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Author

Johnston, Harold S.

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Harold S. Johnston

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Analysis of the Independent Variables in the Perturbation of Stratospheric Ozone by Nitrogen Fertilizers

by

Harold S. Johnston
Department of Chemistry
University of California
Berkeley, California 94720

Abstract

The important variables in the problem of ozone reduction by nitrogen fertilizers are regarded to be: τ, the atmospheric residence time of nitrous oxide; β, the fraction of nitrogen fertilizer that is denitrified within a few decades; and α, the fraction of denitrified gases that is nitrous oxide. With these three parameters, plus the results of the Climatic Impact Assessment Program, the time and degree of ozone reduction can be estimated by ultra-simple equations, which give about the same results as more elaborate model calculations. At the present state of uncertainty concerning the global nitrogen balance, this simple approach may be useful in framing working hypotheses for solution of the full problem.

The Effect of Nitrous Oxide on Stratospheric Ozone

This report accepts the results of the Department of Transportation's Climatic Impact Assessment Program CIAP (Grobecker et al., 1975; National Academy of Sciences, 1975). The findings pertinent to this study are:

(1) The natural abundance of stratospheric ozone is largely determined by the balance between formation from solar radiation and destruction by the oxides of nitrogen (NO and NO_2, or NO_x).

(2) Doubling stratospheric NO_x would reduce ozone by about 20 percent, Figure 1.

(3) Stratospheric NO_x is primarily produced from the oxidation of nitrous oxide (N_2O) in the stratosphere.

(4) Atmospheric nitrous oxide is produced from bacterial action (denitrification) in the soil and in the oceans.

The second conclusion above is illustrated by Figure 1 and it is simply stated by the expression:

$$-\frac{\Delta O_3}{O_3} = \frac{1}{5}\frac{\Delta NO_x}{NO_x} \qquad (1)$$

In this equation NO_x represents the global inventory of natural nitrogen oxides in the stratosphere, $NO_x + \Delta NO_x$ represents a perturbed global inventory of nitrogen oxides sustained over a period of at least 10 years (about three stratospheric residence times for NO_x), O_3 represents the global inventory of natural ozone in the stratosphere, and $O_3 - \Delta O_3$ is the steady-state ozone inventory with the NO_x perturbation. Further study of stratospheric ozone is underway, and the fraction 1/5 may be modified to 1/3 or 1/8 or some other number in the future. However, in view of uncertainties in the global nitrogen cycle, it is suggested that Equation 1 be accepted and used at the present time.

One point (+) in Figure 1 corresponds to the reduction in ozone caused by doubling the amount of nitrous oxide (N_2O) in the atmosphere (Vupputuri, 1974). An ozone reduction of 19 percent was found. This finding and conclusion (3) above suggest that the simple general equation giving global ozone reduction can be expressed in terms of nitrous oxide, the primary source of stratospheric NO_x.

$$-\frac{\Delta O_3}{O_3} = \frac{1}{5}\frac{\Delta N_2O}{N_2O} \qquad (2)$$

The present amount of atmospheric nitrous oxide, N_2O in Equation 2, is about one-quarter part per million by volume in the troposphere and decreasing in the stratosphere. The global inventory of atmospheric nitrogen in N_2O is thus 1.3×10^{15} grams or 1300 MT, millions of metric tons (Schütz et al., 1970).

Nitrogen Fixation

Nitrogen fixation (N_F) is the conversion of atmospheric N_2 to ammonia, nitrogen oxides, nitrates, etc. It occurs through the action of soil bacteria, bacteria in the ocean, other biological agents, lightning, combustion, and synthetic nitrogen fertilizer. There are many reviews of the global aspects of nitrogen fixation, for example, CAST (1976). By summing over recognized sources of nitrogen fixation and extrapolating to global scale, one can identify about 200 to 300 MT (as N) per year as the current rate of nitrogen fixation. Other recent reviews are in general agreement with the magnitude of recognized global rate of nitrogen fixation (McElroy, 1975; Burns and Hardy, 1975).

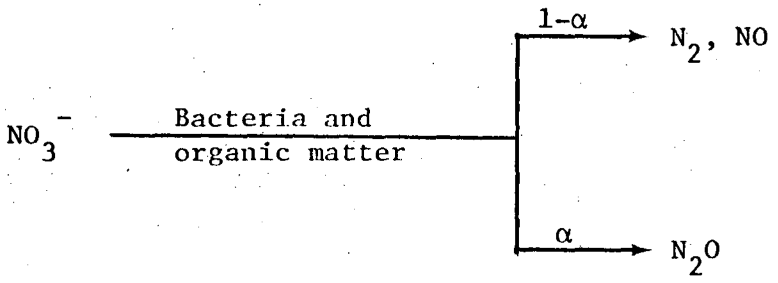
The thermodynamics of nitrogen fixation was reviewed by Safrany (1974), and he emphasized that thermodynamic work must be supplied to bring about the fixation of nitrogen. In terms of thermodynamic possibility, there is one long recognized exception to this energy requirement. Air and water are unstable with respect to becoming dilute aqueous nitric acid (Lewis and Randall, 1923).

