



Project Summary

A Mesoscale Acid Deposition Model: Preliminary Applications and a Guide for User Interface

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In 1984 the U.S. EPA initiated a **Mesoscale Acid Deposition Study**. This study was organized to assess and understand the interactions and importance of local emissions in mesoscale precipitation scavenging. One important component of the project is the simulation of the field events using a detailed meteorological and chemical modeling framework (called **MesoSTEM**). A dynamic meteorological model (**MASS**—meteorological atmospheric simulation system) is used to predict the meteorological fields, including precipitation rates. These fields are used as inputs to a comprehensive chemical model (**STEM-II**—Sulfur Transport Eulerian Model). The 3-dimensional models are used to quantify the relationships between emissions, chemical production and wet deposition on the mesoscale. The linkage of the models, and the application of **MesoSTEM** to the May 2nd and 3rd, 1985 Philadelphia data set is the subject of this progress report.

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

The **STEM** (Sulfur Transport Eulerian Model) models were developed to provide a theoretical basis to investigate the relationships between the emissions, the

atmospheric transport, chemistry and removal processes, and the resultant distribution of air pollutants and depositions. The development of an Eulerian model, the **STEM-I** model, to describe the transport/transformation and removal of SO_2 and sulfate began in 1975. This **STEM-I** model simulates the transport and chemical processes of SO_2 and sulfate in three-dimensions and makes use of a set of 27 reactions to describe SO_2 gas phase photo-oxidation.

Work began in 1980, with NASA funding, to extend the **STEM** model to include a more detailed treatment of N_xO_y , hydrocarbon, and H_xO_y species and wet removal processes. This activity, and subsequent work with Pacific Northwest Laboratories related to wet removal, led to the development of the **STEM-II** model, which currently treats some 60 chemical species. The important atmospheric processes are incorporated into the model using chemical, dynamical and thermodynamical parameterizations having sufficient detail to accommodate boundary layer-free troposphere exchange in cloudy and cloud-free environments, an in-cloud and below-cloud wet removal and chemical processes. The **STEM-II** model and its components have already been used for a variety of applications. Some of these are: (a) transport of SO_2/NO_x /hydrocarbon urban plumes to the background troposphere; (b) sulfate and nitrate formation in the presence of land/sea breeze; (c) effects of in-cloud and below-cloud scavenging on homogeneous gas-phase chemistry, (d) detailed analysis of

mixing-limited chemical reaction of NO emissions; and (e) the investigation of sulfate production in orographic storms. Many other applications are currently ongoing and some will be discussed later in this report. Also, the STEM-II model has been applied to problems on various spatial scales utilizing horizontal grid sizes from 80 km down to 5 km.

In 1984 the U.S. EPA initiated a Mesoscale Acid Deposition Study. This study, involving scientists from EPA, Brookhaven National Laboratory, NASA, Meso, Inc., and the Universities of Iowa and Kentucky, was organized to assess and understand the interactions and importance of local emissions in mesoscale precipitation scavenging. The study consists of a field component, diagnostic calculations, and the application of a combined mesoscale meteorological and chemical modeling framework (called MesoSTEM). The STEM-II model is being used in this project. This report summarizes our activities during the two year period May 1985-May 1987. These activities have focused on the linkage of the dynamic mesoscale meteorological model (i.e., the MASS (Mesoscale Atmospheric Simulation System)) and the STEM-II model, the testing of the MesoSTEM model, and the diagnostic analysis of field data collected on May 2nd and May 3rd, 1985 around Philadelphia, PA.

Overview of STEM-II Model

The diagnostic analysis in this project is being carried out by use of the STEM-II model. The STEM-II model is an Eulerian combined transport/chemistry/removal model which treats chemical species in the gas, cloud, rain and snow phases. Thirty-nine species are advected, while 21 species are short-lived and are modeled using pseudo-steady state methods.

The STEM-II model is structured to treat wet removal processes in detail. A schematic of the processes that are included in the model analysis is presented in Figure 1. In this model, the in-cloud scavenging of sulfate aerosol is presumed to occur totally by nucleation. Both cloud and aerosol size distributions are assumed to be monodispersed. Once the cloud forms, the number of sulfate aerosols activated and dissolved to form aqueous sulfate is assumed to be the same as the number concentration of cloud droplets. Rain drops are also assumed to be monodispersed. Secondary sulfate is treated in the same way

as primary sulfate and is allowed to be reinjected into the gas phase as hydro-meteors evaporate.

In this project the cloud parameters are calculated by the Advanced Scavenging Module (ASM) cloud scavenging model. The ASM model treats the cloud microphysics, and calculates the cloud and precipitation distributions, and interconversion rates. ASM calculates a self consistent and realistic meteorological data set of the simulated storm. The precipitation formation processes are treated in a parameterized fashion. The scheme lumps water into four categories: water vapor, cloud water, rain and snow. The cloud related parameters calculated in ASM are transferred to the STEM-II model where the transport/chemistry/removal of pollutants is calculated.

For the gas phase, the reaction mechanism includes 85 reactions and 60 chemical species. Of these species, 39 long-lived species are advected while the remaining 21 short-lived species such as free radicals are modeled using the Pseudo-Steady State Approximation.

For the liquid phase, 17 equilibrium dissociation reactions, 3 chemical kinetic expressions, and 22 ionic species are included in the STEM-II code. Detailed solution equilibria and chemical kinetics are solved using a modified semi-implicit method while satisfying the electrical-neutrality constraint. The mass transfer associated with absorption into and desorption from droplets is also included.

Application of STEM-II to May 2nd and 3rd Field Data

The STEM-II model described above is being used to analyze field data collected in the U.S. EPA Mesoscale Acid Deposition Study. The model was implemented on the VPS 32 machine at the NASA Langley Research Center. The current application work is focusing on the May 2nd and 3rd, 1985 study conducted in the Philadelphia area.

The modeling domain used for this analysis is shown in Figure 2. Two different grid systems are being used: a coarse grid with horizontal grid spacings of ~ 56 km; and a fine grid with horizontal spacings of 20 km (see Figure 3). The vertical domain is the same in each system with 14 vertical grids non-uniformly spaced between the surface and a height of 6 km. The wind, temperature, and surface precipitation fields predicted by the dynamic meteorological model MASS. The predicted precipitation

fields were used as inputs to the ASM cloud model to generate the microphysical parameters for the wet removal calculations.

