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**Development of a
Gas-to-Particle Conversion Model
for Use in Three-Dimensional
Global Sulfur Budget Studies**

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Project Overview:

This project consists of a one-year study aimed at the development of a description of gas-to-particle conversion for anthropogenic and oceanic sulfate precursor species. The model is to include both gaseous and aqueous conversion pathways, and is to be suitable (i.e., computationally feasible) for inclusion in three-dimensional modeling studies of the global sulfur cycle. The model is to provide some size resolution of particles to allow prediction of CCN (cloud condensation nuclei) activity. Size resolution of particles is also important for the calculation of particle surface area and vapor scavenging rates, which compete with new particle production pathways for available condensable vapors.

Sulfur-bearing aerosols are of particular interest in atmospheric research, and have been focused upon in this work, because of their high solubility and ubiquity. Aerosols affect radiative fluxes at the surface of the Earth through their ability to scatter and/or absorb solar radiation; soluble aerosols also indirectly affect the earth's radiation budget by acting as cloud condensation nuclei and influencing cloud microphysical properties and hence cloud albedo. Thus aerosols, through their effects on radiative fluxes, have a potentially large climate impact. Some studies suggest that increased injection of sulfate into the atmosphere can lead to a substantial cooling effect, masking greenhouse gas warming. However, increased atmospheric mass of sulfate does not directly correspond to increased numbers of particles. An important objective of this work is to develop methods to predict the distribution of sulfate mass between growth of preexisting particles and formation of new numbers of particles from the gas phase.

The research and its results can be broken down into the tasks described below. The model developed (BIMODAM) is based upon previous work with a modal aerosol model (Kreidenweis and Seinfeld, *Atm. Env.* 22: 283-296, 1988). The modal representation was chosen as a basis due to its computational efficiency, but testing (see Task 2 below) revealed that even this simple scheme is too computationally intensive for long-term global simulations. Therefore, the research tasks described have focused upon development of accurate further simplifications and parameterizations, and upon model performance evaluations that compare predictions against a widely-used, detailed sectional aerosol representation (MAEROS; see Task 3).

Scientific Results:

Task 1:

Development of schemes for increasing speed of thermodynamic calculations.

The assumed mechanism for the formation of new particles from the gas phase is the binary nucleation of sulfuric acid / water particles. The nucleation rate is sensitive to ambient relative humidity, acid vapor concentration, and temperature. Tables of the rate of nucleation as a function of these variables were developed using the PI's code, which computes the nucleation rate in the presence of hydrates in the gas phase (Jaecker-Voirol and Mirabel, *J. Phys. Chem.* 92: 3518 - 3521, 1988) and includes detailed thermodynamic data for temperatures above 0 °C. Below that temperature, the published rates computed by those authors were used. The rate tables were further simplified by a three-dimensional polynomial fit, greatly reducing the computational time for this part of the calculation.

Polynomial approximations of particle size as a function of "dry" mass and relative humidity were developed for sulfuric acid and ammonium sulfate. This avoids the need for subroutines which compute solution properties (e.g., density, water activity)

and the equilibrium haze particle size iteratively. Additionally, the user has the option of choosing a "maritime" (ammonium sulfate) or "continental" (ammonium sulfate with 30% insoluble material) aerosol model for calculation of size of haze particle.

Task 2:

Initial feasibility study with GRANTOUR model.

The aerosol model of Kreidenweis and Seinfeld (1988), with the parameterizations described in Task 1, was incorporated into Lawrence Livermore National Laboratory's (LLNL) three-dimensional global transport, transformation and deposition model of the sulfur cycle (GRANTOUR). A stiff ODE solver was employed to solve the aerosol equations, which were decoupled from a simplified gas-phase chemistry scheme that provided source rates of condensable vapor to the aerosol model. The stiff solver proved to be computationally expensive, as expected. However, several short-term (6- to 48-hour) simulations were completed.

In one study, global steady-state sulfate mass distributions, predicted from earlier GRANTOUR studies, were used to initialize the model run by arbitrarily partitioning the mass into 0.1- μm particles. It is expected that, at steady state, the predicted mass would be the same as that used to initialize the model, but the numbers of particles would adjust to satisfy atmospheric sources and sinks. The initialization scheme led to very low particle number concentrations in the upper troposphere. A six-hour simulation was performed and analyzed for regions in which new particle production occurred, compared with regions in which the vapor source led only to growth of existing particles. It was found that the upper troposphere supported significant new particle formation, suggesting that although sulfate masses and production rates are low in this region, cold temperatures and low aerosol surface area may lead to new particle formation. Observational evidence for nucleation of ultrafine, highly acidic particles in the free troposphere has since been obtained (Clarke, *J. Atmos. Chem.* 14: 479 - 488, 1992).

More conclusive statements await the results of a longer-term simulation, continued until a steady-state global aerosol number distribution is achieved. With this objective in mind, further parameterizations to increase the computational speed of BIMODAM were pursued (Tasks 6 and 8).

Task 3:

Modification of sectional aerosol model for calibration of modal aerosol model.

The MAEROS sectional aerosol model (Gelbard and Seinfeld, *J. Colloid Int. Sci.* 78: 485, 1980) was modified to incorporate the same particle size and nucleation rate parameterizations as those used in BIMODAM. Additionally, a postprocessing code was written to analyze the sectional output for mass mean diameter and standard deviation. In addition to nucleation and condensational growth, MAEROS is also capable of simulating coagulation and depositional loss processes. In our application, MAEROS is run with a total of 39 lognormally-spaced bins spanning 0.001 - 10 μm in particle diameter.

Task 4:

Development of condensational growth factors.

Simulations performed with MAEROS were used to estimate the degree of polydispersity achieved when new particles were formed under a range of vapor source rates and relative humidities; this analysis yielded condensational growth factors (α , always less than 1) that are applied in BIMODAM. This factor corrects for the overprediction of particle growth that occurs when the aerosol population is assumed monodisperse (Okuyama, Kousaka, Kreidenweis, Flagan and Seinfeld, *J. Chem. Phys.* 89: 6442-6453, 1988), as in done in the modal model.

