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The object of this paper is to extend the simple ATDL model of urban dispersion to account for chemical reactions. In the simple model for chemically inert substances (Gifford and Hanna, 1970 and 1972; Hanna, 1971), surface concentration [C](ppm) is proportional to local area source strength Q_C(cm^3/m^{2}s) and inversely proportional to the wind speed U(m/sec):

$$[C] = A \frac{Q_C}{U} \quad , \qquad (1)$$

the proportionality factor A is shown in the references to equal about 50, 200, and 600 for unstable, neutral, and stable conditions, respectively. For yearly averages, the factor A is observed to be about 225. Physically, the factor A represents the ratio $\Delta x/Z$, where Δx is the horizontal upwind dimension of the source region and Z is the average height throughout the region of a plume of material released at the surface of the region. In the above references, it is found that the height Z is not strongly dependent on city size; Z equals approximately 2000, 150, and 40 m for unstable, neutral, and stable conditions, respectively.

If photochemical reactions take place, then the equation describing the time rate of change of concentration $[C_i]$ in a box of unit width with height Z, depth Δx is the following:

$$Z \, \Delta x \frac{\partial}{\partial t} [C_i] = Q_{Ci} \, \Delta x - Z \, U \, [C_i]$$

$$- Z \, \Delta x \, \Sigma \, \alpha_{im} \, [C_i]^{a_{im}} \prod_{ikm} [C_j]^{a_{ijm}} \quad . \qquad (2)$$

It is assumed for simplicity that concentration $[C_i]$ is uniform in the box. The last term is based on the law of mass action. The constants α_{im} are called the rate constants; they are inversely proportional to the time required to change the concentration [C] by 50 per cent by means of the chemical reactions im alone. The index ikm indicates the number of substances other than C_i that are involved in reaction im. The constants "a" are stoichiometric coefficients, i.e. the numerical coefficients in the balanced chemical reaction equation. For steady state conditions with no chemical reactions, eq. (2) reduces to the simple ATDL dispersion eq. (1). There are of course additional equations, similar to eq. (2), for other chemical substances that are involved in the chemical kinetic system.

Eq. (2) may be made dimensionless by defining a dimensionless concentration $[C]^*$ and time t^*:

$$[C]^* = \frac{[C] \, UZ}{Q_C \, \Delta x} \qquad t^* = \frac{tU}{\Delta x} \qquad (3)$$

The concentration $[C]^*$ equals unity for steady state conditions with no chemical reactions. That is, the simple disperion equation (1) is in effect used as a scaling factor for non-dimensionalizing the concentration. As a result, eq. (2) takes the dimensionless form:

$$\frac{\partial}{\partial t^*} \ln [C_i]^* = \frac{1}{[C_i]^*} - 1 \qquad (4)$$

$$- \sum_m \left(\prod_{ikm} [C_j]^{*\,a_{ijm}} \right) \left(\alpha_{im} \frac{\Delta x}{U} \prod_{ikm} \left(\frac{Q_j \, \Delta x}{UZ} \right)^{a_{ijm}} \right) [C_i]^{*\,a_{im}-1}$$

The dimensionless numbers,

$$\alpha_{im} \, (\Delta x/U) \prod_{ikm} (Q_j \, \Delta x/UZ)^{a_{ijm}} \, ,$$

completely determine the solution, given the initial conditions. If all the dimensionless numbers are less than about 0.1, then chemical reaction terms are not important in the system by comparison with source terms and advection terms. It is thus possible to assess the relative importance of wind speed, stability, and source strengths in the system.

