Kirk-Othmer Encyclopedia of Chemical Technology.

ATMOSPHERIC MODELING

ematical air quality models provide a powerful framework for understanding the dynamics of pollutants in the atmosphere and for assessing the impact emission sources have on pollutant concentrations. Two classes of models are commonly used. Empirical models provide an understanding of source impacts by statistically analyzing historical air quality data. Diagnostic models provide a comprehensive description of the detailed physics and chemistry of compounds in the atmosphere, following the evolution of pollutant emissions to their ultimate fate. At the heart of the model is a system of mathematical routines that integrate the effects of individual processes. The complexity and computational intensity of modern models have necessitated the development of algorithms for fast and accurate mathematical solution techniques. Air quality models are being applied to solving such problems as urban smog, acid deposition, regional ozone, haze in scenic regions, and the destruction of the protective stratospheric ozone layer.

Mathematical models have grown increasingly detailed in descriptions of air pollutant dynamics and are thus key tools for gaining scientific understanding of atmospheric processes. These models also are the most practical and scientifically defensible means of relating pollutant emissions to air quality. They are widely used in regulatory planning and analysis as indicated in Figure 1. A wide variety of models are used to address problems ranging from indoor air pollution to regional acid deposition and global climate change. The models used are remarkably similar. This article focuses on the models used to understand air pollution dynamics.

Development of a mathematical air quality model proceeds through four stages. In the conceptual stage, a working set of relationships approximating the physical system is derived. Next, these relationships are expressed as mathematical equations, giving a formal description of the idealized system. The third step is the computational implementation of the model, including development of the algorithms and computer code needed to solve the equations given various inputs. The final step is the application of the model, including acquisition and processing of the necessary input data, and evaluation of model results.

1. Air Pollutants

Air pollution (qv) problems are characterized by their scale and the types of pollutants involved. Pollutants are classified as being either primary, that is emitted directly, or secondary, ie, formed in the atmosphere through chemical or physical processes. Examples of primary pollutants are carbon monoxide [630-08-0] (qv), CO, lead [7439-92-1] (qv), Pb, chlorofluorocarbons, and many toxic compounds. Notable secondary pollutants include ozone [10028-15-6] (qv), O_3, which is formed in the troposphere by reactions of nitrogen oxides (NO_x) and reactive organic gases (ROG), and sulfuric and nitric acids.

Models are used extensively to understand a wide range of problems, including indoor air pollution, such as elevated levels of radon [10043-92-2], Rn, and formaldehyde [50-00-0], CH_2O, high concentrations of carbon monoxide and particulate matter in the vicinity of congested roadway intersections, spills of volatile toxic chemicals, urban smog, acid deposition, global climate change, and stratospheric ozone depletion. Each of these problems involves pollutant transport via advection and turbulent diffusion. Several of them also involve

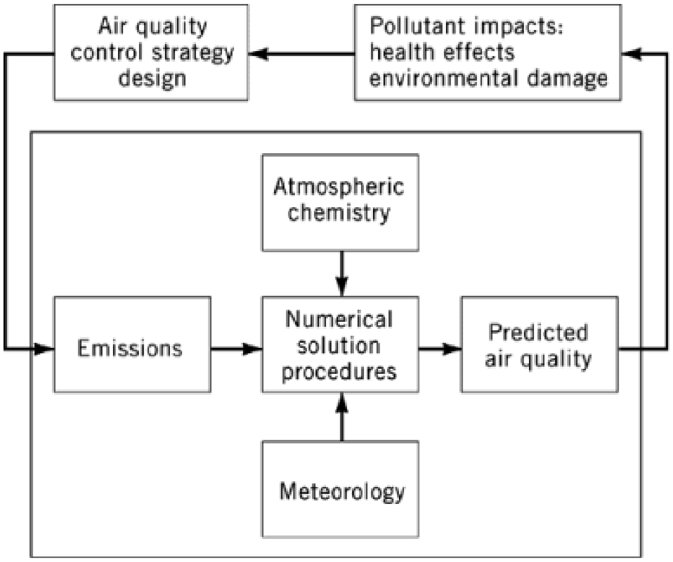

Fig. 1. Schematic of the role of an air quality model, in the air quality control planning process. Some studies, for example, the prediction of indoor air pollutant concentrations, require more than one model.

atmospheric chemistry and processes of wet or dry deposition may also be important. Thus the models used to describe the dynamics in each case primarily vary in temporal and spatial resolution, the chemical transformations being tracked, and the deposition processes included. If a pollutant is strictly primary in nature and is long-lived in the atmosphere, the models used to describe its dynamics need only follow transport. Transport-only models are used when dealing with carbon monoxide, many toxic chemicals, and most components of particulate matter. Following the evolution of secondary or highly reactive pollutants is generally much more complicated because chemical reactions between many compounds must be considered in addition to transport and removal. Chemically active systems include urban and regional smog, acid deposition, and stratospheric ozone depletion.

2. Air Quality Models

Models used in air pollution analysis fall into two classes: empirical–statistical and deterministic as shown in Figure 2. In the former, the model statistically relates observed air quality data to the accompanying emission patterns, and chemistry and meteorology are included only implicitly. In the latter, analytical or numerical expressions describe the complex transport and chemical processes that affect air pollutants. Pollutant concentrations are determined as explicit functions of meteorology, topography, chemical transformation, surface deposition, and source characteristics. A typical schematic is shown in Figure 3. A listing of many of the air quality models, including status, applications, and the model formulations can be found in ref. 2. Each formulation involves approximations and has certain strengths and limitations.

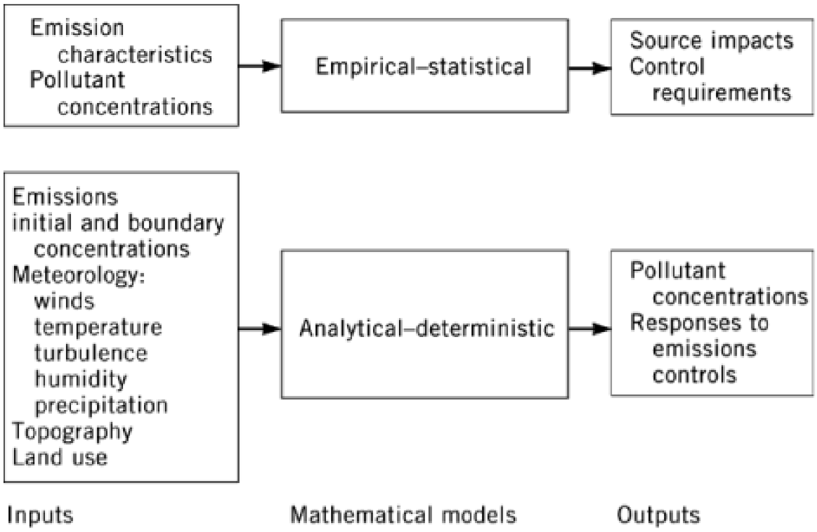

Fig. 2. Inputs, types of models, and outputs used in air quality modeling studies.

3. Empirical–Statistical Models

Empirical–statistical models are based on establishing a relationship between historically observed air quality and the corresponding emissions. The linear rollback model is simple to use and requires few data, and for these reasons has been widely applied (3, 4). Linear rollback models assume that the highest measured pollutant concentration is proportional to the basinwide emission rate, plus the background value; that is,

$$c_{\max} = aE + c_b \qquad (1)$$

where $c_{\max}$ is the maximum measured pollutant concentration, E is the emission rate, c_b is the background concentration resulting from sources outside the modeling region, and a is a constant of proportionality. The constant implicitly accounts for the dispersion, transport, deposition, and chemical reactions of the pollutant. The allowable emission rate E_a necessary to reach a desired ambient air quality goal c_d can be calculated from

$$\frac{E_a}{E_o} = \frac{c_d - c_b}{c_{\max} - c_b} \qquad (2)$$

where E_o is the emission rate that prevailed at the time that $c_{\max}$ was observed. Presumably, pollutant concentrations at other times decrease toward background levels as emissions are reduced. The linear rollback model is a very simplified approach and its application is limited. Nonlinear processes, such as chemical reactions and spatial or temporal changes in emission patterns, are not accounted for in the rollback model.