$$H_2O(\ell) + N_2(g) + \frac{5}{2}\,O_2(g) = 2\ H^+(aq) + 2\ NO_3^-(aq) \qquad (3)$$

At chemical equilibrium at 298°K, the pressure of oxygen at sea level would be reduced to about 0.02 atmosphere, and the pH of the oceans would be about 1.5. Fortunately, the atmosphere and ocean are not in equilibrium with respect to this process. As Lewis and Randall (1923, p. 568) remarked: "It is to be hoped that nature will not discover a catalyst for this reaction, which would permit all of the oxygen and part of the nitrogen of the air to turn the oceans into dilute nitric acid." On the other hand, since chemical equilibrium favors this process, one should be on the lookout for unknown inorganic or biological mechanisms that bring about this reaction to some degree. If some process in the ocean catalyzed this reaction to only a small fractional degree, it could be a significant rate of fixation of nitrogen relative to identified terrestrial sources.

Denitrification

Denitrification is the natural process by which certain bacteria in the soil and in the ocean reduce nitrate to gaseous nitrogen, nitrous oxide, and in some cases nitric oxide NO.



(4)

The term α is the fraction that is N_2O in the gaseous products of denitrification, $N_2O/(N_2 + N_2O + NO/2)$. In soils α varies with temperature, pH, moisture, and local oxygen. For example, in a column of soil in the laboratory at 30°C saturated with water and with oxygen excluded, denitrification of an added sample of nitrate was 99 percent complete in 60 hours, and the products were N_2:N_2O:NO in the ratio (as N) of 8:6:1 (Bailey and Beauchamp, 1973). In agricultural soil under field conditions, denitrification occurs primarily where the soils are nearly saturated with water, where oxygen is largely absent, and where organic matter is available for microbial consumption. The fraction of the nitrogen converted to N_2O in the process of denitrification (α) was estimated to be about 1/16 (CAST, 1976, p. 15). Some measurements indicate only half as much. Environmental conditions that favor a large value of α are low temperature, low pH, and marginal anaerobic conditions; and these factors all lead to low rate of denitrification (CAST, 1976, p. 15). The fraction of N_2O produced when denitrification occurs in the ocean is unknown (CAST, 1976, pp. 16-18). These considerations suggest the following ranges for the fraction α

$$\begin{aligned} &\text{Land} &:&\quad 0.025 < \alpha < 0.1 \\ &\text{Ocean} &:&\quad 0 < \alpha < 1 \\ &\text{Global} &:&\quad 0.025 < \alpha < 0.4 \end{aligned} \tag{5}$$

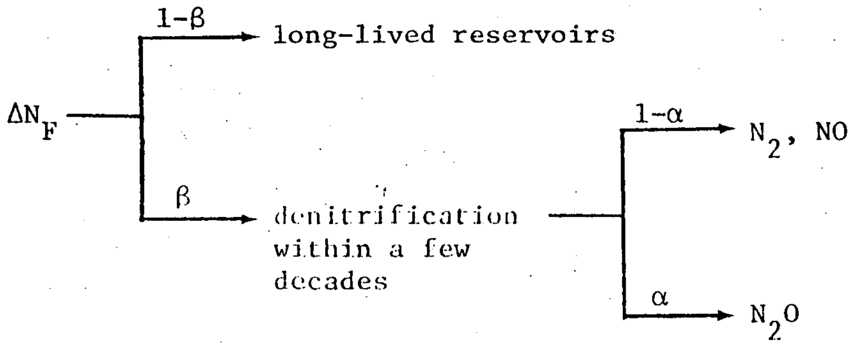
These global limits are not vigorous upper and lower bounds. They are selected from a list where each higher or lower possibility differs from the previous by a factor of two. It seems unlikely that α could be as great as 0.8 or as small as 0.012, and thus the numbers in (5) are taken as a plausible range.

Added to agricultural soils, as little as 1 percent or as much as 75 percent of the nitrogen may be lost to prompt denitrification, but the average amount is probably about 10 to 15 percent (CAST, 1975, p. 14). Such denitrification typically occurs within a few weeks after application of the fertilizer.

If the nitrate fertilizer is incorporated in annual plants, denitrification is typically delayed by a year or more, as the plant is eaten, digested, and in part returned to the soil. If this digested nitrogen is incorporated in the body of animals, denitrification may be delayed by a matter of several years. If the original soil nitrogen is incorporated in bushes or trees, there may be a delay of several decades between fixation and denitrification. It the nitrate goes into deep ocean waters, the time for denitrification may be delayed for 1000 years. Incorporation of fixed nitrogen in soil minerals or sediments may also result in a greatly delayed denitrification time. Liu *et al.* (1976) have emphasized the importance of the deep ocean, sediments, and soil minerals as long-term reservoirs for fixed nitrogen.

