Dynamic-Kinetic Evolution of a Single Plume of Interacting Species

ROBERT J. GELINAS AND JOHN J. WALTON
Lawrence Livermore Laboratory, University of California, Livermore 94550

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ABSTRACT

The coupled dynamic and kinetic evolution of chemical species are considered for an assumed exhaust plume from an SST at proposed flight altitudes of about 20 km. A systematic effort is made to determine whether chemical and radiative interactions seriously alter the exhaust species distributions determined on the basis of scale-dependent diffusion alone. In the present coupled treatment, use is made of the plume dispersion coefficients from previous dynamic calculations, and a moderately complex kinetic mechanism is incorporated. The sensitivity to transport rates is presented, and the role of inhomogeneity correlations is discussed.

1. Introduction

This is the first part of a two-part investigation of a coupled dynamic-kinetic treatment of SST exhaust species distributions over scales of 1 to 1000 km. The first part considers only single plumes; the second deals with multiple plumes in a flight corridor (Walton, 1974). The basic aim is to determine whether the complexities of radiative and chemical interactions must be included in plume dynamics calculations (Walton, 1973a).

To date, most atmospheric models simply compute the distributions of the effluent species over scales of 1 km to global scales on the basis of initial species concentrations, as if interactions were frozen and only dispersive processes were at play (Walton, 1973a, b). The present work is based on an alternative approach that starts at the simplest level of retaining dispersion-dependent terms in coupled kinetic equations for the species and reaction sets of interest.

The extreme cases of no interactions on the one hand, and of peak plume concentration kinetics on the other, may be useful for considering the extremes of inhomogeneity correlations in exhaust plumes. Pertinent cases are developed and discussed. As in all kinetic models, there are parametric uncertainties. Sensitivity to selected parametric variations is considered in an attempt to estimate likely limiting magnitudes of possible effects.

2. Development of basic equations

The dispersal of exhaust products can be gainfully viewed in at least two ways. A conventional approach considers the space- and time-dependent diffusion of these species into an infinite ambient medium—in this case a medium of air and naturally occurring trace species. However, the solution of the full space- and time-dependent problem, with interactions included, is a sizeable task. Thus, a second approach is suggested: We shall consider a Lagrangian box of variable volume, which always encompasses the exhaust species, and which, therefore, moves with the plume in some sense. In such a model the explicit spatial dependence is suppressed, and the resultant time-dependent equations (with a reasonably full representation of interactions) can be readily solved with standard kinetic methods. This generalized case takes the form of conventional space-independent kinetic equations, plus a volume-dependent term expressing the variation of concentrations due to the volume change of the Lagrangian box encompassing the exhaust species.

a. Development of generalized kinetic equations

The specific forms of the generalized kinetic equations can be developed by considering the definition of the total concentration $C_i(t)$ of the $i$th species in terms of an ambient component $C_i^a(t)$ associated with the natural background and a perturbed component $C_i^p(t)$ associated with engine exhausts:

$$C_i(t) = C_i^a(t) + C_i^p(t),$$  

(1)

$$C_i(t) = [N_i^a(t) + N_i^p(t)]/V(t).$$  

(2)

In the present development, $V(t)$ is chosen to be the time-varying volume of a Lagrangian box in which the number of exhaust species $N_i^p(t)$ is constant. Expanding the derivative of $C_i(t)$ is

$$\frac{dC_i(t)}{dt} = \lim_{\delta t \to 0} \frac{1}{\delta t} [C_i(t+\delta t) - C_i(t)],$$  

