
The Nitrogen Cycle: Perturbations Due to Man and Their Impact on Atmospheric N_2O and O_3

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THE NITROGEN CYCLE:
PERTURBATIONS DUE TO MAN AND
THEIR IMPACT ON ATMOSPHERIC N₂O AND O₃

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Features of the global cycle of fixed nitrogen are reviewed with an emphasis on perturbations due to man. It is argued that agricultural practices and combustion may lead to an increase in the concentration of atmospheric N₂O with consequent effects on O₃. The level of O₃ may drop by about 20 % over the next 100 years if world population and the demand for food should continue to grow at anything like rates which prevailed in the recent past. Uncertainties in the model are highlighted and note is taken of areas where there is need for additional data.

1. INTRODUCTION

Ozone is formed in the atmosphere (Chapman 1930) by



followed by



and removed (Crutzen 1970; Johnston 1971) by



followed by



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with additional contributions due to direct recombination of O with O₃ (Chapman 1930), and catalytic cycles involving H, OH and HO₂ (Bates & Nicolet 1950).

Oxides of nitrogen are formed in the stratosphere by reactions of O(¹D) with N₂O (Crutzen 1971; McElroy & McConnell 1971; Nicolet & Vergison 1971), in which O(¹D) is released by photolysis of O₃. Nitrous oxide is formed by microbiological activity at the Earth's surface (Bates & Witherspoon 1952; Bates & Hays 1967), and appears to have a relatively short atmospheric lifetime, about 10 years, as evidenced by spatial and temporal variability detected in measurements of the gas carried out by a number of groups over the past 15 years (Goody 1969; Schütz, Junge, Beck & Albrecht 1970; Junge 1974; Ehhalt, Heidt, Lueb & Pollack 1975; Schmeltekopf 1975; Rasmussen 1975). The primary sink for atmospheric N₂O is uncertain, though recent measurements by Johnston & Selwyn (1975) appear to exclude gas phase photolysis. Bates & Hays (1967) and McElroy, Elkins, Wofsy & Yung (1976) explored the possibility of a sink due to microbiological processes in the ocean. The idea merits further attention, but remains speculative. Additional data are required on an urgent basis in order to refine our knowledge of the marine nitrogen cycle. These data should permit a more quantitative definition of the rôle which the ocean might play in the global budget of atmospheric N₂O, a matter of some current interest, as we shall see below.

Concern has arisen in recent years that a variety of man-related activities might lead to a change in the level of atmospheric ozone. Attention focused initially on the supersonic air transport (Crutzen 1970; Johnston 1971). Exhaust gases of aircraft contain nitric oxide, and a high volume of stratospheric aviation might be expected to accelerate the rate at which ozone was removed by the catalytic cycle described by reaction (3) and (4). A fleet of 500 Boeing-class s.s.ts flying 8 h per day, as contemplated by the United States some six years ago, would be expected to lower the global concentration of ozone by about 5% (Climatic Impact Assessment Program 1975). Larger reductions, exceeding 20% (Wofsy, McElroy & Sze 1975*a*), might be anticipated by the turn of the century, if the volume of stratospheric aviation should grow to the level envisaged by Groebecker (1974). Similarly large effects could ensue due to man's increasing use of chlorofluoromethanes (Molina & Rowland 1974; Cicerone, Stolarski & Walters 1974; Crutzen 1974*a*; Wofsy *et al.* 1975*a*), and there could be an appreciable impact due to agricultural applications of methylbromide, a fumigant whose use has grown rapidly in the past decade (Wofsy, McElroy & Yung 1975*b*).

Chlorofluoromethanes decompose photolytically in the stratosphere, releasing chlorine, which can affect ozone through the reaction scheme



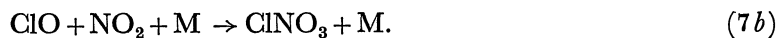
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The Cl_x and NO_x chemistries are coupled, since the abundance of ClO may be influenced by



and by



Reductions in ozone attributable to past use of chlorofluoromethanes are estimated at around 1%, and could grow to about 10% if release of chlorofluoromethanes should continue at rates prevalent today (Inadvertent Modification of the Stratosphere 1975). Larger effects would ensue if the industry should grow at anything like the rates which prevailed in the recent past,

and several of the models presented by Wofsy *et al.* (1975*a*) indicated ozone reductions which exceed 20 %, † similar to projections noted earlier for the high volume air traffic model described by Grobecker (1974).

Methylbromide affects ozone in a manner similar to the chlorofluoromethanes. The gas decomposes in the stratosphere, releasing bromine which can react with ozone through the catalytic cycle



followed by



The impact is currently small, less than 1 %. Future growth patterns for the bromine industry should be viewed cautiously however, since bromine can serve as an exceedingly efficient catalyst for removal of stratospheric ozone. All of the effects discussed above may be eliminated, or at least minimized, by appropriate source regulation. The culpable agents may be considered discretionary, in no sense essential to the survival of modern society. This paper attempts to isolate effects on ozone which might be attributed to the production of food, and explores further the implications of certain practices now employed for the disposal of organic waste. In his attempt to develop a food supply adequate to the needs of this planet's expanding population, man has come to rely to an increasing extent on chemical fertilizers. Industrial fixation of nitrogen for agricultural purposes has grown by rather more than a factor of 10 over the past 25 years. It accounted for less than 3 % of the total nitrogen fixed globally by natural processes in 1950, 3.5×10^6 t (tonnes) as compared to 1.6×10^8 t (Hardy & Havelka 1975; Burns & Hardy 1975; Council for Agricultural Science and Technology 1976). It grew at an average rate of 10.7 % per year between 1950 and 1974 and there are no indications for an imminent decline in the growth pattern. Estimates for nitrogen fertilizer production by the end of the century range from 1×10^8 to 2×10^8 t (Hardy & Havelka 1975; Council for Agricultural Science and Technology 1976). If one adds to the world's inventory of fixed nitrogen quantities of the gas fixed by industrial processes in general, including transportation but excluding fertilizer – 1.5×10^7 t in 1950, 4×10^7 t in 1974, and perhaps 10^8 t in 2000 (Bolin 1970; Keeling 1973) – it is hard to escape the conclusion that man has already had a significant influence on the global cycle of nitrogen, and that his rôle must grow rapidly in the years ahead. One would expect an increase in the rate at which fixed nitrogen should be removed by denitrification. This paper is directed towards an attempt to estimate the associated rise in atmospheric N_2O and its consequent effects on O_3 .

If one accepts for the moment an asymptotic state in which fixation of nitrogen for fertilizer should stabilize at an annual level of 2×10^8 t, with an additional 1×10^8 t supplied by other anthropogenic agents, and if one assumes that the relative amounts of N_2 and N_2O evolved during denitrification should remain constant, one might anticipate an increase in the concentration of atmospheric N_2O at some future date by about a factor of 3. Our model incorporates of course a number of unproven assumptions. It requires that fixation and denitrification should balance on a suitably long time scale. It omits feedback mechanisms which might couple the atmosphere and biosphere, and which might conceivably alter the manner in

† The possible role of ClNO_2 , introduced recently by Rowland, Spencer & Molina (1976), was not considered in early models for the stratospheric impact of fluorocarbons. Preliminary studies indicate that reductions in O_3 quoted here may require downward revision, by perhaps as much as a factor of 3. Further assessment of the complexities introduced by a fully coupled $\text{Cl}_x\text{-NO}_x$ chemical system will require extensive laboratory studies of a large number of potentially important reactions.

which essential nutrients are redistributed under natural conditions. It assumes that the loss process for N_2O should respond in a linear fashion to a change in atmospheric concentration. These limitations seem unimportant in the present context however. Fixation and denitrification must balance, at least on a geologic time scale: the continued presence of N_2 in the atmosphere attests to this fact. The major question concerns the time scale for anthropogenically driven denitrification. A global disruption to the cycle which regulates the natural dispersal of nutrients should entail an environmental perturbation much larger than any discussed here. It is difficult to envisage a loss process for N_2O which might respond in a highly nonlinear fashion to a change in atmospheric concentration. Our model, with its assumptions and inherent limitations, projects a significant rise in the level of N_2O . The predicted drop in O_3 could be as large as 20 % in the near future, as we may see from the more detailed discussion below.

