Potential Ozone Column Increase Resulting from Subsonic and Supersonic Aircraft NO_x Emissions

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A two-dimensional time-dependent photochemical model developed to describe the meridional distribution of the important trace species in the stratosphere and troposphere continuously throughout the year has been used to estimate the effect on ozone of NO_x emissions, supplied by the Federal Aviation Administration (FAA), from a combined fleet of supersonic and subsonic aircraft projected to be operational in 1990. The net effect of this combined fleet is to increase the atmospheric ozone level slightly (maximum local column change $\leq 1.5\%$) for the given chemical system. High-altitude injections of NO_x result in a decrease in the ozone column above approximately 15-16 km, as predicted in numerous previous studies. However, this reduction is smaller than the increase in the ozone column resulting from the production of ozone through the methane-smog chemical cycle resulting from the large amount of NO_x deposited at lower altitudes (L 13 km). Relative latitudinal and seasonal variations of the ozone change are large, being greatest in the fall and least in the late spring and summer seasons. Since the changes in the ozone column are sensitive to the methane-smog reaction system, more information regarding the rates at which these reactions proceed is needed to affirm the present initial estimates.

Introduction

THROUGHOUT this decade there has been concern regarding the effect of various activities of man on the Earth's protective ozone shield. This concern was initiated by the work of Crutzen[1] and Johnston[2] which indicated that oxides of nitrogen (NO_x) deposited in the atmosphere could catalytically reduce the concentration of ozone, resulting in an increase of potentially harmful ultraviolet radiation reaching the Earth's surface. Since then, a number of national programs have been formulated to investigate the chemical and hydrodynamic structure of the natural atmosphere and the effect of pollutants on the stratosphere and troposphere.

Initially, the major concern regarding possible ozone reduction focused on the catalytic destruction by oxides of nitrogen present in the exhaust emissions of supersonic aircraft. This was the primary concern, since supersonic aircraft cruise at high altitudes, where the atmospheric residence time is on the order of a few years. Thus, a large fleet of these aircraft would emit a substantial amount of NO_x, which would be present for a long period of time, during which it would destroy ozone. The Department of Transportation's Climatic Impact Assessment Program (CIAP) was organized to address this NO_x question specifically and to attempt to arrive at an answer. During the program, various photochemical models of the stratosphere were developed to calculate the distribution of important trace chemical species in the atmosphere. Included were time-dependent one-, two-, and three-dimensional photochemical models. Some of the primary modeling results were presented in a review article by Hidalgo.[3] Since then, improvements in some of the models have increased their ability to describe atmospheric distributions of species in the natural atmosphere. Recent estimates of aircraft fleet sizes projected to be operational in 1990, provided by the FAA's High Altitude Pollution Program (HAPP), show a significant reduction in the estimated size of the supersonic aircraft fleet as compared to the upper-bound maximum growth forecasts used in CIAP calculations, a significant increase in the subsonic fleet, and a broad-based latitudinal variation in aircraft flight traffic density. These projections, coupled with the fact that the latitudinal variation of ozone in the natural atmosphere is significant and the population ultimately to be affected by any resultant atmospheric change also is distributed in a highly latitude-dependent manner, make it imperative that a model that considers the latitudinal as well as the altitude variation be utilized to investigate the scope of this problem. A three-dimensional model[4] presently is computer-limited to simulation of the effects of specified NO_x and HO_x distributions on the chemistry and dynamics of ozone, where the distribution of NO_x and HO_x must be obtained from another source. However, a time-dependent two-dimensional model of the atmosphere (latitude and altitude) can take into account all of the presently agreed important chemistry, include the effects of meridional transport by mean winds and large-scale turbulent eddies, and consider latitudinal variations of the injection of pollutants as well as the spatial and time-dependent variation of the location of the sun. Some recent applications of time-dependent two-dimensional models to the prediction of the effect of aircraft NO_x emissions on ozone include Crutzen,[5] Borucki et al.,[6] and Hidalgo and Crutzen.[7] Crutzen[5] and Borucki et al.[6] considered only the problem of emissions from supersonic aircraft, whereas Hidalgo and Crutzen[7] considered separate injections from individual groups of supersonic and subsonic aircraft at three altitude regimes. Reference 7 included the methane-smog cycle and showed that injection of NO_x at low altitudes (≤ 13 km) may result in an increase of ozone rather than a decrease.

Considering the recent FAA-supplied projections of the NO_x emissions from a combined supersonic and subsonic fleet (Table 1) and the fact that approximately 80% of the emissions are from low-flying subsonic aircraft, it is imperative that any modeling estimates consider the methane-smog cycle in evaluating the overall effect of NO_x emissions on atmospheric ozone.

This paper considers a time-dependent two-dimensional phenomenological photochemical model of the atmosphere applied to the problem of estimating the effect on ozone of exhaust NO_x emissions from a more realistic estimate (upper bound) of a combined fleet of subsonic and supersonic aircraft projected to be operational around the year 1990. A description of the model is included, together with a

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discussion of the ability of the model to predict the distribution of trace species in the natural atmosphere.

Model

The model is a time-dependent phenomenological photochemical model of the atmosphere in which the hydrodynamic variables (mean atmospheric density, temperature, turbulent diffusion coefficients, and mean meridional winds) either are specified from observations or are obtained indirectly from observations as a function of time during the year and used to solve the system of species conservation equations for the meridional distribution of trace species throughout the year. The formulation of the model, discussed in Widhopf and Taylor[10] and Widhopf,[11] basically is designed to examine relatively small changes in the ozone concentration as a function of the time of year throughout the meridional plane, since any resultant changes in the species concentration occurring as a result of the introduction of a pollutant are not coupled back to the atmospheric dynamics or temperature distributions.