The emission fields for the simulations are based on Version 5.2 of the U.S. EPA National Acid Precitation Assessment Program (NAPAP) which includes SO_x, NO_x and speciated hydrocarbons. The point and area sources gridded to 20 km are shown in Figures 4-8. Elevated point sources are assigned to vertical grids by distributing the point emissions over a control volume centered around the grid point. Presented are point source and area emissions for NO, SO₂, NH₃, sulfate and toluene. The spatial distributions of the NO, SO₂, sulfate and toluene emissions are similar with the major point sources in the northeast section (around New York) of the model domain and around Philadelphia. The area sources show a similar pattern but with appreciable values at each grid point. The NO area emissions are very large exceeding 1.1×10^{13} molecules/m²-s at several locations. The area emissions of ammonia are quite different from the other species. As shown, there are very low ammonia emissions in New Jersey and relatively large emissions on the Pennsylvania side of the model region.

The May 2nd event was an example of a slow moving frontal system which produced very heavy precipitation in the study area. The flow field in the modeling region at 14:00 LT (local time) was generally from the east and gradually shifted to the northeast after 22:00 LT. The level one wind speeds were high throughout the period with horizontal winds of 15 m/s. The precipitation came from the south and reached Philadelphia at 15:50 LT. Output from the MASS model was used to provide the meteorological inputs for the STEM-II model.

The measured wet deposition loadings of nitrate and sulfate are shown in Figure 9. The general features show that for both species the loadings were higher on the Pennsylvania side. Furthermore, the nitrate loadings were slightly higher than those for sulfate on the New Jersey side.

Coarse Grid Simulations

Coarse grid model predictions have been obtained for an 18 hr period corresponding to 14:00 May 2nd to 8:00 May 3rd, 1985. The model was initialized by starting with rural conditions and then seasoning under no-flow conditions with real emissions for a period of 2-3 days.

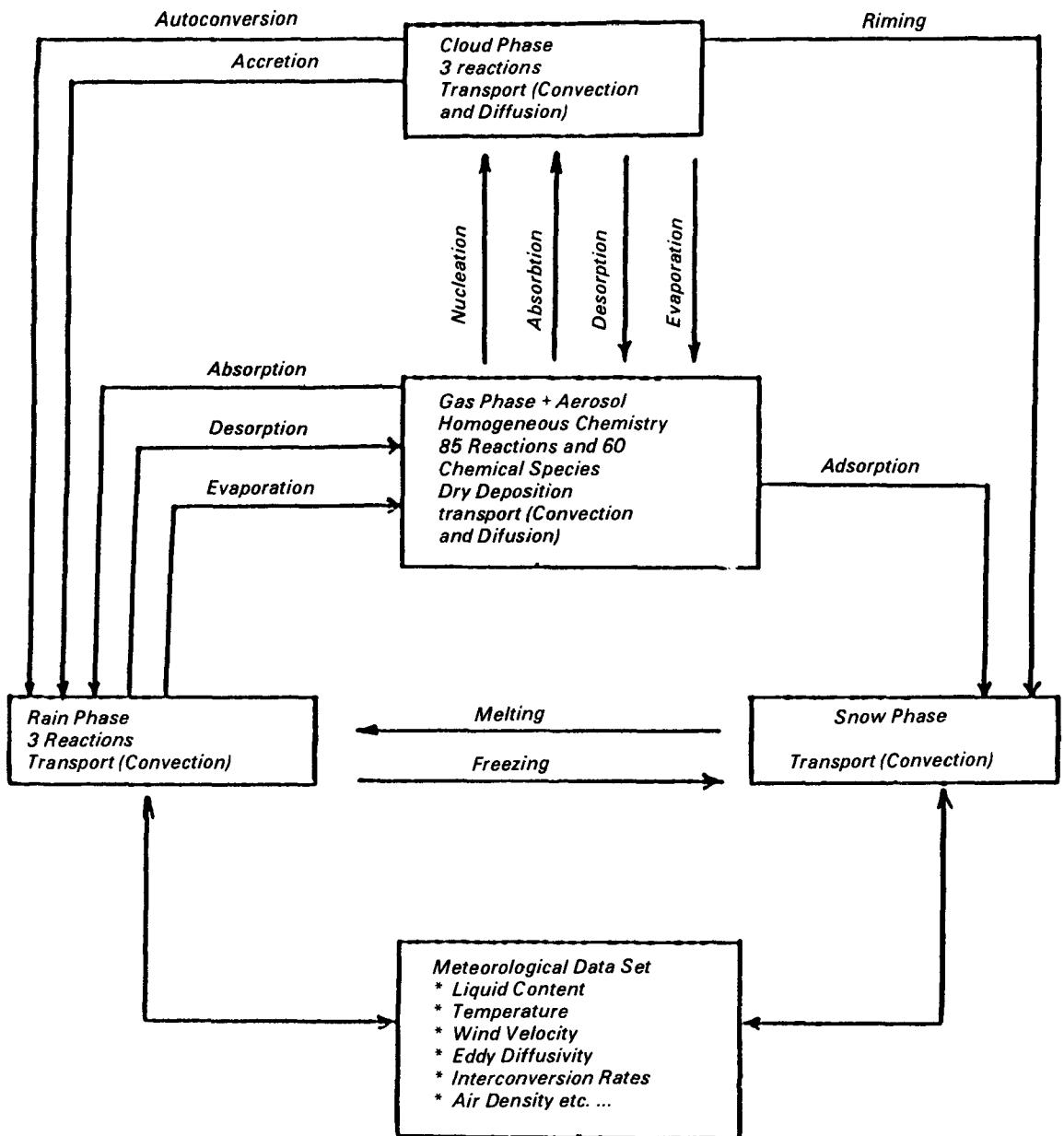


Figure 1. Interaction diagram of chemical/physical processes treated in the STEM+ASM model.

Initialization of the model is difficult because of the small domain size and large horizontal velocities. The model was initialized under no-flow conditions so that the initial conditions would reflect the source characteristics of the model domain. Since no measurements were available to set the inflow boundary conditions, the chemical composition of the air masses transported into the model region (through the eastern and northern boundaries) was estimated by perform-

ing 1-dimensional model calculations reflecting the air mass histories. For example, the air entering through the eastern boundary has relatively low concentrations reflecting that it originated from the south and traveled along a wet trajectory, whereas the air mass entering the northern boundary has high concentrations of pollutants reflecting the high source regions upwind in New York. The results of the coarse grid simulation are discussed in a paper

presented at the 16th International Technical Meeting on Air Pollution Modeling and Its Applications.

