AP42 Section:	9.2.1
Background Ch	2
Reference:	10
Title:	P. J. Crutzen, "Upper Limits on Atmospheric Ozone Reductions Following Increased Application of Nitrogen to the Soil," *Geophysical Letters*, 3(3):169-172, March 1976.

sect. 2
#10

Vol. 3, No. 3 Geophysical Research Letters March 1976

UPPER LIMITS ON ATMOSPHERIC OZONE REDUCTIONS FOLLOWING INCREASED APPLICATION OF FIXED NITROGEN TO THE SOIL

Paul J. Crutzen

National Center for Atmospheric Research, Boulder, Colorado 80303*
and
National Oceanic and Atmospheric Administration, Aeronomy Laboratory, Boulder, Colorado 80302

Abstract. Our understanding of the marine and terrestrial nitrogen budgets is severely limited. For instance, atmospheric data indicate a residence time of N_2O in the atmosphere of about 10 years and consequently sources and sinks of atmospheric N_2O of the order of 130×10^6 ton N/year. Such large sources and especially sinks for atmospheric N_2O have not been satisfactorily identified and it may not be excluded, a priori, that not only the N_2O source, but also its sink is affected by man. The limited knowledge about the earth's N_2O budget so far obtained is in favor of the view that there is no imminent danger of large ozone reductions following the predicted increase in the input of fixed nitrogen in the soil by the year 2000. However, it seems likely that, with unchanged agricultural practices, there will develop serious long term problems, certainly in a world of exponential growth, and, for best action, it is essential that a well balanced, interdisciplinary research effort now be designed to increase our knowledge of all aspects of the earth's nutrient cycles.

Introduction

The release of nitrous oxide (N_2O) from the soil and the oceans has a major controlling effect on the atmospheric ozone content (Crutzen, 1970 and 1971). This is due to the formation of nitric oxide in the stratosphere by the reaction

$$\text{R1} \qquad N_2O + O(^1D) \rightarrow 2NO$$

and the catalytic destruction of ozone by NO and NO_2 through the pair of reactions

$$\text{R2} \qquad NO + O_3 \rightarrow NO_2 + O_2 \quad \text{and}$$

$$\text{R3} \qquad NO_2 + O \rightarrow NO + O_2$$

Variations in the atmospheric N_2O content should, therefore, lead to variations in the atmospheric ozone content.

N_2O, together with N_2, is produced in the soil and in ocean waters by bacteria (see, e.g., Alexander, 1961; Delwiche, 1970; Hahn, 1974). Under natural conditions, a balance is maintained between the processes of nitrogen fixation (i.e., splitting of the strong bond in the N_2 molecule, leading to the formation of combined or fixed nitrogen, $\tilde{N}$ = inorganic odd nitrogen, ammonia, urea, amino-acids) and denitrification (leading to the return of N_2 and N_2O to the atmosphere). The most important contribution to the fixation of nitrogen on land is provided by microbial symbionts of certain leguminous plants, e.g., alfalfas and clovers (Alexander, 1961), while most fixed nitrogen in the oceans seems to be supplied by blue-green algae in tropical ocean waters (Goering et al., 1966). Unfortunately, present knowledge of the global rates of these processes is very limited. This is especially deplorable because, in order to increase agricultural output, man is interfering increasingly with the nitrogen cycle by changing the physical and chemical conditions of the soil and the waters, e.g., by the growing application of inorganic nitrogen fertilizer. The Council for Agricultural Science and Technology (CAST, 1976) reports that the worldwide use of industrial nitrogen fertilizer in the year 1974 amounted to 40 Mton N (1 Mton N = 10^{12}g of nitrogen) and predicts that its use in the year 2000 will be between 100 and 200 Mton N. In comparison, in 1950 only 3.5 Mton N fertilizer was supplied to the soil. The total production of fixed nitrogen for agricultural and industrial purposes and by combustion in the year 1974 amounted to 77 Mton N (CAST, 1976).

The fixation rate of nitrogen by plants on land is estimated by Hardy and Havelka (1975) to be more than 175 Mton N/year. As half of this nitrogen is fixed in agricultural soils, it is clear that, by past management and reshaping of the earth's surface, man has already been affecting significantly the nitrogen budget of the soil even before the recent period of intensified industrial nitrogen fertilization. In addition, there is nitrogen fixation by lightning (10 Mton N/year).