Concern that the increasing use of fertilizer might pose a potential problem for O_3 were raised first by Crutzen (1974*b*) and McElroy (1974). Crutzen seemed to regard the impact as minor. He had the view that the ocean should represent the major source of atmospheric N_2O , a position based primarily on measurements reported by Hahn (1974, 1975). McElroy (1976*a, b*) and McElroy *et al.* (1976) drew rather different conclusions with regard to the rôle of the sea. They thought it improbable that marine activity could dominate the global source of atmospheric N_2O , a conclusion motivated to a large extent by consideration of the global nitrogen cycle. They argued that the marine contribution to N_2O might be ambiguous even with respect to sign. The matter is clearly important in the present context and will be discussed in more detail below, in §2.

Factors which might influence the time scale for anthropogenic perturbations to N_2O are discussed in §3. Consequences for atmospheric O_3 are explored in §5, following an attempt, in §4, to define reasonable models for the future growth in anthropogenic sources of fixed nitrogen.

2. THE NITROGEN CYCLE

This section is directed towards an attempt to estimate a reasonable value for the yield of N_2O associated with particular anthropogenic disturbances. As noted earlier, denitrification is thought to provide the dominant source for N_2O . We need information on the distribution, and on the relative magnitude for individual sources of N_2O in the natural regime. What fraction of the total atmospheric source might be attributed to denitrification in the open ocean? How does this source compare to the contribution from estuaries, soils and fresh water? What fraction of denitrifying events might be expected to lead to emission of N_2O rather than N_2 , and how might this parameter vary as a function of the physical, chemical and biological characteristics of the decay medium? A detailed model for N_2O should require answers to all of these questions, and the available data are quite inadequate to the task.

We shall adopt here a more limited perspective. We shall attempt first to derive a globally averaged value for the *relative* yield of N_2O , using estimates for global fixation, in combination with empirical values for global production of N_2O . We then examine evidence for a large source of N_2O due to microbiological processes in the ocean. We find the evidence unconvincing, and argue that continental sources (soils, fresh waters and estuaries) are likely to play a larger rôle. The empirically defined yield for N_2O will be employed later, in §5, in an attempt to model the response of the atmosphere to specific anthropogenic sources of fixed nitrogen.

The indirect approach adopted here could be eliminated, at least to some extent, if the

microbiological data were such as to allow one to predict the yield of N_2O on the basis of known physical and chemical properties of potential decay sites. This is regrettably not the case however. Field data are sparse, or absent, and most of our present information is derived from laboratory studies, carried out in an environment whose characteristics must differ appreciably from the natural state. Estimates for the fractional yield of N_2O vary all the way from 0 to 100 % (Wijler & Delwiche 1954; Nommik 1956; Cady & Bartholemew 1960; Cooper & Smith 1963; Stefanson 1973). The rate of denitrification may be influenced to a considerable extent by pH. Bacteria active in denitrification have a low tolerance to hydrogen ions and operate with low efficiency in media with pH below about 5.5. It appears that the composition of evolved gases may be similarly affected by pH. Production of N_2O is favoured at pH below 6.5, though extrapolation of the laboratory data to field conditions may lead to significant error in this case. Most of the laboratory data are consistent with a model in which N_2O may be regarded as an obligatory precursor to N_2 (Nommik 1956; Broadbent & Clark 1975). Cooper & Smith (1963) found that nitrate was reduced first to nitrite, and that N_2O appeared later, preceding N_2 . Closed systems, which characterize laboratory experiments, might tend to prejudice results to favour an unrealistically low yield for N_2O . One might expect that N_2O could diffuse away from the decay site under field conditions, and that the yield of N_2 might be lowered accordingly. Such an effect is evident in the curves presented by Focht (1974). It seems advisable under the circumstances that we should attempt to find an independent method with which to estimate the fractional yield of N_2O under natural conditions on a global scale.

Measurements of the spatial and temporal variability of N_2O may be used to derive an empirical value for the lifetime of the gas under normal atmospheric conditions. If we adopt Junge's (1974) value for this parameter, about 10 years, and various estimates (Goody 1954, 1969; Birkeland & Shaw 1959; Rank, Slomba, Gardner & Wiggins 1962; Craig & Gordon 1963; Schütz *et al.* 1970; Rasmussen 1975) for the unperturbed abundance, taken to correspond to a mixing ratio of about 2.6×10^{-7} , we may conclude that the rate for global production of N_2O should correspond to about 1.2×10^8 t (nitrogen) per year. If we combine this result with values quoted earlier for fixation under natural conditions, about 1.6×10^8 t/a (tonnes per year), we may estimate a globally averaged yield factor for N_2O equal to about 0.74.†

It is hard to escape the conclusion based on this analysis that N_2O must be a major product of denitrification. It remains to identify the nature of the source. One might be tempted to attribute production of about 8×10^7 t/a to biological processes in the open ocean, with a further 4×10^7 t/a attributed to denitrification on land. Such a choice would agree well with Hahn's (1974, 1975) conclusion, that the oceans are responsible for about 8.5×10^7 t/a, and that soils contribute an additional 1.5×10^7 t/a. One might assign in this model a source of about 2×10^7 t/a to fresh waters and estuaries, completing a global input of 1.2×10^8 t/a. The distribution is in no sense unique however and, as we shall see below, a careful analysis, incorporating all reasonable constraints, appears to imply a much smaller rôle for the sea. The contribution from continental sources must be raised accordingly, although several of the models to be developed later will allow for a relatively large contribution from the oceans to the global budget of atmospheric N_2O .

Hahn's (1974, 1975) estimate for the marine source of N_2O was based on an analysis of data taken in the North Atlantic, on a series of three cruises by the German research vessel Meteor.

† The yield factor here and in subsequent discussion defines the fractional number of denitrifying events which result in emission of N_2O to the atmosphere.

Measurements were carried out in late spring and summer, during the years 1969–71. Data were obtained for some 42 stations, and included a few measurements of the concentration of N_2O to depths of about 3000 m. Surface waters were analysed for N_2O at 33 distinct locations. Analysis of these data indicated that shallow waters of the North Atlantic were apparently supersaturated in N_2O by about 24 % over the period covered by the observations. Largest supersaturations, exceeding 75 %, were detected in warm waters at $0.6^\circ N$ latitude and at $25.6^\circ N$. An average of all of the surface data obtained at latitudes higher than $37^\circ N$, some 29 samples, could indicate supersaturation by about 13 %. This value is rather small when one considers the uncertainties in the field measurements (*ca.* 10 %), the lack of accurate data on the solubility of N_2O in sea water (*ca.* 10 %), and the possible rôle of bubbling and other physical processes which might influence the concentration of dissolved gases (see McElroy *et al.* 1976). An average of data taken at latitudes below $37^\circ N$, four measurements, would indicate that the surface waters there are supersaturated with respect to ambient air by about 80 %.

The flux of gas across the air/sea interface may be estimated in an approximate fashion from the relation

$$\phi = (D/Z) (C - P\alpha), \quad (10)$$

where ϕ represents flux, D/Z is an effective velocity for diffusion across the boundary, C defines the concentration of gas in solution, P is the pressure of the overlying atmosphere, and α denotes the solubility parameter. Hahn (1974) assumed that the North Atlantic was supersaturated by about 80 % in N_2O under average conditions, and used (10), in combination with an empirical value for D/Z (Broecker & Peng 1974) to derive a value for the magnitude of the resulting flux of N_2O . His analysis suggested an N_2O source of 7×10^6 t/a (nitrogen) from the North Atlantic. Hahn (1974) scaled this result for the North Atlantic to derive an integrated N_2O source for all of the world's oceans equal to 8.5×10^7 t/a (nitrogen). He did not attach too much weight to this result however. He thought that his analysis might be such as to define the source from the North Atlantic to within an order of magnitude. It is clear that the source strength could be much less, and there is no evidence to suggest that it should be greater. All of the measurements were carried out in a period of high biological productivity, and the value assumed for the mean supersaturation of N_2O was heavily weighted by data from a small number of locations (3). Extrapolation to global conditions could introduce large and unpredictable error. Earlier measurements by Craig & Gordon (1963), which will agree well with Hahn's (1974, 1975) data for the tropics, appear to indicate that the high latitude South Pacific may be undersaturated in N_2O , by as much as 32 %. The World's oceans might serve then as a sink for N_2O (McElroy *et al.* 1976). In any event the rôle of the oceans in the atmospheric budget of N_2O remains unclear, and Hahn's (1974) value for the global yield should be viewed with appropriate caution.

Hahn's (1974, 1975) data are important in that they show clear evidence for local sources of oceanic N_2O . Further work, covering a wider range of physical and biological conditions, will be required if one is to hope for a more quantitative model of the marine nitrogen cycle, and it is clear that research efforts should be directed to achieve this goal in the near future.†

† More recent data (Yoshinari 1976) support the view that the open ocean is a very small source of N_2O . Using depth profiles for N_2O and estimates for vertical transport, Yoshinari (1976) calculated an oceanic source of N_2O of order 1×10^6 t/a. His surface measurements show enhanced N_2O supersaturations in near-shore and estuarine waters, consistent with the idea developed here, that the land functions as a nearly closed system for fixed nitrogen.