(3)
or
\[
\frac{dC_i(t)}{dt} = \frac{\partial C_i(t)}{\partial V(t)} \frac{\partial V(t)}{\partial t} + \frac{\partial V(t)}{\partial t} + S^\text{ext}(t),
\]
(4)
where \(S^\text{ext}(t)\) is the net source (or sink) rate of \(i\)th species to (or from) \(V(t)\) due to external factors (e.g., rainout of \(i\)th species). The explicit time variation \(\partial C_i(t)/\partial t\) is due to radiative and chemical interactions and can be written as
\[
\frac{\partial C_i(t)}{\partial t} = \frac{P_i[C(t)] - L_i(C(t))C_i(t)}{V(t)},
\]
(5)
The terms \(P_i[C(t)]\) and \(L_i[C(t)]C_i(t)\) represent interactive production and removal terms for species of the \(i\)th type. The term involving \(\partial C_i(t)/\partial V(t)\) can be evaluated from Eq. (2). One finds
\[
\frac{\partial N_i^A(t)}{\partial V(t)} = 0,
\]
(7)
which is simply a statement of the condition of \(N_i^A(t)\) being constant in the Lagrangian box defined by \(V(t)\). But the number of ambient particles \(N_i^A(t)\) is not constant in \(V(t)\), because under expansion, \(V(t)\) sees an increase in \(N_i^A(t)\) as it overtakes, or entrains, undisturbed air. The term
\[
\frac{\partial N_i^A(t)}{\partial V(t)}
\]
can be evaluated by our definition of the ambient concentration being constant at all \(V(t)\). That is, the evaluation of
\[
\frac{\partial [N_i^A(t)/V(t)]}{\partial V(t)} = 0
\]
simply leads to
\[
\frac{1}{V(t)} \frac{\partial N_i^A(t)}{\partial V(t)} = \frac{1}{V(t)} \frac{\partial V(t)}{\partial t} + \frac{1}{V(t)} C_i(t).
\]
(8)
Thus,
\[
\frac{\partial C_i(t)}{\partial V(t)} = \frac{1}{V(t)} C_i(t) + \frac{1}{V(t)} C_i(t).
\]
(9)
Substitution of Eqs. (5) and (9) into Eq. (4) gives
\[
\frac{dC_i(t)}{dt} = P_i[C(t)] - L_i[C(t)]C_i(t) - \left[\frac{\partial \ln V(t)}{\partial t}\right] [C_i(t) - C_i^A(t)] + S^\text{ext}(t).
\]
(10)

The only remaining task, one which is requisite for a solution of Eq. (10), is to obtain a usable expression for \(\partial \ln V(t)/\partial t\). This term is strictly dynamic in nature and is readily at hand. Let it be given that a perturbation \(C_i(t)\) is governed by the diffusion equation
\[
\frac{\partial C_i^P(t)}{\partial t} = \frac{N_i^T}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \exp \left[-\frac{1}{2} \left(\frac{x^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right],
\]
(11)
with Gaussian solution
\[
C_i^P(t) = \frac{N_i^T}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \exp \left[-\frac{1}{2} \left(\frac{x^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right].
\]
(12)
Here \(N_i^T\) is the total perturbation in the number of species \(i\), and \(\sigma_x, \sigma_y, \sigma_z\) are the standard deviations of the distribution, satisfying the equations
\[
\frac{d\sigma_x^2}{dt} = 2K_x(t), \quad \frac{d\sigma_y^2}{dt} = 2K_y(t), \quad \frac{d\sigma_z^2}{dt} = 2K_z(t).
\]
(13)
The time rate of change of concentration at the plume center \((x,y,z=0)\) due to diffusion only is, from Eq. (12),
\[
\frac{dC_i^P}{dt} = \frac{N_i^T}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \left[\frac{\dot{x}}{\sigma_x^2} + \frac{\dot{y}}{\sigma_y^2} + \frac{\dot{z}}{\sigma_z^2}\right],
\]
\[
= \frac{N_i^T}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \left[\frac{\dot{x}}{\sigma_x^2} + \frac{\dot{y}}{\sigma_y^2} + \frac{\dot{z}}{\sigma_z^2}\right],
\]
\[
= -C_i^P(t) \frac{\partial \ln(\sigma_x \sigma_y \sigma_z)}{\partial t}.
\]
(14)
From Eq. (1) we note that
\[
C_i = C_i^A - C_i^P,
\]
and it will be recognized that \(\sigma_x \sigma_y \sigma_z\) is some constant multiple of the plume volume \(V(t)\); thus, Eq. (14) is just the dispersive term appearing in Eq. (10). The importance of this parallel lies in that we now have
\[
\frac{\partial \ln V(t)}{\partial t} = \frac{\dot{x}}{\sigma_x} + \frac{\dot{y}}{\sigma_y} + \frac{\dot{z}}{\sigma_z},
\]
\[
\frac{\partial \ln V(t)}{\partial t} = \frac{K_x}{\sigma_x} + \frac{K_y}{\sigma_y} + \frac{K_z}{\sigma_z}.
\]
(15)
Eq. (15) is general, in that, given the \(K\)'s, Eqs. (13) define the \(\sigma\)'s in time, which then gives \(\partial \ln V(t)/\partial t\).
b. Method qualifications

