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SENSITIVITY OF TIME-VARYING PARAMETERS IN STRATOSPHERIC MODELING

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ABSTRACT

At present there are few models where the effect of time varying parameters such as seasonal and diurnal changes in the solar zenith angle have been studied in detail. In particular, the possible effects on model estimated environmental impact of aerospace operations in the high atmosphere have not been reported in the literature. Using a one-dimensional model we have studied the sensitivity to the time dependent variations of these parameters and its effect on the model predicted perturbations. This sensitivity seems to limit the interpretability of steady state models.

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1. INTRODUCTION

One-dimensional parameterized models can be particularly useful in studies concerned with the stratospheric distributions of minor chemical constituents, and the possible perturbation effects to these constituents due to stratospheric pollution sources such as the SST. The results of such models can contribute significantly to our understanding of the unperturbed stratosphere and its response to perturbations. However, when dealing with such parameterized models, it is important for us to establish the effect of any and all parameters on the calculated results.

The purpose of this study is to analyze the sensitivity of time varying parameters such as solar zenith angle on the minor chemical species studied and their perturbations in a time-dependent one-dimensional model of the stratosphere. Seasonal and diurnal variations are to be analyzed.

2. MODEL DESCRIPTION

The governing equation (from Colgrove et al., (1965) and Shimazaki (1967)) regarding the temporal variation in the number density of the ith constituent, c_i, is given by the continuity equation

$$\frac{\partial c_i}{\partial t} = P(c) - L(c)\, c_i + \frac{\partial}{\partial z}\left[K_z \left\{\frac{\partial c_i}{\partial z} + \left(\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H}\right) c_i\right\}\right] + S_i \quad (1)$$

where $P(c)$ = production of c_i due to photochemical interaction of the other c_j's;
$L(c)c_i$ = loss of c_i due to chemical interaction of c_i with other c_j's;
S_i = any other possible sinks or sources of c_i;
T = temperature;
H = scale height factor
K_z = vertical eddy diffusion coefficient.

The vertical transport is parameterized by means of the so called eddy diffusion coefficient which is a function of altitude. This vertical profile of K_z has been presented in previous studies (Chang (1974), and Chang and Wuebbles (1974)).

This model extends from the ground to 55 km. The numerical technique used in the computations is a variant of the basic Gear method (Hindmarsh (1972), Byrne and Hindmarsh (1974)), which has been described as used in the one-dimensional model previously (Chang, Hindmarsh and Madsen (1973)).

All together fourteen minor atmospheric constituents (O, O_3, NO, NO_2, HNO_3, N_2O, OH, OH_2, H_2O_2, NO_3, N_2O_5, $O(^1D)$, H, N) are solved for in the model. Vertical distribution of N_2, O_2, H_2O, and CH_4 are held constant throughout the calculation. There are a total of 49 reactions in the model. The list of reactions is shown in Table 1. Where possible, the original measurements are cited, as referenced in Garvin and Hampson (1974). The other reaction rates are either evaluated in Garvin and Hampson (1974) or were evaluated by previous reviews (i.e., Baulch et al. (1973), Wilson (1972), Hampson (1973)).

The solar flux and absorption cross-section data used have been described by Gelinas et al. (1973). The quantum yield for the photodissociation of NO_3 has been changed to $Q_\lambda = .01$ for $NO_3 \xrightarrow{h\nu} NO + O_2$ and $Q_\lambda = .1$ for $NO_3 \xrightarrow{h\nu} NO_2 + O$ based on Johnston (1974).

Most of the previous one-dimensional calculations have utilized a constant sun condition, which means that the solar zenith angle χ is assumed to be constant throughout the calculations. In this type of model calculation, it is hoped that the value of χ assumed will represent the average solar conditions at mid-latitudes in the atmosphere. However, seasonal and diurnal variations in the solar zenith angle make it quite difficult to accurately derive such an average χ. Therefore it is of interest to examine the sensitivity of the model to these time variations in solar zenith angle.