The ocean receives fixed nitrogen from the land, directly by river run-off, and indirectly by rain. Various estimates (Emery, Orr & Rittenberg 1955; Junge 1963; Jones 1971; McConnell 1973; McElroy 1976*a*) for the combined source due to rivers and rain range from about 4×10^7 t/a (nitrogen), to perhaps 8×10^7 t/a. Larger values are based generally on older data (Emery *et al.* 1955), which allow a relatively large contribution due to rain. More recent studies incorporate extensive measurements by Junge (1963), as discussed for example by McConnell (1973). These measurements suggest that the contributions from rain and rivers might be comparable, and imply an annual source of fixed oceanic nitrogen equal to about 4×10^7 t. The net source could be somewhat larger, if *in situ* fixation were to play an important rôle.

Delwiche (1970) suggests that fixation could contribute as much as 10^7 t nitrogen per year to oceanic nitrogen. Earlier work by Goering, Dugdale & Menzel (1966) appeared to indicate that the blue green alga *Trichodesium* might play an important rôle, though more recent data by Goering, Richards, Codispoti & Dugdale (1973) seem to imply that the net global source due to *Trichodesium* should not exceed 4×10^4 t/a. The Council for Agricultural Science and Technology (1976) quotes a range of values for fixation, varying from 4×10^5 to 4×10^6 t/a, with a preference for 1×10^6 t/a. Their conclusion will be adopted for present purposes.

Our 'best' model considers a source of marine fixed nitrogen equal to 4×10^7 t/a, supplied mainly by rain and river run-off. A second model, designed to stretch the various parameters in such a manner as to maximize the rôle of the sea in global denitrification, is taken to include a source of 7×10^7 t/a due to rain and rivers, with an additional 1×10^7 t/a supplied by *in situ* fixation. The fractional yield of N_2O is taken to be the same for land and sea in model 1, about 0.74. The sea is assumed to play a larger rôle in model 2. The fractional yield of oceanic N_2O is set equal to 0.9 in this case and the oceans contribute approximately 7×10^7 t/a to the global budget of atmospheric N_2O , a figure which may be compared to the value assigned to the oceans in model 1, about 3×10^7 t/a. The fractional yield of N_2O for continental denitrification is 0.74 in model 1, 0.58 in model 2. The lifetime for atmospheric N_2O is 10 years in both models, and a third model, model 3, is designed to explore the consequence of a longer lifetime. The lifetime is set equal to 20 years in this case, and the fractional yield for global N_2O is lowered accordingly, to 0.37. The marine budget of fixed nitrogen is handled in model 3 in a manner similar to model 1.

Our discussion of the marine nitrogen cycle is consistent with various analyses which have appeared in the literature over the past several years. A good summary of present knowledge is given by Codispoti (1973). It appears that the oxygen concentration must be quite low, less than 0.1 ml/l, if denitrification is to occur to any appreciable extent in the ocean. The conditions required for denitrification might arise to some extent in the internal organs of certain marine biota, and they might occur locally, and at certain times of the year, when the supply of organic material could exceed the available source of O_2 . The oxygen deficient waters of the eastern North Pacific Ocean may play an important rôle in the global budget of marine nitrogen. Codispoti (1973) estimates that denitrification in these waters could account for a net nitrogen loss of between 2×10^7 and 3×10^7 t/a. Anoxic waters off the coast of Peru, and a similar region in the Arabian Sea should play an additional rôle, and these three regions might represent the dominant sink for marine nitrogen. Codispoti (1973) thought that N_2 should be the major product of marine denitrification. Further measurements will be required to resolve these issues.

3. ANTHROPOGENIC SOURCES OF N₂O

This section is directed towards a study of several ways in which man might influence the net global source of atmospheric N₂O. The discussion, which follows McElroy (1976*b*) will emphasize perturbations associated with agriculture, and will attempt to trace the fate of fixed nitrogen incorporated in the plant–animal–human food chain. What are the factors which might influence the time scale for denitrification? One would hope that a careful study of the anthropogenic nitrogen cycle might suggest likely sites for denitrification. We shall argue on this basis that a large fraction of the net global source of N₂O might arise due to denitrification in aqueous media, and that local sources, for example the immediate vicinities of cattle feed lots, could play an important rôle. The analysis given here will be used later to assess the magnitude of the change in ozone which might be anticipated with several conceptual models for the future development of agricultural and industrial fixation.

The nitrogen content of soils in a natural ecosystem will tend to approach an equilibrium value, if the environmental conditions should remain constant for a relatively prolonged time period. The equilibrium state may be influenced by the nature of the vegetative cover, by physical conditions in the soil, by microbial activity and by climate. Nitrogen may be lost from the system by denitrification, or by the release of volatile compounds such as NH₃, NO or NO₂. It may be removed also by erosion, or by leaching. Loss of nitrogen in the equilibrium state is balanced by *in situ* fixation and by the supply of fixed nitrogen compounds in rain.

Cropping will tend to disturb the local equilibrium. The nitrogen content of the medium will decline as the soil is cultivated. The decline may be minimized to some extent by periodic applications of chemical fertilizer, or if the farmer should choose to plant the land with legumes. There is little doubt though that traditional farm practices will tend to lower the reserve of soil nitrogen, at least in the early stages of agricultural development. The nitrogen content of soils in the North Central United States decreased rapidly during the first 10–20 years of cultivation, with 25 % of the total soil reservoir depleted during the first 20 years, 10 % lost in the subsequent 20 years and about 7 % lost between the 40th and 60th years (Jenny 1941). Similar results under a variety of conditions were reported by Haas, Evans & Miles (1957) for the Great Plains, by White, Holben & Richer (1945) for the Jordan Soil Fertility Plots in Pennsylvania, by Bracken & Greaves (1941) for semi arid regions of Utah, by Giddens & Garman (1942) for Georgia, and by Smith, Thompson, Collier & Hervey (1954) for the blackland soils of Texas. Agricultural soils of the United States lost approximately 1.6×10^9 t of fixed nitrogen, out of an initial reservoir of about 4×10^9 t, in a fifty year period following the first large scale development of the Midwest (Jenny 1941; Council on Agricultural Science and Technology 1976). It is clear from these data that the nitrogen content of soils may be altered by agricultural practice on a relatively short time scale, less than 50 years. The system will adjust to a new equilibrium state, in which fertilizer and various fixing organisms can balance the loss of nitrogen extracted in crops and lost by denitrification, leaching and erosion. It appears, for the United States at least, that this new equilibrium configuration is one in which the nitrogen content of the soil may be reduced to approximately 50 % of its initial value.

Approximately 50 % of the total nitrogen made available in agricultural soils, i.e. the sum of the contributions from humus mineralization and fertilizer, may be taken up by the growing crop, according to data summarized by the Committee on Nitrate Accumulation (1972). Some 25 % of the plant nitrogen may be lost due to a combination of factors, including drought, hail,

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fire, insects, plant pathogens, failure to harvest, processing wastes and spoilage. About 35 % of the initial mineral supply is fed to livestock, and some 15 % of this ultimately reaches the human consumer as meat, poultry, and dairy products such as milk and cheese. Plant sources – fruits, vegetables, potatoes, flour, etc. – account for somewhat less than 30 % of the daily nitrogen requirements of people in the United States, though meat and animal products may be emphasized to a lesser extent elsewhere. A schematic illustration of the manner in which nitrogen may be utilized in the agricultural cycle is shown in figure 1.