The governing species conservation equation is derived following the general procedure outlined by Reed and German[12] for representing the turbulent transport flux due to large-scale eddies. In the meridional plane this equation, written in terms of the mass mixing ratio, is of the form

$$\frac{\partial \rho Y_i}{\partial t} + \frac{\partial \rho w Y_i}{\partial z} + \frac{1}{\cos\phi}\,\frac{\partial \rho v Y_i \cos\phi}{r\partial\phi} = \frac{\partial}{r\partial\phi}\left\{\rho k_{\phi z}\frac{\partial Y_i}{\partial z}\right.$$
$$\left. + \rho k_{\phi\phi}\frac{\partial Y_i}{r\partial\phi}\right\} + \frac{\rho}{r}\left\{(2k_{zz} - k_{\phi z}\tan\phi)\frac{\partial Y_i}{\partial z} + (2k_{z\phi} - k_{\phi\phi}\tan\phi)\right.$$
$$\left. \times \frac{\partial Y_i}{r\partial\phi}\right\} + \frac{\partial}{\partial z}\left\{\rho k_{zz}\frac{\partial Y_i}{\partial z} + k_{\phi z}\frac{\partial Y_i}{r\partial\phi}\right\} + \omega_i + S_i;\ i = 1,2\ldots \quad (1)$$

where Y_i is the mass mixing ratio, ρ_i/ρ, of the ith chemical species; ρ is the local mean atmospheric density; t is the temporal variable; $r = z + R_e$, where R_e is the mean radius of the Earth and z is the altitude measured from and normal to the Earth's surface; ϕ is the latitude; ω_i is the photochemical rate of production/depletion of the ith species; and S_i is the local source/sink effect. The components of the tensor $k_{\alpha\beta}$ represent the diffusion coefficient in the respective directions arising from large-scale eddy motions, whereas v and w are the components of the mean circulation in the meridional and vertical directions, respectively. This equation is solved for each of the trace species considered.

Chemical Model

The chemical system that is considered in this investigation includes the following species: $O(^1D)$, $O(^3P)$, O_2, O_3, NO, N_2O, NO_2, OH, H_2O, HO_2, H_2O_2, HNO_3, N, H, N_2, CO, and CH_4. The distribution of H_2O in the stratosphere is assumed constant (2.5 ppmm), as interpreted from the studies of Mastenbrook,[13] whereas in the troposphere it is specified using a relative humidity formulation.[14] Smog-type reactions initiated by the oxidation of methane by OH, which may be important in the lower regions of the atmosphere, also are included.[15] These reactions also include the species CH_3, CHO, CH_2O, CH_3O, CH_3O_2, and CH_3O_2H. The specific reaction system and the associated reaction rate coefficients used in this investigation are tabulated in Table 2. This chemical system is based essentially on the one recommended by the CIAP Chemical Panel, as outlined in the first and third volumes of the CIAP monographs,[16,17] with additional reactions and updated reaction rates as outlined in the National Academy of Sciences (NAS) report on halocarbons[18] and evaluated by Wuebbles et al.[19]

The computation of the absorption of solar radiation is an integral step in determining the chemical structure of the atmosphere, since many of the important reactions in the atmosphere are photochemical processes. Using the solar flux data compiled by Ackerman,[20] the diurnally averaged local photodissociation rates J_i are calculated at every location in the atmosphere at each time step by a technique developed by Kramer and Widhopf.[21] The time variation of the solar zenith angle with latitude and solar declination is included in the determination of J_i. The absorption cross sections utilized to compute J_i for the various species are outlined in Widhopf.[11].

The effect of chlorine in the atmosphere was not included in this investigation. From NAS studies,[18] the inclusion of chlorine should attenuate the effect of NO_x destruction of ozone due to the formation of $ClONO_2$. N_2O_5 and NO_3, which are produced predominantly during periods of darkness, have not been included in the present study. Some NO_x can be tied up in these compounds, reducing the effect of NO_x reduction on ozone predominantly in regions where there are long periods of darkness, such as the winter polar regions. Since the chemistry of both of these compounds is

Table 1 1990 worldwide aircraft NO_x emissions, high estimates (kg/yr)[a]

	ALTITUDES - km												
Latitude	6-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15	15-16	16-17	17-18	18-19	Total
N 60+	3.35E6	3.03E6	1.43E7	1.31E7	1.46E7	1.31E6	9.99E5	4.06E5	1.72E6	2.59E6	2.10E6	1.43E6	5.894E7
50-60	2.15E7	2.59E7	9.44E7	1.06E8	9.09E7	8.26E6	3.72E6	2.12E6	6.57E6	1.03E7	8.06E6	3.71E6	3.814E8
40-50	7.60E7	8.70E7	1.79E8	2.79E8	1.62E8	2.48E7	4.59E6	2.09E6	4.17E6	6.96E6	5.46E6	2.36E6	8.334E8
30-40	7.74E7	9.20E7	1.67E8	3.09E8	1.72E8	2.97E7	3.11E6	1.74E6	1.30E6	2.73E6	2.07E6	8.63E5	8.589E8
20-30	2.61E7	2.83E7	6.74E7	1.02E8	6.92E7	8.73E6	1.55E6	1.20E6	8.06E5	1.90E6	1.71E6	4.67E5	3.094E8
10-20	1.11E7	1.18E7	2.65E7	4.28E7	3.99E7	3.67E6	4.74E5	1.54E5	3.24E5	5.38E5	4.22E5	1.71E5	1.379E8
0-10	4.80E6	5.14E6	1.50E7	1.82E7	1.36E7	1.26E6	1.73E5	0	2.91E5	4.08E5	3.44E5	1.63E5	5.938E7
10-0	3.31E6	3.77E6	1.22E7	1.38E7	1.09E7	8.65E5	1.38E5	0	3.01E5	4.22E5	3.56E5	1.65E5	4.623E7
20-10	2.74E6	3.21E6	1.14E7	1.52E7	1.15E7	1.11E6	3.15E5	1.32E5	1.10E5	2.19E5	1.58E5	7.52E4	4.617E7
30-20	3.67E6	4.01E6	9.47E6	1.37E7	8.66E6	9.31E5	5.10E4	0	9.85E4	1.38E5	1.16E5	6.63E4	4.091E7
40-30	4.01E6	4.63E6	6.62E6	1.18E7	6.14E6	1.21E6	8.64E4	5.16E4	1.56E4	4.74E4	2.84E4	6.22E3	3.464E7
50-40	2.36E5	3.05E5	3.19E5	8.28E5	4.46E5	9.29E4	1.5 E1	0	0	0	0	0	2.227E6
60-50	4.77E4	3.79E4	2.99E4	2.52E4	1.04E4	1.45E3	0.97	0	0	0	0	0	1.526E5
S 60+	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	2.343E8	2.691E8	6.036E8	9.255E8	5.999E8	8.197E7	1.521E7	7.894E6	1.571E7	2.625E7	2.082E7	9.477E6	2.810E9

[a] Oliver, R. C.[8] and A. D. Little, Inc.[9]

not known completely, the magnitude of their effects is tentative. The effects of these constituents are presently being included and will be investigated in the future. Their exclusion should not affect the overall trend of the present results.