For some given application of nitrogen fertilizer, the degree of denitrification as a function of time might be something like that illustrated in Figure 2. The time scale is deliberately left unspecified in Figure 2. Some of the fertilizer is rapidly denitrified in the soil, some is denitrified at a somewhat slower rate, some nitrogen is incorporated in plants or animals and denitrification occurs later, and some is transported into soil minerals or into the deep ocean, where denitrification is indefinitely delayed. The fraction β is defined as that portion of the original nitrate fertilizer that does not get incorporated in dead reservoirs or in other words the fraction denitrified within one or two decades. The symbol τ_D is the time for the fraction 1/e of the original material to be denitrified. Unless β is very small, the discussion could focus on the first 1/e fraction denitrified, and the great complexities of the long-lived portion could be deferred for future consideration. This definition of residence time τ_D is a bit forced, since the course of denitrification is almost surely not a first order reaction, for example, Figure 2.

The products of a given application of nitrogen fertilizer ΔN_F can be stated in terms of the two fractions, α and β:



(6)

Thus the production of nitrous oxide ΔP_{N_2O} from the addition of a quantity of nitrogen fertilizer ΔN_F is

$$\Delta P_{N_2O} = \alpha\beta\ \Delta N_F \qquad (7)$$

The values of α and β are expected to be different for different modes of application of nitrogen fertilizer.

This analysis is not restricted to nitrogen fertilizer. Other modes of nitrogen fixation, legumes, combustion, lightning, etc. can be discussed in terms of the fraction β that is denitrified within a few decades and the fraction α of denitrified gases that is N_2O.

Natural Atmospheric Nitrous Oxide

In an oversimplified way, one can write a differential equation for the global nitrous oxide inventory, N_2O:

$$\frac{dN_2O}{dt} = P_{N_2O} - \frac{N_2O}{\tau} \qquad (8)$$

where $1/\tau$ is the average first-order rate constant for nitrous oxide destruction, or τ is the "residence time" of nitrous oxide. If the production rate P_{N_2O} and the destruction rate constant $1/\tau$ remained constant over a long period of time, the nitrous oxide inventory would reach a steady-state.

$$P_{N_2O} = N_2O/\tau \qquad (9)$$

Presumably the present nitrous oxide inventory is at or close to its steady-state achieved over geological time periods. The magnitude of the inventory is known, and as stated before it is about 1300 MT (N).

The residence time τ of nitrous oxide can be estimated in various ways. An upper limit on the time can be placed by consideration of the stratospheric photolysis and reactions of nitrous oxide. From the measured (Ehhalt, 1975) distribution of nitrous oxide in the stratosphere, from measured cross sections for ultraviolet radiation (Johnston and Selwyn, 1975), and from measured rate constants for reactions of nitrous oxide with singlet oxygen atoms (Davidson _et al._, 1976), I calculate that the maximum lifetime τ of N_2O is about 160 years. From model calculations Crutzen (1976) finds 140 years and McElroy _et al._ (1976) report 118 years for this quantity. This limit is set from considerations only of the stratosphere. From the variability in time and in space in the troposphere, Junge (1974) estimated the atmospheric residence time of nitrous oxide to be 8 years, with a factor of two uncertainty. This estimate of 4 to 16 year residence time is rounded out to 5 to 20 years in this report. These considerations bracket the possible atmospheric residence time of nitrous oxide as follows:

$$5 \text{ years} < \tau < 160 \text{ years} \tag{10}$$

Within the last two years, one writer or another on this subject has suggested atmospheric residence times within this range.

Perturbed Atmospheric Nitrous Oxide

If the global rate of production of nitrous oxide increased from P_{N_2O} to $P_{N_2O} + \Delta P_{N_2O}$ and if it held constant at the new value for a time long compared to τ, there would be a new steady-state inventory N_2O, which for small perturbations would be $(P_{N_2O} + \Delta P_{N_2O})\tau$, compare

Equation 8. In this case, the ozone Equation 2 can be extended to give

$$-\frac{\Delta O_3}{O_3} = \frac{1}{5}\,\frac{\Delta P_{N_2O}}{P_{N_2O}} \qquad (11)$$

The perturbed production rate ΔP_{N_2O} is related to the perturbed rate of nitrogen fixation. A strict, detailed account would find this relation to be exceedingly complicated. However, a gross first-order approximation is valuable in identifying the important independent variables, and such a simplified relation has been given as Equation 7

$$\Delta P_{N_2O} = \alpha\beta\ \Delta N_F \qquad (7)$$

where N_F is the rate of fixation of nitrogen in the natural background situation, $N_F + \Delta N_F$ is the rate of nitrogen fixation after a step-function perturbation is carried out, β is the fraction of fixed nitrogen that is denitrified within a few decades, and α is the average fraction of denitrification that leads to nitrous oxide. To realize Equation 7 one must consider times long compared to the denitification time τ_D; and to realize Equation 11, one must consider times long compared to τ plus τ_D.

