Atmospheric Transport, Dispersion, and Chemical Reactions in Air Pollution: A Review

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Introduction

IT is difficult for anyone living in an urban area of an advanced industrial society to avoid exposure to deteriorating air quality. But approaches toward its improvement tend to involve a number of interdisciplinary factors. Thus, physical scientists and engineers tend to view pollution problems as technological problems; perhaps soluble, perhaps not, but essentially of a technical or "hardware" nature. To a biologist, the ecological component looms large: The balance of nature, with possible pathological consequences for organisms, is upset. To an economist, it seems largely a matter of resource allocation. While the sociologist sees a behavioral problem in individualistic-materialistic societies. From the various perspectives, environmental planners, legislators, and public administrators must formulate corrective policies with the additional constraint of political viability. In the present review, we deal with one of the scientific and engineering aspects of air pollution; namely, the dispersal and chemical reactions experienced by pollutants entering the atmosphere. But if relevance is desired, the social and economic aspects should be borne in mind as well, since the practical applications of this knowledge lie largely in the formulation of rational pollution-abatement strategies.

At present, pollutant emissions considered most important in the atmosphere are the particulates and various gaseous species including oxides of sulfur (primarily SO_2), oxides of nitrogen (NO and NO_2), carbon monoxide (CO) and hydrocarbons (primarily reactive hydrocarbons, RH). There is, in addition, some concern over other trace materials in the atmosphere such as radionuclides emitted by certain types of nuclear reactors and processing plants. The major air pollutants are, to some degree, introduced into the atmosphere inherently by industrial societies which meet their energy requirements by the combustion of fossil fuels. Of course, the amounts of these contaminants and the space and time distribution of their sources depends on specific patterns of urbanization, industrialization, and land use, and on the effectiveness of pollution abatement devices designed to remove them at the source. Table 1 gives estimated annual emissions of principle pollutants in the United States from different kinds of sources.[1] The bulk of sulfur oxide emissions and over half the nitrogen oxides are produced by the combustion of sulfur-bearing coal and fuel oil for space heating of buildings and electric power generation, while gasoline-powered motor vehicles account for most of the carbon monoxide and hydrocarbons and contribute heavily to nitrogen oxides as well.

Table 1 Estimated emissions of principal pollutants in the United States during 1968 in tonnes/yr × 10^6, from Ref. 1 (1 tonne = 1 metric ton = 10^3 kg)

Source	Particulates	Sulfur oxides (SO_x)	Nitrogen oxides (NO_x)	Carbon monoxide (CO)	Hydrocarbons (HC)
Stationary fuel combustion	8.1	22.1	9.1	1.7	0.6
Mobile fuel combustion	1.1	0.7	7.3	57.9	15.1
Combustion of refuse	0.9	0.1	0.5	7.1	1.5
Industrial processes	6.8	6.6	0.2	8.8	4.2
Solvent evaporation	—	—	—	—	3.9
Total	16.9	29.5	17.1	75.5	25.3

Clearly, between the limiting cases of eliminating all of these emissions by a return to pastoral life, and allowing the present emission levels to continue unabated, a large number of options exist. These range from the banning of motor vehicles in urban cores, to using "low emission" engines in automobiles, to installing desulfurization equipment in fossil fuel power plants, to converting these plants to nuclear power, and to various other remedies that have been proposed. Since many of these are not only costly but in some cases involve disruption of cultural norms (population control, suburban-urban mass transit, etc.), it is desirable to have some idea of their effect on ambient air quality prior to their implementation. In the past, these effects have not always been accurately anticipated by legislative bodies, owing to a lack of understanding of atmospheric processes. A case in point was recently noted by Nobel Laureate physicist Murray Gell-Mann,[2] relating to photochemically produced oxidants (smog) over the Los Angeles basin: Photochemical reactions are known to create oxidants from atmospheric mixing of *both* unburned reactive hydrocarbons and oxides of nitrogen; primarily from motor vehicles, under the influence of solar radiation. But the state of California very early opted to control hydrocarbons as being easier. To conform with these limitations on hydrocarbon emissions, automotive manufacturers responded

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Received August 2, 1971; revision received November 15, 1971; presented as Paper 72-82 at the AIAA 10th Aerospace Sciences Meeting, San Diego, Calif., January 17–19, 1972.

Index categories: Atmospheric, Space and Oceanographic Sciences; Boundary Layers and Convective Heat Transfer—Turbulent; Thermochemistry and Chemical Kinetics.

with engine modifications which raised the flame temperature during combustion, thereby maintaining performance but also increasing NO_x emissions. This largely cancelled the benefit of regulating the hydrocarbons and taking the increased automobile population into account, Gell-Mann believes that smog was not reduced at all.[2]

When a given air quality standard is sought, it is important to understand the various emission levels and distributions which could in fact achieve it, taking into account meteorological factors in atmospheric transport and dispersion, and chemical reactions which create and destroy species in the atmosphere. To this end, one seeks mathematical "dispersion models" to predict with reasonable confidence the concentration distributions associated with arbitrarily distributed pollution sources. The present review is aimed at assessing current understanding of aerophysical processes underlying such models. Various types of dispersion models currently in use or proposed for environmental planning purposes will be discussed as well.

The literature covering the various topics subsumed by this review is rather extensive and we have not attempted to cite all relevant original sources; rather, where prior comprehensive reviews were available these have been employed and are so cited in the text. Since physical processes active in pollution dispersion are in a different context already familiar to many readers with backgrounds in the aerospace sciences, the material presented here is organized to serve primarily as an orientation and starting-point for those interested in applications of turbulent transport theory and chemical kinetics to current modeling problems in air pollution.

Meteorological Factors in Air Pollution

Generally, polluting gases and particulates are deposited directly into the planetary boundary layer where they are transported as active or passive scalars by advection and turbulent diffusion. It is well established that this boundary layer is in a state of turbulent motion with large-scale velocity variations associated with the pressure fields commonly depicted on synoptic meteorological charts. For our present purposes, we seek to describe those features of the flow governing contaminant transport processes, namely: 1) space and time variations of the turbulent wind velocity vector, and 2) the stability of the atmosphere, i.e., its ability to resist or enhance turbulent diffusion of mass, momentum, and energy. In meteorological problems, turbulent diffusion depends not only on wind shear but also on the vertical temperature structure, since buoyancy forces can play an important role in establishing dynamic motion.

Wind Properties

Much progress has recently been made in understanding long range patterns of atmospheric transport and circulation on a planetary scale.[3] Over urban-industrial areas these patterns can well be modified locally by such features as terrain, high-rise structures, and urban heat island effects. For certain very localized problems in pollution transport (e.g., those occurring in "skyscraper canyons" of large cities) it is necessary to consider in detail a complex three-dimensional flowfield; however, for most problems of interest here it is reasonable to assume a turbulent mean wind velocity $\bar{u}(x, y, z, t)$ oriented parallel to the ground. Of course, fluctuation velocities (u', v', w') exist in all directions. Following the usual convection, fluctuating components are denoted by a "prime" and turbulent-mean flow variables by an overbar or (in the case of fluctuation product means) by angular brackets $\langle\ \rangle$. These time averages should be interpreted in a nonstationary meteorological context as discussed by Lumley and Panofsky.[4]

It is often convenient to formulate pollution dispersion problems in a wind-oriented coordinate system with x along the wind axis, y horizontal and normal to the wind, and z vertical, where t is the time. Note, however, that meteorological conditions will, in general, result in changes in wind direction in the (x, y) plane relative to the ground, so that coordinate rotations through a direction angle ϕ may be needed in relating results to surface-fixed grids such as emissions inventories.* Data can usually be obtained at various locales in the United States for $\bar{u}$ and $\bar{\phi}$ measured at some height z above the ground in hourly intervals.† This information is often given statistically in the form of "wind roses" showing the frequency of occurrence of these speeds and directions over monthly, seasonal, or annual periods.