Boundary Conditions

The computational domain considered in this investigation extends from the north to the south pole, with a 10° meridional resolution and from the surface to 50 km, with a vertical resolution of $\Delta z = 1$ km from the surface to 35 km and $\Delta z = 2.5$ km up to the upper boundary. At the polar regions, a zero latitudinal flux is assumed.

A fixed ozone concentration [$5(10)^{11}$ molecules/cm^3] was imposed at the lower boundary, as interpreted from the meridional distributions compiled by Dütsch[22] and Hering and Borden[23-26] (as summarized in the data compilation of Wu[27]). The concentration of N_2O at the lower boundary was prescribed as an average value (0.481 ppmm) interpreted from the tropospheric measurements of Schütz et al.[28] and Goldman et al.[29] The latitudinal variation of the mass mixing ratio of CO at the surface was interpreted from the measurements of Seiler.[30] The mass mixing ratio of CH_4 (0.75 ppmm) at the lower boundary was specified from the measurements of Ehhalt et al.[31] Injection of NO and NO_2 resulting from the anthrophotogenic activities was specified at the lower boundary as interpreted from the estimates of Robbins and Robinson.[32] The species $O(^3P)$, $O(^1D)$, OH, HO_2, N, and H were taken to be in photochemical equilibrium at the lower boundary because of their relatively short lifetimes, whereas HNO_3, NO_2, NO, and H_2O_2 were removed from the troposphere by simulating atmospheric rainout/washout. HNO_3 was removed at the average rates defined by Junge,[33] whereas NO_2, NO, and H_2O_2 were assumed to be removed at one-tenth this rate.

The species $O(^3P)$, $O(^1D)$, O_3, OH, HO_2, H_2O_2, N, and H were assumed to be in photochemical equilibrium at the upper boundary, whereas the mass mixing ratios of NO_2, N_2O, CH_4, CO, and HNO_3 were continued analytically to the upper boundary by a second-order extrapolation in space and time described by Widhopf[11] and Widhopf and Taylor.[10] This extrapolation allows the used of centered spatial differencing at this boundary while also eliminating the necessity of specifying a boundary condition for these species at this location. It is an accurate and stable method of evaluating conditions at computational boundaries[34] when the physical mechanisms interior to the computational domain govern the boundary value. This is the case for N_2O, NO_2, CH_4, CO, and HNO_3, which are being transported up into the higher regions of the stratosphere.

Transport Data

The meridional distributions of both the mean density and temperature were specified using the data obtained from 10 years of observations which were analyzed and compiled by Louis.[35,36] These averaged data are specified from the surface to 68 km for the entire meridional plane and for each of the four seasons.

Luther[37,38] has analyzed the heat-transfer, temperature, and wind variance data of Oort and Rasmussen[39] using the procedure outlined by Reed and German[12] for defining the components of the anisotropic turbulent eddy diffusivity tensor. The three components $k_{\phi\phi}$, $k_{\phi z}$, and k_{zz} are specified for the northern hemisphere from the surface to 60 km. Values for the components of the diffusivity tensor in regions where observational data were not available were obtained by