The use of the above equations is based on the assumption that all perturbed species maintain similar Gaussian profiles and that processes going on over the entire plume may then be described in terms of those taking place at the plume center. This is in contrast to the often-used assumption in kinetic models of instantaneous uniform mixing in a volume, which is not well suited to the class of problems under present consideration. The assumption of similar Gaussian profiles itself leads, through the nonlinear part of the $P_1-LC_1$ term in (10), to a certain type of inherent error. These terms generally contain expressions of the form

$$R = \sum_{i,j} k_{ij} C_i C_j,$$

where the $k_{ij}$ are reaction rate coefficients that may be either positive or negative. If at some instant all perturbations have the same Gaussian profile, then substituting (1) and using (12), we have

$$R = \sum_{i,j} k_{ij} C_i C_j + \{\sum_{i,j} k_{ij} (C_i^2 C_j^2 + C_i^2 C_j^2)\} \exp\left[\frac{1}{2} \left(\frac{x^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right],$$

and

$$\{\sum_{i,j} k_{ij} C_i C_j \} \exp\left[\frac{1}{2} \left(\frac{x^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right].$$

The first term above is just balanced by the ambient transport. That is, if all $C=0$ the reaction and transport terms cancel to give zero total time derivative for each species, providing a stationary ambient concentration. The approximation upon which this paper is based is that the space-dependent part of $R$ has the form

$$\{\{1\}, \{2\}\} \exp\left[\frac{1}{2} \left(\frac{x^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right].$$

Were this in fact the case, then chemical processes would not change the shape of the concentration profile, but only the magnitude of the deviation from ambient. Small-scale transport alone would give a change in shape that would be common to all species. Obviously, at plume center ($x=y=z=0$) the results are identical, but away from this point the spatial coefficient of $\{1\}$ will give rise to a tendency away from the assumed similarity. The level of confidence in results of this analysis rest on the relative magnitude of $\{1\}$ and $\{2\}$ or the logarithmic derivative associated with the terms. Thus, if $\{2\} \ll \{1\}$, the Gaussian profiles will be preserved. On the other hand, if $\{1\}$ and $\{2\}$ are of such magnitude for a species that through the total running time of the problem they make only a small change in the concentration, their relative magnitude is not of importance. With respect to the cases described here, it was found that for NO, NO$_2$ and O$_3$ the first condition was satisfied for times less than $10^9$ sec, and the second condition was satisfied after $10^9$ sec. It should be pointed out that there may be indirect effects through deviations of species such as H, HO, O and N, which do exhibit derivatives that violate the above conditions.

c. Special case

Of special interest in this paper is dispersion by scale-dependent diffusion. The form of the diffusion coefficient $K$ that has been adopted is phenomenological in nature, selected with the specific purpose of giving results that are consistent with similarity theory for small scales and that approach global values $K_m$ asymptotically for large scales. The form used is

$$K = \left(\frac{1}{b^2 \varepsilon^2} + \frac{1}{K_m}\right)^{-1}, \quad (16)$$

where the $K$'s and $\sigma$'s may be different in different coordinate directions. In Eq. (16), $b$ is a dimensionless constant of order 1, and $\varepsilon$ is the atmospheric energy dissipation rate. Upon substitution of (16) into (13), we find

$$\frac{\sigma_x^2 + \sigma_y^2 + \sigma_z^2}{K_m} = \frac{2b^2 \varepsilon^2 + 3}{K_m \varepsilon^2},$$

$\sigma$ being the standard deviation at $t=0$. The substitution of (17) and (16) in Eq. (15) then provides the required entrainment correction for (10).