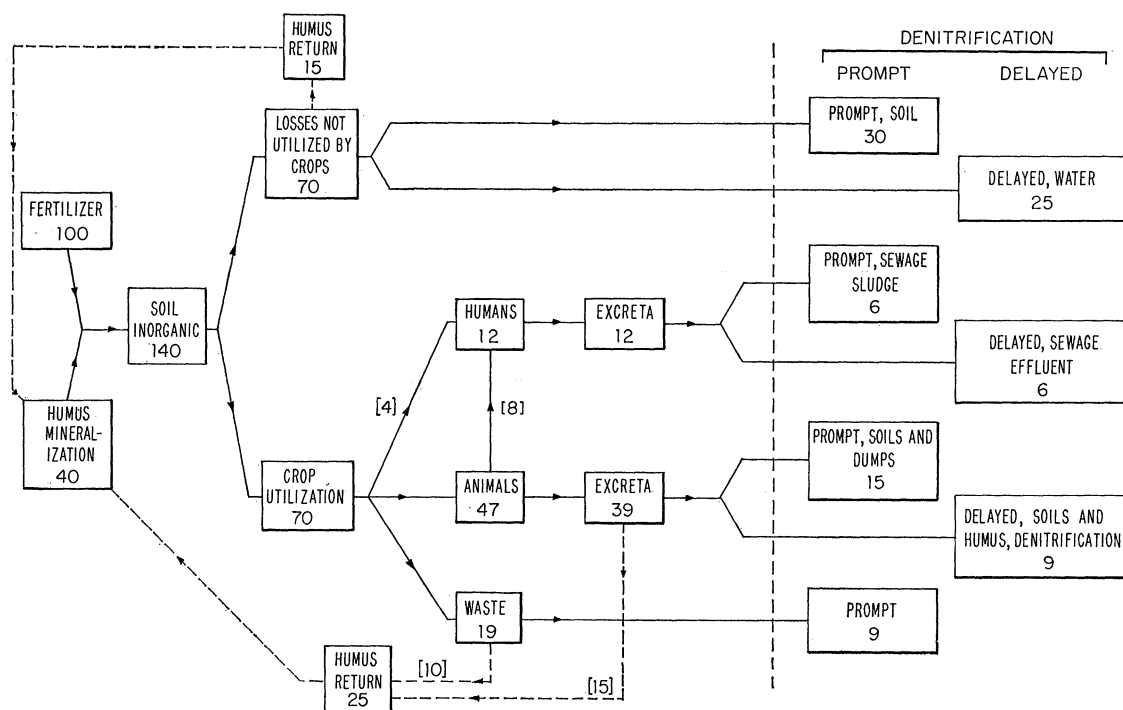


FIGURE 1. Transfer of nitrogen in the agricultural food chain (arbitrary units), adapted from data given by the National Academy of Sciences (1972). The relative contributions of soil nitrogen and fertilizer are intended to model average conditions in the United States. The various time scales for denitrification are discussed in the text.

All of the nitrogen mineralized in agricultural soils, or applied as fertilizer, must be returned ultimately to the atmosphere, either as N_2 or N_2O . The time scale for denitrification will depend fairly critically on agricultural and human practices, and will be influenced also by regional and climatic effects. Some denitrification will occur relatively rapidly, in the field, in cattle feedlots, and in plants for the treatment of human sewage. Some of the available nitrogen will be washed off into streams, lakes and estuaries, where denitrification may proceed on a somewhat delayed basis. We sought in figure 1 to distinguish between prompt and delayed sources of denitrification. It might be reasonable to associate a short time scale, of order 1–10 years, with prompt release. A much longer value, of order 10–100 years should apply to the delayed contribution.

A small amount of nitrogen may percolate ultimately to the deep ocean, where the time scale for denitrification could be as long as several thousands of years. There are reasons to believe that the amount of nitrogen which can penetrate to the deep ocean must be relatively small.

Nitrogen is a limiting nutrient in marine environments (Ryther & Dunstan 1971). Any excess in the supply of nitrogen from the land may be rapidly utilized by the near-shore marine biosphere with only a small amount exported. A similar situation seems to apply to sewage discharges into fresh waters and estuaries. Carpenter, Pritchard & Whaley (1969) showed that nitrogen in sewage is rapidly removed from the Potomac river, and J. Hahn (private communication) found the Rhine to be an extremely active source of N_2O . These results suggest that denitrification, and production of N_2O , may be a major path for nitrogen loss from rivers that receive municipal waste.

Details of the model in figure 1 were influenced to a considerable extent by data and agricultural-human practices prevalent in relatively advanced societies. Denitrification might proceed more rapidly in third world countries, where extensive rice culture might accelerate the rate of anaerobic processes. The denitrification cycle could be promoted also by the agricultural use of human and animal waste, and would be influenced further by climatic conditions – temperature and humidity. Use of marginal land, and the need for land clearance, could contribute further. As noted earlier, mineralization of humic nitrogen proceeds most rapidly in the early stages of soil cultivation, though it may be difficult to extrapolate the U.S. experience to other areas of the globe.

Several of the features of figure 1 merit further discussion. We indicated a fairly large loss of nitrogen from fields due to *in situ* denitrification. The nitrogen loss is well established, though the mechanism may be uncertain. The missing nitrogen does not appear in the soil, and there are four possible interpretations of the data. Nitrogen may be removed by volatilization of ammonium. It may be lost by leaching of soil nitrate, by run-off, or it may be released by denitrification. Measurements by Carter, Bennet & Pearson (1967), using tagged nitrogen under field conditions, show clear indications that a significant amount of nitrogen must be lost in gaseous form, even when denitrification might be considered improbable. Their experiment was carried out on a gently sloping, well-drained fine sandy loam, at Thorsby, Alabama. Loss of nitrogen was unaffected by pH, which was generally rather low, below 7.0, such that volatilization of ammonium should not have been significant. Figure 1 indicates a prompt release of nitrogen equal to 25% of that mineralized. This value may be relatively conservative, on the low side. Denitrification should occur, presumably, mainly in regions of the soil near and below the root system of the crop, where the organic demand for oxygen might be moderately high, but where the supply of O_2 might be inhibited, particularly following periods of relatively heavy rainfall. Figure 1 envisages additional sinks for nitrogen, due to surface run-off, and downward transport, and we suppose that the amount of nitrogen removed by these agents might be comparable to that lost locally by denitrification. The dissolved nitrogen carried off by ground water and surface streams will be lost elsewhere, and these contributions are included in the budget for delayed sources of denitrification in figure 1. The figure does not allow for nitrogen loss due to volatilization of NH_4^+ . We assume that on average the soil would tend to gain a small amount of fixed nitrogen from the air, in part due to combustion processes elsewhere, and we suppose that this source should tend ultimately to stabilize the loss of nitrogen due to mineralization of humus. The various branching paths in figure 1 have been adjusted to ensure an equilibrium condition for soil nitrogen. As noted earlier, this constraint is to be expected for a mature agricultural system, but may tend to underestimate the amount of nitrogen lost to the atmosphere in the early stages of agricultural development.

Animal excretions play a major rôle in the anthropogenic nitrogen budget and might be

expected to provide a favourable medium for denitrification. We may note in this context, the growing tendency in the United States to concentrate cattle in relatively confined areas, to facilitate their ultimate delivery to the consumer market. Their excretionary wastes are not treated with any great care, and feedlots may represent locally important sources of denitrification. The cattle population of the United States currently exceeds 100 million animals (U.S. Department of Agriculture 1974) and there may be as many as 3 billion chickens. The Committee on the Accumulation of Nitrate (1972) included in its report a strong recommendation to encourage the return of animal manure to agricultural soils. Such a recommendation, if implemented, would cut back on the demand for chemical fertilizer, and might reduce the net global release of N_2O . The recommendation cannot easily be implemented however since feedlots are often located in regions of the country far removed from farmlands where the manure might be used.

As may be seen from figure 1, one might anticipate that a major fraction of the nitrogen fixed by various processes on land should be liberated ultimately by denitrification in aqueous media. This view appears to be supported by recent measurements reported by J. Hahn (private communication), as noted earlier. He found that the waters of the Rhine were supersaturated in N_2O by about a factor of 60 during the month of January 1971. To the extent that these data may be considered representative, it would seem difficult to escape the conclusion that fresh water sources should play an important rôle in the global budget of fixed nitrogen. The time scale for N_2O release could be relatively short, and the model displayed in figure 1 might tend to underestimate the short term response of the atmosphere to perturbations due to the impact of an enhanced source of fixed nitrogen. We assume, consistent with the data in figure 1, that approximately 50% of the nitrogen applied as fertilizer may be denitrified within the first 10 years, with a mean value for the time lag in the appearance of N_2O set equal to 7 years. Approximately 40% of the applied nitrogen is assumed to be released with a delay of 50 years, and the balance is emitted on a time scale of about 100 years. We assume that a relatively small fraction, about 20%, of the combustion source may be liberated promptly, in 7 years. A further 20% is assumed to be released in 50 years, and the balance is emitted with a delay time set equal to 100 years. The precise values for the time scales assigned here are to some extent arbitrary and should be refined as new observational data become available. They are unlikely to introduce significant error in the present context however, if our major assumption should prove valid, i.e. that the continents including soils, rivers, lakes, estuaries and near coastal waters, should operate as an essentially closed system for fixed nitrogen.