A second class of empirical–statistical models is the receptor-oriented model, which has been used extensively for estimating the contributions that distinguishable sources such as automobiles or municipal incinerators make to particulate matter concentrations (5–14). Attempts have also been made to track nonreacting gases (15), and under special conditions, reactive organic compounds (16–18), to their sources using receptor modeling methods. Receptor models compare the measured chemical composition of particulate matter at a receptor site to the chemical composition of emissions from the primary sources to identify the source contributions at the monitoring location. There are three principal categories of receptor models: chemical mass

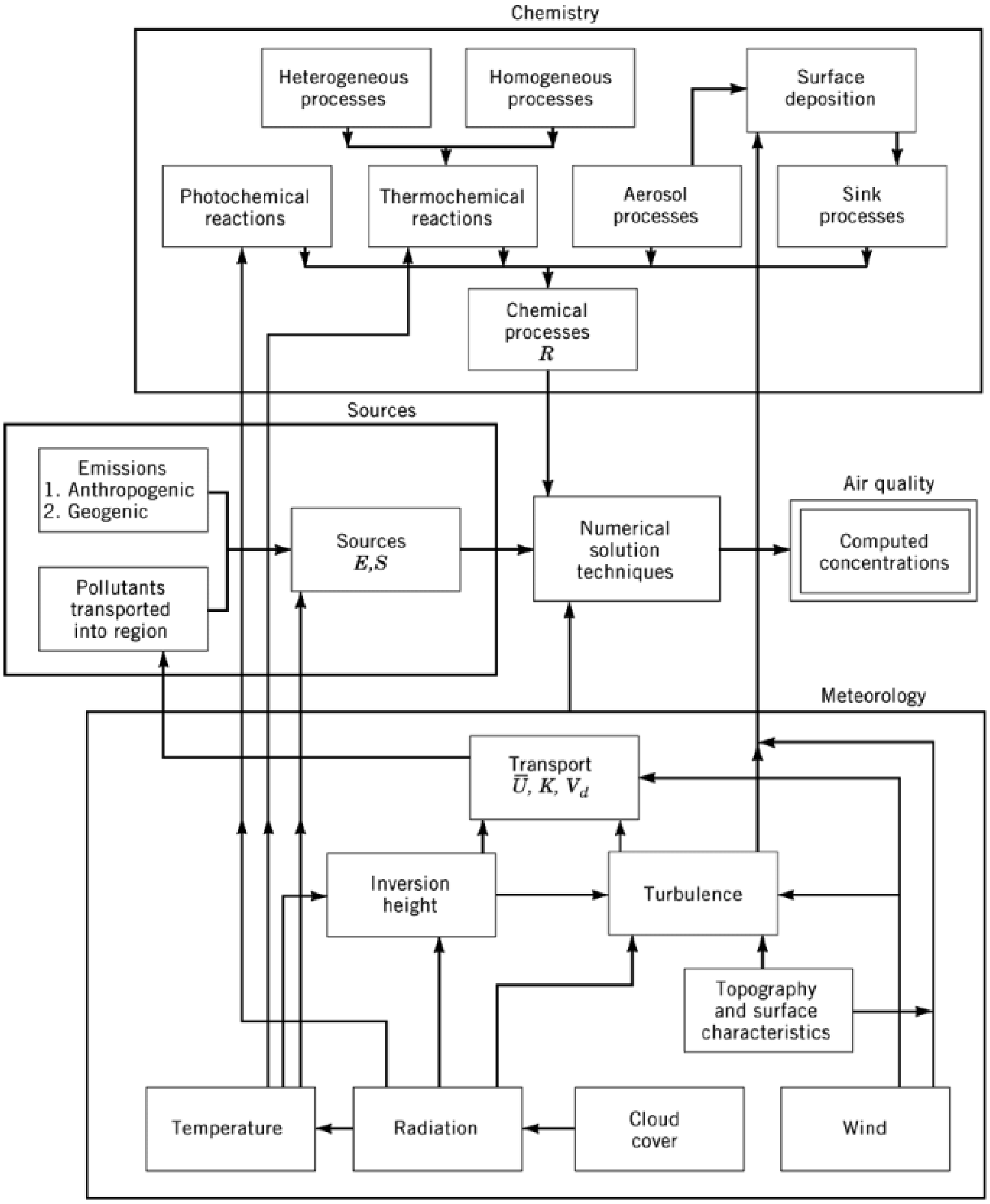

Fig. 3. Schematic diagram of a deterministic air quality model, showing the model components and interactions (1) where each of the boxes involves a large number of individual processes. Terms are defined in text.

balance, multivariate, and microscopic. Hybrid analytical and receptor (or combined source–receptor) models have been used (19), but further investigation into their capabilities is required.

Receptor models are powerful tools for source apportionment of particulates because a vast amount of particulate species characterization data have been collected at many sampling sites worldwide, and because many aerosol species are primary pollutants. Most of the information available is for elemental concentrations, eg, lead, nickel, and aluminum, although more recent measurements have provided data on concentrations of ionic species and carbonaceous compounds. At a sampling (or receptor) site, the aerosol mass concentration of each species i is

$$c_i = \sum_{j=1}^{n} a_{ij} S_j \qquad i = 1, 2, \ldots m \qquad (3)$$

where c_i is the mass concentration of species i at the receptor site; S_j is the total mass concentration of all species at the receptor site that is attributable to source *j;* a_ij is the fraction that species i constitutes of the total mass concentration arriving at the sampling site from source *j; m* is the total number of species measured; and n is the total number of sources. The mass concentration at the receptor site and the coefficients a_ij that describe the chemical composition for the sources are the inputs from which S_j, the mass apportioned to source *j,* is determined. Because a_ij characterizes the source, it is referred to as the source fingerprint and should be unique to the source. When the chemical compositions of the emissions from two source categories are similar, it is extremely difficult for receptor models to distinguish between the sources. The categories of receptor models are differentiated by the techniques used to determine S_j.

If the source fingerprints, a_ij, for each of n sources are known and the number of sources is less than or equal to the number of measured species ($n \leq m$), an estimate for the solution to the system of equations (3) can be obtained. If $m > n$, then the set of equations is overdetermined, and least-squares or linear programming techniques are used to solve for S_j. This is the basis of the chemical mass balance (CMB) method (20, 21). If each source emits a particular species unique to it, then a very simple tracer technique can be used (5). Examples of commonly used tracers are lead and bromine from mobile sources, nickel from fuel oil, and sodium from sea salt. The condition that each source have a unique tracer species is not often met in practice.

Microscopic identification models are similar to the CMB methods except that additional information is used to distinguish the source of the aerosol. Such chemical or morphological data include particle size and individual particle composition and are often obtained by electron or optical microscopy.

Multivariate models, including factor analysis models (14, 22–24), rely on finding the underlying structure of large sets of air quality data in order to determine sources. Models based on factor analysis are the most widely used. Multivariate models operate by identifying groups of elements or species, the concentrations of which fluctuate together from sampling period to sampling period, implying that these groups come from a single “source”. When the composition of the hypothetical source is compared to the known composition of specific sources, it often becomes obvious what the group of cofluctuating chemical elements represents. For example, lead and bromine concentrations are usually highly correlated because they are emitted primarily by the same sources, ie, automobiles burning leaded gasoline. Multivariate techniques do not rely on a detailed knowledge of the source fingerprint a_ij and can be used to refine estimates of the fingerprint.

4. Deterministic Models

Deterministic air quality models describe in a fundamental manner the individual processes that affect the evolution of pollutant concentrations. These models are based on solving the atmospheric diffusion–reaction equation, which is in essence the conservation-of-mass principle for each pollutant species (25):

$$\frac{\delta c_i}{\delta t} + \overline{U} \cdot \nabla c_i = \nabla \cdot D_i \nabla c_i + R_i(c_1, c_2, c_3, \ldots c_n) + S_i(\overline{x}, t) \qquad i = 1, 2, 3, \ldots n \qquad (4)$$

where c_{i} is the concentration of species $i;\overline{U}$ is the wind velocity vector; D_{i} is the molecular diffusivity of species $i;$ R_{i} is the net production (depletion if negative) of species i by chemical reaction; S_{i} is the emission rate of $i;$ and n is the number of species. R can also be a function of the meteorological variables. Equation 4 states that the time rate of change of a pollutant depends on convective transport (term 2), diffusion (term 3), chemical reactions (term 4), and emissions (term 5), together with initial and boundary conditions. Deposition and surface level emissions enter as boundary conditions at the ground:

$$E - v_d c = -K_{zz}\frac{\delta c}{\delta z}$$

where E is the ground level emissions, v_{d} is the deposition velocity, and K_{zz} is the vertical diffusivity. The turbulence closure problem makes it necessary to approximate the atmospheric diffusion equation, usually by K-theory (26, 27):

$$\frac{\delta c_i}{\delta t} + \langle\overline{U}\rangle\cdot\nabla\langle c_i\rangle = \nabla\cdot K\nabla\langle c_i\rangle + R_i(\langle c_i\rangle, \langle c_2\rangle, \ldots\langle c_n\rangle) + \langle S_i(x,t)\rangle$$

$$i = 1, 2, 3, \ldots n \qquad (5)$$

where the braces $\langle\ \rangle$ indicate an ensemble average, and K is the turbulent (eddy) diffusivity tensor. Known analytical solutions exist only for the simplest source distributions and chemical reaction mechanisms, $\langle S_{\mathrm{i}}\rangle$ $R,$ in equation 5.