Great concern has been expressed about the possible ecological consequences and health effects of the increasing supply of fixed nitrogen to the soil (e.g., Commoner, 1970). Furthermore, as the denitrification processes return fixed nitrogen partly as N_2O to the atmosphere, there is now growing concern that a reduction in ozone will result from man's expanding agricultural activities (Crutzen, 1972, 1974, 1975; McElroy, 1975a, b). The increased levels of ultraviolet radiation at ground level resulting from this will not only cause more skin cancer, but may also reduce significantly crop yields. In this context, one should not only consider problems connected with increasing nitrogen fertilizer input, but the whole problem of man's agricultural practices, waste water treatment and his indus-

---

*The National Center for Atmospheric Research is sponsored by the National Science Foundation.

trial activities which all affect the physical and chemical conditions of the soils and waters.

Up to this date, almost all observational work on the global budget of N_2O has been conducted by a research team at the Max-Planck Institute for Chemistry in Mainz, Germany. Much of this work has been summarized by Hahn (1974, 1975), who estimated a global rate of N_2O production in ocean waters of 85 Mton N/year and in soils of 15 Mton N/year. As stated by Hahn, both estimates should be considered uncertain. Especially the extrapolation of information from the north Atlantic ocean to global scale has been strongly criticized by McElroy (1975a), who postulates that the earth's oceans are not a net source, but a net sink for atmospheric N_2O (McElroy, 1975b). Although McElroy's criticism is at least partly justified, his interpretation of the N_2O data from the oceans is speculative. More observations, such as those reported by Yoshinari (personal communication, 1976), are extremely important.

From the variability of measured global N_2O mixing ratios, Junge (1974) estimated an average atmospheric residence time of N_2O of about 10 years (5-20 years), indicating a global source strength of N_2O of about 130 Mton N/year (260-65 Mton N/year), which is far larger than the present use of fixed nitrogen in fertilizer. A source of this size is indeed compatible with a large source of N_2O in ocean waters as estimated by Hahn (1974).

Large variabilities in the atmospheric N_2O content have also been found by other researchers (Goody, 1969; Schmeltekopf, private communication). A very interesting suggestion by Zipf (personal communication, 1976) is that there may be a global production of N_2O of at least about 10 Mton N/year in thunderstorms.

An oceanic net source of N_2O of 85 Mton N/year (Hahn, 1974) seems very large and some recent work by Yoshinari (personal communication, 1976) in the northwest Atlantic indicates a smaller net source of N_2O. It is, therefore, clear that not enough data are available to make a reliable global budget of N_2O. Furthermore, release of N_2O from oceanic surface waters seems to take place in the presence of so much oxygen, that it becomes difficult to reconcile this with present knowledge of denitrification processes. This may, therefore, indicate release of N_2O during assimilation and nitrification (Hahn, 1975; Sillén, 1967).

As nitrogen fixation in the oceans is extremely variable, it is not possible to give a satisfactory estimate of the global oceanic nitrogen fixation rates. A fixation rate of 0.05 Mton N/year as estimated by CAST (1976) seems very low in view of measurements of average N fixation rates of 10^{-8} g litre $^{-1}$ hour $^{-1}$ in tropical oceanic surface waters (Goering et al., 1966). Equally confusing, such a low value does not seem to be in accordance with the results of studies of the relative uptake of newly fixed nitrogen, ranging from 2-40%, in primary production (Dugdale and Goering, 1967; Mague et al., 1974; Koblentz-Mishke et al., 1970). In addition, very active nitrogen fixation occurs in shallow waters, such as in the sediments below sea grass (Patriquin and Knowles, 1972) and on coral reefs (Webb et al., 1975).

Some of our present knowledge of the earth's nitrogen budget has been summarized in Table 1 Most of the tabulated information has been gathered from Burns and Hardy (1975), Hardy and Havelka (1975), CAST (1976), and Hahn (1974 and 1975). Adopting the recently measured absorptio cross sections of N_2O by Johnston and Selwyn (1975), we estimate a destruction rate of 9 Mton N/year ($1.2x10^9$ molecules $cm^{-2}s^{-1}$) of N_2O in the stratosphere. If this were the only destruction process of N_2O, this would lead to an atmospheric residence time of about 140 years. All indications are, therefore, that there is substantial removal of N_2O in the troposphere or at the earth's surface. It is estimated in the presen study that the oxidation of N_2O in the stratosphere will lead to a production rate of NO_x of 0.28 Mton N/year ($8x10^7$ molecules $cm^{-2}s^{-1}$). It is remarkable what small percentage of the odd nitrogen budget is essential for the earth's ozone budget, emphasizing the great role played by the rain and cloud filter in the troposphere in preventing the leakage of tropospheric odd nitrogen into the stratosphere.