3. Single plume applications

The specific examples considered deal with single plumes at an assumed altitude of 20 km and a latitude of 45N. Photodissociation rates in these examples are evaluated using the noon solar flux for the date of the autumnal equinox (23 September) for a purely absorbing standard atmosphere. The detailed description of our solar flux and photodissociation rate calculations and data sources can be found in Gelinas et al. (1973), and only the rate values, per se, are included here. Chemical reaction rate coefficients have been taken primarily from National Bureau of Standard sources (Garvin, 1973). The set of radiative and chemical reaction processes of our kinetic mechanism corresponds to that used in the one-dimensional calculations of Chang et al. (1973), which we have used in conjunction with our strictly time-dependent calculations. This reaction set and the rate values appear in Table 1. Of course, this reaction set is not physically complete. It can only be somewhat representative of the many kinetic mechanisms presently being used by atmospheric modelers. There are also uncertainties associated
with the adopted reaction rates. Sensitivity studies of more or less complete reaction sets and of uncertain rates in kinetic mechanisms are a sizeable task in their own right, and they will not be presented in this particular article. Rather, we shall emphasize the response of our current model to variation in transport rates. This is in recognition of the physical fact that turbulent dispersion is neither a constant nor a continuous process and that this aspect of the dynamic-kinetic problem has not received a great deal of attention (to date) in models.

Table 1. List of reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. O(D)+M → O(PP)+M</td>
<td>5.85×10^{-11}</td>
</tr>
<tr>
<td>2. O(PP)+O+O2 → O3+M</td>
<td>1.15×10^{-14}</td>
</tr>
<tr>
<td>3. O(PP)+O2 → 2O3</td>
<td>4.60×10^{-15}</td>
</tr>
<tr>
<td>4. N2O → NO+O2</td>
<td>3.54×10^{-15}</td>
</tr>
<tr>
<td>5. O(P)+NO → NO+O2</td>
<td>9.1×10^{-15}</td>
</tr>
<tr>
<td>6. NO2+O → NO3+O2</td>
<td>1.4×10^{-15}</td>
</tr>
<tr>
<td>7. NO+O(PP)+M → NO2+M</td>
<td>2.98×10^{-15}</td>
</tr>
<tr>
<td>8. N+NO2 → N2+O+O2</td>
<td>9.0×10^{-15}</td>
</tr>
<tr>
<td>9. N2O2+O(D) → N+O3</td>
<td>1.1×10^{-15}</td>
</tr>
<tr>
<td>10. N2O2+O(D) → 2NO</td>
<td>1.1×10^{-15}</td>
</tr>
<tr>
<td>11. N+NO2 → NO+O(PP)</td>
<td>1.1×10^{-15}</td>
</tr>
<tr>
<td>12. N+NO2 → N2+O2</td>
<td>2.7×10^{-15}</td>
</tr>
<tr>
<td>13. N+NO2 → 2NO</td>
<td>6.0×10^{-15}</td>
</tr>
<tr>
<td>14. O(D)+N+M → N2O+M</td>
<td>2.8×10^{-16}</td>
</tr>
<tr>
<td>15. N+O2 → NO+O2</td>
<td>5.7×10^{-16}</td>
</tr>
<tr>
<td>16. O(D)+H2O → 2HO</td>
<td>3.5×10^{-16}</td>
</tr>
<tr>
<td>17. O(D)+CH3 → OH+CH3</td>
<td>4.0×10^{-16}</td>
</tr>
<tr>
<td>18. HO+O3 → HO2+O2</td>
<td>1.58×10^{-14}</td>
</tr>
<tr>
<td>19. HO+O(PP) → O3+H</td>
<td>4.2×10^{-11}</td>
</tr>
<tr>
<td>20. HO+O3 → HO+O2</td>
<td>3.12×10^{-11}</td>
</tr>
<tr>
<td>21. HO2+O(PP) → HO2+O2</td>
<td>1.0×10^{-11}</td>
</tr>
<tr>
<td>22. H+O3+M → HO2+M</td>
<td>7.9×10^{-12}</td>
</tr>
<tr>
<td>23. H+O3 → HO+O2</td>
<td>2.6×10^{-11}</td>
</tr>
<tr>
<td>24. HO+H2O2 → HO2+O</td>
<td>2.9×10^{-11}</td>
</tr>
<tr>
<td>25. HO+HO3 → HO2+O2</td>
<td>2.0×10^{-10}</td>
</tr>
<tr>
<td>26. HO+HO3 M+HO2</td>
<td>1.35×10^{-10}</td>
</tr>
<tr>
<td>27. HO+HNO2 → H2O+HO3</td>
<td>1.3×10^{-10}</td>
</tr>
<tr>
<td>28. HO+HNO2 → H2O+HO3</td>
<td>2.55×10^{-12}</td>
</tr>
<tr>
<td>29. NO+HO2 → NO3+HO</td>
<td>2.9×10^{-10}</td>
</tr>
<tr>
<td>30. O(D)+H → HO+O(PP)</td>
<td>7.9×10^{-12}</td>
</tr>
<tr>
<td>31. O3+H → HO+O(PP)</td>
<td>2.57×10^{-11}</td>
</tr>
<tr>
<td>32. O3+H → HO2+O2</td>
<td>4.19×10^{-14}</td>
</tr>
<tr>
<td>33. O3+O3 → O3+O3</td>
<td>1.80×10^{-14}</td>
</tr>
<tr>
<td>34. NO+O → NO+O2</td>
<td>9.40×10^{-15}</td>
</tr>
<tr>
<td>35. NO+O3 → NO+O3</td>
<td>2.0×10^{-10}</td>
</tr>
<tr>
<td>36. NO+O3 → N+O3+O(D)</td>
<td>1.46×10^{-12}</td>
</tr>
<tr>
<td>37. NO+O3 → N+O3+O(D)</td>
<td>7.43×10^{-11}</td>
</tr>
<tr>
<td>38. NO+O3 → N+O3+O(D)</td>
<td>4.32×10^{-11}</td>
</tr>
<tr>
<td>39. NO+O3 → N+O3+O(D)</td>
<td>2.28×10^{-10}</td>
</tr>
</tbody>
</table>