The kinetic mechanism proposed by Friedlander and Seinfeld (1969) serves admirably to illustrate the application of the theory. The

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* This paper is a brief summary of a longer paper, in which complete derivations are given, submitted to <u>Envir. Sc. and Tech.</u>

following three dimensionless equations for the rate of production of $[NO]^*$, $[NO_2]^*$, and $[RH]^*$ are obtained:

$$\frac{\partial}{\partial t^*} \ln [NO]^* = \frac{1}{[NO]^*} - 1 - C1 \, [NO_2]^*[RH]^* \quad (5)$$

$$\frac{\partial}{\partial t^*} \ln [NO_2]^* = \frac{1}{[NO_2]^*} - 1 + C2 \, [NO]^*[RH]^* - C3 \, [NO_2]^*[RH]^* \quad (6)$$

$$\frac{\partial}{\partial t^*} \ln [RH]^* = \frac{1}{[RH]^*} - 1 - C4 \, [NO_2]^* - C5 \, [NO_2]^*/[NO]^* \; . \quad (7)$$

The five dimensionless governing parameters in eqs. (5) through (7) are the following:

$$\begin{aligned} C1 &= \alpha \, Q_{NO_2} \, Q_{RH} \, \Delta x^3/(U^3 Z^2) \\ C2 &= \alpha \, Q_{NO} \, Q_{RH} \, \Delta x^3/(U^3 Z^2) \\ C3 &= \lambda \, Q_{NO_2} \, Q_{RH} \, \Delta x^3/(U^3 Z^2) \qquad (8) \\ C4 &= \theta \, Q_{NO_2} \, \Delta x^2/(U^2 Z) \\ C5 &= \mu \, (Q_{NO_2} \, / \, Q_{NO}) \, \Delta x/U \quad . \end{aligned}$$

The rate constants α, θ, μ, and λ equal $1.7 \times 10^{-3} ppm^{-2} sec^{-1}$, $3.3 \times 10^{-5} ppm^{-1} sec^{-1}$, $4.0 \times 10^{-6} sec^{-1}$, and $3.3 \times 10^{-4} ppm^{-2} sec^{-1}$, respectively, according to Friedlander and Seinfeld (1969). If steady-state conditions are assumed, then the three equations (5) through (7) can be solved directly for the three unknowns $[NO]^*$, $[NO_2]^*$ and $[RH]^*$.

Source strengths, meteorological data, and pollutant concentrations observed during the two-day period 29-30 September 1969 in the Los Angeles basin, reported by Weisburd et al. (1971) and Roth et al. (1971), are available to test the above theory. If it is assumed that the simple ATDL dispersion model, eq. (1), is valid at 5 a.m. (i.e. before sunrise), then it can be assumed that

$$Q_{NO_2} = .2 \, Q_{RH} \text{ and } Q_{NO} = .3 \, Q_{RH}.$$

Because the parameter A is equivalent to the ratio $\Delta x/Z$, the parameters (8) can be simplified to:

$$\begin{aligned} &C1 = 3.3 \times 10^{-4} \, Q_{RH}{}^2 \, A^3 Z/U^3, \\ &C2 = 1.5 \, C1, \quad C3 = .2 \, C1, \qquad (9) \\ &C4 = .02 \, C1 \, U/AQ_{RH}, \; C5 = 2.8 \times 10^{-6} \, AZ/U \end{aligned}$$

From the above references, it is found that the average day-time source strength Q_{RH} in the Los Angeles basin is approximately .005 $cm^3/m^2 sec$. The average wind speed U in the basin for the period 6:30 a.m. - 10:30 a.m. on 29 September 1969 was approximately 2 m/sec. For a typical day, the parameter A can be taken to equal 200 and the depth Z to equal 150 m. For these values of the variables Q_{RH} , U A, and Z, the governing parameters C1 through C5 equal 1.25, 1.87, .25, 0.50, and .042, respectively. Because some of these parameters are greater than .1, chemical reactions are important for this system. Since the parameters C1 and C2 are largest, it is clear that slight changes in wind speed can greatly affect smog concentrations, for C1 and C2 are inversely proportional to the cube of the wind speed.