Model Assumptions

In order to calculate possible reductions in ozone, we adopt the same model which was previously used to estimate the possible effects of the chlorocarbon industry on the stratospheric ozone content (Crutzen and Isaksen, 1975). As this model provides theoretical estimates of the profiles of many stratospheric constituents in rather good agreement with observations, we may have some confidence in the prediction of ozone reductions which may result from the increased supply of N_2O to the atmosphere. We assume that the increased supply of fixed nitrogen to the soil is immediately balanced by denitrification although it is clear that there may be some considerable delays due to build-up of inorganic and organic nitrogen in the large soil and water reservoirs.

The build-up of N_2O can be modelled by applying the following equation at the lower boundary

$$-K_z(M)\,\frac{d}{dz}\left\{\frac{(N_2O)}{(M)}\right\} = P_o + \gamma P_1 - w_d(N_2O) \qquad (1$$

In this equation, we equate the net upward flux of N_2O at the lower boundary with the N_2O release rate from soils and waters ($P_o + \gamma P_1$) minus a hypothetical destruction rate at the earth's surface, which we assume to be proportional to the ground level concentration of N_2O. Although, we assume, that the sink of N_2O is at the earth's surface, it is not difficult to formulate the present problem of N_2O increases, if the main sink for N_2O would be atmospheric and the results would be very similar. The deposition velocity w_d is approximately equal to the atmospheric scale height divided by the atmospheric residence time of N_2O and is equal to $2.7x10^{-3}$cm s^{-1}, if we assume a residence of N_2O of 10 years (w_d is tentatively assumed to remain constant). The term P_o-$w_d(N_2O)$ is equal to the present flux of N_2O into the stratosphere, i.e., 9 Mton N/year (or

Table 1. Estimates of important posts in the present nitrogen budgets of soils and oceans, units Mton N/year. Several estimates are very uncertain.

	Land	Oceans
Biological fixation	>175	0.05-100
Fertilizer	40	0
Combustion, industrial use	37	
Lightning	5	5
Stratospheric NO	0.06	0.22
Volatilization (NH_3 and NO_x)	-205	
Return of $\tilde{N}$ (rain and surface deposition)	145	60
River runoff of $\tilde{N}$	-15	15
Net input of fixed nitrogen	>182	80-180
Release of N_2O	15	40-90
Release of N_2	>167	40-90

1.2×10^9 molecules $cm^{-2}s^{-1}$). This defines the magnitude of the term P_o which should be considered as the present production of N_2O at the earth's surface. For an atmospheric residence time of 10 years of N_2O, we adopt $P_o = 1.8 \times 10^{10}$ molecules $cm^{-2}s^{-1}$ ($\simeq$ 133 Mton N/year), based on a ground level volume mixing ratio of N_2O of 2.5×10^{-7}. Finally, the term γP_1 represents a direct response of denitrification to increasing input of fixed nitrogen in the soil, with γ being the relative yield of N_2O in the denitrification process and P_1 the increase in application rate of fixed N. We assume an increase in agricultural fixed nitrogen input from 40 Mton N/year at present to 200 Mton N/year in the year 2000 and no change thereafter. An examination of the data compiled in Table 1 indicates that γ should be less than about 8% (15/182). A number of experiments with agricultural soils suggests a value of γ of about 6% (CAST, 1976). Such a low value for γ can be explained, as soil conditions which are favorable for high relative yields of N_2O (higher acidity, lower temperatures, marginal anaerobic conditions) are at the same time unfavorable for denitrification (CAST, 1976). An average value of γ of less than 5% would follow if the residence time of N_2O in the atmosphere would have been determined by its stratospheric sink. However, the global yield of N_2O in soils is somewhat uncertain and we will make calculations not only for $\gamma = 0.07$, but also for more extreme choices such as $\gamma = 0.2$ and $\gamma = 0.5$. We will also make one calculation for $\gamma = 0.2$, assuming an atmospheric lifetime of N_2O of 20 years, implying about two times smaller values for w_d and P_o than given before.

