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"Effect of Increased Nitrogen Fixation on Stratospheric Ozone: Report 53, Iowa State University", Council for Agricultural Science and Technology, Ames. 1976.

FOREWORD

This report was developed by eleven scientists representing the subject-matter areas of atmospheric chemistry, chemical engineering, environmental science and chemistry, microbiology, oceanography, plant genetics, soil biochemistry, soil physics, and soil chemistry. The task force met in Denver from October 23 to 25 to prepare a first draft of the report. The chairman then prepared a revised version and returned it to members of the task force for review and comment. A second revision was then prepared and returned for further comment. Finally, the report was edited and reproduced for transmittal to the Congressional committees concerned with the matter of ozone depletion.

CONTENTS

SUMMARY

Nitrogen compounds are produced by biological reactions and by industrial processes from the abundant nitrogen gas (N_2) in the atmosphere. The formation of compounds from atmospheric nitrogen is called fixation. In nature, nitrogen compounds undergo many conversions, but under aerobic conditions, characterized by the presence of oxygen, they tend to be converted to the nitrate (NO_3^-) form. Under anaerobic conditions, characterized by the absence of oxygen, the nitrate is denitrified, and the nitrogen contained therein is converted into nitrogen gas (N_2) and nitrous oxide (N_2O), which escape into the atmosphere. The nitrous oxide diffuses into the stratosphere, where it decomposes to yield nitrogen gas and small amounts of nitric oxide (NO) and nitrogen dioxide (NO_2), which react with ozone (O_3) to convert it to oxygen (O_2). The ozone in the stratosphere is produced by the reaction of light with oxygen and is destroyed primarily by reactions with the nitrogen oxides.

As long as the production and destruction are equal, the ozone in the stratosphere is maintained at a constant concentration. Increased nitrogen fixation will lead to increased denitrification, increased amounts of nitrous oxide moving into the stratosphere, and a reduction in ozone concentration.

Ozone in the stratosphere attenuates the ultraviolet light received from the sun. As the ozone concentration decreases, more ultraviolet light will reach the surface of the earth. The fear is that this additional radiation will have detrimental effects on living organisms and possibly on the climate.

Because the global use of fixed nitrogen in fertilizers has increased greatly in recent years and in 1974 amounted to almost 40 million metric tons, the eventual generation of nitrous oxide from the fertilizer nitrogen after application to the soil has been cited as a potential environmental hazard. In response to this concern, this document estimates nitrogen fixation, nitrous oxide production, and ozone reduction based on two methods of calculation and on various increases in nitrogen fixation. Uncertainties and information gaps in the nitrogen cycle are pointed out.

This document does not review either the projected biological effects of ozone depletion or the stratospheric chemistry of ozone. These topics are dealt with at length in other studies.

World fixation of nitrogen in 1974, expressed in millions of metric tons per year (MT/yr), was estimated to be as follows:

MT = metric tons

Mechanism or Location of Fixation	Fixation in 1974	
	MT/yr	Percent of Total
Natural processes on agricultural land	89	38
Natural processes on forested and unused land	60	25
Industrial fixation for fertilizers and industrial purposes	57	24
Combustion	20	9

Mechanism or Location of Fixation	Fixation in 1974 MT/yr	Percent of Total
Lightning	10	4
Ocean	1	--
Total	237	100

Most of the estimates given are based on inadequate data; consequently, actual amounts may be significantly different from those shown. The study of nitrogen fixed in the oceans has not progressed far enough to permit reliable estimates. However, estimates of the amount of nitrogen fixed for fertilizer and other industrial uses in 1974 are considered reliable. The trend of industrial fixation of nitrogen offers some indication of the trend in total amount of nitrogen fixed. It is estimated that 174 MT of nitrogen were fixed by all processes in 1950. Total fixation in 1850 could have been 150 MT of nitrogen.

Nitrous oxide-nitrogen production on land is estimated as 5 to 10 MT/yr; published estimates of production in the ocean, however, range from less than 1 to 100 MT/yr. The higher value was based on reported supersaturation of ocean waters with nitrous oxide.

Two methods of estimating the decrease in ozone concentration in the stratosphere were used. Method I is based on nitrogen fixation. It involves the assumptions that the relative increase in production of nitrous oxide is proportional to the relative increase in total nitrogen fixation and that sufficient time has elapsed for the rate of denitrification to come to equilibrium with fixation; i.e., the lag time between increased fixation and increased denitrification has passed. This method, using fixation estimated for 1950 as a base, suggests that the reduction in ozone would be 5.8 and 11.5% as a consequence of increased fixation of 50 and 100 MT of nitrogen per year, respectively.

Method II is based on nitrous oxide evolution. It involves the assumption that the global rate of production of nitrous oxide is 100 MT/yr (based on supersaturation of this gas in the ocean and on changes in measured concentrations of nitrous oxide in the atmosphere). Method II leads to estimates of ozone reduction much lower than those from Method I. For example, on the assumption that global production of nitrous oxide-nitrogen is 100 MT/yr and that 5% of the nitrogen denitrified is released as nitrous oxide, the estimated ozone reduction is 1% with an increase of 100 MT/yr in nitrogen fixation. This method is forced to assume an unknown source of nitrous oxide in the ocean and an unknown sink for nitrous oxide in the troposphere.

There are great uncertainties in many of the estimates that have been made for nitrogen fixation and for nitrous oxide production, and there are many information gaps that need to be filled before the question of the effects of increased nitrogen fixation on the ozone layer can be answered. Perhaps the biggest information needs are in the areas of nitrogen transformations and the quantities of nitrous oxide pro-

duced in the ocean. Other needs deal with the complexities of the nitrogen cycle on land. The lag time between fixation by various processes and denitrification must be known as a basis for estimating how soon predicted effects based on equilibrium conditions can be expected. Concentrations of nitrous oxide and their fluctuations in the troposphere (lower atmosphere) need to be monitored to provide an index to variations and increases in production. Improved models are needed to relate the ozone concentration in the stratosphere to nitrogen fixation and nitrous oxide production on earth.

In spite of the uncertainties in the predictions of the effects of increased fixation of nitrogen on stratospheric ozone, the potential hazard is sufficiently serious that, in addition to research on the various phases of the global nitrogen cycle that impinge upon the nitrous oxide-ozone question, research on the efficiency of use of all fixed forms of nitrogen should be worthwhile.

INTRODUCTION

Ozone (O_3) is a form of oxygen that exists in minor quantities in the earth's atmosphere. It is found mainly in the stratosphere, where its concentration is maintained in dynamic equilibrium by natural processes that produce it and others that destroy it. Because ozone effectively filters out ultraviolet radiation, which has detrimental effects on exposed living organisms on the earth's surface and perhaps also on the climate, maintenance of the ozone concentration in the stratosphere is important to the well-being of people, animals, and crops.

Ozone is produced by the reaction of light with oxygen (O_2) and is destroyed largely by its reaction with nitric oxide (NO) and nitrogen dioxide (NO_2). These oxides are formed in the stratosphere from nitrous oxide (N_2O) that originates in soils, sediments, and waters. The nitric oxide and nitrogen dioxide produced by various processes in the lower atmosphere are considered to be recycled back to the soil. Thus, the nitrogen oxide of primary importance in controlling the balance of ozone in the stratosphere is nitrous oxide, and a substantial increase in nitrous oxide production might constitute a potential hazard to our health and well-being.

During the period from 1971 to 1974, the U.S. Department of Transportation (DOT), through its Climatic Impact Assessment Program, completed a $21 million research project on the stratosphere, stratospheric ozone, and the vulnerability of stratospheric ozone to man-made perturbations from supersonic transports. This project included a study of probable biological effects and possible climatic effects of a systematic long-term reduction of stratospheric ozone. The U.S. National Academy of Sciences (NAS), through its National Research Council, set up a Climatic Impact Committee to advise the DOT during the course of its research and to evaluate the findings independently. The DOT has published six monographs that contain the full details of the study.[a] A summary report was issued in March, 1975 (Grobecker et al., 1975), and a report by the NAS was issued in April, 1975 (National Academy of Sciences, 1975). In the present report, the findings of the DOT and NAS reports are accepted.

Crutzen (1974) and McElroy (1975) have called attention to the increase in nitrous oxide production that might result from increased fixation of nitrogen (N), i.e., conversion of nitrogen gas (N_2) of the atmosphere into inorganic or organic nitrogen compounds. The postulated cause-and-effect relationship is that increased fixation results indirectly in increased denitrification, i.e., the conversion of nitrate (NO_3^-) into nitrous oxide and nitrogen gas by microorganisms in soils, sediments, and waters. The extra nitrous oxide then migrates to the stratosphere, where a small fraction of it is converted to nitric oxide and nitrogen dioxide which react with ozone to destroy it.

