

On The Origin of Tropospheric Ozone

S. C. LIU, D. KLEY, AND M. MCFARLAND

*National Oceanic and Atmospheric Administration, Environmental Research Laboratories, Aeronomy Laboratory
Boulder, Colorado 80303*

J. D. MAHLMAN AND H. LEVY II

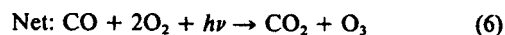
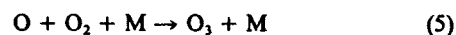
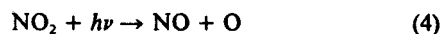
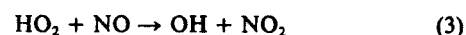
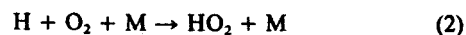
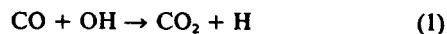
*National Oceanic and Atmospheric Administration, Environmental Research Laboratories
Geophysical Fluid Dynamics Laboratory, Princeton University
Princeton, New Jersey 08540*

The effects of NO_x (NO + NO₂) intrusion from the stratosphere on photochemical ozone production in the upper troposphere are investigated. Using the currently accepted reaction rate coefficients, we find that this upper tropospheric ozone source may be significantly larger than the direct injection of ozone from the stratosphere. Many features of the observed tropospheric temporal and spatial ozone distributions appear to be better explained by this upper tropospheric ozone source hypothesis than by either the classical 'dynamical control' or 'photochemical control' hypotheses. In addition, we find that NO_x emissions from high flying subsonic aircraft in the northern hemisphere may cause an ozone increase in the troposphere. The calculated tropospheric ozone increase due to these NO_x emissions is not inconsistent with the increases observed by the northern hemispheric ozonesonde stations.

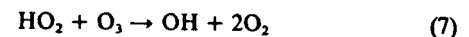
INTRODUCTION

The presence of ozone is very important for tropospheric photochemistry. Levy [1971, 1973] has shown that ozone is a prerequisite in the production of hydroperoxyl and hydroxyl radicals, which control the chemical cycles of many important trace gases (e.g., CO, CH₄, H₂S, CH₃Cl, etc.) in the troposphere [Weinstock and Niki, 1972; Wofsy et al., 1972]. Perturbation of ozone in the troposphere will not only change the chemical lifetimes of these species, but also change the radiation budget and thus may affect the climate [Manabe and Wetherald, 1967; Fishman et al., 1979a; Ramanathan and Dickinson, 1979].

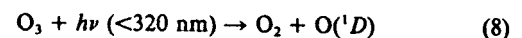
The origin of tropospheric ozone has recently become a controversial subject. From earlier analyses of the ozone distributions, Junge [1962] accepted the classical view that ozone is transported from the stratosphere and destroyed at the surface. This view continues to be favored by Junge and Czeplak [1968], Pruchniewicz [1973], Fabian and Pruchniewicz [1977], Chatfield and Harrison [1977], Singh et al. [1978], and Hussain et al. [1979]. On the other hand, Chameides and Walker [1973], Crutzen [1974], Fishman and Crutzen [1977], Liu [1977], Stewart et al. [1977], Chameides [1978], and Fishman et al. [1979b] have argued that gas phase photochemical production and destruction of ozone in the troposphere may be more important than injection of ozone from the stratosphere. The proposed ozone formation reactions are similar to the so-called smog chamber reactions [Heicklen et al., 1971]:



Odd hydrogen (H, OH, HO₂, and H₂O₂) and NO_x act as catalysts in producing ozone from CO and O₂. The efficiency of this cycle is proportional to the concentrations of these catalysts in the atmosphere. In the troposphere the radicals OH, H, NO₂, and O generally follow the above reaction mechanisms. However, low concentrations of NO allow competition with (3) for the HO₂ radical. This means that the efficiency of producing ozone depends critically on the amount of NO in the atmosphere. A competing reaction to (3) is



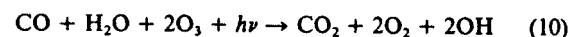
Coupling this with (1) and (2) and with reactions



