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Analytic solutions of reaction diffusion equations and implications for the concept of an air parcel

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Abstract. In the atmosphere, hydroxyl radical concentrations can be estimated by considering the relative change in the concentration of two hydrocarbons of differing reactivity. This approach is based on three assumptions: (1) that background concentrations of the two hydrocarbon are zero; (2) that transport processes will influence all hydrocarbon concentrations equally; that is, hydrocarbon changes can be separated into the product of a chemical term and a transport term; and (3) that hydrocarbons have the same spatial and temporal emission pattern. In this paper, analytical solutions to a steady state reaction diffusion equation are derived. The general solutions to this problem are nonseparable, with the degree of nonseparability defined by a single parameter that is a simple function of the system's intrinsic timescales. When this parameter is evaluated for diffusivities typical of the boundary layer ($\sim 10^2$ m^2/s) and hydrocarbon reactivities that are sufficiently slow to be practically useful, it can be readily shown that for all practical purposes, separability can be assumed. This separability influences the spatial distribution of loss but not the net global loss. Thus even under nonseparable conditions, although the apparent local loss rate may be considerably less than the actual kinetic loss rate implied by hydrocarbon reactivity, when the apparent local loss rates are integrated to deduce a global loss rate, there will be no underestimate in the global loss rate, since the chemical loss rate is a linear function of hydrocarbon concentrations. It is conjectured that when much higher dispersion rates common in photochemical transport models ($\sim 10^5$–10^6 m^2/s) are invoked, local photochemical balances may be perturbed when chemical loss rates are either spatially inhomogeneous or influenced by reactant concentrations. Thus in highly diffusive models the influence of highly reactive chemical species may be extended further from the source regions than is realistic, even though the globally averaged loss rates would still be consistent with the magnitude of the globally averaged sink.

1. Introduction

Although the hydroxyl radical plays a crucial role in most aspects of tropospheric photochemistry, direct measurements have proved difficult because of the high sensitivity required to measure ambient concentrations. This has led several groups to make indirect estimates of time-averaged hydroxyl radical concentrations by examining the differential loss of hydrocarbons whose principal sink is reaction with the OH radical [*Calvert*, 1976; *Singh et al.*, 1981; *Roberts et al.*, 1984; *McKenna et al.*, 1995]. By determining concentration changes for two hydrocarbons of differing reactivities and assuming that the influence of "transport" on hydrocarbon concentrations will be the same irrespective of hydrocarbon reactivity, total hydroxyl radical exposures can be derived which can be used to estimate the mean hydroxyl concentration once an exposure time has been estimated.

Analytical solutions for the concentration field of a pollutant, emitted at a constant rate, subject to both advection by a constant wind and eddy diffusion by steady isotropic homogeneous turbulence, have been known for some time [*Sutton*, 1953]. Although it must be acknowledged that the treatment of atmospheric dispersion as a Fickian process is unrealistic in important aspects and can lead to erroneous results, solutions of the governing equations for this class of problem continue to be discussed because of the conceptual utility provided by simple analytic expressions with obvious physical interpretations.

In order to discriminate between the influences of chemistry and transport on pollutant concentrations, many experimental studies have compared the change in the relative concentrations of two species of differing reactivity. The validity of this approach is based on three main assumptions: (1) the effect of transport is confined to a simple dilution of the sampled air parcels; (2) the diluent air contains negligible concentrations of either of the reactive gases; and (3) hydrocarbons have the same spatial and temporal emissions pattern. The steady state concentration field χ of a reactive gas is governed by

$$K\left\{\frac{\partial^2\chi}{\partial x^2}+\frac{\partial^2\chi}{\partial y^2}+\frac{\partial^2\chi}{\partial z^2}\right\}-u\,\frac{\partial\chi}{\partial x}-L\chi+S(x,y,z)=0 \qquad (1)$$

where the gas is emitted from a continuous steady source distribution of magnitude $S(x, y, z)$, subject to advection with uniform velocity u, uniform turbulent dispersion represented by a constant isotropic eddy diffusivity K, and a loss rate $L\chi$ proportional to the local concentration χ, the reactive species in question.