Increased fixation of nitrogen by industrial processes for fertilizers and industrial purposes is the special concern of this report, but the same effect would ultimately result from increases in fixation of nitrogen by biological processes and high-temperature combustion. Biological processes that could be significant

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[a] Available through the National Technical Information Service, Springfield, Virginia 22151.

in this regard include the fixation that would occur if acreages of leguminous crops were increased or if current efforts of biologists to develop the nitrogen-fixing capabilities of nonleguminous crops were brought to fruition. Thus, the amounts of nitrogen being fixed and the probable increases in fixation by all processes are important aspects of the problem. Other important aspects are (1) the delay time between fixation and denitrification for various uses of fixed nitrogen, (2) the ratio of nitrous oxide to nitrogen gas produced during denitrification in soils, sediments, and waters, and (3) uncertainties and information gaps concerning complexities of conversion of nitrogen gas to fixed forms and their subsequent conversion back to nitrogen gas and nitrous oxide. Item 2 is of special concern because nitrogen gas is innocuous and only nitrous oxide is involved in ozone depletion. No method is currently available by which the ratio of nitrogen gas to nitrous oxide produced by denitrification under field conditions can be determined.

This report does not deal with the possible effects of stratospheric ozone on plants, animals, and climate. Details can be obtained from the DOT and NAS reports. The main concerns are (1) that decreased ozone will result in less attenuation of the radiation in the ultraviolet (uv) spectrum from 295 to 320 nanometers, which nearly coincides with the 280- to 315-nanometer band (called uv-B), and (2) that more skin cancer will be induced if more of this uv-B radiation reaches the earth's surface. The National Academy of Sciences (1975) and Grobecker et al. (1975) give the figure of a 20% increase in skin cancer from a 10% decrease in ozone.

All values in this report are expressed in the metric system and are also expressed on an elemental basis. Thus, the quantities of the various forms of nitrogen mentioned can be compared directly because the values are expressed as quantities of nitrogen contained in the various forms.

ESTIMATES OF NITROGEN FIXATION

This section contains estimates of nitrogen fixation by all known processes. Nitrogen fixation is defined as the conversion of nitrogen gas from the atmosphere into combined forms, which may be organic or inorganic and may occur as gases, liquids, or solids. The amounts fixed and hypothetical increases in amounts fixed are used in a following section to estimate possible decreases in stratospheric ozone. Unless otherwise stated, estimates are expressed as nitrogen in units of millions of metric tons per year (MT/yr) on a global basis.

Agriculture

Nitrogen in fixed forms is essential for all living organisms and is thus needed to grow the green plants which use energy from the sun to produce the food, feed, and fiber needed by the human population and domesticated animals. Fixed nitrogen from many sources can be used by green plants, but the ultimate source is nitrogen gas in the atmosphere, which is converted to fixed forms by natural or industrial processes.

Nitrogen is the plant nutrient most extensively required for crop production in world agriculture, and fertilizer nitrogen has contributed substantially toward the dramatic increases in crop yields during the past two decades. World consumption of fertilizer nitrogen has increased rapidly since World War II, and it will no doubt continue to increase because world needs for food and fiber cannot be met

without it.

The estimates of nitrogen fixation in agriculture by Burns and Hardy (1975) of 35, 9, and 45 MT/yr for cultivated legumes, nonlegumes, and meadows and grasslands, respectively, are reasonable and probably as accurate as possible with present knowledge of the nitrogen cycle.

There is no evidence that the total amount of nitrogen fixed by legumes on a worldwide basis has decreased as the use of fertilizer nitrogen has increased from about 3.5 MT/yr in 1950 to about 40 MT/yr in 1974. Depending on the amount of fertilizer nitrogen used to meet expanding needs for food and fiber and the success of research on increasing the yield and nitrogen fixation capacity of leguminous crops, nitrogen fixation by these crops could increase by 50 to 100% (from 35 MT/yr) during the next 25 years. Increases in nitrogen fixation by leguminous crops for the period 1850 to 1950 are speculative but could have been as great as 20 MT/yr.

Forests

There are a few scattered direct measurements of nitrogen fixation by bacteria and blue-green algae in soils and on leaf surfaces in temperate and tropical forests. Many of these forests also contain some nitrogen-fixing, root-nodulated legumes, but there are very few data on the quantities of nitrogen fixed by these plants. Overall nitrogen-balance studies on forests frequently give greater nitrogen accretion rates than can be accounted for by inputs from rainfall. On the basis of very patchy evidence, it seems reasonable to assume an average nitrogen fixation rate of 10 to 15 kg/ha/yr occurring over 4.1×10^9 ha of forests to give a global total of 40 to 60 MT/yr (Burns and Hardy, 1975; Knowles, 1975).

Unused Land

Unused land, which includes areas classed as desert, tundra, marsh, bog, alpine, and savannah, is the most diverse of all categories considered. Nitrogen fixation ranges from zero in some deserts to potentially very high levels in some aquatic or semi-aquatic sites such as areas of marshes and fresh-water emergent plants. Many of the areas included here also contain nodulated legumes with largely unknown contributions to nitrogen fixation. Thus, it is possible to arrive at only a very rough global average value for the amount of nitrogen fixed on unused land. The value of 2 kg/ha/yr occurring over 4.9×10^9 ha of land surface for a global total of 10 MT/yr is suggested on the basis of papers by Burns and Hardy (1975), Erus (1970), and Knowles (1975).

Ocean

Few data are available on the quantity of nitrogen fixed biologically in the ocean. Certain species of marine phytoplankton and bacteria can use nitrogen gas as a source of nitrogen for growth. Large expenditures of energy are required for this process, and so it would not be expected to occur where there are adequate supplies of other readily utilized forms of fixed nitrogen. However, growth of phytoplankton in the upper zone of temperate, stratified waters and, in particular, in the upper zone of permanently stratified, tropical and semitropical waters, often reduces available forms of combined nitrogen to minute concentrations. Under

these conditions, phytoplankton and bacteria capable of utilizing nitrogen gas may have a competitive growth advantage and may flourish.

The blue-green alga Trichodesmium has been recognized since the early 1800's as a bloom-forming species in the offshore waters of tropical oceans. The Atlantic, Pacific, and Indian Oceans have been reported to contain blooms of this alga, but their distribution and duration are poorly known. The presence of this species in offshore waters, where the concentration of dissolved inorganic combined nitrogen compounds is low, led to the investigation of its capacity to fix nitrogen. Several studies with Trichodesmium collected from the Atlantic, Pacific, and Indian Oceans have confirmed its ability to fix nitrogen (Dugdale et al., 1964; Goering et al., 1966; Carpenter, 1971; and Carpenter and McCarthy, 1975). Rates of nitrogen fixation in excess of 0.3 µg/liter/hour in water containing this species have been reported (Goering et al., 1966; Carpenter, 1971). Integration of the fixation profiles measured in the upper zone of water at several locations in the tropical Atlantic Ocean and the Caribbean Sea gives an estimated nitrogen fixation rate of about 350 µg/ m^2/year. The distribution of Trichodesmium is poorly known, but the organism seems to be most abundant in tropical oceans between 20°N and 20°S latitudes. If one assumes, therefore, that fixation occurs at the above rate in this region of the ocean (133 x 10^6 km^2), about 4.6×10^{10}g or 0.046 MT of nitrogen is fixed annually in the tropical ocean. This amount will not greatly alter the yearly input of combined nitrogen into the ocean.

Nitrogen fixation by blue-green algae of the genera Calothrix and Nostoc, and by bacteria in bottom sediments is important in the nitrogen economy of certain intertidal zones, but on a worldwide basis they probably do not contribute significant amounts of combined nitrogen to the ocean. Nitrogen fixation by organisms associated with atolls has also been reported (Weibe et al., 1975). But, again, their contribution to the total budget of combined nitrogen in the ocean is probably unimportant. If all known nitrogen-fixing organisms are considered, however, the amount of nitrogen fixed in the ocean could be as high as 0.4 to 4.0 MT/yr.

Lightning

Nitric oxide is produced in any high-temperature process occurring in air, and the nitric oxide may be oxidized to nitrogen dioxide. Lightning produces transient high temperatures and thus presumably produces nitric oxide and nitrogen dioxide, which are then incorporated into precipitation as nitrate (NO_3^-) and nitrite (NO_2^-). Estimates of nitrogen fixed by this process vary tremendously. McElroy (1975) used a figure of 10 MT/yr which was probably based on an estimate by Delwiche (1970) and involves attributing a portion of the fixed nitrogen in rainfall to lightning.

Various summaries (Allison, 1965; Stevenson, 1965) of the amounts of nitrogen brought down in rain indicate an average of about 7 kg/ha, of which an average one-third or 2.3 kg is in the form of nitrate (the ratio of nitrogen in ammonium (NH_4^+) to that in nitrate may vary from 1:1 to 10:1). No significant correlation has been found between the nitrate concentration in precipitation and the number and frequency of lightning discharges (Vienmeister, 1960; Wetselaar and Hutton, 1963; Gambell and Fisher, 1964; and Reiter, 1970), even when the data were integrated over several days to a month to allow for the time delay between formation of nitric oxide and its appearance in rainfall as nitrate (Visser, 1964). However, Junge (1958) has

observed that nitrate in rainwater is bound to geographical areas to a lesser degree than other rainwater constituents, indicating that nitrate formation may not necessarily occur in the same location as the nitric oxide from which it is derived. Various extrapolations of the nitrate-nitrogen in rainfall over land and over the ocean (Emery et al., (1955) and Holland (1973) presented estimates of total nitrogen in rainfall over the ocean) suggest that perhaps 10 to 20 MT of nitrogen are fixed per year by lightning. These estimates are nearly the same as that made by Delwiche (1970) but are considerably greater than the estimate of 0.02 MT/year made by Uman (1971), who, however, suggested that considerably larger amounts of nitrogen could be fixed by corona discharges in all types of precipitating clouds and along the ground under these clouds.