Neglecting buoyancy effects on turbulent diffusion momentarily, the vertical profile associated with velocity $\bar{u}$ can be obtained from dimensional considerations. It is customary to characterize the intensity of turbulent diffusivity of momentum in the vertical direction by a "friction velocity,"

$$u^* \equiv \langle u'w' \rangle^{\frac{1}{2}} \tag{1}$$

For the first 10–100 m above the surface where this flux is known to be roughly constant, dimensional analysis yields a logarithmic form of the mean velocity profile,[5]

$$\bar{u}(z) = (u^*/k)\ln(z/z_0) \tag{2}$$

where z_0 is an experimentally determined roughness length associated with surface texture, and von Kármán's constant is found empirically to be $k \simeq 0.4$. Knowing z_0, wind measurements of $\bar{u}_1$ at some height z_1 permit calculation of the associated u^*. The velocity profile is then available from Eq. (2). Though lacking the physical basis of the logarithmic profile, power laws of the form $\bar{u} = \bar{u}_1(z/z_1)^p$, where the exponent $(0 \leq p < 1)$ is found by curve fitting, are sometimes used in urban dispersion models.

Defining the vertical turbulent diffusion coefficient for momentum by

$$\varepsilon_z \equiv -\langle u'w' \rangle/(\partial\bar{u}/\partial z) \tag{3}$$

gives $\varepsilon_z(z) = ku^*z$ for the logarithmic profile. Table 2, using values of z_0 compiled in Refs. 6–8, indicates u^* and ε_z when $\bar{u}_1 = 5$ m/sec at $z_1 = 2$ m.

Table 2 Typical experimental values of z_0 in logarithmic wind profile and corresponding friction velocity u^* and eddy diffusivity $\varepsilon_z = ku^*z$ under adiabatic conditions (evaluated for $u_1 = 5$ m/sec at $z_1 = 2$ m; $k = 0.4$), from Refs. 6–8

Type of surface	z_0, m	u^*, m/sec	ε_z, m^2/sec
Mud flats, ice	1×10^{-5}	0.16	0.13
Smooth sea	2×10^{-4}	0.22	0.18
Level desert	3×10^{-4}	0.23	0.18
Snow surface, lawn to 1 cm high	1×10^{-3}	0.26	0.21
Lawn to 5 cm	1.5×10^{-2}	0.41	0.33
Lawn to 60 cm	6.5×10^{-2}	0.58	0.46
Fully grown root crops	1.4×10^{-1}	0.75	0.60

In pollution problems, one is after the effect of turbulent diffusion on the concentration c_i of some generic species i, rather than diffusion of momentum within the atmosphere per se. Turbulent diffusion coefficients normal to the wind for species concentrations‡ can be defined by

$$K_y \equiv -\langle c_i'v' \rangle/(\partial\bar{c}_i/\partial y); \quad K_z \equiv -\langle c_i'w' \rangle/(\partial\bar{c}_i/\partial z) \tag{4}$$

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* An *emissions inventory* can be defined as a tabulation of sources, including the rate and type of emissions, their locations in a ground-fixed coordinate system and their temporal pattern.

† For example, from the Environmental Data Service, National Oceanic and Atmospheric Administration, National Climatic Center, Asheville, N. C. 28801.

‡ Various units are used to express concentration in the air pollution literature. In the present work, ρ_i is the partial density of species i, $c_i = \rho_i/\rho$ is its mass fraction, and $X_i = (M/M_i)c_i$ its volume or molar concentration; where M_i is the molecular weight of i, $M \simeq 29$ the molecular weight of air, and $\rho \simeq 1.23 \times 10^9$ μg/m^3 the mass density of air at sea level. For ρ_i in μg/m^3 and X_i in parts per million (ppm): $\rho_i = 42.5M_iX_i$.

If, as is customary in two-dimensional boundary-layer problems over aerodynamic bodies, a turbulent Schmidt number of order unity ($\varepsilon/K \simeq 1$) is assumed, one obtains $K_z \simeq \varepsilon_z$ for $\bar{u}$ a function of z only. This corresponds to the case of Fickian diffusion discussed by Sutton[9] where the size of effective eddies in a smoke plume are independent of distance from the source. As Sutton recognized, it is more likely that effective concentration eddy size increases with distance of the diffusing cluster from the source, so that K_y is initially finite, and both K_y and K_z increase with x even when ε_z is z dependent only.

Stability of the Lower Atmosphere

In addition to mechanical turbulence driven by wind shear, fluctuations in the atmosphere are affected by net buoyancy forces which may either enhance or retard the tendency of perturbations to grow. It can easily be verified that net buoyancy forces on a fluid element vanish when adiabatic pressure variations $dp = \rho C_p dT$ are exactly balanced by those associated with hydrostatic equilibrium $dp = -\rho g\, dz$, where g is the gravitational acceleration, and a perfect gas is assumed with pressure p, temperature T, density ρ, and specific heat at constant pressure C_p. Equating the pressure differentials gives the vertical temperature gradient associated with this neutral stability condition, the so-called dry adiabatic lapse rate,

$$\partial T/\partial z = -g/C_p = -\Gamma \tag{5}$$

where $\Gamma \simeq 9.8°\text{C/km}$ at sea level. It is useful also to introduce the potential temperature Θ, defined as the temperature that air would have were it adiabatically brought to sea level conditions. In the atmosphere, $\partial\Theta/\partial z$ is related to $\partial T/\partial z$ by

$$\partial\Theta/\partial z = \partial T/\partial z + \Gamma \tag{6}$$

Generally, one speaks of unstable conditions for superadiabatic lapse rates, $-\partial T/\partial z > \Gamma$ ($\partial\Theta/\partial z < 0$), neutrally stable conditions for adiabatic lapse rates, $-\partial T/\partial z = \Gamma$ ($\partial\Theta/\partial z = 0$), and stable conditions for subadiabatic lapse rates, $-\partial T/\partial z < \Gamma$ ($\partial\Theta/\partial z > 0$); where these essentially characterize the degree to which shear-driven mechanical turbulence is intensified, unmodified and retarded, respectively, by buoyancy effects. A condition does exist wherein vertical turbulent diffusion can be inhibited to the point where it is effectively blocked, the so-called *temperature inversion* where $\partial T/\partial z$ becomes positive ($\partial\Theta/\partial z > \Gamma$). Typically, the vertical temperature structure observed over urban regions begins with $\partial T/\partial z$ negative near the surface and rises to some height, commonly known as the mixing depth l_m, where the gradient changes sign, $\partial T/\partial z \geq 0$.

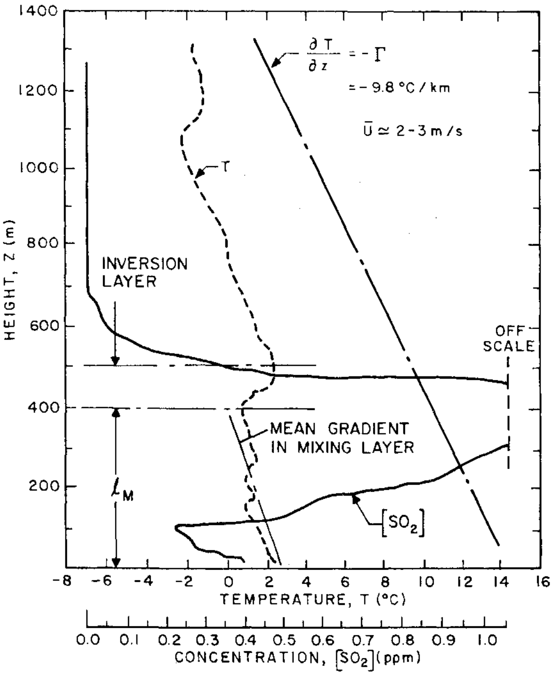

Fig. 1 Vertical temperature and sulfur dioxide concentration profile measurements at Battery Park, New York City, at 0738 EST, on 9 March 1966 (from Ref. 10). A pronounced temperature inversion beginning at $l_m \simeq 400$ m inhibits vertical diffusion of the SO_2 above the lower mixing layer. The dry adiabatic lapse rate is also shown.