Fine Grid Simulation

Results using a fine grid of 20 km horizontal mesh spacing for the May 2nd and 3rd, 1985 case have also been obtained. The fine grid domain is shown in Figure 3 and covers a region 180 km x 180 km x 6 km with 1400 grid points (i.e., 10x10x14). The emissions inventory

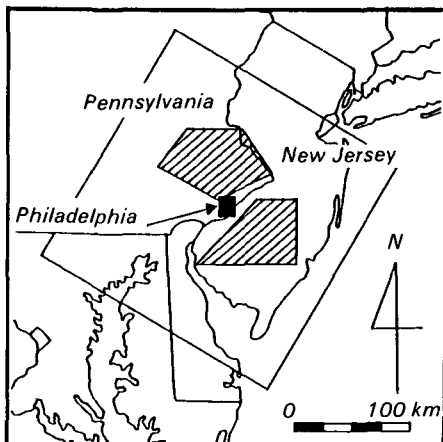


Figure 2. Philadelphia mesoscale acid deposition study domain. The shaded regions denote the areas where the monitoring stations were deployed. The large slanted square represents the modeling region.

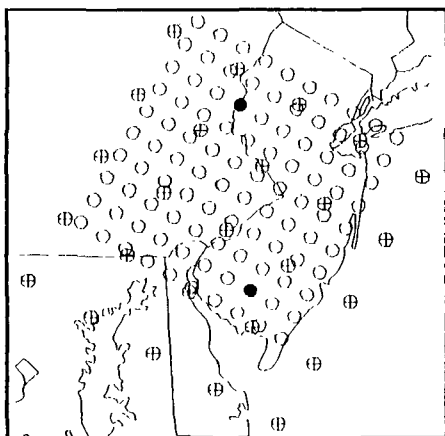
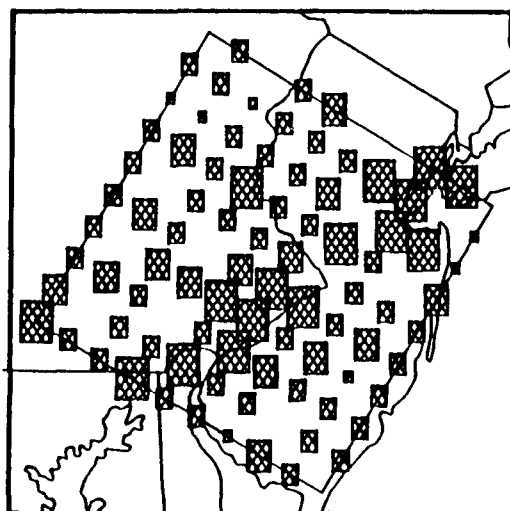


Figure 3. Model region for MesoSTEM application. Coarse grid and fine mesh grid systems are shown. Solid dots show grid points (8,2) and (4,8) in the New Jersey and Pennsylvania regions, respectively.

was discussed earlier and plotted for selected species in Figures 4 to 8. The initial conditions of the primary pollutants (e.g., NO, NO₂, and SO₂) showed large concentrations around New York City and Philadelphia areas. The initial conditions of ammonia reflected the large area sources on the Pennsylvania side of the model domain. Ground level NH₃ concentrations exceeded 5 ppb in much of this region. The initial concen-

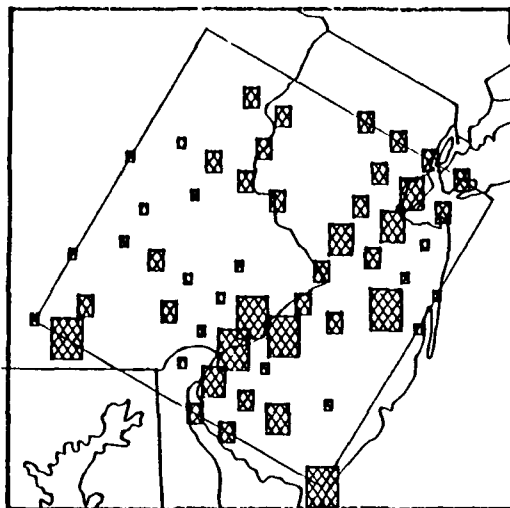
NO Emissions



molecls. m⁻² sec⁻¹

- .1E+13 < 0
- .5E+12 < 0 < .1E+13
- 1E+12 < 0 < .5E+12
- .1E+11 < 0 < .1E+12

NO Emissions(P)



molecls. m⁻³ sec⁻¹

- .2E+09 < E
- .1E+09 < E < .2E+09
- .1E+08 < E < .1E+09
- .1E+07 < E < .1E+08

Figure 4. Elevated point sources (at level 2 corresponding to a height 200 m) and area emissions for NO.

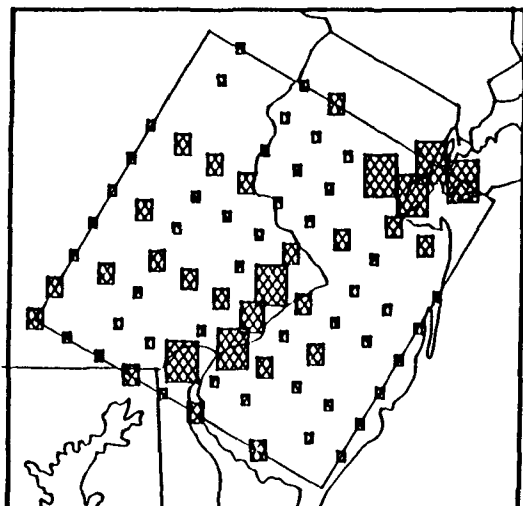
trations of the secondary pollutants (e.g., HNO₃, H₂O₂, O₃, and sulfate) showed quite different behavior than the primary species. For example, the H₂O₂ surface concentrations were rather uniform from 3-6 ppb. The spatial distribution of the nitrate and sulfate initial conditions reflected the structure in the emissions of NO_x and SO₂, respectively. The surface O₃ initial concentrations were low reflecting the high NO_x emissions over the entire modeling region. The boundary conditions for the fine grid domain were derived from the predictions of the coarse grid simulations.

The surface concentrations of sulfate and H₂O₂ at various times are shown in

Figures 10 and 11. The rain enters the domain around 14:00 on May 2nd and is completed by 6:00 on May 3rd. The sulfate and H₂O₂ surface concentrations reflect the rain patterns, with low values during the rain and the build up of concentration after the rain ends.

Results for the total wet deposition of selected species are presented in Figures 12 and 13. The most structure is seen in the nitrate deposition plot. There is high nitrate deposition in the northwest and southwest corners of the domain, reflecting the emissions distribution and the general flow patterns. The sulfate deposition plot shows a much more uniform distribution from east to west.