3. SEASONAL MODEL RESULTS

Seasonal variations were included in the model by utilizing the well-known relationship for the cosine of the solar zenith angle:

$$\cos\chi = \sin\theta \sin\delta + \cos\theta \cos\delta \cos\left(\frac{2\pi t}{12}\right) \quad (2)$$

where θ = latitude
δ = solar angle from noontime equator (ranges from -23.5° to +23.5° depending on season)
t = time in hours.

A latitude of 45°N is used for all of the model computations and t is assumed to be noon for the seasonal model (δ only variable in seasonal model).

Because of the importance of horizontal motion in determining seasonal variations in such constituents as ozone in the stratosphere, a one-dimensional model cannot adequately represent the seasonal ambient distributions or minor strato-

TABLE I. Reaction rates.

REACTION	RATE COEFFICIENT	REFERENCE
1. $NO + O \xrightarrow{M} NO_2$	$3.96 \times 10^{-33} \exp(940./T)$	
2. $NO + O_3 \rightarrow NO_2 + O_2$	$9. \times 10^{-13} \exp(-1200./T)$	
3. $NO_2 + O \rightarrow NO + O_2$	9.1×10^{-12}	Davis, et al. (1972)
4. $O + O_3 \rightarrow 2O_2$	$1.9 \times 10^{-11} \exp(-2300./T)$	
5. $O + O_2 \xrightarrow{M} O_3$	$1.07 \times 10^{-34} \exp(510./T)$	Huie, et al. (1972)
6. $O(^1D) \xrightarrow{M} O$	5.85×10^{-11}	
7. $O_2 \xrightarrow{h\nu} O + O$	J_1	
8. $O_3 \xrightarrow{h\nu} O + O_2$	J_2	
9. $O_3 \xrightarrow{h\nu} O(^1D) + O_2$	J_3	
10. $NO_2 \xrightarrow{h\nu} NO + O$	J_4	
11. $N + NO_2 \rightarrow N_2O + O$	$9. \times 10^{-12}$	(1)
12. $N_2O + O(^1D) \rightarrow N_2 + O_2$	1.1×10^{-10}	
13. $N_2O + O(^1D) \rightarrow 2NO$	1.1×10^{-10}	
14. $N + O_2 \rightarrow NO + O$	$1.1 \times 10^{-14}\ T \exp(-3150./T)$	
15. $N + NO \rightarrow N_2 + O$	2.7×10^{-11}	
16. $N + NO_2 \rightarrow 2NO$	$6. \times 10^{-12}$	(1)
17. $O(^1D) + N_2 \xrightarrow{M} N_2O$	2.8×10^{-36}	
18. $N + O_3 \rightarrow NO + O_2$	5.7×10^{-13}	
19. $O(^1D) + H_2O \rightarrow 2OH$	3.5×10^{-10}	
20. $O(^1D) + CH_4 \rightarrow OH + CH_3$	$4. \times 10^{-10}$	
21. $OH + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-1000./T)$	
22. $OH + O \rightarrow O_2 + H$	4.2×10^{-11}	
23. $HO_2 + O_3 \rightarrow OH + 2O_2$	$1. \times 10^{-13} \exp(-1250./T)$	
24. $NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.23 \times 10^{-13} \exp(-2470./T)$	Johnston (1973)
25. $HO_2 + O \rightarrow OH + O_2$	$4. \times 10^{-11} \exp(-500./T)$	
26. $H + O_2 \xrightarrow{M} HO_2$	$2.08 \times 10^{-32} \exp(290./T)$	
27. $H + O_3 \rightarrow OH + O_2$	2.6×10^{-11}	
28. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$3. \times 10^{-11} \exp(-500./T)$	
29. $OH + HO_2 \rightarrow H_2O + O_2$	$2. \times 10^{-10}$	Hochanadel, et al. (1972)
30. $OH + NO_2 \xrightarrow{M} HNO_3$	$\frac{4. \times 10^{-11}\ [M]}{(1.12 \times 10^{18} + [M])}$	based on Tsang (1973)
31. $OH + HNO_3 \rightarrow H_2O + NO_3$	1.3×10^{-13}	
32. $OH + H_2O_2 \rightarrow H_2O + HO_2$	$1.7 \times 10^{-11} \exp(-910./T)$	
33. $NO + HO_2 \rightarrow NO_2 + OH$	$2. \times 10^{-13}$	
34. $O(^1D) + H_2 \rightarrow OH + H$	2.9×10^{-10}	
35. $OH + OH \rightarrow H_2O + O$	$1. \times 10^{-11} \exp(-550./T)$	
36. $H_2O \xrightarrow{h\nu} H_2 + O(^1D)$	J_5	
37. $NO \xrightarrow{h\nu} N + O$	J_6	
38. $HNO_3 \xrightarrow{h\nu} OH + NO_2$	J_7	
39. $H_2O_2 \xrightarrow{h\nu} 2OH$	J_8	
40. $NO + NO_3 \rightarrow 2NO_2$	8.7×10^{-12}	Harker & Johnston (1972)
41. $NO_2 + O \xrightarrow{M} NO_3$	$1. \times 10^{-31}$	
42. $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$	$2.3 \times 10^{-13} \exp(-1000./T)$	
43. $NO_2 + NO_3 \xrightarrow{M} N_2O_5$	$\frac{2.9 \times 10^{-12}\ [M]}{(7. \times 10^{22} \exp(-2670./T) + [M])}$	(2)
44. $N_2O_5 \xrightarrow{M} NO_2 + NO_3$	$\frac{6. \times 10^{14}\ [M] \exp(-10970./T)}{(7. \times 10^{22} \exp(-2670./T) + [M])}$	(2)
45. $N_2O_5 + O \rightarrow 2NO_2 + O_2$	$1. \times 10^{-14}$	Davis (1973)
46. $N_2O_5 + H_2O \rightarrow 2HNO_3$	$1. \times 10^{-20}$	Morris & Niki (1973)
47. $N_2O_5 \xrightarrow{h\nu} 2NO_2 + O_2$	J_9	
48. $NO_3 \xrightarrow{h\nu} NO + O_2$	J_{10}	
49. $NO_3 \xrightarrow{h\nu} NO_2 + O$	J_{11}	