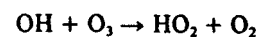
and



we obtain the net ozone destruction reaction:



The two crucial rate constants (3) and (7) have been measured recently [Howard, 1979; Zahniser and Howard, 1980]. The rate constant of (3) is sufficiently fast that HO₂ reacts predominantly with NO rather than with O₃ in the troposphere, provided the NO mixing ratio is 10 pptv or more. This results in a net production of ozone in the troposphere. Above the tropopause, however, the ratio of O₃ to CO [Seiler and Warnock, 1972; Fabian et al., 1979] increases rapidly, so that instead of (1), OH reacts preferentially with O₃,



Thus in the lower stratosphere, (7) and (11) become a catalytic sink for ozone and compete efficiently with (1) through (5).

The NO_x profiles used by Chameides [1978] and Fishman et al. [1979b] have mixing ratios of about 100 pptv at the surface and decrease sharply with increasing height. This causes most of the predicted ozone production to be in the lowest 3 km. These profiles were obtained by assuming that the major

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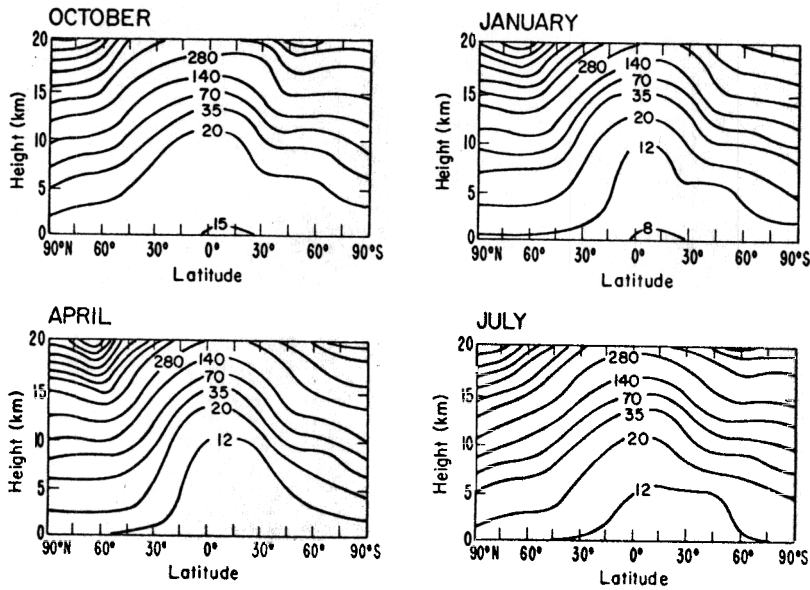


Fig. 1. Calculated troposphere NO_x ($\text{NO} + \text{NO}_2$) distributions. These were scaled according to the tracer distributions in the work by *Mahlman et al.* [1980] and the method of *Levy et al.* [1980] by assuming only the stratospheric NO_x source of $3 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. The NO_x amount is then obtained by using the averaged NO_x/NO_y ratios derived by KDML. Units are in pptv.

sources of NO_x are combustion and lightning near the surface and that the major sink is conversion of NO_2 to HNO_3 by OH and subsequent removal by precipitation. However, this picture of NO_x distribution is now doubtful in view of the recent work by *Kley et al.* [1980] (hereafter referred to as KDML), who find more than 100 pptv of NO_x in the upper troposphere, which is a factor of 10 greater than the values used in the above-mentioned models.

In the following sections we will examine the implication of the NO_x distribution given by KDML on the production of tropospheric ozone and related photochemistry.

