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LIMITATION OF FERTILIZER INDUCED OZONE REDUCTION BY THE LONG LIFETIME

## OF THE RESERVOIR OF FIXED NITROGEN

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Abstract. Stratospheric ozone is destroyed catalytically by nitrogen oxides originating from N_2O produced by denitrifying bacteria at the surface of the earth. Concern has been expressed that major perturbations in N_2O production will result by the beginning of the 21st century because of increased use of industrially produced fertilizers. It is pointed out here that the reservoir of fixed nitrogen is so large that the time required to produce a significant increase in N_2O production from denitrification is probably many hundreds of years.

1. The Nitrogen Cycle and Stratospheric Ozone

Primary chemical control over the ozone abundance in the stratosphere is exerted by nitrogen oxides through the catalytic cycle

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

$$NO_2 + O \rightarrow NO + O_2 \qquad (2)$$
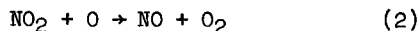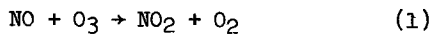
The nitric oxide is created mainly by reaction of $O(^1D)$ with N_2O in the stratosphere. The nitrous oxide in turn emerges from the Earth's surface where it is generated along with N_2 in soil and in water by denitrifying bacteria. Where oxygen is deficient these bacteria use fixed nitrogen in the form of NO_3^- or NO_2^- as electron acceptors to oxidize organic compounds. Fixed nitrogen is thus reduced to N_2 and N_2O. The relative amounts of N_2 and N_2O generated in this denitrifying process depends on the acidity of the medium. When the pH of the medium is lower than 6.5 generation of N_2O compared to N_2 is favored; as much as half of the gas produced may be nitrous oxide, although the rate of the entire process is reduced [Alexander, 1971]. No animals and almost no plants can use nitrogen in the form of N_2 to produce nitrogen compounds such as amino acids and eventually proteins. Plants utilize nitrogen after it has been made available to them in a "fixed" form - that is after the N_2 has been dissociated and the atomic nitrogen used to form compounds such as ammonium, nitrate, or nitrite ions (NH_4^+, NO_3^-, NO_2^-) in the medium in which the plants grow. Under natural conditions (after the natural abundance of NH_3 in the atmosphere reached present levels) biological fixation of nitrogen on land has been performed mainly by organisms symbiotically associated with leguminous plants - although

other biological fixation mechanisms also exist [Burns and Hardy, 1975]. In aqueous media - the ocean in particular - biological fixation is accomplished mainly by blue-green algae. Another source of fixed nitrogen in the ocean is accretion of fixed nitrogen produced on the land in rainwater and river runoff. Ionizing processes in the atmosphere (lightning) are also natural sources of fixed nitrogen for the land and the oceans.

There is presumably a steady state in the nitrogen cycle in nature. The fixed nitrogen is interchanged repeatedly between biomass and humus, humus and inorganic form, inorganic form and biomass. Eventually, in inorganic form, it is combined by denitrifying bacteria with organic material and returned to the atmosphere as N_2 or N_2O. The global rate of fixation has presumably balanced the glocal rate of denitrification. (It is conceivable of course that there have been sizeable variations in these rates. For example, a maximum usage of fixed nitrogen might have occurred during the Carboniferous). Estimates vary for the biological rates of fixation. They are particularly uncertain for the oceans. Hardy and Havelka [1975] put the rate of fixation by plants on land at 17.5×10^7 metric tons (N)/year, or higher. Delwiche [1970], on the other hand, used a value of only 4.4×10^7 tons (N)/year. Estimates of the atmospheric ionization source run from 0.75×10^7 tons (N)/year [Delwiche, 1970] to 1×10^7 tons (N)/year [Burns and Hardy, 1975; Hardy and Havelka, 1975].

Recently, however, man has begun to intervene in the global nitrogen cycle through the production of significant quantities of fixed nitrogen. Combustion processes are estimated to contribute about 4×10^7 tons (N)/year to the land [Burns and Hardy, 1975]. But a potentially more serious perturbation is the growing use of inorganic nitrogen fertilizers. In 1950, this source was only 0.35×10^7 tons (N)/year but by 1974 had grown to 4×10^7 tons (N)/year and at a yearly growth rate of 6% will reach 20×10^7 tons (N)/year by the year 2000 [Hardy and Havelka, 1975]. In 1974, according to these estimates, the total annual fixation rate on land was about 26×10^7 tons (N). Concern over the possible detrimental effects of this anthropogenic intervention in the nitrogen cycle has been expressed [Keeny and Gardner, 1970; Delwiche, 1970; Commoner, 1975]. Recently, it has been pointed out that increased fertilization might possibly lead to a significant perturbation in the global

rate of denitrification, and N_2O generation and consequently an erosion of the Earth's ozone shield [McElroy, 1974, 1975; Crutzen, 1974; Bishop, 1975]. Attention has been drawn to the fact that the rate of industrial fixation of nitrogen (combustion aside) is now comparable with the biological rate on land and threatens to almost the double the present rate by the year 2000. If the denitrification rate balances the fertilization rate and if a significant fraction of the reduced nitrogen is N_2O, the effect on the ozone abundance through the NO_x cycle (1,2) could be significant.