4. THE DEMAND FOR FERTILIZER AND PROJECTIONS FOR THE FUTURE GROWTH IN INDUSTRIAL SOURCES OF FIXED NITROGEN

Fixation of nitrogen for use in chemical fertilizers has grown rapidly, at an average rate of about 10.7% per year, over the past 25 years. The past history of development is illustrated in figure 2. The figure excludes the source due to combustion. The growth in fixation of nitrogen by combustion averaged 4% between 1950 and 1975, and may be projected from data presented by Bolin (1970) to grow by about 3% per year between 1975 and 2000. Hardy & Havelka (1975) estimate that fixation of nitrogen for fertilizers could climb to about 2×10^8 t/a by the year 2000, corresponding to an average growth rate of 6% per year over the last quarter of this century. The Council for Agricultural Science and Technology (1976) quotes a range of values,

between 1×10^8 and 2×10^8 t/a, by the turn of the century, and it seems clear that the immediate prospects for the fertilizer industry are optimistic.

Table 1 gives a summary of data available for current construction of fertilizer plants in a number of major countries (Keyes 1973). If we assume that all of these plants should be operational by late 1977, it is clear that production of fertilizer nitrogen should grow to about 5.4×10^7 t/a by 1978. Harre, Bridges & Shields (1975) quote a range of values between 5.3×10^7 and 6×10^7 t/a by 1980, an estimate which seems conservative in light of the information presented in figure 2 and table 1. It seems reasonable to suppose, that in the future a relatively larger fraction of the total nitrogen fixed as synthetic ammonia may be used to produce fertilizer. Harre *et al.* (1975) give a range of values between 8.1×10^7 and 8.7×10^7 t/a (nitrogen) for global fixation of synthetic ammonia in 1980. Estimates for fertilizer use in the range 1×10^8 to 2×10^8 t/a by the year 2000 seem quite reasonable in light of the discussion above.

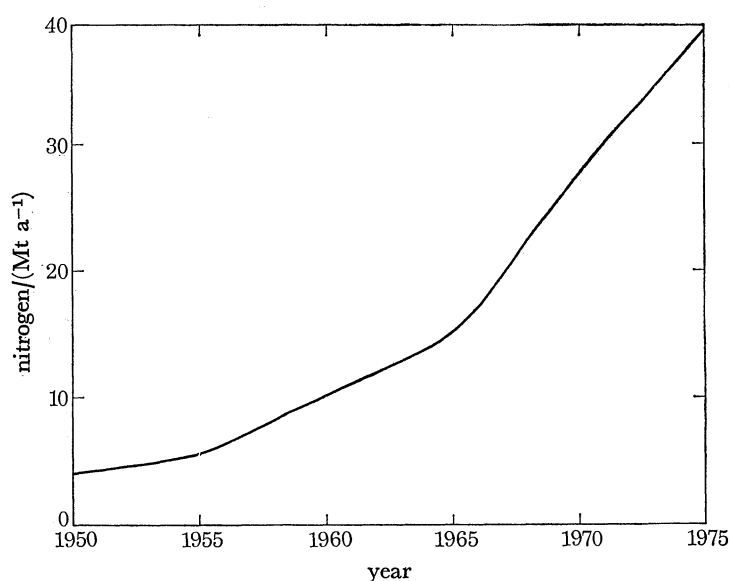


FIGURE 2. The past history of fertilizer use. The units are 10^6 t/a of nitrogen. Data are from Minerals Yearbook, 1950-73.

There are several factors which might be expected to influence the future demand for fertilizer nitrogen. The World's population is expected to grow from its present level of 4×10^9 to about 6.5×10^9 by the year 2000, corresponding to a mean rate of increase of 2% per year (Walters 1975). This estimate is consistent with figures released recently by the United Nations (Demographic Year Book 1970). Approximately 1.3×10^9 ha were devoted to agriculture in 1973, of which roughly 5×10^8 ha were taken up for the production of major grain crops, excluding rice. The amount of land devoted to agriculture has remained relatively constant over the past 15 years, though production of food crops has increased by nearly 50% in the same time period. The increase in productivity may be attributed directly to the influence of fertilizer. The yield for grain crops, which averaged 1.94×10^3 kg ha⁻¹ in 1973, was achieved through the application of almost 4×10^1 kg of nitrogen per hectare in the form of chemical fertilizer. If the World's living standards are to remain relatively constant on a per capita basis over the next 35 years, and if the allotment of land for agriculture should remain stable at its present value, then the demand for fertilizer should grow to about 1.10×10^8 t/a (nitrogen) by the year 2000.

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TABLE 1. PROJECTED CONSTRUCTION OF FERTILIZER PLANTS

country	(1) plant capa- city (N)† 10 ⁶ t a ⁻¹	product	capital investment 10 ⁶ \$	financial source or technical sponsor	operational date
Angola	0.04	ammonium sulphate	ua.‡	ua.	1976
	0.08	fertilizer	ua.	ua.	
Bahrain	0.15	fertilizer	115	India	under study
	0.32	ammonia			
	0.28	urea			
Bangladesh	0.17	ammonia	80	India	ua.
Bolivia	0.32	ammonia	ua.	Argentina	ua.
	0.27	urea	ua.	Argentina	ua.
Brazil	0.32	ammonia	60	Kellogg International	1975
	0.14	urea			
	0.32	ammonia	ua.	Brazil	ua.
	0.11	urea	ua.	Brazil	ua.
Canada	0.32	ammonia	ua.	Canada	ua.
	0.28	urea	ua.	Canada	ua.
China	0.96	ammonia	70	U.S.A. (Kellogg)	ua.
	0.62	ammonia	ua.	Japan	ua.
	2.36	urea	55	Holland (Kellogg)	1976
Egypt	0.19	fertilizer	ua.	World Bank	ua.
Hungary	0.32	ammonia	ua.	Hungary	1975
India	0.48	ammonia	220	Britain and W. Germany	ua.
	0.32	ammonia			
	0.28	urea			
	0.32	ammonia			
Iran	0.12	urea	ua.	France	ua.
Iraq	0.42	urea	100	Japan	ua.
	0.26	ammonia	—	—	
Ireland	0.32	ammonia	50	Ireland	1977
Italy	0.13	ammonium nitrate	ua.	Italy	1975
S. Korea	0.44	ammonia	181	U.S.A. and Japan	1976
	0.12	urea			
	0.05	ammonium nitrate			
Libya	0.32	ammonia	—	Libya and Germany	1976
Pakistan	0.04	urea ammonium phosphate	—	World Bank	ua.
	0.32	ammonia	100	Kellogg and World Bank	ua.
	0.07	nitro-phosphate			
	0.56	ammonia			
Romania	0.04	fertilizer	ua.	Romania	ua.
Spain	0.26	ammonia	ua. } ua. } 4 }	Spain	1975
	0.08	urea			
	0.15	ammonia			
Sudan	0.18	urea	60	France	
Taiwan	0.26	ammonia	ua.	Taiwan	ua.
	0.05	urea	ua.	Taiwan	ua.
Trinidad	0.35	ammonia	50	Trinidad	1976
Turkey	0.32	ammonia	57 } ua. }	World Bank and W. Germany	1976
	0.16	urea			
U.S.S.R.	2.40	ammonia	§	U.S.A.	ua.
	0.69	urea	§	U.S.A.	ua.
	0.80	ammonia	—	Italy	ua.
	0.23	urea	—	Italy	ua.

† The net nitrogen content of various industrial products were estimated by using the following percentages by mass: ammonia 82 %, urea 46 %, ammonia phosphate and sulphate 18 %, ammonia nitrate 32 %, and fertilizer 30 %.

‡ ua., Information unavailable.

§ Part of the \$8 billion deal between Occidental Petroleum and the U.S.S.R.