SO₂ Emissions



SO₂ Emissions(P)

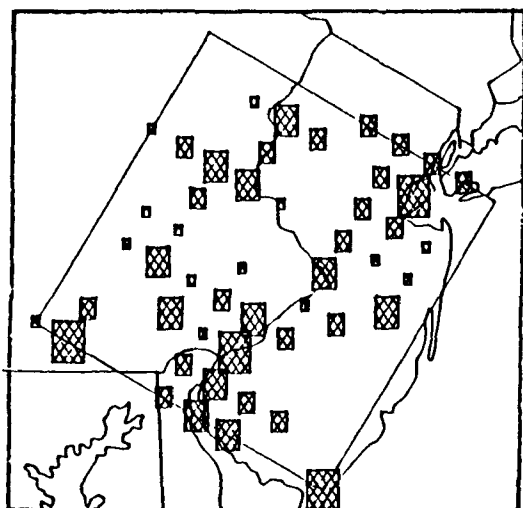


Figure 5. Elevated point sources (at level 2 corresponding to a height 200 m) and area emissions for SO₂.

The uniformity in the wet deposition is reflected by the situation that the gas phase concentrations of nitric acid and sulfate in the high source regions are only 20-30% higher than those in the rural areas in spite of the fact that the concentrations of the primary pollutants are 5-10 times higher.

Further details of the deposition at the New Jersey measurement sites and the Pennsylvania sites can be seen by examining the deposition as a function of time at grid points (8,2) and (4,8) (see Figure 3). The time profiles of surface gas phase and rain phase concentrations of

selected species are presented for comparison in Figure 14. The New Jersey site is an area of low NO_x and SO_x sources and for the meteorological conditions on May 2nd the wind direction is from the east; thus, relatively clean air is passing to this site through the eastern boundary. Precipitation occurs at this grid point for the first 16 hours of the event. The rain phase concentrations at this grid point show that the soluble pollutants are removed rapidly by the initial rain and that the bulk of the deposition loading occurs in the first hour of the rain event. The liquid phase concentrations of

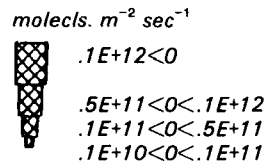
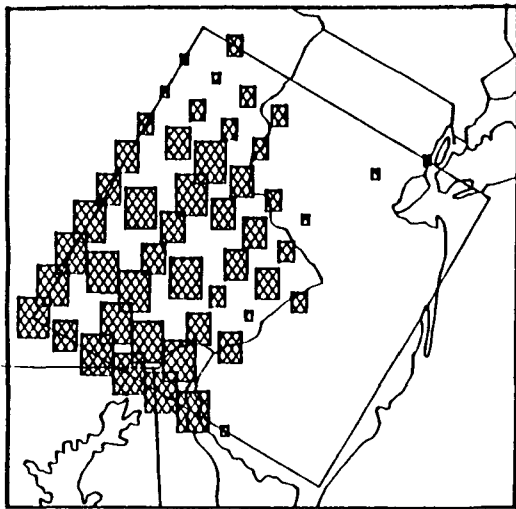
nitrate and H⁺ build up beginning at 5:00 LT on May 3rd. This corresponds to the time that the wind shifts to a northeasterly flow transporting the polluted air mass from New York.

The Pennsylvania site (grid point (4,8)) is located in a region with high SO_x and NO_x emissions. The site is also downwind of major sources throughout the meteorological conditions of May 2nd, 1985. Precipitation began at this site at 17:00 LT May 2nd and continued until 4:00 LT on May 3rd. The time profiles of liquid phase concentrations at this site are also presented in Figure 14. The time profiles are quite different than those at the New Jersey site. The liquid phase concentrations of most species reach maximum values at 19:00 LT. The sulfate and nitrate concentration maximums are about 150 μM. The liquid phase concentration profiles of H₂O₂ and bisulfite show opposite trends. The H₂O₂ is high initially and decreases as time progresses. This indicates that at early times H₂O₂ is present in excess of bisulfite, and the bisulfite is consumed by the reaction with H₂O₂ to produce sulfate. At later times the H₂O₂ is depleted from the system and the bisulfite concentration increases. The gas phase profiles (not shown) indicate that gaseous H₂O₂ is depleted from the area by 22:00, whereas gaseous SO₂ is maintained by local emissions.

The total deposition at the two sites is also plotted. The total H⁺ deposition is about 1500 μmole/m² at the Pennsylvania site and ~ 1000 μmole/m² at the New Jersey site. The nitrate deposition exceeds the sulfate deposition at each point.

Budget calculations for various processes over the modeling domain for the 18 hour simulation are presented for HNO₃, sulfate and SO₂ in Figure 15. These results provide useful insights into the relative importance of various processes. The SO₂ inventory shows that local emissions during the 18 hour period is equivalent to about 1/3 of the mass of SO₂ initially present. (Furthermore, the net advection (i.e., inflow-outflow) into the region is equivalent to about 1/3 of the amount emitted.) The wet deposition and dry deposition are of equal importance and together are equivalent in magnitude to the emissions. The wet removal processes consist of wet deposition of S(IV) at the surface and the conversion of S(IV) to sulfate in cloud and rain water. As indicated, the importance of liquid phase transformation of S(IV) is much more important than the gas phase reactions of SO₂. The predominant liquid

Ammonia Emissions



Ammonia Emissions(P)

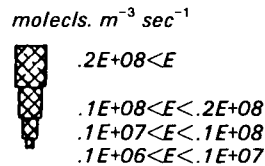
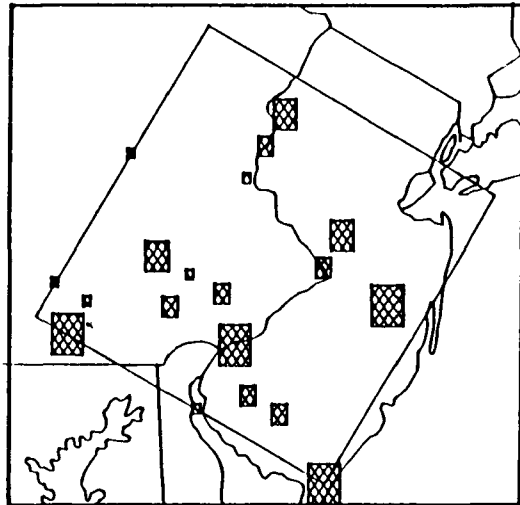


Figure 6. Elevated point sources (at level 2 corresponding to a height 200 m) and area emissions for ammonia.

phase reaction for this simulation is the reaction of S(IV) with H_2O_2 to produce sulfate. The inventory for sulfate reveals that the contribution of primary emissions is very small, that wet deposition is much more important than the dry deposition process for this event, that sulfate production by liquid phase processes greatly exceeds that in the gas phase, and that an appreciable fraction is transported out of the model domain. (The net advection term for sulfate is negative.) The nitrate inventory is similar to that for sulfate except that the gas phase production of nitric acid domi-

nates. Also, for nitrate the net advection of mass is out of the model domain.