2. The Fertilizer Issue

Although very little has yet to appear in the scientific literature there is a lively debate in progress concerning the seriousness of this effect. Attention has been focused on the rates of fixation and denitrification, particularly on the flux of N_2O into the atmosphere, its atmospheric lifetime and the size and sign of the ocean source. Hahn [1974], for example, estimated a biological production of N_2O from soil sources of about 1.5×10^7 tons (N)/year compared to a presumed total denitrification rate of 23×10^7 tons (N)/year. He found a source of N_2O in the oceans of 8.5×10^7 tons (N)/year These rates, compared to the total atmospheric burden of N_2O, imply a 20 year lifetime for N_2O in the atmosphere. Since the known stratospheric sink implies a lifetime of about 150 years, an unknown tropospheric or surface sink for N_2O must exist according to this model. A 10-20 year atmospheric lifetime for N_2O has been indirectly inferred from the observed fluctuations in atmospheric N_2O densities [Goody, 1969; Schutz et al., 1970]. In contrast with this model McElroy [1975] has taken a 20-year lifetime for atmospheric N_2O, a stratospheric sink of 1×10^7 tons (N)/year and the concept that the oceans are a net sink for N_2O of strength 2.5×10^7 tons (N)/year and the land a source of 3.5×10^7 tons (N)/year. In his model a 20% reduction in ozone by the end of the first quarter of the 21st century would be a result of current and future use of industrial fertilizer. The model assumes that denitrification keeps step with fixation.

3. The Long Lifetime of the Fixed Nitrogen Reservoir

In this note we draw attention to an important, but overlooked factor relating the industrial input to the global reservoir of fixed nitrogen and the output rate of N_2 and N_2O. We note the immense amount of fixed nitrogen contained in the reservoirs compared to the input and output rates under discussion. So far attention has been concentrated on the relative magnitudes of the various sources of fixed nitrogen and the ratio of N_2O to N_2 produced by denitrifying bacteria and not enough attention paid to the very long lifetime of fixed nitrogen in the land and in the oceans. The implication of this long lifetime of naturally fixed nitrogen is that the time delay between the fertilizer input and a larger response in denitrification will be measured in thousands of years. This will be so unless a mechanism should develop that would reduce drastically the lifetime of industrially fixed nitrogen against denitrification.

The reservoirs of fixed nitrogen according to McElroy [1975] and Delwiche [1970] are shown in Table 1 in metric tons (N).

A major disparity between the two models is in the estimated reserves of organic nitrogen. It is possible that Delwiche's estimates are too large. According to Bolin [1970], the reservoir of organic carbon on land is 7×10^{11} tons, and with a C/N ratio of 12 [Allison, 1973] this implies a soil reservoir of about 6×10^{10} tons (N). Our own inventory of global soils yields about 1×10^{11} tons of organic N in soils [Kononova et al., 1961; Gerasimov and Glazovskaya, 1965; Buckman and Brady, 1971; Allison, 1973]. Similarly in the oceans, we estimate about 6×10^{11} tons of inorganic N and about 2×10^{11} tons of organic N [cf., Sverdrup et al., 1942] in agreement with McElroy.

Of the inorganic nitrogen on land, only about 1% is in soluble form, i.e., NO_3^-, NO_2^- and NH_4^+, and therefore readily available for use by plants. The remainder is present as insoluble clay-bound ammonia, in weak equilibrium with NH_4^+ [Burns and Hardy, 1975]. The availability of clay-bound ammonia to nitrifying bacteria is probably greater than 5% per year [Allison, 1973], giving a maximum lifetime for clay-bound ammonia of

Table 1

Fixed Nitrogen Reserves in Metric Tons (N)

	Land		Oceans	
	McElroy	Delwiche	McElroy	Delwiche
Inorganic	1×10^{11}	1.4×10^{11}	6×10^{11}	1×10^{11}
Organic (dead)	6×10^{10}	7.6×10^{11}	2×10^{11}	9×10^{11}
Organic (living)	1×10^{10}	1.4×10^{10}	8×10^8	1×10^9
Total	1.7×10^{11}	9.14×10^{11}	8×10^{11}	10^{12}
Global Total	9.7×10^{11}	1.9×10^{12}		

about 20 years. The lifetime of living organic nitrogen (mostly plants) is also less than 20 years [Whittaker and Likens, 1973]. The mineralization rate of dead organic nitrogen is about 1 to 2% per year which implies a 50 to 100 year lifetime. The above lifetimes imply yearly turnover rates of 100×10^7 tons (N)/year or more. Similarly, in the ocean, the lifetime of dead organic nitrogen against decomposition is 25 years [Reiner, 1973] and implies a turnover rate of 800×10^7 tons (N)/year. Thus, unless the natural or industrial fixation rate is comparable to these rates the equilibrium between living organic, dead organic, and inorganic nitrogen on land and in the oceans will remain unperturbed.