An example of this situation is depicted in Fig. 1, adapted from Davidson,[10] which shows vertical temperature and sulfur dioxide concentration profiles measured over New York City. Qualitatively, this structure is fairly typical of observed urban temperature inversions. Note the strong inversion beginning approximately at $l_m \simeq 400$ m. For $0 \leq z \leq l_m$, a mixing layer exists with turbulent diffusion of SO_2 proceeding at rates associated with the stable temperature gradients present in this region at the time of the measurement. Notice that SO_2 concentrations drop off sharply through the inversion layer (400–500 m), illustrating the wall-like blockage of vertical transport characteristic of elevated regions over urban regions where $\partial T/\partial z \geq 0$. The importance of the mixing depth in pollution problems is that it limits the ability of the atmosphere above a community to dilute contaminants by vertical diffusion. Estimates of mean maximum mixing depths in the contiguous United States have been compiled by Holzworth[11] for monthly averaging periods.

While turbulent diffusion in the mixing layer depends in a fundamental sense on temperature structure, an empirical system due to Pasquill[8] is often used in urban dispersion models to denote stability. Here, common meteorological observations—insolation (incident-solar-radiation) during the day or degree-of-cloudiness at night—are used in lieu of temperature profile measurements for reasons of practicality and availability of data. Stability classes defined in this system are given in Table 3.

Table 3 Relation of turbulence types to weather conditions (after Pasquill[8])

A: Extremely unstable conditions
B: Moderately unstable conditions
C: Slightly unstable conditions
D: Neutral conditions[a]
E: Slightly stable conditions
F: Moderately stable conditions

				Nighttime conditions	
Surface wind speed $\bar{u}$, m/sec	*Daytime insolation* Strong	Moderate	Slight	Thin overcast or $\geq 4/8$ cloudiness[b]	$\leq 3/8$ cloudiness
<2	A	A–B	B		
2–3	A–B	B	C	E	F
3–5	B	B–C	C	D	E
5–6	C	C–D	D	D	D
>6	C	D	D	D	D

[a] Applicable to heavy overcast, day or night.

[b] The degree of cloudiness is defined as that fraction of the sky above the local apparent horizon which is covered by clouds.

Although this system has proved quite useful, and will be referred to later, it is desirable to relate stability to more fundamental physical quantities. One such quantity is the turbulent heat flux in the vertical direction

$$H \equiv \rho C_p \langle T'w' \rangle \tag{7}$$

which plays an analogous role to u^* in turbulent momentum transport. Also, it is useful to introduce the Richardson number Ri, defined as the ratio of turbulent energy consumed by buoyancy to that produced by wind shear. It can be shown to take the dimensionless form[5]

$$Ri = (g/T)[(\partial\Theta/\partial z)/(\partial\bar{u}/\partial z)^2] \tag{8}$$

The atmospheric boundary layer is generally regarded as the region within which the fluxes u^* and $H/\rho C_p$ can be taken as constant. Also, as implied by Eq. (8), for arbitrary velocity and potential temperature gradients the effects of buoyancy are embodied in the parameter g/T. From these three quantities which taken together characterize velocity and temperature profiles in the surface layer, Monin and Obukhov[12,13] formed the unique length

$$L \equiv -u^{*3}\rho C_p T/(kgH) \tag{9}$$

Further, they hypothesized that their length scale was a constant characterizing a particular state of atmospheric stability. The Monin-Obukhov length L is important insofar as it forms a physically significant normalization factor for the height coordinate and leads to a "similarity" theory for profiles in the constant-flux boundary layer which accounts for stability effects through the variable (z/L). Correspondingly, assuming a unit turbulent Prandtl number, the velocity and potential temperature profiles for general diabatic (not necessarily adiabatic) lapse rates can be put into the "universal" forms,[4]

$$\bar{u}(z) = (u^*/k)[\ln(z/z_0) - \psi(z/L)] \tag{10}$$

$$\Theta(z) - \Theta_0 = \Theta^*[\ln(z/z_0) - \psi(z/L)] \tag{11}$$

where $\Theta_0 = \Theta(z_0)$ is the potential temperature at $z = z_0$, $\Theta^* = H/(\rho C_p k u^*)$ is a scaling temperature, and ψ is a universal function of the height normalized to the Monin-Obukhov length.

In view of the desirability of expressing stability in terms of more fundamental physical properties of the mixing layer, Pasquill and Smith[14] have recently estimated the Richardson numbers and Monin-Obukhov lengths associated with the stability classes defined in Table 3. These values are quoted in Table 4.

Table 4 Estimates of the correspondence between Pasquill's stability categories, *Ri* and *L*, for short grass, after Ref. 14

Stability category	*Ri* (at $z_1 = 2$ m)	*L*, m
A	-1.0 to -0.7	-2 to -3
B	-0.5 to -0.4	-4 to -5
C	-0.17 to -0.13	-12 to -15
D	0	∞
E	0.03 to 0.05	35 to 75
F	0.05 to 0.11	8 to 35

At present, the Monin-Obukhov similarity theory represents a reasonably adequate description of the constant-flux part of the atmospheric boundary layer immediately above the Earth's surface. Above the constant-flux layer there exists the so-called Ekman layer where fluxes and gradients of fluxes in the transverse direction become important. A review of recent progress in developing a theory for the atmospheric boundary layer as a whole is given by Sheppard.[15]

Atmospheric Dispersion

In this section, methods for describing pollutant concentration distributions associated with various emission sources will be reviewed. Initially, only localized dispersion will be treated, both from single sources or in multiple source urban dispersion models, in the context of the gaussian plume and gaussian puff approximations. Subsequently, dispersion modeling, using the "box model" concept applicable to longer ranges, will be discussed.

Under present assumptions, horizontal advection is balanced by vertical and transverse turbulent diffusion and terms arising from creation or depletion of species i by various internal sources or sinks. In the wind-oriented coordinate system, the conservation of species mass equation takes the form

$$\frac{\partial \bar{c}_i}{\partial t} + \bar{u}\frac{\partial \bar{c}_i}{\partial x} = \frac{\partial}{\partial y}\left(K_y \frac{\partial \bar{c}_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial \bar{c}_i}{\partial z}\right) + \dot{\bar{c}}_i \tag{12}$$

where diffusivities K_y and K_z are defined by Eq. (4) and the source $\dot{\bar{c}}_i$ represents rates of gain or loss by chemical reactions, precipitation (washout) or adsorption by suspended particles. It can be assumed that for particulates with diameters less than 10 μm the material remains suspended in the ambient environment so that Eq. (12) applies to these species as well.[16]

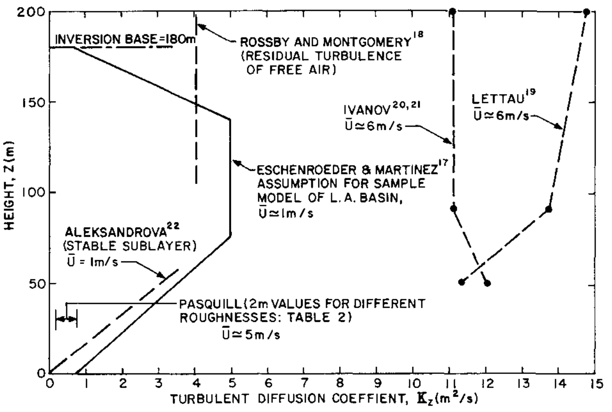

Fig. 2 Height-variation of vertical turbulent diffusion coefficient for different average wind speeds compiled from various sources by Eschenroeder and Martinez.[17]

Clearly, the solution of Eq. (12) requires some knowledge of K_y and K_z. One possible representation used, for example, by Eschenroeder and Martinez[17] involves taking $K_z \simeq \varepsilon_z$, as discussed previously, and treating an essentially two-dimensional ($K_y = 0$) problem. Figure 2 shows diffusivity data compiled from various sources[18–22] and used by Eschenroeder and Martinez to construct an empirical turbulent diffusion profile for the Los Angeles basin. Note that their diffusivity model assumes a decrease approaching the inversion base to reflect the wall-like inhibition of vertical turbulent motion by buoyant stability. Assuming $K_z(z)$ in this way permits integration of Eq. (12) either analytically or by numerical methods. However, the approach has the drawback that extensions to three-dimensional problems, where K_y is not negligible, are not straightforward. Moreover, as will be shown, it appears that characterizing plume diffusivities in terms of z variations only is somewhat inconsistent with physical diffusion processes and with measurements of plume growth. Nonetheless, in multiple-species reacting flow problems, where nonlinearities may be introduced by source terms, such approximations are very useful in obtaining numerical solutions and can give valuable insights into the more general problem.