There is seeming agreement that almost all of the ammonium-nitrogen and most of the nitrate-nitrogen in rainwater are of terrestrial origin, but there is sufficient evidence from differences in ratio of nitrate to ammonium and other constituents of rainwater over tropical and temperate regions to justify an estimate of 10 MT of nitrogen fixed annually by lightning and other electrical discharge phenomena in the atmosphere.

Combustion

The combustion of fuels of fossil origin has become the principal means of energy generation for heat (space, water, and industrial), electric power, and transportation. Since air containing 78% nitrogen is the oxidizer, an ever-present side reaction is the formation of nitrogen oxides. The bulk of this fixed nitrogen is emitted to the atmosphere as nitric oxide with only small amounts as nitrogen dioxide and little, if any, as nitrous oxide. Despite this composition, it has been customary to express these emissions by weight as though they were nitrogen dioxide, and thus this mixture of gases will be referred to as nitrogen dioxide.

Since the nitrogen oxides have been recognized for 25 years as important pollutants of the lower atmosphere, fairly extensive emission measurements and inventories have been developed in recent years, especially for the United States. There is general agreement that use of energy for transportation, electric power generation, industrial heat, and other purposes makes an important contribution to the total amount of nitrogen fixed. The Federal responsibility for these estimates rests with the United States Environmental Protection Agency, which has published inventory studies from time to time (Cavender et al., 1973). The 1973 study reports 6.9 MT of nitrogen dioxide-nitrogen fixed per year in the United States during 1970, with transportation sources and stationary-source fuel combustion each contributing about half of the total.

Emissions measured from light-duty passenger vehicles indicate a major fractional contribution from gasoline-powered vehicles. Emissions from these vehicles are in the range of tenths of a gram of nitrogen dioxide-nitrogen per mile, with U.S. Federal emission standards in recent years being 0.6 to 0.9 gram of nitrogen dioxide-nitrogen per mile. For this calculation, we take 1.2 grams per mile as representative of the current fleet. With 125,000,000 vehicles in the United States, burning 290,000,000 gallons of gasoline daily with an average fuel economy of 12 miles per gallon, there are 3.5×10^9 vehicle miles/day. At 1.2 grams of nitrogen dioxide-nitrogen per mile, this is 42×10^9 grams/day, 1.5×10^{12} grams/year, or 1.5 MT/year.

The emissions from trucks per mile exceed those from passenger cars, but trucks have lower fuel economy, and these two factors approximately compensate for each other in the calculation made here. To the emissions from automobiles and trucks must be added the emissions from ships, planes, and trains to obtain a transportation total.

The Los Angeles County Air Pollution Control District (1971) estimated that, in their area, transportation sources accounted for 254 tons of nitrogen dioxide-nitrogen per day out of total emissions of 345 tons per day. This estimate attributes a larger share to transportation than the national inventory given by the EPA. If this 254 tons per day is multiplied by the ratio of U.S. to L.A. populations (about 30) and by 365, we obtain 2.8 MT per year for the U.S. transportation source. The two estimation procedures are reasonably consistent with the EPA national inventory.

To arrive at a figure for the entire world requires a method of extrapolation since no worldwide inventories are available. One simple way is to assume that emissions of nitrogen dioxide are proportional to total fuel usage. The United States uses about 1/3 of the world's energy, and so we may estimate the world total by multiplying the U.S. figure by 3[b/]. Multiplying the EPA figure of 6.9 MT of nitrogen dioxide-nitrogen per year in the United States (Cavender et al., 1973) by 3 yields 20.7 MT per year as an estimate of the world total. This 20.7 MT/yr figure is somewhat higher than the 15.2 MT/yr cited by Robinson and Robbins (1968).

The Robinson and Robbins report cited above also gives a figure of 138 MT/yr for the production of nitrogen dioxide-nitrogen from natural sources based on assumptions that (1) the worldwide background concentration of nitrogen dioxide-nitrogen is 0.3 part per billion and that (2) the residence time for nitrogen dioxide is the same as for sulfur dioxide, which is estimated to be 1 week. The first assumption led to a worldwide atmospheric burden of about 3 MT, which was multiplied by 52 weeks to obtain an estimated production of about 156 MT of nitrogen dioxide-nitrogen per year. The uncertainties in these assumptions and the lack of identification of any natural source to account for the production make this estimate difficult to accept. In a later paper, Robinson and Robbins (1970) revised their procedure and increased the estimate to 194 MT of nitrogen dioxide-nitrogen per year. This value was derived from estimates of the deposition rates for nitrogen compounds and the worldwide background concentration. If nitric oxide and nitrogen dioxide are oxidized to nitrate and removed from the atmosphere by rainfall in accordance with current understanding, the estimated production is far in excess of the nitrate content of world rainfall based on experimental measurements. Because of this disagreement and because no natural sources of these amounts of nitrogen dioxide-nitrogen have been identified, these estimates by Robinson and Robbins have been disregarded in the development of estimates of nitrogen fixation.

Although nitric oxide is not rapidly oxidized at low concentrations by atmospheric oxygen, photochemical and other atmospheric processes (e.g., oxidation by natural ozone) probably convert it to nitrate, which then is washed out by rainfall.

[b/] This extrapolation seems plausible because the big sources of nitrogen oxides are from advanced technologies, and these are fairly uniform worldwide.

Nitric oxide, therefore, probably makes only a minor contribution to the stratospheric burden of nitrogen oxides. After it reaches the land surface, however, the nitrate produced in the atmosphere is subject to the same denitrification reactions as nitrate from any other source. Thus, it should be counted in the total inventory of nitrogen fixation.

Industrial Ammonium Fixation

The records on the worldwide amounts of fixed nitrogen used in fertilizers are plotted in Figure 1 for the period 1962 through 1974. Nitrogen consumed in fertilizers increased from 11.5 to 38.7 MT/yr over this 13-year period, and the annual average increase was 10.7%. Estimates of the amounts of nitrogen consumed in fertilizers are available for periods prior to 1962, but the data are less reliable. Nitrogen is fixed as synthetic ammonia (NH_3) to supply the demand for fertilizers and other nitrogen-bearing chemicals. Losses occur during handling and transporting the various nitrogen-bearing chemicals and during conversion of ammonia into fertilizer chemicals such as nitric acid and urea. Records are not available to show annual amounts of nitrogen fixed as ammonia to supply the fertilizer demands and the demands of the chemical industry, including that which is fixed and lost before use. However, 65 to 70% of the total nitrogen fixed as ammonia is estimated to be used in fertilizers, the remaining 30 to 35% representing the sum of the ammonia nitrogen lost and that used for purposes other than fertilizers. In the United States, about 20% of the nitrogen fixed is used for purposes other than fertilizers, but data on worldwide consumption for such purposes are not available. On the basis of this range of percentages, the total worldwide amount of nitrogen fixed as ammonia in 1974 was estimated to be 55 to 60 MT.

It is estimated that the worldwide consumption of nitrogen in fertilizers in 1950 was 3.8 MT, although this figure has not been refined to the same extent as data for the 1962-74 period. The percentage of the total fixed nitrogen consumed in fertilizers was assumed to be the same in 1950 as it is now--65 to 70%. On this assumption, the total nitrogen fixed in 1950 was estimated to be in the range of 5.4 to 5.8 MT.

It is difficult to make accurate long-range predictions of the amount of nitrogen that will be fixed to supply fertilizer and chemical industry demands. According to a recent estimate (Harre et al., 1975), 53 to 60 MT of nitrogen equivalent will be used in fertilizers in 1980. A middle value of 57 MT was given. From this, it is assumed that the total nitrogen fixed as synthetic ammonia in 1980 will be in the range of 81 to 87 MT. Longer range predictions of the total amount of nitrogen fixed as ammonia would involve greater uncertainty, but might be somewhere between 100 and 200 MT/yr by the year 2000.