Table 2 Chemical reactions and rate coefficients

	REACTION	RATE COEFFICIENT[a]		REACTION	RATE COEFFICIENT[a]
1.	$O(^3P) + O_3 \rightarrow 2O_2$	$1.9(10)^{-11}\exp[-2300/T]$	26.	$NO + h\nu \rightarrow N + O(^3P)$	J_{26}
2.	$O_2 + h\nu \rightarrow 2O(^3P)$	J_2	27.	$N + O_2 \rightarrow NO + O(^3P)$	$1.02(10)^{-14}T\exp[-3130/T]$
3.	$O_3 + h\nu \rightarrow O(^3P) + O_2$	J_3	28.	$N + NO \rightarrow N_2 + O(^3P)$	$2.7(10)^{-11}$
4.	$NO_2 + h\nu \rightarrow O(^3P) + NO$	J_4	29.	$N + NO_2 \rightarrow NO + NO$	0.0
5.	$O(^3P) + O_2 + M \rightarrow O_3 + M$	$1.07(10)^{-34}\exp[510/T]$	30.	$N_2 + O(^1D) + M \rightarrow N_2O + M$	$2.8(10)^{-36}$
6.	$O(^3P) + NO_2 \rightarrow O_2 + NO$	$9.1(10)^{-12}$	31.	$NO_2 + N \rightarrow N_2O + O(^3P)$	$1.4(10)^{-12}$
7.	$O_3 + NO \rightarrow O_2 + NO_2$	$9(10)^{-13}\exp[-1200/T]$	32.	$O(^1D) + H_2O \rightarrow OH + OH$	$2.32(10)^{-10}$
8.	$O_3 + NO_2 \rightarrow O_2 + NO_3$	$1.23(10)^{-13}\exp[-2470/T]$	33.	$O(^1D) + CH_4 \rightarrow OH + CH_3$	$1.38(10)^{-10}$
	$\lvert NO_3 + h\nu \rightarrow 2/3[NO_2 + O(^3P)] + 1/3[NO + O_2]\rvert$		34.	$OH + O(^3P) \rightarrow O_2 + H$	$4.2(10)^{-11}$
9.	$O_3 + OH \rightarrow O_2 + HO_2$	$1.6(10)^{-12}\exp[-1000/T]$	35.	$H + O_2 + M \rightarrow HO_2 + M$	$2.08(10)^{-32}\exp[290/T]$
10.	$NO + HO_2 \rightarrow OH + NO_2$	$2.3(10)^{-13}$	36.	$H + O_3 \rightarrow OH + O_2$	$1.23(10)^{-10}\exp[-562/T]$
11.	$O(^3P) + H_2O \rightarrow OH + OH$	0.0	37.	$NO + O(^3P) + M \rightarrow NO_2 + M$	$3.96(10)^{-33}\exp[940/T]$
12.	$OH + NO_2 + M \rightarrow HNO_3 + M$	$\frac{2.76(10)^{-13}\exp[880/T]}{1.166(10)^{18}\exp[220/T] + [M]}$	38.	$OH + OH \rightarrow H_2O + O(^3P)$	$1(10)^{-11}\exp[-550/T]$
13.	$HNO_3 + h\nu \rightarrow OH + NO_2$	J_{13}	39.	$N + O_3 \rightarrow NO + O_2$	$5.7(10)^{-13}$
14.	$HO_2 + O_3 \rightarrow OH + O_2 + O_2$	$1(10)^{-13}\exp[-1250/T]$	40.	$HO_2 + h\nu \rightarrow OH + O(^3P)$	J_{40}
15.	$HO_2 + O(^3P) \rightarrow OH + O_2$	$3(10)^{-11}$	41.	$OH + CH_4 \rightarrow H_2O + CH_3$	$2.36(10)^{-12}\exp[-1710/T]$
16.	$OH + HO_2 \rightarrow H_2O + O_2$	$2(10)^{-11}$	42.	$2OH + M \rightarrow H_2O_2 + M$	$2.5(10)^{-33}\exp[2500/T]$
17.	$OH + HNO_3 \rightarrow H_2O + NO_3$	$8.9(10)^{-14}$	43.	$H_2O_2 + O(^3P) \rightarrow OH + HO_2$	$2.75(10)^{-12}\exp[-2125/T]$
	$\lvert NO_3 + h\nu \rightarrow 2/3[NO_2 + O(^3P)] + 1/3[NO + O_2]\rvert$		44.	$CO + OH \rightarrow H + CO_2$	$\log_{10}K = -12.95 + 3.94(10)^{-4}T$
18.	$H_2O_2 + h\nu \rightarrow OH + OH$	J_{18}	45.	$CH_2O + h\nu \rightarrow H_2 + CO$	J_{45}
19.	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$1.7(10)^{-11}\exp[-910/T]$	46.	$CHO + O_2 \rightarrow HO_2 + CO$	$5(10)^{-12}$
20.	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.7(10)^{-11}\exp[-500/T]$	47.	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$2.6(10)^{-31}$
21.	$O_3 + h\nu \rightarrow O_2 + O(^1D)$	J_{21}	48.	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$1.5(10)^{-12}\exp[-500/T]$
22.	$O(^1D) + M \rightarrow M + O(^3P)$	$2.2(10)^{-11}\exp[92/T]$	49.	$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$	$3.0(10)^{-11}\exp[-500/T]$
23.	$N_2O + h\nu \rightarrow N_2 + O(^1D)$	J_{23}	50.	$CH_3O_2H + h\nu \rightarrow CH_3O + OH$	J_{50}
24.	$N_2O + O(^1D) \rightarrow N_2 + O_2$	$5.7(10)^{-11}$	51.	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$1.6(10)^{-13}\exp[-3300/T]$
25.	$N_2O + O(^1D) \rightarrow NO + NO$	$5.7(10)^{-11}$	52.	$CH_2O + h\nu \rightarrow H + CHO$	J_{52}
			53.	$CH_2O + OH \rightarrow H_2O + CHO$	$1.4(10)^{-11}$

[a] Units in sec^{-1}, cm^3 sec^{-1} and cm^6 sec^{-1} for unimolecular, bimolecular and trimolecular reactions.

Luther by extrapolation, using the results of Wofsy and McElroy[40] and Newell et al.[41] These coefficients are specified for each month and initially were used to parameterize the components of the turbulent diffusivity tensor. The values for the southern hemisphere were obtained by reflecting the northern hemispheric values, shifted by six months, and applying them appropriately in the southern hemisphere. However, in testing these transport coefficients against the dispersion of inert tracers in the atmosphere, they were found to be not totally adequate[11] and were improved by numerical experimentation described in a subsequent section.

The mean meridional circulation was obtained from the work of Louis et al.[35,36] who calculated the circulation patterns by solving the continuity and energy equations using compiled observations of the local meridional temperature distributions and heat-transfer rates. These are the same data sources used to define the thermal structure of the atmosphere, as previously discussed. The circulation patterns are specified for the entire meridional plane for each season from the surface to 50 km. In order to insure that total mass conservation was satisfied, the vertical wind component obtained by Louis was specified and the meridional component calculated from the global continuity equation. In order that smooth variations of all of these parameters would exist throughout the year, the temperature, density, and transport parameters (k_{zz}, $k_{\phi z}$, $k_{\phi\phi}$, and w) were specified at each location by temporally fitting the data previously described using a five-term Fourier series.

Numerical Scheme

An accurate (second-order in space and time) time-dependent numerical finite-difference scheme developed by Widhopf and Victoria,[42] which is explicit in space and implicit in time and efficiently overcomes the "stiff" nature of the chemical system, is used to solve the governing individual species conservation equations. Details of the scheme as applied to this problem are discussed in Widhopf[11] and Widhopf and Taylor.[10]

Inert Tracer Studies

Previous model calculations[11] using the turbulent diffusion coefficients of Luther and the mean meridional winds of Louis resulted in an inadequate simulation of the atmospheric dispersion of carbon-14 and concentration of ozone at high latitudes. Therefore, modifications to these transport coefficients were made using the carbon-14 data as a guide. This excess atmospheric carbon-14 resulted from nuclear weapon detonations in 1961-1962 at approximately 70°N (Telegadas[43] and Johnston et al.[44]). The results of these simulations at 30°N for a period of approximately 3 yr, using the original transport of Luther and Louis and the improved transport developed by Glatt and Widhopf,[45] are shown in Fig. 1. It is evident from this figure that the improved model transport very adequately simulates the dispersion of carbon-14 over a number of years. Although not shown here, the model underpredicts the carbon-14 in the altitude regime of 9-13 km at the high latitudes.