Dispersion from an Isolated Source

In treating the simplest case of dispersion from an isolated source, we note first that sources need not be located at the Earth's surface. A number of pollutants are emitted from elevated sources such as industrial chimneys or power plant stacks at some height h_s above the ground. These usually continue to rise an incremental height Δh either by virtue of buoyancy forces acting on the heated effluent or because their momentum carries them aloft, or both. Various factors influence the ultimate height $h = h_s + \Delta h$ the plume attains but the most important is probably the state of ambient temperature stratification (i.e., the atmospheric stability in the sense of the preceding section). The major problem in describing this behavior arises from the fact that the plume is, itself, a three-dimensional turbulent shear flow imbedded in a turbulent atmospheric boundary layer. Nonetheless, progress has been made in understanding this process and in devising semi-empirical correlations for the plume rise Δh, much of which is summarized in a series of publications by Briggs.[23–25] In what follows, we assume the horizontal scale for dispersion is sufficiently great so as to justify representing the plume as emanating from a virtual source having the x, y coordinates of the real source, but located at height h.

For the special case of a uniform wind where K_z and K_y are constants, where an isolated source located at $(0, 0, h)$ continuously emits a mass per unit time of species i at a constant rate Q_i, and where the removal rate from internal sinks is governed by linear processes, $\dot{\bar{c}} = -\bar{c}_i/\tau_c$ with τ_c a characteristic decay time; Eq. (12) has the solution[26]

$$\bar{c}_i(x,y,z) = \frac{Q_i/\rho}{2\pi\sigma_y\sigma_z\bar{u}}\exp\left[-\frac{x}{\bar{u}\tau_c}\right]\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\left\{\exp\left[-\frac{1}{2}\left(\frac{z-h}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+h}{\sigma_z}\right)^2\right]\right\} \tag{13}$$

where the dispersion coefficients or "spreads" in the gaussian profiles are

$$\left\{\ \sigma_y \equiv (2K_y x/\bar{u})^{\frac{1}{2}}, \qquad \sigma_z \equiv (2K_z x/\bar{u})^{\frac{1}{2}}\right. \tag{14}$$

Associated initial and boundary conditions on Eq. (12) are

$$\begin{aligned} &\text{at } x = 0: && \bar{c}_i \to Q_i\delta(y)\delta(h-z)/(\rho\bar{u}) \\ &\text{at } z = 0: && \partial\bar{c}_i/\partial z = 0 \\ &\text{at } z = \infty: && \bar{c}_i = 0 \end{aligned}$$

where δ is the Dirac delta function; these conditions specify that the source is located at the effective stack height, that there is a total reflection at the Earth's surface (no deposition or chemical reaction at $z = 0$), and that the dispersion is not limited in the vertical direction. Further, it can be verified that the mass flux of X_i across a plane perpendicular to the plume axis is

$$\dot{m}_i(x) \equiv \int_{-\infty}^{\infty}\int_{0}^{\infty} \rho_i\bar{u}\,dz\,dy = Q_i e^{-\bar{u}x/\tau_c}$$

so that the emission rate $\dot{m}_i(0) = Q_i$ is recovered at the virtual plume origin.

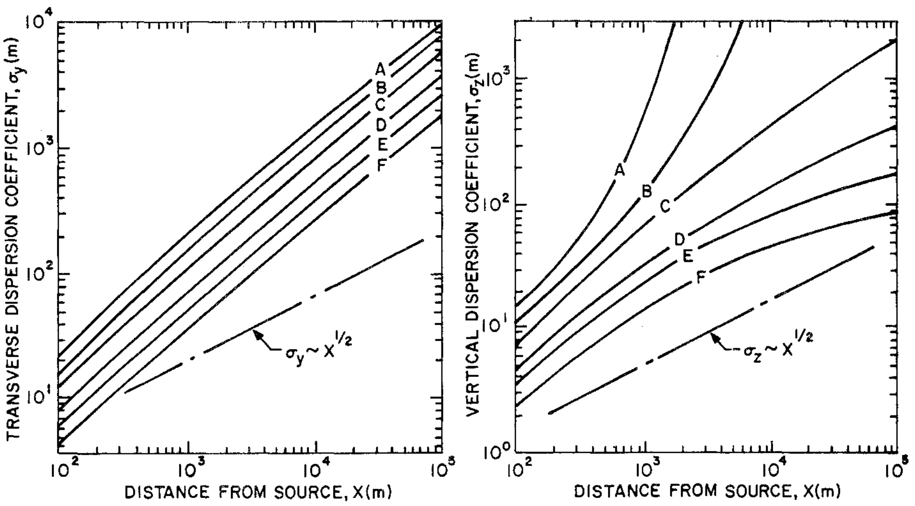

Fig. 3 Empirical transverse and vertical dispersion coefficients in the gaussian plume vs downwind distance for the stability classes of Table 3; after Pasquill, as interpreted by Gifford.[30]

Despite the approximations involved, the appeal of analytical solutions is so great that the gaussian plume formula [Eq. (13)] has found widespread use in predictions of pollution dispersion, albeit with certain ad hoc assumptions made as to the dependence of σ_y and σ_z on distance from the source and on stability of the atmosphere, as discussed by many authors including Gifford,[5] Sutton,[6] Pasquill,[8] Smith,[27] Anderson et al.,[28] and Turner.[29] The reliance on some empiricism stems, in part, from the fact that theoretical relationships between turbulent diffusion and atmospheric stability are not well established and, in part, from the fact that within a stability class plume growth is not experimentally found to follow the $x^{\frac{1}{2}}$ growth law predicted by Eq. (14). This is illustrated in Fig. 3 which shows correlations for vertical and transverse dispersion coefficients derived from smoke plume observations by Pasquill and reinterpreted by Gifford.[30] The letters labeling the family of curves refer to stability classes defined in Table 3. Alternately, stability categories can be related to Richardson number or Monin-Obukhov length using Table 4, so that in principle $\sigma_y(x, L)$ and $\sigma_z(x, L)$ are available from Fig. 3. Note that plume mixing is anisotropic with vertical dispersion showing a greater sensitivity to stability as one would expect.

At present, common practice is to use the gaussian plume formula in estimates of concentration profiles for nonreacting species and those with first-order internal sinks. Figure 4 shows normalized ground-level concentrations computed from Eq. (13) with "frozen" removal rates ($\tau_c \to \infty$) at $y = 0, z = 0$, for an effective source at $h = 30$ m. The curves correspond to the growth laws of Fig. 3 for different stability classes. The ground-level concentrations peak downstream of the source, with the most unstable case peaking first, and then decay as they become dominated by dilution in the expanding plume.

It is often desired to describe concentrations over distances greater than those where the upper plume boundary encounters an elevated inversion lid which blocks further vertical diffusion. Following Turner's analysis,[29] this can be considered to occur when $l_m \simeq 2.15\sigma_z + h$. The vertical dispersion coefficient at this point has the value $\sigma_z(x_m) = (l_m - h)/(2.15)$ with the corresponding downstream distance x_m available from Fig. 3. Up to this point the plume has a gaussian vertical distribution, but Turner assumes that by the time the plume has traveled a distance $2x_m$ it attains a uniform distribution between l_m and the Earth's surface, as shown in Fig. 5. Turner's model for inversion-limited vertical mixing leads to the suggestion that Eq. (13) be replaced by

$$\bar{c}_i(x,y,z) = \frac{Q_i/\rho}{(2\pi)^{\frac{1}{2}}\sigma_y(l_m - h)\bar{u}}\exp\left[-\frac{x}{\bar{u}\tau_c}\right]\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \tag{15}$$

when $x \geq 2x_m$.