Conclusion

Table 1 contains data for the Task Force's best estimates of nitrogen fixation from all known sources. These values are used as the basis for calculating possible effects of future increases in nitrogen fixation on stratospheric ozone. Estimates for nitrogen fixation in 1850 and 1950 are 150 and 174 MT, respectively. The 1950 estimate assumes some reductions in fixation for industrial uses and by combustion

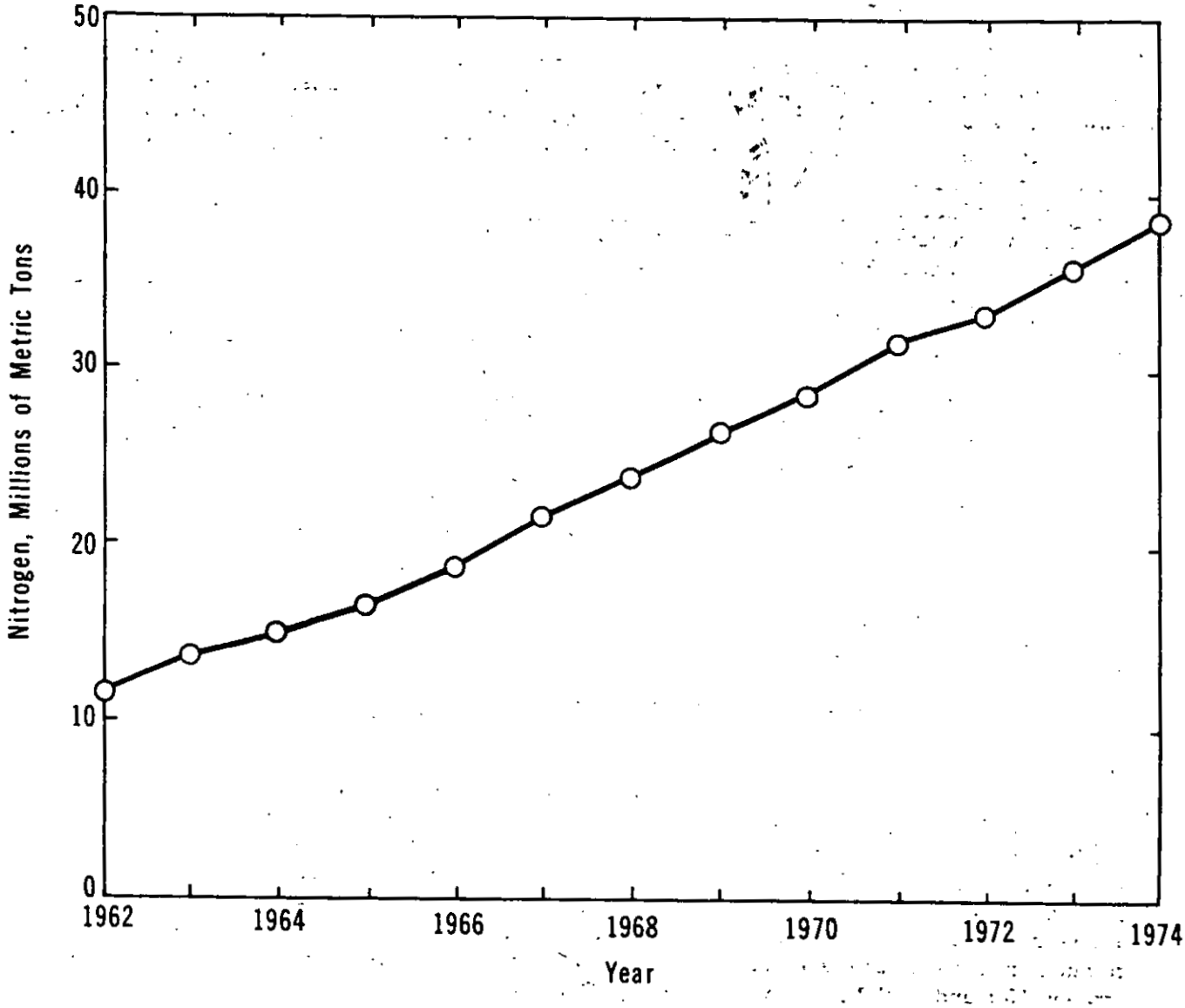

Figure 1. Worldwide consumption of nitrogen in fertilizers, 1962-74.

Table 1. Estimates of total nitrogen fixation for the year 1974

Location or Mechanism of Fixation	Nitrogen Fixed	
	MT/yr	% of Total
Agriculture		
Legumes	35	14.8
Nonlegumes	9	3.8
Grasslands	45	19.0
Forests	50	21.1
Unused land	10	4.2
Ocean	1	0.4
Atmosphere (lightning, etc.)	10	4.2
Combustion	20	8.4
Industrial ammonium fixation		
Use as fertilizers	39	16.5
Industrial uses	11	4.6
Inefficiencies (losses)	7	3.0
Total	237	100.0

along with a substantial reduction in fertilizer nitrogen. The estimate for 1850 assumes that (1) no commercial fertilizers were used, (2) fixation for industrial uses and by combustion was very small, and (3) fixation by leguminous crops was considerably smaller than in 1940 or 1974.

Nitrogen fixed by lightning and also by high-temperature combustion of fossil fuels is assumed to reach the earth's surface as nitrate in rain. Thus, according to the estimates in Table 1 the nitrate-nitrogen in rainfall should be about 30 MT/yr, which is about three times the quantities that have been reported. Many, if not most, of the measurements of nitrate in rain were made before the large increase in fossil fuel combustion during the past few decades, and so present measurements would perhaps show greater amounts of nitrate in rainfall.

ESTIMATES OF DENITRIFICATION

Land Surface

Biological denitrification is a natural process carried out by microorganisms in an oxygen-deficient environment. Denitrification involves a series of reductions of nitrogenous compounds starting with nitrate and ending with nitrogen gas. The commonly accepted sequence is as follows (Payne, 1973):

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

The normal end-product of denitrification is nitrogen gas. However, if the rate of conversion of nitrous oxide to nitrogen gas is slower than the rate of diffusion of nitrous oxide from the system, some nitrous oxide escapes to the atmosphere. Numerous studies have shown that nitrous oxide is formed within microbial cells and released into the medium.

Denitrification occurs in soil only when a portion of the soil is saturated or nearly saturated with water (anaerobic zones, or zones without oxygen, are present) and when a source of available carbon for microbial respiration is present in the anaerobic zone. Denitrification losses of nitrogen from fertilizers added to soils have been reported to vary between 1 and 75% of that applied. However, many soil scientists feel that a 10 to 15% loss of applied nitrogen due to denitrification is a good average value (Broadbent and Clark, 1965).

The proportion of the total nitrogenous gases liberated as nitrous oxide during denitrification in soils has been reported to vary between 0 and 100%, depending upon the conditions existing in the zone of denitrification (Cady and Bartholomew, 1960; Cooper and Smith, 1963; Nommik, 1956; Stefanson, 1973; and Wijler and Delwiche, 1954). The ratio of nitrogen released to nitrous oxide released is lowest during denitrification in soil where about 10% of the total soil pores are filled with air (Focht et al., 1975). There is no proven method for the determination of the ratio of nitrous oxide to nitrogen produced by denitrification in the field in soil or the ocean. Thus far, such ratios have been determined in sealed systems that differ significantly from field situations.

It is interesting to note that under all environmental conditions reported to favor production of nitrous oxide relative to nitrogen (low temperature, low pH, marginal anaerobic conditions) the rate of denitrification is relatively low. Consequently, the amounts of nitrous oxide produced under these conditions would be low even though the ratio of nitrogen to nitrous oxide is low. It has been reported (Woldendorp, 1962; Michoustine, 1965) that the presence of plants in a soil system tends to increase denitrification rates and to increase the ratio of nitrogen to nitrous oxide. Therefore, it is difficult to extrapolate the results of the many studies on denitrification carried out with soil in the absence of plants to actual cropland situations. However, compilation of results from about 20 studies dealing with gaseous compounds of nitrogen produced by denitrification in soil suggests that a nitrogen to nitrous oxide ratio of 16 (about 6% nitrous oxide) would be typical for conditions normally found during denitrification episodes in agricultural soils.

Direct measurements of nitrous oxide flux from soils in California suggest that from 0.5 to 1 kg of nitrous oxide-nitrogen is liberated per hectare per year (Focht et al., 1975). Measurements of the nitrous oxide concentration in the gas phase of soils in other locations in California and in Australia suggest that the flux measurements given above are within a reasonable range. It is regrettable that very limited data are available on the flux of nitrous oxide from soils.

Data and concepts developed above can be used to arrive at some approximations of total nitrous oxide production from the land surface. It has been estimated that the average loss of nitrogen from cropland is 16 kg/ha/yr (Hauck, 1969). If we accept a ratio of 16 for nitrogen to nitrous oxide, about 1 kg of nitrous oxide-nitrogen is liberated per hectare of cropland per year. This approximation agrees well with measurements of nitrous oxide flux from fertilized soils in California. There are about 1.5 billion hectares of harvested cropland on earth. If we assume that nitrous oxide-nitrogen is produced at the rate of 1 kg/ha/yr, the total release from world cropland may be estimated at 1.5 MT/yr. There are about 13.4 billion hectares of noncropped land on earth. If we assume that 0.2 kg of nitrous oxide-nitrogen is released per hectare per year, the total nitrous oxide-nitrogen released from noncropped areas may be estimated at 2.7 MT/yr. The total nitrous oxide-nitrogen production from land surfaces would therefore be 4.2 MT/yr. Hahn (1974) estimated the nitrous oxide evolution from all land surfaces to be 12.8 to 16 MT/yr. These estimates, however, are based on measurements at only a few sites using techniques that might have accelerated the diffusion of nitrous oxide from soils and reduced the conversion of nitrous oxide to nitrogen, thus giving unusually high estimates.

