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Sources and sinks of atmospheric N_2O and the possible ozone reduction due to industrial fixed nitrogen fertilizers

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ABSTRACT

The terrestrial and marine nitrogen cycles are examined in an attempt to clarify how the atmospheric content of N_2O is controlled. We review available data on the various reservoirs of fixed nitrogen, the transfer rates between the reservoirs, and estimate how the reservoir contents and transfer rates can change under man's influence. It is seen that the sources, sinks and lifetime of atmospheric N_2O are not understood well. Based on our limited knowledge of the stability of atmospheric N_2O we conclude that future growth in the usage of industrial fixed nitrogen fertilizers could cause a 1 % to 2 % global ozone reduction in the next 50 years. However, centuries from now the ozone layer could be reduced by as much as 10% if soils are the major source of atmospheric N_2O.

1. Introduction

Conversion of N_2O gas to NO in the upper atmosphere and the catalytic cycle

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (2)$$

is an important natural process for destroying stratospheric ozone (Crutzen, 1970; Johnston, 1971; Crutzen, 1971; Johnston, 1975). Hence, a significant increase in the flux of N_2O into the atmosphere means a significant reduction in global ozone. The monographs of the U.S.A. Climatic Impact Assessment Program (CIAP, 1975) present the quantitative relationships that have been deduced for O_3 losses due to added NO and NO_2, and the relevant experimental evidence from laboratory and atmosphere.

The possibility that man's activities could alter the physical and chemical conditions of the soil and alter the N_2O flux into the atmosphere appears to have been raised first by Crutzen (1972). In a later paper (Crutzen, 1974) he noted the rapidly increasing usage of industrially produced nitrogen fertilizers and the consequent possibility of increased flux of N_2O. More recently, Hardy & Havelka (1975) have attracted the attention of atmospheric scientists by pointing out that the use of artificial fertilizers, growing at a rate of 6% per year, could increase from 40 Mtons (N)/yr in 1974 to 200 Mtons (N)/yr by the year 2000. Since the natural fixation rate from all sources on land and ocean is estimated to be about 250 Mtons (N)/yr, an increase of 200 Mtons (N)/yr would be a significant fraction of the present total terrestrial fixation rate. McElroy (1975a, b; McElroy, 1976) has estimated that the resulting reduction in total ozone could be 20% or more by the year 2025. The calculation on which these estimates were based assumed a 20-year lifetime for N_2O in the troposphere, and a sink for N_2O in the oceans. It also assumed that there will be no important time lag between fertilizer input and denitrification, i.e. an increase of 200 Mtons in the annual rate of fixation via artificial fertilizer by the year 2000 would be followed by an essentially simultaneous increase of 200 Mtons in the denitrification rate. Crutzen (1976), using a similar estimate for the atmospheric lifetime for N_2O as did McElroy but assuming the ocean to be a source of N_2O rather than a sink following Hahn (1975), finds a much smaller effect from the increased burden of fertilizer. He assumed atmospheric lifetimes of 10 to 20 years

for N_2O and allowed the marine source to range from 50% to 93% of the global source. Competing with such a large source in the seas the fertilizer input becomes a much less significant fraction of the total atmospheric N_2O input rate even in the year 2000. To obtain an upper limit O_3 reduction, Crutzen assumed that the time of denitrification does not significantly lag the time of fixation. He calculated reductions of O_3 between 1.5% and 9% by the year 2025. In a recent review paper McElroy et al. (1976) have noted that major uncertainties surround the role of the oceans in controlling atmospheric N_2O. As had Bates & Hays (1967), they deduced that the oceans would represent a net sink of 40 Mtons of N_2O–N per year and that global ozone reductions of the order of 20% by the year 2013 are not improbable, given fertilizer-usage projections stated above.

We (Liu et al., 1976) on the other hand, have addressed the question of the delay to be expected between the time that application of fertilizers to arable land reaches a certain rate and the time that the return of denitrified N_2O and N_2 to the atmosphere attains that same rate. We drew attention to the fact that the global reservoir of fixed nitrogen is very large compared to the present or projected yearly fixation rates. We have pointed out that, even neglecting the ocean pool, according to current estimates about 2×10^5 Mtons (N) is in various terrestrial reservoirs while fixation is occurring on land at a current rate of about 200 Mtons (N) annually. This leads to a doubling time of the order of 1000 years for fixed nitrogen. Thus, barring the operation of special mechanisms that might come into play when large quantities of soluble nitrogen are injected directly into the soil, increasing the use of fertilizers from 40 to 200 Mtons (N)/yr between the years 1974 and 2000 will produce a relatively small change in the fixed nitrogen reservoir. The consequence is that attainment of a steady state will take a long time. In fact, assuming a 20-year atmospheric lifetime for N_2O and neglecting the oceanic source we arrived at an estimate of only 1% reduction in O_3 by the year 2025 due to the projected increased use of industrial fertilizers.