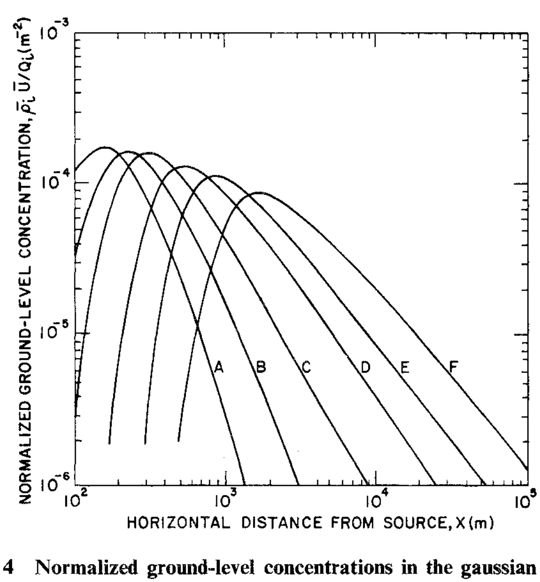

Fig. 4 Normalized ground-level concentrations in the gaussian plume model for the stability classes of Table 3 where the effective source height is at $h = 30$ m and the chemistry is frozen ($\tau_c \to \infty$).

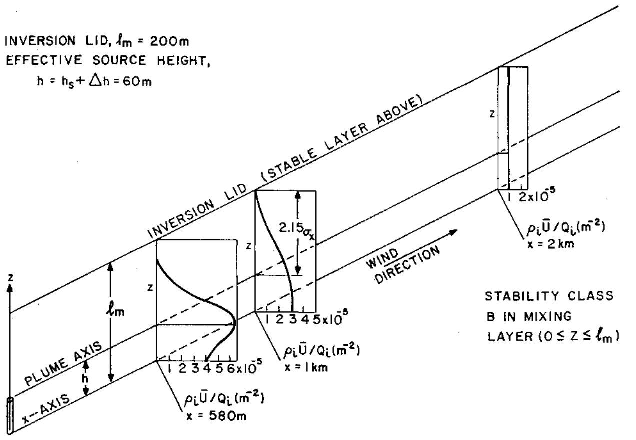

Fig. 5 Vertical concentration profiles in the mixing layer beneath an inversion lid at $z = l_m$ for frozen ($\tau_c \to \infty$) chemistry.[29]

A number of useful semiempirical formulae have been proposed in the context of gaussian distributions for other than continuous point sources. These include line sources, area sources, and instantaneous point sources (gaussian puffs). These relationships and their applicability to concentration estimates for isolated sources are discussed by Anderson et al.[28] and Turner.[29]

Multisource Gaussian Plume Urban Dispersion Models

For environmental planning purposes, one seeks the concentration fields resulting from large numbers of distributed urban and industrial sources. Methods currently in use to model such problems for species with linear decay processes will now be reviewed. Discussion of recent efforts to model more complex nonlinear reacting systems is deferred to following sections.

Consider a time interval, say, one hour, over an urban-industrial region within which meteorological conditions and pollution emission rates can be treated as sensibly constant. It is assumed that spatial distributions of pollution sources are available from an emissions inventory; also, surface wind velocity and direction, stability class (e.g., one of the categories of Table 3) and mixing depth are assumed known, and for simplicity taken as spatially uniform over the region.§ Using gaussian plume formulae and other relations developed previously, it is then possible to compute ground level concentrations $\bar{c}_i(x_0, y_0, 0)$ at any receptor point (x_0, y_0) in the region resulting from each of the isolated sources in the emissions inventory. Since Eq. (12) is linear for zero or linear decay terms, superposition of solutions applies, and the concentration distribution is available by computing the values of $\bar{c}_i$ at various receptors and summing over all sources. If concentration contours (isopleths) are desired, interpolation of values at these receptors may be needed.

This representation is often extended to describe concentrations over much longer time periods where conditions will vary, by considering the unsteady situation as a succession of steady states each having a duration of the order of an hour. Since the x axis in Eqs. (14) or (15) is defined by mean wind direction, and source distributions are given in ground-fixed coordinates, standard formulas are required for rotation of (x, y) coordinate axes as wind direction changes from one hour to the next.

The procedure just described is limited insofar as it cannot account for pollution accumulation during air pollution "episodes" since each steady state is legislated as independent of the preceding one, thereby erasing the "memory" of prior concentrations. Also, the model will break down for species with nonlinear chemistry since superposition no longer applies. Nevertheless, this approach forms the basis of a proliferating number of multisource urban dispersion models aimed at describing ground level concentration contours when meteorological and emission properties are known either from historical data or predictions. A fairly representative list of such efforts includes the work of Pooler[31] (Nashville, SO_2), Turner[32] (Cincinnati, SO_2), Clark[33] (Cincinnati, SO_2, NO_x), Miller and Holzworth[34] (Washington, D.C., SO_2, NO_2), Koogler et al.[35] (Jacksonville, SO_2), Johnson et al.[36] (Washington, D.C., St. Louis, CO), Fortak[37] (Bremen, West Germany, SO_2), and Martin[38] (St. Louis, SO_2).

It should be clear that, with the help of high-speed electronic computers to carry out the large number of routine calculations, concentration variations over time can be obtained by the quasi-steady gaussian plume approach. However, when the average concentrations over long times (for example, seasonal or annual periods) is desired, a modification of the method is employed. First, it is useful to digitize wind speed and direction data as was done for stability. Winds can be grouped into discrete classes whose speed range is denoted by index k, and direction by l. Also, let stability classes be labeled by index m. Martin,[38] for example, uses 6 wind speed classes, 16 wind direction classes (corresponding to the 16 compass points, N, NNE, ..., NNW), and 5 stability classes. Now define the joint probability function $f(k, l, m)$ as the relative frequency of winds in a given speed class k, direction l, and stability m. This function can be evaluated for a characteristic location in an urban region from historical meteorological data. If emission rates are taken constant at their mean values for the seasonal or annual period, the corresponding concentrations $\bar{c}_i(k, l, m)$ can be computed for gaussian plumes for all combinations of meteorological conditions. Long-term averages are then available from the frequency-weighted mean

$$\langle \bar{c}_i \rangle = \sum_k \sum_l \sum_m f(k, l, m) \bar{c}_i(k, l, m)$$

where the joint probability function is normalized to

$$\sum_{k'} \sum_l \sum_m f(k, l, m) = 1$$

Annual average sulfur dioxide concentration contours computed in this way[39] in the metropolitan New York region are indicated in Fig. 6. For comparison, average values derived from aerometric network measurements at locations in the region[40] are also shown.

Recently, attempts have been made to characterize the nonsteady situation more accurately using so-called instantaneous gaussian puff expressions. Here pollution emission from any source is regarded as a series of instantaneous releases which may follow different trajectories at different diffusion rates. Examples of this approach are the work of Shieh et al.[41] (New York, SO_2) and Roberts et al.[42] (Chicago, SO_2). While these models have greater flexibility than the steady-state gaussian plumes, the improvement is bought at the price of very detailed knowledge required to predict both trajectories and dispersion coefficients of individual puffs in an ambient urban environment. Perhaps the most sophisticated dispersion model along these lines is that recently devised by Lamb and Neiburger[43] (Los Angeles, CO), who used general analytical solutions to the unsteady linear diffusion equation. These were obtained for arbitrary source distributions by finding the appropriate Green's function. As with the quasi-steady gaussian plumes, these methods are limited to species with linear decay properties. Further discussion of urban dispersion modeling by gaussian plumes and puffs can be found in the reviews by Wanta[44] and Calder.[45]

Numerical Solutions and Box Models

The gaussian plume methods of the previous section have at least three important deficiencies which limit their applicability to general dispersion modeling problems: 1) it is difficult to adapt them to account for effects of pollutants accumulating in an air-shed over a period of time (say, during a persistent inversion or "episode" period); 2) they are somewhat inappropriate for studies of long-range dispersion since turbulent diffusion becomes