Our studies have determined that the factor α is critical in computing numbers of nucleated particles; if $\alpha = 1$ is assumed, particle number is underpredicted, since growth occurs too quickly during the burst. However, subsequent condensational growth is fairly insensitive to the exact choice of α . Hence, we have developed polynomial expressions for α based upon MAEROS nucleation runs, and apply these expressions, which are a function of vapor source rate and relative humidity, throughout the simulation (Figure 1).

Task 5:

Development of mode merging criteria.

BIMODAM represents an aerosol distribution by up to two monodisperse modes, each represented by its mass mean diameter and total number concentration. As the particles grow by condensation, the particles with the smaller diameter will eventually approach in size those of the other mode, since the condensational growth is (approximately) inversely proportional to diameter. It is desirable to combine the two modes when they become indistinguishable, both to eliminate a set of equations and to empty one mode so that it is available to accept particles nucleated from the gas phase.

The merging is accomplished by reference to a criterion that is the ratio of the sum of the condensation rates onto the individual bins to the condensation rate onto the merged bin; the merged bin mean diameter is computed by summing total aerosol mass and dividing by total number. The criterion is always less than one since the monodisperse (merged) representation will predict greater condensational growth rates than the bimodal representation. Allowing merging only when the criterion is greater than 0.95 constrains the overestimation of condensational growth to be less than 5%.

Task 6:

Parameterization of nucleation of new particles from the gas phase.

The five independent variables in BIMODAM are mass and number of aerosol particles in each bin, and the gas-phase condensable vapor saturation ratio. The rate equations represent a system of five coupled ordinary differential equations. In a typical scenario, the vapor phase builds up due to chemical reaction in the gas phase and is simultaneously slowly depleted as it is scavenged by existing particles. At some time, a "critical" saturation ratio may be reached that is high enough to support new particle formation, which occurs as a "burst". The nucleation phenomenon occurs on a relatively short time scale, and results in rapid changes in the vapor saturation ratio; thus, during

the "burst" the ODE solver is forced to take computationally-expensive short time steps.

An approach has been developed to algebraically predict the number of new particles nucleated and the duration of the "burst" from knowledge only of vapor source rate and relative humidity. The method is based upon the approximation of the time-dependent nucleation rate during the burst as a triangular function (Figure 2). The value J_{crit} is uniquely related to a critical saturation ratio, S_{crit} , which, along with the slope of the $J(t)$ curve at that point, has been correlated to the two independent parameters from the results of a large number of runs.

The method has been tested for a wide range of vapor sources and for relative humidities between 50% and 100%, and predicts the correct number of particles nucleated to within 10%. An example calculation is compared to the full integration (using the ODE solver) in Figure 3. The parameterized nucleation scheme was completed in 0.21 sec CPU, whereas the full integration required 3.09 sec CPU. Thus a substantial savings in computational time can be realized with this method.

Additionally, a means for applying the technique in the presence of preexisting particles has been developed, in which the vapor loss due to condensation onto the aerosol is subtracted to obtain an "effective" vapor source rate, which can be utilized in the same manner described above. Results from tests with this application are very encouraging, and show that accurate (within 10%) predictions are obtained for about 70% of the cases studied.

Task 7:

Intercomparison studies between aerosol models.

Although each component of the fully-parameterized BIMODAM model has been tested against MAEROS and against the original aerosol model, intercomparison studies which simulate a realistic atmospheric situation and which can be used to compare accuracy and total computational costs between models were also performed. An example calculation is shown in Figure 4. The situation modeled is the steady-state marine boundary layer concentrations of sulfate from the reaction of dimethylsulfide (DMS). Vapor source rates and particle loss rates have been taken from the work of Bates *et al.* (Bates, Johnson, Quinn, Goldan, Kuster, Covert, and Hahn, *J. Atmos. Chem.* 10: 59-81, 1990); these authors also present steady-state aerosol and vapor mass concentrations that can be used to compare with the results of our simulations.

The advantage of using the derived condensational growth factors (α) is evident, as the modal model will overpredict growth and underpredict number if $\alpha=1$ is used. However, with the derived value of α , BIMODAM predicts a steady-state number, mass, and particle size that is in excellent agreement with MAEROS, and uses less than 0.5 sec CPU in comparison with the 141 sec CPU required by MAEROS.

An additional comparison of three methods - MAEROS, BIMODAM with full integration of the particle number balance equations, and BIMODAM with the parameterized nucleation scheme discussed in Task 6 - is shown in Figure 5. In the fully-integrated case, a low continuous source of particles by homogeneous nucleation is predicted at steady state. The parameterization cannot represent a continuous source of particles, but assumes a cyclical steady state in which particle "bursts" are followed by periods of particle number depletion until the vapor phase again builds to a level that

can support a "burst". The average of the steady-state cycle agrees well with the continuous steady states predicted by MAEROS and BIMODAM.

Task 8:

Testing of analytical solution for condensational growth of particles.

The most substantial improvement in overall computational costs will occur if use of the ODE solver can be eliminated completely. By applying the parameterized nucleation scheme and eliminating integration during that part of the simulation, the only remaining numerical integration is in the growth calculation. We have derived an analytical solution to the particle growth equation that depends upon the diameter remaining approximately constant. This requirement is satisfied to within 10% if the particle mass increases by not more than 3%; after this point, the constant which represents terms dependent upon diameter must be updated.

Task 9:

Development of simple model of uptake of volatile sulfur and aqueous chemical conversion and application to conversion of SO₂ to sulfate in GCM clouds.

A model for computing the uptake and conversion of gas-phase species by a cloud droplet was developed and tested against published results from similar models. The model considers the effects of liquid water content, drop size, mass transfer limitations, solubility limitations, and chemical kinetics in both phases in a zero-dimensional framework. The model is documented in an LLNL Report, as the work was jointly supported by a subcontract from LLNL.

Latitudinally- and vertically-dependent atmospheric ozone and hydrogen peroxide concentrations were taken from a two-dimensional global gas-phase chemistry model run supplied by LLNL, and used as input to the aqueous-phase model. The ambient SO₂, liquid water content, and temperature were varied; runs were performed for a range of pH observed in clouds. (Although the model is capable of computing pH in the drops, the calculated pH is sensitive to the assumptions made about availability of buffering and neutralizing species such as ammonia, for which little observational information exists; therefore, "typical" pH's were assumed and held constant.) Six-hour runs were performed to match the time steps taken in the GRANTOUR model. The objective was to map out those combinations of input variables for which one of the reagents was limiting, and to use the model results to predict the overall SO₂-to-sulfate percentage conversion as a function of input variables.