Examination of equation 5 shows that if there are no chemical reactions, ($R = 0$), or if R is linear in $\langle c_{\mathrm{i}}\rangle$ and uncoupled, then a set of linear, uncoupled differential equations are formed for determining pollutant concentrations. This is the basis of transport models which may be transport only or transport with linear chemistry. Transport models are suitable for studying the effects of sources of CO and primary particulates on air quality, but not for studying reactive pollutants such as O_3, NO_2, HNO_3, and secondary organic species.

4.0.1. Lagrangian Models

There are two distinct reference frames from which to view pollutant dynamics. The most natural is the Eulerian coordinate system which is fixed at the earth's surface and in which a succession of different air parcels are viewed as being carried by the wind past a stationary observer. The second is the Lagrangian reference frame which moves with the flow of air, in effect maintaining the observer in contact with the same air parcel over extended periods of time. Because pollutants are carried by the wind, it is often convenient to follow pollutant evolution in a Lagrangian reference frame, and this perspective forms the basis of Lagrangian trajectory and Lagrangian marked-particle or particle-in-cell models. In a Lagrangian marked-particle model, the center of mass of parcels of emissions are followed, traveling at the local wind velocity, while diffusion about that center of mass is simulated by an additional random translation corresponding to the atmospheric diffusion rate (28, 29).

Lagrangian trajectory models can be viewed as following a column of air as it is advected in the air basin at the local wind velocity. Simultaneously, the model describes the vertical diffusion of pollutants, deposition, and emissions into the air parcel as shown in Figure 4. The underlying equation being solved is a simplification of equation 5:

$$\frac{\delta c_i}{\delta t} = \frac{\delta}{\delta z}K_{zz}\frac{\delta c_i}{\delta z} + S_i(t) + R(\bar{c}, t) \qquad (6)$$

Trajectory models require spatially and temporally resolved wind fields, mixing-height fields, deposition parameters, and data on the spatial distribution of emissions. Lagrangian trajectory models assume that vertical

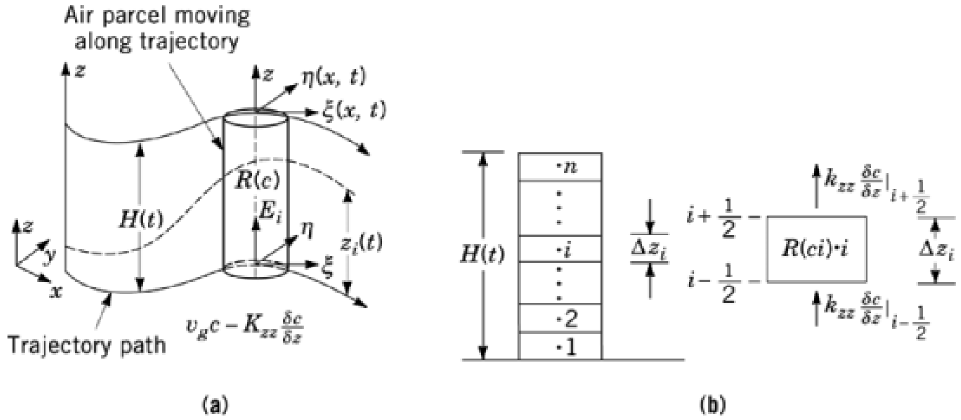

Fig. 4. Schematic diagram of a Lagrangian trajectory model where $H(t)$ represents the air column height in both Eulerian (x,y,z) and Lagrangian (ξ, η, z) coordinates; c, the pollutant concentration; R, chemical reactions; v_g, deposition of pollutants; and K_{zz}, vertical diffusion. (**a**) The column of air being modeled is advected at the local wind velocity along a trajectory path across the modeling region; $z_i(t)$ represents the mixing height variation along the trajectory path; E_i, the emissions of the ith pollutant. Within the moving air parcel, the model describes the important processes affecting the pollutant evolution and concentration. (**b**) Vertical resolution is gained by dividing the column into a number of cells in the vertical direction; $R(c_i)$ represents the concentration produced by chemical reactions within the ith cell of which Δz_i is the height.

wind shear and horizontal diffusion are negligible. Other limitations of trajectory and Eulerian models have been discussed (30).

4.0.2. Gaussian Plume Model

One of the most basic and widely used transport models based on equation 5 is the Gaussian plume model. Gaussian plume models for continuous sources can be obtained from statistical arguments or can be derived by solving:

$$\overline{U}\frac{\delta c}{\delta x} = K_{yy}\frac{\delta^2 c}{\delta y^2} + K_{zz}\frac{\delta^2 c}{\delta z^2} \qquad (7)$$

where $\overline{U}$ is the temporally and vertically averaged wind velocity; x, y, and z are the distances in the downwind, crosswind, and vertical directions, respectively; and K_{yy} and K_{zz} are the horizontal and vertical turbulent diffusivities, respectively. For a source with an effective height H, emission rate Q, and a reflecting (nonabsorbing) boundary at the ground, the solution is

$$c(x, y, z) = \frac{Q}{2\pi\overline{U}\sigma_y(x)\sigma_z(x)}\exp\left[\frac{-y^2}{2\sigma_y^2(x)}\right]\left[\exp\frac{-(z-H)^2}{2\sigma_z^2(x)} + \exp\frac{-(z+H)^2}{2\sigma_z^2(x)}\right]$$

This solution describes a plume with a Gaussian distribution of pollutant concentrations, such as that in Figure 5, where $\sigma_z(x)$ and $\sigma_z(x)$ are the standard deviations of the mean concentration in the y and z directions. The standard deviations are the directional diffusion parameters, and are assumed to be related simply to the turbulent diffusivities, K_{yy} and K_{zz}. In practice, $\sigma_y(x)$ and $\sigma_z(x)$ are functions of x, $\overline{U}$, and atmospheric stability (2, 31–33).

Gaussian plume models are easy to use and require relatively few input data. Multiple sources are treated by superimposing the calculated contributions of individual sources. It is possible to include the first-order chemical decay of pollutant species within the Gaussian plume framework. For chemically, meteorologically, or geographically complex situations, however, the Gaussian plume model fails to provide an acceptable solution.

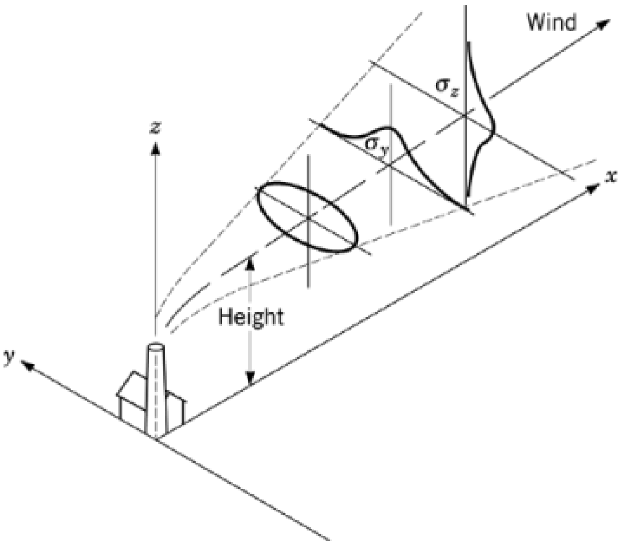

Fig. 5. Diffusion of pollutants from a point source. Pollutant concentrations have separate Gaussian distributions in both the horizontal (y) and vertical (z) directions. The spread is parameterized by the standard deviations (σ) which are related to the diffusivity (K).

4.0.3. Eulerian Models

Of the Eulerian models, the box model is the easiest to conceptualize. The atmosphere over the modeling region is envisioned as a well-mixed box, and the evolution of pollutants in the box is calculated following conservation-of-mass principles including emissions, deposition, chemical reactions, and atmospheric mixing.