If we multiply this value of 4.2 MT/yr for the estimated nitrous oxide-nitrogen produced from land surfaces by 16, the estimate of total denitrification is 71.4 MT/yr. Delwiche (1970) estimated a total denitrification of 50 MT/yr from the world's land surfaces. Considering the uncertainties of these estimates and assuming they might be on the conservative side, one might be justified in setting a possible upper limit of total denitrification on land surfaces of 100 MT/yr, for an estimate of about 7 MT of nitrous oxide-nitrogen per year.

Ocean

The annual rate of denitrification in the marine environment is generally

arrived at by assuming that the ocean is in a steady state with respect to nitrogen. That is, the annual excess of nitrogen added to the ocean over that trapped by sediments is assumed to be denitrified.

Various scientists have constructed nitrogen budgets of the ocean from the very limited data available. Estimates vary, and it is difficult to judge which ones are better than others.

Emery et al. (1955) published the following budget:

	MT of Nitrogen
Reserves in the ocean	920,000
Annual use by phytoplankton	9,600
Annual contribution by rivers	19
Annual contribution by rain	59
Annual loss to sediments	9

Thus, the annual contributions from rivers and rain, 78 MT, exceed the annual loss to the sediments, 9 MT, by about 69 MT. If the nitrogen reserves in the ocean are, indeed, about 920,000 MT, the annual excess of nitrogen would double the oceanic reserves in about 13,000 years on the assumption that the annual consumption by phytoplankton represents a recycling. At this rate of increase in the oceanic reserves, the supply of atmospheric nitrogen would be exhausted in about 50×10^6 years. There is no evidence that the nitrogen content of the ocean is increasing, and the ocean is assumed to be in a steady state with respect to nitrogen; i.e., denitrification equals the annual input. From these data, we estimate that denitrification in the ocean is about 70 MT of nitrogen per year.

Holland (1973) presented a somewhat different budget:

	MT of Nitrogen
Reserves in the ocean	920,000
Annual input from the atmosphere	10
Annual input from rivers	10
Annual loss to sediments	10

The major difference in the two budgets is the estimate of the contribution from atmospheric input. Holland's budget implies an annual input excess over loss of 10 MT. If a steady state is to be maintained, return of gaseous forms of nitrogen to the atmosphere is required, and oceanic denitrification is the mechanism whereby this is accomplished. From these data, the estimate of denitrification in the ocean is about 10 MT of nitrogen per year.

Richards (1971) has summarized the available estimates of oceanic denitrification reported by various authors. These are:

Origin of Observations	Rate of Denitrification (MT of nitrogen/yr)
Black Sea	
a) Goering et al. (1973)	0.007
b) Goering et al. (1973)	0.2
Cariaco Trench	
Goering et al. (1973)	0.01
Eastern Tropical North Pacific	
a) Goering et al. (1973)	10
b) From respiratory rates	
Packard (1969)	1
Riley (1951)	50
From nitrate reduction estimates made in Darwin Bay (Galapogos Islands) and applied to the eastern tropical North Pacific by Richards (1971)	230

The above estimates suggest that sulfide-bearing waters (e.g., those of the Black Sea and the Cariaco Trench which have long-term, oxygen-deficient, stagnant waters) are not major sites of denitrification, but other low-oxygen, less stagnant regions may well be important. The oxygen-deficient zone of the eastern tropical Pacific seems to be an important region of denitrification. Other oxygen-deficient regions in the Arabian Sea and the subtropical Atlantic may also be important sites of denitrification. These estimates of denitrification are so diverse that no conclusions concerning total denitrification in the ocean can be made.

The gaseous product of denitrification in the marine environment has been reported to be nitrogen gas (Goering, 1968; Kioke and Hattori, 1975). Nitrous oxide has not been identified as a denitrification product. However, supersaturation of ocean surface waters with nitrous oxide has been reported (Hahn, 1974; Yoshinari, 1973, 1975). The supersaturation appears to be too great to result from physical processes such as air injection during storms or the mixture of water masses of different temperatures. One must, therefore, postulate that nitrous oxide is produced in seawater. The mechanism of production is uncertain. Yoshinari (1973, 1975) found an inverse correlation between nitrous oxide and oxygen contents in the Atlantic. As nitrous oxide increased, oxygen decreased. This observation suggests that nitrous oxide production is closely related to biological activity, but it is not known whether the release is biochemical or chemical. The activity of microorganisms is the most probable source since the maximum supersaturation with nitrous oxide generally occurs in the layer of the ocean with the least dissolved oxygen (Yoshinari, 1973, 1975). Hahn (1974) estimated an annual global production rate of 100 MT of nitrous oxide-nitrogen from the ocean, based on the nitrous oxide supersaturation of the North Atlantic Ocean.

Conclusion

Estimates of denitrification are less certain than are estimates of nitrogen fixation. Perhaps the estimates for denitrification on land surfaces (soils) are more reliable than those for the oceans, but the total uncertainty is great.

If denitrification on land areas is 70 to 100 MT of nitrogen per year, denitrification of the order of 100 MT of nitrogen per year in the ocean would be necessary for fixation and denitrification to be roughly in balance on a global basis. And, if the ratio of nitrogen gas to nitrous oxide is 16, the nitrous oxide production in the ocean would be about 6 MT/yr. The problem is that we have no idea what the nitrogen gas to nitrous oxide ratio is for denitrification in the ocean.

Calculations based on the data for supersaturation of the ocean with nitrous oxide suggest that about 10 times more nitrous oxide is produced from the ocean than can be calculated from nitrogen balances in the ocean or than are consistent with the nitrogen gas to nitrous oxide ratios for denitrification in soils.

POSSIBLE EFFECTS ON STRATOSPHERIC OZONE

The findings of the Department of Transportation and National Academy of Sciences studies that are most pertinent to the problem of increased nitrogen fixation are as follows:

(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 -- nitric oxide and nitrogen dioxide.

(2) The nitric oxide and nitrogen dioxide in the stratosphere arise primarily from oxidation of nitrous oxide in the stratosphere.

(3) Atmospheric nitrous oxide is produced from bacterial action in the soil and in the ocean.

Model

Through application of certain models developed in the DOT and NAS studies as background information to assess the effect of injection of nitrogen oxides into the stratosphere from supersonic transports, it appears that doubling the stratospheric nitrogen dioxide equivalent would reduce the ozone concentration by about 20%; or, more generally, the percentage reduction of ozone is one-fifth of the percentage increase in stratospheric nitrogen dioxide equivalent. A different model (Crutzen, 1974) leads to the same end result, which may be expressed in the formula,

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

where $-\Delta O_3$ is the decrease of ozone brought about by the increase of nitrogen

oxides, ΔNO_x (NO_x is the sum of nitric oxide and nitrogen dioxide calculated as nitrogen dioxide equivalent), and where O_3 is the amount of ozone and NO_x is the amount of nitrogen oxides present before the changes occurred.

Since the principal source of natural stratospheric nitrogen oxides is atmospheric nitrous oxide (N_2O), formula 1 may be rewritten in terms of nitrous oxide to an excellent approximation:

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

Formula 2 will be used as a basis for quantitative inference in this report, with the individual terms referring to global amounts.

In the natural nitrogen cycle, fixation of atmospheric nitrogen to biologically useful forms is eventually followed by denitrification, which yields a mixture of nitrogen gas and nitrous oxide. There is no evidence of a 1:1 ratio between increased fixation of nitrogen and increased denitrification within a few decades or centuries. Some of the fixed nitrogen can be deposited in various forms that take it out of circulation for indefinite periods of time. However, burial of nitrogen in various forms is balanced to some extent by release of nitrogen by weathering of geological deposits that become exposed to land surfaces. As a first approximation, therefore, the rate of denitrification would tend to equal the rate of fixation, and the nitrogen cycle would be approximately balanced if the rate of nitrogen fixation were to remain constant for a long period of time. Although the ratio of nitrogen gas to nitrous oxide produced by denitrification varies with pH, moisture content of soils, and other environmental factors, one could assume as a global average that the amount of nitrous oxide produced would be proportional to the rate of nitrogen fixation. If the world went from a particular long-term constant rate of nitrogen fixation, N_F, to a new long-term constant rate of nitrogen fixation, $N_F + \Delta N_F$, at the new steady state one could assume that the ratio $\Delta N_2O/N_2O$ would be approximately equal to the ratio $\Delta N_F/N_F$. In this case, the equation for reduction of ozone becomes

$$\frac{-\Delta O_3}{O_3} = \frac{1}{5} \frac{\Delta N_F}{N_F} \qquad (3)$$

Some nitrogen from soil, plant and animal residues, and fertilizer is denitrified within a few days after it is made available to the denitrifying organisms. Overall, however, there is a substantial delay between the time the nitrogen is fixed and the time it is returned to the atmosphere by denitrification. Nitrogen added to, or made available from, soil for plant use is distributed among plants, animals, plant and animal waste products, soil organic matter, soil inorganic fractions, microorganisms, fixed nitrogen of terrestrial origin in the atmosphere, etc., cycling from one nitrogen pool to another. The reactions and processes are many, and the average time delay between fixation and denitrification is not known.