This model has recently been revised and expanded to allow for more aqueous species, including sea salt nuclei. It will be used as a basis for the incorporation of aqueous chemistry into a detailed cloud model.

Recommendations and Conclusions:

A fully-parameterized model for the formation and growth of aerosols via gas-to-particle conversion has been developed and tested. A particularly significant contribution is a new method for the prediction of numbers of particles nucleated using information on the vapor

source rate, relative humidity, and preexisting aerosol alone, thus eliminating the need to solve a system of coupled ODEs. Preliminary tests indicate substantial reduction in computational costs, but it is recommended that the BIMODAM model be incorporated into a large-scale model of the sulfur cycle in order to more fully test its computational feasibility.

Education and Human Resources:

The following graduate students have been partially supported by this project:

Debra Youngblood is currently completing work on her M.S. thesis, and expects to receive the degree in December 1993. She has worked on several aspects of the project which will constitute the bulk of her thesis work, including development of the nucleation parameterization, development of the condensational growth factor correlations, and the intercomparison studies. Her work will be presented at the 1993 Annual Meeting of the American Association for Aerosol Research. Upon completion of the thesis, we will prepare and submit 1 - 2 journal articles describing the results of this work.

Wendy Richardson is currently working toward a second graduate degree under the advisement of Prof. Kreidenweis. Dr. Richardson has contributed to the revision of the aqueous aerosol model and performed the series of runs aimed at developing the parameterization for the global model. She is applying the modified aqueous chemistry model to her thesis work, which will involve incorporating aerosol and aqueous chemistry into a simulated marine stratocumulus cloud.

Publications Resulting from Grant Support

Youngblood, D.: Development and Testing of a Bimodal Aerosol Dynamics Model. *M.S. Thesis*, Colorado State University, December 1993.

Kreidenweis, S. and Youngblood, D.: Dynamic Aerosol Model for Use in Large Scale Simulations. Paper accepted for presentation at the 1993 Annual Meeting of the American Association for Aerosol Research, Oak Brook, Illinois, October 1993.

Kreidenweis, S.: A model for aqueous chemistry in cloud droplets. Lawrence Livermore National Laboratory Report, 1991.

Kreidenweis, S., Penner, J., and Walton, J. Development of an aerosol source term for global sulfur budget studies. Presented at the XX General Assembly of the IUGG, Vienna, Austria, 1991.

Kreidenweis, S.: "Development of a Gas-to-Particle Source Term for Global Sulfur Budget Studies," presented at the 1991 Annual Meeting of the American Association for Aerosol Research, Traverse City, Michigan, October 1991.

List of Figures:

- Figure 1: The condensational growth factor, α , as a function of condensable vapor source rate and relative humidity. The factors are derived from studies of nucleation from the gas phase using the MAEROS model, and are used to bring BIMODAM predictions into agreement with the sectional model.
- Figure 2: The time-dependent rate of homogeneous binary nucleation, $J(t)$. The function $J(t)$ is approximated as triangular to derive the parameterization described in the text. J_{crit} is the time when the nucleation burst begins; Δt is the half-width of the burst. The value of J_{prime} is used to deduce the slope of the $J(t)$ curve, which, when multiplied by $2 \times \Delta t$, yields total number nucleated during the burst.
- Figure 3: Comparison of BIMODAM calculations using integration of the aerosol number balance equation and using parameterized nucleation scheme.
- Time-dependent gas-phase concentration of sulfuric acid. The parameterized run assumes a linear relationship until the nucleation burst time. During the burst, vapor production is exactly balanced by increase of aerosol mass in the parameterized case. Overpredicted gas-phase concentrations quickly correct to agreement with the integrated run.
 - Time-dependent aerosol mass.
 - Time dependent aerosol number concentration. No aerosol is assumed present in the parameterized case until the burst is completed.
 - Time-dependent particle size. The slight underprediction of total number in the parameterized case leads to a slight overprediction in diameter.
- Figure 4: Steady-state calculation modeled after the observations of Bates *et al.* (1990).
- Aerosol number concentration. Note that the assumption of monodispersity ($\alpha=1$) results in underpredicted aerosol number and overpredicted mean particle size (Figure 4b), whereas the derived condensation growth factor brings the BIMODAM calculation into good agreement with MAEROS.
 - Steady-state particle size distribution computed by MAEROS. The "distribution" calculated using the BIMODAM model is shown as the delta function at the computed mass mean diameter. D_{pm} (MAEROS) = 0.485 μm ; D_{pm} (BIMODAM) = 0.488 μm .
- Figure 5: Comparison of three methods for computing time-dependent aerosol number and mass concentrations, as explained in the text.
- Time-dependent aerosol mass.
 - Time dependent aerosol number concentration.