Using the above values of the governing parameters, the steady-state concentrations $[NO]^*$, $[NO_2]^*$, and [RH] were calculated to be .40, 1.45, and .82, respectively. These values are plotted as crosses on the right-hand-side of Figure 1. Also plotted are the observed time variations of the dimensionless concentrations of these substances. Since it was assumed

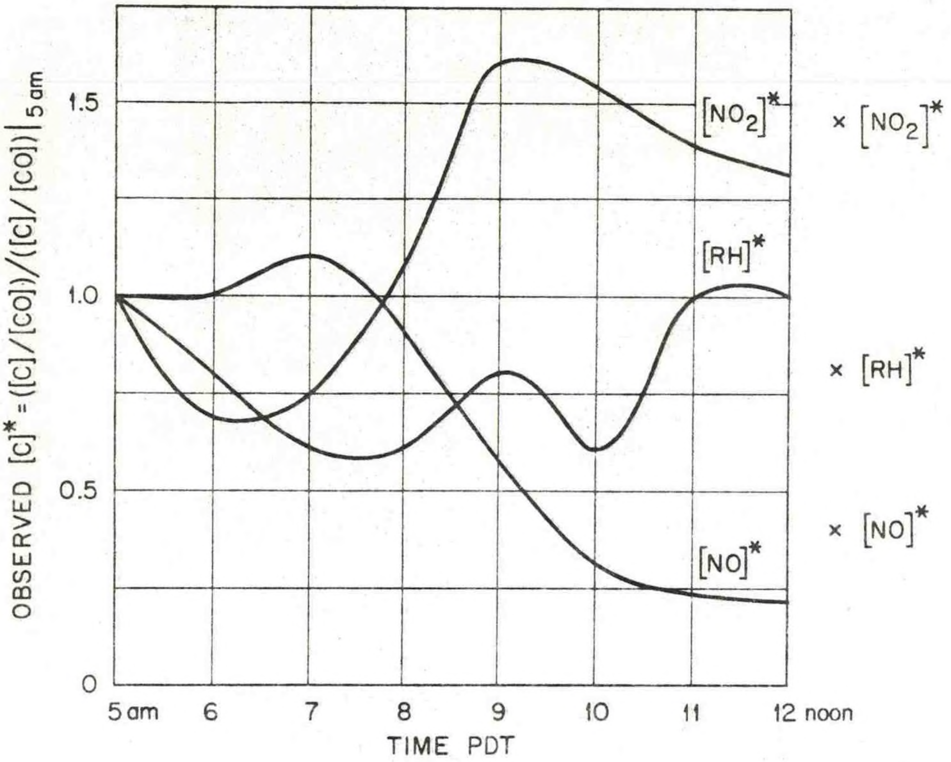

Figure 1: The observed hourly dimensionless concentrations $[C]^* = ([C]/[CO])/ ([C]/[CO])|_{5a.m.}$ of NO_2, RH, and NO, plotted as a function of time for 29 September 1969 in the Los Angeles basin. The steady state dimensionless concentrations, calculated by eqs. (5) through (7), are shown as crosses on the right hand side of the figure.

that the concentration of the inert substance [CO] follows the predictions of the simple ATDL dispersion model, and also that the concentrations of all pollutants at 5 a.m. (before sunrise) follow the simple model, then it follows that $[C]^*$ is equivalent to the ratio $([C]/[CO])/([C]/[CO])|_{5a.m.}$. Observed concentrations of NO, NO_2, and RH, averaged over the basin, are normalized in this manner and plotted as a function of time in Figure 1. The observed dimensionless concentrations at noon and the calculated steady-state concentrations are seen to be in fair agreement.

Table 1

Values of predicted and observed steady-state dimensionless concentrations in the Los Angeles basin for noon on 29 September 1969.

Substance	$[NO]^*$	$[NO_2]^*$	$[RH]^*$
Predicted	.40	1.45	.81
Observed	.22	1.32	1.00

The above calculations are just one example of the insight that can be gained from this kind of analysis. Other applications are given in a more complete paper (Hanna, 1972). For example, if it assumed that photochemical reactions become important when the parameter Cl is greater than 0.1, then it is possible to estimate "critical" values of wind speed and source strength. It is clear from the present study that the wind speed is a dominant factor in the determination of concentrations of photochemical smog, since the wind speed appears cubed in the governing parameter Cl, and also appears in the simple eq. (1). For eleven stations in the Los Angeles basin at noon on 29 September 1969, the correlation between oxidant concentration and inverse wind speed is .66. The strong correlation between wind speed and inert pollutant concentration has been documented by Hanna (1971) and Gifford and Hanna (1972).

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