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RESULTS FROM THE ONE BOX KINETICS - TRANSPORT CODE

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RESULTS FROM THE ONE BOX KINETICS - TRANSPORT CODE

In this note we will look at some preliminary results concerning the kinetics and transport of a single SST exhaust plume. Shown will be curves exhibiting the effect of different transport rates on the on axis ozone concentration and total ozone destruction per unit plume length.

We look at the equation for some chemical species i

$$\frac{\partial c_i}{\partial t} = P_i(c) - L_i(c) c_i + T_i \quad (1)$$

where P_i , L_i and T_i are respectively, production, lose and transport of the species. If in the one box model we have a steady state corresponding to ambient then

$$P_i(c_a) - L_i(c_a) c_{ai} + S_i = 0, \quad (2)$$

$S_i = T_{ai}$ being an apparent source or sink due to transport processes which characterize the dynamic equilibrium in a multi-dimensional problem. By this we mean that in a problem with one or more dimensions while the kinetics tries to carry the system to some equilibrium distribution, transport in the form of diffusive fluxes acts to smooth out irregularities. Equillibrium is then reached when these two processes balance. In a zero dimensional model this effect of transport must be specified using information obtained from observation or from some model calculation in one or more dimensions.

If the equilibrium defined by (2) is perturbed then (1) becomes

$$\frac{\partial c_i}{\partial t} = P_i(c_i) - L_i(c)c_i + S_i + T_i' \quad (3)$$

The assumption implicit in (3) is that the transport can be separated into parts characteristic of the ambient S_i and the perturbation T_i' . In Section II of Note 6 the nature of the term T_i' was discussed and found for the diffusive transport of a two dimensional gaussian profile to be

$$T_i' = -(c_i - c_{ai}) \left(\frac{K_y}{\sigma_y^2} + \frac{K_z}{\sigma_z^2} \right) \quad (4)$$

where the K 's and σ 's are the diffusion coefficients and standard deviations.

The form of K is that given in my Denver paper (J.J. Walton, "Dispersion of Exhaust Plumes in the Stratosphere", 1973 AIAA/AMS International Conference on Environmental Impact of Aerospace Operation in the High Atmosphere).

$$K = \frac{1}{\frac{1}{b\epsilon^{1/3}\sigma^{4/3}} + \frac{1}{K_m}} \quad (5)$$

K_m the global diffusion coefficient, ϵ the atmospheric energy dissipation rate and b a dimensionless constant of order 1. This gives for σ

$$\frac{\sigma^2}{K_m} + 3 \frac{\sigma^{2/3}}{b\epsilon^{1/3}} = 2t + \frac{\sigma_0^2}{K_m} + 3 \frac{\sigma_0^{2/3}}{b\epsilon^{1/3}} \quad (6)$$

where $\sigma_0 = \sigma(t=0)$.

For this note the perturbation by a single exhaust plume of the ambient atmosphere at 20 Km altitude was studied. Ambient concentrations c_{ai} and transport S_i were obtained from J. Chang's one dimensional vertical mode. The reactions and rate coefficients (table 1) were essentially those used by Chang. Species assumed fixed were H_2 , CH_4 , N_2 and O_2 while the species O^1D , HO , H , HO_2 , O_3 , H_2O , H_2O_2 , HNO_3 , NO_3 , NO_2 , N_2O , O , NO and N were free to vary. Perturbations of H_2O , NO and NO_2 corresponding to the end of Lockheed's wake dispersion regime were used (H. Hoshizaki, et al "Study of High-Altitude Aircraft Wake Dynamics," Lockheed Palo Alto Research Laboratory report no: DOT-TST-90-4). In table 2 are the ambient and perturbed values of the various species plus the ambient transport terms obtained from Chang.

Initial plume dimensions were taken from Lockheed and were 8.3187×10^4 cm in the horizontal and 1.335×10^4 cm in the vertical. These dimensions translate into horizontal and vertical standard deviations of 1.935×10^4 cm and 3.105×10^3 cm (section III, note 6).

In Figs. 1 are time histories of the concentration of O_3 , NO , NO_2 and $NO_x = NO + NO_2$ at the center of a single plume. In addition is included an estimate of the net chemical destruction of ozone per cm plume length. This is obtained from a time integration of the chemical derivative weighted by the plume area ($2\pi \sigma_y \sigma_z$)

$$\Delta O_3(t) = \int_0^t 2\pi \sigma_y \sigma_z \left. \frac{d[O_3]}{dt} \right|_{chem} dt' \quad (7)$$

