Methods for Assessing the Effects of Mixtures of Chemicals
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Predicting Concentrations of Atmospheric Pollutants

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ABSTRACT

Transport and transformation of chemical mixtures occur continuously and simultaneously in the atmosphere. Starting with experimental data and fundamental concepts, models have been developed to predict exposure concentrations to which biological receptors are exposed within a given time interval. Because the interactions between transport dynamics in the atmosphere and the atmospheric chemistry of air pollution are very complex, models to predict exposure concentrations represent many compromises and simplifications regarding coupled processes.

The combined effects of chemical transformations and media dynamics determine exposure concentrations for mixtures of chemicals in the atmosphere. To better understand the nature of the interactions between these coupled processes and the criteria used to assign negligible importance to individual processes, the steps for developing models to predict ground level concentrations of mixtures of air pollutants are presented. From this discussion, recommendations are given regarding refinements to these models.

1 INTRODUCTION

Formation of new chemical mixtures occurs continuously in all phases of the environment. The cycling of important elements is the result of many simultaneous processes. The concentrations of individual chemicals and mixtures of chemicals to which biological receptors are exposed are due to the combined effects of these environmental transport and transformation processes. Because transformations and transport dynamics for chemicals are coupled processes, models to predict exposure concentrations must take this situation into account.

Within a designated time interval and spatial location, interactions among naturally occurring chemicals and chemicals entering the environment as a result of industrial synthesis and commercial use have three possible outcomes: (1) chemicals remain unchanged; (2) chemicals are partially altered; and (3) chemicals are completely remineralized. The most important characteristics of chemicals that determine the outcomes of these interactions for a specified set of intensive environmental conditions are the molecular structures of the constituents of the mixture. Empirical relationships for specific arrangements of atoms and functional groups in molecules, and theoretical models based on molecular orbital theories, have made it possible to predict with an increasingly high degree of accuracy the outcomes of different types of interactions once a specific mechanism has been proposed and a set of environmental conditions specified. Even with this increased predictive capability, these relationships and theories have been developed for single chemicals, and at most two chemicals plus a solvent or other carrier medium which usually does not exert a passive role. For a mixture of chemicals in either a highly mobile phase like the atmosphere or a condensed phase like the hydrosphere, there are many interactions that are possible. The significance and impact on the rate of transport and transformation and the composition of new mixtures cannot always be predicted from single chemical models.

There are instances, however, in which simple models can be very effective in predicting outcomes of complex processes. For this reason, the steps in developing predictive models for air pollutants will be analysed because the models are attempts to represent complex interactions of mixtures by simple process dynamics.

2 ATMOSPHERIC TRANSPORT AND TRANSFORMATIONS

The formation of mixtures of ozone and photochemical oxidants in the atmosphere above many urban areas is the result of a series of complex photochemical and chemical reactions between oxides of nitrogen and hydrocarbons. The accumulation of significant concentrations of photochemical oxidants at ground level is due to the combination of atmospheric chemical reactions and lack of dispersion resulting from insufficient atmospheric turbulence. Photochemical smog episodes are the result of these two abiotic processes occurring simultaneously.

The atmospheric chemistry and meteorology of photochemical smog have been studied by many investigators (Altshuller, 1979; Altshuller and Bufalini, 1971; Anderson, 1978; Calvert and McQuigg, 1975; Calvert *et al.*, 1978; Dimitriades, 1972; Friedlander and Seinfeld, 1969; Graedel, 1980; Haagen-Smit, 1952; Hecht and Seinfeld, 1972; Hecht *et al.*, 1974; Lioy and Samson, 1979; Martinez *et al.*, 1973). The chemical reactions of photochemical smog begin with photodissociation of nitrogen dioxide into nitric oxide and an oxygen free radical. The very reactive oxygen free radical reacts with abundant oxygen to produce ozone, which in turn reacts with nitric oxide to produce nitrogen dioxide. Thus the cycle is repeated and will continue as long as there is sunlight and nitrogen dioxide. In the absence of other chemicals that compete for oxygen free radicals, a pseudo steady state will be reached producing a constant level of ozone in the lower atmosphere. The cyclical nature of this process is illustrated in Figure 1 (NAS, 1977).

Of the atmospheric chemicals, nitrogen dioxide is the only chemical that can absorb radiant energy in the visible portion of the electromagnetic radiative energy spectrum and undergo photodissociation. Ozone requires the higher-energy ultraviolet portion of this spectrum for dissociation to occur. The dissociation of ozone occurs in the stratosphere and is responsible for shielding the earth's surface from very high-energy solar radiation. It is ironic that ozone is an important constituent of the upper atmosphere for safeguarding life on the earth's surface, but is considered life threatening when present at significant concentrations at ground level.