Results and Discussion

The results of the computations as presented in Figure 1, do not substantiate the very large ozone reductions of 30% by the end of this century, which were mentioned elsewhere (Bishop, 1975), but point rather to the possibility of a long term effect on the ozone layer, certainly if the present interpretations of the earth's N_2O budget (Hahn, 1974 and 1975; Junge, 1974; CAST, 1976) are even approximately correct (corresponding to Case I in Figure 1). It does not seem likely that there will be an imminent danger of serious ozone depletions due to an increase in the application rate of fertilizer in the soils. However, a disturbing feature is that there seem to exist rather significant short and long term variations in atmospheric N_2O, which indicate large and not well understood sources and sinks of N_2O. Attention should, therefore, be directed not only to the possibility of man's influence on the source of atmospheric N_2O, but also its sink. If the main loss of N_2O would occur by microbes in soils, then it seems likely that consumption of N_2O will decrease, when soils become more acid. This factor is partly under man's control.

Variations in the atmospheric N_2O content should be followed after some years by variations in the stratospheric ozone content and atmospheric N_2O should therefore be monitored. As there are indications that the N_2O content of the atmosphere has been increasing by about 15% from 1968 to 1971 (see compilation of data by Hahn, 1975), one may speculate whether this may not have been at least partly the reason for the observed decrease in total ozone from 1970-1974 (Machta, private communication).

While we have indicated the unlikelihood of an imminent danger of serious ozone depletions due to increasing applications of fixed nitrogen, we also realize that there are many gaps in our knowledge of the earth's nitrogen cycle. It is,

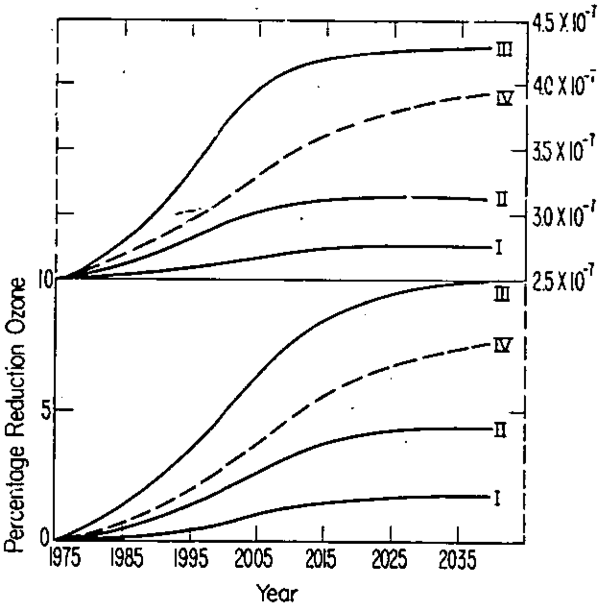

Figure 1. Calculated maximum percentage reductions of total ozone due to increasing application of fixed nitrogen in the soil (lower curves, left scale) and corresponding growth of volume mixing ratios of N_2O (upper curves, right scale). Curves, labeled IV, assume an atmospheric residence time of N_2O of 20 years, otherwise a residence time of 10 years is assumed. The assumed relative denitrification productions of N_2O in agricultural soils were as follows: I (7%), II and IV (20%), III (50%). Growth rate of nitrogen fertilizer: 6% per year from 1975 to 2000 and constant thereafter.

therefore, crucial that a well-balanced, interdisciplinary research program now be designed to the many aspects of this and other important nutrient cycles. To solve some of the increasingly pressing environmental and energy problems connected with future food production, it seems unavoidable to review agricultural practices and waste water treatment. With regard to the latter, it seems likely that release of N_2O in the denitrification processes can be reduced to very low values (Lance, 1972). Best of all, more efficient "recycling" of fixed nitrogen can reduce pressures on the environment and energy use.

References

Alexander, M., *Introduction to Soil Microbiology*, Wiley and Sons, Inc., New York, 472 pp., 1961.

Bishop, J. E., Earth's ozone shield may be imperiled by more fertilizer use, scientist says, *The Wall Street Journal* (article alledgedly based on interview with M. B. McElroy), November 13, 1975.

Burns, R. C., and R. W. F. Hardy, *Nitrogen Fixation in Bacteria and Higher Plants*, Springer-Verlag, New York, 189 pp., 1975.