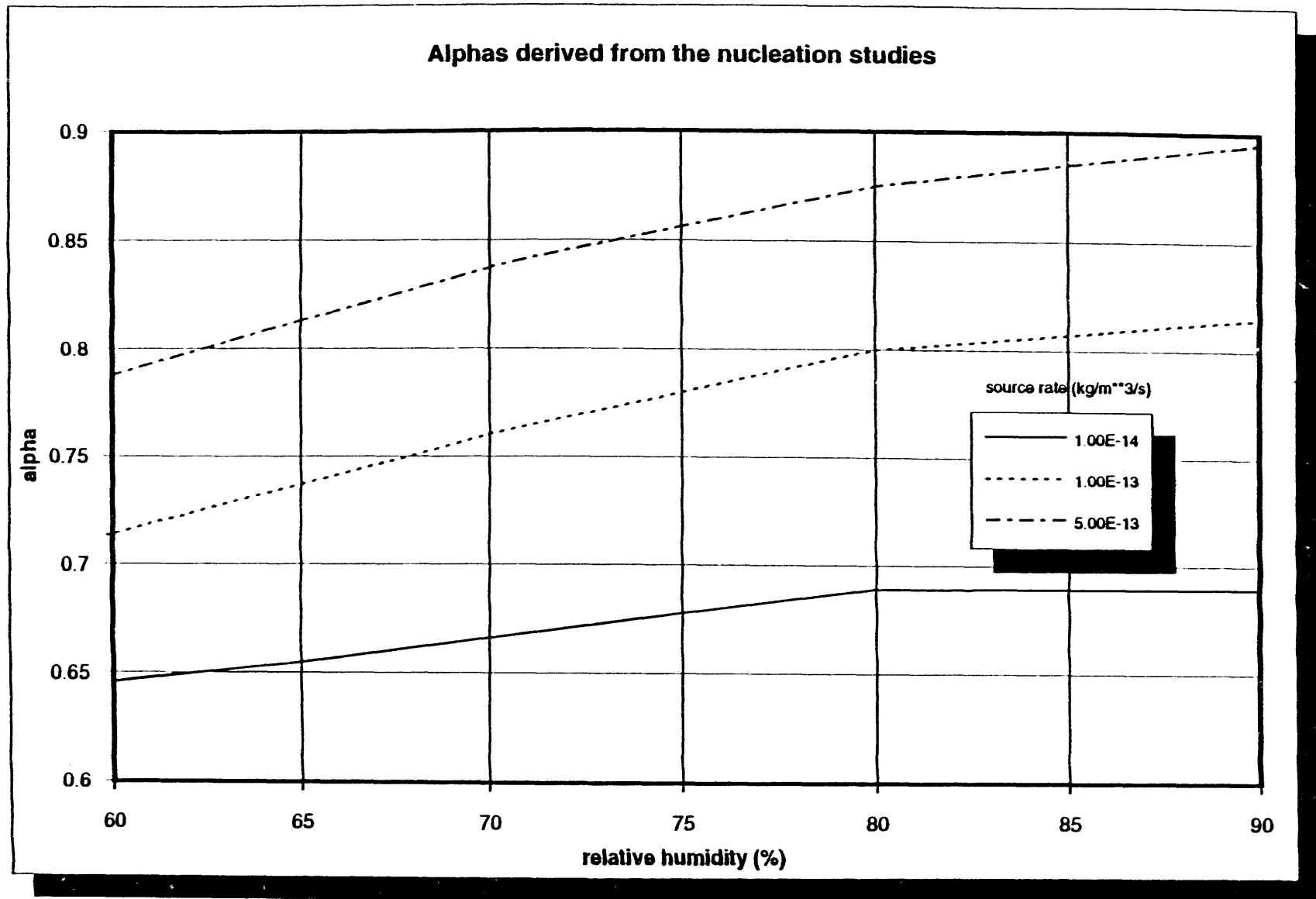


Figure 1.

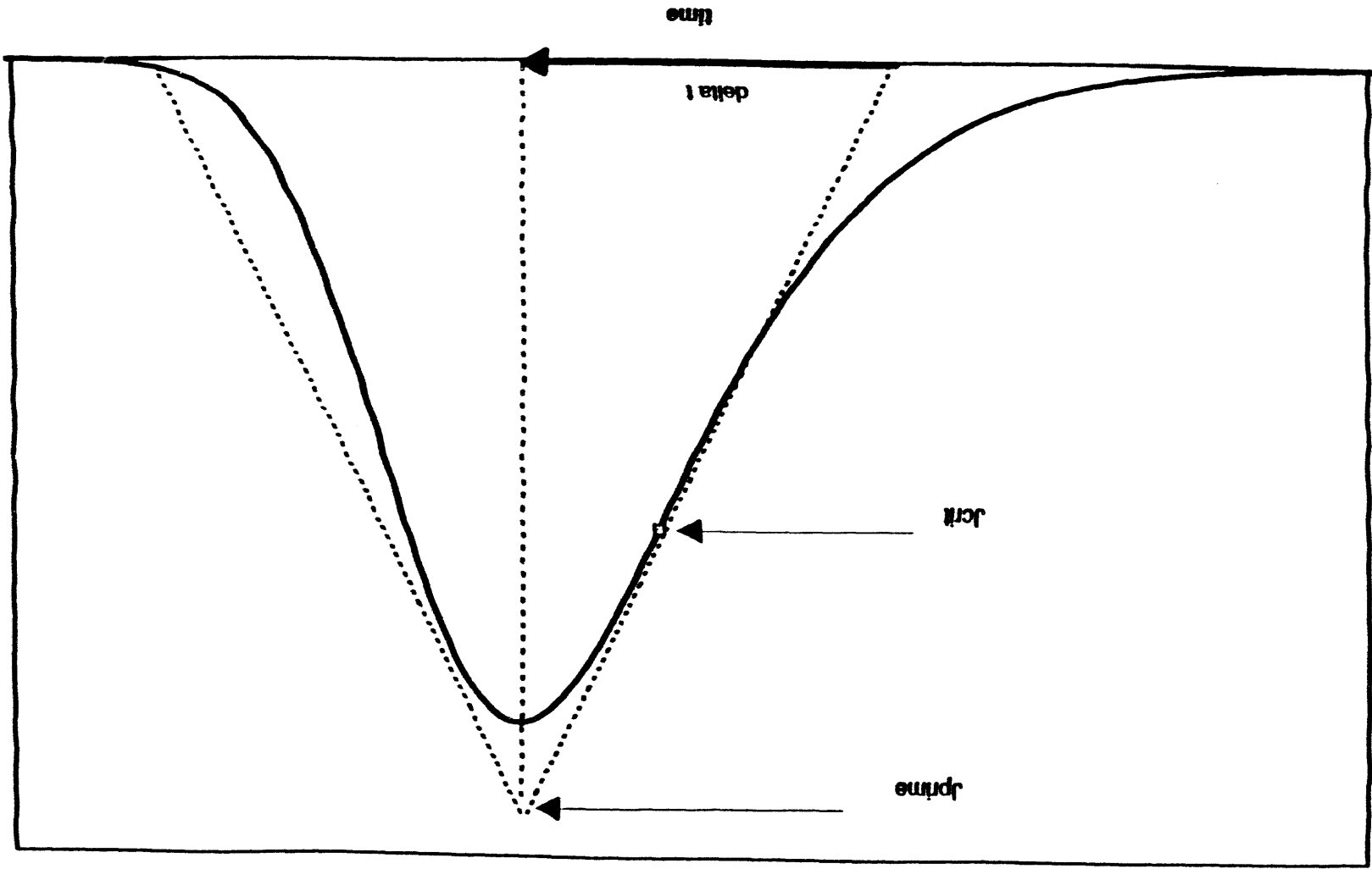


Figure 2.