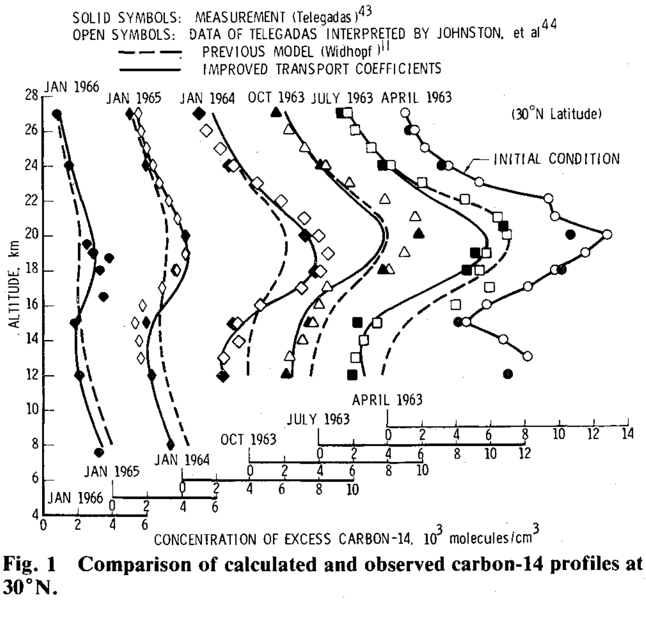

Fig. 1 Comparison of calculated and observed carbon-14 profiles at 30°N.

Since the carbon-14 data were used as a guide for transport modifications, independent tests were performed by calculating the dispersion of other atmospheric radioactive debris, namely, tungsten-185 and Zr-95, using the same improved model transport. Both of these tracers resulted from atmospheric nuclear detonations: tungsten-185 from a detonation at approximately 11°N in the summer of 1958,[46] and Zr-95 from a detonation at approximately 40°N in the summer of 1967.[47] Thus, these three simulations cover the northern hemisphere fairly adequately, and subsequent testing against the atmospheric movement of these tracers should be a good test of the model meridional transport. The results of the computations are shown in Figs. 2 and 3. For

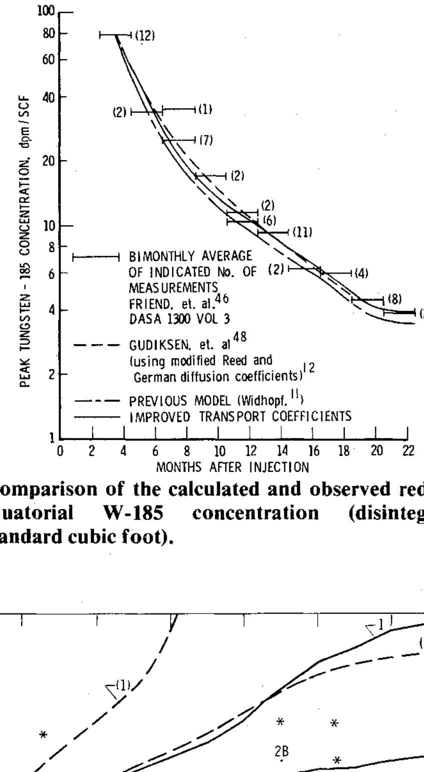

Fig. 2 Comparison of the calculated and observed reduction of the peak equatorial W-185 concentration (disintegrations per minute/standard cubic foot).

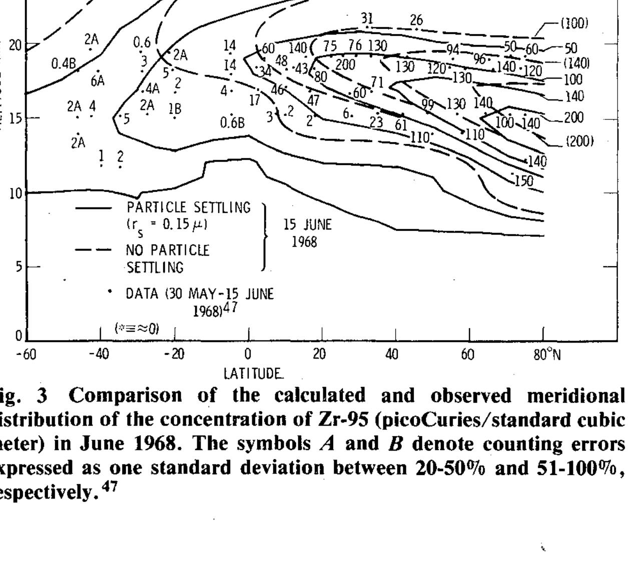

Fig. 3 Comparison of the calculated and observed meridional distribution of the concentration of Zr-95 (picoCuries/standard cubic meter) in June 1968. The symbols *A* and *B* denote counting errors expressed as one standard deviation between 20-50% and 51-100%, respectively.[47]

tungsten-185, the agreement is very good, both in the decay of the equatorial maximum concentration (Fig. 2) and in the altitude-time history of this maximum concentration. The agreement of the calculated results and the measurements was good for the original transport; however, the agreement was even better using the improved transport. In order to simulate properly the time variation of the atmospheric burden of Zr-95, which is a particulate, it was found necessary to account for particle settling.[48] The data for the period June 1968, along with the corresponding numerical results for the cases where particle settling was neglected and where the settling of particles was approximated using a mean particle radius of 0.15μ, are shown in Fig. 3. For no particle settling, the agreement with the available measurements below 20 km is relatively good, but above 20 km it is poor. Corresponding comparison of the time variation of the total atmospheric burden also was shown to be poor. However, when particle settling was accounted for in a parametric way ($r_s = 0.15\mu$ and $\rho_s = 6.44$ g/cm^3), the agreement with data is good in both respects.