Equations 7 and 9 can be substituted into Equation 11 to give

$$-\frac{\Delta O_3}{O_3} = \frac{1}{5}\,\frac{\Delta N_F}{N_2O}\,\alpha\beta\tau \qquad (12)$$

The natural inventory N_2O is known, and the increased rate of nitrogen fixation can be specified to assess its effect. The three unknowns, α, β, and τ appear as a single product. If one takes 100 MT (N)/yr as the increased rate of fixation of nitrogen, Equation 12 assumes the numerical form

$$-\frac{\Delta O_3}{O_3} = 1.5 \times 10^{-2}\ \alpha\beta\tau \qquad (13)$$

where τ is in years.

Of the three terms, α, β, τ, in Equation 13, the fraction rapidly (within a few decades) denitrified β is the most difficult to assess. There are independent physical arguments that set limits on the other two terms: Equation 5 for α, the fraction of denitrification that yields N_2O; Equation 10 for τ, the atmospheric residence time for N_2O. If one divides both sides of Equation 13 by the unknown fraction β, one obtains an upper bound for the ozone reduction, subject to assumed values of α and τ

$$\frac{\Delta O_3}{O_3} \le \frac{1}{\beta}\,\frac{\Delta O_3}{O_3} = -\ 1.5 \times 10^{-2}\ \alpha\tau \qquad (14)$$

If all increased nitrogen fixation leads to denitrification within a few decades, then the maximum ozone reduction occurs. Otherwise the reduction of ozone is less than $1.5 \times 10^{-2}\ \alpha\tau$ by the factor β.

For an assumed rate of increased nitrogen fixation of 100 MT (N) yr^{-1}, the maximum percentage ozone reduction is presented in Table 1 for the range of α (Equation 5) and for the range of nitrous oxide residence time τ (Equation 10). The indicated ozone reductions vary from 0.2 to 50 percent. With such a wide range of possibilities, the subject appears to be hopelessly amorphous. However, the situation is not as indefinite as it seems to be from Table 1.

that suggests such a large source of nitrous oxide, there is no known process that destroys atmospheric nitrous oxide at such a rate. For several years, Junge and co-workers (Schütz, 1970) have pointed out the need to identify a major new sink for atmospheric nitrous oxide. This model has the following indications with respect to the natural nitrous oxide balance:

(ii) N_2O production occurs largely in oceans
N_2O fraction in denitrification close to 1 in ocean and the expected 0.05 on land
N_2O production rate about 130 MT (N) yr^{-1}
N_2O destruction largely by unknown process
N_2O residence time about 10 years

Various Models of Ozone Reduction by Nitrogen Fertilizer

There have been a number of recent papers and discussions of this problem, and in many cases the points made by different authors can be simply expressed in terms of Tables 1 and 2.

In an unpublished memorandum circulated in December 1975, Crutzen carried out the calculation for the limiting case of only stratospheric destruction of nitrous oxide, case (i) above. For a steady input of 200 MT (N) yr^{-1} of fertilizer, he found an upper limit 8 percent ozone reduction by the year 2100 and a 14 percent steady-state ozone reduction. For the same assumptions ($\alpha = .04$, $\beta = 1$, $\tau = 130$ yr), the simple Equation 12 gives a steady-state ozone reduction of 16 percent.

Crutzen (1976) also explored the lower limiting case concerning atmospheric residence time for nitrous oxide, namely 10 years. By assuming β to be 1.0, he regarded his calculations as giving the upper limit on atmospheric ozone reduction. He considered an exponential growth of nitrogen fertilizer production from 1975 to 2000 and then constancy thereafter. Three values of α were considered, .07, .2, and 0.5. Also one calculation was carried out with nitrous oxide atmospheric residence time τ of 20 years and with $\alpha = 0.2$. By the year 2050 steady-state ozone reductions were between 1.5 and 10 percent.

Liu _et al_. (1976) reviewed the entire field and emphasized the large reservoirs of fixed nitrogen in the deep ocean and in soil minerals. These large reservoirs have a very slow rate of exchange with biologically available forms of nitrogen. However the product of the large values in the reservoirs and the small rates of exchange gives a turnover rate of available nitrogen that is large compared to industrial sources of fixed nitrogen. They emphasized that unless industrial rates of nitrogen fixation rate are comparable to the natural turnover rate, "the _equilibrium_ between living organic, dead organic, and inorganic nitrogen on land and in the oceans will remain unperturbed." For industrially fixed nitrogen to have an immediate (decades) effect on atmospheric nitrous oxide, the added fertilizer would have to follow a mechanism other than the natural equilibrium between free nitrate and day-bound fixed nitrogen. In the language of this article, Liu _et al_. emphasized the quantity $1-\beta$, the fraction of added fertilizer that enters the long-lived reservoirs.

