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Newly Recognized Vital Nitrogen Cycle

(nitrogen oxides/stratospheric photochemistry/ozone balance)

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Contributed by Harold Johnston, May 22, 1972

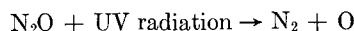
ABSTRACT Soil and sea bacteria produce a small amount of nitrous oxide (N₂O); a small part of this N₂O is photochemically converted to nitric oxide (NO) in the stratosphere. This process has recently been shown to be the principal source of the active oxides of nitrogen (NO and NO₂) in the stratosphere. The active oxides of nitrogen catalytically destroy ozone, and NO and NO₂ appear to be a principal factor in the natural ozone balance. Stratospheric ozone is the only effective shield for the surface of the Earth against the harsh ultraviolet radiation between 300 and 250 nm. Thus, soil bacteria indirectly control the intensity of ultraviolet radiation reaching the Earth's surface. This subcycle of the major nitrogen cycle involves a relatively small amount of nitric oxide, estimated to be between 0.26 and 1.2 × 10⁹ kg of NO per year on a world-wide basis. A recent estimate of the future nitric oxide emission in the stratosphere by the Concord supersonic transport is 0.37 × 10⁹ kg/year on a world-wide basis, which is similar to the amount estimated from the natural source.

The fixation of atmospheric nitrogen, its utilization by plants and then animals, and its return to the atmosphere by denitrifying bacteria constitute a well-known cycle, vital to all life on Earth (1). Recent considerations of the probable environmental impact of supersonic transports (SST) have identified several specific processes, which link up to constitute another vital cycle. This minor loop of the nitrogen cycle couples the activity of soil bacteria (through oxides of nitrogen in the stratosphere) with the level of ultraviolet radiation at the surface of the Earth.

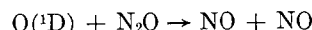
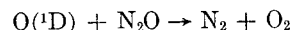
In the soil there are certain bacteria—for example, *Pseudomonas denitrificans* (1)—that use oxygen to oxidize organic material when it is abundant but use nitrates or nitrites to oxidize organic compounds under anaerobic conditions. In this process, most of the nitrates and nitrites are reduced to molecular nitrogen, N₂. However, a small amount of this reduction terminates with nitrous oxide, N₂O. The formation of nitrous oxide occurs actively in rich, wet soil (1-4) and in surface ocean waters (5). Nitrous oxide is a rather inert gas, resembling carbon dioxide in several respects. It is unreactive toward air and water, and it is essentially unaffected by solar radiation in the troposphere. Nitrous oxide is thus a natural trace constituent in the troposphere at about 0.25 parts per million (ppm) (3, 4). Nitrous oxide slowly diffuses upward from the turbulent, well-mixed troposphere into the stratosphere, which by virtue of its steep temperature inversion is relatively stable against vertical mixing. As slow eddy diffusion processes lift nitrous oxide up to elevations of about 20-30 km, it is destroyed both chemically and photochemically. The mean lifetime of nitrous oxide from formation

in the soil to destruction in the stratosphere is estimated to be between 10 and 70 years (5).

Bates and Hayes (3) worked out the quantitative problem of the eddy diffusion of nitrous oxide into the stratosphere and its photochemical destruction there

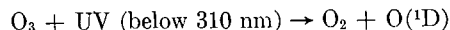


The oxygen atom adds to an oxygen molecule to form ozone, which is an exceedingly minor source of stratospheric ozone. Nitrous oxide reacts with singlet oxygen atoms (6)



These two fast reactions occur with very nearly equal probability.

The principal source of singlet oxygen atoms is the photolysis of ozone at wavelengths shorter than 310 nm (7, 8)



Singlet oxygen atoms are rapidly deactivated by collision with either nitrogen or oxygen (9)



However, on rare occasion a singlet oxygen atom collides with nitrous oxide to form two molecules of nitric oxide. Nitric oxide, NO, unlike nitrous oxide, is chemically very active, and it undergoes many fast reactions in the stratosphere (10, 11).

Crutzen (10b) appears to be the first to propose that nitrous oxide is the principal natural source of "odd nitrogen" (NO and NO₂) in the stratosphere. There is a large uncertainty concerning the rates of atmospheric motions and an additional smaller uncertainty about the rate constants for the reactions of singlet oxygen atoms in the stratosphere. Within the range of uncertainty, Crutzen estimated the worldwide average flux of nitric oxide into the stratosphere from this source to be between (0.29 and 1.5) × 10⁸ molecules cm⁻² sec⁻¹. Similar calculations were made by McElroy and McConnell (12) and by Nicolet and Vergison (13). The formation of nitric oxide occurs largely between 20 and 30 km.