Eulerian "grid" air quality models are the most complex, but potentially the most powerful, involving the least-restrictive assumptions. They are also the most computationally intensive. Grid models solve a finite approximation to equation 5, including temporal and spatial variation of the meteorological parameters, emission sources, and surface characteristics. Grid models divide the modeling region into a large number of cells, horizontally and vertically, which interact with each other by simulating diffusion, advection, and sedimentation (for particles) of pollutant species. Input data requirements for grid models are similar to those for Lagrangian trajectory models, but, in addition, data on background concentrations (boundary conditions) at the edges of the grid system are required. Eulerian grid models predict pollutant concentrations throughout the entire airshed. Over successive time periods the evolution of pollutant concentrations and how they are affected by transport and chemical reaction can be tracked.

4.0.4. Modeling Chemically Reactive Compounds

A number of compounds are formed or destroyed in the atmosphere by a series of complex, nonlinear chemical reactions, eg, stratospheric ozone. Models that not only describe pollutant transport, but also account for complex chemical transformations, $R(\bar{c},t)$ in equation 5, are necessary for these systems. Such models are also required to study the dynamics of chemically reactive primary pollutants such as nitric oxide [10102-43-9], NO, and pollutants that are primary as well as secondary in origin, for example, nitrogen dioxide [10102-44-0], NO_2, and formaldehyde. Addition of the capability to describe a series of interconnected chemical reactions greatly increases requirements for computer storage as well as computing time and input data requirements. Increased computational demands arise because the evolution of the interacting species must be followed simultaneously, leading to a system of coupled, nonlinear differential equations.

Box, Lagrangian trajectory, and Eulerian grid models have all been developed to include nonlinear chemical reactions. Box models assume that the pollutants are mixed homogeneously within the modeling region, an assumption that is often inappropriate. Trajectory and grid models resolve pollutant dynamics spatially and have been used widely and with success particularly for studying photochemical smog and acid deposition problems (26, 34–45).

4.1. Temporal and Spatial Resolution

The temporal and spatial resolutions of models can vary from minutes to a year and from meters to hundreds of kilometers. The minimum meaningful resolution of a model is determined by the input data resolution and the structure of the model. Statistical models generally rely on several years' worth of measurements of hourly or daily pollutant concentrations. The resolution of the input data represents the minimum resolution of a statistical model. Resolution of analytical models is limited by the spatial and temporal resolution of the emissions inventory, the meteorological fields, and the grid size chosen for model implementation. For modeling urban air basins, the size of individual grid cells is on the order of a few kilometers per side, whereas for modeling street canyons, the cell size must be reduced to a few meters on each edge. At the other extreme, regional models have horizontal resolutions varying from 20 to 100 km, and global models may have a resolution as coarse as a few thousand km. The temporal resolution of models ranges from about 15 minutes to a few hours or days.

The information desired from modeling studies often depends on processes that occur on spatial scales much smaller than the resolution of most air quality models. The modeling of NO_x air quality in street canyons involves small-scale processes of this sort. Introduction of point-source emissions into grid-based air quality models likewise involves a mismatch between the high concentrations that exist near the source versus the lower concentrations computed by a model that immediately mixes those emissions throughout a grid cell of several kilometers on each side. Because of computational time constraints, it has often been considered impractical to describe fully the processes that take place on a scale smaller than the main model grid, ie, subgrid scale. Nevertheless, values obtained from large-scale calculations should be accurate over the spatial averaging scale adopted by the model.

5. Model Components

A model's ability to correctly predict pollutant dynamics and to apportion source contributions depends on the accuracy of the individual process descriptions and input data, and the fidelity with which the framework reflects the interactions of the processes.

5.1. Turbulent Transport and Diffusion

There are two pollutant transport terms in equation 5: an advection term, in which pollutants are carried along with the time-averaged mean wind flow; and a dispersion term representing transport resulting from local turbulence. The averaging time that determines the mean winds is related to the spatial scale of the system being modeled. Minutes may be appropriate for urban-scale simulations, multihour averages for the regional scale, and daily to weekly averages for determining long-term concentrations of nonreactive pollutants.

Turbulent transport is determined by complex interactions between meteorological conditions and topography. In addition to gross topographical features, surface "roughness" scales have been devised to parameterize surface characteristics according to land-use categories. Very small values, are assigned to smooth water or ice, and increasingly higher values to grasslands, croplands, residential areas, and urban-industrial centers.

In general, the rougher the surface, the greater the local turbulence. Often, particularly during sunny days, atmospheric turbulence is generated by the heating of the earth's surface.

Turbulent fluxes are difficult to measure, and hence there are uncertainties in the various methods employed by models to describe them. As in equation 5, these fluxes are typically parameterized as being proportional to the gradient of mean pollutant concentrations. Further simplifying the problem, the components of the eddy diffusivity tensor, K, are assumed to be constant along their respective axes. An obvious need when applying K-theory is some algorithm for establishing the value of K. As a result of the large variety of processes involved, there are also a number of methods to parameterize the horizontal and vertical diffusion coefficients (46). The usual limitation to the accuracy of diffusion calculations in a practical application is determined by the extent of measurements of the atmospheric structure taken during the period to be simulated. For most model applications, the number of observed factors relating to atmospheric turbulence are few and include only ground-level winds and temperatures, surface roughness, and cloud cover. At a few locations and times, the inversion base, or mixing height, wind speeds aloft, and vertical temperature gradient may also be known. As the amount and accuracy of information characterizing atmospheric structure increases, confidence in model predictions of dispersion increases.

5.2. Removal Processes

Pollutant removal processes, particularly dry deposition and scavenging by rain and clouds, are a primary factor in determining the dynamics and ultimate fate of pollutants in the atmosphere.

5.2.1. Dry Deposition

Dry deposition occurs in two steps: the transport of pollutants to the earth's surface, and the physical and chemical interaction between the surface and the pollutant. The first is a fluid mechanical process (see Fluid mechanics), the second is primarily a chemical process, and neither is completely characterized at the present time. The problem is confounded by the interaction between the pollutants and biogenic surfaces where pollutant uptake is enhanced or retarded by plant activity that varies with time (47, 48). It is very difficult to measure the depositional flux of pollutants from the atmosphere, though significant advances were made during the 1980s and early 1990s (49, 50).

Many factors affect dry deposition, but for computational convenience air quality models resort to using a single quantity called the deposition velocity, designated v_d or v_g, to prescribe the deposition rate. The deposition velocity is defined such that the flux F_i of species i to the ground is

$$F_i = v_d c_i(z_r) \qquad (9)$$

where $c_\mathrm{i}(z_\mathrm{r})$ is the concentration of species i at some reference height z_r, typically from one to several meters. For a number of pollutants, v_d has been measured under various meteorological conditions and for a number of surface types (50).

Early models used a value for v_d that remained constant throughout the day. However, measurements show that the deposition velocity increases during the day as surface heating increases atmospheric turbulence and hence diffusion, and plant stomatal activity increases (50–52). More recent models take this variation of v_d into account. In one approach, the first step is to estimate the upper limit for v_d in terms of the transport processes alone. This value is then modified to account for surface interaction, because the earth's surface is not a perfect sink for all pollutants. This method has led to what is referred to as the resistance model (52, 53) that represents v_d as the analogue of an electrical conductance

$$v_d = (r_a + r_b + r_s)^{-1} \qquad (10)$$

where r_a is the aerodynamic resistance controlled primarily by atmospheric turbulence, r_b is the resistance to transport in the fluid sublayer very near the plant surface, and r_s is the surface (or canopy) resistance. Of the three resistances, r_a is essentially the same for all species, r_b is the same for gaseous species with the same diffusivities, though it can be considerably greater for aerosols, and r_s depends greatly on the surface affinity for the diffusing species. For example, nitric acid [7697-37-2], HNO_3, which reacts rapidly with most surfaces, has a very low surface resistance, usually taken as zero (49, 54, 55), whereas CO is not very reactive and has a high r_s value. Significant differences between the deposition of gases and aerosols are that aerosols have a much lower diffusivity, the rate of gravitational settling can be significant for larger particles, and the surface resistance for aerosols is not determined by species reactivity, alone. Recent models account for the variation of surface resistance and diurnal change in fluid mechanical transport. These parameterizations have been used to quantify the deposition flux of various compounds (49, 56).