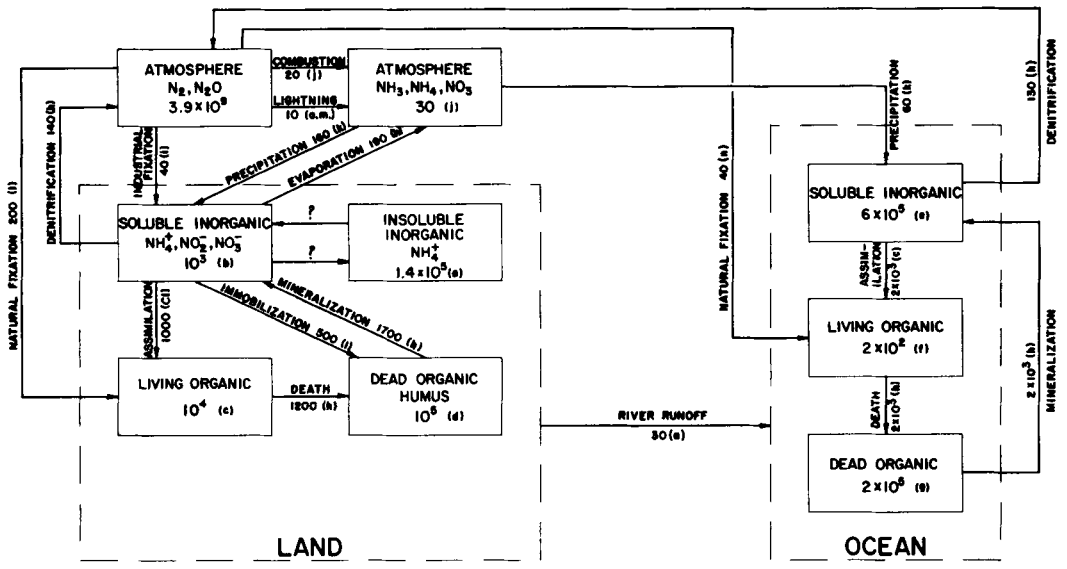
In making this estimate we assumed that the soluble inorganic nitrogen in the soil remains in equilibrium with plants, humus, and the insoluble inorganic nitrogen sequestered in clay particles. Our calculation allowed for a possible immediate denitrification of 10% of the soluble inorganic nitrogen (NH_4^+, NO_3^-, and NO_2^-) added to the soil whether it was produced by mineralization of nitrogen that had been immobilized in humus, by nitrification of ammonium sequestered in clays or by injection of soluble inorganic fertilizers into arable land by man.

Sze & Rice (1976) noted that our earlier model assumed that the prompt denitrification rate will vary linearly with the amount of soluble inorganic N added to the soil even when the rate of fertilization is five times the present rate (and comparable to the present rate of mineralization per unit area). They have pointed to evidence that the efficiency of utilization of fixed nitrogen in producing plant mass diminishes as fertilizer use per unit area increases, a possibility that we discuss later. Assuming that the unused nitrogen is lost mostly in denitrification they have estimated that the reduction of ozone by 2025 might be as large as 10% if 60% of the fertilizer applied to arable lands is denitrified promptly. In agreement with our model, they calculated a reduction in ozone of 1.4% if only 10% of the fertilizer is immediately denitrified.

The objective of this paper is to examine the nitrogen cycle, especially N_2O sources and sinks, to evaluate the uncertainties and to critically look into the assumptions made in the calculation of stratospheric ozone reductions due to artificial fertilizer usage. Experts in several disciplines (e.g., soil science, microbiology) will note that we have employed a black-box approach. This was necessary because we are not knowledgeable enough to appreciate many of the microprocesses at play in soils and elsewhere, but also because there are legitimate large scale input–output questions that do not necessarily interest soil scientists or other specialists. The present scarcity of basic information can be partially alleviated by more interdisciplinary studies.

2. Nitrogen cycle

In Fig. 1 we illustrate the elements in the nitrogen cycle as we interpret them, drawing from available studies. The boxes represent the various reservoirs of nitrogen on land and in the ocean. The largest reservoir is the atmosphere where N_2 and N_2O contribute a mass of 3.9×10^9 Mtons (N). We



(a) DELWICHE (1970)
(b) ABOUT 1% OF INSOLUBLE INORGANIC NITROGEN.
(c) WHITTAKER AND LIKENS (1973), ASSUMING C/N = 80.
(ci) WHITTAKER AND LIKENS (1973), ASSUMING C/N = 40.
(d) OUR OWN ESTIMATE.
(e) VACCARO (1965).
(f) WHITTAKER AND LIKENS (1973), ASSUMING C/N = 12.
(g) SKIRROW (1965), ASSUMING C/N = 12.
(h) FORCED VALUE TO MAINTAIN STEADY STATE.
(i) HARDY AND HAVELKA (1975).
(j) ROBINSON AND ROBBINS (1968).
(k) BURNS AND HARDY (1975) & REFS. THEREIN; TSUNOGAI (1971)
(l) ABOUT 1/2 OF ASSIMILATION, SEE TEXT.
(m) CHAMEIDES, et al (1977)
(n) SEE TEXT

Fig. 1. Nitrogen cycle of the land and the ocean, units are in million tons (N) for reservoir contents or million tons (N) per year for transfer rates.

neglect the large reservoirs of nitrogen in primary and sedimentary rocks in this discussion because it is generally agreed that the transfer rate between this reservoir and all others is very small—about 10 Mtons (N)/yr. Microbial symbionts of leguminous plants and nitrogenase in general are responsible for most of the nitrogen fixation at present (Hardy & Havelka, 1975). They effectively cause a splitting of the N_2 bond, and supply fixed nitrogen to living plants at a rate of about 200 Mtons (N)/yr. (References to our sources are given in the figure.) According to the carbon inventory of Whittaker & Likens (1973) there are 1×10^4 Mtons (N) of fixed nitrogen in plants if the ratio of carbon to nitrogen is taken to be 80 (Deevey, 1973). Most of the nitrogen fixed in living plants has a lifetime of the order of 15 years, although it is obvious that a lifetime of one year applies in many cases, e.g. cereal crops and leaves of trees. After the death of plants, their fixed nitrogen is transferred to the reservoir of dead organic material where according to our estimate (Table 1) reside 10^5 Mtons (N) compared with 6×10^4 Mtons (N) that follow from the carbon inventory of Bolin (1970) and a C/N ratio of 12 (Allison, 1973). On the other hand, Delwiche's (1970) estimate of 7.6×10^5 Mtons (N) is a factor of 7 greater than ours. From 1 to 5% of the fixed nitrogen in humus is mineralized annually —transformed to soluble NH_4^+, NO_3^-, and NO_2^-— according to most estimates (Burns & Hardy, 1975; Bartholomew, 1975; Bremner & Tabatebai, 1973; Hauck, 1971). The reservoir of soluble fixed nitrogen in the soil is also fed by industrial fertilizers into tilled farm lands (present rate 40 Mtons (N)/yr), and by precipitation of NH_3, NH_4^+, NO_3^- in rainwater at a rate of 160 Mtons/yr (Burns & Hardy, 1975, and references therein). The precipitating and depositing fixed nitrogen is supplied from an atmospheric reservoir of 30 Mtons resulting from evaporation or volatilization of soluble soil nitrogen at a rate of 190 Mtons (N)/yr, by lightning at a rate of 10 Mtons (N)/yr, and by combustion at a rate of 20 Mtons (N)/yr. (60 Mtons (N)/yr falls in rain and dry deposits in the