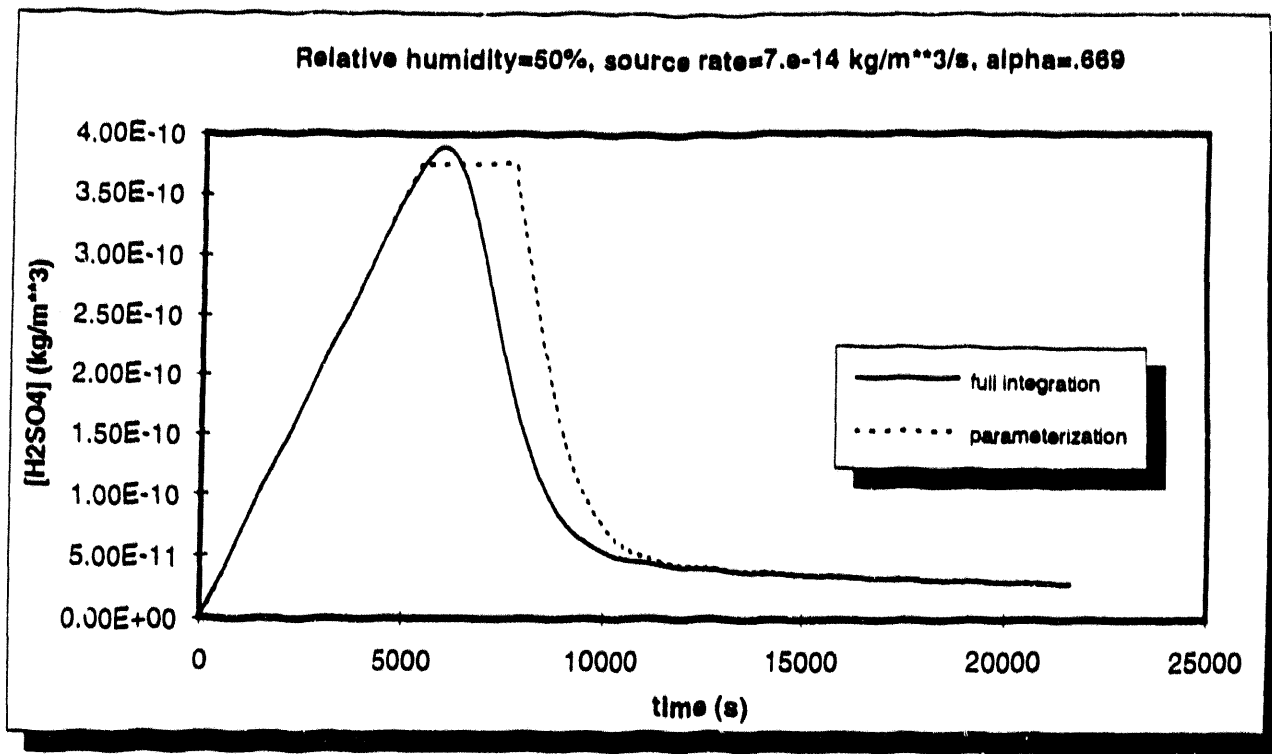


Figure 3a.

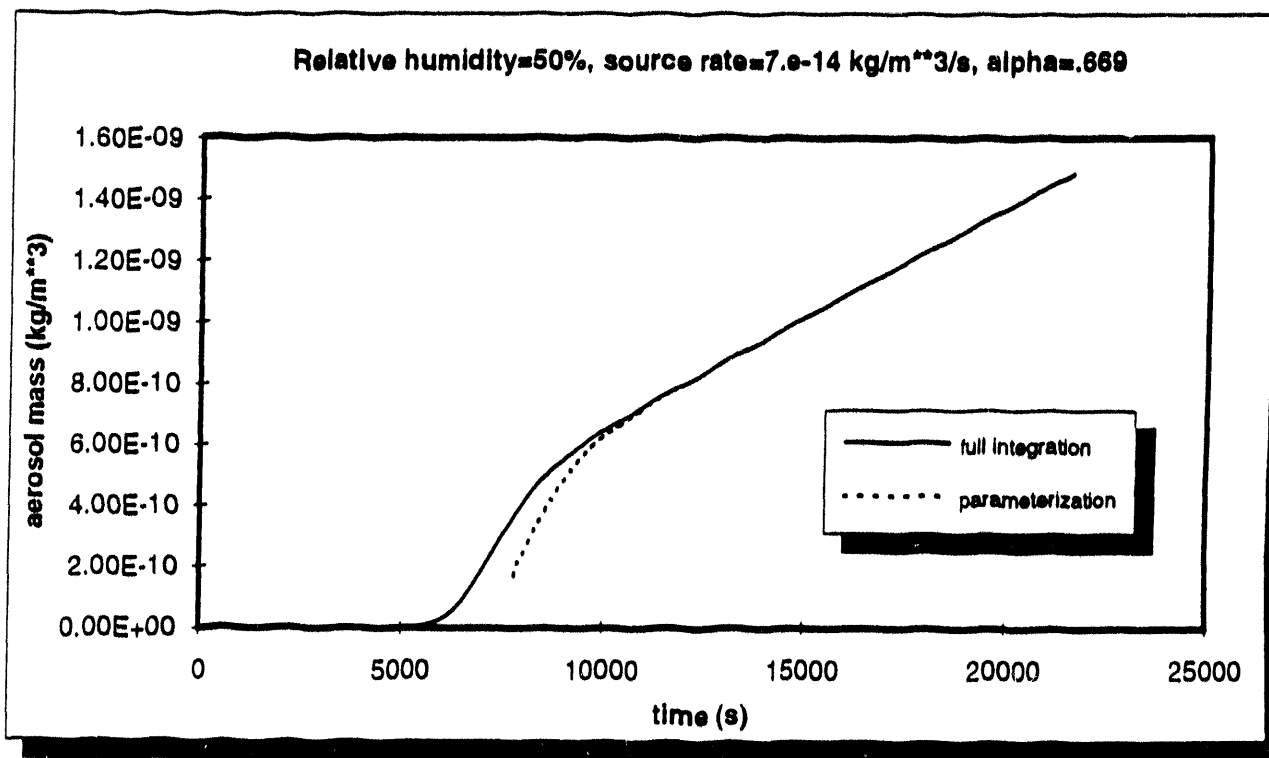


Figure 3b.