Nitrogen fixed by industrial and combustion processes increased significantly year by year between 1950 and 1975, but the rate of nitrogen fixation probably changed

much faster than the rate of attainment of a steady state in the nitrogen cycle. Thus, Equation 3 cannot be used to calculate the year-by-year expected reduction of ozone, because it applies only to equilibrium conditions when denitrification equals fixation. However, it can be used to examine the sensitivity of ozone to various assumed increases in rate of nitrogen fixation. Two methods of calculation are used here.

Method I

The first method used to estimate the effect of increased industrially fixed nitrogen on stratospheric ozone is based on Equation 3. An inventory of total nitrogen fixed is presented in Table 1. The fixation of nitrogen in 1950 was estimated to be 174 MT, and the 1974 estimate was 237 MT (an increase of 63 MT/yr from fertilizers, industrial uses of fixed nitrogen, and nitrogen fixation by combustion. If this increased rate of fixation were sustained long enough for fixation and denitrification to come into balance, the destruction of stratospheric ozone would be 7.2%:

$$\frac{-\Delta O_3}{O_3} = \frac{1}{5} \quad \frac{63}{174} = 0.072.$$

However, there is no evidence to suggest that during the 1940-1974 period the ozone concentration in the stratosphere has either increased or decreased[b/].

If recent trends are extrapolated 25 years into the future, considering the increases in nitrogen fixation from all sources, one can arrive at rates of industrial fixation somewhere between 100 and 200 MT/yr. These two numbers are considered here as sensitivity tests of what might happen, subject to the assumptions and approach of Method I and not as predictions for any specific time in the future. If the level of nitrogen fixation were 274 MT/yr for sufficient time for denitrification to equilibrate with fixation, the eventual steady-state reduction of ozone, relative to the level of ozone in the stratosphere in 1950, would be

$$\frac{-\Delta O_3}{O_3} = \frac{1}{5} \quad \frac{100}{174} = 0.115$$

If the increase in nitrogen fixation were 200 MT per year above the 1950 level, the new steady state would see the ozone reduced by 23%.

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b/ A somewhat analogous "natural" event in history passed without evident adverse effects. George Stanford (Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland) has estimated that U.S. soils have lost roughly 1.6 billion metric tons of nitrogen as a result of cultivation. Most of this loss occurred within a period of 50 years when the soils of the Midwest were first cultivated. The average annual rate of loss during this period in the United States alone may be estimated at 30 million metric tons of nitrogen. If half of the loss was due to erosion and half to decomposition of the organic matter and release of nitrate, the nitrogen "fertilization" still amounted to 15 million metric tons annually, an addition approximately equivalent to the worldwide consumption of nitrogen in fertilizers in 1964 (Fig. 1).

Figure 2 presents estimated reductions in stratospheric ozone calculated using Method I. The upper line for a beginning nitrogen fixation rate of 150 MT/yr gives the reductions in ozone calculated for various increases in nitrogen fixation over a level that might approximate the situation in 1850 before commercial fertilizers were available and before substantial fixation by combustion, and when there was substantially less fixation by leguminous crops than at present. If the fixation in 1850 and 1974 were as assumed and if Method I is reliable, the reduction in ozone could have been 11.6% for the period 1850 to 1950, assuming no lag between fixation and denitrification. The center line applies to a beginning fixation rate of 174 MT/yr (1950), and the lower line applies to a beginning fixation rate of 237 MT/yr (1974). The values of ozone reduction in the figure were calculated on the assumption that denitrification and fixation rates are the same. Because of an unknown lag time between fixation and denitrification, no time schedule can be stated.

Method II

The second method of estimating the decrease in stratospheric ozone associated with various increases in nitrogen fixation is based on Equation 2 and considerations of measurements of nitrous oxide in the atmosphere and in the ocean.

Experiments on soils in the laboratory and in the field suggest that, under average natural conditions, nitrous oxide-nitrogen constitutes only about 5 or 10% of the nitrogen in the nitrogenous gases produced by denitrification. There is uncertainty in this number, but the uncertainty can be recognized by making calculations on the basis of 2.5, 5, and 10% nitrous oxide-nitrogen. With this assumption, the increase in nitrous oxide (ΔN_2O in Equation 2) is obtained by multiplying the increase in nitrogen fixation, N_F, by the fraction of nitrous oxide-nitrogen in the nitrogen evolved by denitrification. Values to be considered for ΔN_2O are those presented in Table 2.

To carry out a calculation with Equation 2 and the increased rate of formation of nitrous oxide with increased nitrogen fixation, an estimate of the natural rate of production of nitrous oxide is required. The actual concentration of nitrous oxide in the troposphere is readily measured, although there are difficulties with absolute calibrations. The concentration of nitrous oxide in the troposphere is about 0.25 part per million (by volume), and the total amount is about 1300 MT of nitrogen. An estimate of the global rate of production, however, is more difficult to obtain.

Two observations have yielded some direct evidence on the rate of production of nitrous oxide. During late 1966 through 1968, Schuetz et al. (1970) made day-by-day measurements of atmospheric nitrous oxide in Mainz, West Germany. The concentration of nitrous oxide increased from 0.25 part per million in late 1966 to 0.30 part per million in late 1968. (The values measured by the same group decreased to about 0.25 ppm 2 or 3 years later.) The 0.25 ppm of 1966 corresponds to a global figure of 1300 MT of nitrous oxide-nitrogen; the 0.30 ppm of 1968 represents 1560 MT; the difference is 260 MT. Thus, the rate of change of nitrous oxide-nitrogen averaged 130 MT/yr over the two-year period. At the same time, Goody (1969) measured the atmospheric nitrous oxide over an 18-month period in Boston, Massachusetts. There is a discrepancy of 20% in the absolute values (due, perhaps, to the difficulty of establishing absolute calibrations) between the two series of data, but the same increasing trend in nitrous oxide concentration was

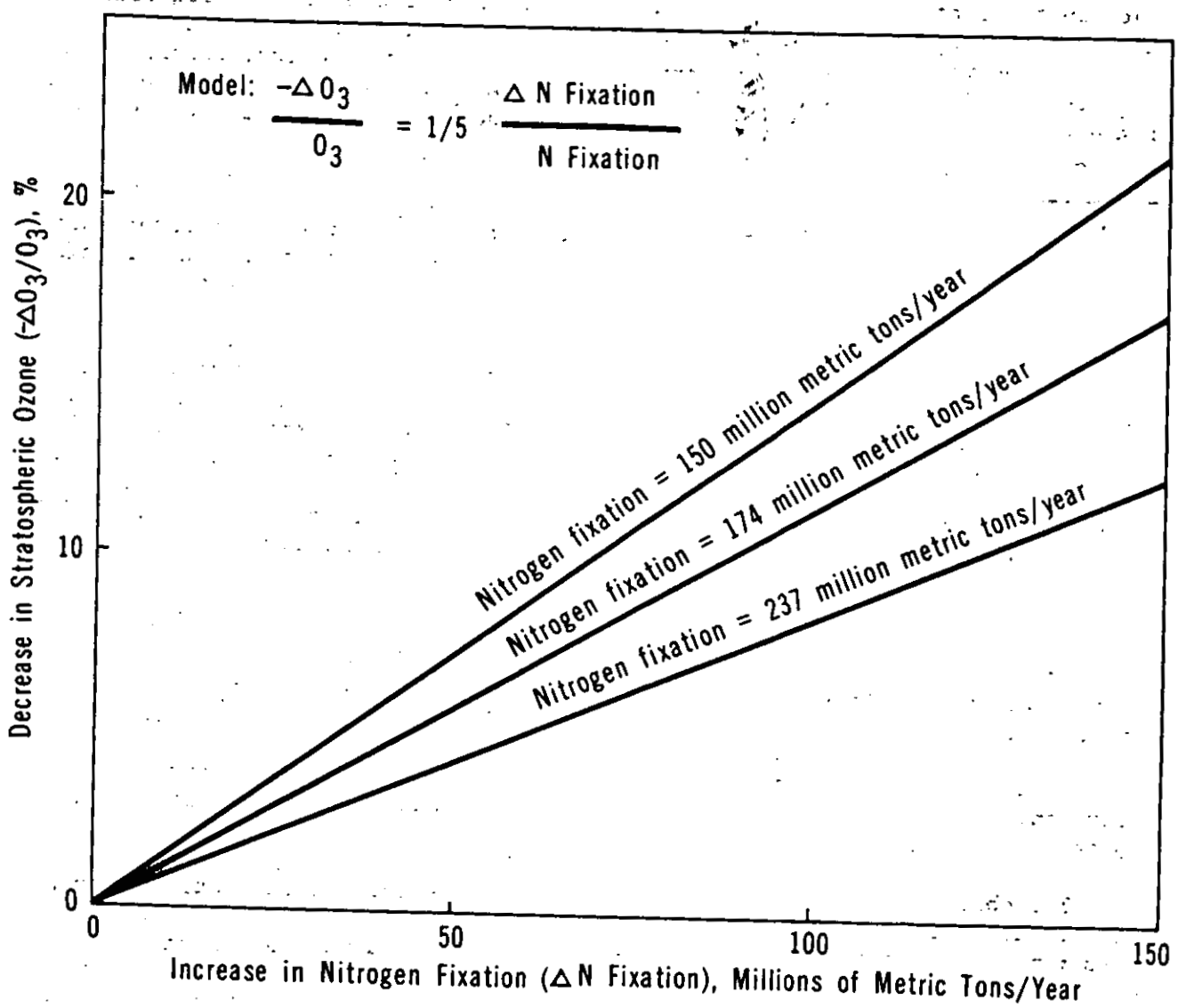

Figure 2. Reduction in stratospheric ozone as affected by increased nitrogen fixation. The calculations were made by Method I for three levels of background or beginning global nitrogen fixation, 150, 174, and 237 million metric tons per year.