These comparisons should be interpreted with a realization that the data base is limited and has implicit measurement errors due to instrumentation and spatial and temporal frequency of the measurements, among other reasons. However, because of the necessarily empirical nature of the two-dimensional transport, these types of comparisons provide a basis with which to test the model transport without including chemical effects (as do tests against the distribution of O_3, N_2O, CH_4, etc.), which have their own inherent inaccuracies and unknowns. The availability of more data of this type, as well as additional tests, will allow for a further refinement of the model transport in the future.

Natural Atmosphere

Before any atmospheric model can be used to investigate the effect of a particular pollutant on the chemical structure of the atmosphere, it *must* be able to reproduce realistically the seasonal (monthly) variation of the ozone distribution in the natural atmosphere, as well as the distribution of other trace species. In fact, this can be considered as another test of the model transport, as well as the chemistry. In this regard, the model was run for a period of 7 yrs using the outlined chemical model, transport parameters, and boundary conditions. The model reached a periodic yearly variation in about 4 yrs of simulation, with an average variation in the

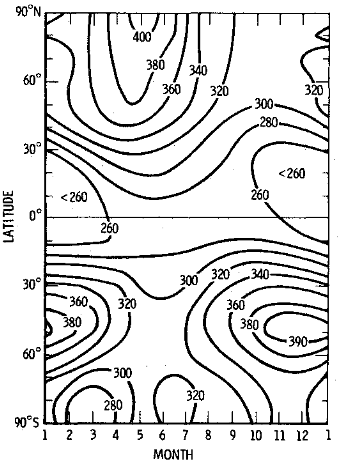

Fig. 4a Calculated monthly variation of the total ozone column as a function of altitude (m-atm-cm).

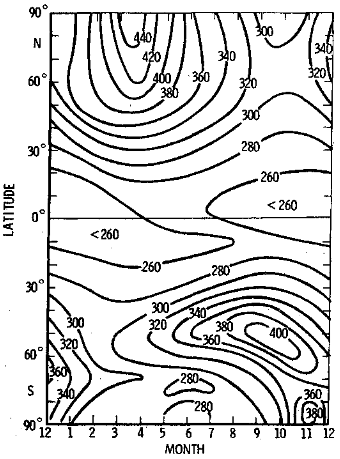

Fig. 4b Observed monthly variation of the total ozone column as a function of latitude (m-atm-cm).[22,49]

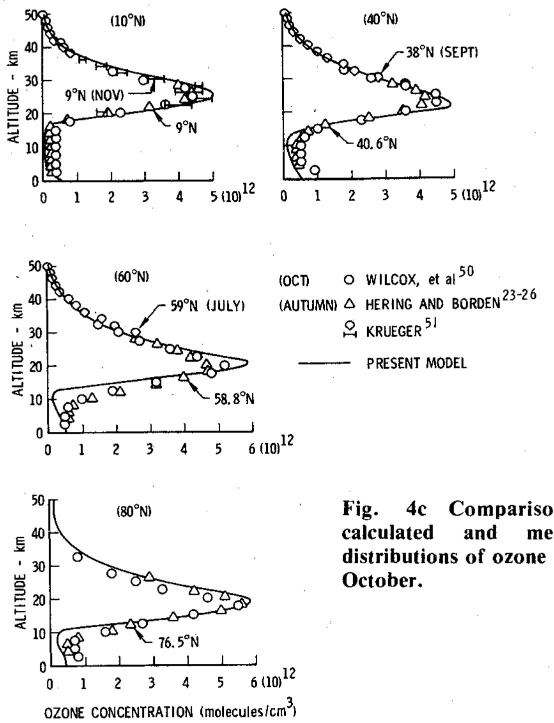

Fig. 4c Comparison of calculated and measured distributions of ozone during October.

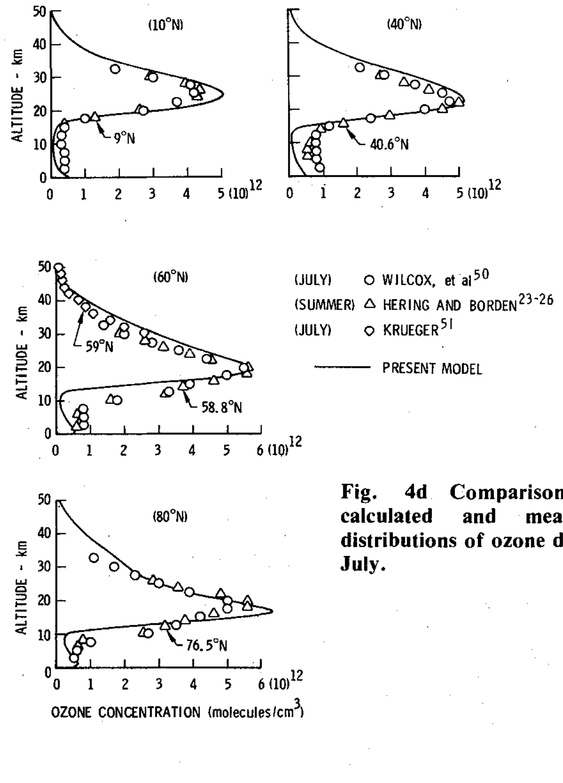

Fig. 4d Comparison of calculated and measured distributions of ozone during July.

ozone column of approximately 0.1%. The results are shown in Figs. 4a-4d. These figures include a comparison of the monthly variation of the ozone column with observations for the northern and southern hemispheres (Figs. 4a and 4b) and a comparison of individual ozone profiles in the northern hemisphere at various latitudes during October (Fig. 4c) and July (Fig. 4d).

As can be seen, the reproduction of the observed ozone column variation is very good in the northern hemisphere, with a maximum error of approximately 9% during the spring season at very high latitudes. The model adequately simulates the variation of the ozone column in the southern hemisphere.