(1) Derived from reaction rate given by Baulch, et al. (1973) and branching ratios given by Phillips and Schiff (1965).

(2) Hinshelwood mechanism fitted to the high and low pressure limiting rates quoted in Garvin and Hampson (1974) and based on review by Baulch, et al. (1973).

spheric constituents. However, as a sensitivity study, it is valid to compare the SST perturbation effect on total ozone for the seasonal model with similar calculations for the constant sun model. This comparison is shown in Fig. 1.

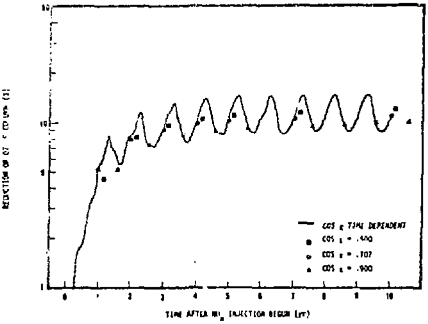

Figure 1. Comparison of ozone reduction from SST perturbation for seasonal solar flux model with constant sun model calculations.

The constant sun model gives approximately the same amount of ozone destroyed as does the seasonal model for the case that corresponds to average seasonal zenith angle, cosχ = .707. A similar correspondance between the seasonal model and the constant sun model is found for cosχ = .900. However, for the case of low cosine of the solar zenith angle, cosχ = .500, there is approximately 2% more ozone destroyed by the seasonal model than by the constant sun model. This difference is due to the fact that the seasonal model is not in a quasi-steady state during the periods of low cosχ because of the continuously changing solar zenith angle. In fact there is comparatively more ozone in the ambient seasonal model during the period around cosχ = .500 than is found in the constant sun model at equilibrium. This extra amount of ozone in the seasonal model is not supported by local photochemical production, and consequently represents a net loss under the SST perturbation. Therefore there is more ozone reduction in a seasonal model during low cosχ than would be calculated by a constant sun model.