Nested Grid Capabilities

The results discussed previously indicate that the deposition on the mesoscale is strongly influenced by the transport of material into the region. In order to better specify the flux of materials into the mesoscale area of interest we are planning to use a regional-scale model simulation to provide boundary conditions for the MesoSTEM model. A one-way nesting of a regional-scale version of STEM-II with the MesoSTEM model

is planned. The regional scale grid system is shown in Figure 16. The regional scale study of precipitation scavenging using STEM-II is being conducted for Battelle Pacific Northwest Laboratories in conjunction with the PRECP program. The meteorological fields are being obtained by objective analysis using radiosonde data and gridded precipitation is prepared objectively using a program developed by David Powell at PNL. There are two options available for the regional scale simulations. One option is to use the same detailed version of STEM-II for the regional simulation that is used for the mesoscale simulations. The other option is to use an "engineering" version of STEM-II for the regional simulation. The engineering version of STEM-II has the same numerics and treatment of wet removal processes, but utilizes a simplified chemical mechanism. The engineering model executes about 10-20 times faster than the detailed version of STEM-II. For either option, the regional simulation is done first and output files are used to specify the boundary input files for a separate simulation of STEM-II on the mesoscale.

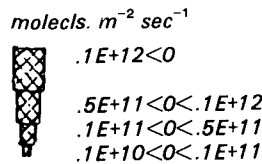
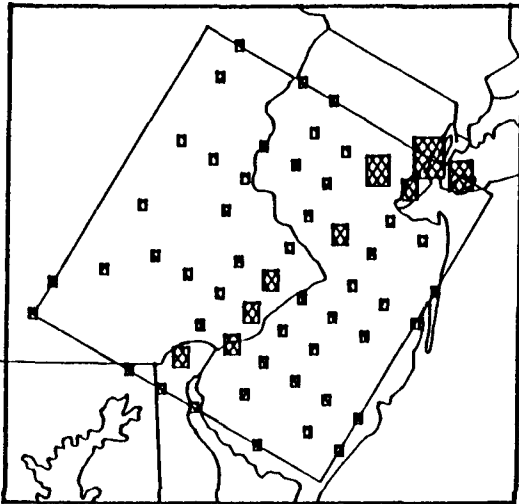
The engineering version of the model is currently undergoing extensive testing. The regional scale meteorological fields will be available by early summer, and regional scale simulations for the May 2nd and 3rd, 1985 conditions from both options will be available this summer.

Simulation Execution Times

The fine grid simulation utilizing 1400 grid points requires 4.5 CPU hours on NASA Langley Cyber VPS 32 per 18 hours simulated. The STEM-II plus ASM model was transferred to the VPS 32 machine and optimized. It was found that option - 0 with the FORTRAN compiler was the best. The following timing profile was obtained for the May 2nd and 3rd simulation.

ion concentration calculation	28%
aqueous phase mass transfer	30%
aqueous phase transport	6%
gas phase reaction	9%
aqueous phase reaction	10%
gas phase transport	<1%
input, output, bookkeeping, print ...	
traffic control	16%

SO_4^- Emissions



SO_4^- Emissions(P)

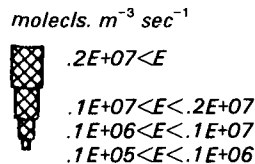
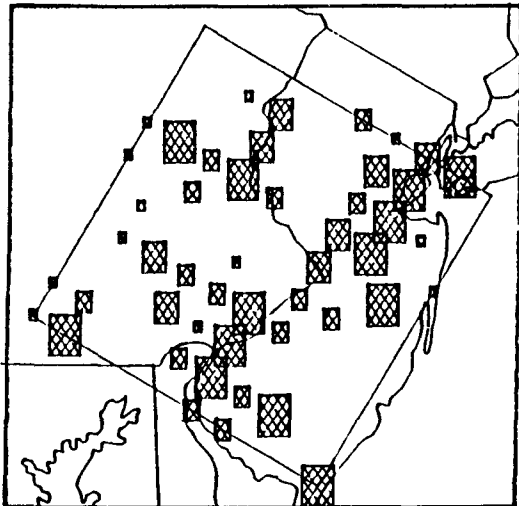


Figure 7. Elevated point sources (at level 2 corresponding to a height 200 m) and area emissions for SO_4^- .

Philadelphia field data. Coarse grid simulations have been examined and analyzed in detail, and sensitivity runs and a fine mesh simulation have been completed and are currently being analyzed. The coarse and fine mesh simulations, in addition to providing insights into the processes affecting acid deposition in mesoscale precipitation events, will also provide valuable information as to the effect of horizontal and vertical grid resolution on model predictions.

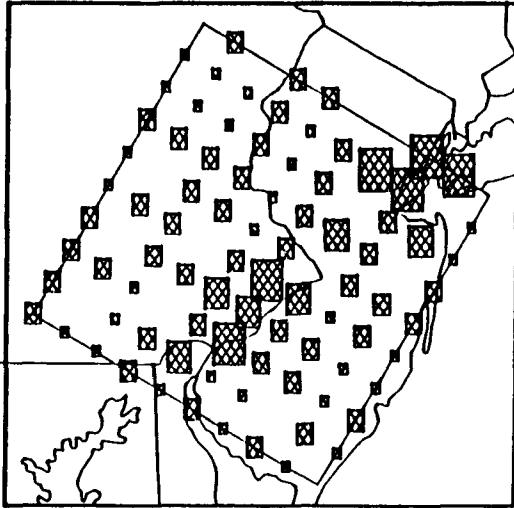
The major efforts for the next project period will be the application of the one-way nested version of the model (to provide boundary conditions for the MesoSTEM application) and the analysis of two additional data sets corresponding to the April 4, 1984 and December 3, 1984 Philadelphia field studies.