The vertical ozone profiles are seen to be in good agreement with available data except generally below 14 km. A similar feature was found in the inert tracer studies between 13 and 9 km, and improvement in this area presently is being sought. The magnitude and altitude of the ozone peaks are well reproduced in all months. Calculated distributions of NO, NO_2, N_2O, HNO_3, CH_4, CO, and OH are in relatively good agreement with available measurements summarized and/or reported by Ackerman,[52] Anderson,[53] Ehhalt et al.,[31] Goldman et al.,[29] Schütz et al.,[28] and Seiler,[30] among others.[54]

Atmosphere Perturbed by NO_x Emissions

Shown in Table 1 is an estimate (upper bound) supplied by the FAA regarding the NO_x emissions from a combined fleet of subsonic and supersonic aircraft projected to be operational in 1990. This table includes emissions from present subsonic-type aircraft that cruise at nominally 9-11 km, advanced subsonic aircraft that will cruise in the altitude range of approximately 12.5-14.5 km, and supersonic aircraft of the Concorde-Tupolev type that cruise at nominally 18 km. These emission levels correspond to approximately 140 Concorde-Tupolev-type supersonic aircraft and approximately 10,000 present and advanced types of supersonic aircraft. (More details regarding the emission levels are contained in Ref. 8.) As can be seen, the variation of the NO_x emissions with altitude and latitude is very large. Estimates of the seasonal variations were not made; thus, these emissions were distributed uniformly throughout the year at the indicated locations. The areas of high NO_x injection cover the more populated industrial regions in the northern hemisphere from 20°-60°N latitude. The major portion of emissions (about 80%) results from the subsonic fleet and is deposited mainly at altitudes between 9 and 13 km. The total amount of NO_x emissions from the combined fleet is 2.81 $(10)^9$ kg/yr.

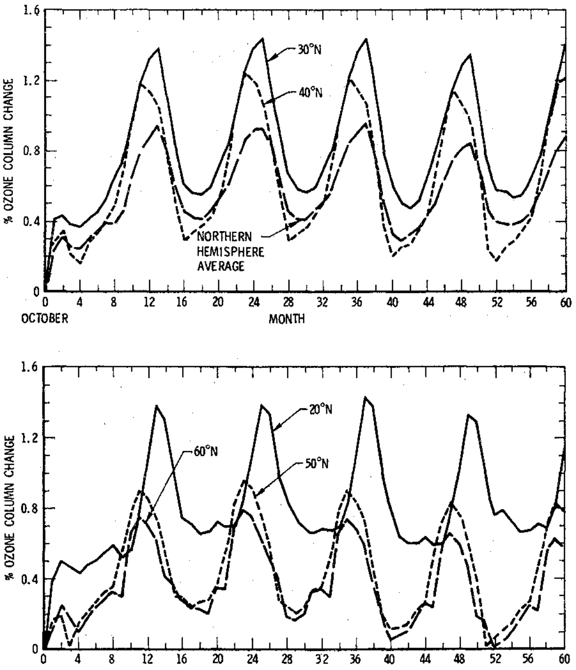

Fig. 5 Calculated temporal ozone change resulting from aircraft NO_x emissions from a combined subsonic and supersonic fleet projected to be operational in 1990, as described in Table 1.

The natural atmosphere calculation previously described was used as a starting condition (converged to 0.1% in ozone column) from which both the natural atmosphere and perturbed atmospheric calculations were continued for an additional 5 yrs. This procedure was followed in order to improve the sensitivity of the calculation by reducing any differences in the natural and perturbed atmospheric results which may arise due to incomplete convergence of the natural atmosphere. The results are shown in Fig. 5, which depicts the total ozone column change with time at various latitudes in the northern hemisphere over a 5-yr period starting in October. As can be seen, there is an overall increase in ozone as a result of the introduction of the NO_x emissions from this combined aircraft fleet. This, at first, seems to be a contradiction to the CIAP findings,[55] which concluded that ozone would be reduced because of aircraft NO_x emissions for both subsonic and supersonic aircraft; however, it should be remembered that in CIAP, methane-smog reactions were not included, and, thus, the possibility of ozone production due to NO_x emissions was not considered in model calculations of NO_x effects on ozone. A careful examination of the current results show a decrease in ozone column above approximately 15-16 km, in agreement with previous CIAP study trends, whereas below this altitude regime the NO_x emissions tend to increase the ozone concentration. At any given altitude, the calculated change in the corresponding overhead ozone column is less than a few percent. For the case under investigation, the major portion of the NO_x is injected at altitudes lower than 13 km, where the methane-smog chemistry can and does lead to an increase in ozone, and the net result of the combined fleet for this chemical system is a slight increase in ozone column, with a very large seasonal and latitudinal variation.

In order to understand the physical mechanisms that cause the resultant changes in ozone, various chemical cycles that are occurring in the atmosphere must be investigated. As proposed by Crutzen[1] and Johnston,[2] ozone is destroyed through the following catalytic cycle (cycle I):

$$\text{R6:}\quad NO_2 + O \rightarrow NO + O_2$$

$$\text{R7:}\quad NO + O_3 \rightarrow NO_2 + O_2$$

which results in a net reduction of O_3, whereas the net concentration of $NO + NO_2$ is not reduced similarily. This cycle occurs to some degree throughout the atmosphere, together with the destruction of ozone due to the presence of HO_x (see list of reactions in Table 2).

Analysis of the numerical results shows that in the troposphere the methane-smog reactions are important in determining the ozone concentration. When the smog reactions are considered, the following chain is found to be important in producing ozone (cycle II):

$$\text{R10:}\quad HO_2 + NO \rightarrow OH + NO_2$$

$$\text{R4:}\quad NO_2 + h\nu \rightarrow NO + O(^3P)$$

$$\text{R5:}\quad O(^3P) + O_2 + M \rightarrow O_3 + M$$

The initiation of cycle II occurs predominantly through the following chain (cycle III):

$$\text{R41:}\quad CH_4 + OH \rightarrow CH_3 + H_2O$$

$$\text{R47:}\quad CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

R49: $CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$

R50: $CH_3O_2H + h\nu \rightarrow CH_3O + OH$

R51: $CH_3O + O_2 \rightarrow CH_2O + HO_2$

R45: $CH_2O + h\nu \rightarrow CO + H_2$

R44: $CO + OH \rightarrow H + CO_2$

R35: $H + O_2 + M \rightarrow HO_2 + M$

where R35 is the major producer of HO_2. Cycles II and III are similar to those proposed by Crutzen.[15] Cycles II and III can be important in the troposphere, whereas cycle I is most important in the stratosphere. These cycles compete with each other and result in the distribution of O_3 and NO_x present in the natural atmosphere.