4. DIURNAL MODEL RESULTS

Based on the sensitivity found between the constant sun model and the seasonal model, it was decided to analyze the effect of having diurnal variations in solar zenith angle in the one-dimensional model.

For these calculations, δ in Eq. (2) is assumed to be 0 which corresponds to the equinox. The latitude is again 45° and the time allowed to vary diurnally. The initial distributions for the ambient calculation of the diurnal model were derived by the constant sun model.

Figure 2 depicts the time variation of total ozone in an ambient calculation with the diurnal model. During the first 120 days, the amount of total ozone decreased, reached a minimum, and then increased to reach equilibrium after approximately four years. The increase during the first 120 day period is primarily due to chemical readjustment above 30 km where the chemical response time for O_3 is very short (less than a week). After this time, the vertical transport slowly brings the system to a total chemical-transport equilibrium, which is reached after 1320 days with a total ozone column concentration of 8.504×10^{18} molecules/cm^2. This latter increase is instigated by the decrease of net amount of NO and NO_2 between 20 and 30 km (through conversion to N_2O_5 and NO_3).

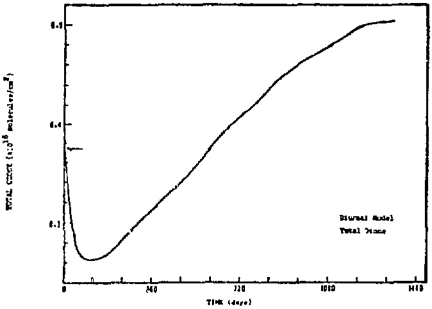

Figure 2. Variation of total ozone with time in diurnal model (noontime).

The previous diurnal models for the stratosphere (Whitten and Turco (1974); Shimazaki and Ogawa (1974)) have stopped calculations at a model time which is less than or equal to the time for the minimum in total ozone. While the change in the total ozone column in Fig. 2 is only a few percent over the four year period, the changes in the other minor chemical species are much more significant (Figs. 5, 6, and 7). Due to the sharp transition of some of the species at sunrise and sunset, all model calculations must verify that the particular computational techniques used is sufficiently accurate so as to be able to hold onto a diurnal steady state once it is reached (i.e., no drifting away due to computational error).

To ensure that the present diurnal model can indeed reach a numerically accurate time dependent equilibrium state a special test problem was calculated in which the transport coefficient, K_z, was constant at $3 \times 10^5 cm^2/sec$ over the entire stratosphere. This corresponds to approximately a factor of 100 increase in K_z over most of the stratosphere, thus giving the model a much shorter transport residence time with which to reach equilibrium. As seen in Fig. 3, equilibrium was reached after approximately 100 days and the model continued to maintain this equilibrium state. The total ozone column remained constant to within four significant figures in the continued calculations after reaching the steady state. This confirms the numerical accuracy of our model.

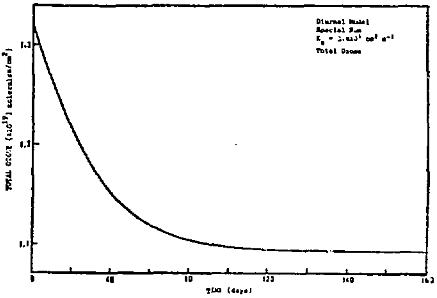

Figure 3. Time variation of total ozone for fast transport diurnal model (special run).