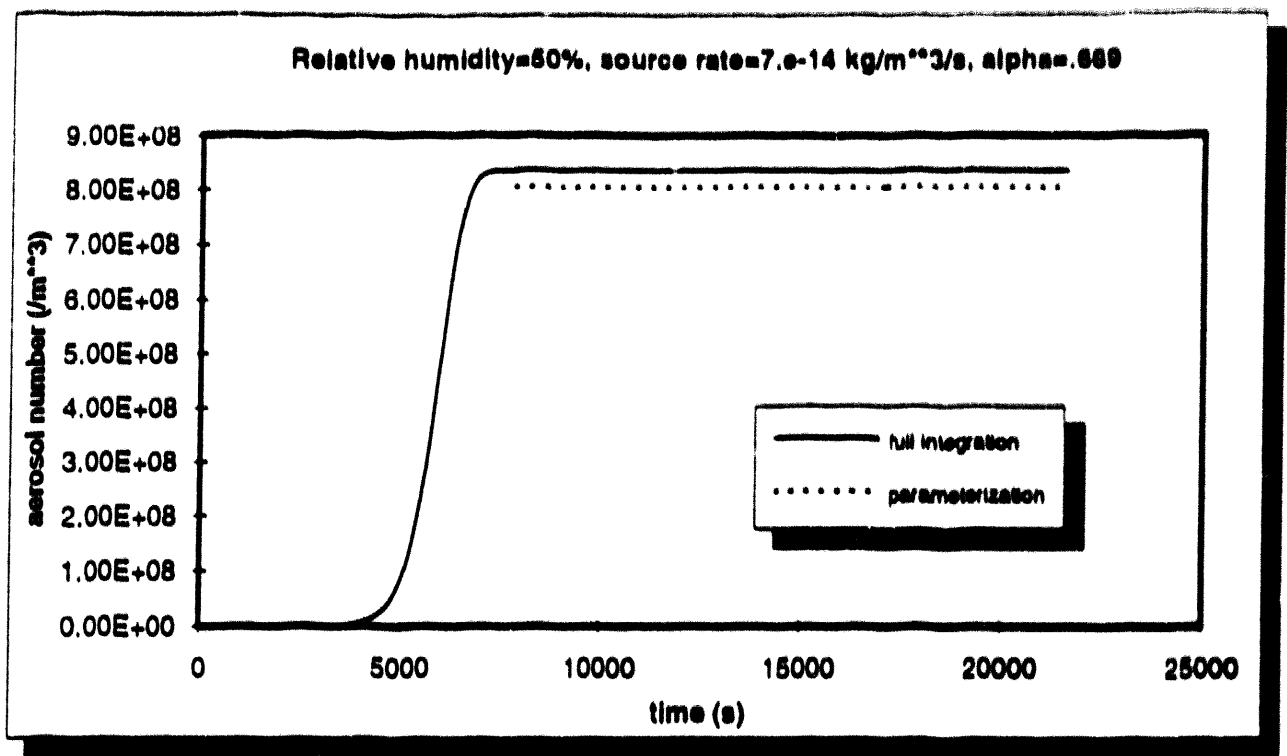


Figure 3c.

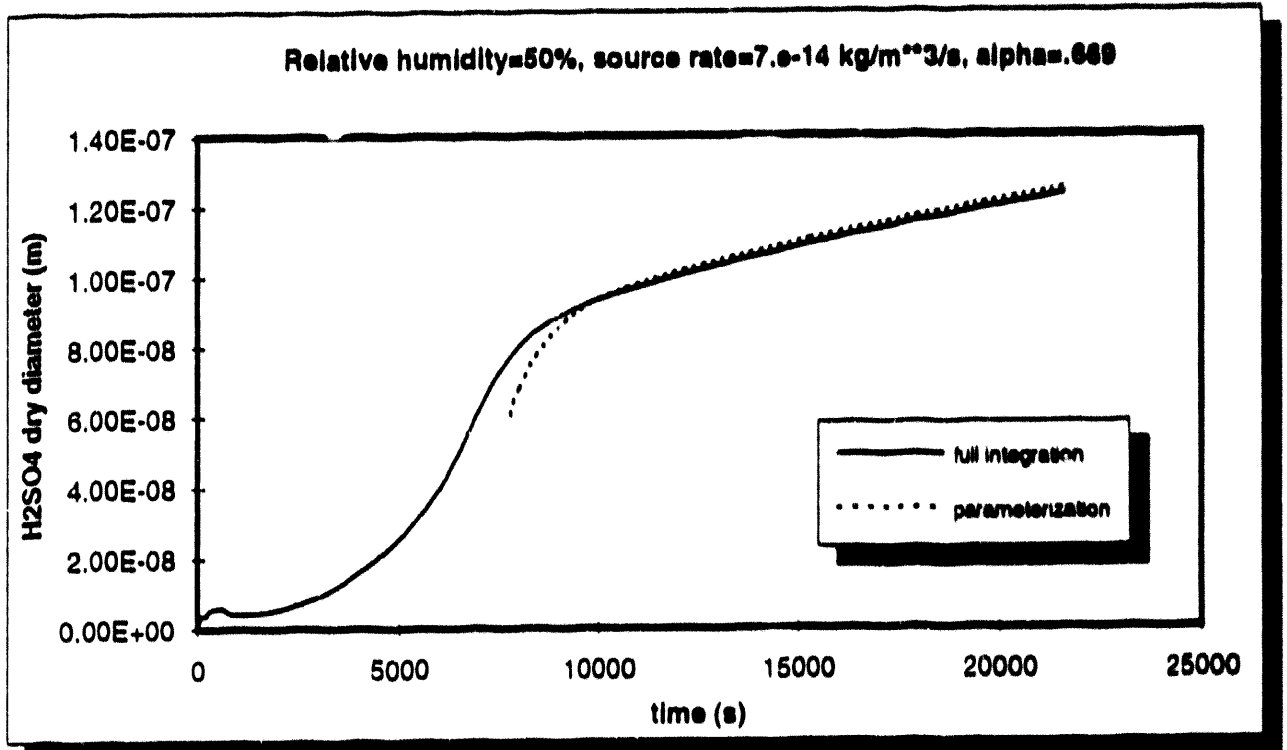


Figure 3d.

