United States
Environmental Protection
Agency

Atmospheric Sciences
Research Laboratory
Research Triangle Park NC 27711

Research and Development

EPA/600/S3-87/021 Sept. 1987

EPA

Project Summary

Development of Computer Modules of Particulate Processes for Regional Particulate Model

A. Belle Hudischewskyj, Pradeep Saxena, and Christian Seigneur

The development of an aerosol model for inclusion in the EPA Regional Particulate Model is described. Existing computer models of particulate processes developed under contract to the EPA are compared to determine efficient and accurate methods of simulating particulate behavior. These methods are then incorporated into an aerosol model, which is both accurate and efficient in its treatment of the dynamics, thermodynamics, and chemical composition of atmospheric aerosols.

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

In the past, air pollution monitoring and modeling studies have generally focused on the study of photochemical smog formation and related impacts. Recently, however, more attention has been paid to such concerns as high levels of particulate matter with diameters less than 10 μm (PM10), visibility impairment, and acid deposition. A knowledge of the concentration, chemical composition, and size distribution of atmospheric aerosols over the entire range of relative humidities is required to model these phenomena.

During the course of this work, we installed and evaluated numerous computer models of particulate processes developed under contract to the EPA to select efficient and accurate models for incorporation into the regional model. These models were developed to treat the dynamics, thermodynamics, and chemistry of atmospehric particulate matter. The evaluation took into consideration the computational requirements, predictive accuracy, and application range of the models.

Aerosol Dynamics

For our study of the treatment of aerosol dynamics, we compared four models: COAGUL and CONFEMM, developed at the University of Texas by Professor J. R. Brock and co-workers; AGRO, developed at the University of Minnesota by Professor K. T. Whitby, Mr. E. E. Whitby, and co-workers; and ESMA P, developed at the California Institute of Technology by Professor J. H. Seinfeld and co-workers. These four models represent the three major approaches to solving the General Dynamic Equation (GDE) that governs the treatment of aerosol coagulation and condensation. COAGUL and CONFEMM are examples of a continuous representation of the GDE for coagulation and condensation, respectively. ESMA P is an example of a discrete representation in which the size distribution is sectionalized. AGRO represents a parameterized

approach in which the size distribution is assumed to be lognormal.

Coagulation

COAGUL, AGRO, and ESMA P were used to simulate aerosol coagulation over 12 hours for atmospheric aerosol concentrations typical of clear, hazy, and urban conditions. ESMA P was applied with two different size resolutions, 12 and 39 sections, over the 0.001 μm to 10 μm size range. COAGUL was shown to provide an accurate solution of the coagulation equation. AGRO performed well for case studies involving both clear and hazy conditions (in which coagulation has little effect on the initial size distributions) but was less accurate for the urban case study. ESMA P, with both 12 and 39 sections, performed well relative to COAGUL.

The computational times were compared on a Prime 750 computer. AGRO required less than 1 C PUs; COAGUL from 100 to 1000 C PUs; and ESMA P from 180 to 2500 C PUs for 39 sections, and from 40 to 350 C PUs for 12 sections.

Condensation

CONFEMM, AGRO, and ESMA P were compared in the simulation of aerosol condensation over 12 hours for atmospheric concentrations typical of clear, hazy, and urban conditions. ESMA P was again applied with two different size resolutions, 12 and 39 sections, over the 0.001 μm to 10 μm size range. CONFEMM provided an accurate solution of the condensation equation. The performance of ESMA P with 39 sections was satisfactory for all cases; with 12 sections it produced reasonable results when condensation occurred primarily in the accumulation mode, but poorer results when condensation occurred on smaller aerosols. AGRO overestimated the peak concentration of the accumulation mode, but predicted the median diameter of the mode fairly well. As in the coagulation study, AGRO required the least amount of time, less than 1 C PUs. CONFEMM required about 150 C PUs; ESMA P required 90 C PUs with 12 sections and 300 C PUs with 39 sections.

Comparison Results

On the basis of the results of the coagulation and condensation simulation results, we selected the sectional representation with a size resolution of 12 sections over a size range of 0.001 μm to 10 μm to simulate aerosol dynamics. This approach provides a reasonable compromise between model accuracy and computational requirements.

Aerosol Thermodynamics

Treatment of the thermodynamic equilibrium between the aerosol phases is central to determination of the chemical composition of aerosols that results from the condensation of sulfuric acid, nitric acid, ammonia, and water. Other species, such as HCl and organic compounds, also affect the thermodynamic equilibrium of aerosols. Since HCl is generally present in low concentrations in the atmosphere, and sulfate and nitrate aerosols generally occur in significant concentrations in polluted areas and are of primary interest in the consideration of acid deposition and visibility impairment, we focused on models of sulfate/nitrate/ammonium/water aerosols.