McKeen et al. [1990] considered (1) for an infinite continuous line source and concluded that the chemical and mixing processes could not, in general, be separated. That result is confirmed by analytical solution, and a new analytical result for a continuous point source is presented. From these analytical

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solutions the definition of a coupling parameter in terms of the fundamental properties of the system naturally emerges. This coupling parameter may also be expressed as a simple function of the intrinsic timescales. By considering the apparent changes to local loss rates in terms of this coupling parameter, it is possible to define the circumstances under which chemistry and transport may be considered as uncoupled. Finally, the coupling constant is used to discuss the concept of a Lagrangian air parcel.

2. Dispersal and Removal of Chemically Reactive Species

Sutton [1953, p. 136] has given the solutions to (1), for an inert tracer ($L = 0$), for several specific source distributions. Here it will be shown that some of these solutions are applicable to the related reactive species problem provided a suitable change of variable is applied. Following *Seinfeld* [1986], we make the substitution $\eta = \chi \cdot e^{kr}$, where $k = u/2K$, because then the first-order derivative with respect to χ can be eliminated and (1) reduces to

$$K \cdot \nabla^2\eta - k^2\left(1 + \frac{4KL}{u^2}\right)\eta + S(x, y, z)e^{-kr} = 0 \qquad (2)$$

similar to *Seinfeld* [1986, equation (2), p. 555] except for the term $4KL/u^2$. Solutions to this class of problem can be described by the general expression

$$\chi = \frac{A_S}{4\pi}f\left(\frac{ur}{2K}(1 + \alpha)^{1/2}\right) \exp\left(-\frac{ux}{2K}\right) \qquad (3)$$

where

$$A_s = \int_V S(x, y, z) \exp\left(\frac{ux}{2K}\right) dV \qquad (4)$$

and f is a solution of the differential equation

$$\nabla^2 f - k^2(1 + \alpha) \cdot f = 0 \qquad (5)$$

where

$$\alpha = \frac{4KL}{u^2} \qquad (6)$$

The term α plays a special role, since it is this parameter which defines how much interaction there will be between the chemical and the physical processes. The physical significance of α is clarified when it is related to the fundamental time constants for the system under consideration. By definition,

$$t_a = \frac{r}{u} \qquad (7)$$

where t_a is the time to advect an air parcel at distance r.

$$\tau_D = \frac{r^2}{4K} \qquad (8)$$

where τ_D is the time for diffusion acting on a concentration gradient over a distance r to reduce that gradient by $1/e$, and

$$\tau_c = \frac{1}{L} \qquad (9)$$

where τ_c is the time for chemical removal to reduce a concentration by $1/e$. It then follows that

$$\alpha = \frac{t_a}{\tau_D} \cdot \frac{t_a}{\tau_c} \qquad (10)$$

and (3) becomes

$$\chi = \frac{A_S}{4\pi}f\left[2\,\frac{\tau_D}{t_a}\left(1 + \frac{t_a^2}{\tau_D \cdot \tau_c}\right)^{1/2}\right] \exp\left(-2\,\frac{\tau_D x}{t_a r}\right) \qquad (11)$$

The term α can be regarded as a coupling constant which links chemical and mixing processes in a diffusive atmosphere. Thus from a mathematical point of view the chemical and physical process described by (1) are not decoupled, and it is not generally possible to express the contribution of chemistry and diffusive transport as

$$\chi = \frac{A_S}{4\pi}f\left[\left(2\,\frac{\tau_D}{t_a}\right) \exp\left(-2\,\frac{\tau_D}{t_a} \cdot \frac{x}{r}\right)\right] \exp\left(-\frac{t_a}{\tau_c}\right) \qquad (12)$$

However, if we adopt the same approach as *McKeen et al.* [1990] and equate (11), the exact formal expression, with (12) but substitute an apparent chemical loss rate L_{app} for the actual loss rate L, the ratio of the apparent to the actual loss rate can be expressed as

$$\frac{L_{\text{app}}}{L} = \frac{\tau_c}{t_a} \log\left[\frac{f\left(2\,\frac{\tau_D}{t_a}(1 + \alpha)^{1/2}\right)}{f\left(2\,\frac{\tau_D}{t_a}\right)}\right] \qquad (13)$$

3. Special Cases

In order to understand the implications of these results, we will consider two special cases: a continuous point source situated at the origin and an infinite line source passing through the origin with advection acting perpendicular to the line source.