NO_x DISTRIBUTION IN THE CLEAN TROPOSPHERE

Levy et al. [1980] have discussed a procedure for deriving the tropospheric NO_x (i.e., total odd nitrogen = $\text{NO}_x + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{HNO}_2 + \text{HNO}_3 + \text{HNO}_4 + \text{ClONO}_2 + \text{PAN}$) by scaling the concentrations of the 'stratified tracer' experiment of the general circulation/tracer model by *Mahlman et al.* [1980]. To facilitate comparison of the observations of NO_x with the values predicted by models, KDML have calculated NO_x from the NO_y distributions by semi-empirically deriving the NO_x/NO_y ratio. We have followed the same procedure and calculated the two-dimensional tropospheric NO_x distributions shown in Figure 1. In deriving these distributions, we have included only the NO_y source from the stratosphere which is mainly from oxidation of N_2O . Following KDML, we have used the value $3 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ for the column production rate of NO_y in the stratosphere. We have also used the 'averaged value' for the NO_x/NO_y ratio derived by KDML to calculate the NO_x distribution from the calculated NO_y distribution. Because these NO_x distributions compared favorably with measured values (KDML), we have used these NO_x values in the following calculations unless specified otherwise. To explore the possible effects of a much lower NO_x distribution, we have also adopted the smaller value of $1.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ for the column production rate of NO_y in the stratosphere as calculated by *Levy et al.* [1980] and the 'smallest value' for the NO_x/NO_y ratio derived by KDML. This results in a 'low

NO_x ' distribution that is about a factor of 4 lower than the distribution in Figure 1. KDML infer from measured NO profiles that the upper tropospheric NO_x distribution is dominated by the stratospheric source. It would appear that the anthropogenic emissions contribute mainly to the boundary layer NO_x and then, probably only regionally [*Levy et al.*, 1980], despite the fact that the anthropogenic source strength is much greater than the stratospheric source. The reason is that water soluble gases in the lower troposphere have a much shorter lifetime against heterogeneous removal than in the upper troposphere [e.g., *Ehhalt*, 1973; *Mahlman and Moxim*, 1978]. More details, including a discussion on the importance of lightning as a source of NO_x , can be found in KDML. However, they concluded that the lightning contribution to the natural NO_x is probably not important.

The calculated NO_x distribution shown in Figure 1 is about a factor of 2 lower than the observed values in the 'clean' troposphere as measured by KDML. Given the uncertainties involved in deriving the NO_x distribution, we consider our derived NO_x distributions to be consistent with the measured values. We will show in the next section that with this NO_x distribution the ozone produced in the upper troposphere by (1) to (5) can be more than 3 times as high as the ozone flux from the stratosphere. Even with the 'low NO_x ' distribution, the ozone produced in the upper troposphere can be comparable to the ozone flux from the stratosphere.

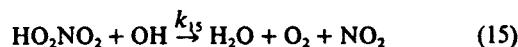
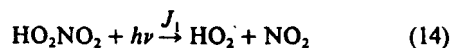
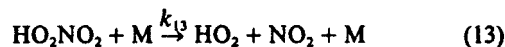
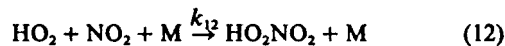
Another noteworthy feature of Figure 1 is the factor of about 1.8 difference in the NO_x distributions between the northern hemisphere (NH) and the southern hemisphere (SH). This asymmetry is due to the interhemispheric difference in the net vertical transport calculated by the general circulation/tracer model [*Manabe and Mahlman*, 1976; *Mahlman et al.*, 1980].

NO_x emissions from high flying subsonic aircraft were estimated to reach about $1.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ above 9 km in the NH by the year 1980, according to the 'modified emissions estimates' by *Oliver et al.* [1977]. This represents an important addition to the NO_x distribution in the NH. To estimate the

NO_y increase due to the aircraft NO_x emissions, we have simply superposed the NO_x emissions above 9 km on the stratospheric NO_y source. For the 'low NO_x ' distribution this means an 80% increase in the NO_x distribution in the NH. For the NO_x distribution in Figure 1 the increase in the NH is about 40%. The increase of NO_x in the SH due to aircraft emissions is negligible.