Figure 4 shows the change in the distribution of O_3 from the constant sun model results to the diurnal model equilibrium state. The increase in ozone at the ozone peak at 25 km accounts for the increase in total ozone shown in Fig. 2. The distribution of NO has decreased by as much as a factor of 2 during this same period and is presented in Fig. 5. If the NO distribution for the diurnal model at equilibrium (day 1320) is compared with existing measurements, it is found that the NO profile above 20 km is now well within range of the data by Ackerman et al. (1973). Note that after 120 days, NO has decreased by only about half of the eventual decrease at equilibrium.

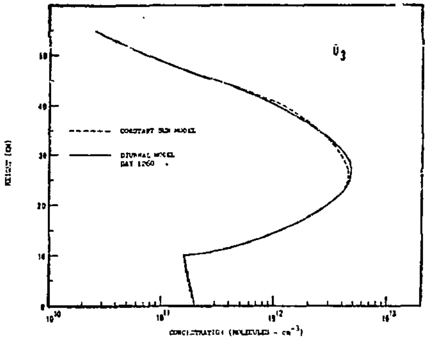

Figure 4. Comparison of constant sun model ozone profile with ambient ozone distribution for diurnal model (noontime).

As seen in Figs. 6 and 7 NO_2 and HNO_3 have also, respectively, decreased in concentration in the stratosphere from the values derived by the constant sun model. However, both constituents are still within the lower limits of the measurements in the stratosphere.

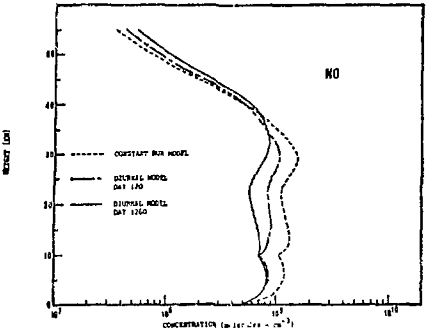

Figure 5. NO distribution for diurnal model (noontime) (for day 120 and day 1260) compared with profile for constant sun model.

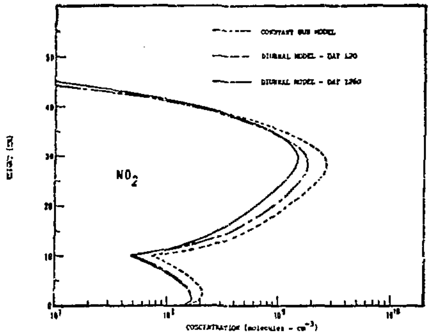

Figure 6. NO_2 distribution for diurnal model (noontime) (for day 120 and day 1260) compared with profile for constant sun model.

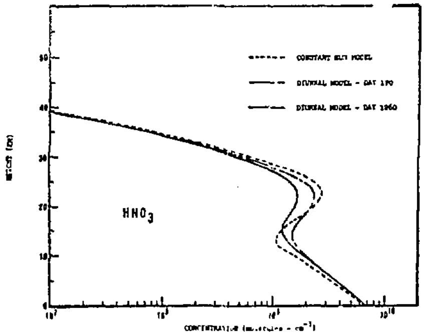

Figure 7. HNO_3 distribution for diurnal model (noontime) (for day 120 and day 1260) compared with profile for constant sun model.

The diurnal behavior of NO and NO_2 at various altitudes are indicated in Fig. 8. The diurnal behavior of NO_2 indicates a monotonic increase in concentration between sunrise and sunset at all altitudes in the stratosphere. At 120 days this was not found except at high altitude. This implies downward propagation of this behavior as the model progresses. For NO, at 30 km, the daily variation agrees with the trend measured by Patel et al (1974). However there is a difference in magnitude of approximately 3 between the diurnal model NO and Patel et al (1974).

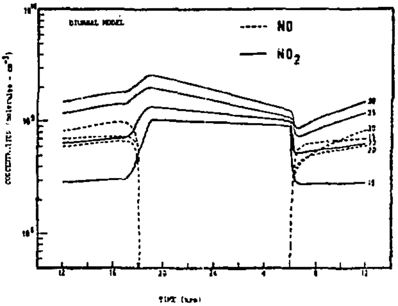

Figure 8. Diurnal behavior of ambient NO and NO_2 at various altitudes.