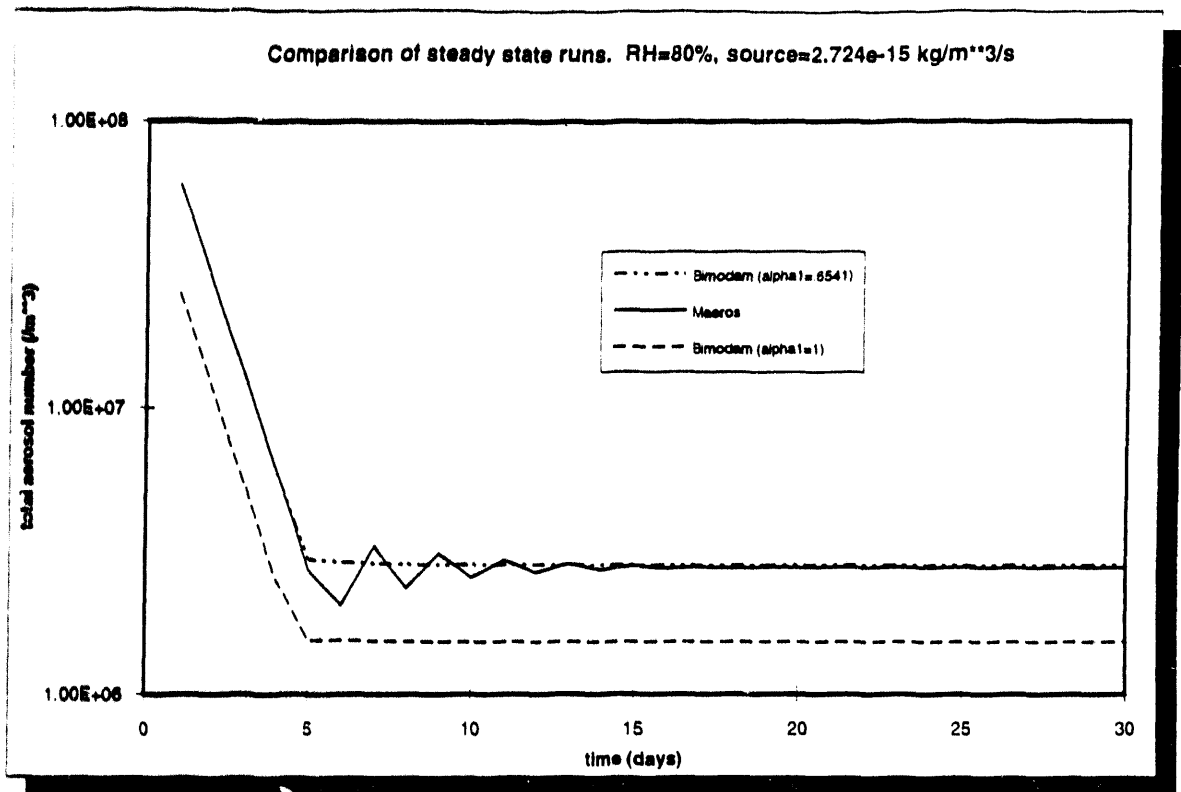


Figure 4a.

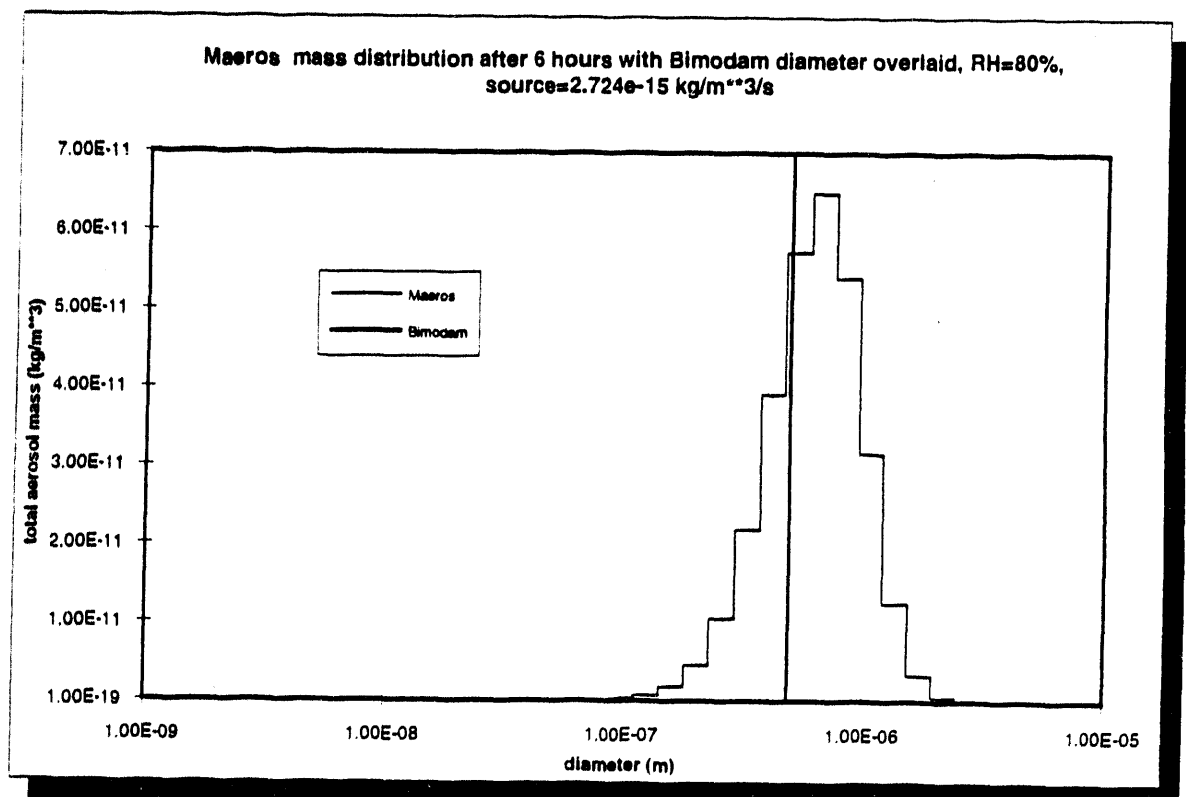


Figure 4b.