The nitric oxide produced from nitrous oxide very rapidly reacts with ozone to produce nitrogen dioxide (6)



Singlet oxygen atoms also react with water to form hydroxyl radicals (14)



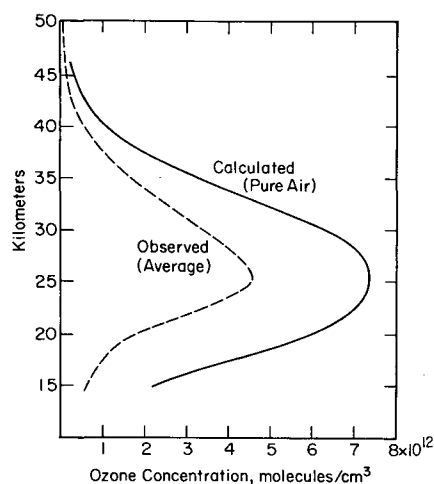
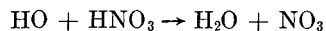
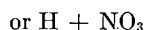
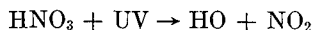


FIG. 1. Comparison of calculated and observed ozone at the equator (solar equinox). The observed ozone is based on Dütsch's (20) long-term average profile. The calculation is based on pure air and a static atmosphere.

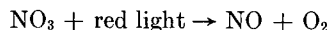
Among other reactions, these radicals in the lower stratosphere form and destroy nitric acid (11d)



Nitric acid has been observed in the lower stratosphere (15), and the integrated column of nitric acid vapor is about 6×10^{-9} of the total column of air above 15 km. This nitric acid slowly diffuses downward into the troposphere, where it is rapidly removed by rain, and it slowly diffuses upward where it is destroyed by short wavelength ultraviolet radiation (16)



As recently observed in this laboratory, the free radical NO_3 is rapidly destroyed by visible light to reform nitric oxide



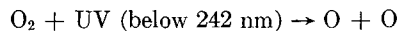
and nitric acid strongly absorbs ultraviolet radiation around 200–210 nm; it is destroyed with a quantum yield close to one.

Although the stratosphere has a strong temperature inversion, with consequent stability against vertical mixing, there is some vertical turbulent diffusion, which acts toward the equalization of inhomogeneities of composition. The vertical turbulence itself is a random mixing process, and the direction of flow of any substance is from a high mole fraction towards a low mole fraction. Nitrous oxide (N_2O) is formed at the Earth's surface, mixed throughout the troposphere, and destroyed chemically and photochemically in the stratosphere. Thus, the gradient of nitrous oxide is a decrease with elevation, and the direction of turbulent diffusional flux is upward. On the other hand, the active oxides of nitrogen, NO_x , (NO and NO_2) are produced in the ionosphere, in the stratosphere, and in the troposphere; the principal sink (interconversion of NO , NO_2 , NO_3 , N_2O_5 , HNO_3 , and HNO_2 does not constitute a sink) of NO_x is wash-out by rain in the troposphere. The average, natural composition of NO_x in various regions of the

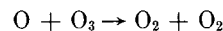
atmosphere is about: 50 parts per billion [10^9] (ppb) in lower mesosphere, 3–12 ppb in the stratosphere, and 1–3 ppb in the troposphere, with the lower limit applying in the upper troposphere. The direction of turbulent diffusion of NO_x is downward from the mesosphere, through the stratosphere, to the troposphere. In the course of the same turbulent diffusional process, N_2O moves upward from troposphere to stratosphere and NO_x moves downward from the stratosphere to the troposphere. Thus, the sources of NO_x in the troposphere (combustion, etc.) have little or no effect on the NO_x composition of the stratosphere. Nitric acid is formed from NO_x between 15 and 25 km ($\text{HO} + \text{NO}_2 \rightarrow \text{HNO}_3$); it is destroyed photochemically above 25 km, and it is washed out by rain in the troposphere. The turbulence in the lower stratosphere, which transports N_2O up and NO_x down, moves nitric acid both up and down to its two regions of destruction and removal.

