United States
Environmental Protection
Agency

Atmospheric Sciences Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S3-84-095 Jan. 1985

EPA

Project Summary

Continued Research in Mesoscale Air Pollution Simulation Modeling

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The work described in this Project Summary is contained in three project reports that comprise the completion of a seven volume series. The first four volumes covered evaluative and research studies that were exploratory in nature in an attempt to lay the groundwork for various refinements to an Urban Airshed Model developed under EPA sponsorship. The final three volumes discuss the completion of these studies and the incorporation of several refinements to the urban airshed model.

Specifically, the reports contain: (1) details of model refinement activities concerned with the improvement of numerical integration techniques, the incorporation of surface removal processes, the development of automated, objective procedures for preparing wind inputs, the treatment of atmospheric chemical reactions, and the estimation of rate constants for photolysis reactions; (2) discussion of microscale modeling efforts aimed at the estimation of eddy diffusivities and the improved treatment of point and line sources; and (3) progress in the development of aerosol modeling capabilities.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Since the time of the original version of the Urban Airshed Model developed in 1973, a number of modifications have been implemented in the computer codes to account more fully for the physical and chemical phenomena believed to be important in influencing urban air quality. A synopsis of the current features of the model is presented below.

Basically, the Urban Airshed Model accepts emissions, meteorological chemical, and air quality data as inputs and produces predictions of pollutant concentrations during specified time intervals within the cells of a three-dimensional grid encompassing the region of interest. Thirteen chemical species are considered: ozone (O_3); nitrogen dioxide (NO_2); nitric oxide (NO); sulfur dioxide (SO_2); carbon monoxide (CO); peroxyacetylnitrate (PAN); total aerosol; olefins (other than ethylene); paraffins; aromatics and ethylene; aldehydes; nitrous acid (HNO_2); and hydrogen peroxide (H_2O_2). The aerosol component consists of primary particulate matter and secondary nitrate, sulfate, and organic aerosols.

The model simulates pollutant transport through the action of advection and turbulent dispersion. As mentioned above, wind inputs are time-varying and fully three-dimensional. Only horizontal wind components are input; appropriate vertical velocities are calculated using a mass balance constraint. Thus, the influence of convergence and divergence zones in the

windfield can be handled properly. Eddy diffusivity coefficients are estimated from an algorithm that accounts for the effects of atmospheric stability, surface roughness, wind speed, and inversion height.

Chemical transformations are represented by the 42-step chemical mechanism mentioned above. Organics are segmented into four classes that are based primarily on carbon bond characteristics and to a lesser extent on reactivity and reaction products. The mechanism can account for the effects of hourly temperature variations on reaction rate constants through the use of the Arrhenius relationship. Photolysis rate constants are allowed to vary in time as well as in space. Aerosol predictions in a column of grid cells are used to estimate the effect of light scattering on the photolysis rate constants in each grid cell of that column.

Removal of pollutants by surface sinks is treated by means of the deposition velocity concept. The effects of both atmospheric turbulence and surface uptake characteristics are considered. Model inputs include a spatial array of surface types corresponding to the land use in each grid cell.

Several microscale features are incorporated in the model. Subgrid-scale concentration variations arising from the spatial characteristics of point and line sources can affect the spatially averaged predictions obtained from a grid model. However, these effects are only important when a contaminant emitted from a point or line source reacts rapidly with another pollutant. One such example is the reaction of NO with O_3 to form NO_2 and O_2.

To account for the subgrid-scale influences of line sources, the model treats the lowest layer of grid cells in a special manner. First, this layer is considered to have a depth of only about 20 m. Second, NO emissions from motor vehicles are allowed to react immediately with only the O_3 in close proximity to the roadway. This treatment of the lowest layer also considers ground-level emissions from areal sources and surface removal processes. In addition to predicting "ground-level" concentrations, the algorithm developed for the lowest layer also predicts the net flux of each pollutant into the second layer of grid cells.

Emissions from large point sources are distributed in grid cells aloft through the use of a plume rise algorithm. Consideration is given to whether a plume penetrates an elevated inversion layer, and, if so, whether it ultimately breaks through the layer.