Sze and Rice (1976) responded to the suggestions of Liu _et al_. (1976), but they emphasized the fraction β of fertilizer that is promptly (decades) denitrified. They made the point that to some extent, the nitrogen fertilizers applied to agricultural soils have significantly different histories than nitrogen cycling in natural ecosystems. They assumed a 20 year atmospheric residence time for nitrous oxide, and they assumed that the N_2O fraction of denitrified gases was 0.26 for both land and ocean. They considered three different possible values for the fraction of fertilizer that is promptly denitrified, namely, 0.10, 0.35, and 0.6. Thus in the language of this article, they consider the cases of $\alpha = 0.26$; $\beta = 0.1$, 0.35, and 0.6; $\tau = 20$ yr; and the rate of application of nitrogen fertilizer is 200 MT (N) yr^{-1}. For the year 2025, they calculated ozone reductions from nitrogen fertilizer to be between 1.6 percent and 9 percent. From Equation 12 one finds ozone reductions ranging from 1.8 to 10 percent for these same values of α, β, and τ.

McElroy et al. (1976) reviewed this subject with emphasis on the question of the ocean as a source or sink for nitrous oxide. They conclude, in disagreement with Hahn (1974), that the oceans as a whole are a net sink for atmospheric nitrous oxide. McElroy et al. assume a 20 year atmospheric lifetime for nitrous oxide, a value of 0.23 for α (they stated it as 0.3 for the ratio of N_2O to N_2 in denitrified gases), the value of one for β, and 200 MT (N) yr^{-1} as fertilizer input. They conclude that "reductions in ozone of the order of 20 percent during the first half-quarter of the twentieth century, due to current and future use of fertilizer, are not improbable." For the same values of α, β, and τ, Equation 12 gives a 14 percent reduction of ozone essentially in agreement with the value deduced by McElroy et al.

Thus the simple use of Table 1 (subject to restrictions of Table 2) gives very nearly the same results as those from extensive model calculations. The time to achieve the ozone reduction is the sum of the time for the fraction β to be denitrified (one or two decades, by definition), the time for the atmosphere to reach equilibrium with respect to the new source of N_2O (τ represents the time for this process to go to 1 - 1/e toward completion), and the time for ozone to relax following NO_x production (a time short compared to the nitrous oxide residence time).

Preferred Range of Values

For nitrogen fertilizer applied to agricultural soils, the important values of the fractions α and β concern the agricultural soils and nearby land and water areas. The values of α and β for the ocean have only secondary effect on how much of the fertilizer is converted to atmospheric nitrous oxide. The oceans could be important in determining the global atmospheric residence time τ of nitrous oxide, and uncertainties about the role of the ocean leaves this residence time uncertain between the limits of 10 to 100 years. Nitrogen fertilizer applied to land would be expected (CAST, 1976) to produce nitrous oxide between 5 and 10 percent of that denitrified, $\alpha = 0.05$ to 0.1, and this range is embraced by solid lines in Table 3. The upper limit to ozone reduction occurs if all added nitrogen fertilizer is promptly (decades) denitrified, that is $\beta = 1$. It is my personal judgment that the long-term effect of 100 MT (N) yr^{-1} of nitrogen fertilizer is given by Table 3. There could be a large (about 10 percent) reduction of ozone, but it would take hundreds of years to build up to this steady-state. On the other hand, the ozone reduction could occur within a few decades, but the amount of ozone reduction is only a matter of 1 or 2 percent. Also, it could be any values in between, for example, a 5 percent ozone reduction with a

50 year relaxation time. If a large fraction, 1-β, of the fertilizer goes into deep soil or oceanic reservoirs, the short-term ozone reductions would be less by the factor β. Some models discussed above do not fall within the solid lines of Table 3; and this merely illustrates that there are current disagreements with respect to details of this subject. As new information is developed, the actual situation may fall within the solid lines of Table 3 or it may be something well off to one side or another.

The Important Variables

Although the actual situation is exceedingly complicated and this analysis is extremely simple, it is felt that Table 1-3 go a long way twoard reflecting the broad aspects of current knowledge and uncertainty in this problem. The important variables are: (1) τ, the global atmospheric residence time of nitrous oxide, which is determined by all the natural sources and sinks of N_2O. (2) β, the fraction of nitrogen fertilizer applied to land that will be denitrified within a few decades, as opposed to the fraction 1-β that is transferred to long-lived oceanic or lithospheric reservoirs of fixed nitrogen. (3) α, the fraction of denitrified nitrogen fertilizer (or its organic nitrogen descendants) that is converted to nitrous oxide, as opposed to the fraction 1-α that is produced as N_2 or NO. (4) The factor 1/5 connecting ozone decrease and NO_x increase in Equation 1 and incorporated in Tables 1-3 is subject to further investigation and refinement. With these four factors, α, β, τ, and 1/5, one can simply calculate the long-term ozone reduction from any assumed increase in nitrogen fertilizer usage ΔN_F(MT yr^{-1}):

$$-\frac{\Delta O_3}{O_3} \doteq \frac{1}{5}\,\frac{\Delta N_F}{1300}\,\alpha\beta\tau \qquad (15)$$

For time varying application of fertilizer, this simple equation is, of course, not applicable. It is recognized that the terms α and β are widely variable over the world, and use of loosely defined average values is not satisfactory. However, these terms, at present, are treated the same way in detailed model calculations and in the simple method used here. Until there are experimental data that give the detailed structure of the functions, α and β, this ultra simple method may be sufficient to answer a number of the questions that may be asked.