The concentrations of ozone and photochemical oxidants increase in the air space above urban areas because of the presence of significant concentrations of reactive hydrocarbons and meteorological conditions in the troposphere that reduce the rate of dispersion and dilution of air pollutants. The presence of

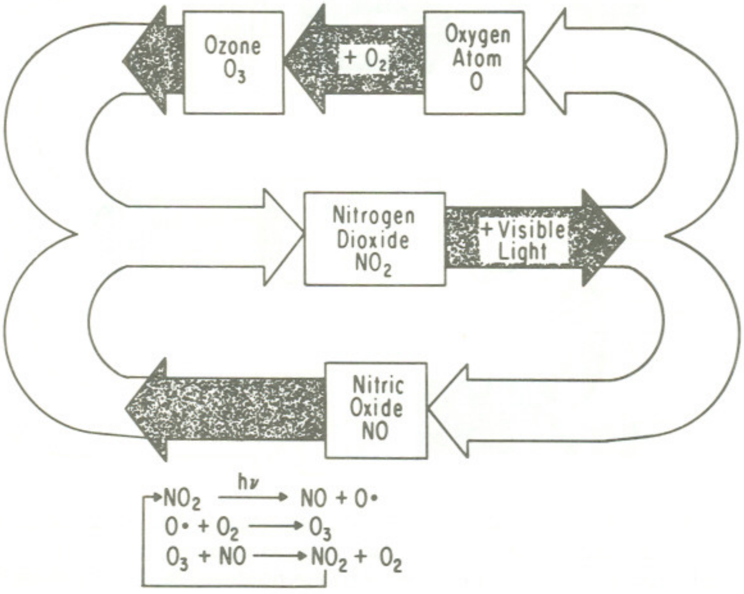

Figure 1 Photodecomposition of nitrogen dioxide. Cycle continues as long as sun shines. Net result is a steady-state concentration of ozone in the lower atmosphere. The thickness of the connecting arrows indicates steady state equality of concentrations of ozone, nitrogen dioxide and nitric oxide. From NAS (1977). *Reproduced by permission of the National Academy of Sciences*

reactive hydrocarbons, particularly low molecular weight alkenes from automobile exhaust and other mobile and stationary sources, is important because they can react with oxygen atoms produced by the photochemical dissociation of nitrogen dioxide to produce aliphatic free radicals. These new free radicals can either react with nitric oxide to generate nitrogen dioxide or form additional free radicals. By reacting with nitric oxide, the more abundant hydrocarbon free radicals slow down the removal process of ozone with nitric oxide, allowing ozone concentration to increase. The impact on the concentration of ozone in the troposphere of reactive hydrocarbons and their reaction products is shown mechanistically in Figure 2 (NAS, 1977). An example of the time-dependent increase and decrease of ozone, nitric oxide, and nitrogen dioxide concentrations is shown in Figure 3, which has been compiled from several investigations (Ball, 1976; Derwent and Stewart, 1973; USDHEW, 1970).

The observed changes in the concentration of ozone, nitric oxide, and nitrogen dioxide are due not only to chemical reactions, but also to changes in atmospheric dispersion. Before 8 a.m. it is not uncommon for a nocturnal temperature

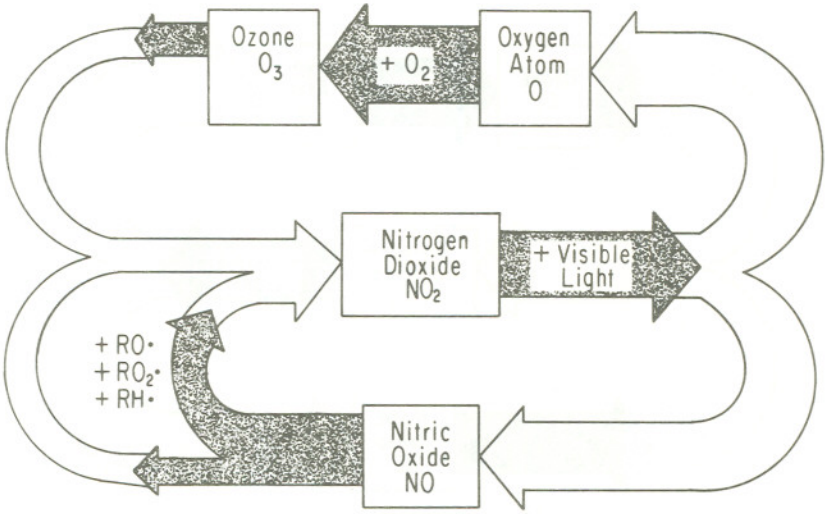

Figure 2 Atmospheric chemistry of photochemical smog. The presence of reactive hydrocarbons adds chemicals that can react with oxygen atoms to form free radicals. These free radicals (indicated as RO, RO_2, and RH) are produced rapidly by chain transfer mechanisms and also react with nitric oxide, thus competing with the reaction between ozone and nitric oxide. Because there are many hydrocarbon free radicals and their rate constants for reaction with nitric oxide are much greater than for the reaction of nitric oxide and ozone, there is little remaining nitric oxide to react with ozone which then accumulates in the lower atmosphere. From NAS (1977). *Reproduced by permission of the National Academy of Sciences*