The governing equations of the model are solved through the use of finite difference relationships. The three-dimensional equation is split into the following four fractional steps:

- Advection and diffusion in the x-direction.
- Advection and diffusion in the y-direction.
- Advection and diffusion in the z-direction.
- Chemistry.

Emissions, removal, and microscale considerations are included in the third step. The SHASTA algorithm is employed to calculate pollutant transport, and the trapezoidal rule is used in the chemistry step.

Results and Discussion

In project report V, two numerical integration methods identified as having features that provided significant improvements over the technique originally embedded in the Airshed model have been evaluated. Of particular concern was the treatment of horizontal transport. The methods examined were the SHASTA and Egan-Mahoney methods. In several numerical experiments involving the transport of an inert pollutant in both one and two dimensions, we found that the SHASTA method seems to possess the best blend of computational speed coupled with minimum error propagation. Further tests with a problem involving both transport and chemical transformations confirmed the enhanced reliability of this method over that used previously. In a final set of experiments, the SHASTA method was employed in an actual airshed simulation of the Los Angeles Basin. The resulting predictions differed no more than about 20 percent from those generated using the original method.

Uptake by the ocean, ground, and biota is generally acknowledged to be of considerable importance for some air pollutants, especially when they are transported over long distances. The possible importance of including these processes in an urban-scale air quality model has been reviewed, but very little information exists regarding the rates of uptake of photochemical pollutants by characteristic urban materials. The uptake rates are parameterized through use of the deposition velocity concept, in which the rate of uptake is assumed to be proportional to the pollutant concentration just above the surface. The proportionality constant (i.e., the deposition velocity) is influenced by the stability of the atmosphere and the type of surface. An algorithm that relates the overall effective deposition velocity to these two influences has been implemented. Sensitivity studies using best estimates of the deposition velocities indicate that surface removal processes may significantly affect the concentrations of O_3, NO_2, and SO_2 in the Los Angeles Basin. The specification of uptake parameters for the Los Angeles Basin is discussed in detail to aid model users in estimating these inputs for other urban areas.

Theoretical assessments and model sensitivity studies indicated the importance of treating the full three-dimensional nature of the windfield. As a result, the model was modified to accept time-varying, fully three-dimensional wind inputs (namely, a one-hour-average wind speed and direction for each grid cell). An objective analysis technique to prepare such a windfield using available measurements both at the surface and aloft has been developed. This technique also attempts to account for urban heat island effects. It should be directly applicable to relatively flat areas, such as St. Louis. However, it should also be possible to extend the technique for application to areas with greater relief.

A chemical kinetic mechanism is one of the most important components of any model capable of predicting the concentrations of secondary air contaminants. A 42-step mechanism suitable for describing the chemical transformations of organics, nitrogen oxides (NO_x), O_3, and SO_2 and the production of sulfate, nitrate, and organic aerosols is presented The organic/NO_x/O_3 mechanism consists of 32 steps. A unique feature of this mechanism is the explicit consideration given to the carbon bonds making up each organic molecule. In simulations of smog chamber experiments, this mechanism overcomes some deficiencies exhibited by reaction schemes previously employed in the Urban Airshed Model. For the addition of SO_2 and sulfate aerosol prediction capabilities to the model, a seven-step mechanism describing the conversion of SO_2 to sulfate aerosol has been assembled. Three reaction steps were postulated to describe the formation of organic and nitrate aerosols.

A discussion of the treatment of rate constants for photolysis reactions used in the chemical mechanism is also provided, and through the use of our Multi-Layer Light-Scattering Model, the influence of aerosols on the attenuation of sunlight within a column of polluted air is examined. The results led to the formulation of

a linear relationship with height above the terrain for the photolysis rate constants In effect, the total integrated aerosol mass in a column of grid cells is used in conjunction with nominal estimates of the clean air values of the photolysis rate constants to calculate values of the rate constants for each grid cell in that column

In project report VI, techniques for modeling the microscale phenomena associated with urban air pollution were developed. In this context, the term "microscale" refers to all phenomena that have characteristics temporal or spatial scales that are too small to be resolvable in an explicit, deterministic manner in urban-scale air pollution models. Examples of microscale phenomena include turbulent diffusion, turbulent concentration fluctuations, and subgrid-scale variations in the time-averaged concentration field.