As indicated 83% of the CPU time is spent performing the chemistry calculations with 58% spent in the ion concentration and the aqueous phase mass transfer. Work on increasing the execution speed must focus on these subroutines. Work was conducted investigating the possibility of using half-word (32 bit) arithmetic. This could speed up the current code by 20-30%, with little degradation of the precision of the final results.





Summary

The major activities related to the use of the STEM-II model in the Mesoscale Acid Deposition Project have been summarized in this progress report. The installation of the STEM-II model on the NASA Langley Cyber VPS machine and the interface with the MASS model has been completed. The MesoSTEM model framework has been applied to the analysis of the May 2nd and 3rd, 1985

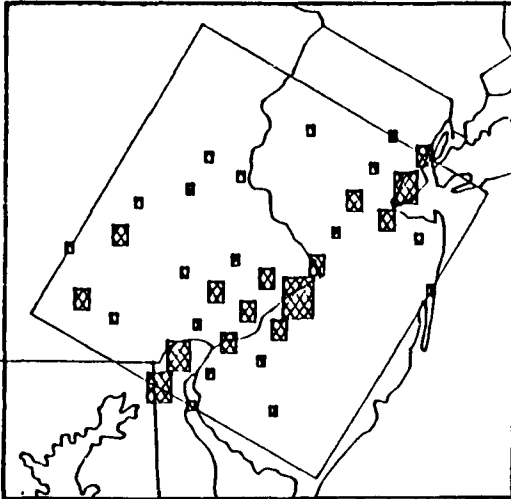
Toluene Emissions



molecls. $m^{-2} sec^{-1}$

-  $.1E+12 < 0$
-  $.5E+11 < 0 < .1E+12$
-  $.1E+11 < 0 < .5E+11$
-  $.1E+10 < 0 < .1E+11$

Toluene Emissions(P)



molecls. $m^{-3} sec^{-1}$





-  $.2E+07 < E$
-  $.1E+07 < E < .2E+07$
-  $.1E+06 < E < .1E+07$
-  $.1E+05 < E < .1E+06$

Figure 8. Elevated point sources (at level 2 corresponding to a height 200 m) and area emissions for toluene.

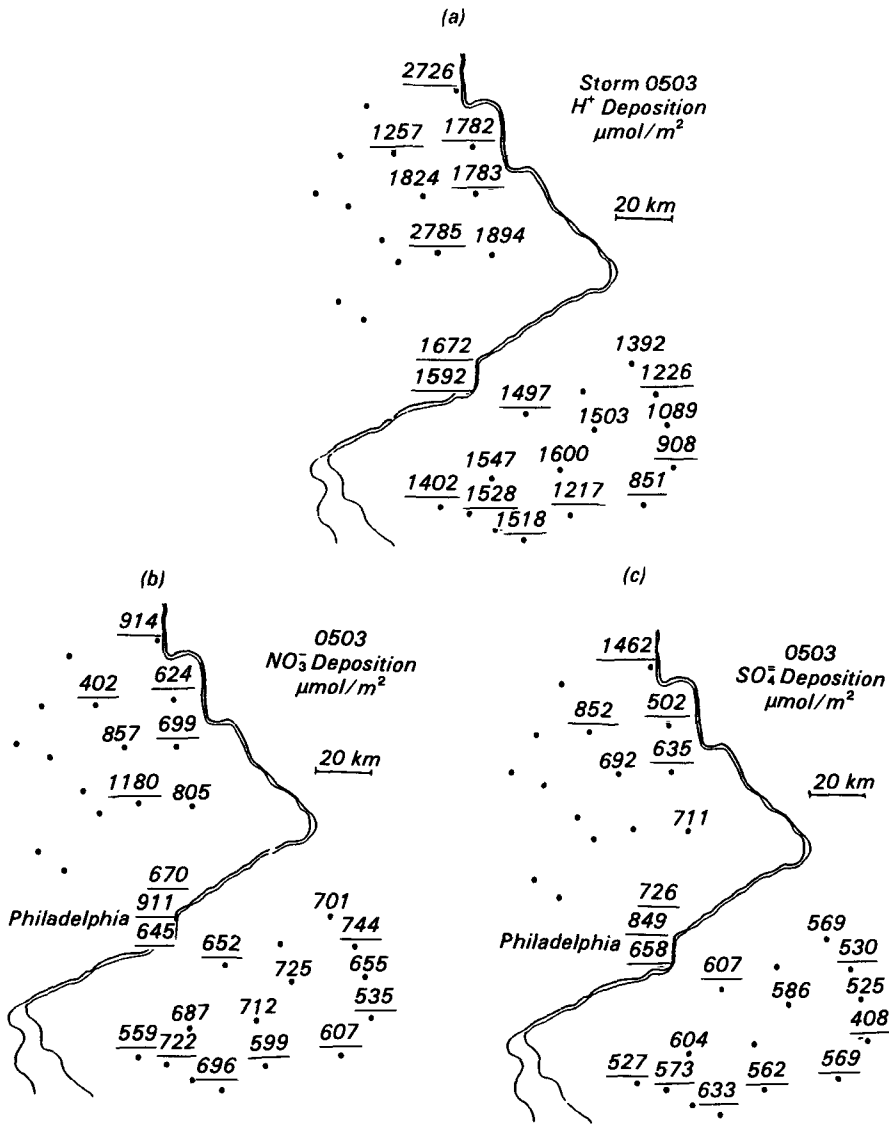
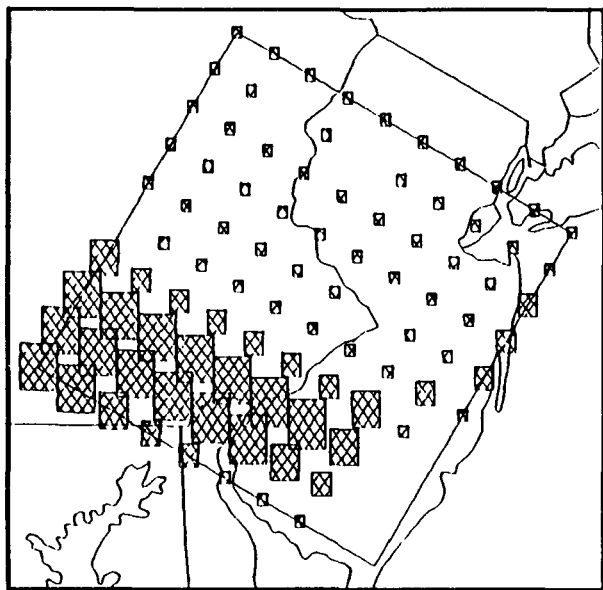
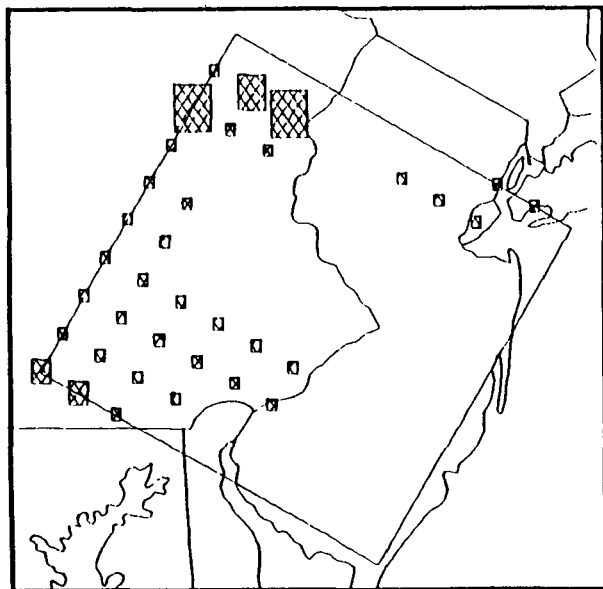
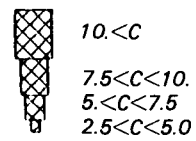