Table 2. Increases in nitrous oxide (ΔN_2O) for various increases in nitrogen fixation (ΔN_F) and various ratios of nitrous oxide (N_2O)-nitrogen to the total nitrogen released as gases by denitrification

ΔN_F MT of Nitrogen per Year	$\frac{N_2O}{N_2O + N_2}$	ΔN_2O MT of Nitrogen per Year
50	0.025	1.25
	0.050	2.5
	0.10	5.0
100	0.025	2.5
	0.050	5.0
	0.10	10.0
150	0.025	3.75
	0.05	7.5
	0.10	15.0

found. If atmospheric nitrous oxide increased at the same rate on both sides of the Atlantic, as witnessed by observations made by two different experimental methods, the change would appear to be a global effect. The indicated net increase in nitrous oxide-nitrogen was 130 MT/yr, but the annual gross formation rate must have been greater. These numbers are probably subject to fairly large errors.

Junge (1974) correlated the time and space fluctuations of observed tropospheric constituents with their atmospheric residence time. Oxygen, carbon dioxide, hydrogen, methane, carbon monoxide, ozone, and radon are well correlated on this basis. Extensive measurements were made by Schuetz et al. (1970) on the time and space variations of nitrous oxide in the troposphere which in turn indicate (Junge, 1974) an atmospheric residence time of about 10 years. The uncertainty is estimated to be a factor of two. These studies indicate a global source of nitrous oxide-nitrogen of 130 MT/year, with an uncertainty range of 65 to 260 MT/yr.

Measurements of nitrous oxide in the Atlantic Ocean were reported by Junge and Hahn (1971) and by Hahn (1974). They found the ocean to be supersaturated with respect to nitrous oxide, and thus they concluded that the ocean is a source of atmospheric nitrous oxide. From the degree of supersaturation in surface waters and from a theory of gaseous transport through liquid surface films, Hahn (1974) calculated a global rate of production of nitrous oxide-nitrogen from the ocean of 100 MT/yr. This figure was regarded as probably of the correct order of magnitude. Thus, Junge and his coworkers have three independent studies indicating that nitrous oxide has a short atmospheric residence time of about ten years.

These considerations of measured nitrous oxide in the atmosphere and in the oceans indicate that the natural source rate for production of nitrous oxide-nitrogen is about 100 MT/yr. This figure is in strong disagreement with the findings of soil scientists and the features discussed in connection with Method I. If the background rate of nitrogen fixation is 174 MT/yr and if the rate of production of nitrous oxide-nitrogen is 5 to 10% of the fixation rate, the global rate of formation of nitrous oxide-nitrogen is 9 to 17 MT/yr, or about 13 MT/yr for the most probable value.

Figures 3 and 4 present calculated reductions in ozone versus increases in nitrogen fixation, using Method II, for various ratios of nitrous oxide-nitrogen to nitrous oxide nitrogen + nitrogen gas in the denitrification products. In Figure 3 the present nitrous oxide-nitrogen production is taken as 100 MT/yr. For an additional nitrogen fixation of 100 MT/yr over the 1950 base value, the calculated reduction of ozone is 0.5 to 2%; for an increased nitrogen fixation of 200 MT/yr, the calculated decrease is 1 to 4%. In Figure 4 the present production of nitrous oxide-nitrogen is taken as 50 MT/yr. The 50 MT/yr figure involves the assumption that the rate of production of nitrous oxide-nitrogen in the ocean is only about 40 MT/yr and that Hahn's (1974) calculations overestimated the nitrous oxide production from the ocean by a factor of 2.5. The indicated ozone reduction is 1 to 4% for an increase of 100 MT/yr in nitrogen fixation using a present production of nitrous oxide-nitrogen of 50 MT/yr.

Comparison of Methods

The ozone reduction estimated by Method II using a nitrous oxide-nitrogen

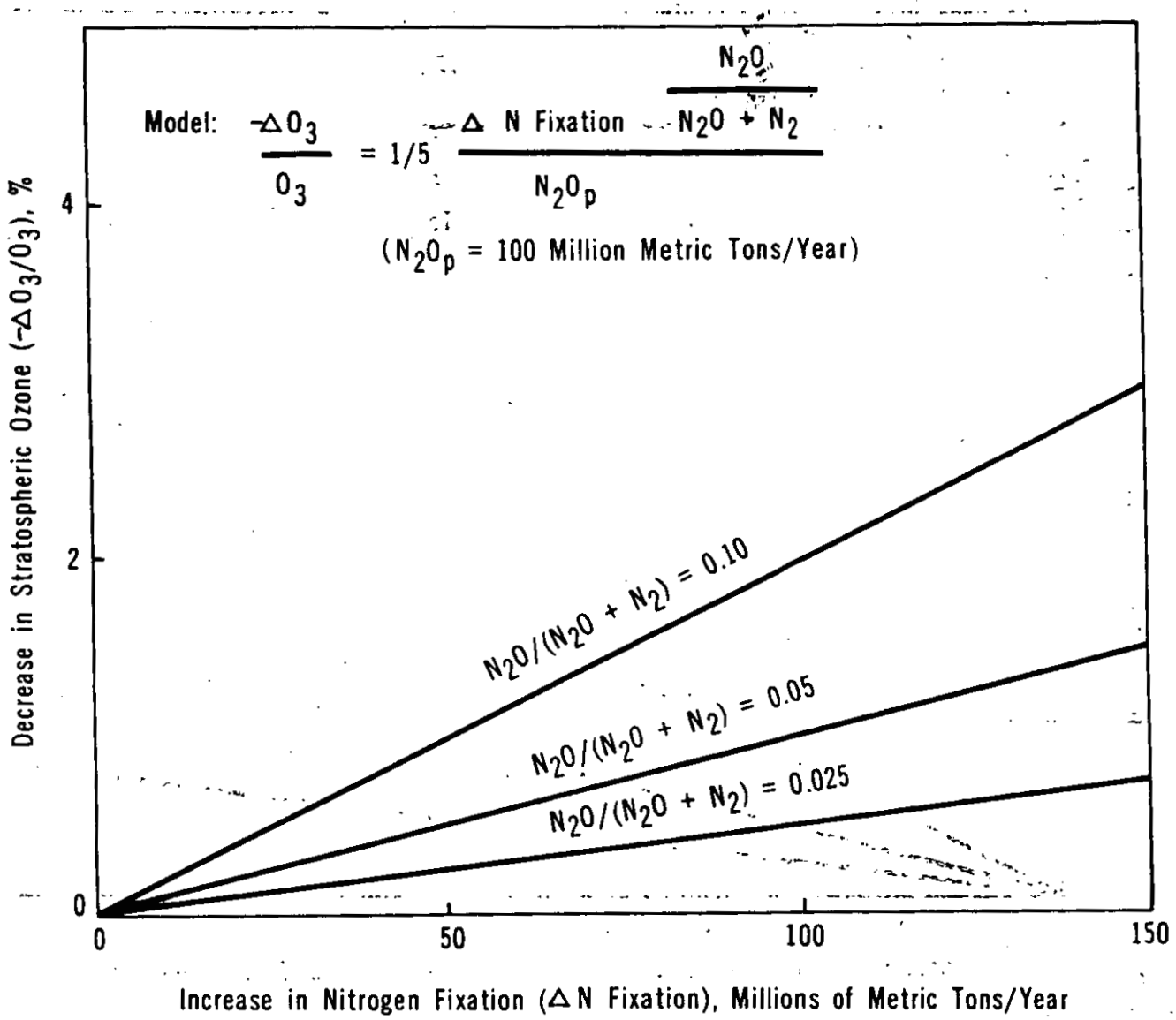

Figure 3. Reduction in stratospheric ozone as affected by increased nitrogen fixation. The calculations were made by Method II for three ratios of nitrous oxide to nitrogen plus nitrous oxide ($N_2O/[N_2 + N_2O]$) produced by denitrification with a beginning level of global nitrous oxide production (N_2O_p) of 100 million metric tons of nitrogen equivalent per year.