CAST (Council for Agricultural Science and Technology), *Effect of increased nitrogen fixation on stratospheric ozone*, Report No. 53, January 19, 1976.

Commoner, B., Threats to the integrity of the nitrogen cycle: nitrogen compounds in soil, water, atmosphere and precipitation, *Global Effects of Environmental Pollution* (S. F. Singer, Ed., Reidel Publ. Cy., Dordrecht, Holland), pp. 70-95, 1970.

Crutzen, P. J., The influence of nitrogen oxides on the atmospheric ozone content, *Quart. J. Roy. Met. Soc.*, *96*, 320-325, 1970.

Crutzen, P. J., Ozone production rates in an oxygen, hydrogen, nitrogen oxide atmosphere, *J. Geophys. Res.*, *76*, 7311-7327, 1971.

Crutzen, P. J., SST's: a threat to the earth's ozone shield, *Ambio*, *1*, 41-51, 1972.

Crutzen, P. J., Estimates of possible variations in total ozone due to natural causes and human activities, *Ambio*, *3*, 201-210, 1974.

Crutzen, P. J., Physical and chemical processes which control the production, destruction and distribution of ozone and some other chemically active minor constituents, *GARP Publications Series* (WMO, Geneva, Switzerland), pp. 235-243, 1975.

Crutzen, P. J., and I. S. A. Isaksen, The impact of the chlorocarbon industry on the ozone layer, submitted to *J. Geophys. Res.*

Delwiche, C. C., The nitrogen cycle, *Scientific American*, *223*, 137-146, 1970.

Dugdale, R. C., and J. J. Goering, Uptake of new and regenerated forms of nitrogen in primary productivity, *Limnol. Oceanog.*, *12*, 196-206, 1967.

Goering, J. J., R. C. Dugdale, and D. W. Menzel, Estimates of in situ rates of nitrogen uptake by trichodesmium sp. in the tropical Atlantic ocean, *Limnol. Oceanogr.*, *11*, 614-620, 1966.

Goody, R., Time variations in atmospheric N_2O in Eastern Massachusetts, *Planet. Space Sci.*, *17*, 1319-1320, 1969.

Hahn, J., The North Atlantic Ocean as a source of atmospheric N_2O, *Tellus XXVI*, 160-168, 1974.

Hahn, J., N_2O measurements in the Northeast Atlantic Ocean, *"Meteor" Forsch. Ergebnisse, A*, *16*, 1-14, 1975.

Hardy, R. W. F., and U. D. Havelka, Nitrogen fixation research: a key to world food?, *Science*, *188*, 633-643, 1975.

Johnston, H. S., and G. Selwyn, New cross sections for the absorption of near ultraviolet radiation by nitrous oxide (N_2O), to be published in *Geophys. Res. Ltrs.*, 1975.

Junge, C. E., Residence time and variability of tropospheric trace gases, *Tellus XXVI*, 477-488, 1974.

Koblentz-Mishke, O. J., V. V. Volkovinsky, and J. G. Kabanova, Plankton primary production of the world ocean, *Scientific Exploration of the South Pacific* (W. S. Wooster, Editor), U. S. National Academy of Sciences, Washington, D. C. 183-193, 1970.

Lance, J. C., Nitrogen removal by soil mechanisms, *Journal WPCF*, *44*, 1352-1361, 1972.

Mague, T. H., N. M. Weare and O. Holm-Hansen, Nitrogen fixation in the North Pacific Ocean, *Marine Biology*, *24*, 109-119, 1974.

McElroy, M. B., Chemical processes in the solar system: a kinetic perspective, to be published in *MTP International Review of Science*, 1975a.

McElroy, M. B., Sources and sinks for atmospheric N_2O, manuscript, November 1975b.

Patriquin, D., and R. Knowles, Nitrogen fixation in the rhizosphere of marine angiosperms, *Marine Biology*, *16*, 49-58, 1972.

Sillén, L. G., The ocean as a chemical system, *Science*, *156*, 1189-1197, 1967.

Webb, K. L., W. D. DuPaul, W. Wiebe, W. Sottile, and R. E. Johannes, Enewetak (Eniwetok) Atoll: Aspects of the nitrogen cycle on a coral reef, *Limnol. Oceanogr.*, *20*, 198-210. 1975.

(Received December 1, 1975;
revised January 12, 1976;
accepted January 21, 1976.)