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Restrictions Imposed by the Natural Nitrogen Balance

Although various authors and modelers have recently proposed residence times for N_2O as short as 5 years and as long as 160 years and although the global average value of α could be between 0.025 and 0.4, there are many pairs of the variables (α,τ) that can be shown to be extremely improbable. Some pairs of α and τ imply impossible values of the natural rate of nitrogen fixation. The present, natural rate of nitrogen fixation N_F depends on the same variables (Equations 7 and 9):

$$N_F \geq \beta N_F = \frac{N_2O}{\alpha\tau} = \frac{1300}{\alpha\tau}\,\frac{MT}{yr} \qquad (15)$$

Since the present situation is presumably a steady-state between nitrogen fixation and denitrification, the factor β should be unity in this equation. The rates of nitrogen fixation implied by the various values of α and τ are given in Table 2, which has the same format as Table 1. A column is added giving the implied nitrous oxide production rate P_{N_2O} for each value of N_2O residence time, τ.

Experts in soil science, oceanography, and related sciences can identify sources of nitrogen fixation that add up to 200 to 300 MT (N) yr^{-1} (CAST, 1976). These estimates have increased over the last decade as new sources have been identified (compare Delwiche, 1970). The thermodynamics of Equation 3 suggest the possibility of an unrecognized oceanic source of nitrogen fixation. These considerations suggest that global nitrogen fixation rates between 160 and 650 in Table 2 be regarded as within the expected range, but that values above and below this range are extremely improbable. The implied nitrogen fixation rates between these limits are enclosed by a solid line.

The destruction of nitrous oxide in the stratosphere sets an upper limit of 160 years to the atmospheric residence time of N_2O, and this quantity is enclosed in dashed lines in Table 2. The situation in the natural nitrous oxide balance implied by this upper limiting case is as follows:

(i) N_2O production occurs almost exclusively on land
N_2O fraction in denitrification about 0.05
N_2O production rate 10 to 20 MT (N) yr^{-1}
N_2O destruction only in stratosphere
N_2O resident time 100 to 160 years

A model can be associated with the lower limit of the nitrous oxide residence time, which is based on measurements in the atmosphere and in the ocean (Schütz _et_ _al_., 1970; Junge, 1974; Hahn, 1974). The entries in Table 2 involving residence times 5, 10, or 20 years are circled with a dashed line to illustrate this situation. The overlap between the solid line and dashed lines are the possible cases according to this model. For a 10 year nitrous oxide residence time and a 300 MT (N) yr^{-1} rate of nitrogen fixation, the implied global average value for the fraction of nitrous oxide from dentrification (α) is 0.4. The indicated value for this factor on land is between 0.05 and 0.1 (CAST, 1976), and this seems to indicate that denitrification in the ocean would yield almost 100 percent nitrous oxide. The rate of production of N_2O according to this model is about 130 MT (N) yr^{-1}, and there must then be an equal rate of natural destruction of nitrous oxide. Whereas Hahn (1974) has limited oceanic data

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Figure Titles

Figure 1. The percentage decrease of ozone as a function of the percentage increase in stratospheric nitrogen oxides as found by the Climatic Impact Assessment Program, 1975. The line represents the equation $-\Delta O_3/O_3 = (1/5)\ \Delta NO_x/NO_x$.

Figure 2. A semiquantitative statement of the denitrification of a particular sample of fixed nitrogen added to agricultural soil. A portion is rapidly denitrified, the fraction β is denitrified over a relatively short period of time (a few decades), and the fraction $1-\beta$ is converted to long-lived reservoirs of fixed nitrogen.