A relatively modest rise in global living standards by the year 2000, a grain production of 3.75×10^3 kg per person per year as compared to the present value of 2.5×10^3 kg per person per year, should require approximately 1.70×10^8 t (nitrogen) fertilizer per year, similar to the figure quoted by Hardy & Havelka (1975). If all of the World's population were to achieve the dietary affluence now enjoyed by the United States, 1.1×10^3 kg grain per person per year, the demand for fertilizer would grow to 4.00×10^8 t/a (nitrogen) by 2000.†

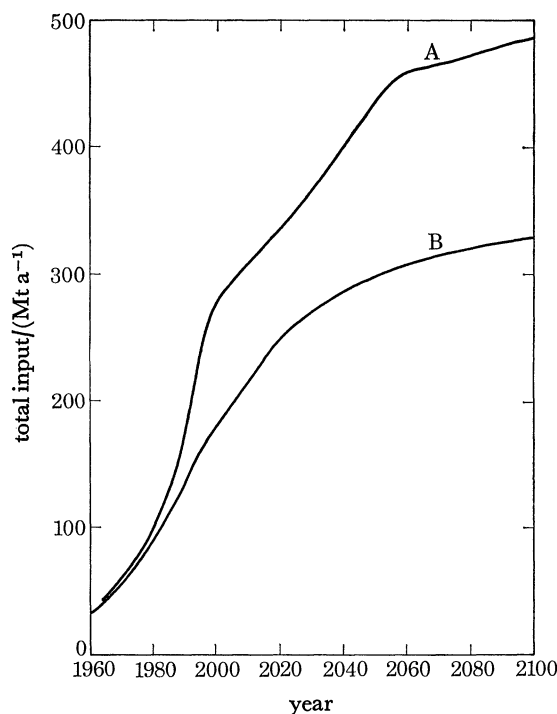


FIGURE 3. Projections for total anthropogenic nitrogen fixation (10^6 t/a nitrogen). The assumptions behind models A and B are discussed in the text.

Several conceptual models for the future production of fertilizer nitrogen, together with estimates for the growth in fixation due to combustion, are shown in figure 3. The projections are regarded as relatively conservative. They assume a moderately stable World population by the middle of the next century. They assume that climatic conditions should remain favourable for agriculture over the next 150 years, though it may be argued that weather has been unusually cooperative in the recent past. They allow modest improvement in living standards, with model A, but continue to project major dietary deprivation with model B.

It is probable that economic and political factors will play a major rôle in regulating and delimiting the future course of world agriculture. The growing demand for food and fertilizer may be directly attributed to the needs of third world countries. Current expansion in fertilizer production capacity depends heavily on resources of a small number of more prosperous capitalistic economies: the United States, Japan and Western Germany are notably prominent,

† The values quoted here for fertilizer demand were obtained from a linear extrapolation of data presented by Hardy & Havelka (1975), linking grain productivity to fertilizer use for various contemporary agricultural systems. The linear relationship is unlikely to hold for large yields, and it seems probable that the demand for fertilizer should be larger rather than smaller than the values given here.

as may be inferred from a casual inspection of the data in table 1. The demand for fertilizer envisaged in model A for the year 2000, will require a capital investment, in plant, of about $\$3.3 \times 10^{10}$.† Sociological and political considerations dictate that these resources should be made available. The economic demands may be offset to some extent, by the natural resources of the third world.

5. ANTHROPOGENIC PERTURBATIONS TO N_2O AND O_3

This section is devoted to an attempt to predict the changes in N_2O and O_3 which might arise due to future growth in agricultural and industrial fixation of nitrogen. The variation to be expected for N_2O will depend on the growth pattern assumed for fixation, the yield factor adopted for N_2O , and the delay time assessed for denitrification. As discussed above, we shall investigate two models for the future course of fixation, and three models for the fractional yield of N_2O . The models, with obvious notation, are denoted by the symbols A1–A3 and B1–B3.

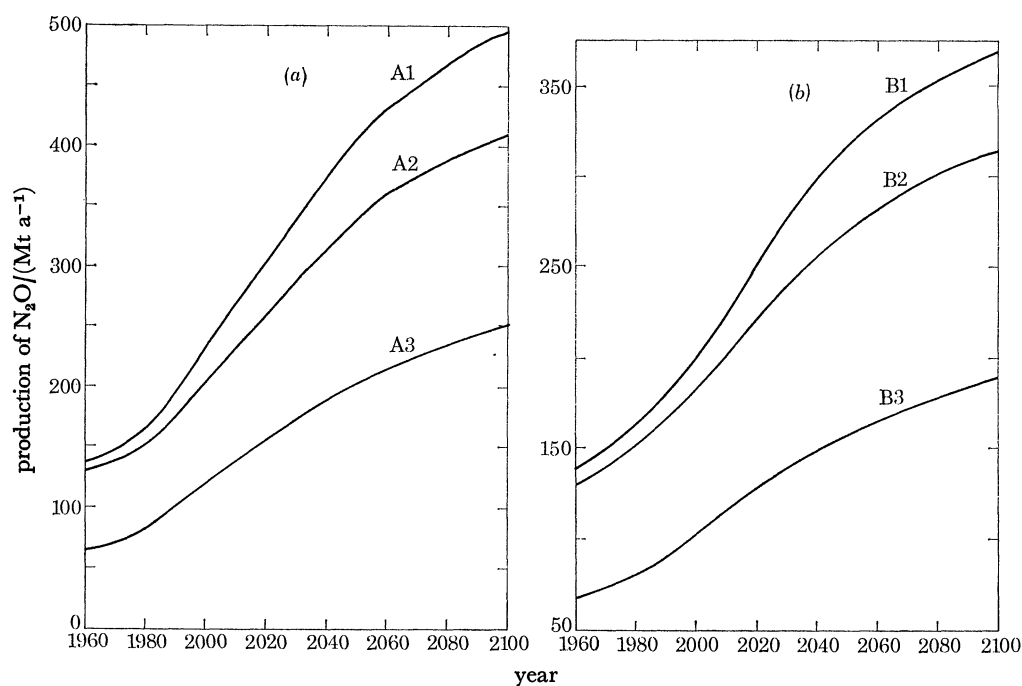


FIGURE 4. (a) The global production rate for N_2O (10^6 t/a nitrogen) as a function of time, for three cases corresponding to demand curve A in figure 3 and models 1, 2 and 3 described in the text. (b) Same as (a), using demand curve B in figure 3.

Models A_2 and B_2 assume that the sea should play a predominant rôle in the budget of atmospheric N_2O under unperturbed conditions. As noted earlier, we consider this unlikely. The weight of the observational evidence appears to favour a condition intermediate to models A(B)1 and A(B)3. The delay time for denitrification will be treated in the manner described in §3. Results for the time history of the N_2O source are shown in figure 4. The corresponding change in atmospheric N_2O is illustrated in figure 5 and results for O_3 are given in figure 6.

† Dollar figures quoted here reflect monetary standards and costs in fiscal 1973. They should be adjusted accordingly to reflect past and anticipated inflation.

The perturbations to O_3 summarized in figure 6 were derived using procedures described by McElroy, Wofsy, Penner & McConnell (1974). The concentration of O_3 at high altitude, where the chemical time constant, τ_c , is less than 30 days, was derived subject to the assumption of chemical equilibrium. The concentration at low altitude ($\tau_c > 30$ days) was obtained by applying a suitable scale factor (the scale factor was estimated by considering the magnitude of the perturbation to O_3 at the level for which τ_c equalled 30 days) to the unperturbed distribution of O_3 , as measured for example by Hering & Borden (1967). Details of the chemical model, updated to reflect recent laboratory measurements, are given by Wofsy (1976). Vertical profiles for N_2O , NO_x , CH_4 , CO and Cl_x were obtained by using the simple empirical scheme employed in most recent studies of atmospheric O_3 (see, for example, the Climatic Impact Assessment Program 1974). Diffusion coefficients, based mainly on analyses of the spatial distribution of C^{14} (Johnston, Kattenhorn & Whitten 1976) and CH_4 (Wofsy & McElroy 1973) were taken from Wofsy (1976).

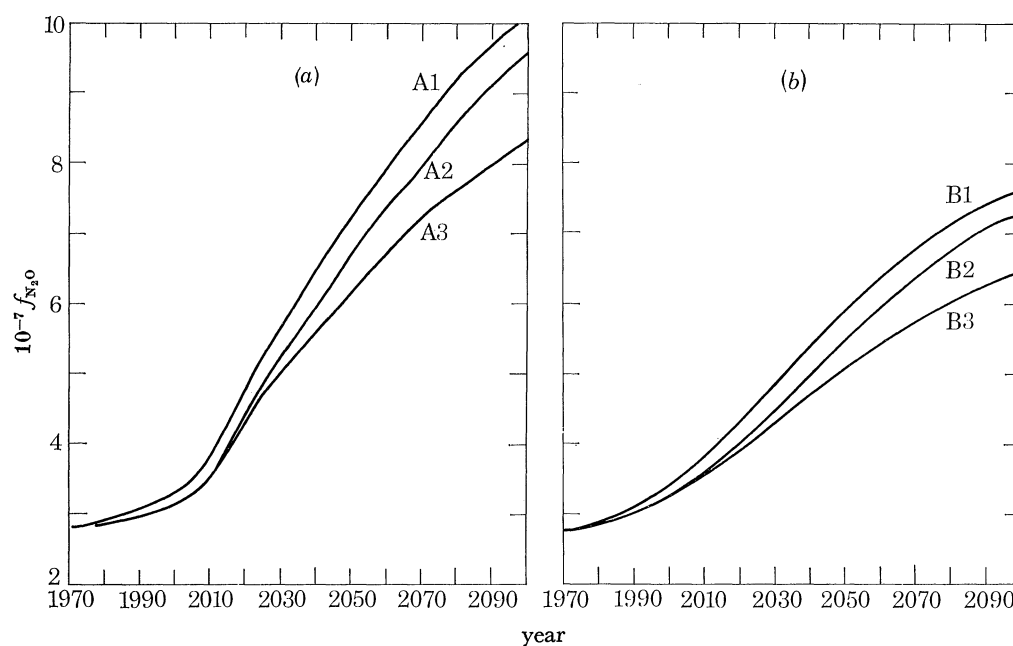


FIGURE 5. (a) The global mixing ratio of N_2O ($v/v \times 10^{-7}$) as a function of time, for the three cases given in figure 4a. (b) The global mean mixing ratio of N_2O ($v/v \times 10^{-7}$) as a function of time, for the three cases given in figure 4b.