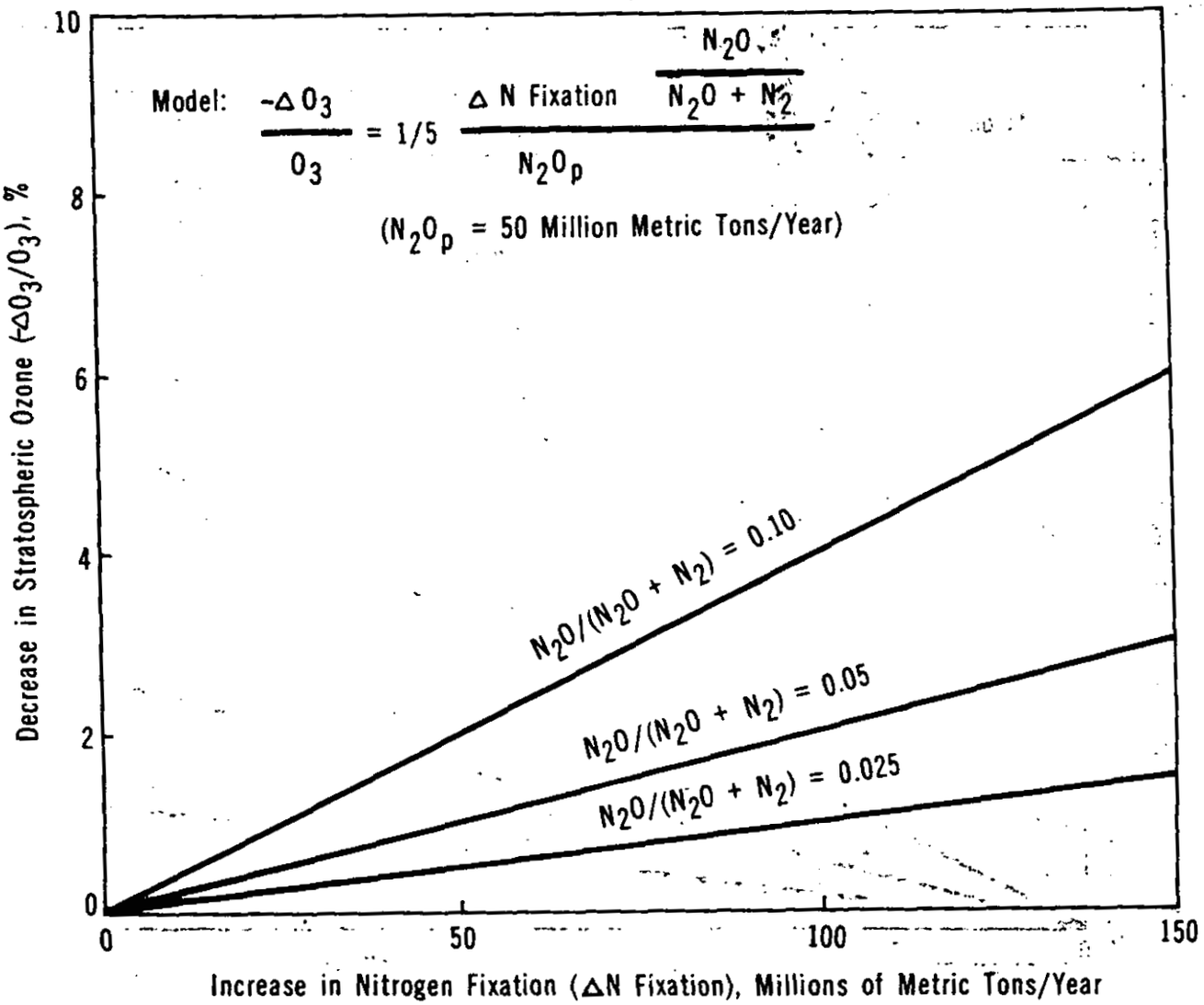

Figure 4. Reduction in stratospheric ozone as affected by increased nitrogen fixation. The calculations were made by Method II for three ratios of nitrous oxide to nitrogen plus nitrous oxide ($N_2O/[N_2O + N_2]$) produced by denitrification with a beginning level of global nitrous oxide production (N_2O_p) of 50 million metric tons of nitrogen equivalent per year.

production value of 100 MT/yr agrees very well with that estimated by Crutzen (1974). The ozone reduction estimated by Method I agrees fairly well with that estimated by McElroy (1975). Crutzen (1974) included in his calculations the oceanic source of nitrous oxide reported by Hahn (1974), as is done in Method II. McElroy (1975) excluded the large oceanic source of nitrous oxide, as is done in Method I.

It is obvious that these two methods disagree by a large factor. The source of the disagreement is readily apparent. Method I sums the amounts of nitrogen fixed by recognized sources, the oceans being regarded as a minor source. Method II uses observed trends in atmospheric nitrous oxide and measured gradients of nitrous oxide in the ocean to infer that there must be a large unknown source of nitrous oxide, probably in the ocean. The measurements behind Method II imply an unknown source and an unknown sink for an enormous mass of nitrous oxide-nitrogen, about 100 MT/yr. Either there are unknown systematic errors in the measurements, or there are some large unknown aspects of the natural nitrogen cycle.

Summary Evaluation

Until the uncertainty is resolved, one must consider the possibility of any effect within at least the range given by Methods I and II. The range between the greatest ozone reduction and the least ozone reduction due to a given amount of additional fixation of nitrogen is a full factor of 10.

In view of the uncertainties involved in many phases of the global nitrogen cycle, the formulation of a number of methods of estimating possible ozone reduction as a result of increased nitrogen fixation is not surprising. Crutzen (1975), in a recent paper, presented a method and a rationale which predicts that increased nitrogen fixation will reduce stratospheric ozone by less than 1% by the year 2000 and less than 10% by the year 2100. These predictions are based on a 6% increase in the annual use of nitrogen in fertilizers and on assumptions that nitrous oxide-nitrogen is 7% of the gaseous nitrogen produced by denitrification in soils and that evolution of nitrous oxide from the ocean is too small to be important relative to production on the land.

INFORMATION NEEDS

Members of the Task Force support without reservation the conclusion that inadequate information is available for making a decisive estimate of the effects of increased nitrogen fixation on stratospheric ozone. The quantitative data from field research are inadequate to inspire confidence in any of the predictions that have been made.

Perhaps the greatest information gap is in the area of nitrogen transformations in the ocean. We need to know the amounts of nitrogen fixed, the amounts denitrified, the ratio of nitrous oxide to nitrogen in the gaseous products of denitrification, and the physical chemistry of nitrous oxide in ocean waters in the presence of other atmospheric gases. If large amounts of nitrous oxide are produced in the ocean, as indicated by the data on supersaturation of the ocean with this gas, we must then identify the sources in the ocean and the sinks elsewhere in the environment. The possibility that the ratio of nitrous oxide to nitrogen gas in biological denitri-

fication in the ocean is much higher than is indicated by laboratory studies needs to be explored.

Techniques for making quantitative field measurements of nitrous oxide evolution from soils need to be developed further and widely applied so that quantitative data on production on the land surfaces of the earth can be obtained. At the same time, the total denitrification and the ratio of nitrous oxide to nitrogen evolved from land surfaces throughout the world must be determined in relation to various environmental parameters.

The total amounts of nitrogen fixed by natural processes on the earth's land surfaces need to be determined much more accurately. Present estimates involve a great deal of extrapolation from measurements in very few places.

More precise and detailed information on cycling of fixed nitrogen through all possible channels, including cycling in forests, grasslands, unused lands and agricultural lands, industrial uses, and food and fiber channels. This information can be used along with better understanding of nitrogen movements and reactions in waters of all types to calculate lag times between fixation and denitrification. Another aspect of the time delay between increased nitrogen fixation and a possible effect of nitrous oxide on stratospheric ozone that needs to be investigated is the time required for nitrous oxide to migrate from the surface of the earth to the stratosphere.

The possibility of a process of nitrous oxide production that does not involve denitrification needs to be explored. The operation of such a process in the ocean might explain some of the apparent supersaturation of the ocean with nitrous oxide and thus might resolve the question that now exists regarding the global production of this gas.

Certainly one important and immediate need is to initiate a continuous accurate monitoring of nitrous oxide in the trosphere at several continental and oceanic sites. Changes in nitrous oxide concentrations can not only alert society to impending problems or lack thereof but can also provide a key to the behavior of the worldwide nitrogen cycle. The U.S. Environmental Protection Agency would seem to be an appropriate organization to do the monitoring.

Nitrogen is lost when ammonia is processed into other compounds for fertilizer use, and the handling and transporting of fertilizers result in additional losses. About 15% of the nitrogen applied to soils is lost from the soil-crop system. Technical studies to decrease nitrogen losses would be worthwhile. New fertilizer materials and agricultural practices need to be developed to reduce the losses that occur after nitrogen fertilizer is applied to the soil. Furthermore, improved worldwide statistics are needed on industrial nitrogen fixation and on the amount of fixed nitrogen consumed by the chemical industry.

Much nitrogen is fixed during the combustion of fuels and in transportation. A national program is now under way to replace relatively scarce natural gas and petroleum fuel with coal. Greater amounts of nitrogen are fixed during burning of coal than of oil or natural gas. Although the nitrogen oxides produced by combustion are not implicated directly in ozone depletion, they contribute to it indirectly, as do all sources of fixed nitrogen. Efforts to develop combustion processes that do not result in fixation of large amounts of nitrogen may be justified on this

basis.

And, finally, further work is needed to develop theoretical models that will represent more accurately than those now available the relationship between the ozone concentration in the stratosphere and the nitrogen fixation and nitrous oxide production on the earth.

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