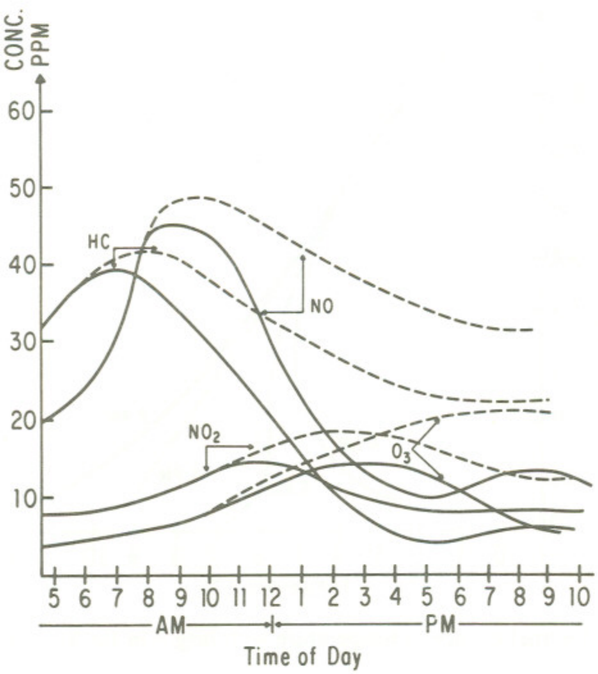

Figure 3 Combined effects of meteorology and atmospheric chemistry in causing photochemical smog. Dotted lines indicate concentrations during a sustained daylight temperature inversion

inversion to exist in the atmosphere. At midday, during periods of sunlight, the rate of change of atmospheric temperature with altitude, or atmospheric lapse rate, is usually negative, indicating that atmospheric temperature decreases with increasing altitude above the earth's surface. The magnitude of the lapse rate is a good measure of the dispersion rate because it represents the magnitude of the temperature gradient in the atmosphere. The relationship between vertical temperature gradient and atmospheric stability is an important determinant of the dispersion and dilution capability of the lower atmosphere (Blackadar, 1957, 1962; Lumley and Panofsky, 1964; Monin, 1970; Monin and Yaglom, 1971; Pasquill, 1962; Turner, 1964, 1970). A typical diurnal pattern of changes in stability that are related to the temperature gradient in the atmosphere is shown in Figure 4. In the stable atmosphere of early morning, concentrations of ozone, nitric oxide, and nitrogen dioxide will increase, not only because of atmospheric chemical reactions but also because in a stable atmosphere the rate of removal by air motion is much lower than the rate of entry from exhaust emissions during peak rush hour traffic. Referring to Figure 3, as the sun warms the earth's surface at a higher rate than the air above it, the lapse rate changes from positive to

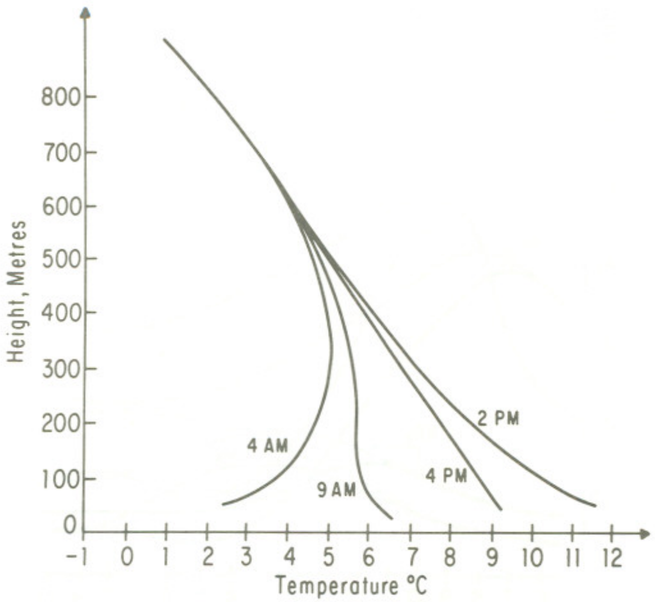

Figure 4 Diurnal change in temperature with height in the lower atmosphere

negative, the atmosphere becomes more unstable, and enhanced vertical mixing causes concentrations of air pollutants to decline rapidly. The effect of an unstable atmosphere is seen during the peak afternoon traffic load. The dispersing capability of the atmosphere is near its daily maximum in the absence of conditions that cause prolonged temperature inversions and concentrations of air pollutants will remain below their early morning levels.

In addition to the daily pattern of low-level temperatures that alternate from unstable during the day to stable at night, more persistent inversions aloft that extend through the diurnal cycle act as a physical barrier or 'lid' to vertical mixing. Subsidence inversions caused by the subsiding air in the vicinity of high-pressure regions and marine inversions with flow from above cool water over warmer land are examples. These inversions limit vertical mixing, pollutants will not be dispersed, and concentrations will remain high throughout the day and night. In an analysis of ozone concentration patterns for the north-eastern section of the United States, Lioy and Samson (1979) observed that extended levels of high ozone concentrations were due to prolonged periods of high pressure.

2.1 Models for Predicting Concentrations of Air Pollutants

Models of many types have been developed for predicting ground level concentrations of air pollutants at locations downwind of their points of entry.