3.1. Point Source Steady State Solution

Seinfeld [1986] has given the solution for a point source of magnitude q as

$$\chi = \frac{q}{4\pi Kr} \exp\left(-\frac{u}{2K}(r - x)\right) \qquad (14)$$

Given this solution, straightforward substitution in (13) leads to the simple expression

$$\frac{L_{\text{app}}}{L} = \frac{2}{\alpha}\left(\sqrt{1 + \alpha} - 1\right) \qquad (15)$$

The ratio L_{app}/L is depicted in Figure 1 as a function of α. At low values of α the coupling between chemistry and transport is negligible, and the loss rate factor L_{app}/L is equal to unity; as α increases through unity, the coupling implied by α increases and the loss rate factor decreases, implying that the local concentrations change at a rate slower than that consistent with kinetic loss rates alone.

Point source solution timescales. From (11) and (15) it is obvious that it is not the individual chemical and transport timescales that should be compared with the advection timescale but their geometric mean $(\tau_c \cdot \tau_D)^{1/2}$. To understand why this particular combination is important, consider what effect mixing has on an air parcel for different values of τ_c and τ_D. When t_a is small in relation to $(\tau_c \cdot \tau_D)^{1/2}$, then α will be small and there will be little interaction; air will be mixed slowly and will not suffer a significant chemical loss over time

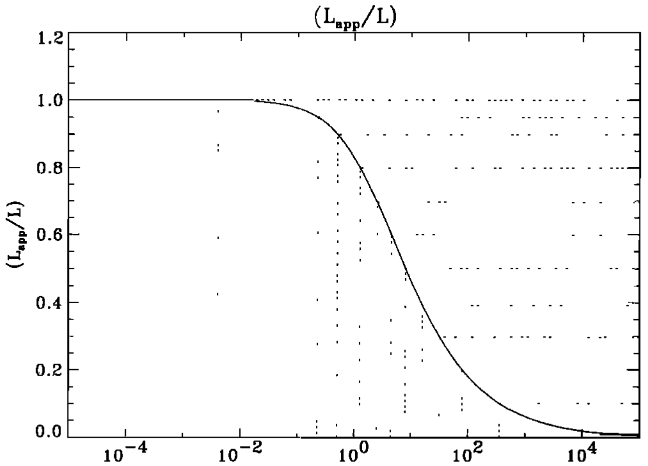

Figure 1. Change in L_{app}/L as a function of the coupling constant α for the continuous point source solution. See Table 1 for some examples of α and L_{app}/L. Values correspond to the contour values in Figure 2.

t_a. However, when t_a becomes sufficiently large that $t_a > (\tau_c \cdot \tau_D)^{1/2}$, then mixing can bring air from parts of the plume where a significantly different degree of chemical loss has taken place. The apparent age of the air parcel is actually the mass-weighted mean of a mixture of air with different chemical ages. Typically, the mean age of the air parcel will be shorter than the age of the air parcel centroid, and mixing will bring in younger air from upstream and older air from downstream. However, because of the logarithmic dependence of age on concentration, the age of the downstream air will not be sufficient to compensate for the youth of the upstream air. Thus the apparent age will be biased toward younger air, and L_{app} will be less than L.

Point source solution velocity scales. Although in a steady state solution the concentration distribution does not change with time, it is illuminating to consider the intrinsic velocity scales that apply to this problem. First, consider the concentration of an inert gas; the speed at which a diffusive signal would propagate through the system is given by

$$u_D = 4K/x \tag{16}$$

When u is less than u_D, the concentration will be dominated by diffusion rather than advection. However, eventually, x will be sufficiently large that u is greater than u_D, and it is appropriate to think of air parcels with an intrinsic length scale of

$$x_D = \frac{4K}{u} \tag{17}$$

Clearly, from (17), the greater the diffusion the greater the apparent air parcel size. Next consider a chemically reactive gas; the natural velocity scale that is a system invariant becomes

$$u_c = 2(KL)^{1/2} \tag{18}$$

u_c indicates how quickly a chemical signal from adjacent air parcels may propagate; if u_c is greater than u, then concentration gradients are dominated by the mixing of air parcels of differing age, and the air parcel concept will not be applicable. If u exceeds u_c, then air moves away from the source region faster than modified signals from adjacent air masses, characterized by a different release time of contaminants, can mix into an air parcel, and the plume may be considered as air parcel like, with an intrinsic length scale

$$x_c = 2\left(\frac{K}{L}\right)^{1/2} \tag{19}$$

x_c will typically be much greater than x_D, which is a measure of the intrinsic eddy length scale implied by a particular K value, while x_c is a measure of the largest size that an air parcel may have and still reasonably be attributed with a single age. Table 1 shows some illustrative calculations for a range of hydrocarbon reactivity, wind speeds, and eddy diffusivities.