MODEL CALCULATIONS

The model numerical methods and photochemical reactions, as well as the equations used to calculate ozone production and destruction, are as given in the work by Liu [1977]. Since we have fixed the distribution of all species that are sensitive to transport (i.e., CO , O_3 , CH_4 , H_2 , NO_x , NO_y , and H_2O), the model can be regarded as a diurnal one-dimensional photochemical calculation. The steady state diurnal distributions for all compounds not fixed are found by integrating through 10 diurnal cycles. The reaction rate constants are updated to the values listed in *NASA Reference Publication 1049* [1979] except for the following reactions: $\text{HO}_2 + \text{HO}_2$ from Cox and Burrows [1979], $\text{OH} + \text{H}_2\text{O}_2$ from Keyser [1980] and Sridharan *et al.* [1980], and the addition of reactions involving HO_2NO_2 as follows:



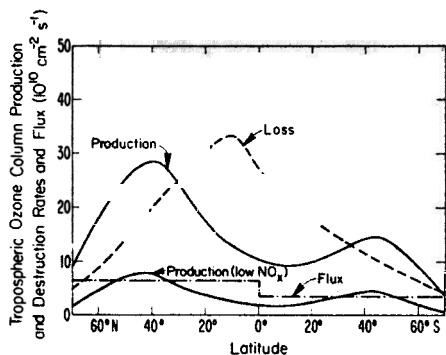


Fig. 2. Model calculated tropospheric ozone column production and destruction rates. The 'production' used the NO_x distributions of Figure 1. The 'production (low NO_x)' used the 'low NO_x ' distributions described in the text. The 'flux' is the averaged hemispheric ozone flux across the tropopause calculated by *Mahlman et al.* [1980].

these reactions are still lacking. The sinks of odd hydrogen in the upper troposphere are $\text{OH} + \text{H}_2\text{O}_2$ (50%), $\text{OH} + \text{HO}_2$ (30%), and $\text{OH} + \text{HNO}_3$ (10%). In addition, the reaction $\text{OH} + \text{HO}_2\text{NO}_2$ could be as large as a 50% sink if its rate constant is as large as $3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, the upper limit given by X. Barker (private communication, 1980). This reaction can also be an important sink for odd hydrogen in the lower stratosphere [Cicerone and Walters, 1980; Wuebbles and Duewer, 1980]. So the calculation of the odd hydrogen distribution in the upper troposphere is probably the largest single source of uncertainty in evaluating ozone production rates. The uncertainty of the ozone loss rate is much smaller since the reaction $\text{O}(^1D) + \text{H}_2\text{O}$ depends only on the concentrations of ozone and water vapor in the lower troposphere.

Another source of uncertainty arises from the nonlinear effect due to highly variable reactants that are positively or negatively correlated resulting from various transport processes. For instance, NO_x is positively correlated with O_3 , while both CO and H_2O are negatively correlated with O_3 . This type of effect cannot be calculated directly in the one-dimensional model used here. However, it is possible to estimate the errors produced through the omission of such effects. Consider a reaction $a + b \rightarrow c + d$ for which the reaction rate is calculated for a time average at a single point. Then

$$\overline{n_a n_b} = \overline{n_a} \overline{n_b} + \overline{n_a' n_b'} \quad (16)$$

$$\overline{n_a n_b} = \overline{n_a} \overline{n_b} + \rho_{a,b} (\overline{n_a'^2})^{1/2} (\overline{n_b'^2})^{1/2} \quad (17)$$

$$\overline{n_a n_b} = \overline{n_a} \overline{n_b} (1 + \rho_{a,b} V_{r(a)} V_{r(b)}) \quad (18)$$

Where \overline{n} denotes time average of number density, $n' = n - \overline{n}$, $\rho_{a,b}$ the correlation coefficient between a and b , and $V_{r(a)} \equiv (\overline{n_a'^2})^{1/2} / \overline{n_a}$, the relative standard deviation. This correction term can now be estimated from previous knowledge about $V_{r(i)}$'s for various trace gases and their expected correlations. The important reactions to be considered are the production and loss terms of ozone. The easiest term to assess is the ozone loss term $\text{O}(^1D) + \text{H}_2\text{O}$. Since this is important only in the lower troposphere, we have $V_{r(\text{O}(^1D))}$ and $V_{r(\text{O}_3)}$ being of the order of 0.3, and $V_{r(\text{H}_2\text{O})}$ which may be nearly 1.0, and a small anticorrelation factor $\rho_{\text{O}_3, \text{H}_2\text{O}}$ which is assumed to be of the order of -0.3 [see *Routhier and Davis*, 1980]. Thus the correction to this loss term is only about -10% . The correction to the production terms can be expressed as