In this work the so-called optimal eddy diffusivities were reexamined to determine whether (1) the diffusivities are unique, (2) they have a universal form when properly scaled, and (3) they are dependent on source height. Optimal diffusivities are designed to make the predictions of the diffusion equation agree as closely as possible with the mean concentration distributions derived from a sophisticated numerical model of turbulence in the planetary boundary layer. Using a test case for which the analytic solution of the diffusion equation is available, it can be shown that the method used to derive the optimal diffusivity produces unique results that agree very closely with the true value. Using concentration data for two different unstable cases, namely, $z_i/L = -4.5$ and $z_i/L = -1100$, for all stabilities in the range $z_i/L \leq 4.5$, it can be shown that the optimal vertical diffusivity $K_z(z)$ appears to have a universal form when z is normalized by z_i, the depth of the mixed layer, and when K_z is scaled with $w^* z_i$, where w^* is the convective velocity scale. The universal form of K_z for a source near ground level has also been determined. Finally, using concentration data for sources of different heights in the same flow, it was found that the optimal diffusivity depends quite strongly on the source elevation.

A model for describing the effects of turbulent concentration fluctuations on second-order chemical reactions has also been developed, implemented, and tested. The model equation contains a reaction parameter, whose value can be approximated by unity in most problems of air pollution, and two mixing parameters, whose functional forms are determined solely by the nature of the turbulence and the configuration of reactant sources. For given source characteristics, the mixing parameters can be expressed as universal functions of the flow conditions. Approximate expressions for the mixing parameters applicable to the case where one reactant is emitted from a point source into an atmosphere containing a uniform concentration of a co-reactant have been derived. Using these expressions, we applied the model to the case of NO emanating from a point source into an O_3 laden atmosphere and found that the rate of conversion of NO to NO_2 is greatly inhibited by turbulent concentration fluctuations, even under stable conditions. The predictions of the model compare well with empirical data from both atmospheric and laboratory studies.

A method of parameterizing the effects of chemical reaction rates of both subgrid-scale concentration variations arising from ground-level sources and turbulence-induced concentration fluctuations has also been developed In essence, the parameterization scheme is simply a modified lower boundary condition on the concentration field that takes into account the effect of subgrid-scale concentration variations. This scheme has been implemented in the Airshed Model and is currently undergoing tests.

The resolution of point source plumes in grid models of urban air pollution has been studied and a sub-model capable of restoring point spatial resolution to any grid model was developed, but is applicable only to inert and first-order reactants.

Finally, theoretical frameworks for two models of pollutant levels around roadways have been developed. The more general of the two models can treat photochemical pollutants; the effects of turbulent concentration fluctuations produced by vehicle wake and ambient turbulence; calm winds or winds parallel to the roadway; exhaust buoyancy effects; elevated, depressed, or at-grade highways; pollutant deposition; and other phenomena normally included in air pollution models.

In project report VII, a simplified model of the dynamics of photochemical aerosols has been developed, and initial applications of it have been presented. The model, which can be incorporated in or coupled to a photochemical air quality simulation model, takes into consideration the emissions of particles with diameters of 0.01 μm to 1.0 μm and their growth in this size range by the formation of secondary aerosol. The formation of very small particles by homogeneous nucleation and their subsequent growth is treated as a boundary condition on the particle size distribution function at a diameter of 0.01 μm. Although coagulation is not included in the model, methods were studied for obtaining solutions to the coagulation equation with computational efficiency.

In the aerosol model, the formation of particulate matter is assumed to occur in two stages—condensable material first forms in the gas phase and then diffuses to the particles. A pseudo-steady-state is assumed in which the rate of formation of condensable material in the gas phase is set equal to the rate at which condensation occurs on particles. Calculations are presented that justify this assumption for secondary aerosol production rates and particle concentrations typical of moderate smog conditions in the Los Angeles Basin. Estimates are made of the rate of formation of sulfuric acid droplets by homogeneous nucleation as a function of the aerosol number density, the rate of production of condensable material, and the relative humidity.