These models combine important meteorological characteristics and chemical reaction characteristics of pollutants (Chang and Weinstock, 1973; Clarke, 1964; Egan and Mahoney, 1972; Eschenroeder *et al.*, 1972; Friedlander and Seinfeld, 1969; Gifford and Hanna, 1973; Hanna, 1971, 1973; Heines and Peters, 1973; Hoffert, 1972; Johnson *et al.*, 1973; Lamb and Neiburger, 1971; Lamb and Seinfeld, 1973, 1974; Martin, 1971; McCollister and Wilson, 1975; Pack, 1964; Reynolds *et al.*, 1973, 1974; Reynolds and Seinfeld, 1975; Roth *et al.*, 1974; Trijonis, 1974; Turner, 1970). The models use different methods of solution of the equations of motion for turbulence required to describe air pollutant transport and transformation. A major obstacle in the development of predictive models for air pollution is a lack of understanding of the theory of turbulent dispersion with simultaneous chemical reaction for homogeneous turbulence. A fundamental understanding of multicomponent reactions occurring in the heterogeneous turbulence of the atmosphere is even less well understood.

Even with these limitations, two approaches have been developed for predicting ground level concentrations of air pollutants emitted from stationary and mobile sources in urban areas. The Eulerian approach describes the behaviour of pollutant species relative to a fixed coordinate system, and the Lagrangian approach describes concentration changes relative to a moving fluid. Both approaches provide valid descriptions of turbulent dispersion but, due to the unknown characteristics of many of the transport properties, such as velocities and dispersion coefficients, as well as a precise knowledge of the atmospheric chemistry of photochemical smog, exact solutions with either method are impossible. However, with the use of reasonable assumptions, approximate solutions can be obtained that incorporate and couple important meteorological and chemical reaction variables.

The problems of finding solutions with the Eulerian approach to turbulent dispersion originate in the fluctuating character of concentration and velocity fields. In the equations of motion for turbulent dispersion these terms create more dependent variables than defining equations—referred to as the closure problem of turbulence. The problem becomes even worse when the chemical reactions are non-linear, thus introducing into the defining equations additional fluctuating components that include dependent variables. The derivation of the equations for turbulent transport in the atmosphere and the complications arising from these additional components are given in Pasquill (1962) and Seinfeld (1975). By using the Boussinesq approximation many of the closure problems in the Eulerian approach can be overcome, and the turbulent mass balance equations for individual species can be given as

$$\frac{\partial\langle C_j\rangle}{\partial t}+\sum_{i=1}^{3}\bar{V}_i\frac{\partial\langle C_j\rangle}{\partial X_i}=\sum_{i=1}^{3}\frac{\partial}{\partial X_i}\left(K_{ii}\frac{\partial\langle C_j\rangle}{\partial X_i}\right) \tag{1}$$

$$+W_j(\langle C_1\rangle,\ldots\langle C_N\rangle+S_j(X,t);\quad j=1,2,\ldots N$$

where

$\langle C_j \rangle$ is an approximation to the concentration term for chemical species j, $C_j + C'_j$, composed of the instantaneous concentration C_j, plus the turbulent concentration fluctuation, C'_j. $\langle C_j \rangle$ is defined as the time-smoothed concentration of species j in the turbulent mass transfer equation;

$\bar{V}_i$ is the time-smoothed velocity component in the i-direction;

K_{ii} is the eddy diffusivity, defined as the ratio of the product of the fluctuating components of instantaneous concentration and velocity field to the gradient of the time-smoothed concentration of species j in the i-direction; for example,

$$\frac{\langle C'_j V'_i \rangle}{\dfrac{\partial \langle C_j \rangle}{\partial X_i}}$$

W_j $(\langle C_1 \rangle \ldots \langle C_N \rangle)$ is the chemical reaction rate term in which the complexities of reaction rate terms have been removed by replacing instantaneous concentrations with time-smoothed concentrations;

S_j (X, t) is a source term for species j located at position X emitting species j at a specified rate.

Even with these simplifications, the problem of finding solutions that provide reasonable predictions is still a difficult proposition. Comparison of observed concentrations with predicted values indicates that, during periods of prolonged stagnant air motion and intense solar irradiation, reactive intermediates play a much greater role in forming stable air pollutants for which few toxicity data are available (Calvert *et al.*, 1978). In these situations, the use of theoretical chemical models to examine most probable reaction pathways and to identify the reaction products from competing and parallel reactions would make an important contribution.

For photochemical smog, where ozone is both a chemical of concern from a toxicological viewpoint and a surrogate for other photochemical oxidants, it can be shown that the rate of increase of ozone in the atmosphere is a function of atmospheric concentrations of reactive hydrocarbons (RH) and nitric oxide (NO) (Haagen-Smit, 1952). Using this simplification for a very complex set of atmospheric chemical reactions, the rate of accumulation of ozone (O_3) is proportional to the atmospheric concentration of reactive hydrocarbons and nitric oxide as follows:

$$\frac{d[O_3]}{dt} = k[\mathrm{RH}] \cdot [\mathrm{NO}] \tag{2}$$

Friedlander and Seinfeld (1969) used this simplified kinetic model, and developed an equation to calculate ground level concentration of ozone for different levels of atmospheric turbulence. With this simple model, the amount of ozone at a location downwind from the emitting source depends on the ratio [RH]/[NO] and the Damköhler number for a bimolecular reaction (Damköhler, 1936). The Damköhler number is given as