$$\rho_{a,b} V_{r(a)} V_{r(b)} = \rho_{\text{NO}_x, \text{HO}_x} V_{r(\text{NO}_x)} V_{r(\text{HO}_x)} \quad (19)$$

Since the major source of ozone is located at the upper troposphere, the source of HO_x is proportional to the concentration of CH_2O and the sink is approximately proportional to the square of the HO_x concentration. We estimate the value of (19) to be a small negative number because both $V_{r(\text{NO}_x)}$ and $\rho_{\text{NO}_x, \text{HO}_x}$ appear to be less than 0.5.

Also plotted in Figure 2 are the averaged downward ozone fluxes in the NH and the SH calculated by *Mahlman et al.* [1980]. These values are in reasonable agreement with the values derived by *Reiter* [1971], *Cunnold et al.* [1975], and *Danielsen and Mohnen* [1977]. These values are probably reliable within a factor of 2 or so. Estimated destruction of ozone at the surface is about the same as the estimated flux from the stratosphere [Aldaz, 1969; Fabian and Junge, 1970; Danielsen and Mohnen, 1977; Fabian and Pruchniewicz, 1977]. However, surface destruction estimates are probably subject to larger uncertainties because of the different surface and meteorological conditions involved.

Our calculated globally averaged tropospheric column production of ozone is $1.5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ for the NO_x in Figure 1 and $0.4 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ for the 'low NO_x ' case. The averaged tropospheric column loss rate calculated is $1.9 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. These values are significantly greater than or comparable to the estimated ozone flux across the tropopause and the surface destruction rate. Even with the large uncertainties involved in the calculations, we believe that these numbers indicate the importance of the 'in situ' tropospheric production and loss of ozone in determining the tropospheric ozone distribution. Therefore we hypothesize that tropospheric ozone is mainly produced in the upper troposphere and transported from the stratosphere, while it is destroyed in the lower troposphere and at the surface.

DISCUSSION

Here we will review the evidence in favor of the two hypotheses on the origin of tropospheric ozone and will discuss how our hypothesis fits into the picture. The evidence supporting the classical 'dynamical control' of tropospheric ozone is as follows:

1. The tropospheric mixing ratios of ozone at all latitudes and seasons in the NH increase with height [Chatfield and Harrison, 1977]. The net flux due to atmospheric mixing is always downward, indicating that ozone is injected from the stratosphere. Furthermore, the spring maximum in the ozone concentration in mid-latitudes always occurs first in the upper troposphere and propagates down to the surface with a time delay of about a month.

2. The enhancements of ozone in the troposphere have been found to coincide with stratosphere-troposphere exchange processes [Briggs and Roach, 1963; Penn, 1964; Berggren and Labitzke, 1966; Danielsen, 1968; Danielsen et al., 1970]. Seasonal variations of ozone also correlate with variations in the exchange processes between the stratosphere and troposphere [e.g., Chatfield and Harrison, 1977]. For example, variations of ozone have been observed to coincide with the variations of ^{90}Sr and ^7Be , which are of stratospheric origin [e.g., Fabian et al., 1968; Hussain et al., 1979].

3. There is a lack of clear diurnal variations in the clean tropospheric ozone concentrations, as would be expected if photochemistry controls the ozone level [Chatfield and Harrison, 1976; Fabian and Pruchniewicz, 1977; Singh et al., 1978]. However, this argument is weak because the current predicted photochemical lifetime for ozone is about 10 days [Chameides,

1978], which implies the diurnal variation should be only about 10%.

4. Recent general circulation model calculations [Mahman *et al.*, 1980; Gidel and Shapiro, 1980] predict that a larger downward flux of ozone from the stratosphere is expected in the NH. This is qualitatively consistent with the observations of larger tropospheric ozone amounts in the NH.