Here it should be pointed out that the methane-smog chemical system and rates at which these reactions proceed are not that well known and in some cases have had to be estimated. Thus, the effect shown here is somewhat preliminary and points to the need for more work regarding this important chemical system. Also, recent work by Duewer et al.,[56] shows the sensitivity of model predictions to the HO_x chemical system and rates that also are not known to a sufficient degree. This can have an impact on the overall result for the calculation of the effect of the introduction of a pollutant but, with the exception of the troposphere, should not affect significantly the prediction of the distribution of ozone in the natural atmosphere.

In the atmosphere perturbed by aircraft NO_x emissions, the injected NO_2 comes into immediate equilibrium with NO. The NO deposited and eventually transported to altitudes above approximately 15-16 km catalytically reduces O_3 primarily through cycle I. Below this altitude regime, NO also catalytically reduces O_3 through this cycle; however, ozone also is produced through cycles II and III. Since most of the NO_x is deposited by subsonic aircraft cruising at low altitudes (≤ 13 km), the result of the release of these emissions in the atmosphere is a decrease in ozone above approximately 15-16 km and an increase in ozone concentration below, resulting for this chemical system in a net small increase in ozone as depicted. The magnitude and sign of the net result are, of course, dependent on the distribution of the NO_x emissions with altitude and latitude as well as the transport/residence time of these emissions within the atmosphere, especially in the upper troposphere and lower stratosphere. As pointed out previously, it also is subject to the accuracy of the chemical system and rates used. With significant increases in higher-altitude traffic, the net result (with everything else fixed) conceivably could be a decrease in ozone. Similar results and conclusions were obtained by Hidalgo and Crutzen[7] where they parametrically investigated the effect of separate NO_x emissions at various altitudes using a two-dimensional atmospheric model developed by Crutzen.[5]

Figure 6 shows latitudinal cross sections of the resultant ozone change in February, June, and October of the fifth year of NO_x injection. Included as an insert is the latitudinal variation of the NO_x emissions. As can be seen from this figure, the variation is very latitudinal-dependent, peaking at approximately the latitudes where the NO_x injection is largest. The seasonal variation is large in the northern hemisphere and smaller in the southern hemisphere. Although there is not any significant NO_x injected in the southern hemisphere, there is a relatively significant change in the ozone column.

One may interpret this southern hemisphere effect as being due to the transport of the NO_x emissions from the northern hemisphere in a manner similar to the dispersion of Zr-95 depicted in Fig. 3. Here, the initial amount of Zr-95 was deposited at approximately 40°N in July 1967. The interhemispherical mixing of Zr-95 is seen to occur primarily in the altitude regimes corresponding to the aircraft NO_x injection, and the model simulation of this mixing is seen to be in relative agreement with measurements. Newell et al,[57] have shown that the upper layer of the troposphere is the chief interhemispheric mixing zone, with the mixing time scale on the order of 1 yr to 30°S. In the present case, from 0° to 30°S the peak effect occurs in approximately 1 yr, whereas at latitudes farther south the effect of the NO_x emission does not become significant until the beginning of the third year. Further analysis and testing has to be performed before the southern hemisphere results can be interpreted with the same objectivity as the northern hemisphere results, since almost all of the model testing and development has been done in the northern hemisphere.

It is apparent from Fig. 5 that the year-to-year variation in the ozone column change repeats itself very well after about the first year. This is indicative of the chemistry that has been outlined previously for cycles II and III, which are fast and are the predominant mechanism for the resultant change in ozone. However, cycle I, whose full effect depends on the transfer of NO_x to higher altitudes, has time scales on the order of months to years. This is reflected in the fact that there is a steady reduction in the ozone column increase with time in the northern hemispherically averaged ozone column, especially at 50° and 60°N lat. If the numerical simulation were to be carried on further in time, there probably would be a reduction in the overall ozone column increase shown here. However, it is felt that this 5-yr simulation is representative of the results and would be affected significantly only during the spring-summer at the higher latitudes.

The results in Fig. 5 show the largest effect on the ozone column occurring during the fall season and the least effect during the late spring and summer seasons. For the constant injection rate with time considered in this study, the resulting relative increase in local NO_x concentration during the summer season is less than that for the fall season, therefore contributing to larger effects in the fall season.

As stated previously, the methane-smog reaction rates are very difficult to measure, and one of the main conclusions of this work is to emphasize the need for more accurate information regarding this system and associated reaction rates, since the methane-smog cycle can be important in determining the magnitude of the aircraft NO_x problem. Therefore, these results should be considered as preliminary until more accurate rates are available. Also, the effect of these emissions is dependent on the transport/residence times in the upper troposphere and lower stratosphere, the heterogeneous removal of NO_x and HNO_3 in the troposphere, and an accurate picture of the HO_x chemical reaction rates. Thus, these results point toward a greater interest in the troposphere, and in future modeling efforts more emphasis should be placed in this region of the atmosphere, since it can have a potentially significant impact on the aircraft pollution problem.

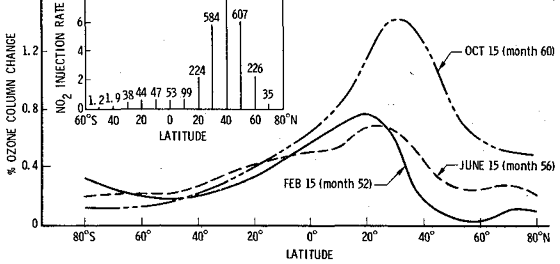

Fig. 6 Latitudinal variation of ozone column change.

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