$$N_{\mathrm{DA}} = kQ_{\mathrm{A}_0}/V^{*}L^2 \tag{3}$$

where

k = a rate constant which includes the photochemical dissociation of nitrogen dioxide as well as the effects of temperature on the reaction rate constants of the other chemical reactions in the competing and sequential set of photochemical smog reactions;
Q_{A_0} = initial concentration of nitric oxide;
V^{*} = average horizontal wind speed composed of vertical and horizontal components of wind velocity;
L = Monin–Obukhov length (Monin and Yaglom, 1971) defined as:

$$L = (-1)\left(\frac{V^{*3}}{K(g/T)(q/\rho C_{\mathrm{p}})}\right) \tag{4}$$

where

K = von Karman's constant given as 0.40 by some authors and 0.36 by others;
g = acceleration of gravity;
T = average absolute temperature;
q = average vertical heat flux due to convective, conductive and radiative heat transfer (q is positive when temperature decreases with height above the earth's surface, e.g. normal lapse rate of the atmosphere, and q is negative when there is a temperature inversion);
ρ = average density of the atmosphere;
C_{p} = average heat capacity of the atmosphere at constant pressure.

The Monin–Obukhov length, L, is a measure of atmospheric stability. When the atmosphere is stable, L is positive because q is negative—a temperature inversion. For unstable air, q is positive and L is negative. The sign and magnitude of L are a measure of the stability of the atmosphere and a measure of its diluting potential. Thus the criteria for stability are

$L < 0$ (q is positive) unstable, rapid dilution
$L > 0$ (q is negative) stable, temperature inversion, rapid accumulation
$L = \infty$ (q is zero, adiabatic) unstable, rapid dilution.

If the height of the source, h, measured in the Z-direction, is substituted for L, the ground level concentrations of ozone produced from the coupling of atmospheric chemical reactions and meteorological phenomena are given as (Friedlander and

Seinfeld, 1969):

$$[O_3] = [NO]_0 \frac{\left\{1 - \exp\left(-\frac{A}{2b} N_{DA}(\sigma - 1)(1 - h^2/Z^2)\right)\right\}}{\left\{1 - \frac{1}{\sigma}\exp\left(-\frac{A}{2b} N_{DA}(\sigma - 1)(1 - h^2/Z^2)\right)\right\}} \tag{5}$$

where

$$N_{DA} = \frac{k[NO]_0}{V^* h^2}. \tag{6}$$

$$\sigma = \frac{[RH]_0}{[NO]_0} \tag{7}$$

It can be shown that for fixed values of σ, the largest ground level concentrations of ozone are observed when wind velocity is minimal (a temperature inversion or stagnant high-pressure system) and initial nitric oxide concentrations in the atmosphere are high. The interactions of the controlling phenomena and the responses for different sets of variables are shown in Figure 5.

Lagrangian approaches produce predictive models that are based on probability density functions. The density functions can only be solved by knowing the entire past history of the particle whose trajectory is being determined. However, by using a Markov process, it can be shown that the present state depends only on the immediately prior state and not on any earlier states. With this approximation, the function that describes the probability of finding the particle between position $x + dx$, $y + dy$, and $z + dz$, can be greatly simplified. One of the most commonly used probability density functions is the Gaussian distribution. For non-reactive air pollutants such as fly ash particles from coal combustion for heating and electrical power production characterized as continuous point sources, the Gaussian plume model gives the ground level concentration of particles as

$$\langle C(x, y, z = 0) \rangle = \left(\frac{S_j(x, t)}{\pi \sigma_y \sigma_z V^*}\right) \exp\left(-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right) \exp\left(-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right) \tag{8}$$

where

$S_j(x, t)$ = emission rate of the source of chemical species j;
x, y, z = coordinates locating the source;
H = the height of the source above ground level;
σ_y, σ_z = crosswind and vertical dispersion coefficients that have dimensions of length and are functions of atmospheric stability.

2.2 Predicting Air Pollutant Concentrations

The Eulerian and Lagrangian models include the combined effects of chemical transformations and meteorological dynamics to calculate ground level concen-