For the 41 reactions listed in Table 1 there are 19 atomic or molecular species involved. Of these, we hold CH4, H2, N2 and O2 fixed and simply allow CH4 to accumulate, because there is no removal process for CH4 in this kinetic mechanism. The differential equations for the remaining species, O(D), HO, H, HO2, O3, H2O, HNO3, NO2, NO3, N2O, NO and N2, are solved using the LLL variant of the Gear method (Hindmarsh, 1972). The procedure is the following: We start with a steady state [from J. Chang’s one-dimensional (1D) model] representing the ambient atmosphere in an arbitrary “box” of constant volume. From Eq. (10) the steady-state equation for this case is

\[ P_i(C_i) - L_i(C_i)C_i + S_i = 0, \quad i = 1, 14, \quad (18) \]

where \( S_i = T_i \) is an apparent source of species \( i \) due to transport processes associated with the dynamic equilibrium of the ambient atmospheric state. By working in conjunction with the steady-state solution of the 1D model, we are able to explicitly incorporate computationally consistent diffusive flux terms \( T_i \), which in the presence of perturbations \( T_i \), simulate the ongoing mechanisms associated with the “natural” atmosphere. In the absence of perturbations, the system simply returns to the appropriate ambient state. Thus, for the

Fig. 2. As in Fig. 1 except for a single plume with low-level, scale-dependent transport of perturbed species: \( K_{zm} = 10^4 \) cm² sec⁻¹, \( K_{zm} = 10^8 \) cm³ sec⁻¹, and \( \epsilon = 2 \times 10^{-4} \) cm² sec⁻¹.
perturbed cases of interest we will use Eq. (10) in the form

\[
\frac{dC_i(t)}{dt} = P_i[C(t)] - L_i[C(t)]C_i(t) + T_i^a(t) + T_i^r,
\]

\(i = 1, 14.\) (19)