5.2.2. Scavenging by Rain, Fog, and Clouds

Wet removal, or precipitation scavenging, can be effective in cleansing the atmosphere of pollutants, and depends on the intensity and size of the raindrops (57). Fog and cloud droplets can also absorb gases, capture particles, and promote chemical reactions. Precipitation scavenging is not as important on an urban scale as on a regional scale and is not included in most urban-scale models. Fog chemistry can be important to human health on an urban scale, as evidenced in London in 1952 when thousands of persons died during an episode of excess industrial air pollution and fog (27). Cloud, rain, and fog processes are often important in regional and global scale modeling.

5.2.3. Representation of Atmospheric Chemistry Through Chemical Mechanisms

A complete description of atmospheric chemistry within an air quality model would require tracking the kinetics of many hundreds of compounds through thousands of chemical reactions. Fortunately, in modeling the dynamics of reactive compounds such as peroxyacetyl nitrate [2278-22-0] (PAN), $C_2H_3NO_5$, O_3, and NO_2, it is not necessary to follow every compound. Instead, a compact representation of the atmospheric chemistry is used. Chemical mechanisms represent a compromise between an exhaustive description of the chemistry and computational tractability. The level of chemical detail is balanced against computational time, which increases as the number of species and reactions increases. Instead of the hundreds of species present in the atmosphere, chemical mechanisms include on the order of 50 species and 100 reactions.

Three different types of chemical mechanisms have evolved as attempts to simplify organic atmospheric chemistry: surrogate (58, 59), lumped (60–63), and carbon bond (64–66). These mechanisms were developed primarily to study the formation of O_3 and NO_2 in photochemical smog, but can be extended to compute the concentrations of other pollutants, such as those leading to acid deposition (40, 42).

Surrogate mechanisms use the chemistry of one or two compounds in each class of organics to represent the chemistry of all the species in that class. For example, the explicit chemistry of butane [106-97-8], C_4H_{10}, might be used to describe the chemistry of the alkanes.

Lumped mechanisms are based on the grouping of chemical compounds into classes of similar structure and reactivity. For example, all alkanes might be lumped into a single class, the reaction rates and products of which are based on a weighted average of the properties of all the alkanes present. For example, as shown in Table 1, the various alkanes, CH_{2n+2}, react with OH in a similar manner to form alkyl radicals, C_nH_{2n+1}. When expressed explicitly, over 30 species and 20 reactions are involved. By lumping, the series of reactions can be reduced to one, and the number of required organic compounds is reduced to two. Thus lumping yields a tremendous savings in computational time, yet maintains the necessary chemical detail.

The carbon bond mechanism (64–66), a variation of a lumped mechanism, splits each organic molecule into functional groups using the assumption that the reactivity of the molecule is dominated by the chemistry of each functional group.

Table 1. Alkane–Hydroxide Radical Reactions

Explicit reactions

$$\left.\begin{array}{l} C_2H_6 + OH \longrightarrow C_2H_{\dot{5}} + H_2O \\ C_3H_8 + OH \longrightarrow C_3H_{\dot{7}} + H_2O \\ \vdots \\ C_nH_{2n+2} + OH \longrightarrow C_nH_{\dot{2}n+1} + H_2O \end{array}\right\} \begin{array}{c}\text{initial reaction} \\ \text{with OH}\end{array}$$

$$\left.\begin{array}{l} C_2H_{\dot{5}} + O_2 \longrightarrow C_2H_5O_{\dot{2}} \\ C_3H_{\dot{7}} + O_2 \longrightarrow C_3H_7O_{\dot{2}} \\ \vdots \\ C_nH_{\dot{2}n+1} + O_2 \longrightarrow C_nH_{\dot{2}n+1}O_{\dot{2}} \end{array}\right\} \begin{array}{c}\text{alkyl radical} \\ \text{oxidation reaction}\end{array}$$

Lumped representation

$$\text{alkane} + OH \longrightarrow RO_{\dot{2}}$$

5.3. Aerosol Dynamics

Inclusion of a description of aerosol dynamics within air quality models is of primary importance because of the health effects associated with fine particles in the atmosphere, visibility deterioration, and the acid deposition problem. Aerosol dynamics differ markedly from gaseous pollutant dynamics in that particles come in a continuous distribution of sizes and can coagulate, evaporate, grow in size by condensation, be formed by nucleation, or be deposited by sedimentation. Furthermore, the species mass concentration alone does not fully characterize the aerosol. The particle size distribution, which changes as a function of time, and size-dependent composition determine the fate of particulate air pollutants and their environmental and health effects. Particles of about 1 μm in diameter or smaller penetrate the lung most deeply and represent a substantial fraction of the total aerosol mass as shown in Figure 6. The origin of these fine particles is difficult to identify because much of the fine particle mass is formed by gas-phase reaction and condensation in the atmosphere.

Simulation of aerosol processes within an air quality model begins with the fundamental equation of aerosol dynamics which describes aerosol transport (term 2), growth (term 3), coagulation (terms 4 and 5), and sedimentation (term 6):

$$\frac{\delta n}{\delta t} + \nabla\cdot\overline{U}n + \frac{\delta I}{\delta v} = \frac{1}{2}\int_0^v \beta(\overline{v}, v-\overline{v})n(\overline{v})n(v-\overline{v})\,d\overline{v} - \int_0^\infty \beta(\overline{v}, v)n(\overline{v})n(v)\,d\overline{v} - \nabla\cdot Cn \qquad (11)$$

where n is the particle size distribution function; $\overline{U}$ is the fluid velocity; I is the droplet current that describes particle growth and nucleation resulting from gas-to-particle conversion; v is the particle volume; β is the rate of particle coagulation; and C is the sedimentation velocity. Modeling the formation and growth of aerosols is done by sectioning the size distribution n into discrete ranges. Then the size and chemical composition of an aerosol is followed as it evolves by condensation, coagulation, sedimentation, and nucleation.

5.3.1. Air Quality Model Inputs

Inputs to analytical air quality models can be broadly grouped as those dealing with meteorology, emissions, topography, and atmospheric concentrations. Meteorological inputs generally control the transport rate of pollutants and are used to determine reaction rates and the depositional flux of compounds. Topography influences transport and deposition. Observed compound concentrations are used to specify both initial and boundary conditions for model simulations. Especially for pollution problems involving organic compounds,

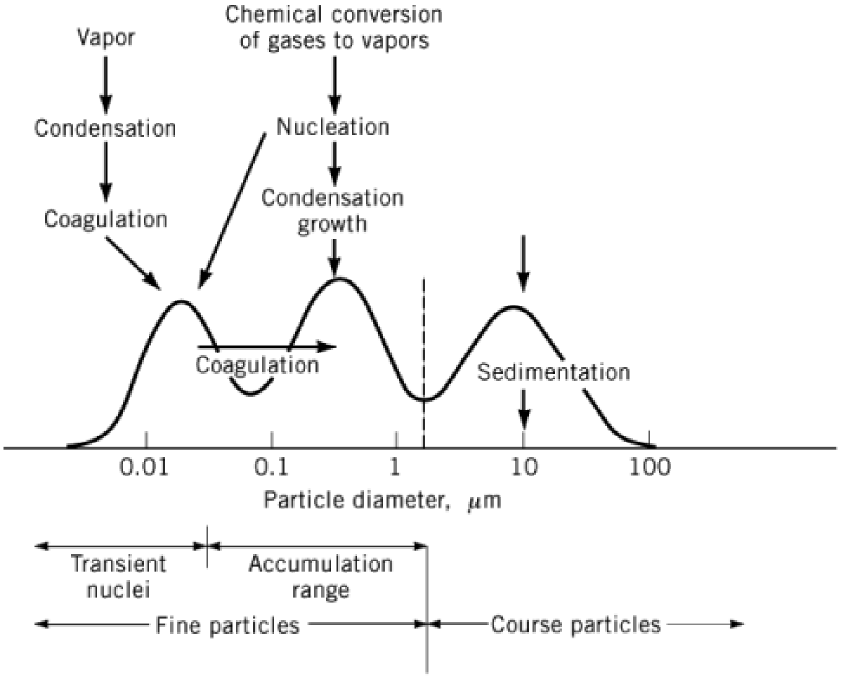

Fig. 6. Size distribution of an urban aerosol showing the three modes containing much of the aerosol mass. The fine mode contains particles produced by condensation of low volatility gases. The mid-range, or accumulation mode, results from coagulation of smaller aerosols and condensation of gases on preexisting particles. Coarse particulates, the largest aerosols, are usually generated mechanically.

emissions are a key input subject to considerable uncertainty. Although emissions from primary industrial facilities or utilities may be reasonably well known, emissions from residential or commercial facilities, mobile sources, and natural sources are often roughly estimated and difficult to verify.