TABLE I

Reaction	Rate Coefficient	Reaction	Rate Coefficient
$\text{CH}_4 + \text{O}^1\text{D} = \text{CH}_3 + \text{HO}$	4.0×10^{-10}	$\text{N} + \text{O}_3 = \text{NO} + \text{O}_2$	5.7×10^{-13}
$\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2$	1.47×10^{-13}	$\text{N}_2\text{O} + \text{O}^1\text{D} = \text{N}_2 + \text{O}_2$	1.1×10^{-10}
$\text{H} + \text{O}_3 = \text{HO} + \text{O}_2$	2.6×10^{-11}	$\text{N}_2\text{O} + \text{O}^1\text{D} = 2\text{NO}$	1.1×10^{-10}
$\text{H}_2 + \text{O}^1\text{D} = \text{H} + \text{HO}$	2.9×10^{-10}	$\text{N}_2\text{O} + h\nu = \text{N}_2 + \text{O}^1\text{D}$	2.02×10^{-9}
$\text{H}_2\text{O} + \text{O}^1\text{D} = 2\text{HO}$	3.5×10^{-10}	$\text{NO} + \text{O} \xrightarrow{\text{M}} \text{NO}_2$	5.57×10^{-13}
$\text{H}_2\text{O}_2 + \text{HO} = \text{H}_2\text{O} + \text{HO}_2$	2.55×10^{-13}	$\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$	3.54×10^{-15}
$\text{H}_2\text{O}_2 + h\nu = 2\text{HO}$	4.83×10^{-6}	$\text{NO} + h\nu = \text{N} + \text{O}$	1.46×10^{-26}
$\text{HNO}_3 + \text{HO} = \text{H}_2\text{O} + \text{NO}_3$	1.3×10^{-13}	$\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$	9.1×10^{-12}
$\text{HNO}_3 + h\nu = \text{NO} + \text{NO}_2$	7.53×10^{-7}	$\text{NO}_2 + \text{O}_3 = \text{NO}_3 + \text{O}_2$	1.4×10^{-18}
$\text{N}_2 + \text{O}^1\text{D} \xrightarrow{\text{M}} \text{N}_2\text{O}$	5.18×10^{-18}	$\text{NO}_2 + h\nu = \text{NO} + \text{O}$	9.49×10^{-3}
$2\text{HO} = \text{H}_2\text{O} + \text{O}$	7.93×10^{-13}	$\text{O} + \text{O}_2 \xrightarrow{\text{M}} \text{O}_3$	2.09×10^{-15}
$\text{HO} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$	2.0×10^{-10}	$\text{O} + \text{O}_3 = 2\text{O}_2$	4.66×10^{-16}
$\text{HO} + \text{NO}_2 \xrightarrow{\text{M}} \text{HNO}_3$	2.49×10^{-12}	$\text{O}_2 + h\nu = 2\text{O}$	2.57×10^{-13}
$\text{HO} + \text{O} = \text{H} + \text{O}_2$	4.2×10^{-11}	$\text{O}^1\text{D} \xrightarrow{\text{M}} \text{O}$	1.08×10^8
$\text{HO} + \text{O}_3 = \text{HO}_2 + \text{O}_2$	1.58×10^{-14}	$\text{O}_3 + h\nu = \text{O} + \text{O}_2$	4.19×10^{-4}
$2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	2.98×10^{-12}	$\text{O}_3 + h\nu = \text{O}^1\text{D} + \text{O}_2$	1.86×10^{-5}
$\text{HO}_2 + \text{NO} = \text{HO} + \text{NO}_2$	2.0×10^{-13}	$\text{N}_2\text{O} + h\nu = \text{N} + \text{NO}$	2.02×10^{-11}
$\text{HO}_2 + \text{O} = \text{HO} + \text{O}_2$	1.0×10^{-11}	$\text{NO}_3 + h\nu = \text{NO} + \text{O}_2$	2.28×10^{-2}
$\text{HO}_2 + \text{O}_3 = \text{HO} + 2\text{O}_2$	3.12×10^{-16}	$\text{N} + \text{NO}_2 = \text{NO} + \text{NO}$	6.0×10^{-12}
$\text{N} + \text{NO} = \text{N}_2 + \text{O}$	2.7×10^{-11}	$\text{N} + \text{NO}_2 = \text{N}_2\text{O} + \text{O}$	9.0×10^{-12}
$\text{N} + \text{O}_2 = \text{NO} + \text{O}$	1.16×10^{-18}		