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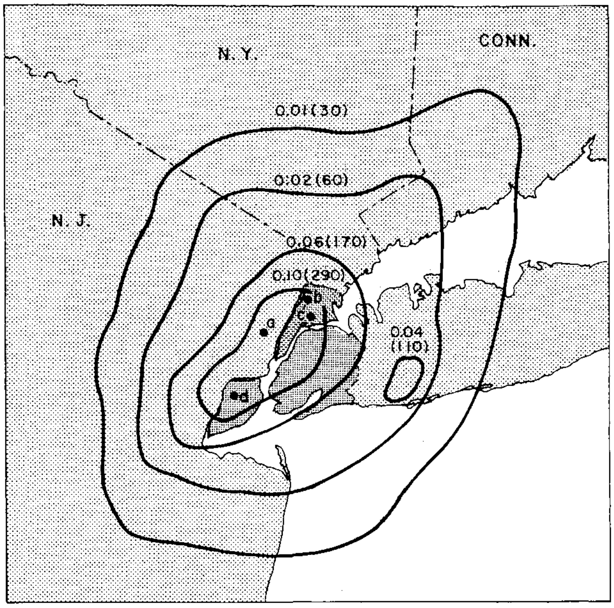
§ Often, meteorological variables are only measured on a routine basis at one location in a region (usually an airport) and the spatial uniformity assumption becomes a practical necessity imposed by lack of data.



AEROMETRIC DATA[40]		
STA.	CONCENTRATION	
	(ppm)	($\mu g/m^3$)
a	0.14	400
b	0.15	430
c	0.15	430
d	0.09	260

Fig. 6 Theoretical annual average sulfur dioxide concentration contours in ppm and $\mu g/m^3$ (in parentheses) over metropolitan New York computed with gaussian plume multiple-source urban diffusion model.[39] A linear decay was assumed with a half-life of 3.0 hr (τ_c = 4.3 hr).

relatively less important than advection over large spatial scales (also, the dispersion coefficients of Fig. 3 generally used with gaussian plumes are somewhat speculative and grounded in a limited data base for distances greater than a few kilometers[8]); finally, 3) these techniques do not account for nonlinear interactions among different species arising from chemical reactions.

Probably the most general scheme to account for the broad regimes of physics which one desires to model is numerical solution of the three-dimensional turbulent conservation of species equations with variable wind speeds and turbulent diffusivities. As discussed previously, this is complicated by the fact that general relationships for K_y and K_z have not yet been established in terms of windspeed and stability. Pasquill[14] has suggested $K_z \simeq [(\epsilon^{1/3}\lambda_m^{4/3})/15]$ on physical grounds, where ϵ is the rate of energy dissipation and λ_m is the wavelength corresponding to the peak in the turbulent spectrum of the vertical velocity component. But until more is known of ϵ and λ_m in the atmosphere the practical utility of this approach is somewhat limited. Moreover, the computational and computer storage problems associated with solution of three-dimensional partial differential equations by finite-difference methods are formidable. Nonetheless, the work of Eschenroeder and Martinez[17] suggests that the finite-difference approach can yield useful results with reasonable computer resources when the advective wind direction does not change and transverse diffusion can be neglected. Another numerical approach, used by Wayne et al.,[46] is to solve a simpler form of the conservation equations for a parcel of air as it moves in a dynamic emission and meteorological environment along a given urban wind trajectory. This is somewhat similar to the gaussian puff concept of the previous section but includes chemical as well as diffusive effects. The problem here is that numerical integration along a large number of streamlines, each following a complex trajectory, is required to derive an output in isopleth form.

What is needed is some method which overcomes the problems of the gaussian plumes and puffs, but is computationally less demanding than a finite-difference solution of the full partial differential conservation of species equations with turbulent diffusion. One approach which meets these requirements is the so-called box model of which there are a number of versions. One of the earliest box models was proposed by Smith[47] to account for unsteady pollution accumulation effects over a city. Essentially, he assumed instantaneous homogeneous mixing in a box whose volume is defined by the dimensions of a hypothetical square city at the base and the mixing depth. The spatially uniform concentration in the box is then described by an ordinary differential equation giving the concentration rate-of-change proportional to the rate at which pollutants enter the box from urban emissions less the rate at which they are removed by advection, chemistry, and precipitation. Note that the homogeneous mixing assumption effectively bypasses the problem of specifying turbulent mixing processes within the box. However, the neglect of vertical diffusion requires the existence of a well-defined inversion layer. More recently, more advanced versions of the box model have been proposed by Reiquam,[48,49] Seinfeld,[50] and MacCracken et al.,[51] with multiple boxes to account for spatial nonuniformities in concentration. These are all conceptually rather similar, but Seinfeld's analytical development seems the most straightforward and will be followed here to describe the method.

Consider the pollutants as a multicomponent mixture of N species all of which can, in principle, react chemically with each other. The specification of an appropriate source term $\dot{\bar{c}}_i(c_1, \ldots, c_N, t)$ for this system will be discussed in a later section. Now suppose the airshed over an urban region is divided into an array of L rectangular volumes or cells, each covering a square of side b_j in an emissions inventory, and extending upwards a height $l_{mj}(t)$ corresponding to the time-dependent mixing depth. The volume of the kth cell is $\vartheta_k(t) = b_k^2 l_{mk}(t)$. Let $Q_{ik}(t)$ be the mass per unit time of specie i emitted into box k from all pollution sources (assumed known). Further, assume that horizontal velocity components in Earth-fixed coordinates $\bar{u}_k(t)$ and $\bar{v}_k(t)$ perpendicular to the vertical cell walls are known a priori. Let q_{jk} be the volumetric flow rates from adjacent cells into cell k and q_{jk} the corresponding flow rates out of cell k. Finally, assume that each cell is a well-mixed reactor with inflows and outflows between cells. That is, we neglect diffusive transport across cell walls and consider only advective transport among cells. Taking a mass balance for the kth cell leads to an ordinary differential equation for the concentration of species i in box k as a function of time.

$$\frac{d\bar{c}_{ik}}{dt} = \frac{\bar{c}_{ik}}{\vartheta_k}\frac{d\vartheta_k}{dt} + \frac{1}{\vartheta_k}\sum_{j=0}^{L} q_{jk}\bar{c}_{ij} - \frac{-\bar{c}_{ik}}{\vartheta_k}\sum_{j=0}^{L} q_{kj} + \frac{Q_{ik}}{\rho\vartheta_k} + \dot{\bar{c}}_{ik}(\bar{c}_1, \ldots, \bar{c}_N, t) \tag{16}$$

Note that q_{jk} and q_{kj} are formed by taking the product of the appropriate velocity component, either $\bar{u}_k$ or $\bar{v}_k$, with the cell wall area $b_k l_{mk}$. In general, one must solve $L \times N$ ordinary differential equations of this type simultaneously for each of N specie concentrations in each of L cells (or boxes).

Numerical techniques for accomplishing these integrations are well known and available as standard subroutines for computer program applications. Concentration isopleths can be found from interpolation between values in the cells. Note that input requirements are restricted to a reasonably small number of parameters: b_j, $l_{mj}(t)$, $Q_{ij}(t)$, $\bar{u}_j(t)$, $\bar{v}_j(t)$, and initial values of the concentrations $(\bar{c}_{ij})_0$. This compares favorably with input requirements of finite-difference solutions to the three-dimensional partial differential conservation equations which require detailed information on vertical concentration profiles as initial data.

Thus far, the box model approach has only been applied to dispersion model calculations for nonreacting species, primarily by Reiquam[49] (elemental sulfur in Western Europe) and MacCracken et al.[51] (CO in the San Francisco Bay Area). However, future applications to the more complex, reacting systems appear promising.

Atmospheric Chemistry Effects

Attention will now be given to chemical reactions which modify, in some cases severely, the concentrations one would expect on the basis of nonreacting dispersion models. In the case of photochemical smog, entirely new species are formed which are themselves considered pollutants, and their concentrations are explicitly dependent on chemical processes.