Table 1. *An estimate of the amount of organic nitrogen in the world's soils**

Soil type	tons (N)/ha	% of soil type over world	tons (N)
Podzolic	6.6	0.09	8×10^9
Chernozems	24	0.06	19×10^9
Chestnut and red-brown	13	0.07	12×10^9
Serozems	7.5	0.17	17×10^9
Krasnozems	11	0.19	26×10^9
Gray-brown forest	9.4	0.05	6×10^9
Alluvial	30	0.04	16×10^9
Mountain and tundra	6	0.20	16×10^9
Snows and glaciers		0.12	0
			120×10^9 tons

* References = Kononova et al. (1961); Gerasimov (1965); Buckman & Brady (1971).

ocean.) A recent paper (Chameides et al., 1977) deduced a possibly larger lightning fixation rate. In the soil, almost all of the fixed inorganic nitrogen—1.4×10^5 Mtons according to Delwiche—is sequestered as insoluble ammonium bound in clay particles. The exchange between this vast reservoir and the soluble pool (that contains only about 1% of the fixed inorganic nitrogen in the soil) as a result of sequestration and nitrification by soil bacteria is apparently very slow and inefficient. Following Delwiche (1970) we show the reservoir of soluble fixed nitrogen on land as about 10^3 Mtons.

The assimilation rate of carbon on land is 4.8×10^4 Mtons (C)/yr (Whittaker & Likens, 1973). If we divide this rate by the C/N ratio of 80 we get 600 Mtons (N)/yr, but Hitchcock & Wechsler (1972) found the global nitrogen assimilation rate to be 7900 Mtons (N)/yr. For land alone, Hitchcock (private communication, 1976) estimates a range of 1600 to 2400 Mtons (N)/yr for assimilation, excluding bacteria and fungi. The discrepancy reflects partly the uncertainties in the estimates and partly the fact that nitrogen-rich plants (e.g. crops, grasses) as well as parts of plants (e.g. leaves of trees) have shorter lifetimes than the woody parts of trees. We choose the nitrogen assimilation rate on land to be 1000 Mtons (N)/yr. It will be shown later that this choice of assimilation rate combined with the estimated immobilization rate will imply a mineralization rate of 1.7% per year which is consistent with the generally accepted values of 1 to 5%.

Soluble inorganic nitrogen is immobilized into dead organic matter by bacteria. The rate (500 Mtons (N)/yr) is about $\frac{1}{2}$ the rate at which soluble inorganic fixed nitrogen is assimilated by plants. This estimate follows from experiments performed with tagged ^{15}N in which recovery of nitrogen in crops was between 40% and 70% and total organic recovery (crop plus soil) was between 60% and 90% (Allison, 1973; Hauck, 1971). The nitrogen recovered in the soil (between 20% and 30%) had been immobilized by bacteria. For comparison, Hitchcock (private communication, 1976) estimates 1500 Mtons (N)/yr for the rate of immobilization of fungi and bacteria. 1200 Mtons (N) must be transferred annually from living to dead organic material in order to conserve the 200 Mtons fixed in plants annually by symbionts and the 1000 Mtons assimilated from the soil. Adding to these 1200 Mtons the 500 Mtons immobilized by bacteria it follows that the mineralization rate must be 1700 Mtons (N) annually. This annual rate is 1.7% of the pool of dead organic fixed nitrogen, a value that compares well with the previously quoted estimates of 1 to 5%.

An alternative approach to the determination of transfer rates in the soil nitrogen cycle is as follows. Nitrogen depletion in agricultural soils has been observed carefully in several regions of the U.S.A. and elsewhere. Typical results, discussed by Allison (1973), are that a roughly exponential decay of soil nitrogen occurs under poor agricultural practices, at least for the initial 30 to 40 years in the midwestern U.S. and Canada. Fig. 2, from Allison il-

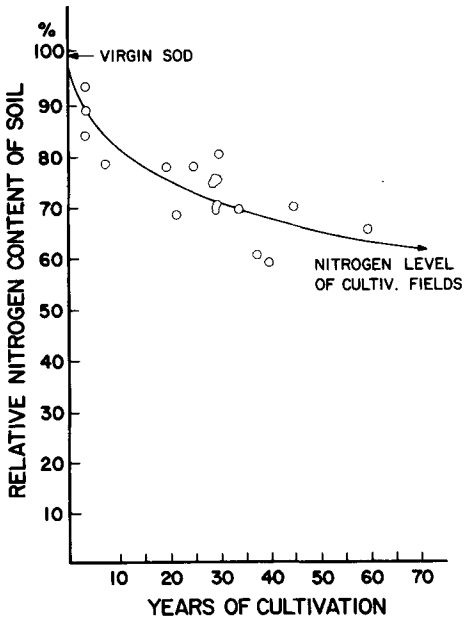


Fig. 2. Decline of soil nitrogen with length of cultivation periods under average farming practices in the Middle West. This figure was taken from Allison (1973); original data are from Jenny (1933) as Allison discussed. We use these data to estimate mineralization rates as discussed in the text.

lustrates these results. C. C. Delwiche (private communication, 1976) warns us, however, that not all soils demonstrate N loss when first cultivated; crop type, climate and seasonal effects are involved. With these limitations in mind, we proceed to employ the data of Fig. 2 because such data allow us to deduce the lifetime, τ, of soil nitrogen against uncompensated mineralization, and to write four algebraic equations for the unknowns: I, A, M, D, where

I = immobilization rate
A = assimilation rate
M = mineralization rate
D = biomass N death rate, as in the lower left hand corner of Fig. 1.

