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## Stratospheric Ozone: The Possible Effects of Tropospheric-Stratospheric Feedback

Abstract. *The existence of tropospheric-stratospheric feedback mechanisms affecting variations in stratospheric ozone indicates the need to model the complete tropospheric-stratospheric system. For instance, a decrease in stratospheric ozone results in increased photolytic destruction of nitrous oxide in the troposphere and thereby reduced production of nitric oxide in the stratosphere. Estimates indicate that this mechanism will result in a recovery in atmospheric ozone of about 6 to 13 percent of the initial perturbation.*

As a result of recent studies, the prediction has been made that the release of stratospheric pollutants, such as nitrogen oxides, $NO_x$, from supersonic transports and ClX (Cl, ClO, HCl) from the photolytic destruction of chlorofluoromethanes will cause a significant diminution in the atmospheric $O_3$ content (*1–3*). In order to quantitatively assess the effects of these and other perturbations, several photochemical models have been constructed (*2, 4, 5*). In these models it is generally assumed, as a lower boundary condition, that the tropospheric mixing ratios of long-lived gases, such as $N_2O$, $CH_4$, and $CH_3Cl$, are constant and do not vary with changes in the $O_3$ column above (*2, 4, 5*). This practice effectively decouples the tropospheric-stratospheric system, not allowing for possible feedback between the troposphere and stratosphere. In fact, it is likely that a perturbation in the stratospheric $O_3$ content will, because of the resultant change in near-ultraviolet radiation penetrating the tropopause, cause changes in tropospheric photochemistry.

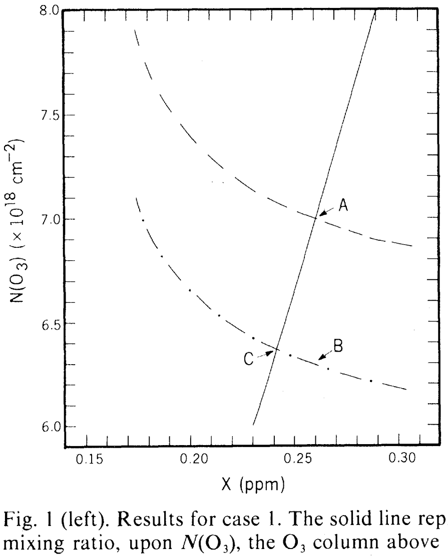
Calculations, based on a model similar to that of Chameides (*6*), indicate that a 10 percent decrease in the $O_3$ column above 15 km, $N(O_3)$, results in an approximate 13 percent increase in the photolytic destruction rate of $N_2O$ and a 20 percent increase in the tropospheric concentration of OH radicals. These increases will cause a decrease in the tropospheric concentration of $N_2O$, and in the concentration of $CH_4$ and $CH_3Cl$, both of which are destroyed by OH (*7*). Thus a decrease in $N(O_3)$ may result in a decrease in the tropospheric input of $NO_x$, $CH_4$, $H_2O$, odd hydrogen (OH, $HO_2$, $H_2O_2$, H), and ClX to the stratosphere, possibly leading to feedback effects.

We estimate that these feedback effects are small but not insignificant, an indication that the entire tropospheric-stratospheric system must be modeled. The largest of the tropospheric feedback mechanisms that we have identified thus far involves tropospheric $N_2O$ and is discussed below.

The major source of stratospheric $NO_x$ is the oxidation of $N_2O$ (*8*) by excited oxygen atoms: $O(^1D) + N_2O \rightarrow 2NO$. Since catalytic destruction by $NO_x$ is the major sink of stratospheric $O_3$ (*1*), the stratospheric abundance of $N_2O$ plays a major role in determining the atmospheric $O_3$ content. Crutzen (*9*) reports that, with no $N_2O$ in the atmosphere, the total atmospheric $O_3$ content would be 60 percent higher, whereas twice as much $N_2O$ would yield 20 percent less atmospheric $O_3$.