Air pollutants are generally present in extremely dilute (parts-per-million) concentrations so that local thermodynamic equilibrium does not apply and chemical effects must be evaluated by considering the influence of finite-rate production and removal processes on individual conservation of species equations. Consider a general multicomponent mixture of chemically reacting trace gases. Each specie A_i $(i = 1, 2, 3, \ldots, N)$ can participate in any of M individual reactions denoted by subscript r, and represented by

$$\sum_{i=1}^{N} \nu'_{ir} A_i \xrightarrow{k_r} \sum_{i=1}^{N} \nu''_{ir} A_i$$

where ν'_{ir} and ν''_{ir} are the stoichiometric coefficients and k_r the reaction rates. Let X_i be the molar (per-unit-volume) concentration of A_i and $\dot{X}_i$ the net chemical source term for this specie. Summing over-all reactions, phenomenological chemical kinetics gives,[52]

$$\dot{X}_i = \dot{X}_i(X_1, \ldots, X_N, t) = \sum_{r=1}^{M} (\nu''_{ir} - \nu'_{ir}) k_r(t) \prod_{i=1}^{N} X_i^{\nu'_{ir}} \tag{17}$$

Note that we permit a time variation in the reaction rates. This is necessary since reaction rates for photochemical processes $k_1(t) = \Phi k_a(t)$ (where Φ is the quantum yield and k_a the specific absorption rate) depend on the flux of solar photons; hence on the zenith angle, and hence on the time t. If mass concentrations are being used, the appropriate source term is $\dot{c}_i = (M_i/M)\dot{X}_i$ and can be evaluated in terms of mass fractions by letting $X_i = (M/M_i)c_i$ in Eq. (17). When forming the source terms in the turbulent conservation equations, the approximation

$$\bar{\dot{c}}_i = \langle \dot{c}_i(c_1, \ldots, c_N, t) \rangle \simeq \dot{c}_i(\bar{c}_1, \ldots, \bar{c}_N, t)$$

is generally used, implying that terms of order $\langle c_i' c_j' \rangle$ are negligible compared to terms of order $\bar{c}_i \bar{c}_j$. It is not yet clear whether this is entirely justified. In any event, taking the gaseous contaminants of Table 1 as those of greatest interest in urban dispersion modeling, one requires information on reaction paths and reaction rates of sulfur oxides, nitrogen oxides, hydrocarbons, and carbon monoxide under urban atmospheric conditions.

As with most pollutants, sulfur dioxide emitted into the atmosphere is thought to follow a cycle wherein it is "scavenged" or removed from the air. First the SO_2 oxidizes to SO_3 and reacts with water vapor to form sulfuric acid mist; subsequently the sulfuric acid in the aerosol reacts with other substances to form sulfates which precipitate out.[53] However, there is some disagreement as to the reaction paths and rates by which this takes place, particularly as regards the initial oxidation step. A number of mechanisms have been postulated for the conversion of SO_2 to SO_3, including photooxidation by solar radiation in the near ultraviolet (3000–3400 Å), solution in small water droplets present in the atmosphere at high humidity and homogeneous or heterogeneous reactions involving moisture and other constituents or catalysts in fly ash.[54] Levy et al.[55] suggest that the reaction $O + SO_2 + O_2 \rightarrow SO_3 + O_2$ may be important. We shall discuss presently where the O atoms needed by this reaction might come from. In any event, most authors tend to discount the noncatalyzed gas phase reaction with molecular oxygen, $2SO_2 + O_2 \rightarrow 2SO_3$, as too slow to account for observations. Based on a linear process, $d[SO_2]/dt = -[SO_2]/\tau_c$, current estimates of the half-life of sulfur dioxide in the atmosphere range from two hours to several days.[56,57]

The pollution-related chemistry of nitrogen oxides and hydrocarbons is best understood in the context of the system of sunlight-induced reactions whose products are known as *photochemical smog*. This concept was originally introduced by Haagen-Smit[58] to explain the formation of ozone and other oxidants over the Los Angeles basin, a region characterized by large emissions of nitrogen oxides and unburned but reactive hydrocarbons from motor vehicle exhausts into a relatively stagnant air mass in the presence of high levels or solar radiation. In addition to the oxidants, light-scattering aerosols are formed which result in decreased visibility. In subsequent studies, evidence of photochemical smog has been found in other major cities which rely on internal-combustion powered automobiles for urban transportation.

Some ten years ago, Leighton published his now-classic treatise *Photochemistry of Air Pollution*[59] reviewing absorption rates for primary photochemical reactions of various nitrogen oxides, hydrocarbons, and other species, and concluded that among these pollutants the strongest absorber was nitrogen dioxide which photodissociates by

1) $NO_2 + h\nu \xrightarrow{k_1} NO + O$

to form nitric oxide and atomic oxygen. Leighton gives $k_1 = \Phi k_a \simeq 0.33\ \text{min}^{-1}$ for a solar zenith angle of 45° in the absorption band 2900–3850 Å. Atomic oxygen produced by this reaction readily reacts with the "ocean" of molecular oxygen in which it is immersed to yield ozone by

2) $O + O_2 + M \xrightarrow{k_2} O_3 + M$

where the third body M is either O_2 or N_2. Generally speaking, nitric oxide is present either directly from emissions or is produced by other reactions and it reacts with the ozone by

3) $O_3 + NO \xrightarrow{k_3} NO_2 + O_2$

to give nitrogen dioxide. Some interesting insights emerge from considering these reactions, although we shall shortly have to also consider the role of hydrocarbons to develop a complete picture of the photochemical smog process. Applying Eq. (17) gives the formation rate of nitrogen dioxide:

$$d[NO_2]/dt = -k_1[NO_2] + k_3[O_3][NO]$$

In practice a quasi-steady state is established in a sunlit atmosphere within a few minutes[60,61] and the derivative can be neglected compared to terms on the right-hand side so that

$$[O_3] \simeq k_1[NO_2]/k_3[NO]$$

This expression is found to hold reasonably well in field measurements[60] and illustrates the intimate relationship between the ratio of nitrogen dioxide to nitric oxide concentrations and ambient ozone levels.

However, reactions 1–3 alone do not account for the high ozone concentrations observed in photochemically polluted air since insufficient amounts of NO_2 would be produced. As Stephens[61] has shown, what is needed is an additional process which is slow compared to the steady state, but which converts NO to NO_2 without consuming an equivalent amount of ozone. It is now known that this function is performed by organic radicals (RCO_x) which yield an oxygen atom to nitric oxide to form nitrogen dioxide. These organic radicals are produced in the atmosphere by the oxidation of the emitted reactive hydrocarbons (RH) via complex reaction paths involving long reaction chains. In addition to ozone (O_3), final products of the smog reactions include peroxyacetal nitrate (PAN), aldehydes (RHCO), and often aerosols as well. While specific reaction steps in the hydrocarbon oxidation are difficult to ascertain experimentally, photochemical smog is often studied in the laboratory in "smog chambers," where dilute mixtures of RH and NO_x are exposed to artificial ultraviolet radiation and measurements made of the time-history of their disappearance and the subsequent appearance of O_3, PAN, RHCO, and aerosols. From such data, attempts have been made to infer underlying reaction paths and postulate kinetic mechanisms. Further discussion of many studies in this vein can be found in the reviews by Altshuller and Bufalini.[62,63]

Recently, computer solutions based on kinetic models have been obtained and compared with smog chamber concentration histories by Westberg and Cohen.[64] These solutions are found by numerical integration of a set of coupled rate equations of the form of Eq. (17) using rate constants and stoichiometric coefficients associated with the model. The Westberg-Cohen results showed good agreement with smog chamber data; but in attempting to represent in detail each individual reaction step, they required a total of 71 reactions for the propene/NO_x system; rather a large number if one hopes to incorporate finite-rate processes into urban dispersion models since, in principle, each specie, including intermediates, must be represented by its own conservation equation. With a view toward dispersion model applications, Eschenroeder and Martinez[17] suggested a "lumped parameter" kinetic model where hydrocarbon reaction chains and organic radical reactions are lumped into composite forms, thereby limiting species and reactions considered to more manageable numbers. In addition to reactions 1–3, Eschenroeder and Martinez propose