To write the four equations, let us assume that globally averaged quantities are appropriate. For our first equation, we employ the rate of decay of soil N from Fig. 2 discussed above, and similar data also discussed by Allison (1973). We write

$$\frac{\text{Soil N reservoir}}{100} = M - \frac{D}{5} - I \qquad (3)$$

The left hand side approximates a 1% loss of soil N per year observed for the initial 30 years. As much as half of these soil nitrogen losses could have been due to erosion (CAST, 1976; Allison, 1973). This would probably happen mostly during the first few years of cultivation and become small thereafter. We use a small retention of crop residue (20%) to take into account the erosion loss. The right hand side shows a mineralization loss, M, of soil nitrogen, and a replenishment by immobilization, I.

A second equation expresses an assumed steady state biomass:

$$A + F = D \qquad (4)$$

where F is the total fixation rate on land, taken to be 200 Mtons (N) per year (Hardy & Havelka, 1975). Equation 5 is an analogous relation for the soil organic pool

$$D + I = M \qquad (5)$$

According to previous discussion, we have the fourth equation

$$I = \frac{A}{2} \qquad (6)$$

Solution of these four simultaneous equations yields the following globally averaged rates:

D = 1250 Mtons/year
I = 500 Mtons/year
M = 1700 Mtons/year
A = 1000 Mtons/year

These values agree very well with our previous estimates.

Quantitatively, one of the most poorly understood processes in the nitrogen cycle is the rate of sequestering of soluble ammonium in its clay-fixed form as well as the subsequent nitrification or return of the ammonium to the soluble state. It is generally believed that an equilibrium exists among three forms of ammonium in the soil: soluble, exchangeable and clay-bound (Allison, 1973). The coupling between the bound and exchangeable forms is probably weak. But so long as the exchange rate is unknown our only recourse in this analysis is to parameterize the rate. For a relatively strong equilibrium, we shall choose a transfer rate

of 500 Mtons (N)/yr and for a weak equilibrium, a rate of 10 Mtons (N)/yr.

The combined annual rate of volatilization and denitrification on land is 330 Mtons (N)/yr and is forced by continuity considerations. It is interesting that this gaseous production rate is about 17% of the total input of soluble inorganic nitrogen to the soil pool (2000 Mtons (N)/yr). This is consistent with the percentage of N in fertilizers that cannot be accounted for in many fertilizer tracer studies and is usually attributed (with little experimental proof) to gaseous loss. In fact, in many studies, the loss is loosely attributed to denitrification although the experimental arrangements used in open systems do not permit a gas analysis. Thus, there is no way in these studies of deciding the apportionment of the gas produced among N_2O, N_2, and NH_3, for example, or even in demonstrating that gas is produced. Large losses by volatilization of NH_3 are possible under some circumstances. For example, the concentration of ammonium in rainwater over Israel exhibited a maximum during spring, correlating more with soil temperature than with air temperature (Yaalon, 1964; see also Lodge et al., 1968). This was attributed to increased biological decomposition of organic matter in the soil. Yaalon's NH_4^+ concentrations in 1962–1963 were approximately ten times higher than corresponding measurements made from 1922–1924. The heavy fertilization of Israel during the intervening forty years was believed a probable cause for this enhancement. In 1963, the nitrogen as nitrate and ammonia deposited by rainfall over Israel annually was approximately equivalent to the annual consumption of fixed nitrogen as chemical fertilizer. Also, data from grazed fields show significant fluxes of ammonia (Denmeade et al., 1974). Our own inventory suggests that the gaseous N loss is about equally divided between denitrification and volatilization. It is obviously very important to know under field conditions what fraction of fertilizer added to the soil is denitrified. In fact, the variation of the process with fertilizer input and the ratio of N_2O to N_2 are data essential to an understanding of the problem to which we now address ourselves.

The question of fixation and denitrification in the oceans is a subject of lively debate. The inventory and exchange rates in the oceans are even more uncertain than those on land. Runoff of fixed nitrogen from the continents to the ocean is at a rate of about 30 Mtons (N)/yr (Delwiche, 1970) or less (Tsunogai, 1971). Dry deposition and rainfall contribute 60 Mtons (N)/yr to the seas. The latter figure, 60 Mtons (N)/yr, from Burns & Hardy (1975) and references therein, is larger than the corresponding rate of 20 Mtons (N)/yr deduced by Tsunogai (1971). The total global fixation rate in oceans is uncertain. Delwiche (1970) suggested 10 Mtons (N)/yr, while the CAST report (1976) quoted a range of values between 0.4 and 4 Mtons (N)/yr. But very high values, 90 to 130 Mtons (N)/yr are suggested by Soderlund & Svensson (1976) (reported to us by P. J. Crutzen). We choose a median value, 40 Mtons (N)/yr, to display in Fig. 1.