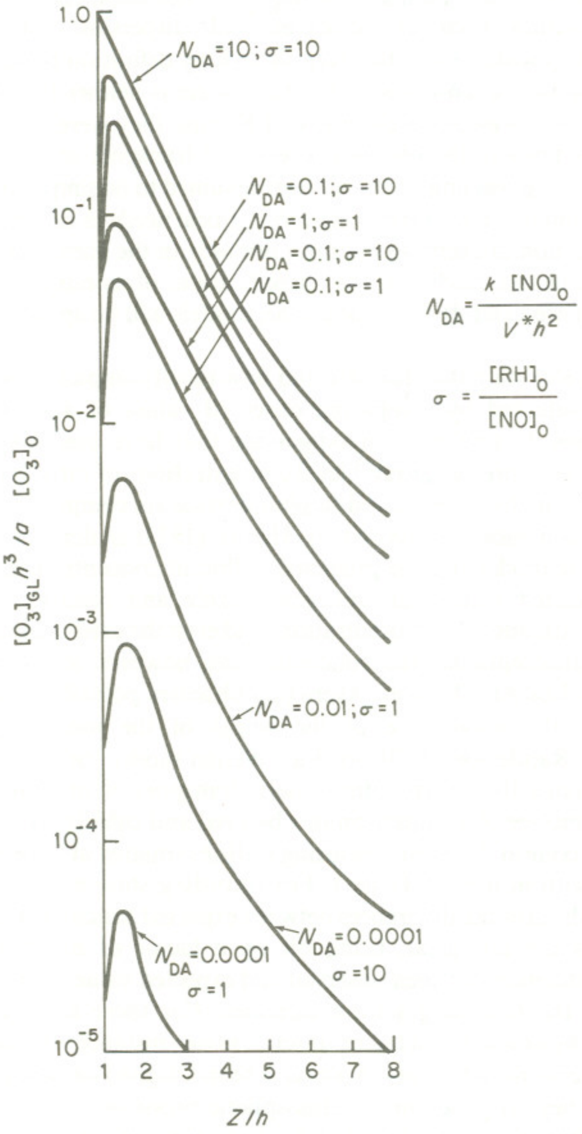

Figure 5 Ground level ozone concentrations as a function of meteorological conditions and concentration ratios of reactive hydrocarbons (RH) and nitric oxide. *Reprinted with permission from Friedlander and Seinfeld* (Environ. Sci. Technol., *3*, *1175–1182*). *Copyright* (1969) *American Chemical Society*

trations of air pollutants. In developing these expressions, many simplifications regarding complex interactions were required. The detailed characteristics of transport variables such as velocities and dispersion coefficients were approximated by scalar quantities even though by definition these variables are first- and second-rank tensors and the atmosphere is neither homogeneous nor isotropic. Many processes were eliminated because they were assumed to make minor contributions to the overall processes of transport and transformation. Interactions among reacting chemicals were assumed to be simple and expressible by linear reaction rate laws. One of the most critical needs in modelling transport and transformation of chemical mixtures not only in the atmosphere but also in other environmental media is the identification of conditions when these simplifications are valid. If this is not done, models will be applied wrongly and inappropriately.

How valid these simplifications are and how much complexity is required can partially be evaluated by comparing observed values of air pollutants with predicted values. Examples of investigations that have used Lagrangian and Eulerian models to predict ground level concentrations of nitric oxide, nitrogen dioxide, reactive hydrocarbons, and sulphur dioxide are compiled in Table 1. The simple dispersion model proposed by Hanna (1973) is derived from a basic Gaussian plume model and the predicted pollutant concentrations are given in Table 1. Predicted values for nitrogen dioxide and reactive hydrocarbons compare well with observed concentrations and even the predicted value for nitric oxide is not unacceptable. The concentrations, however, are averages for 11 stations in the Los Angeles area. Averaging obscures point-by-point variations and discounts the importance of the height of the measuring station to concentration. Randerson (1970) used a Eulerian model and a finite difference solution technique to simulate atmospheric transport of sulphur dioxide over Nashville, Tennessee. A comparison of observed and calculated concentrations for sulphur dioxide at different measuring stations situated at different heights is given in the bottom half of Table 1. For recording stations situated at 10–20 metres above the ground, differences between expected (calculated) and observed concentrations are not great, being off by a factor of no more than two. Substantial differences between observed and expected values begin to appear as the height of the recording station increases. For these stations, the model underpredicts by as much as a factor of seven in one instance. One explanation is the use of dispersion coefficients which have been assigned constant values in this model, when they are functions of atmospheric pressure.

In models that are designed for localized phenomena, underpredicting is not serious, but it does point out a substantial limitation in applying these models to long-range transport at higher altitudes and in representing complex localized chemical interactions in a meaningful fashion. Because long-range transport is important in understanding problems of acid rain and modification of the

Table 1 Comparison of observed values of air pollutant concentration with values calculated from Lagrangian and Eulerian models

I. Lagrangian model (Hanna, 1973)[a]

Substance	Dimensionless observed conc.	Dimensionless calculated conc.
NO	0.22	0.40
NO_2	1.45	1.32
RH	0.81	1.00

II. Eulerian model (Randerson, 1970)

Observation station no.	Elevation (metres)	Observed SO_2 (pphm) at 1800 CST	Calculated SO_2 (pphm) at 1800 CST
19	15	5.8	5.1
48	15	13.6	6.5
52	50	2.9	0.4
56	35	6.9	0.9
60	20	10.9	14.0
82	10	13.2	4.2
90	20	4.9	2.7

[a] Concentrations were averaged for 11 stations in the Los Angeles region at 1200 PST, 29 September 1969.

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stratosphere, it is important to include more detail on the variability of meteorological and chemical variables as functions of intensive properties of the atmosphere. Applying localized models to predict long-range effects is inappropriate because important chemical reactions that occur at different heights have not been included.

In the development of their model, Friedlander and Seinfeld (1969) represented the air space above an urban area as a large chemical reactor. In chemical reactor theory, it is well known that contacting patterns, mixing characteristics, reaction kinetics, reactor size, and concentrations of chemicals introduced at different times can sharply change the product distributions for chemicals being produced from a complex set of series and competing reactions (Levenspiel, 1962). There is no reason to suspect that these same complexities do not affect ground level concentrations of smog products. In the development of more precise predictive models, it is important that these factors and interactions be represented in more detail.