According to the estimates of Hardy and Havelka [1975] the rate of natural nitrogen fixation in soil is $\sim 20 \times 10^7$ tons (N)/year. According to Delwiche [1970] it is 5×10^7 tons (N)/year. The fixation rate in the ocean is always acknowledged to be very uncertain, 5×10^7 tons (N)/year from rivers, rain and local fixation according to McElroy [1975], and 4×10^7 tons (N)/year according to Delwiche [1970] including 3×10^7 tons (N)/year in runoff. From the size of the reservoir and the fixation rates, we can estimate doubling times in various ways, but they are all long. Using these sources we estimate the doubling times of fixed nitrogen from natural sources on land ranging from about 850 years to 18,300 years. If we consider the global reservoirs we would have total fixation rates of about 23×10^7 tons (N)/year [Hardy and Havelka, 1975] and 6×10^7 tons (N)/year [Delwiche, 1970]. The resulting doubling times for fixed nitrogen in the global reservoir would be 4,200 years and 32,000 years, respectively.

We can calculate an upper limit to the reduction in the ozone column by N_2O originating from the projected use of industrially produced fertilizers (4×10^7 tons yearly in 1974 increasing annually by 6%). For this upper limit calculation we assume (a) the only source of N_2O is on land, (b) the lifetime of fixed nitrogen on land is only 850 years, (c) N_2O has a 20 year lifetime in the atmosphere, (d) the rate of denitrification is linearly proportional to the abundance of NO_3^- and NO_2^- in the soil. We find an increase in the N_2O mixing ratio of 4% by the year 2025 and 20% by the year 2050. The corresponding ozone reductions [CIAP Final Report, 1975] are about 1% and 4% respectively. If one should instead assume that the rate of denitrification will remain always equal to the rate of fixation he would find an increase in the N_2O mixing ratio of 220% by the year 2025 and an order of magnitude increase by the year 2050. On the other hand, we must point out that if the use of artificial fertilizers should be maintained at the year 2025 rate for 1000 years an eventual increase of 4000% in the N_2O mixing ratio would result. On this long time scale the problem would be serious.

4. Discussion

Therefore, if the fixed nitrogen introduced into fields, rice-paddies or other crop-producing media by man are to produce a rapid response in the atmosphere as a result of denitrification,

special mechanisms will have to be invoked. These mechanisms would have to balance the addition of fertilizers to the soil with denitrification hundreds or even thousands of times faster than natural biological denitrification or chemodenitrification. Several processes must be understood before any final assessment can be made of the time scale on which denitrified man-made fertilizers can affect the ozone layer. They are those processes that govern the distribution and denitrification of these artificial forms of fixed nitrogen. Will these injections into the fixed nitrogen reservoir stimulate a corresponding rapid response in the production of organic wastes and denitrifying bacteria in oxygen-poor media so that the return of N_2 and N_2O to the atmosphere can keep step with the increased fixation rate? Will this response that would balance fixation with denitrification develop as fixed nitrogen increases in the world reservoir? What appears to be required for a rapid increase in N_2O production is a special mechanism whereby a significant portion of the nitrogen fixed by man is transported to an anaerobic environment where organic matter would be preferentially oxidized by the fixed nitrogen ions rather than being returned to living organisms. Another possibility is that chemodenitrification rates would grow [see e.g., Stevenson et al., 1970]. Also, it is commonly observed in ^{15}N-tracer studies that 15% of the applied fertilizer is lost to the atmosphere within days [Hauck, 1971]. What portion of this gaseous loss is due to denitrification (possibly N_2O) and what to volatization of NH_3 is not known.

These appear to be questions even more fundamental than those concerning the ratio of N_2O and N_2 in the released gas, the nature of the tropospheric sink or whether the ocean is a large source or sink for N_2O. If such special mechanisms do not develop, it would seem most likely that adding fixed nitrogen at rates of the order of 10^8 tons (N)/year would begin to produce a noticeable response in the release of N_2 and N_2O only hundreds of years after the process began. Furthermore, if the artificial or industrial source persists for times measured only in tens of years the response in denitrification will be a small one lasting a long time. But if the artificial fixation persists for times comparable to the natural residence time of fixed nitrogen in the soils and seas the response of the system in producing N_2O may be delayed but large and persistent. It is essential to understand what will be the response of the denitrifying processes to the rapid increase in the introduction of fixed nitrogen in selected small areas of the surface. This appears to be a central problem posed by the increased use of artificial fertilizer as far as its effect on the atmospheric ozone is concerned.

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