Model simulations are presented for a batch system (with constant rates of aerosol production) both with and without sources of primary aerosol and for a trajectory system. Model simulations and smog chamber experiments are in qualitative agreement.

Conclusions and Recommendations

Investigation of numerical methods appropriate for the solution of the species transport equation have identified the SHASTA and Egan-Mahoney algorithms as numerical integration methods offering greater accuracy than the existing Price algorithm currently used in the Urban Airshed Model. In addition, both the SHASTA and Egan-Mahoney techniques have shown promise of being as computationally efficient as the Price method. The following conclusions can be drawn on the basis of the examination of the SHASTA and Egan-Mahoney algorithms:

- Of all the variants of the SHASTA technique, the non-flux-limited, non-mass-conservative formulation appears to be the most accurate, as well as the most computationally efficient.
- The non-flux-limited, non-mass-conservative SHASTA algorithm is substantially more accurate than the Price integration method. In the two-dimensional reactive and nonreactive

analyses, the predictions of the SHASTA algorithm were superior to those of the Price algorithm.

- The SHASTA algorithm, unlike the Price method, is stable for all values of the parameter ε less than 1/2. Hence, simulations over long time intervals do not exhibit the instability observed when the Price algorithm is used.
- Although more accurate, the Egan-Mahoney method requires considerably more computational time and substantially more computer storage than the SHASTA method. For a nonreactive species, such as CO alone, this technique could most probably be optimized to produce superior results at reasonable computing costs for a three-dimensional problem. In cases involving many species, however, the computational costs and storage requirements for the necessary generating moments would be exorbitant.
- In the future, efforts should be devoted to optimizing the computer codes and simulation scheme so as to increase program efficiency and to reduce execution time. Searching for an optimal time step, putting the kinetic mechanism into an individual step, and computing the reaction rates of every other time interval are some of the possible ways in which this objective could be achieved. In addition, efforts should be made to keep abreast of the latest developments in the literature concerning integration of partial differential equations and changes in computer technology to permit implementation of methods that are currently unattractive with the existing technology.

A simple model for the removal of gaseous pollutants by surface sinks has been incorporated into the Urban Airshed Model. The surface sink model considers surface removal to occur in two phases—transport to the surface followed by adsorption on the surface. The resistance to surface uptake (the reciprocal of the deposition velocity) was determined from deposition velocities measured under atmospheric conditions that lead to rapid transport to the surface (that is, so that surface removal was limited by the surface uptake rate).

Deposition rates have been measured under the widest range of conditions for SO_2, but even for this pollutant, few surface types have been studied. Because of this lack of data, it is necessary to make crude estimates for deposition rates over surfaces found in the urban environment. The improvement of these estimates for the Los Angeles Basin awaits additional measurements of deposition velocities under a variety of meteorological conditions over surfaces common to the Basin. Sensitivity studies performed with our estimated deposition rates indicate that surface uptake of SO_2, NO_2, and O_3 in the Basin can have a significant effect on the concentration of these pollutants.

A new objective-analysis wind field algorithm has been evaluated and implemented in the Urban Airshed Model on the basis of general principles and prior experience. This algorithm will miss some significant wind-field features, such as the bending of the thermal cell in the boundary layer shear zone and effect of surface friction variations. However, it is also anticipated that the analysis will reproduce the most important phenomena known to influence the urban boundary layer and will, in particular, avoid introducing the large spurious features that might be expected from any algorithm that depends on influence factors or other unconstrained interpolation techniques.

The computed horizontal velocity is not irrotational unless soundings show it to be so. The total velocity vector is irrotational about a vertical axis. This is, of course, not perfectly true in nature, but in most cases the dominant perturbations to the mean flow are irrotational. In this case, the only perturbance addressed is the heat island effect, which is a potential flow disturbance except to the extent that it couples to the mean shear profile. Since the momentum and energy equations were not used, these second-order effects could not be addressed.