3 CONCLUSIONS

The main focus of this discussion has been to review the approaches and considerations in the development of predictive models for atmospheric concentrations of air pollutants. Because the concentrations of these chemicals strongly depend on both the mechanism of formation and the dynamics of transport, it is not enough to be concerned only with the mechanisms and kinetics of chemical transformations. Without the transport dynamics, appropriate consideration is not being given to all the determinants of exposure concentration. The discussions on model development have stressed the need to refine existing methods for analysing and interpreting transformation kinetics and media dynamics.

In short, the discussion has been directed towards a method of analysis of complex interactions that emphasizes the determination of the rate-controlling step or steps as a function of environmental conditions and participating chemical reactants. Simplifications made during model development must be carefully documented to protect the validity of the final model. When it is possible, attempts should be made to identify conditions when simple models can be used to interpret complex interactions of chemical mixtures. Methods to determine what the rate-controlling steps are as a function of environmental conditions are important, but it is also equally important to identify conditions when simple models fail, and why they fail.

4 REFERENCES

Altshuller, A. P. (1979). Model predictions of the rate of homogeneous oxidation of sulfur dioxide to sulfate in the troposphere. *Atmos. Environ.*, **13,** 1653–1661.

Altshuller, A. P., and Bufalini, J. J. (1971). Photochemical aspects of air pollution: a review. *Environ. Sci. Technol.*, **5,** 39–64.

Anderson, L. G. (1978). Effects of nighttime chemistry upon the transport of ozone and ozone precursors. *J. Air Pollut. Control Assoc.*, **29,** 970–973.

Ball, D. J. (1976). Photochemical ozone in the atmosphere of Greater London. *Nature*, **263,** 580–582.

Blackadar, A. K. (1957). Boundary layer wind maxima and their significance for the growth of nocturnal inversions. *Bull. Am. Meteorol. Soc.*, **38,** 283–290.

Blackadar, A. K. (1962). The vertical distribution of wind and turbulent exchange in a neutral atmosphere. *J. Geophys. Res.*, **67,** 3095–3102.

Calvert, J. G., and McQuigg, R. D. (1975). The computer simulation of the rates and mechanisms of photochemical smog formation. *Int. J. Chem. Kinet. Symp.*, **1,** 113–154.

Calvert, J. G., Su, F., Bottenheim, J. W., and Strausz, O. P. (1978). Mechanisms of the homogeneous oxidation of sulfur dioxide in the troposphere. *Atmos. Environ.*, **12,** 197–226.

Chang, T. Y., and Weinstock, B. (1973). Urban CO concentration and vehicle emissions. *J. Air Pollut. Control Assoc.*, **23,** 691–696.

Clarke, J. F. (1964). A simple diffusion model for calculating point concentrations from multiple sources. *J. Air Pollut. Control Assoc.*, **14,** 347.

Damköhler, G. (1936). Effects of heat, mass, and momentum transport on the performance of chemical reactors. I. General considerations for transfer in chemical processes. *Z. Elektrochem. Angew. Phys.*, **42,** 846–862 (in German).

Derwent, R. G., and Stewart, H. N. M. (1973). Elevated ozone levels in the air of central London. *Nature*, **241,** 342–343.

Dimitriades, B. (1972). Effect of hydrocarbon and nitrogen oxide on photochemical smog formation. *Environ. Sci. Technol.*, **6,** 253–260.

Egan, B. A., and Mahoney, J. R. (1972). Applications of a numerical air pollution transport model to dispersion in the atmospheric boundary layer. *J. Appl. Meteorol.*, **11,** 1023–1039.

Eschenroeder, A. Q., Martinez, J. R., and Nordsieck, R. A. (1972). *Evaluation of a Diffusion Model for Photochemical Smog Simulation.* EPA-R4-73-012a. General Research Corp., Santa Barbara, California: 226 pages.

Friedlander, S. K., and Seinfeld, J. H. (1969). A dynamic model of photochemical smog. *Environ. Sci. Technol.*, **3,** 1175–1182.

Gifford, F. A., and Hanna, S. R. (1973). Modelling urban air pollution. *Atmos. Environ.*, **7,** 131–136.

Graedel, T. E. (1980). Atmospheric photochemistry. In Hutzinger, O. (Ed.) *Handbook of Environmental Chemistry*, pp. 107–143. Springer-Verlag, Heidelberg.

Haagen-Smit, A. J. (1952). Chemistry and physiology of Los Angeles smog. *Ind. Eng. Chem.*, **44,** 1342–1346.

Hanna, S. R. (1971). A simple method of calculating dispersion from urban area sources. *J. Air Pollut. Control Assoc.*, **21,** 774–777.

Hanna, S. R. (1973). A simple dispersion model for the analysis of chemically reactive pollutants. *Atmos. Environ.*, **7,** 803–817.

Hecht, T. A., and Seinfeld, J. H. (1972). Development and validation of a generalized mechanism for photochemical smog. *Environ. Sci. Technol.*, **6,** 47–57.