All six models in figure 6 indicate moderately large reductions in O_3 on a relatively immediate time scale. The reduction in O_3 for model A approaches 20% in the latter half of the 21st century, consistent with projections given earlier by McElroy (1976a). It is interesting to note that the impact is relatively independent of assumptions made with regard to the rôle of the sea in the natural state. Our conclusions are predicated primarily on the rationale developed in §3, i.e. that the continents operate as an essentially closed system for anthropogenically fixed nitrogen. If we assume that as much as 40% of the nitrogen fixed on land might escape to the open ocean in rivers and rain, reflecting an assumption that 7×10^7 tonnes of fixed nitrogen should escape to the open oceans in the natural state, the anthropogenic influence on O_3 , as indicated by models A2 and B2 could be reduced by a factor of about 0.8.

The results in figure 6 appear to violate upper limits proposed by Crutzen (1975), for the impact of fertilizer over the next 125 years. Crutzen (1975) argued that the largest possible perturbation to O_3 should result if one assumes that the delay in denitrification should be vanishingly small compared to the atmospheric lifetime for N_2O . He considered a growth in fertilizer production from the 1974 value of 4×10^7 t/a to 2×10^8 t/a by the year 2000, with a constant level of production thereafter. He concluded that the reduction in O_3 should not exceed 1% by the year 2000 and that it should be less than 10% by 2100. His results depend critically however on an assumption that the time constant for change in O_3 should not be affected by the lifetime for N_2O . The source of N_2O due to denitrification was set equal to the magnitude of the sink due to stratospheric photolysis, about 9×10^6 t/a. This result would imply a lifetime for atmospheric N_2O of about 130 years, and would correspond to a yield factor of 4%. It is clear though that the yield for N_2O must be raised as the atmospheric lifetime for the gas is reduced. A short lifetime implies a large source of N_2O and a rapid atmospheric response. The relatively small reductions in O_3 derived by Crutzen (1975) are valid only if the atmospheric lifetime for N_2O should exceed 100 years. They may not in any sense be regarded as upper limits to the real impact of fertilizer.

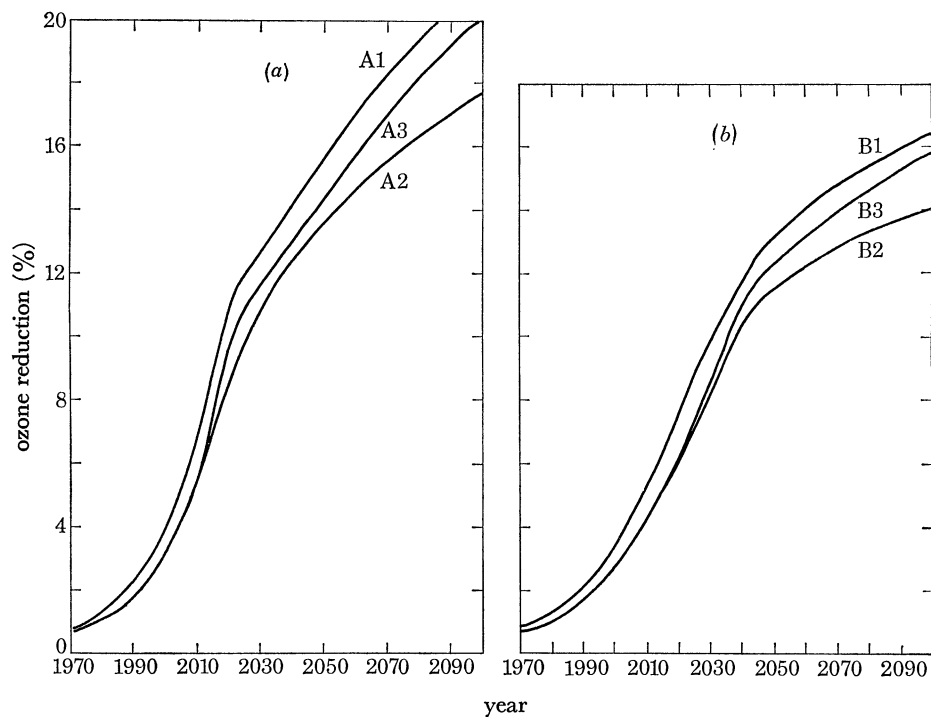


FIGURE 6. (a) Reductions in ozone as projected with models A1–3. (b) Reductions in ozone as projected with models B1–3.

It appears that inconsistencies of the earlier work have been removed in a more recent study Crutzen (1976). His discussion in this case was heavily weighted by Hahn's (1974, 1975) estimate for the land source of N_2O , 1.5×10^7 t/a. This result was used to estimate an N_2O yield factor for terrestrial denitrification, of less than about 8%. He omitted however continental denitrification associated with fresh water media, and, as noted above, there are reasons to believe that a major fraction of the global source of N_2O may arise in this compartment. He

presented results for a range of N₂O yield factors, from 7 to 50 %. His models did not include nitrogen fixation associated with combustion and assumed a zero growth situation for fertilizer after the year 2000. As before, denitrification was taken to proceed without delay, and results were presented as upper limits to the fertilizer effect on O₃. His model should be adjusted to allow for higher yields of N₂O. If combustion and agricultural growth in the 21st century were included in his source input, the conclusions should be compatible with the present discussion.

A recent paper by Liu, Cicerone, Donahue & Chameides (1976) raises a different issue. They argue that the response of the atmosphere to change in the rate for fixation of nitrogen might require an exceedingly long time period. They discussed a range of values for the land reserve of fixed nitrogen, varying from 1.7×10^{11} t to 9.1×10^{11} t (nitrogen). If one considers a fixed nitrogen input of 2×10^8 t/a, it would appear that the time constant for significant change in soil nitrogen should lie between 8×10^2 and 5×10^3 a. This conclusion depends critically however on a value quoted by Delwiche (1970) for the reserve of fixed soil nitrogen, about 9×10^{11} t. It appears that Delwiche's result may rely on an earlier paper by Stevenson (1965), which contains an unfortunate typographical error. Estimates for the nitrogen content of humus are based on measurements of the C:N ratio and on extrapolated values for the global accumulation of humic material (Stevenson 1965). Delwiche's (1970) data for organic and inorganic soil nitrogen should be reduced therefore by about a factor of 10. McElroy (1976*a*) quotes a value of 1×10^{10} t (nitrogen) for the inorganic reservoir,† with 6×10^{10} t (nitrogen) included in the humic compartment. The time constant for soil nitrogen should be lowered accordingly, to about 400 years. It should be emphasized that this result refers to the natural state. It is consistent with the recovery pattern observed for nitrogen on the recessional moraines of an Alaskan glacier (Crocker & Major 1955), in spoil banks of Minnesota strip mines (Leisman 1957), in soils on the shores of Lake Michigan (Olson 1958), and in sand dunes at Blackney Point, England (Salisbury 1925). The time constants are much shorter in agricultural land. The levels of biological activity and the loss of nitrogen to surface waters are accelerated by cultivation and the response of the system to a perturbation is consequently more immediate. Field measurements (Jenny 1941; Haas *et al.* 1957; White *et al.* 1945; Bracken & Greaves 1941; Giddens & Garman 1942; and Smith *et al.* 1954) imply a mean lifetime of about 50 years, in harmony with the analysis given here.