4) $O + RH \xrightarrow{k_4} 2.5\,RCO_x + 0.12\,RHCO$

5) $O_3 + RH \xrightarrow{k_5} 2.5\,RCO_x + 0.12\,RHCO$

6) $RCO_x + NO \xrightarrow{k_6} NO_2$

7) $RCO_x + O_2 \xrightarrow{k_7} 0.5\,O_3$

8) $RCO_x + NO_2 \xrightarrow{k_8} 0.67\,PAN$

as representative of the complete photochemical smog system for RH/NO_x mixtures; where effective stoichiometric coefficients on the right-hand side of reactions 4, 5, 7, and 8 apply when RH = trans-2-Butene. In practice, the rate constants are found by computing time-histories based on estimates of k_r in the literature and adjusting certain values to obtain agreement with experiments. Figure 7 shows results of the above method compared with smog chamber measurements by Tuesday,[65] where rate constants used in these calculations can be found in Ref. 17. Although it can be argued that a global chemistry approach has elements of nonuniqueness, the Eschenroeder-Martinez model does appear to give a qualitatively correct picture of the over-all kinetic process.

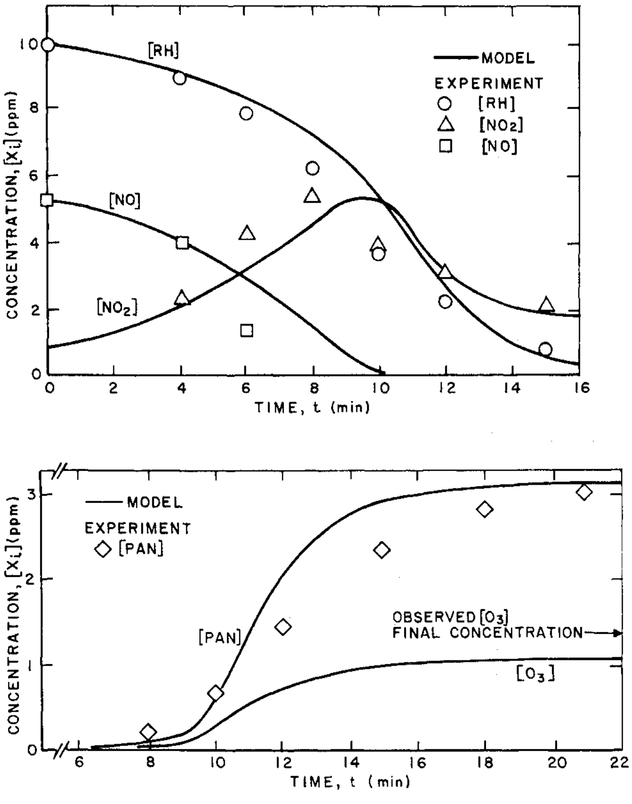


Fig. 7 Time-histories of photochemical smog reactants and products computed with Eschenroeder-Martinez lumped-parameter kinetic model (for *RH* = trans-2-Butene) compared with smog chamber measurements by Tuesday[65] (from Ref. 17).

Photochemical smog is also important insofar as its presence can affect the chemistry of other constituents such as sulfur dioxide and carbon monoxide. Renzetti and Doyle[66] who did smog chamber experiments on $RH/NO_x/SO_2$ systems suggested that sulfur dioxide might be oxidized by photochemical smog products or intermediates. The possible importance of the reaction $O + SO_2 + O_2 \rightarrow SO_3 + O_2$ mentioned previously is now understandable since O atoms are produced by reaction 1. It has also been suggested[59,66] that organic radicals of the peroxyalkyl type $(RO\dot{O})$ might cause oxidation by $RO\dot{O} + SO_2 \rightarrow R\dot{O} + SO_3$. More recent experiments by Wilson and Levy[67] led to the conclusion that photochemical smog greatly increases the decay rate of SO_2 and that maximum oxidant levels are decreased when SO_2 is present. But as Altshuller and Bufalini[63] have noted, an adequate understanding of the oxidation of SO_2 in photochemical smog is still lacking, particularly as regards the influence of water vapor, where experimental data are confusing and often contradictory.

Until recently, carbon monoxide was thought to be essentially inert over urban-atmospheric residence times. But Westberg, Cohen, and Wilson[68] were able to show that hydroxyl radical intermediates present in photochemical smog could attack CO molecules yielding the net reaction $CO + O_2 + NO \rightarrow CO_2 + NO_2$. This accelerates the conversion of NO to NO_2 and the production rate of O_3. Originally suggested by computer simulations, this effect has since been verified in smog chamber experiments with $RH/NO_x/CO$ systems.[68] Hecht and Seinfeld[69] have attempted to account for the hydroxyl attack on CO, and other factors as well, including the influence of water, in a 15-step lumped-parameter kinetic model which they propose for photochemical smog formation. In preliminary tests their model gave rather good descriptions of smog chamber results for various olefin and paraffin hydrocarbons both in the presence and absence of CO.

It should be clear that the development of kinetic models which accurately characterize the rate chemistry of pollutants is a rapidly developing art, but one which should be vigorously pursued if physically meaningful dispersion models are to emerge for the major pollutants.

Concluding Remarks

For applications to environmental planning and policymaking, the over-all question which dispersion models must ultimately address can be stated in general terms as follows. Given the space and time distributions of emission sources and meteorological data on wind velocity fields, inversions and atmospheric stability, what are the resulting concentration distributions generated over air quality regions of the major pollutants (particulates, SO_2, NO_x, CO, hydrocarbons, and photochemical oxidants)? We have attempted here to survey the methods currently used or proposed for modeling this problem or parts of it. Based on our review, the areas which appear to require further research can be grouped into two categories: 1) aerophysical problems and 2) computational problems.

As for the aerophysical problems, a number of phenomena are still inadequately understood. We suffer from a lack of data and theory relating to turbulent transport of contaminants in the atmospheric boundary layer, particularly over distances greater than a few kilometers. Also, a theory for inversion and stability effects on diffusion in terms of first principles is still lacking, although the Monin-Obukhov similarity theory in the constant-flux layer is a good starting point. Moreover, most of the important chemical removal and production processes have not yet been incorporated into well-verified models. Because of space limitations, we have not discussed other removal processes, perhaps equally important (but poorly understood), such as precipitation scavenging and absorption by the Earth's surface or oceans. But even if all of these elemental physical processes were better understood, considerable computational problems still have to be overcome to develop dispersion models of sufficient generality. It is likely that the gaussian plume and gaussian puff approximations have been stretched too close to the limits of their usefulness. A direct attack on the diffusion equations by finite-difference techniques has a very definite virtue when the wind direction is spatially and temporally uniform, and a convenient coordinate system can be chosen. But this is generally not the case, since most urban regions are characterized by fairly complex streamline patterns, at least in the horizontal plane, and three-dimensional finite-difference solutions to the diffusion equation are at present a distant prospect. For this reason we have pointed out the potential of box models, which are somewhat intermediate to gaussian plumes and finite-difference solutions in their ability to describe episodes, long-range effects and nonlinear chemical interactions.

To keep the scope of the review within reasonable bounds we have not discussed a number of allied topics such as the use of dispersion models in pollution control schemes, effects of pollutants dispersing over global scales, problems of monitoring instrumentation, the role of field measurements in validating dispersion models; and, perhaps the most important motivating factor, the changing social environment within which these problems are perceived as important. Nonetheless, even within our self-imposed limitations in scope, the research problems in dispersion modeling emerge as formidable and challenging, and much work remains to be done.

Finally, we might note that the physically complex, interdisciplinary nature of air pollution dispersion modeling in many ways parallels the problems of modeling the chemically reacting flowfields generated by atmospheric entry vehicles, an area which has yielded up many of its mysteries to analysis since the national commitment to conquer space. There is, therefore, some reason to hope that progress will be made with the class of problems treated here as well, given a similar commitment to the environment of Spaceship Earth.

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