3.2. Infinite Line Source

If instead of a point source we consider an infinite line source, the symmetry of the problem implies that (5) is best expressed in cylindrical coordinates and can be rearranged to correspond to the modified Bessel equation of the order of zero [*Abramowitz and Stegun*, 1972, p. 374]. The solution of this equation, which remains bound at infinity is the zeroth-order modified Bessel function of the second kind ($K_0(x)$):

$$f = \frac{\sigma}{2\pi} K_0(2\tau_D/t_a) \tag{20}$$

where σ is the source strength per unit length. No general simplification to (13) similar to (16) arises for this class of solution. However, if we note that $K_0(x) \to (\pi/2x)^{1/2} e^{-x}$, as $x \to \infty$, then

$$\frac{L_{\mathrm{app}}}{L} \to \frac{2}{\alpha}\left(\sqrt{1+\alpha} - 1 + \frac{1}{8}\frac{t_a}{\tau_D}\log(1+\alpha)\right) \tag{21}$$

as $t_a/\tau_D \to 0$. *Sutton* [1953] uses the limiting form of K_0 to present an approximate solution for an infinite line source.

Clearly then for small values of t_a/τ_D the apparent loss rate ratios are equivalent for the point source solution (PSS) and the line source solution (LSS). Figure 2 shows contours of constant L_{app}/L for the infinite line source solution as a function of t_a/τ_D and α along with the equivalent contours for a point source. The four quadrants marked on this contour plot can be associated with different regimes. Regions I and II involve advection times that are short in relation to the dispersion timescale; that is, air parcels are well defined. In region I, loss processes are slow in relation to advection, and so well-defined air parcels that can be treated as uniform can be said to exist. In region II, although coherent well-defined air masses exist, the local loss rate is sufficiently rapid that different parts of an air parcel will not behave as if they have a common chemical age. In regions III and IV, advection times are short in relation to the dispersion timescale. In region III, although dispersion is rapid, the chemical loss rates are still sufficiently fast that inhomogeneities due to differing chemical histories can exist. As the loss rates decrease, and we consider points in region IV, dispersion dominates the local concentration change so that most of the physical domain will have a uniform concentration and therefore a uniform loss rate. The mixing together of adjacent fluid elements cannot modify the apparent loss rate, since all elements have similar concentrations.

4. Relationship to Other Work

We can evaluate the ratio of the apparent loss rate to the actual loss rate as a function of the two natural time constant