The data requirements for applying models differ greatly among model types. For a Gaussian plume model, the required data could include as little as the mean wind velocity, source emission rate, atmospheric stability (and hence diffusivity), effective source height and air quality data for comparison with model predictions (67). At the other extreme, a large grid model that incorporates chemical kinetics requires considerably more information. Ideally a comprehensive model evaluation study would incorporate spatially and temporally resolved meteorological data, eg, winds, temperature, and solar insolation, temporally varying emissions for every species in each cell of the modeling region, topographical data, eg, land use and elevation, initial species concentrations, boundary conditions for each species, and concentration data for comparison against model predictions (44).

5.3.2. Meteorological Inputs

Meteorological conditions determine how fast and to where pollutants are dispersed, rates of chemical reactions, and losses resulting from deposition. Inputs vary depending on the type of model being applied. Simpler models, eg, Gaussian plume models with no chemical reactions, may require only a single wind velocity and cloud cover. On the other hand, a complex, three-dimensional, chemically active model requires hourly vertically and horizontally resolved wind fields, as well as hourly temperature, humidity, mixing depth, and solar insolation fields. The spatial and temporal resolution of the meteorological inputs must match the resolution of the air quality model. Much of the time the necessary inputs are determined directly from observations and relatively little mathematical modeling is used. In other cases, it is necessary to interpolate relatively sparse observations over a modeling domain using objective analysis techniques. Because of the sparseness of the data, newer air quality model applications have used dynamic, or prognostic, meteorological models. Use of dynamic models based on fundamental equations is intended to improve the accuracy of the meteorological inputs over the modeling domain.

Objective analysis techniques use a prescribed method with observations collected at a few discrete locations and times to calculate meteorological variables over the modeling domain. Usually this involves two- and three-dimensional spatial interpolation, and does not involve solving for any time dependency of the flow. Particular care must be taken in developing wind fields from sparse data because the wind field should be mass consistent. Objective analysis, including diagnostic procedures, is used to reduce the divergence of interpolated wind fields and account for some topographical features (68–71). A field of input values generated by interpolation over a large geographic area from sparse data is intrinsically uncertain and leads to uncertainty in model predictions. Upper-level variables such as temperature structure (mixing depths) and wind fields are particularly susceptible to this uncertainty, and have led to the wider use of dynamic models.

Dynamic meteorological models, much like air pollution models, strive to describe the physics and thermodynamics of atmospheric motions as accurately as is feasible. Besides being used in conjunction with air quality models, they are also used for weather forecasting. Like air quality models, dynamic meteorological models solve a set of partial differential equations (also called primitive equations). This set of equations, which are fundamental to the fluid mechanics of the atmosphere, are referred to as the Navier-Stokes equations, and describe the conservation of mass and momentum. They are combined with equations describing energy conservation and thermodynamics in a moving fluid (72):

$$\text{mass} \quad \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \overline{U} = 0 \qquad (12)$$

$$\text{momentum} \quad \frac{\partial \rho \overline{U}}{\partial t} + \overline{U} \cdot \nabla \rho \overline{U} = D \nabla^2 \overline{U} + \overline{F} - \nabla P \qquad (13)$$

$$\text{energy} \quad \frac{\partial \rho e}{\partial t} + \nabla \cdot (\rho e \overline{U}) = \dot{Q} - \dot{W} \qquad (14)$$

$$\text{thermodynamics} \quad \frac{p}{\rho} = RT \qquad (15)$$

where ρ is the local density of the atmosphere, $\overline{U}$ is the wind velocity vector, D is the molecular diffusivity, F represents external forces such as gravity, p is pressure, e is the local internal energy of the atmosphere, and $Q\cdot$ is the heat flux in and $W\cdot$ is the work done by, the fluid, friction. The last equation is the Ideal Gas Law. Often it is also necessary to follow the transport of water, eg, for predicting clouds.

$$\frac{\partial q}{\partial t} + \overline{U} \cdot \nabla q = S \qquad (16)$$

where q is the water concentration and S is the source or sinks of water, including rainout, etc. These equations form a set of coupled, nonlinear partial differential equations that are as formidable as those describing the chemical and physical dynamics of trace pollutants.

Experience in the solution of these governing equations is extensive, primarily because they are used in weather forecasting. This experience has led to useful simplifications and to the realization that the system is very sensitive to initial conditions. The sensitivity to initial conditions leads to the temporal amplification of any errors in the initial or boundary conditions, or of computational errors. The growth of these errors seriously limits the period of time that can be simulated for use in air pollution studies unless a separate mechanism is used to dampen error growth. This same limitation makes longer range weather forecasts increasingly uncertain. A method that has been developed to reduce the growth of errors arising from initial and boundary conditions when reconstructing historical conditions is to use observations to adjust the solution back towards the actual. This is referred to as “Newtonian nudging” or four-dimensional data assimilation (FDDA) (73). In essence, the predicted solution from the dynamic model is averaged, using various weightings, and the meteorological fields developed by objective analysis.

The equations governing air motion are generally assumed to be independent of those describing the chemical pollutant dynamics. This is because for problems such as urban smog and acid deposition, pollutant concentrations are so low that they do not significantly impact radiative transfer, and hence future weather. This may not be the case for problems such as stratospheric ozone depletion, and is not true for global climate change. In the latter case, the chemical evolution of the greenhouse gases, eg, carbon dioxide [124-38-9], CO_2, and chlorofluorocarbons (CFC), is currently assumed to be slow, and the pollutant distribution is found using little or no description of the chemistry. The radiative forcing is then found using expected concentrations.

5.4. Mathematical and Computational Implementation

Solution of the complex systems of partial differential equations governing both the evolution of pollutant concentrations and meteorological variables, eg, winds, requires specialized mathematical techniques. Comparing the two sets of equations governing pollutant dynamics (eq. 5) and meteorology (eqs. 12–14) shows that in both cases they can be put in the form:

$$\underset{\text{response}}{\frac{\partial A}{\partial t}} + \underset{\text{convective terms}}{\overline{U}\cdot\nabla A = \nabla\cdot K\nabla A} + \underset{\text{source}}{S} \qquad (17)$$

where A is the variable being modeled, eg, pollutant concentrations, wind velocities, temperature, and water vapor, $\overline{U}$ is the wind velocity vector, K is the turbulent diffusivity, and S is a generalized source or sink, eg, chemical production-destruction and emissions for modeling pollutant concentrations; pressure gradients, gravity, and coriolis forces for momentum conservation; thermal heating for energy conservation; and evaporation for water vapor modeling. Equation 17 is the general transport equation, which can be complex and nonlinear for most atmospheric systems. The nonlinearity and coupling arise as a result of the second and fourth terms. Because the systems of equations used in pollutant dynamics and meteorological modeling have the same general form, similar mathematical techniques are used to solve them.

The generalized transport equation, equation 17, can be dissected into terms describing bulk flow (term 2), turbulent diffusion (term 3) and other processes, eg, sources or chemical reactions (term 4), each having an impact on the time evolution of the transported property. In many systems, such as urban smog, the processes have very different time scales and can be viewed as being relatively independent over a short time period, allowing the equation to be “split” into separate operators. This greatly shortens solution times (74). The solution sequence is

$$\left.\frac{\partial A}{\partial t}\right|_H = -U\cdot\nabla A + \nabla\cdot K\nabla A = L_H(A) \qquad (18)$$

$$\left.\frac{\partial A}{\partial t}\right|_V = -W\frac{\partial A}{\partial z} + \frac{\partial}{\partial z}K_z\frac{\partial A}{\partial z} = L_V(A) \qquad (19)$$

$$\left.\frac{\partial A}{\partial t}\right|_S = S = L_S(A) \qquad (20)$$

$$\left.\frac{\partial A}{\partial t}\right|_{Total} = (L_H + L_V + L_S)(A) \qquad (21)$$