TABLE 2

Specie	c_{ai} , ambient conc. cm^{-3}	c_i , perturbed conc. cm^{-3}	S_i , transport $\text{cm}^{-3} \text{sec}^{-1}$
CH_4	2.775×10^{12}	-	-
H	2.100×10^{-3}	-	0.0
H_2	4.459×10^{11}	-	-
H_2O	3.981×10^{12}	2.074×10^{13}	-3.887×10^2
H_2O_2	1.132×10^8	-	1.245
HNO_3	2.877×10^9	-	-7.124×10^1
HO	3.984×10^5	-	7.709×10^{-4}
HO_2	1.367×10^7	-	1.678×10^{-3}
N	3.237	-	0.0
N_2	1.48×10^{18}	-	-
N_2O	4.103×10^{11}	-	-8.880×10^2
NO	1.801×10^9	8.360×10^{10}	-1.503×10^1
NO_2	2.406×10^9	3.010×10^{10}	1.435×10^1
NO_3	5.368×10^5	-	0.0
O	2.061×10^6	-	2.919×10^{-1}
O^1D	6.182×10^{-1}	-	0.0
O_2	3.700×10^{17}	-	-
O_3	3.590×10^{12}	-	-3.448×10^4

In Fig. 1a are results obtained when there is no transport of the perturbed species, that is T_1 is identically zero. The rapid (~ 1 min) readjustment of the equilibrium between NO and NO₂ is characteristic of all cases studied regardless of transport of perturbed species. Significant deviation of O₃ from its ambient value is not observed until approximately one day after which time the NO, NO₂ balance recrosses. The slight drop-off of NO_x at late times occurs because the fixed N₂ and O₂ concentrations provide infinite baths of these species. Thus, if any chemical path leads from NO and NO₂ to N₂ and O₂, these species will finally settle back to the ambient level.

Figs. 1b and 1c represent the effect of different levels of transport on the perturbed species. From (4) it is seen that this transport not only acts to decrease concentrations which exceed ambient but will tend to fill in "holes" which might develop in a concentration profile. It will be seen, however that the NO_x concentration is dropping off with sufficient rapidity that significant local depletion of O₃ does not have time to occur. On the other hand the number of molecules of O₃ destroyed is increased when there is transport, the explanation being that while it is true NO₂ concentration is decreasing the region over which the reactions are taking place is being significantly increased by the transport process.

Figs. 2 exhibit the effect of transport on the O₃ minimum reached at the center of a single plume. In Fig. 2a $K_z = 0$ and K_y took constant values between 0 and 10^{10} cm²/sec. In Fig. 2b the case for scale

dependent diffusion with $\epsilon = 0.02 \text{ cm}^3/\text{sec}^3$ in (5) is presented. In this figure the abscissa is now the asymptotic value of K_y . It will be seen that the difference in this and the above case is negligible. The last of these figures 2c corresponds to the case of scale dependent diffusion and non-zero vertical transport, here $K_z = 10^3 \text{ cm}^2/\text{sec}$.

In Figs. 3 is total O_3 destruction after 10^6 sec. for the three cases described above. Here again with no vertical transport, the difference between scale dependent and constant transport is slight. The most interesting aspect of figs. 3a and 3b is that there exists some optimum transport rate at which a maximum destruction occurs. Fig. 3c for which $K_z = 10^3 \text{ cm}^2/\text{sec}$ shows a broad maximum as a function of K_{ym} since the presence of vertical transport has already moved us up along the destruction curve. It should be noted from this set of curves that between the extremes of transport there is only about 25% variation in the total ozone destruction.

In figs 4 we look at a cause discussed by G. Hilst (G. R. Hilst and C. du P. Donaldson, "Preliminary Estimates of the Fate of SST Exhaust Materials Using a Coupled Diffusion/Chemistry Model," 1973 AIAA/AMS International Conference on Environmental Impact of Aerospace Operations in the High Atmosphere). Here the initial NO concentration was taken to be 2 ppm ($3.7 \times 10^{12} \text{ cm}^{-3}$) all other initial concentrations being those in table 2. In fig. 4a the curves correspond to the case of no transport while in fig. 4b we have the case for scale dependent diffusion with $\epsilon = 0.02 \text{ cm}^2/\text{sec}^3$, $K_{ym} = 5.0 \times 10^9 \text{ cm}^2/\text{sec}$ and $K_{zm} = 1.0 \times 10^3 \text{ cm}^2/\text{sec}$. As in figs. 1 we see an equilibration of NO and NO_2 in a matter of minutes, followed, when there is no transport, by a rapid drop-off in O_3 concentration, reaching a new equilibrium in approximately 10 days. When

relatively strong transport acts the maximum O_3 change is less than 50%, lasting for less than a day. Total O_3 destruction is seen however, to be substantially increased by the diffusive process which as stated above extends the region in which relatively high NO_x concentrations are present. Finally, the greatly elevated O_3 destruction over that seen in figs. 1 is, of course, due to the fact that there is an almost fifty-fold higher initial NO_x concentration present in the same plume area.

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fig 1 a

fig. 1 b

fig 1c

Fig. 2

Fig. 3

a

b

c

Fig 44

fig 4 b