Table 1. Sample Calculations of α and L_{app}/L, u_c, and x_c

Species	k_{OH}†	L*	u_c, m/s	u_c, m/s	α	α	α	α	α	α
K	1.00E−12	1.00E+06	1.00E+02	1.00E+06	1.00E+02	1.00E+02	1.00E+02	1.00E+06	1.00E+06	1.00E+06
u					5	10	50	5	10	50
CO	0.24	2.40E−07	6.93E−03	6.93E−01	3.84E−06	9.60E−07	3.84E−08	3.84E−02	9.60E−03	3.84E−04
CH_4	0.00084	8.40E−10	4.10E−04	4.10E−02	1.34E−08	3.36E−09	1.34E−10	1.34E−04	3.36E−05	1.34E−06
C_2H_6	0.27	2.70E−07	7.35E−03	7.35E−01	4.32E−06	1.08E−06	4.32E−08	4.32E−02	1.08E−02	4.32E−04
C_3H_8	1.2	1.20E−06	1.55E−02	1.55E+00	1.92E−05	4.80E−06	1.92E−07	1.92E−01	4.80E−02	1.92E−03
C_4H_{10}	2.5	2.50E−06	2.24E−02	2.24E+00	4.00E−05	1.00E−05	4.00E−07	4.00E−01	1.00E−01	4.00E−03
C_5H_{12}	3.9	3.90E−06	2.79E−02	2.79E+00	6.24E−05	1.56E−05	6.24E−07	6.24E−01	1.56E−01	6.24E−03
C_2H_2	0.9	9.00E−07	1.34E−02	1.34E+00	1.44E−05	3.60E−06	1.44E−07	1.44E−01	3.60E−02	1.44E−03
C_2H_4	8.5	8.50E−06	4.12E−02	4.12E+00	1.36E−04	3.40E−05	1.36E−06	1.36E+00	3.40E−01	1.36E−02
C_3H_6	26.3	2.63E−05	7.25E−02	7.25E+00	4.21E−04	1.05E−04	4.21E−06	4.21E+00	1.05E+00	4.21E−02
C_4H_8	31.4	3.14E−05	7.92E−02	7.92E+00	5.02E−04	1.26E−04	5.02E−06	5.02E+00	1.26E+00	5.02E−02
Species	**k_{OH}†**	**L***	**x_c (km)**	**x_c (km)**	**L_{app}/L**	**L_{app}/L**	**L_{app}/L**	**L_{app}/L**	**L_{app}/L**	**L_{app}/L**
K	1.00E−12	1.00E+06	1.00E+02	1.00E+06	1.00E+02	1.00E+2	1.00E+02	1.00E+06	1.00E+06	1.00E+06
u					5	10	50	5	10	50
CO	0.24	2.40E−07	40.8E+01	4.08E+03	1.00	1.00	1.00	0.99	1.00	1.00
CH_4	0.00084	8.40E−10	690.0E+02	6.90E+04	1.00	1.00	1.00	1.00	1.00	1.00
C_2H_6	0.27	2.70E−07	38.5E+01	3.85E+03	1.00	1.00	1.00	0.99	1.00	1.00
C_3H_8	1.2	1.20E−06	18.3E+01	1.83E+03	1.00	1.00	1.00	0.96	0.99	1.00
C_4H_{10}	2.5	2.50E−06	12.6E+01	1.26E+03	1.00	1.00	1.00	0.92	0.98	1.00
C_5H_{12}	3.9	3.90E−06	10.1E+01	1.01E+03	1.00	1.00	1.00	0.88	0.96	1.00
C_2H_2	0.9	9.00E−07	21.1E+01	2.11E+03	1.00	1.00	1.00	0.97	0.99	1.00
C_2H_4	8.5	8.50E−06	6.86E+00	6.86E+02	1.00	1.00	1.00	0.79	0.93	1.00
C_3H_6	26.3	2.63E−05	3.90E+00	3.90E+02	1.00	1.00	1.00	0.61	0.82	0.99
C_4H_8	31.4	3.14E−05	3.57E+00	3.57E+02	1.00	1.00	1.00	0.58	0.80	0.99

Read 1.00E−12 as 1.00×10^{-12}.
*Assuming [OH] = 10^6 molecules cm^{-3}.
†*Atkinson* [1990].

ratios t_a/τ_C and t_a/τ_D. The results of employing these coordinates are shown in Figure 3 (Note that $xu/4k = \tau_D/t_a$ and $L\Delta t = t_a/\tau_c$). *McKeen et al.* [1990] have performed numerical calculations on this problem, and the result in their Figure 2b is indistinguishable from the analytical solution presented in Figure 3. On the basis of their Figure 2b, *McKeen et al.* [1990] concluded that irrespective of the dispersion time constant, there would be no underestimate in the loss rate provided observations satisfy $t_a/\tau_c < 1$. This result appears to be at variance with common sense, because there must be strong interaction between the dispersion and the chemical processes when they have similar timescales. However, by considering Figure 2, it is reasonably obvious that this result arises for quite different reasons when $t_a/\tau_D > 1$ (regions III and IV) than when $t_a/\tau_D < 1$ (regions I and II). For values of $t_a/\tau_D < 1$, reductions in the apparent loss rates will not occur provided $\alpha < 1$; this condition will be satisfied for all $t_a/\tau_c < 1$; while for $t_a/\tau_D > 1$, the situation is quite different. In the simple point source model we would expect that $t_a/\tau_D > 1$ would imply that dispersion dominated over advection, so that only for chemical processes that are slower than the mixing processes would a proper estimate of the loss rate be possible, i.e.,