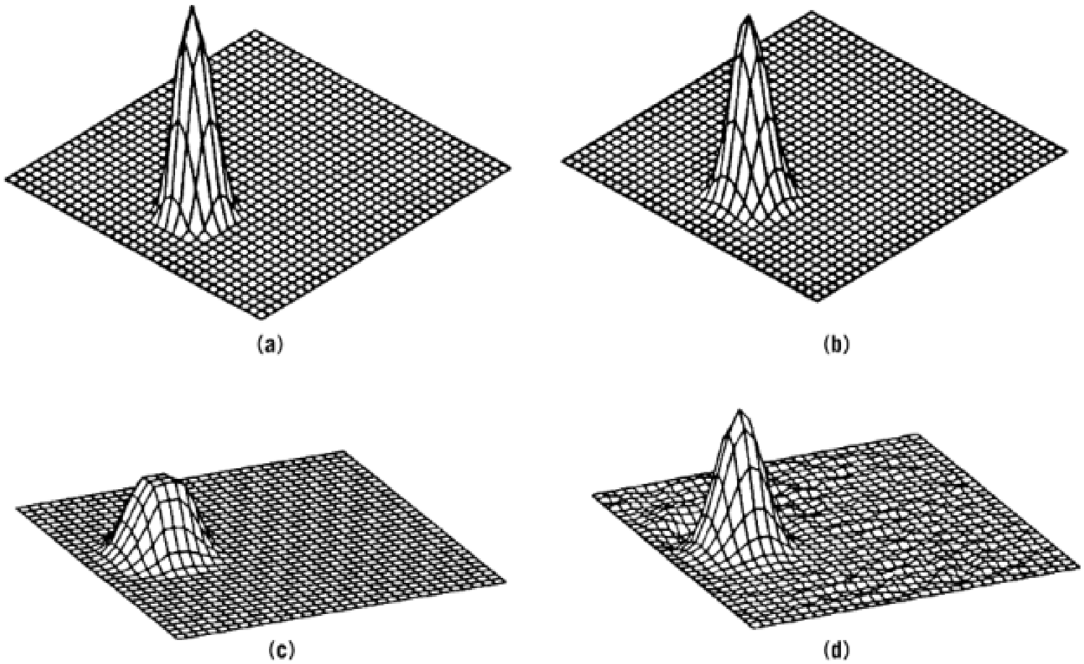

Fig. 7. Comparison of various transport schemes for advecting a cone-shaped puff in a rotating windfield after one complete rotation: (**a**), the exact solution; (**b**), obtained by an accurate numerical technique; (**c**), the effect of numerical diffusion where the peak height of the cone has been severely truncated; and (**d**), where the predicted concentration field is very bumpy, showing the effects of artificial dispersion. In the case of (**d**), spurious waves are formed that impair the predictions, though the peak height is better maintained.

where L_{H} is the horizontal transport operator, L_{V} is the vertical transport operator, and L_S is the operator describing other processes, such as chemistry. Modifications of the splitting process can be used to improve accuracy and computational speed. Besides leading to smaller systems of coupled equations, splitting also allows use of solution techniques that are designed to effectively describe specific processes. For example, in a photochemical air quality model, one routine is used for horizontal transport resulting from bulk winds, another for vertical motions, which are generally diffusive processes, and a third for the chemistry.

Historically, numerical schemes used to calculate the rate of transport have been based on finite difference and, more recently, finite element techniques. Spectral methods have also shown promise, but nonlinear chemical effects tend to degrade solution accuracy in some tests (75, 76). A problem with solving the set of equations is that the spatial discretization of the modeling region leads to artificial numerical dispersion, which is manifested by the formation of spurious waves and by pollutant peaks being spread out. For example, Figure 7 shows how various proposed schemes perform when following the rotation of a cone-shaped pollutant puff. In one instance, the original cone is virtually lost as a result of numerical errors. This remains a classic problem in computational fluid mechanics.

Tracking the chemical dynamics, eg, R in the atmospheric diffusion equation (eq. 5) and S (in eq. 20), is particularly difficult and time-consuming. This is because of the wide range of compound lifetimes, or more specifically, the characteristic reaction times. Some species, such as the O atom, have atmospheric lifetimes on the order of microseconds whereas others last for weeks. It is impractical to use a standard technique, eg, Runga Kutta, having a time-step corresponding to the shortest-lived species. This would be both excessively time-consuming and lead to the accumulation of numerical errors, making the computed solution invalid. Gear methods can be used, but are computationally slow. Instead, the chemical nature of the process is used to motivate a solution procedure. For a compound experiencing chemical production and destruction, the species concentration can be found using:

$$\frac{\partial c_i}{\partial t} = S_i = A_i - B_i c_i$$

where A_i is the production of species i from chemical reactivity and direct emissions, and $B_i c_i$ is the loss of i from chemical reactivity and deposition. In general, A_i and B_i are time varying and depend on concentrations of other compounds. As it turns out, even though species i might react very rapidly, A_i and B_i are rather constant over periods of a minute or so. Thus an approximate analytical solution to the above equation is used. Such techniques have been shown to be very accurate and an order of magnitude faster than others (74, 77). However, solution of the chemical kinetics is still the most computationally intensive part of a chemically active air quality model, consuming about 85% of the computer time.

Historically, the computational intensity of the more complex chemically active models have limited their application. For example, modeling only the gas-phase dynamics over an area like Los Angeles requires solving about 500,000 simultaneous, nonlinear equations. Until the late 1980s, computational power severely limited the use of chemically active models, and particularly inhibited the development and use of regional oxidant and acid deposition models. The rapid increase in computational power is making it possible to address much larger problems, for example, regional and global scale pollution. One aspect of air quality models is that they are highly parallelizable. The development of parallel computers should allow for significantly more detailed modeling of large systems.

6. Application of Air Quality Models

Both receptor and analytical air quality models have proven to be powerful tools for understanding atmospheric pollutant dynamics and for determining the impact of sources on air quality.

6.1. Receptor Models

Receptor models, by their formulation, are effective in determining the contributions of various sources to particulate matter concentrations. In classic studies, sources contributing to airborne particle loadings have been identified in Washington, D.C. (78), St. Louis (9, 24), Los Angeles (7, 12), Portland, Oregon (78), and Boston (79–81), as well as other areas including the desert (82).

A receptor model (78) and a source-oriented deterministic model were combined as part of a particulate air quality control strategy analysis in Portland, Oregon. Using CMB techniques, source contributions to the ambient aerosol were identified and then dispersion modeling was used to confirm the source contributions. The results obtained with the two models were compared, and a revised particulate emissions inventory was input into the source-dispersion model. Finally, the revised emissions inventory was used in dispersion modeling of emission control strategy alternatives. This approach utilized the strengths of both types of models. Receptor models are suitable for predicting the outcome of perturbations in some sources but not others. They are, however, good for determining the sources of particulate matter when an accurate emissions inventory is not available. Disperson models, on the other hand, are well-suited for modeling the impact of a wide variety of emissions changes that would result from changed emission control regulations, but rely totally on an input emissions inventory, which may be uncertain or difficult to obtain.

6.1.1. Analytical Modeling Studies

Analytical air quality models have been used the most in modeling the dynamics of pollutants at local and urban scales. Nonreactive, mass conservation models based on solving equation 3, including Gaussian plume models, have been used extensively for source apportionment, control strategy analysis, and source impact modeling of nonreactive pollutants, such as CO, and of carbonaceous aerosol. Models of this type have also been used to study the sources that contribute to secondary sulfate aerosol formation and they have been used to follow releases of toxic gases in local spills. Variants of the Gaussian plume model are often employed for regulatory purposes. The modest input requirements of these models are the key advantage. Frequently the goal is to estimate the maximum likely impact, so "worst case" meteorological conditions, ie, conditions that cause local pollutant accumulation, are modeled along with the maximum emissions rate that is allowed at the facility.

Of great interest is the use of chemically active air quality models for studying and controlling urban air pollution. This is because of the high costs of controls, the complexity of the system, and the historic lack of success in reducing ozone levels in urban areas. Interest in extending the application of chemically active models to the regional scale has heightened because the ozone problem has been recognized as extending well beyond urban areas.

The lack of success in reducing ozone levels can be partially ascribed to the nonlinearity of the system. An incremental change in the emissions of precursors to a secondary pollutant such as ozone need not lead to a proportional change in the pollutant concentration, or any change at all. For example, both NO_x and organics are precursors to the formation of O_3, but increasing the emissions of one can have a very different result from increasing those of the other. In fact, decreasing NO_x emissions may increase O_3 concentrations nearby while at the same time decreasing O_3 concentrations downwind. On the other hand, reducing emissions of reactive organic gases (ROGs) can lead to significant decreases in ozone in some cities, such as New York, but have little effect in other cities and in rural areas. A common representation of the relationship between maximum O_3 concentrations and initial concentrations of NO_x and ROGs is an O_3 isopleth diagram as shown in Figure 8. Regions of both high and low sensitivities to NO_x and ROG emissions are shown. Analysis of the effect of emission controls on O_3 air quality is further complicated by the fact that the effect of controlling two emission sources together is not necessarily equal to the sum of the incremental improvements from controlling each source alone. Thus definitively assessing the impact that a single source has on air quality is clouded in that its impact responds dynamically to changes in other sources and to varying meteorological conditions.