The assumption implicit in Eq. (19) is that the transport processes are separable into terms characteristic of the ambient and perturbing mechanisms. The ambient concentrations \(C_i^a(t)\) and transport terms \(T_i^a(t)\) used in our examples are given in Table 2. We introduce perturbations in the concentrations of \(H_2O, NO\) and \(NO_2\) based on the values presented in a Lockheed study (Hoshizaki et al., 1973) that correspond to the end of the so-called wake dispersion regime. For these components we have, at \(t=0\),

\[
\begin{align*}
C_{H_2O}(0) &= C^a_{H_2O}(0) + C^p_{H_2O}(0) = 2.074 \times 10^{18} \text{ cm}^{-3}, \\
C_{NO}(0) &= C^a_{NO}(0) + C^p_{NO}(0) = 8.360 \times 10^{10} \text{ cm}^{-3}, \\
C_{NO_2}(0) &= C^a_{NO_2}(0) + C^p_{NO_2}(0) = 3.010 \times 10^{10} \text{ cm}^{-3}.
\end{align*}
\]

The term \(T_i^r\) is evaluated for a two-dimensional Gaussian profile in accordance with Eqs. (1), (16) and (17) on the basis of initial plume dimensions of \(8.3187 \times 10^4\) cm in the vertical (from the Lockheed study). This translates into horizontal and vertical standard deviations of \(1.935 \times 10^4\) cm and \(3.105 \times 10^4\) cm.

4. Results

Figs. 1–3 present the temporal evolution of \(O_3, NO, NO_2\) and \(NO_2 = NO + NO_2\) concentrations at the center of a single plume for three choices of \(K_{xm}, K_{ym}\) and \(\epsilon\). With respect to the right-hand ordinate on these figures, an estimate is plotted of the net chemical destruction of ozone, integrated over the area of the plume. That is, at time \(t\),

\[
\Delta O_3(t) = \int_0^t dt' \frac{\partial(O_3)}{\partial t'}_{\text{chem}}.
\]

This quantity is the total number of ozone molecules destroyed per unit length of the plume.

Fig. 1 shows the results obtained when there is no transport of the perturbed species, that is, when \(T_i^r = 0\). The rapid (~1 min) readjustment of the equilibrium between NO and \(NO_2\) is characteristic of all cases studied at 20 km, regardless of transport of perturbed species. Significant deviation of the on-axis \(O_3\) concentration from its ambient value is not observed until after approximately one day. The slight drop-off of \(NO_2\) at late times occurs because the fixed \(N_2\) and \(O_2\) concentrations provide infinite baths of these species. Thus, the chemical paths that lead from NO and \(NO_2\) to \(N_2\) and \(O_2\) cause these trace species to eventually settle back to the ambient level.

Figs. 2 and 3 represent the effect of different levels of transport on the perturbed species. From Eq. (10) it can be seen that this transport acts to decrease concentrations that exceed the ambient concentrations. Likewise, this mechanism will tend to fill in “holes” that might develop in a concentration profile. Along this line, an interesting result appears for the local on-axis \(O_3\) concentration when comparison is made between the “no-small-scale-transport” case (Fig. 1) and the cases in which small-scale transport is operative (Figs. 2 and 3). In the absence of transport, the perturbed \(NO_2\) levels remain well above their ambient values for very long times (on the order of months), giving rise to a local on-axis \(O_3\) depletion that becomes evident after approximately one day. But in the cases of Figs. 2 and 3, the small-scale diffusion is sufficiently strong for the \(NO_2\) levels to approach ambient levels in less than a day because of plume expansion, and the local on-axis \(O_3\) concentration shows little, or no, response to these more or less brief \(NO_2\) perturbations. Figs. 4 and 5 quantify these results for selected parameter ranges.

The first set of figures (Fig. 4) exhibits the effect of transport on the \(O_3\) minimum reached at the center of a single plume. In Fig. 4a, \(K_{x}=0\) and \(K_{y}\) takes constant values between 0 and \(10^6\) cm² sec⁻¹. In Fig. 4b the case for scale-dependent diffusion with \(\epsilon=0.02\) cm² sec⁻¹ in Eq. (16) is presented. In this figure the abscissa is now the asymptotic value of \(K_{y}\). It will be seen that the difference between this and the above case is negligible. Finally, Fig. 4c corresponds to the case of scale-dependent diffusion and nonzero vertical transport; here \(K_{x}=10^8\) cm² sec⁻¹.