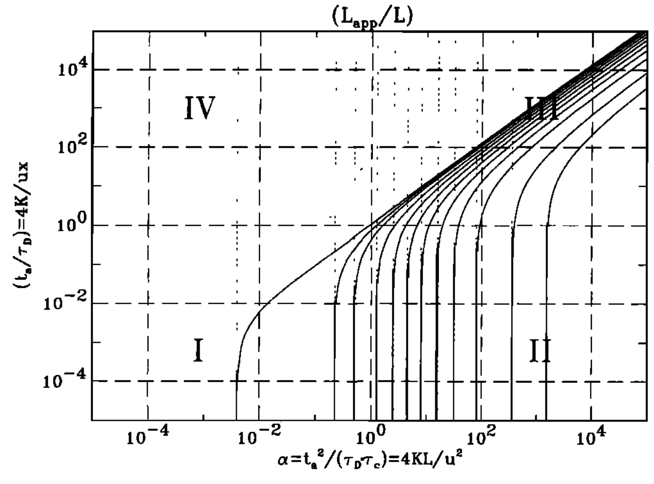

Figure 2. Contours of the apparent loss rate parameter (L_{app}/L_p) for a range of t_a/τ_D and α. Infinite line sources (solid lines), point source (dotted lines).

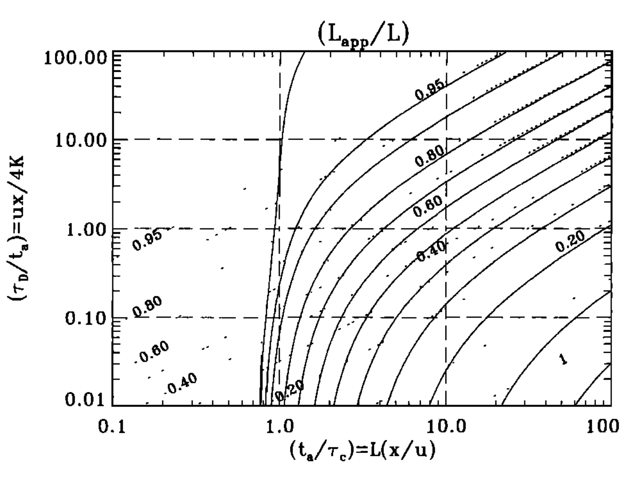

Figure 3. Diagram equivalent to Figure 2b in *McKeen et al.* [1990]. Infinite line sources (solid lines), point sources (dotted lines).

$t_a/\tau_c < t_a/\tau_D$, a more restrictive criterion than $t_a/\tau_c < 1$. In the region bounded by $t_a/\tau_c > 1$, $t_a/\tau_D > 1$, and $t_a/\tau_c > t_a/\tau_D$ the loss rate is not underestimated, since the diluent air has similar concentrations, as it has been influenced by adjacent sources. Thus in the regime where advection times are long in relation to dispersion, the lack of a discrepancy between the actual and the apparent loss rates is not a fundamental property of the mixing processes but is a function of the nature of the source distribution, whereas in the slow dispersion regime, the departure from local loss rates is intimately bound up with the nature of the mixing process.

5. Discussion

5.1. Contrasts Between Solutions

The differences between the point source and the line source solutions can give useful insight into the role of mixing in the atmosphere. The point source solution illustrates under what conditions a simple Lagrangian approach is likely to be successful with both the dispersion and the chemical timescales being equally important in defining the range of suitable chemical and physical timescales. The infinite line source solution, by contrast, indicates how the contribution from many sources may influence the interpretation of local losses. In the PSS case, the deviations from a simple decoupled situation arise because the dispersive transport from the source is efficient in relation to the advection, and so new reactant is supplied more quickly than it is removed either by chemical loss or by advection downstream. In addition, the LSS shows how the influence of adjacent sources can result in the apparent local loss being very different from the local removal rate. The LSS is an idealized example of the impact that a failure to take account of background sources may have on the local determination of hydrocarbon loss rates.

These two solutions neatly illustrate the consequences of the breakdown of the two assumptions given in the introduction. The departure of the loss rate from its expected value for large values of α is a consequence of the inability to express the influence of transport and chemistry as the result of two independent processes.