Figure 9. Measured total deposition of (a) H^+ , (b) HNO_3 , and (c) SO_4^{2-} . The underlined values are for manually deployed bottle-funnel collectors and the others are for automatic wetfall collectors.



(a)

ppb



(b)

ppb

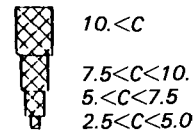
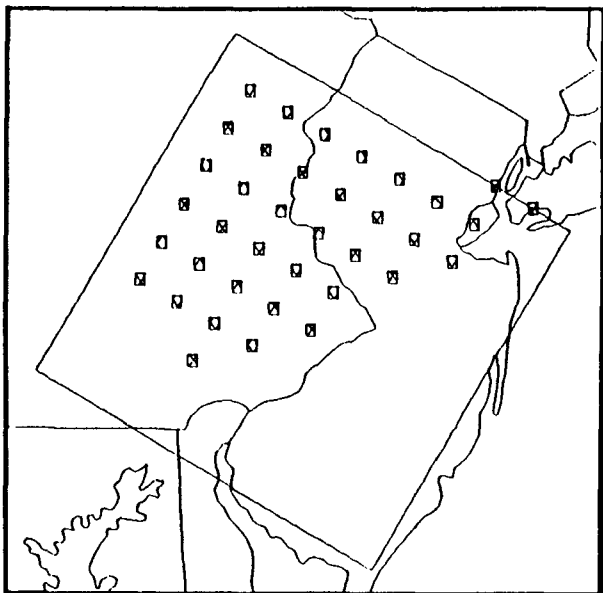


Figure 10. Ground-level aerosol SO_4^{2-} concentration at (a) 2 p.m., (b) 4 p.m., (c) 2 a.m., and (d) 8 a.m.



(c)

ppb

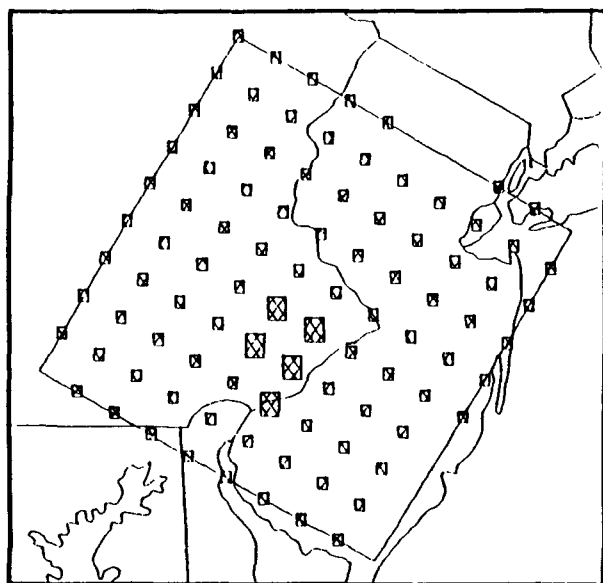


10.<C

7.5<C<10.

5.<C<7.5

2.5<C<5.0



(d)

ppb



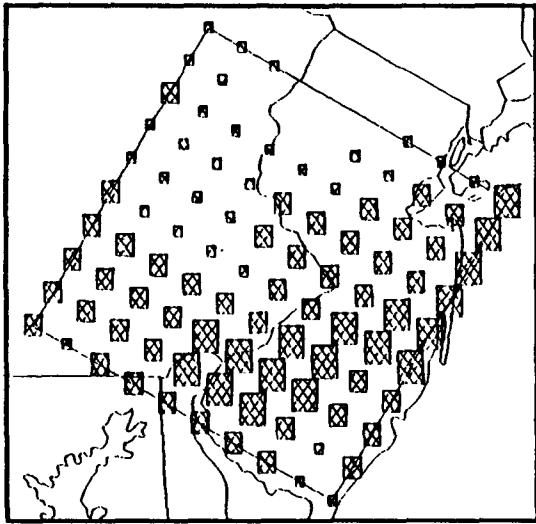
10.<C

7.5<C<10.

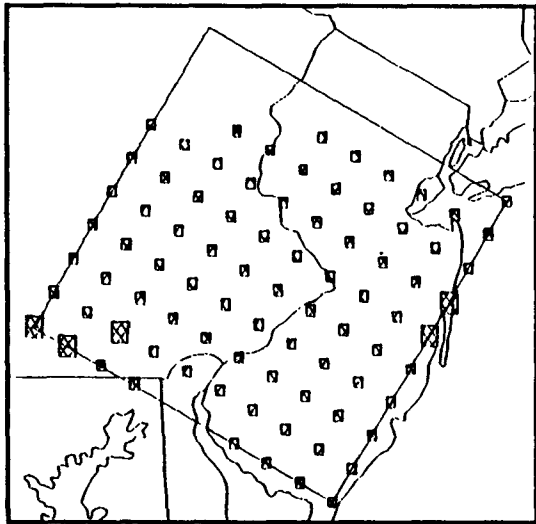
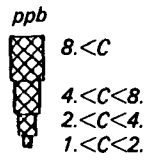
5.<C<7.5

2.5<C<5.0

Figure 10. (continued).