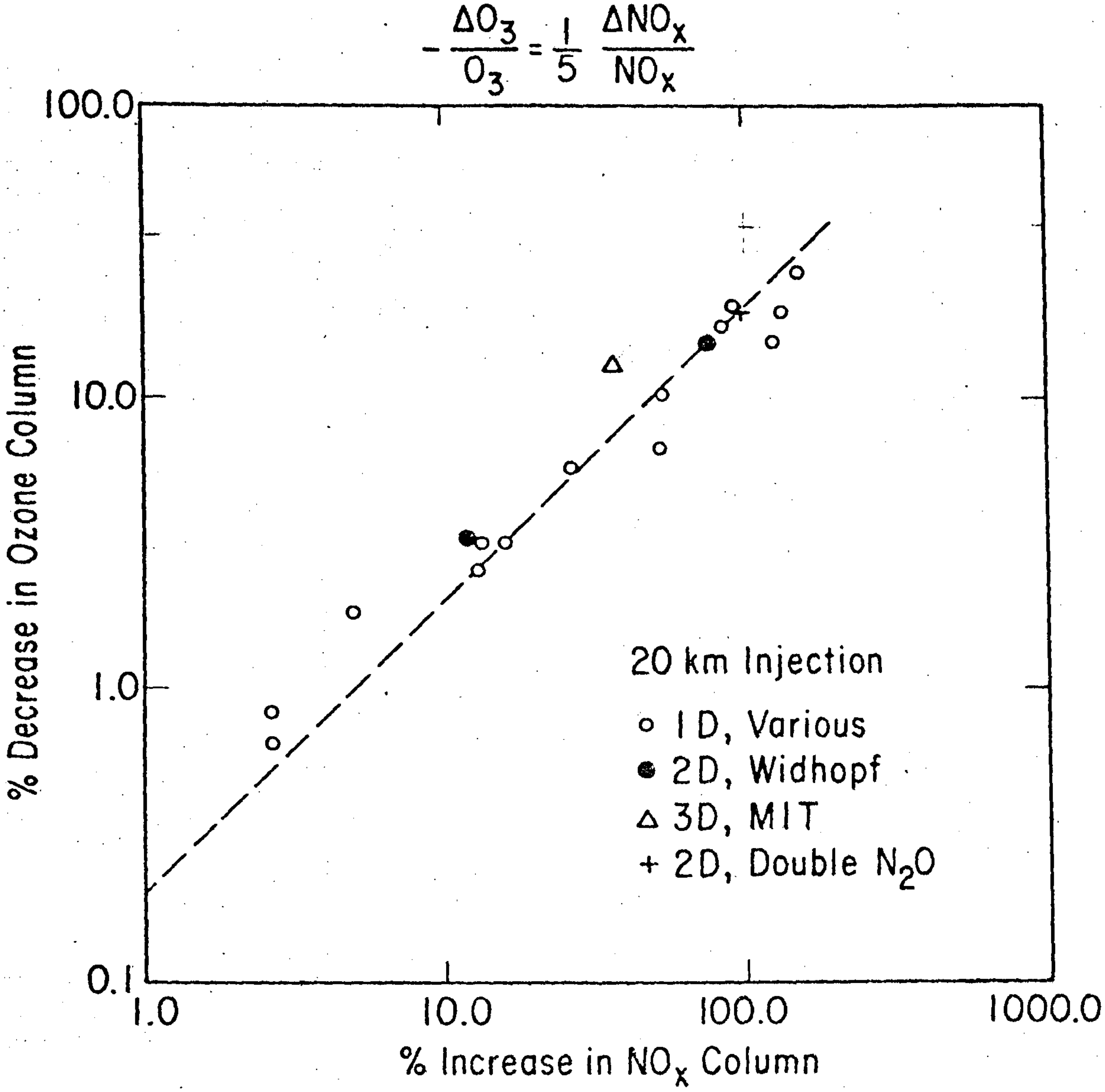
$-\frac{\Delta O_3}{O_3} = \frac{1}{5}\frac{\Delta NO_x}{NO_x}$
100.0
10.0
1.0
0.1
% Decrease in Ozone Column
1.0
10.0
100.0
1000.0
% Increase in NO_x Column
20 km Injection
○ 1 D, Various
● 2D, Widhopf
△ 3D, MIT
+ 2D, Double N_2O