However, since $N_2O$ is produced at the earth's surface by denitrification and is then transported upward (*10*), the stratospheric $N_2O$ abundance is determined by the $N_2O$ mixing ratio at the tropopause. Tropospheric observations indicate that $N_2O$ is well mixed with a residence time of 10 years or more (*11, 12*). Although tropospheric $N_2O$ is destroyed by photodissociation (*10*), measurements of $N_2O$ production in oceans and the temporal variability of $N_2O$ concentrations (*11, 12*) suggest the existence of another unidentified, but dominant, tropospheric sink. (Our calculations include the effects of this unknown sink on the variability of $N_2O$.)

Although photolysis of $N_2O$ is energetically possible for wavelengths below



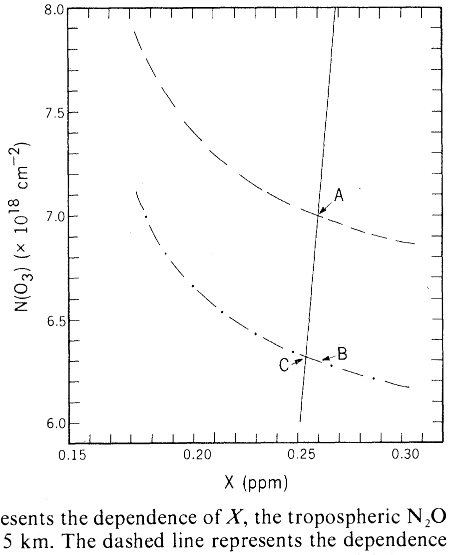


Fig. 1 (left). Results for case I. The solid line represents the dependence of *X*, the tropospheric $N_2O$ mixing ratio, upon $N(O_3)$, the $O_3$ column above 15 km. The dashed line represents the dependence of $N(O_3)$ upon *X* after Crutzen (*9*). The dashed-dotted line represents the dependence of $N(O_3)$ upon *X* with an assumed uniform 10 percent perturbation. Under present-day conditions, the coupled system is in equilibrium at *A*. The initial effect of an assumed 10 percent perturbation would be to move the system from *A* to *B*. Equilibrium is reestablished at *C*, reducing the effect of the perturbation. Fig. 2 (right). Results for case II. For an explanation of the abbreviations used, see the legend to Fig. 1.

3370 Å, observations of the $N_2O$ cross section indicate that the process is not effective for wavelengths greater than about 3100 Å (*10*). Since the $O_3$ absorption cross section decreases by a factor of 20 from 2900 to 3100 Å, leading to a variation in the atmospheric optical depth from 15.2 to 0.8 (*13*), the rate of photolytic destruction of tropospheric $N_2O$ and hence the tropospheric and stratospheric $N_2O$ abundance is sensitive to the atmospheric $O_3$ content. We find that for equinoctial conditions near the ground at 30°N, the daily averaged $N_2O$ photodissociation frequency, $J$, varies from $3.8 \times 10^{-10}$ to $2.8 \times 10^{-10}$ $sec^{-1}$ when the $O_3$ column above varies from $8 \times 10^{18}$ to $1 \times 10^{19}$ $cm^{-2}$ (*14*).

It follows, therefore, that, if the stratospheric $O_3$ content decreases, more solar radiation in the 3000-Å region reaches the troposphere, increasing $J$, thereby decreasing $N_2O$ in the troposphere and the $N_2O$ flux into the stratosphere. This change in turn causes a decrease in stratospheric $NO_x$ and a subsequent increase or recovery in stratospheric $O_3$. A similar but opposite effect occurs if the stratospheric $O_3$ content is initially increased. This mechanism tends to reduce the amplitude of perturbations in $N_2O$ and $O_3$ caused by changes in the $N_2O$ flux (for example, by fertilizers) (*15*).