The second set of figures (Fig. 5) displays the total \(O_3\) destruction in the plume per centimeter of plume length 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. A most interesting aspect of Figs. 5a and 5b is that there is some optimum transport rate at which a maximum destruction occurs. Fig. 5c, for which \(K_{y}=10^6\) cm² sec⁻¹, shows a broad maximum as a function of \(K_{y}\), since the presence of vertical transport has already moved us “up” along the destruction curve. This set of curves indicates that there is only about 25% variation in total \(O_3\) destruction over the extremes of the transport ranges considered.
Fig. 4a. Minimum ozone concentration reached at the center of a single plume being dispersed by constant diffusion, as a function of horizontal diffusion coefficient $K_y$, with no vertical transport, $K_z=0$.

Fig. 4b. As in 4a except for scale-dependent diffusion, as a function of maximum horizontal diffusion coefficient $K_{ym}$, with $r=2 \times 10^{-2}$ cm$^3$ sec$^{-3}$ and no vertical transport, $K_z=0$.

Fig. 4c. As in 4b except for $K_{ym}=10^9$ cm$^3$ sec$^{-3}$.

5. Summary

An efficient means has been developed for performing coupled transport-kinetic calculations in a single box. Specifically addressed is the matter of local stratospheric ozone depletion in the diffusive transport regime due to NO$_x$ injections characteristic of an SST exhaust plume. Cumulative effects of multiple plumes were not considered here. This approach has allowed extensive parametric variations to be studied—particularly the sensitivity of trace species in a perturbed atmospheric regime to variations of transport rates. The major result is that, for an extremely wide range of transport rates, the total ozone destruction in a plume varies by only 25%, or less. Within this major result lie some interesting observations about single plumes of interactive species. First, if the dispersion rate is small, the increase or decrease of local concentrations can be large. But, by this very fact, the above effect can only occupy a very small physical volume (the plume doesn’t grow appreciably). It is then found that the total destruction of ozone in the volume spanned by the plume tends to be less for small dispersion rates than for cases with larger dispersion rates. Second, the extreme case of no dispersion can be viewed as corresponding to a highly correlated non-dispersive eddy. Regardless of how long such inhomogeneous correlations may persist, it has been indicated that this is the least serious case that we viewed in terms of total plume ozone destruction. Third, in recognition that atmospheric transport is not a constant, or even a continuous process, we have obtained a guide to understanding possible worst-case examples of the effects of intermittent atmospheric transport. Recall from above that the total ozone destruction in a plume is sensitive to high NO$_x$ pollutant concentrations on the one hand, and large effective volumes on the other. But it has been noted that these two mechanisms tend to cancel each other. Thus, it is not surprising that there are optimal ranges of plume dispersion, as seen in Fig. 5. Fig. 5 also indicates that, beyond a certain point, further increases of dispersion rates do not further increase this destruction within a given time. Given these limiting features, it is suggested that, for single plumes, the worst cases of total ozone destruction may occur when atmospheric dispersion rates lie continuously in the optimal ranges for O$_3$ destruction (Fig. 5).

Cases in which plume dispersion rates vary either continuously or intermittently from their optimal range would necessarily lead to less total ozone destruction in a given time than the possible worst case above—unless some rather complex synergistic effects can occur within

Fig. 5a. Total ozone destruction within a single plume being dispersed by constant diffusion, as a function of horizontal diffusion coefficient $K_y$, with no vertical transport, $K_z=0$.

Fig. 5b. As in 5a except for scale-dependent diffusion, as a function of maximum diffusion coefficient $K_{ym}$, with $r=2 \times 10^{-2}$ cm$^3$ sec$^{-3}$, and no vertical transport, $K_z=0$.

Fig. 5c. As in 5b except for $K_{ym}=10^9$ cm$^3$ sec$^{-3}$.
a single plume. The burden of demonstrating the existence or non-existence of such effects in a plume must lie with other treatments than our simple sensitivity approach.

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