Figure 9 shows the simultaneous diurnal behavior of NO_x at 20 km for the diurnal model equilibrium state. As expected, at sunset, the NO is no longer produced by the photodissociation of NO_2. N_2O_5 increases slowly during the night due to the reaction $NO_2 + NO_3 \overset{M}{\rightarrow} N_2O_5$ and decreases slowly during the day due to photodissociation.

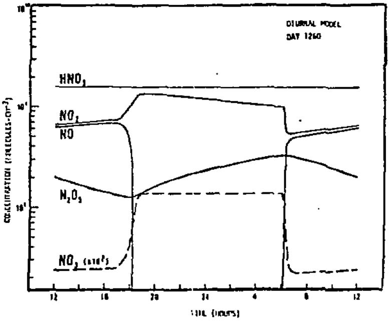

Figure 9. Simultaneous diurnal distribution of NO_x at 20 km for diurnal model equilibrium state.

At equilibrium in the diurnal model, N_2O_5 has increased by approximately a factor of 3 from the value at 20 km derived by the constant sun model, whereas all other NO_x have decreased.

The equilibrium diurnal model distributions were used as the initial condition in a calculation of the diurnal model SST perturbations. An SST input of 2.5 x 10^{12} gm/yr of NO_2 (injected at 20 km) was used both in the diurnal and constant sun model. As represented in Fig. 10, the constant sun model reached a perturbation steady state in approximately 9-10 years with 10.14 percent reduction of ozone.

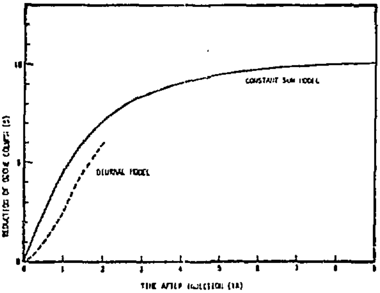

Figure 10. Time variation of SST reduction of ozone for diurnal model compared with constant sun model .

The perturbed diurnal model was run 2 years with an decrease of 6% in total ozone as compared to 7.2% for the constant sun model after 2 years. The diurnal model results seem to follow the trend of the ozone column loss derived by the constant sun model, but without continued calculation it is difficult to conclude on the final results.

Figure 11 includes the 2 year diurnal model's results for the SST perturbations on a graph from Chang and Johnston (1974), which compares the reduction of ozone column vs. increase of NO_x column for various model calculations (represented by □ and △). The present diurnal model calculation is represented by the dark triangle. This graph shows that the diurnal model tends to predict slightly less ozone destruction when compared to other models. Most models presented on this curve are constant sun models. On this graph the fact that the diurnal results are only run for 2 years is no longer very important, since it is a direct correlation of perturbed NO_x and perturbed ozone.

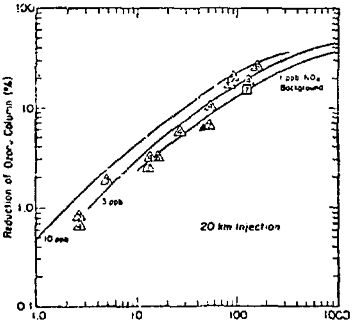

Figure 11. Diurnal model (▲) reductions of vertical ozone column in terms of relative perturbation of NO_x vertical column from Chang and Johnston (1974).

5. CONCLUSION

In conclusion, for the SST perturbation of ozone studies, the correction factors due to the effects of seasonal and diurnal variations in the solar zenith angle are both small and in fact are opposite in sign. Consequently we may expect the net global effect to be small.

However, the detailed trace constituent distributions are seriously effected by these time-dependent variations in solar zenith angle. This indicates the care that may be necessary in comparing local measurements of trace constituents with theoretical calculations.

6. ACKNOWLEDGEMENTS

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