$ approach already accounts for the fraction of N_2O produced from livestock manure and human sewage that is derived from anthropogenically-fixed nitrogen.

An atmospheric box model, which assumes an anthropogenic source proportional to the rate of anthropogenic nitrogen fixation, can reproduce much of the historic growth in N_2O . According to this box model, future increases in anthropogenic N fixation could increase atmospheric N_2O to 400-500 ppbv by the year 2100. A two-dimensional model predicts that the associated increase in stratospheric NO_x could produce a 1-2.5% reduction in total column O_3 , which would be superimposed on a larger increase in O_3 due to the phaseout of anthropogenic halocarbons and to decreases in stratospheric temperature. This predicted impact on O_3 is greater than that currently predicted due to NO_x emissions from proposed supersonic aircraft, largely because an increase in N_2O would put more NO_x into the middle stratosphere where NO_x dominates O_3 loss. Key uncertainties to better understanding the future impact of anthropogenic nitrogen fixation on atmospheric N_2O and stratospheric O_3 revolve around trends in ΔN_f , α' , and fixed nitrogen storage, and continuing uncertainties in stratospheric chemistry.

Finally, we note that the classical view of N_2O production by microbial nitrification and denitrification and destruction by stratospheric photolysis and oxidation is generally in balance and consistent with independent estimates of N_2O sources and sinks. The observed increase in atmospheric N_2O also is consistent with ongoing large-scale disturbances to the global nitrogen cycle, which are dominated by anthropogenic N fixation and also include industrial production of N_2O and releases of naturally fixed N from cultivated and deforested land. The uncertainties in the N_2O budget do not preclude the existence of new sources and sinks when independent evidence argues for them. Our analysis

suggests, however, that the frequently cited need to identify new N_2O sources based on a perceived budget gap may not be justified. Rather, the budget may be balanced by a closer examination of existing sources. We have shown that simple considerations of the global nitrogen cycle can provide a useful consistency check on N_2O budget estimates.

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