Because of the severity of the smog problem in Los Angeles, this location is the most studied area with regard to the role of NO_x and ROG emissions in the formation of ozone and other photochemical pollutants. The effect of NO_x and ROG emissions on ozone formation was found to vary throughout the region (83). Near downtown Los Angeles, ozone formation is inhibited by increasing NO_x emissions, and is effectively reduced by lowering ROG emissions. Downwind, however, where the highest ozone levels are found, ozone is relatively insensitive to ROG emissions, and is effectively reduced by lowering NO_x emissions. Modeling studies have also shown that concentrations of associated pollutants, such as nitric acid, aerosol nitrate, NO_2, and peroxyacetyl nitrate (PAN), are lowered when NO_x emissions are controlled (45). Another application of chemically active air quality models has been to study the effectiveness of using alternative automotive fuels, such as methanol (see ALCOHOL FUELS), compressed natural gas (see GAS, NATURAL), and electric power (see BATTERIES), for reducing smog (84).

Regional oxidant and acid deposition models came into use later than urban photochemical models because of the increased computational intensity, the need to describe more physical and chemical processes, and the later regulatory mandate for development and use. Regional models are very similar to urban-scale photochemical models, differing primarily in their horizontal resolution, 20–100 km vs 4–5 km, and in their treatment of cloud processes and liquid-phase chemistry. Applications of regional models also cover longer periods because of the increased residence time of polluted air masses within their domain. For example,

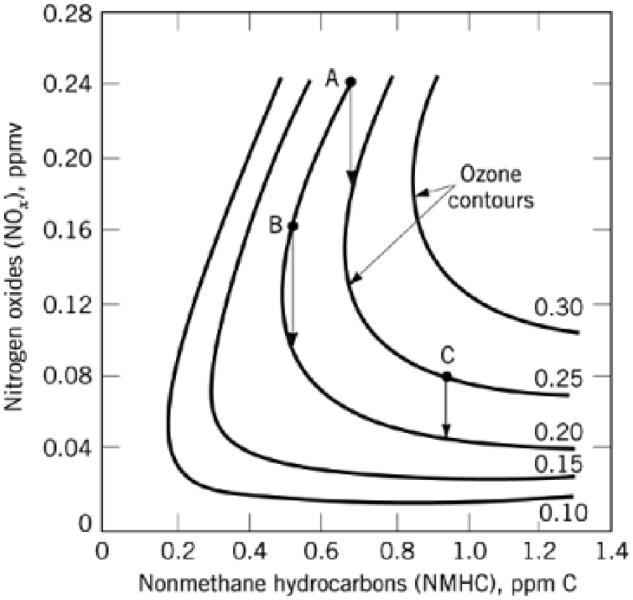

Fig. 8. O_3 isopleth diagram showing the response of O_3 concentrations to changes in initial NO_x and nonmethane hydrocarbon concentrations expressed as parts per million of carbon atoms (ppm C). The response to NO_x reductions is dependent on the particular initial concentrations. At point A, the graph indicates that decreasing NO_x would increase O_3 formation, and at point C, a decrease in the NO_x concentration results in a much larger decrease in O_3 concentrations than a similar decrease at point B on the same isopleth.

applications have followed the evolution of regional pollution episodes of over a week in the northeastern United States, compared to local episodes of two or three days in Los Angeles.

Regional ozone modeling of the Northeast has shown that air pollution problems across cities within this region are linked (85). Air masses starting in Washington, D.C. can travel up the coast, impacting downwind cities such as Baltimore and New York. Emissions in New York further impact Connecticut and Massachusetts. These studies have shown that the type of controls that are most effective in one city may be counterproductive in another. For example, modeling studies have found NO_x control to be effective for controlling ozone in Boston, Washington D.C., and Philadelphia, but lead to increased concentrations in New York (85). The horizontal resolution of the model used for this study was about 20 km, giving some detail in urban areas but not as much as urban-scale models provide.

A variety of models have been developed to study acid deposition. Sulfuric acid is formed relatively slowly in the atmosphere, so its concentrations are believed to be more uniform than ozone, especially in and around cities. Also, the impacts are viewed as more regional in nature. This allows an even coarser horizontal resolution, on the order of 80 to 100 km, to be used in acid deposition models. Atmospheric models of acid deposition have been used to determine where reductions in sulfur dioxide emissions would be most effective. Many of the ecosystems that are most sensitive to damage from acid deposition are located in the northeastern United States and southeastern Canada. Early acid deposition models helped to establish that sulfuric acid and its precursors are transported over long distances, eg, from the Ohio River Valley to New England (86–88). Models have also been used to show that sulfuric acid deposition is nearly linear in response to changing levels of emissions of sulfur dioxide (89).

In the mid-1980s, the destruction of the ozone layer above the Antarctic was recognized to be a potential environmental disaster, and chemically active transport models were used to identify the most important processes leading to depleted stratospheric ozone levels. As with ground-level chemistry, the gas-phase chemistry that occurs in the stratosphereis relatively well understood, but the incorporation of heterogeneous chemistry is an ongoing challenge. In addition, the models that have incorporated stratospheric chemistry in the greatest detail have oversimplified the transport and dynamics of stratospheric circulations. Conversely, three-dimensional models that focus on the dynamics of the atmosphere have used limited treatments of stratospheric chemistry.

Zero- through three-dimensional models have been used to simulate the stratospheric ozone problem. Zero-dimensional models focus on radiative transfer and chemistry at a single point. One-dimensional models incorporate vertical diffusive transport as well. Two-dimensional models currently represent the best compromise between computational tractability and chemical detail (90), and are resolved by latitude, as well as in the vertical dimension. Stronger flows and greater homogeneity over changes in longitude make two-dimensional treatments reasonable, except in the polar regions. Three-dimensional models are needed to study the dynamics of polar regions, including exchanges with air at lower latitudes.

Meridional circulation in two-dimensional stratospheric models has been specified based on observations or general circulation model calculations; recently efforts have been undertaken to calculate circulations from first principles, within the stratospheric models themselves. An important limitation of using models in which circulations are specified is that these cannot be used to study the feedbacks of changing atmospheric composition and temperature on transport, factors which may be important as atmospheric composition is increasingly perturbed.

The key gas-phase reactions occurring in the stratosphere are generally known. Comprehensive reviews of kinetic data have led to general consensus on the rate parameters that should be used in stratospheric models (91). Nevertheless, discrepancies are still apparent when the chemical components of different stratospheric models are compared. Disagreements arise from differing estimates of photolysis conditions in the stratosphere, depending in part on whether or not light scattering in the troposphere is included in the model (91).

Heterogeneous chemistry occurring on polar stratospheric cloud particles of ice and nitric acid trihydrate has been established as a dominant factor in the aggravated seasonal depletion of ozone observed to occur over Antarctica. Preliminary attempts have been made to parameterize this chemistry and incorporate it in models to study ozone depletion over the poles (91) as well as the potential role of sulfate particles throughout the stratosphere (92).

Models can be used to study human exposure to air pollutants and to identify cost-effective control strategies. In many instances, the primary limitation on the accuracy of model results is not the model formulation, but the accuracy of the available input data (93). Another limitation is the inability of models to account for the alterations in the spatial distribution of emissions that occurs when controls are applied. The more detailed models are currently able to describe the dynamics of unreactive pollutants in urban areas.

Because of the expanded scale and need to describe additional physical and chemical processes, the development of acid deposition and regional oxidant models has lagged behind that of urban-scale photochemical models. An additional step up in scale and complexity, the development of analytical models of pollutant dynamics in the stratosphere is also behind that of ground-level oxidant models, in part because of the central role of heterogeneous chemistry in the stratospheric ozone depletion problem. In general, atmospheric liquid-phase chemistry and especially heterogeneous chemistry are less well understood than gas-phase reactions such as those that dominate the formation of ozone in urban areas. Development of three-dimensional models that treat both the dynamics and chemistry of the stratosphere in detail is an ongoing research problem.

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ARMISTEAD G. RUSSELL
Carnegie Mellon University
JANA B. MILFORD
University of Connecticut

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