Figure 1

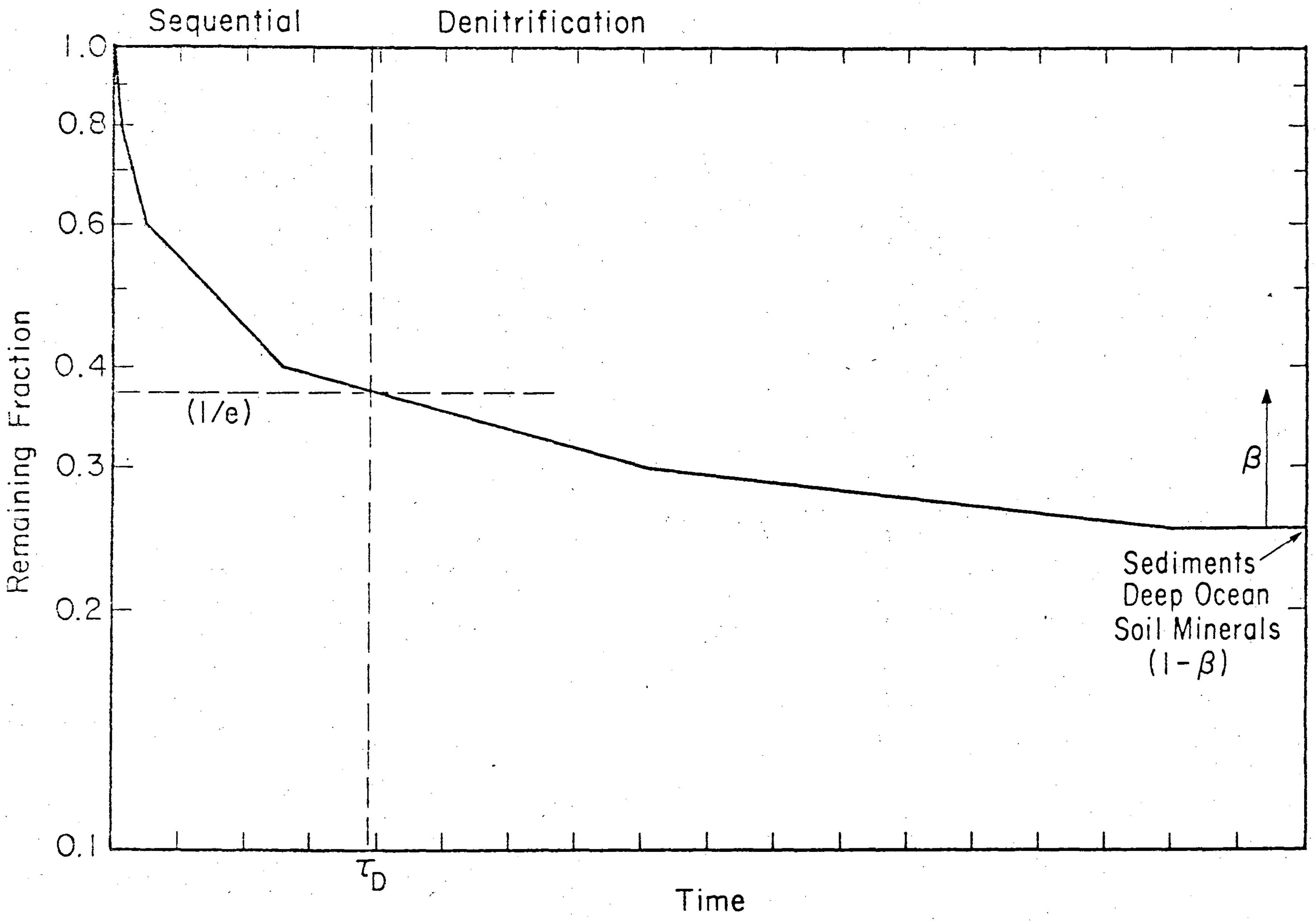
Sequential Denitrification
Remaining Fraction
1.0
0.8
0.6
0.4
0.3
0.2
0.1
(1/e)
τD
Time
β
Sediments
Deep Ocean
Soil Minerals
(1-β)

Figure 2

Table Titles

Table 1. The maximum ($\beta = 1$) percentage reduction of ozone for various possible values of nitrous oxide lifetime τ, for various fractions, $\alpha = N_2O/(N_2O + N_2)$, following denitrification, and for addition of 100 MT (N) yr^{-1} of nitrogen fertilizer.

Table 2. The natural global rate of nitrogen fixation implied by the values of α and τ in Table 1. The probable range of α on land. The possible range of α including land and ocean. The global rate of production of nitrous oxide implied by the residence time τ. The solid line encloses rates of nitrogen production consistent with present knowledge. The dashed lines include two models of atmospheric N_2O lifetime.

Table 3. Table 1 reduced to range of probable values preferred by this author for nitrogen fertilizer applied to land. At one extreme there is a relatively large ozone reduction and a long time of attainment of the ozone reduction. At the other extreme there is a small ozone reduction but much sooner realized.

$$-\frac{1}{\beta}\frac{\Delta O_3}{O_3} = 1.5\,\alpha\tau\ \%$$

α τ	0.025	0.05	0.1	0.2	0.4
5	0.19	0.38	0.75	1.5	3
10	0.38	0.75	1.5	3	6
20	0.75	1.5	3	6	12
40	1.5	3	6	12	24
80	3	6	12	24	48
160	6	12	24	48	–
yr					

ΔN_F = 100 MT/yr, assumed

Table 1

$$N_F = \frac{N_2O}{\alpha\tau} = \frac{1300}{\alpha\tau}\,\frac{MT}{yr}$$

	α (Including Ocean)					
		(α) Land				
τ \ α	0.025	0.05	0.1	0.2	0.4	P_{N_2O}
5	10,400	5200	2600	1300	650	260
10	5200	2600	1300	650	325	130
20	2600	1300	650	325	160	65
40	1300	650	325	160	80	38
80	650	325	160	80	40	19
160	325	160	80	40	-	9.5
yr						MT/yr

Natural Global Nitrogen Fixation Rate

Table 2

$$-\frac{1}{\beta}\frac{\Delta O_3}{O_3}\%$$

	α (Including Ocean)				
		α Land			
τ \ α	0.025	0.05	0.1	0.2	0.4
5		0.4	0.8		
10		0.8	1.5		
20		1.5	3		
40		3	6		
80		6	12		
160		12	-		
yr					

ΔN_F = 100 MT/yr, added to land.

Table 3

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720