Thus, tropospheric $N_2O$ variations act to stabilize stratospheric $O_3$. The effectiveness of this negative feedback mechanism depends upon the sensitivity of tropospheric $N_2O$ to changes in stratospheric $O_3$ as well as the sensitivity of stratospheric $O_3$ to changes in tropospheric $N_2O$. Qualitatively consistent with our predictions are observations of an increase in total $O_3$ in the Northern Hemisphere from 1961 to 1970 (*16*) and an increase in tropospheric $N_2O$ during the late 1960's (*11, 12*). However, these measurements are not conclusive. Continued monitoring of tropospheric $N_2O$ along with $O_3$ are needed to test this hypothesis.

To determine the effectiveness of this stabilization mechanism, we have calculated the likely variation in the tropospheric $N_2O$ mixing ratio, $X$, due to changes in $N(O_3)$ (*17*). The results are presented for two cases. In case I we assume photolysis to be the only sink for $N_2O$, implying a tropospheric $N_2O$ lifetime of about 50 years. In case II an unidentified $N_2O$ sink, with a destruction frequency of $1.7 \times 10^{-9}$ $sec^{-1}$, is assumed to balance the large $N_2O$ production rate from oceans deduced by Hahn (*12*). The solid lines in Figs. 1 and 2 illustrate the calculated dependence of $X$ upon $N(O_3)$ for cases I and II, respectively. Crutzen's (*9*) prediction that $N(O_3)$ is dependent upon $X$ is represented by the dashed lines in Figs. 1 and 2. The coupled system of stratospheric $O_3$ and tropospheric $N_2O$ is in equilibrium where the two lines cross, labeled $A$ in Figs. 1 and 2. If an additional $O_3$ destruction mechanism is introduced, for example, chlorofluoromethanes, the $O_3$ equilibrium curves tend to move downward. Assuming a uniform 10 percent perturbation, this hypothetical perturbed $O_3$ equilibrium is shown in Figs. 1 and 2 as dashed-dotted lines. Thus, the initial effect of the perturbation would be to move the system from $A$ to $B$, along a line of constant $X$, as shown in Figs. 1 and 2. At $B$, however, the rate of loss of $N_2O$ exceeds production, causing $X$ to decrease and $N(O_3)$ to increase. Equilibrium is reestablished for both constituents at $C$ in Figs. 1 and 2. Hence the curves indicate that an initial 10 percent perturbation in $N(O_3)$ is reduced to 8.7 percent for case I and 9.4 percent for case II. Thus, the final reduction in $O_3$ is about 6 to 13 percent smaller than it would have been in the absence of the $N_2O$ stabilization mechanism.

In case I, because the tropospheric residence time of $N_xO$ is about 50 years, this feedback mechanism would not take effect until about 50 years after an initial perturbation. In case II, on the other hand, tropospheric $N_2O$ has a residence time of about 15 years, implying a much shorter delay.

Calculations indicate that the $CH_4$ feedback mechanism, involving variations in tropospheric OH, will also result in an approximate 100 percent recovery in atmospheric $O_3$, initially perturbed by $NO_x$ or small amounts of ClX (*18*). We expect a significantly smaller effect from variations in $CH_3Cl$. However, quantitative modeling of the complete coupled system is needed to fully determine the importance of these and other possible tropospheric-stratospheric feedback mechanisms. In the case of $N_2O$, a redetermination of the $N_2O$ absorption cross section in the critical 3000-Å region would also be useful.

Although our results do not refute warnings of serious perturbations to the $O_3$ layer due to stratospheric pollutants, the existence of tropospheric feedback should not be ignored when one is attempting to assess the impact of perturbations upon the $O_3$ layer. We believe that future calculations should include tropospheric photochemical processes as well as those of the stratosphere and mesosphere.

*Note added in proof:* Recent laboratory measurements of the $N_2O$ cross section by Johnston and Selwyn (*19*) and in situ measurements of $J$ by Stedman *et al.* (*20*) indicate that $N_2O$ is not dissociated in the troposphere. Thus, the $N_2O$ cross sections quoted by Bates and Hays (*10*) and used in this work may be erroneous. Nevertheless, we believe that the effects of tropospheric-stratospheric feedback, as illustrated in the $CH_4$ and $CH_3Cl$ mechanisms, should be included in future stratospheric calculations.

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