An estimate of 6×10^5 Mtons (N) for the soluble inorganic pool in the ocean is given by Vaccaro (1965). Using a carbon inventory of Whittaker & Likens (1973) and a figure of 12 for the C/N ratio, we conclude that the living organic reservoir in the ocean should be 200 Mtons (N) and the assimilation rate 2×10^3 Mtons (N)/yr. The dead inorganic mass of 2×10^5 Mtons (N) has been estimated by Skirrow (1965) from a carbon inventory and a C/N ratio of 12 in dead organic matter. A rate of exchange between the living and dead reservoirs along with the mineralization rate of 2×10^3 Mtons (N)/yr is forced to maintain a steady state. The exchange with sediments is only about 10 Mtons (N)/yr (Burns & Hardy, 1975). Neglecting this exchange, the denitrification rate in the ocean will have a forced value of 130 Mtons (N)/yr.

It is important to note that once nitrogen from the atmosphere is fixed in the soil and ocean it will spend most of its time within the cycle of plants–animal–humus-soluble nitrogen. In the soil, only about 10% of the time does the fixed nitrogen go to denitrification and in the ocean only 6% of the time. In other words, the total fixed nitrogen (mainly humus + plants) in the soil and oceans serves as a buffer between nitrogen fixation and denitrification. To increase the rate of denitrification substantially, one has to increase the total fixed nitrogen abundance. With the projected 200 Mtons (N)/yr fixation rate by year 2000, the doubling time of fixed nitrogen will be about 600 years for the land and more than 4000 years for the ocean. Therefore, the denitrification rate in the ocean will not be changed appreciably by man's nitrogen fixation activities in the next few centuries.

In Fig. 3 we isolate the source and sinks of soluble inorganic nitrogen on land. The percentages

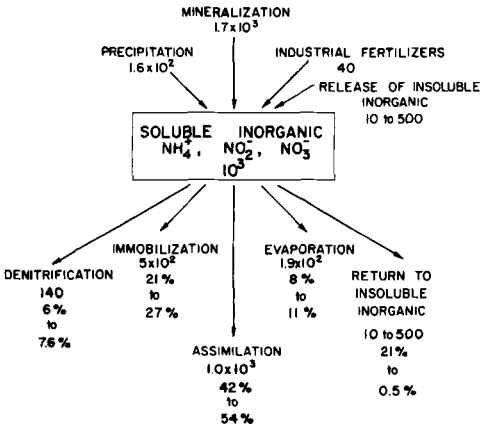


Fig. 3. Sources and sinks of soluble inorganic nitrogen in the land, units are the same as Fig. 1.

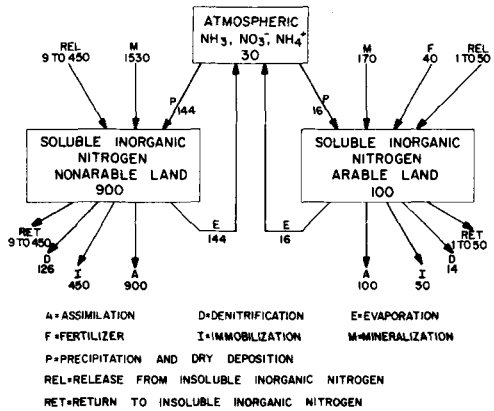


Fig. 4. Same as Fig. 3 except divided into arable and non-arable land.

of the fluxes into various pools are shown in the two extreme cases chosen for the rates of sequestration of ammonium in clay. In Fig. 4 we divide the land area into two parcels, the roughly 10% that is arable and the 90% that is not. We apportion the sources and sinks of soluble nitrogen between them in the ratio of their areas (this assumption does not affect the outcome of the calculations) except for industrial fertilizer which is assigned entirely to the 10% of the land area that is farmed. Using this chart, we can compare the mineralization rate we assign to arable land with Hauck (1971). His analysis of crop lands assigns only 80 kg (N)/ha/yr which gives a source of 1200 Mtons (N)/yr globally. This is a factor of 1.4 less than our estimate.

3. Sources and sinks of N_2O

In early discussions of atmospheric N_2O, Bates & Hays (1967) and others before them speculated that biological denitrification in soils is its major source. It is difficult to assess the percentage of the denitrified gas that enters the atmosphere as N_2O because of a lack of definitive measurements. Stefanson (1973) showed that the ratio of N_2O/N_2 evolved from denitrification of NO_3^- varied from 1/0.06 to 1/6 depending on the soil–water potential. The N_2O to N_2 ratio depends also on the type of soil and fertilizer added and soil pH. Lower pH favors generation of N_2O compared to N_2 although the overall rate of denitrification is reduced (Alexander, 1971). Typically ^{15}N tracer studies, summarized by Hauck (1971), have been conducted without identification of gaseous products or gaseous products have been measured in nontracer studies, e.g., Burford & Stefanson (1973) who measured N_2O releases indirectly. Due to large variations of the N_2O to N_2 ratio with the soil properties, frequent and large scale field observations are needed to provided definitive answers. CAST (1976), after reviewing all available data, suggested a global average ratio of N_2O/N_2 in denitrification of 0.06.