In addition to a wide variety of turbulent motions that tend to transfer material to and from the stratosphere, there may be a systematic component of wind vertically upward near the equator and downward near the poles and elsewhere. A direct vertical wind from the troposphere into the stratosphere would tend to increase N_2O in the stratosphere, but it would decrease the active oxides of nitrogen (NO and NO_2), since it would displace NO_x -rich stratospheric air by the much lower mole fraction of NO_x of the troposphere.

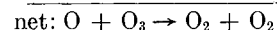
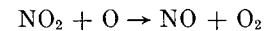
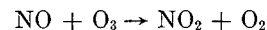
Ozone in the stratosphere is the only significant shield for the Earth against radiation between 250 and 300 nm. Such radiation is damaging or lethal, depending on wavelength and dosage, to plants and animals on the Earth's surface (17). Ozone is formed by the photolysis of molecular oxygen in a two-step process



In the natural atmosphere, "odd oxygen" (O and O_3) is destroyed primarily by two processes. One of these is the direct reaction of an oxygen atom and ozone



and the other is a catalytic cycle brought about by the oxides of nitrogen (10, 11)



where the second reaction is the rate-determining step (11a, b). The oxides of nitrogen are true catalysts; they may be reused over again in this catalytic cycle. A year ago it was thought (on the basis of an extrapolations from room temperature) that the rate constant for the reaction $\text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}$ was about 5000 times larger (11a, b) than that for $\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$; however, recent direct measurements (18) of these reactions at stratospheric temperatures shows the factor to be just over 10,000. Thus, if NO_2 is 0.01% of ozone, the NO_x (NO plus NO_2) catalytic cycle will destroy ozone at a rate equal to the destruction rate in pure air. In the principal ozone layer, ozone is present at a mole fraction the order of magnitude of 10^{-6} , nitric acid is about 10^{-8} , and NO_2 is estimated (11d) to be about 10% of HNO_3 —or 10^{-9} at 20 km—and to be greater than HNO_3 above 30 km. Even at these low values, NO_2 is an

important factor in the current natural balance of ozone (11e).

Ozone profiles and vertical columns have been measured for many years at numerous stations around the world (19). Dütsch has been a leading adviser in this enterprise, and he summarized a large volume of data in 1969 (20). Fig. 1 shows the average observed ozone profile at the equator (solar equinox) as derived by Dütsch (20). Included in Fig. 1 is the ozone profile calculated with the latest available photochemical constants (21) on the basis of static, pure air. Because of the model of static air, the quantitative details of the calculated curve in Fig. 1 are not exactly 100%, especially below 25 km. Above 30 km, the photochemical rates are fast compared to North-South transport rates, and these calculations based on static air are fairly realistic, even if not exact. On a worldwide basis, the instantaneous rate of ozone production is three times faster than the rate of destruction, calculated on the assumption of pure air. The only known mechanism sufficient to explain this ozone deficit (11e) is catalytic destruction of ozone by the oxides of nitrogen. Ozone profiles at the equator for various uniform distributions of NO_x throughout the stratosphere are given in Fig. 2 for a model of static air. Because of the assumption of a static atmosphere, the quantitative aspects of Fig. 2 are not 100% exact, but the capacity of NO_x to reduce ozone is so powerful that this approximation does not change the essential argument. A comparison of Figs. 1 and 2 shows that NO_x between 1 and 10 ppb is sufficient to explain the ozone deficit at the equator. From the observed distribution of nitric acid vapor in the stratosphere, it is probable that NO_x is about 1 ppb around 20 km, and about 10 ppb above 30 km. These quantities are very nearly what is needed to explain the ozone deficit on a world-wide basis. It appears that nitric oxide naturally produced from nitrous oxide is the dominant factor in controlling the present ozone concentration.