The three thermodynamic models we reviewed and compared are (1) the Model for an Aerosol Reacting System (MARS), developed for this study by Saxena and Seigneur at Systems Applications, Inc.; (2) EQUIL, developed by Bassett and Seinfeld at the California Institute of Technology; and (3) KEQUIL, also developed by Bassett and Seinfeld at the California Institute of Technology. EQUIL and KEQUIL are rigorous models that explicitly solve for 17 species in eight phases by minimizing the Gibbs free energy of the systems. There are 13 equilibrium reactions among these species, and the temperature dependence of all thermodynamic properties is taken in to account. KEQUIL and EQUIL are identical in all respects, except KEQUIL incorporates the Kelvin effect (the effect of aerosol surface curvature), and EQUIL does not. MARS is based on fundamental thermodynamics. Its treatment of chemical and interfacial equilibrium focuses only on major species for given sets of ambient conditions. Therefore, the number of equations to be solved is minimized. MARS, like EQUIL, does not consider the Kelvin effect. The distinguishing feature of MARS is its division of the entire regime of aerosol species into several subdomains. Since each subdomain contains fewer viable species than does the entire domain of concentrations, the number of equations to be solved is reduced, and the computational costs are thus minimized.

Comparison Results

Since KEQUIL is the most comprehensive model currently available, the results of MARS and EQUIL were compared with those of KEQUIL. Comparisons were made for a broad spectrum of atmospheric conditions. Results were compared for concentrations of aerosol-phase ammonium, nitrate, total mass, and light scattering coefficients (b_{scat}). Computational times were compared on a Prime 750 computer. Calculations by EQUIL and MARS agreed closely with those of KEQUIL; however, MARS was on the order of 400 times faster than KEQUIL and about 60 times faster than EQUIL. This substantial difference in computational efficiency was attained without significant loss of accuracy. On the basis of this study, we selected MARS as an efficient and accurate model of aerosol thermodynamics for incorporation into the regional model.

Aerosol Model

Formulation

On the basis of the results of the previously mentioned model evaluations and comparisons, we formulated an aerosol model that uses a sectional approach to treat the dynamics and the methodologies incorporated into MARS to treat the thermodynamics of atmospheric aerosols. The processes that affect aerosol concentration, size, and chemical composition were also explored. These processes include advection; diffusion; coagulation; gas-to-aerosol conversion of sulfate, nitrate, and organic species; chemical kinetics; sedimentation; dry deposition on surfaces; and emissions of new aerosol formation in clouds.

The aerosol model that we incorporated into the regional particulate model consists of seven sections in the fine aerosol range with diameters between 0.01 μm and 2.5 μm, and two sections in the coarse aerosol range with diameters between 2.5 μm and 10 μm. The chemical species treated in the fine mode include primary aerosol, sulfate, nitrate, ammonium, organics, and water. Species treated in the coarse aerosol mode include primary aerosol and nitrate. The model can be applied to the entire range of relative humidities. It treats the evolution of the concentration, chemical composition, and size distribution of aerosols undergoing the following processes: coagulation; growth from diffusion-limited condensation of sulfuric acid and organic species; growth/shrinkage from condensation/evaporation of HNO_3, NH_3, and H_2O; oxidation of SO_2 to sulfate by H_2O_2 in the liquid-

coated aerosols; and formation of small sulfate and organic aerosols.

The gas-phase chemistry is treated by means of the Carbon-Bond Mechanism IV (CBM-IV) developed by Whitten and Gery of Systems Applications, Inc. The mechanism describes the chemistry of oxidants, nitrogen oxides, and anthropogenic and natural hydrocarbons. The Carbon-Bond Mechanism X (CBM-X), developed by Whitten and co-workers, was also examined for incorporation into the regional particulate model, and the number of reactions was condensed through variational sensitivity analysis.

Evaluation

To evaluate the aerosol model, we simulated both a regional environment and an urban plume, using a plume trajectory model, PLMSTAR, developed by Godden and Lurmann of ER&T, into which our aerosol model was incorporated. This trajectory/aerosol model, which also employs the Carbon-Bond Mechanism for the treatment of gas-phase chemistry, was developed under contract to Southern California Edison Company.

Two simulations were conducted for 36-hour periods (23-24 August 1987) to simulate both daytime and nighttime chemistries. The first simulation, for Columbus, Ohio, was selected to represent a regional environment. The second, for St. Louis, Missouri, was selected to represent an urban plume. In addition to the two base case studies, six sensitivity studies were conducted. Five of these studies were based on the data for the regional environment and consisted of simulations performed with (1) the base case SO_2 emissions and initial SO_2 concentrations reduced by 50 percent, (2) the base case NO_x emissions and initial NO_x concentrations reduced by 50 percent, (3) the base case NH_3 emissions and initial NH_3 concentrations reduced by 50 percent, (4) the base case reactive hydrocarbon (RHC) emissions and initial RHC concentrations reduced by 50 percent, and (5) the season changed from summer to winter. (Modification to the summer base case input parameters to represent winter conditions included a change in date, a decrease in temperature, lowering the H_2O_2 and O_3 initial concentrations, lowering the mixing height, and shortening the daylight period.) The sensitivity study based on the data from the St. Louis urban plume consisted of increasing the relative humidity from 60 percent to 85 percent.

Conclusions

Results for all the studies were compared and evaluated, and it was concluded that the aerosol model performs well under a variety of atmospheric and meteorological conditions. These results indicate that the aerosol model is a useful tool for studies of PM10, visibility, and acid deposition.

A. Belle Hudischewskyj, Pradeep Saxena, and Christian Seigneur are with Systems Applications, Inc., San Rafael, CA 94903.
***Harold M. Barnes** is the EPA Project Officer (see below).*
The complete report, entitled "Development of Computer Modules of Particulate Processes for Regional Particulate Model," (Order No. PB 87-227 278/AS; Cost: $24.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Officer can be contacted at:
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

EPA/600/S3-87/021