Arguments that support the 'photochemical control' of the tropospheric ozone are as follows:

1. The calculated ozone loss rate is about a factor of 4 larger than the estimated values of ozone flux from the stratosphere.

2. The increase of ozone in urban polluted air is an example of photochemical ozone production in the troposphere.

3. The ozone concentrations in the NH are higher than values in the SH, in spite of probable higher destruction rates at the surface in the NH due to the larger land area [Fishman *et al.*, 1979b]. This is consistent with the fact that anthropogenic NO_x emission is much higher in the NH.

Our ozone production hypothesis presented in the last section offers a consistent unification of the two seemingly contradictory hypotheses. Our proposed ozone production is mainly in the upper troposphere, with the ozone precursor (NO_x) being transported down from the stratosphere in a manner very similar to that of ozone itself [Levy *et al.*, 1980]. Therefore it is consistent with arguments 1, 2, and 4 of the 'dynamical control' theory, provided that there is no appreciable time delay between the NO_x injection and ozone production. The doubling time of ozone in our calculation is about 15 days, which is short in comparison with the time delay between the spring maxima in the upper troposphere and those in the lower troposphere in mid-latitudes. This doubling time also implies that the diurnal variation for ozone is 10% or less, thus satisfying argument 3 of the 'dynamical control' theory.

It is clear that our ozone production hypothesis automatically satisfies arguments 1 and 2 of the 'photochemical control' theory. With regard to argument 3, we note that the level of tropospheric ozone is probably controlled by photochemical production and destruction because they are significantly larger than the stratospheric flux and the surface destruction. In fact, even the 'low NO_x ' case shows the production to be comparable to the cross-tropopause flux (Figure 2). Since the calculated NO_x in the NH is about 1.8 times the value in the SH, our predicted ozone distribution in the NH is about 1.8 times larger than the value in the SH. This is about 50% larger than the asymmetry shown in the ozone data analyzed by Fishman *et al.* [1979b]. Recent measurements [Routhier *et al.*, 1980] support this higher asymmetry. However, there are too few data on the distribution of ozone in the SH to establish a clear picture of the asymmetry that exists between the two hemispheres.

Although the near balance between our calculated ozone production by NO_x in the upper troposphere and the photochemical loss of ozone in the lower troposphere suggests that there is no need for other ozone sources, it does not rule out sources such as the production by the near-surface NO_x [Chameides, 1978; Fishman *et al.*, 1979b]. The balance could, of course, be fortuitous because of the large uncertainties in our calculations. A prerequisite for the evaluation of the near-surface source of ozone is the knowledge of the NO_x distribution in the lower troposphere. KDML have estimated the boundary layer NO_x over the rural United States to be a few

tenths of a ppbv at the surface and decreases with a scale height of 2 km. If this NO_x distribution prevails over a significant portion of the globe, then according to the current understanding of photochemistry, the ozone production [Fishman *et al.*, 1979b] could be greater than the value we calculated in the last section. On the other hand, this near-surface ozone production should be negligible if this NO_x distribution is appropriate only over industrialized nations and there are negligible NO_x concentrations over the rest of the globe.

If indeed the tropospheric ozone production is dominated by the upper tropospheric NO_x , then it is important to look into the effect of the emissions of high flying subsonic aircraft. As was mentioned before, the emissions from subsonic aircraft can increase the upper tropospheric NO_x in the NH by about 40% as compared to the NO_x distribution of Figure 1. Hence for this case according to our calculations, the NH tropospheric ozone could already have increased by about 30%. This scales to be about a 3% increase in the total ozone column density. For comparison, the predicted ozone reduction for the year 1980 by the emission of CFCl_3 and CF_2Cl_2 is only about 2.5% [NASA Reference Publication 1049, 1979]. For the 'low NO_x ' case the calculated increase in the NH tropospheric ozone is about 15% to date.