Hecht, T. A., Seinfeld, J. H., and Dodge, M. C. (1974). Further development of generalized kinetic mechanism for photochemical smog. *Environ. Sci. Technol.*, **8,** 327–339.

Heines, T. S., and Peters, L. K. (1973). An analytical investigation of the effect of first order chemical reaction on the dispersion of pollutants in the atmosphere. *Atmos. Environ.*, **7,** 153–162.

Hoffert, M. I. (1972). Atmospheric transport, dispersion and chemical reactions in air pollution: a review. *Am. Inst. Aeronaut. Astronaut. J.*, **10,** 377–387.

Johnson, W. B., Ludwig, F. L., Dabberdt, W. F., and Allen, R. J. (1973). An urban diffusion simulation model for carbon monoxide. *J. Air Pollut. Control Assoc.*, **23,** 490–498.

Lamb, R. G., and Neiburger, M. (1971). An interim version of a generalized urban air pollution model. *Atmos. Environ.*, **5,** 239–264.

Lamb, R. G., and Seinfeld, J. H. (1973). Mathematical modeling of urban air pollution: general theory. *Environ. Sci. Technol.*, **7,** 253–261.

Lamb, R. G., and Seinfeld, J. H. (1974). A simple dispersion model for the analysis of chemically reactive pollutants. *Atmos. Environ.*, **8,** 527–529.

Levenspiel, O. (1962). *Chemical Reaction Engineering.* John Wiley & Sons, New York: 501 pages.

Lioy, P. J., and Samson, P. J. (1979). Ozone concentration patterns observed during the 1967–1977 long-range transport study. *Environ. Int.*, **2,** 73-83.

Lumley, J. L., and Panofsky, H. A. (1964). *The Structure of Atmospheric Turbulence.* Wiley Interscience, New York: 239 pages.

Martin, D. O. (1971). An urban diffusion model for estimating long-term average values of air quality. *J. Air Pollut. Control Assoc.*, **21,** 16–19.

Martinez, J. R., Nordsieck, R. A., and Eschenroeder, A. Q. (1973). Morning vehicle-start effects on photochemical smog. *Environ. Sci. Technol.*, **7,** 917–923.

McCollister, G. M., and Wilson, K. R. (1975). Linear stochastic models for forecasting daily maxima and hourly concentrations of air pollutants. *Atmos. Environ.*, **9,** 417–423.

Monin, A. S. (1970). The atmospheric boundary layer. In *Annual Review of Fluid Mechanics* 1970, pp. 225–250. Annual Reviews Inc., Palo Alto, California.

Monin, A. S., and Yaglom, A. M. (1971). Turbulence in a thermally stratified medium. In *Statistical Fluid Mechanics*, Vol. I, pp. 417–526. MIT Press, Cambridge, Massachusetts.

NAS (1977). *Ozone and Other Photochemical Oxidants.* National Academy of Sciences, Washington, DC: 719 pages.

Pack, D. H. (1964). Meteorology of air pollution. *Science*, **146,** 1119–1128.

Pasquill, F. (1962). *Atmospheric Diffusion.* Van Nostrand, London: 297 pages.

Randerson, D. (1970). A numerical experiment in simulating the transport of sulfur dioxide through the atmosphere. *Atmos. Environ.*, **4,** 615–632.

Reynolds, S. D., and Seinfeld, J. H. (1975). Interim evaluation of strategies for meeting ambient air quality standards for photochemical oxidant. *Environ. Sci. Technol.*, **9,** 433–447.

Reynolds, S. D., Roth, P. M., and Seinfeld, J. H. (1973). Mathematical modeling of photochemical air pollution. I. Formulation of the model. *Atmos. Environ.*, **7,** 1033–1061.

Reynolds, S. D., Liu, M. K., Hecht, T. A., Roth, P. M., and Seinfeld, J. H. (1974). Mathematical modeling of photochemical air pollution. III. Evaluation of the model. *Atmos. Environ.*, **8,** 563–596.

Roth, P. M., Roberts, P. J. W., Liu, M. K., Reynolds, S. D., and Seinfeld, J. H. (1974). Mathematical modeling of photochemical air pollution. II. A model and inventory of pollutant emissions. *Atmos. Environ.*, **8,** 97–130.

Seinfeld, J. H. (1975). *Air Pollution, Physical and Chemical Fundamentals.* McGraw-Hill, New York: 523 pages.

Trijonis, J. C. (1974). Economic air pollution control model for Los Angeles County in 1975. General least cost air quality model. *Environ. Sci. Technol.*, **8,** 811–826.

Turner, D. B. (1964). A diffusion model for an urban area. *J. Appl. Meteorol.*, **3,** 83–90.

Turner, D. B. (1970). *Workbook of Atmospheric Dispersion Estimates.* Publication No. AP-26, 2nd edition. US Environmental Protection Agency, Research Triangle Park, NC: 84 pages.

USDHEW (1970). *Air Quality Criteria for Photochemical Oxidants.* National Air Pollution Control Administration Publication AP-63. US Department of Health, Education and Welfare, Public Health Service. US Government Printing Office, Washington, DC: 182 pages.