The distribution of O₃ in the lower stratosphere is set by a complex interchange of chemistry and dynamics. The problem may be approached in a variety of ways. A scaling procedure was employed in the present study. Other investigations (Climatic Impact Assessment Program 1974; Crutzen & Isaksen 1976; Donahue, Cicerone, Liu & Chameides 1976) make use of the one dimensional eddy diffusion concept throughout the atmosphere, in precisely the same manner in which it was employed here for N₂O, NO_x, CH₄, CO and Cl_x. Diffusion coefficients are based on models for the distribution of various passive tracers. Methane and ¹⁴C are especially valuable. We may note however that the distribution of O₃ may depart significantly from that of either ¹⁴C or CH₄. The discrepancies are exhibited in figure 7 and are quite marked for all altitudes above about 20 km.

The scaling procedure is designed to circumvent these difficulties. Figure 8 shows a comparison of results obtained using various approaches to treat the problem. We may note that the scaling procedure favoured here gives a much smaller result for the magnitude of the perturbation to

† In the context of ecosystems where inorganic nutrients are seasonally reduced to *ca.*, as in certain grasslands, the term 'inorganic' is intended to include readily available N temporarily incorporated into the biomass.

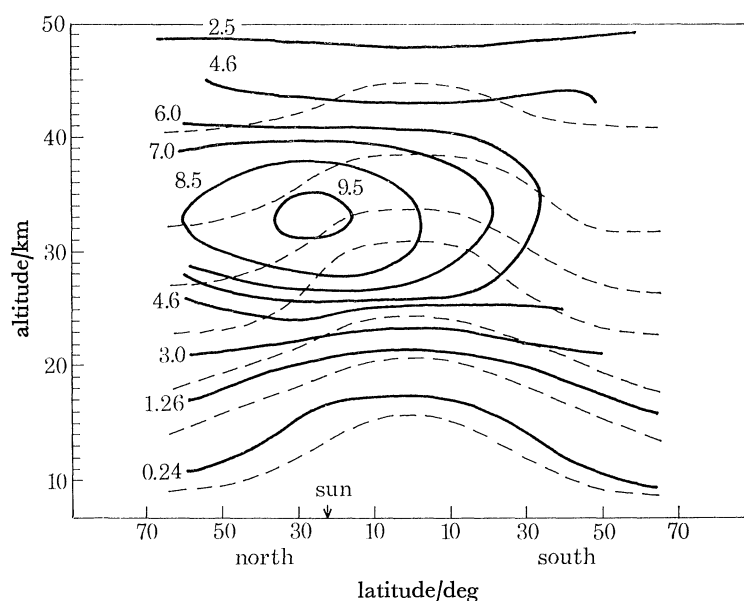


FIGURE 7. The meridional cross-sections for the ozone mixing ratio (p.p.m.v.) in July. Above 30 km the isopleth contours are calculated assuming photochemical steady state. Ozone data are used below 30 km (see Wofsy 1976 for details). The dashed lines correspond to isopleths observed for long-lived tracers like $^{14}\text{CO}_2$, ^{86}Sr , CH_4 and CO (McElroy *et al.* 1976; Wofsy 1976).

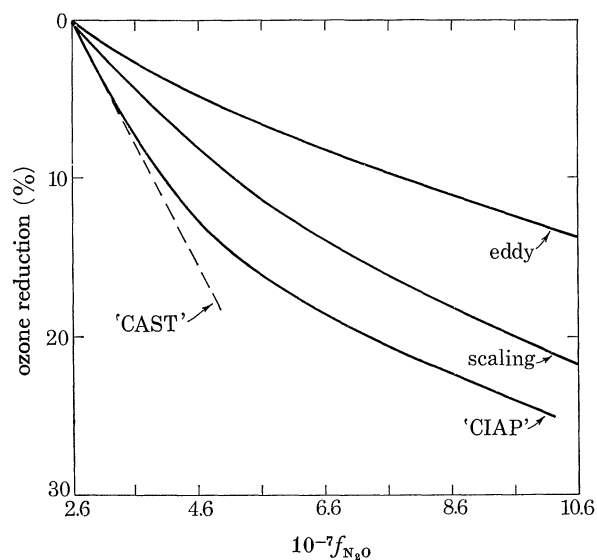


FIGURE 8. Ozone reduction (%) as a function of the tropospheric N_2O mixing ratio ($v/v \times 10^{-7}$). The curves reflect different methods for calculating ozone profiles: 'eddy', one dimensional 'eddy diffusion'; 'scaling', procedure of McElroy *et al.* (1974); 'CIAP', response curve from CIAP Monograph 3 (1975), allowing for the response of stratospheric NO_x to changes of N_2O in our models; 'CAST', the perturbation formula discussed by the Committee for Agricultural Science and Technology (1976), which corresponds to the initial slope of the 'CIAP' curve.

O_3 than would be obtained had we adopted the simple recipe given by the Council for Agricultural Science and Technology (1976). Had we followed their formula to estimate the effect of a given N_2O perturbation, we would have been obliged to increase the magnitude of the reduction predicted for O_3 , to about 20% by 2030 in model A1, and to an impossibly large value by the year 2100. The scaling procedure yields somewhat larger results than the one dimensional eddy model. The eddy model depends critically however on values assumed for the diffusion coefficient between 20 and 30 km. The difference between the several curves shown in figure 8 may be taken to provide some indication of the uncertainty in current models for the anthropogenic impact on O_3 .

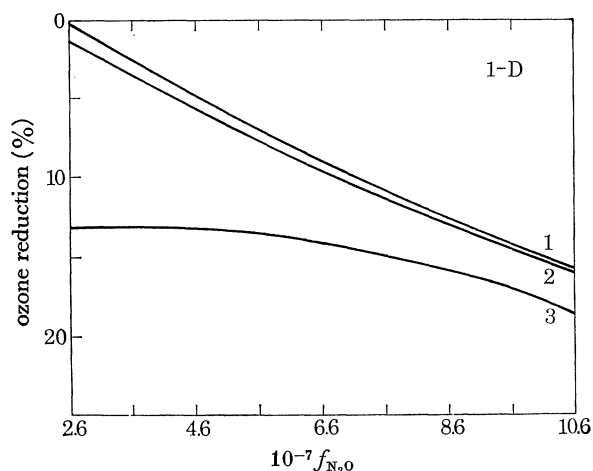


FIGURE 9. Ozone response to increased N_2O , with several assumed values for the stratospheric chlorine burden. Curve 1, stratospheric chlorine taken equal to a quarter of today's value; curve 2, stratospheric chlorine at today's value, corresponding to the data of Lazrus *et al.* (1976) and Ackerman *et al.* (1976); curve 3, stratospheric chlorine taken equal to five times today's level. The effect of reaction (7b) was not explicitly considered in these computations due to current uncertainties in relevant reaction rates.

It should be emphasized that the computations described above do not allow for effects due to future growth in stratospheric chlorine, which might arise, for example, due to continued release of chlorofluoromethanes. The results would not be altered much had we allowed for the present burden of stratospheric chlorine, as shown in figure 9. The non-linear interactions between Cl_x and NO_x chemistry however, could be quite important, if the chlorine content were to increase by about a factor of 2. The effect of a 5-fold increase is depicted in figure 9. An increase of this magnitude might occur by the early part of the next century, should the release of chlorofluorocarbons continue to grow at a moderate rate. The results in figure 9 were obtained by using one dimensional eddy diffusion. The figure clearly illustrates that anthropogenic perturbations to O_3 may not be additive if the impact on O_3 should exceed about 5%.

6. SUMMARY

The issues raised here are complex. They involve a variety of assumptions, and define clear needs for additional research in a number of important areas.

The paper should not in any sense be regarded as an appeal for regulation of fertilizer. It calls rather for additional study, and for agricultural practices which might cut back on the

need for fertilizer, while minimizing the impact on food production. Re-use of animal waste would be helpful in this regard, but might involve considerable economic dislocation.

The model developed here is based on three primary postulates: that the land, including fresh water media and estuaries, should represent an essentially closed system for fixed nitrogen; that the rate for natural fixation should not greatly exceed the value assumed here; and that the lifetime for atmospheric N_2O should be relatively short, between 10 and about 50 years.

Studies of the marine nitrogen cycle could help clarify the first of these issues. The second seems relatively soundly based. Application of nitrogen fertilizer at a rate of 25 kg ha^{-1} is known to produce a significant effect on the productivity of agricultural soil (Hardy & Havelka 1975). If we assume that the background fixation rate should not exceed this value, we may place an upper limit on the rate for natural fixation, equal to about $3 \times 10^8 \text{ t/a}$.

It seems clear that man's growing rôle in the global nitrogen cycle merits further, and indeed more broadly based, scrutiny than the preliminary analysis presented here.

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