The apparently contradictory result, that if mixing is rapid, the apparent loss rate is close to the actual loss rate, is a consequence of the influence that dispersed sources (in this case, dispersed uniformly along an infinite straight line) have on local concentrations and as such represents a breakdown of the second assumption, namely that background concentrations are small. The reason that this leads to a ratio close to unity is that to the left of the 0.999 line in Figure 3, mixing is sufficiently efficient in relation to chemistry that the entire physical domain will take on a uniform concentration. However, even though the apparent loss rate would not be underestimated, it is difficult to see how one would determine L in practice under these conditions. Figure 4 shows a three-dimensional view of the value of L_{app}/L as a function of the logarithms of α and t_a/τ_D. This view neatly illustrates the link between the PSS and LSS suggested by (15) and (21).

5.2. Relevance to Empirical Loss Rate Determinations

It is also instructive to consider the relationship between these simple analytical solutions and the representation of these processes in the atmosphere. Consider the range of values of the two critical parameters t_a/τ_D and α which would apply for the oxidation of aliphatic hydrocarbon by a constant hydroxyl radical concentration of 10^6 molecules/cm^3 assuming a wind speed of 10 m/s and eddy diffusivity between 5 and 50 m^2/s, typical of what might apply to a plume in a turbulent boundary layer [*Sutton*, 1953; *Holton*, 1992]. With these parameter values specified, $\alpha \sim 10$. Under these circumstances the apparent loss rate factor will equal unity everywhere, and (12) reduces to

$$\chi = \frac{q}{4\pi K r} \exp\left[-\frac{u}{2K}(r-x) - \frac{L}{u} r\right] \qquad (22)$$

for a continuous point source, i.e., is identical to (12) when the proper substitutions have been made.

Thus for all practical purposes we can assume separability of chemical and dispersive processes in line with common practice among experimentalists.

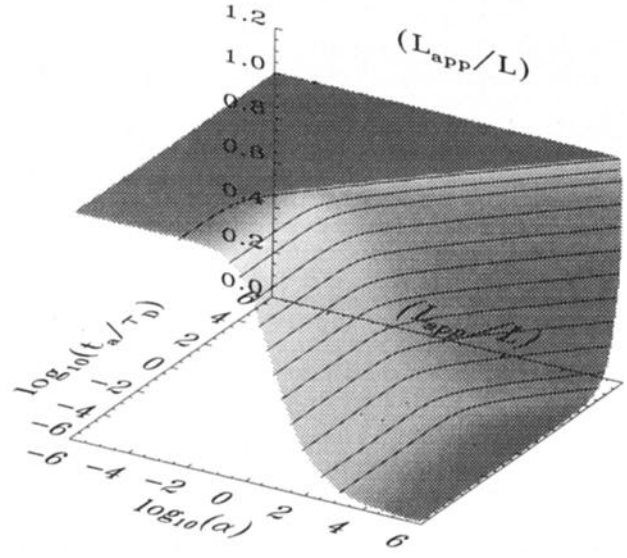

Figure 4. 3-D view of L_{app}/L for LSS. C.f. the PSS and the LSS when t_a/τ_D is small. Infinite line sources (solid lines) corresponding to the contour values in figures 2 & 3.

5.3. Relevance to the Representation of Mixing in Photochemical Transport Models

If eddy diffusivity is many orders of magnitude greater than the values typical of a turbulent boundary layer, then in principle, it is possible for the chemical and physical processes to become coupled. *McKeen et al.* [1990] noted that deviations from uniform loss rates are consistent with such a model provided an eddy diffusivity of 1.2 × 10^6 m^2/s was assumed. Large-scale eddy diffusivities of the order of 10^6–10^7 m^2/s have been deduced from atmospheric measurements by several workers, including *Murgatroyd* [1969], who based his estimate on the spread of geostrophic constant pressure trajectories; these diffusivities, however, are best interpreted as a representation of the statistical distribution of initially adjacent portions of a plume as they are differentially advected by synoptic and planetary scale motions and do not imply that those dispersed parts of a plume interact in any way, as is necessary for the plume model to be meaningful. As such, they are not suitable estimates of the rate of local mixing. Although diffusivity values of 10^6–10^7 m^2/s are physically unrealistic for plume models, they are comparable with those adopted in large-scale photochemical transport models [*Prather et al.*, 1987; *Müller and Brasseur*, 1995]. Thus in principle, such models may suffer from spurious reductions in local loss rates, leading to greater transport ranges for short-lived pollutants. In practice, if either the diffusivity is large enough or the reaction rate is fast enough to make L_{app} significantly different from L, then the applicability of an eddy diffusivity approach is doubtful [*Schumann*, 1989; *Karamchandani and Peters*, 1987], since one of the assumptions inherent in a mixing length model has been violated, namely that the value of the property being mixed is constant on the timescale of an eddy that mixes it.