Similarly, uncertainty exists in the ocean production rate of N_2O. A large oceanic source has been deduced by Hahn (1974) from measurements in the North Atlantic. He extrapolated from his observations to a global N_2O source of 85 Mtons (N)/yr. McElroy et al. (1976) on the other hand, argued that the data base of Hahn is too limited to permit this extrapolation and suggested that a study of the observations by Craig & Gordon (1963), and those of Hahn and correlation of these with ocean productivity would imply that the ocean is a sink (see also Bates and Hays, 1967) in some regions and a source in others. As a system they concluded that the sea is a net sink for 25 Mtons (N) of N_2O each year. Experiments by Yoshinari (1976) in the Western North Atlantic and Caribbean imply a small, perhaps 1 Mton (N)/yr source. If the N_2O produced in oceans is only 1 Mton (N)/yr and the total denitrification rate there is 100 Mtons (N)/yr then N_2 would be the dominant denitrification product in oceans. The pioneering studies of Craig & Gordon (1963) showed signs of different oceanic regions being undersaturated and supersaturated but in their discussion they noted the difficulty one

has in interpreting data from their first measurements. The basic problem (now solved by Craig et al., 1976) has been that hot wire detection gas chromatography is not sensitive enough to permit the required accuracy and precision. The latter authors find, for example, no significant latitudinal, seasonal, or daily change of N_2O in marine air, as seen in the first two samples by Craig & Gordon (1963). The most recent data of Craig et al. (1976) not only indicate that the crude latitudinal gradient of N_2O in marine air from Craig & Gordon (1963) was not real, but that N_2O is a long-lived atmospheric gas. Lifetimes of about 100 years would mean that the atmospheric N_2O burden—(1400 Mtons (N) corresponding to 0.3 ppm mixing ratio) could be maintained by steady sources of N_2O as small as 14 Mtons (N)/yr.

There also may be other land-based sources of N_2O, e.g., in nitrification (Ritchie & Nicolas, 1972) or (less likely) in chemodenitrification (Stevenson et al., 1970). Sewage and nitrogen waste treatment plants could also produce N_2O. At least one other N_2O source must be considered, namely combustion. Pierotti & Rasmussen (1976) have measured N_2O in smokestacks of coal-burning and gas-burning power plants and deduced a possible 2.2 Mtons (N)/yr N_2O source (see also Weiss & Craig, 1976). By analogy, volcanoes and forest fires could also be sources of N_2O.

The only known sink for atmospheric N_2O is photolysis in the stratosphere (Bates & Hays, 1967; Johnston & Selwyn, 1975; Stedman et al., 1976) which destroys only about 10 Mtons (N)/yr and gives N_2O a lifetime of about 150 years. Certain gas-phase reactions are not completely ruled out. Biogenic sinks for N_2O are observed in many experiments. N_2O reduction into N_2 might be a major reaction of nitrogenase (Hardy & Knight, 1966) and many denitrifying bacteria can reduce N_2O (Barbaree & Payne, 1967, Tiedje, private communication, 1976). However, no quantitative estimates of these sinks are available.

Without good estimates of either sources or sinks of N_2O we cannot determine its atmospheric lifetime directly. However, Junge (1974) using an approximate mathematical analysis related the lifetime of a trace gas to its standard spatial deviation. Some of his assumptions (e.g. relatively uniform sink and source function) might not apply to N_2O. Nevertheless with a derived standard deviation of 8%, coupled with measurements by Hahn (1974) he deduced the lifetime of N_2O to be 8 years with a factor of two uncertainty. Recent measurements of N_2O in the atmosphere (R. F. Weiss, private communication, 1976; Craig et al., 1976; Yoshinari, 1976; Singh et al., 1976; Rasmussen et al., 1976) have shown different results. Each of these workers has multiple observations of N_2O in marine and/or rural continental air that show little or no significant variability from day to day, that is, standard deviations of 2% or less except the latter reference, which showed 2.8%. The Scripps Institute data (the former two references above), perhaps the most convincing, were gathered between 70° N and 70° S in the mid-Pacific over several seasons and years. Little, if any, difference between 1964 and 1974 values was seen, except for a 1.5% increase with time, possibly due to combustion sources of N_2O (Weiss & Craig, 1976). Careful separation preceded detection (in ratio to CO_2) by gas chromatographic, ultrasonic phase shift detection. Yoshinari employed an independent method, helium ionization GC detection. The Scripps group finds average N_2O mole fractions of 0.296 ppm as did Singh while Yoshinari found (0.328 $\pm$ 0.005) ppm, although Yoshinari's systematic accuracy is $\pm$10%. Rasmussen et al. (1976) find a mean value of 0.330 ppm.

Earlier N_2O measurements by Goody (1969), Craig & Gordon (1963), Hahn (1974), Schutz et al. (1970), Lahue et al. (1970) and others showed about 0.250 ppm with significant variations that clearly implied a relatively short (10 years) N_2O atmospheric lifetime if Junge's (1974) analysis holds. While much of the statistical variability of these data may be artifacts of early analytical methods and of sampling near sources (Hahn, 1975) there are seasonal trends (Goody, 1969; Schutz et al., 1970) that one should not dismiss. By putting more weight on the recent measurements and taking into account the lack of positive identification of either a significant source or sink (greater than 40 Mtons (N)/yr) we estimate the lifetime of N_2O to be between 30 and 100 years. This implies, respectively, an annual N_2O production of 50 and 14 Mtons (N). If denitrification (270 Mtons (N)/yr; see Fig. 1) is the source of N_2O, it also implies an N_2O to N_2 ratio respectively of 1 : 4.4 and 1 : 16, assuming the ratio to be the same in the denitrification from the land and the ocean. A 1 : 16 ratio was considered likely by CAST (1976).