It is recommended that subgrid-scale bias be investigated for a typical St. Louis site by collecting and statistically analyzing wind records from several (say 5 to 10) surface anemometers placed within the same grid cell.

Since gas-to-particle conversion is an important factor in aerosol behavior, one must understand to a large extent the gaseous processes as a prerequisite to understanding aerosol processes. Aerosols are influenced not only by the same advection-diffusion processes that influence gases, but also by such complex processes as diffusion of gaseous species to surfaces, chemical reactions within particles, and coagulation. Modeling aerosols is thus more complicated than modeling gaseous pollutants. Characterizing an aerosol requires, in principle, the distribution of particles by size, composition, location, and time, which is indicative of the complexity of aerosol modeling.

The chemical and physical data necessary for detailed modeling of the size and composition of an urban aerosol do not exist at present. Nevertheless, it is important that modeling be considered now so that the types of data needed for modeling can be elucidated. This report represents the first phase of an effort to develop mathematical models for urban aerosols. We developed much of the theoretical basis that will ultimately be required for aerosol modeling. However, we adopted a somewhat limited objective—to develop a model capable of predicting the overall submicron aerosol size distribution (and therefore the total aerosol volume and surface area). The model was formulated in such a way that it could be included within a gas-phase model.

Although the chemical composition of a particle influences its rate of growth by vapor condensation, and the chemical composition changes with time, explicitly including particle chemical composition in a model cannot be justified at this time. As first approximation, it has been assumed that the transfer of vapor species to the aerosol occurs independently of the particle composition. In spite of the neglect of particle composition, the integration of the aerosol model into the airshed models gas-phase module will not be a straightforward task because of the new independent variable, particle diameter. With only 10 particle diameters characterizing the aerosol size distribution, which spans two orders of magnitude, an additional 6.25K of storage would be required to include the aerosol model into the gas-phase module with a 25 x 25 grid and no vertical resolution. Furthermore, in a simulation of a seven-hour period, the current aerosol model would add roughly 10 minutes of CPU time (CDC 7600 computer) to the computing time, which represents approximately a 100 percent increase over the current execution time for the gas-phase module alone.

The aerosol model developed in this study is capable of predicting the dynamics of the size distribution, and its inclusion in the gas-phase module would represent a justifiable effort. The portion of the aerosol model that predicts the rate of secondary aerosol formation has been incorporated into the Airshed Model to predict the total aerosol mass concentration as a function of location and time.

The major question to be considered at this point is the direction of further research. We could add complexity to the aerosol model by explicitly including

particle chemical composition and by developing microscale source-oriented models that consider coagulation. Another path would be to integrate the current model into the gas-phase module and thoroughly test it with pertinent available data. Thus, the second path would not center on further model development but would focus on application and use of the current aerosol model. It is recommended that future work follow the second path.

It is recommended that the following studies be carried out in conjunction with the continued development of an urban aerosol model:

1. The total mass concentration aerosol model, currently integrated into the Airshed Model, should be tested on available data for Los Angeles and St. Louis. Sensitivity studies should be carried out with respect to gas-to-particle conversion rates.
2. The aerosol model developed in this study should be integrated into the Airshed Model. The model should then be tested on available data for Los Angeles and St. Louis. Sensitivity studies should be carried out with respect to primary source emission rates and particle size distributions, background aerosol, and gas-to-particle conversion rates.

This approach will serve the purpose of providing a usable urban aerosol model in the minimum period of time.

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The complete report consists of three volumes, entitled "Continued Research in Mesoscale Air Pollution Simulation Modeling:"
"Volume V. Refinements in Numerical Analysis, Transport, Chemistry, and Pollutant Removal," (Order No. PB 85-137 362; Cost: $20.50)
"Volume VI. Further Studies in the Modeling of Microscale Phenomena," (Order No. PB 85-137 370; Cost: $23.50)
"Volume VII. Mathematical Modeling of Urban Aerosol Dynamics," (Order No. PB 85-137 388; Cost: $19.00)
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