The system analyzed here is linear, since it is assumed that the loss reaction has no influence on the reaction rate; that is, the OH concentration remains unchanged; therefore the losses integrated over the entire domain will still be the same even though reactive species will be advected further from the source than is realistic. Thus it is clear that the mixing process in a model has no effect on the global removal rate of the reactive species but only appears to have an effect with reduced losses close to the source compensated for by increased losses farther away. However, if genuinely nonlinear chemistry or spatial inhomogeneities in loss processes are considered, it is conjectured that complex errors may occur when evaluating local losses that, unlike the processes considered in this paper, will not, in general, average out over the domain as a whole. Which reactions will be affected will depend on which chemical timescales become comparable with the implied transport timescales.

6. Conclusions

For all practical experimental purposes, interaction between chemical and transport timescales may be ignored, although care must still be paid to the potential influence of background sources [*McKenna et al.*, 1995]. Although no general separability of diffusive transport and chemical loss processes can be demonstrated when account is taken of likely values of atmospheric parameters, reasonable separation can be shown for a range of hydrocarbons with lifetimes that are comparable with those often used in Lagrangian studies.

The degree of nonseparability can be expressed as a single parameter that is the product of the dispersive and chemical timescales both measured in relation to the advective timescale. Coupling between chemistry and transport only occurs in the limit of rapid dispersion, which violates a basic assumption of the eddy diffusion approximation.

Deviations from the implied kinetic loss rates are only apparent as the global effect is independent of the mixing processes. Thus loss rate deviations are only apparent and not "effective."

In highly dispersive situations, where locally there can be large discrepancies, the intrinsic linearity of the loss processes means that although the local estimates of loss rate will be in error, when local estimates are integrated to produce a global estimate of the loss rate, that estimate will be the same as the one based on separable chemistry and mixing. Global loss rates are unaffected because reduced losses close to source regions are compensated for by increases in more distant losses. In situations where rapid dispersion is implied (i.e., in numerical models with unrealistically large values of eddy diffusion), this may lead to an increase in the inferred lifetime of reactive species, increasing the range of distances over which they will be estimated to persist in significant concentrations.

However, strong nonlinearity present in model chemical systems may result in errors in the local rates of change which will not average out over the domain as a whole. An example of this type of nonlinearity would be in the local balance between production and loss of two species in photochemical balance, such as the balance between OH and HO_2, controlled by the O_3 and NO reactions with peroxy radicals and oxidation of CO and CH_4 by hydroxyl radicals. This potential for nonlinearity should not generally influence atmospheric processes but may become important in model representations where the effective diffusivity can be as high as 10^6 m^2/s.

Thus model estimates of hydrochlorofluorocarbons and hydrocarbon lifetimes may be predicted in an entirely self-consistent way with model-predicted hydroxyl radical amounts. However, where nonlinearity exists, as it does in photostationary state balances, errors in the local rates may influence the local balance and through that model predictions of OH amounts.

This simple model system also indicates how the timescales of advection, mixing, and chemical reactivity may be combined. Furthermore, they offer, albeit under very restrictive conditions, criteria for when it is meaningful to consider a volume of air as an air parcel; that is, it is a volume of air that satisfies the dual criteria that the advection time is short in relation to the dispersion time, necessary for a volume of air to remain intact, and that the chemical timescales must be short in relation to the diffusion-moderated advection timescale $t_a(t_a/\tau_D)$ since chemistry will then be too fast to be influenced by the diffusion of air of a different chemical character into the air parcel.

Provided the first of these conditions is satisfied and an air parcel physically exists, the second condition is satisfied even for timescales longer than the advection timescale. Just how much longer is dictated by the value of (t_a/τ_D).

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