4. The effect of industrial fertilizers on ozone

To evaluate the effect that projected industrial fertilizer usage might have on the ozone layer during the next 50 years, we shall make the following assumptions: (a) the source of atmospheric N_2O is denitrification and (b) the rate of denitrification is linearly proportional to the abundance of soluble inorganic nitrogen. Assumption (b), that of linearity, is essentially that the kinetics of denitrification are first order in NO_3^- concentration. In reality, the order of the kinetics depends on many parameters as shown by Bowman & Focht (1974). Their data (for two distinct soil types) showed regimes of first-order kinetics and zero-order kinetics (i.e. denitrification rate independent of NO_3^- concentration when NO_3^- is very high). Similarly, Porter (1976) has presented data on ^{15}N-tagged fertilizer recovered in corn fertilized at three different dosages, 125, 252, and 376 kg/ha; the latter two rates are very high. He found that 50–52% of the fertilizer N was recovered in the plants, independent of fertilizer rate. Also, indications that fertilizer losses are mostly due to immobilization (Hauck, 1971) should not be ignored. There would be little incentive for farmers to use more nitrogen fertilizers if the combined loss of nitrogen through immobilization and denitrification is more than 70%. Thus, it may not be realistic to assume that fertilizer loss percentages increase with fertilization rate. Nonetheless, to explore a wide range of possible effects later in this section, we shall alter assumption (b) as suggested by Sze & Rice (1976). We also assume: (c) the N_2O to N_2 ratio in denitrification is the same for the land and the ocean, but we will discuss the case where oceans are not a source of N_2O. We will parameterize the atmospheric lifetime of N_2O to 30 years and 100 years (assumption (d)).

As we have pointed out most of the nitrogen fixed as artificial fertilizer will go through the plant–humus cycle at least ten times. The rate of fixation, of exchange from one reservoir to another and of denitrification will all change with time. Thus, the fluxes and concentrations involved in the nitrogen cycle will have to be calculated with a time-dependent model.

The flux of N_2O from arable land at time t, will be given by

$$\phi_a = \phi_a^0 \frac{(n_{si})_a}{(n_{si}^0)_a} \tag{7}$$

where the subscript (a) is for arable land and (n_{si}) denotes soluble inorganic nitrogen abundance, the superscript (0) denotes the value when appreciable use of artificial fertilizer begins. The total N_2O flux, however, will be composed of the sum of that from cultivated and untilled land and ocean.

$$\phi = \phi^0 \frac{(n_{si})_a + (n_{si})_w}{(n_{si}^0)_a + (n_{si}^0)_w} + \phi_{ocean}^0 \tag{8}$$

where the subscript (w) stands for wild or unfarmed land. For the reasons already given ϕ_{ocean} will be constant within the next century. The column abundance, N_{N_2O}, of N_2O in the atmosphere N_{N_2O} will be given by the continuity equation

$$\frac{\partial N_{N_2O}}{\partial t} = \phi - \frac{N_{N_2O}}{\tau_{N_2O}} \tag{9}$$

where τ_{N_2O} is the atmospheric lifetime of N_2O.

To obtain the N_2O flux we need to know how the amount of soluble fixed nitrogen n_{si} varies with time. Since the lifetime of soluble inorganic nitrogen in the soil is less than one year we can take the amount at any time to be proportional to the rate at which it is then being produced, that is

$$p_{si} = \frac{n_{si}}{\tau_{si}} \tag{10}$$

where p_{si} is the production rate and τ_{si} is the lifetime of soluble inorganic nitrogen. Furthermore, we assume this lifetime to be constant year after year even if n_{si} and p_{si} change. Therefore,

$$n_{si} = n_{si}^0 \frac{p_{si}}{p_{si}^0} \tag{11}$$

Now, according to Figs. 3 and 4

$$p_{si} = p_r + p_f + \frac{n_h}{\tau_h} + \frac{n_{ii}}{\tau_{ii}} \tag{12}$$

where p_r is the contribution of precipitation and dry deposition, p_f that of industrial fertilizer, n_h/τ_h the mineralization rate of humus, n_h and τ_h being respectively the amount of humus and its lifetime and finally n_{ii}/τ_{ii} is the rate of release of insoluble inorganic nitrogen from clay by nitrifying bacteria. p_r is assumed not to vary with time, because the contribution of arable land to the total amount of fixed nitrogen in the atmosphere will be small com-

pared to that from all the land even when $(p_r)_a$ is twice the present rate.

We must know how the amount of fixed nitrogen in humus and clay-bound nitrogen varies with time to determine the rate of production of soluble inorganic nitrogen. Since the lifetime of nitrogen immobilized in humus and sequestered in clay is long, we must determine these quantities by solving the differential equations

$$\frac{dn_h}{dt} = p_h - \frac{n_h}{\tau_h} \tag{13}$$

and

$$\frac{dn_{ii}}{dt} = p_{ii} - \frac{n_{ii}}{\tau_{ii}} \tag{14}$$

where the meaning of the symbols should be clear.

In the case where the yearly sequestration and nitrification rates are 500 Mtons the percentages for the losses of soluble inorganic nitrogen in the upper line of Fig. 3 apply. Immobilization and the death of plants contribute to p_h. If we neglect natural fixation as unimportant when we are growing crops using fertilizer then 42% plus 21% of the total rate of production of soluble inorganic nitrogen is the rate of production of fixed nitrogen immobilized in humus

$$p_h = 0.63\, p_{si} \tag{15}$$

Thus

$$\frac{dn_h}{dt} = 0.63 \left(p_r + p_f + \frac{n_{ii}}{\tau_{ii}} \right) - 0.37 \frac{n_h}{\tau_h} \tag{16}$$

By assuming that τ_h and τ_{ii} do not change with time, we get

$$\frac{dn_h}{dt} = 0.63 \left(p_r + p_f + p_{ii}^0 \frac{n_{ii}}{n_{ii}^0} \right) - 0.37\, p_h^0 \frac{n_h}{n_h^0} \tag{17}$$

Similarly, for the amount of sequestered nitrogen

$$p_{ii} = 0.21 \left(\frac{n_h}{\tau_h} + p_r + p_f + \frac{n_{ii}}{\tau_{ii}} \right) \tag{18}$$

$$\frac{dn_{ii}}{dt} = 0.21 \left(p_r + p_f + p_h^0 \frac{n_h}{n_h^0} \right) - 0.79\, p_{ii}^0 \frac{n_{ii}}{n_{ii}^0} \tag{19}$$

Since p_r is known and p_f has projected values, (17) and (19) may be solved together to give n_h and n_{ii}, hence p_{si} and n_{si} at any time t. As we have pointed out the flux of N_2O from arable land is proportional to $(n_{si})_a$ according to (7), and the total flux of N_2O is given by (8).