The newly recognized nitrogen cycle is given by the right-hand portion of Fig. 3. Life processes on the surface of the Earth deposit nitrate in the soil; bacteria under relatively anaerobic conditions produce some N₂O from nitrates, N₂O diffuses up to the stratosphere to form some NO, NO₂, and HNO₃, and some nitric acid diffuses back to the troposphere to be returned to the Earth's surface by rain. This cycle is only a small fraction of the main nitrogen cycle, in that only a small fraction of soil nitrate is converted to N₂O, and only a small fraction of the N₂O is converted to NO_x. However, this cycle is vital to life on Earth because it controls the concentra-

TABLE 1. Comparison of estimates of natural and artificial source of nitric oxide in the stratosphere on an annual, world-wide basis

Estimated natural flux, kg/year	Refs.
(2.3-12) × 10 ⁸	Crutzen (10b)
(4-20) × 10 ⁸	Nicolet (13)
(2.0-5.1) × 10 ⁸	McElroy (12)
Avg (2.6-12) × 10 ⁸	
Estimated flux from the Concorde in 1985, kg/year	
3.7 × 10 ⁸	(22)

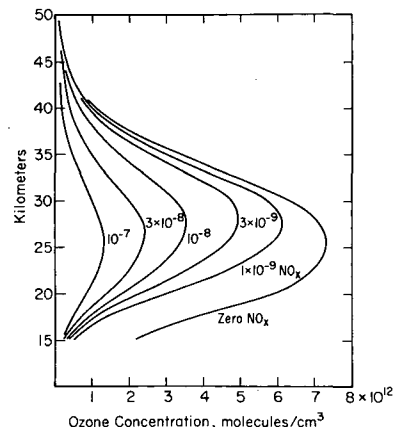


FIG. 2. The effect of oxides of nitrogen on the calculated ozone profile at the equator (solar equinox). The calculations are based on uniform NO_x (NO and NO₂) distributions and a static atmosphere.

tion of ozone in the stratosphere and, thus, the ultraviolet radiation flux at the Earth's surface. Plants and animals have active mechanisms for repairing damage from ultraviolet radiation, and there is now a dynamic balance in living things between ultraviolet radiation damage and repair (17). Thus, the biological process of anaerobic dinitrification is coupled through the stratosphere with the biological struggle against ultraviolet radiation damage.

This new nitrogen cycle has been recognized from consideration of the probable environmental impact of supersonic aircraft operating in the stratosphere. The natural flux of nitric oxide in the stratosphere from nitrous oxide according to three different investigators is given in Table 1. The average estimated range is between (2.6-12) × 10⁸ kg/year for the entire world. According to estimates made by the Australian Academy of Sciences (22), the fleets of Concorde SST in 1985 would constitute a world-wide average flux of NO in the stratosphere of 102 × 10⁴ kg/day or 3.7 × 10⁸ kg/year. This figure is compared with estimates of the natural NO flux in Table 1. It can be seen that the stratospheric source of nitric oxide from the Concorde, as given by the Australian Academy of Sciences, is approximately equal to the natural source of nitric oxide in the stratosphere. The Concorde gives 1.4 times as much NO as the average minimum estimate in Table 1 and 31% as much NO as the average maximum estimate of the natural source. The American SST would have emitted about 3 or 4 times as much NO_x as the Concorde, by virtue of its greater fuel consumption.

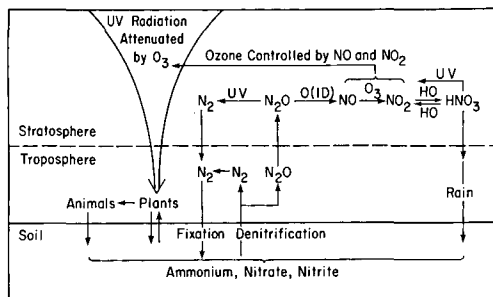


FIG. 3. The nitrogen cycle and the newly recognized secondary cycle involving stratospheric NO_x and ozone.

The stratosphere is a highly complicated system of air motions and photochemistry. A complete understanding of global air circulation coupled with photochemistry and radiative heat balance is not available, and it appears to be several years away, even with a "crash" research program devoted to the subject (23). The active oxides of nitrogen now naturally formed in the stratosphere from nitrous oxide are subject to the great complexities of the stratosphere: a wide range of horizontal and vertical motions, slow transport to the troposphere, the intense ultraviolet radiation field, formation and destruction of nitric acid, and many other reactions involving trace substances. In spite of these poorly understood complexities, the oxides of nitrogen appear now to be a dominant factor in the natural ozone balance. Unless information is developed to the contrary, it is reasonable to assume that artificial oxides of nitrogen will have an effect in the stratosphere similar to the natural oxides of nitrogen. Since the natural NO_x reduces ozone by about a factor of two below the value it would otherwise have (world-wide) an artificial doubling (more or less) of the present input of NO_x could be a major intrusion on this vital nitrogen cycle.

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