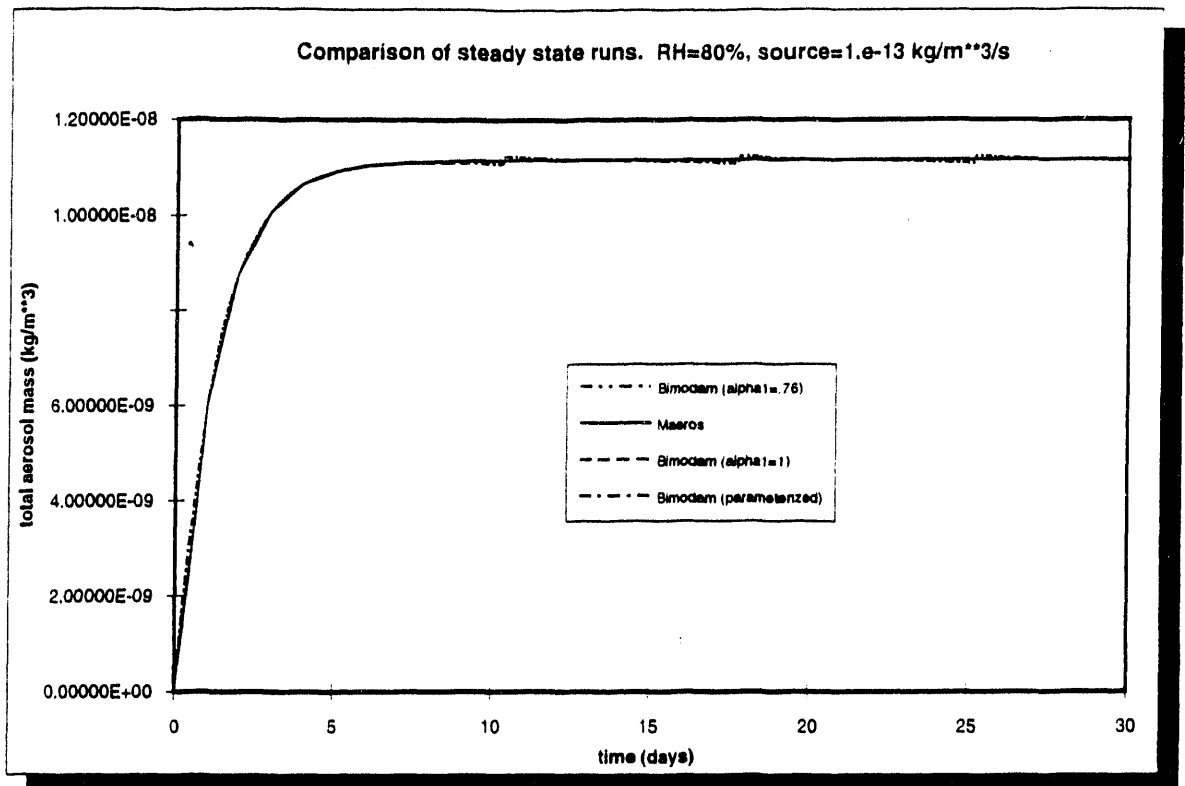


Figure 5a.

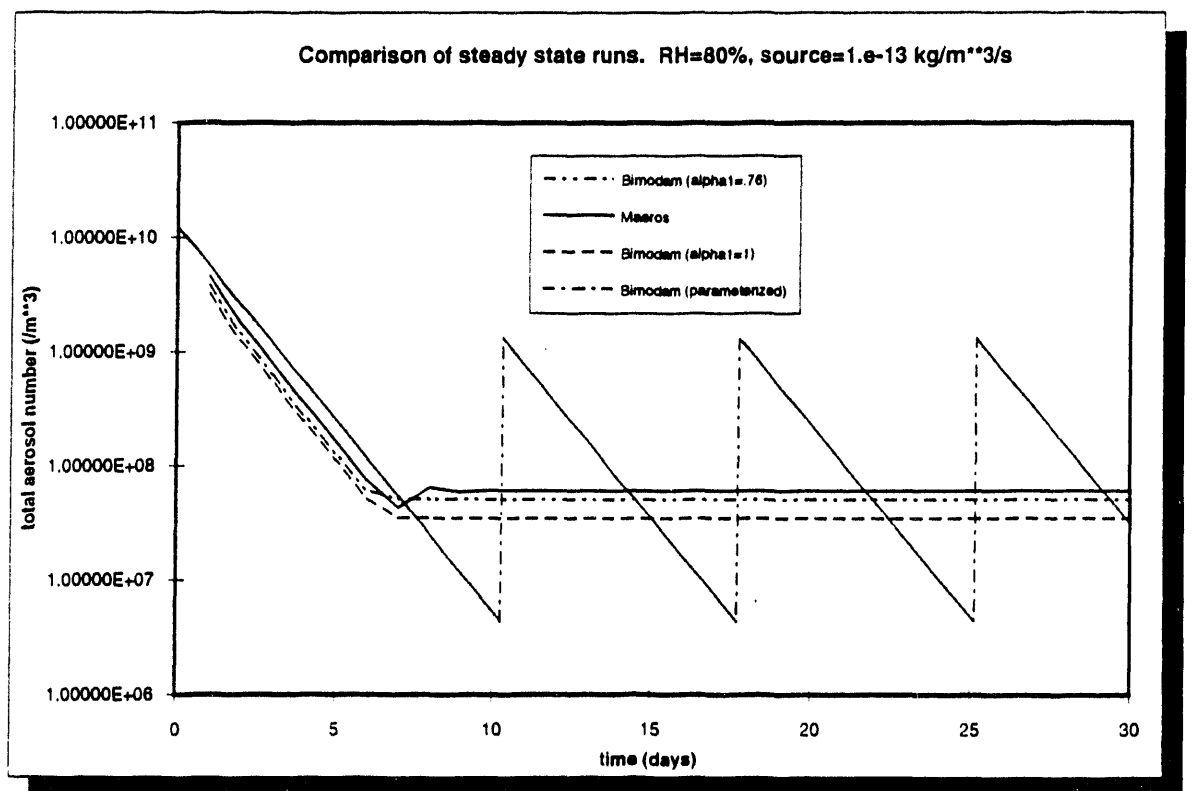


Figure 5b.

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