If ϕ is to be large compared to ϕ° because of the use of fertilizer then $(n_{si})_a$ must be large compared to $(n_{si})_w$. $(n_{si}^0)_a$ at the present time is only about 10% of $(n_{si}^0)_w$. For $(n_{si})_a$ to grow large, then it is necessary that p_f becomes a very important term in p_{si}^a; under present circumstances p_f is only $\frac{1}{5}$ of p_{si}^a. Increasing p_f by a factor of 5 by the year 2000 will bring this ratio to about 1, an increase in $(n_{si})_a$ that leaves it still small compared to $(n_{si})_w$. It is for this reason that the contribution of artificial fertilizers to the total N_2O budget by the early 21st century is expected to be small.

We have carried out calculations of the amount of ozone reduction to be expected by the year 2025 under the following assumptions: 6% increase in fertilizer use per year from 40 Mtons (N)/yr in 1974 to 200 Mtons (N)/yr in the year 2000, constant use thereafter, a 30-year lifetime of N_2O in the troposphere and a 100 year lifetime, an exchange rate of 500 Mtons (N) per year and a rate of 10 Mtons (N) per year between the soluble and insoluble inorganic reservoir via sequestering and nitrification. Finally, we take the annual denitrification rate to be its deduced natural value, 7% of the total annual input to the soluble N pool (see Fig. 3), and triple that value (Sze & Rice, 1976). The scaling factor between atmospheric N_2O change and ozone reduction was taken as 5 in the CIAP Final Report (Grobecker et al., 1974), but recent OH measurements (Anderson, 1976) imply the factor should be around 10. Future stratospheric concentrations of inorganic molecules containing Cl atoms could alter the stratospheric sensitivity to added N_2O. We choose 8 as our scaling factor. The results are summarized in Table 2.

In Table 2 it can be seen that increasing the rate of exchange between the soluble and insoluble pools has the effect of lowering the increase of fixed nitrogen in the soluble reservoir, but only very slightly for a 50-fold change in the rate. Obviously, a strong departure from linearity in the relationship between the rate of denitrification and the rate of application of fertilizer to croplands has a large effect on the ozone reduction. Tripling the denitrification percentage of applied industrial fertilizers more than doubles the ozone reduction, in agreement with the finding of Sze & Rice (1976).

Table 2. *Calculated ozone reduction by the year 2025 due to projected industrial nitrogen fertilizers*

N_2O Lifetime (yrs)	Industrial fertilizer denitrification percentage	Exchange rate between soluble and insoluble inorganic nitrogen (Mtons (N)/yr)	Same N_2O/N_2 in ocean and land denitrification	Land is the only source of N_2O
			Percentage O_3 reduction	
100	8.4	500	0.17	0.33
	10.5	10	0.21	0.4
	25	500	0.37	0.7
	32	10	0.5	0.9
30	8.4	500	0.6	1.0
	10.5	10	0.7	1.3
	25	500	1.3	2.4
	32	10	1.5	2.8

If the total denitrification rate is truly set by the system just described, a change in the tropospheric lifetime implies a change in the ratio of N_2O to total gas (N_2 + N_2O) in the emergent flux. Thus, the flux of N_2O when the N_2O tropospheric lifetime is 30 years, is about 3 times as great as when it is 100 years, although the total denitrification flux remains the same. Hence, the ozone reduction possible by A.D. 2025 is much smaller when the lifetime of N_2O is longer.

5. Conclusion

There are still many uncertainties in our inventory of the nitrogen cycle. The sources and sinks of N_2O are very poorly understood. We do not even know that denitrification of the fixed nitrogen in soils and oceans is the dominant source of atmospheric N_2O. Furthermore, the lifetime of N_2O is quite uncertain. By assuming denitrification to be the major source of atmospheric N_2O, and based on our limited knowledge, we estimate the ozone reduction due to possible future growth in the usage of industrial fixed nitrogen fertilizers to be between 0.2 and 2.8% by the year 2025. But long term (>300 years) ozone reductions could be as high as 10%. Because of the long time constants involved, the threat posed by extensive large scale use of artificial fertilizers may eventually be serious for the biosphere. It is essential for interdisciplinary research to be undertaken now to further our understanding of the nitrogen cycle, as Crutzen (1976) and McElroy (1976) have also advised.

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ИСТОЧНИКИ И СТОКИ АТМОСФЕРНОГО $И_2О$ И ВОЗМОЖНОЕ УМЕНЬШЕНИЕ ОЗОНА БЛАГОДАРЯ ПРОМЫШЛЕННЫМ АЗОТНЫМ УДОБРЕНИЯМ

В попытке уяснить, как контролируется содержание в атмосфере $И_2О$, рассматриваются почвенный и морской циклы азота. Мы даем обзор доступных данных по различным резервуарам связанного азота, по скоростям обмена между этими резервуарами и оцениваем, как содержания резервуаров и скорости обмена могут меняться под влиянием человека. Оказывается, что источники, стоки и времена жизни атмосферного $И_2О$ пока недостаточно хорошо известны. На основе наших ограниченных знаний об устойчивости атмосфернрго $И_2О$ мы делаем вывод, что будущий рост в использовании азотных удобрений, производимых промышленностью, может вызвать в течение следующих 50 лет глобальное уменьшение озона на величину от 1 до 2%. Однако, спустя столетия, слой озона может быть уменьшен на величину до 10%, если почва является основным источником атмосферного $И_2О$.