Our calculations also show that about half of the increase (i.e., 7 to 15%) in the NH tropospheric ozone due to subsonic aircraft should have taken place during the period from 1968 to 1978. An increase of this magnitude should appear as a detectable trend in the ozone records of the ozonesonde stations from which tropospheric ozone observations have been made over the last 10 years or longer. Unfortunately, only nine stations in the NH have continuous data records for most of the last 12 years (see *Ozone Data for the World*, published by the Canadian Department of the Environment). We have examined the ozonesonde data from 1969 to 1976 for the Kagoshima, Sapporo, Tateno, Uccle, and Wallops Island stations; from 1968 to 1977 for the Hohenpeissenberg, Payerne, and Goose Bay stations; and from 1966 to 1977 for the Resolute station. We have excluded all surface ozone data to avoid the possible effects of industrial pollution and surface destruction. However, we note that the two clean surface stations (Mauna Loa and Barrow) that have made continuous ozone measurements since 1973 have shown little increase over the 6 years from 1973 to 1978 [Oltmans, 1980]. Among the nine ozonesonde stations, ozone increases have been found in all but the Tateno station, which shows about a 10% decrease over the 7-year observations. The average ozone increase for all the stations is 8%, with a 4% standard error of the mean. Detailed analysis of these data will be given by J. London *et al.* (manuscript in preparation, 1980). This result is consistent with the ozone increase between 2 and 8 km for the ozonesonde stations reported in NASA Reference Publication 1049 [1979], which is based on the analysis of Angell and Korshover [1979]. The increase is even more significant when we compare it with the decrease of about 20% in the tropospheric ozone found for the SH station at Aspendale during the period from 1965 to 1978. The possibility that the increase in the observed NH tropospheric ozone could be caused by changes in stratospheric ozone does not seem likely, since there were no obvious trends in the lower stratospheric ozone at these stations [Angell and Korshover, 1979].

There are no long-term data available to estimate how much of this increase in ozone is affected by natural variabilities of upper tropospheric ozone. The ozone increases

found in the ozonesonde data fall within our calculated range. It is interesting to note, however, that for the ozonesonde stations located in the north temperate zone where the air traffic is most concentrated, the observed ozone increase is lower than our calculated values for the standard NO_x case, but rather close to those we calculate for the 'low NO_x ' case. Given the uncertainties in both the calculations and ozonesonde data, we believe these ozone observations are not inconsistent with our proposed role of high-flying aircraft. More extensive measurements of tropospheric ozone and model calculations with realistic dynamics are needed to help resolve this problem.

SUMMARY

The previous measurements of KDML, in conjunction with the modeling works of Levy *et al.* [1980] and Mahlman *et al.* [1980], indicate strongly that the upper troposphere NO_x distribution is dominated by the stratospheric source. Because of efficient heterogeneous removal of NO_x , the near-surface anthropogenic NO_x emissions appear to be important only in the lower troposphere and probably only near industrialized regions. In this case the stratospheric source may even be important in determining the surface NO_x distribution in clean remote areas [Levy *et al.*, 1980].

The upper tropospheric NO_x acts as a catalytic precursor in the photochemical ozone production. With the current reaction rate coefficients we calculate that the photochemically produced ozone in the upper troposphere can be significantly greater than the ozone injected from the stratosphere. Hence we hypothesize that this upper tropospheric ozone source provides the primary origin of ozone in the natural troposphere. This source is probably also the largest one throughout the entire troposphere, except for those surface regions dominated by anthropogenic NO_x emissions. We have shown that our hypothesis offers a consistent unification of the two seemingly contradictory views of the origin of tropospheric ozone, i.e., the classical 'dynamical control' versus the 'photochemical control.'

High-flying subsonic aircraft may contribute significantly to the NO_x distribution in the NH upper troposphere. According to our calculations, the aircraft NO_x emissions already could have increased the NH tropospheric ozone by about 15 to 30%. Examination of the ozonesonde data in the NH over the period between 1969 and 1977 shows an increase of about 8%. This is not inconsistent with our calculated value for the same period. However, if this apparent trend is real, considerably more work would be required before a specific cause could be assigned.

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