(a)



(b)

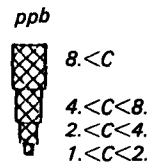
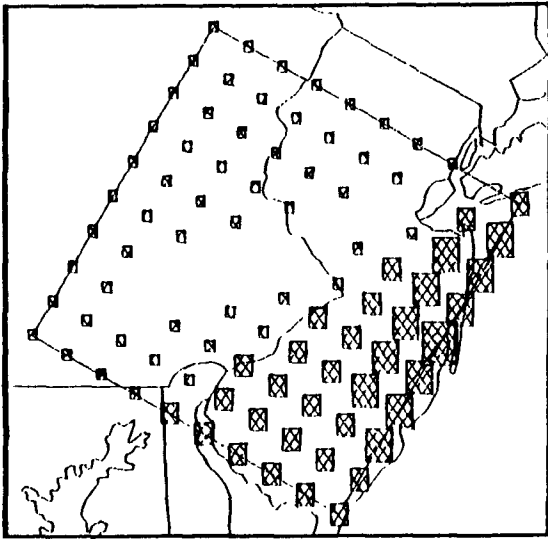
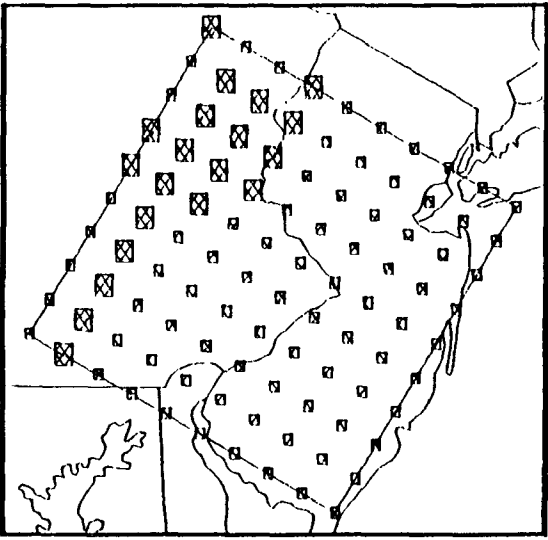
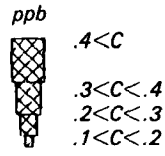


Figure 11. Ground-level gas phase H_2O_2 concentration at (a) 2 p.m., (b) 4 p.m., (c) 2 a.m., and (d) 8 a.m.



(c)



(d)

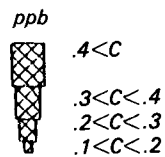


Figure 11. (continued).

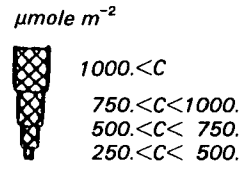
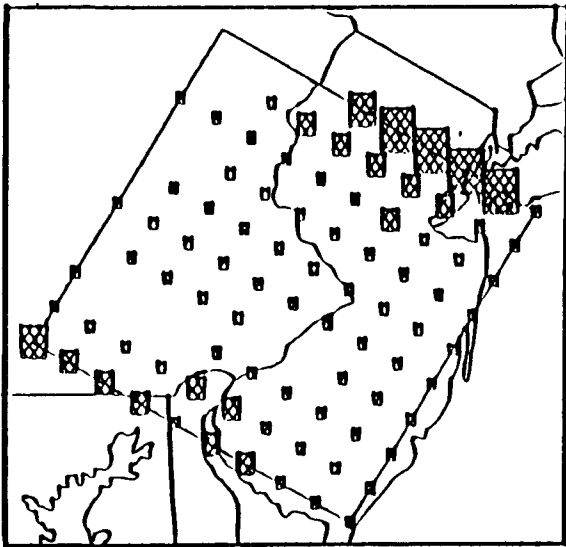
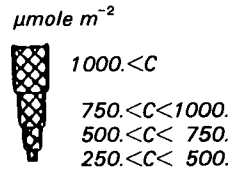
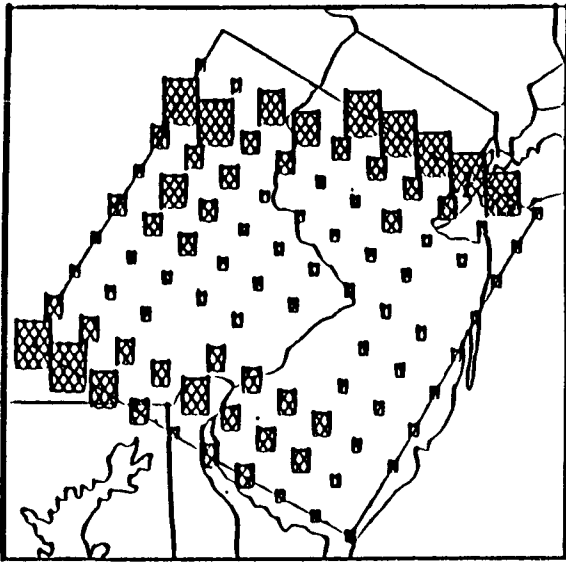


Figure 12. Total 18 hour wet deposition amounts of nitrate (top) and sulfate (bottom) predicted by the fine grid simulation.

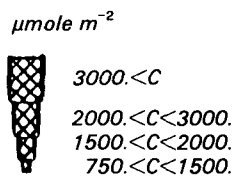
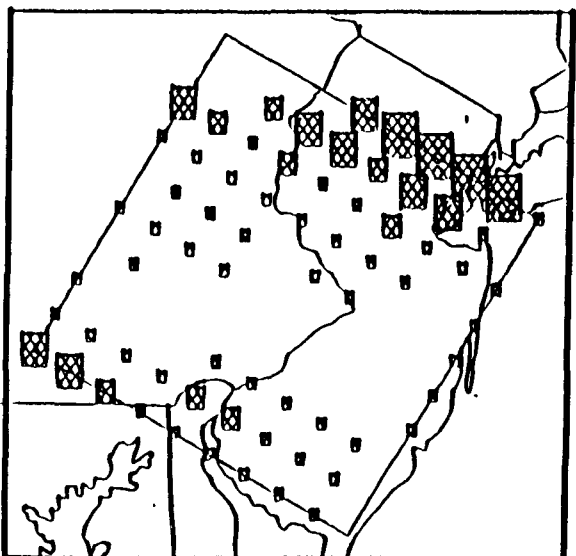
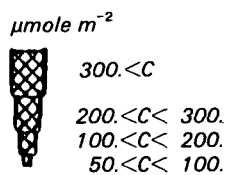
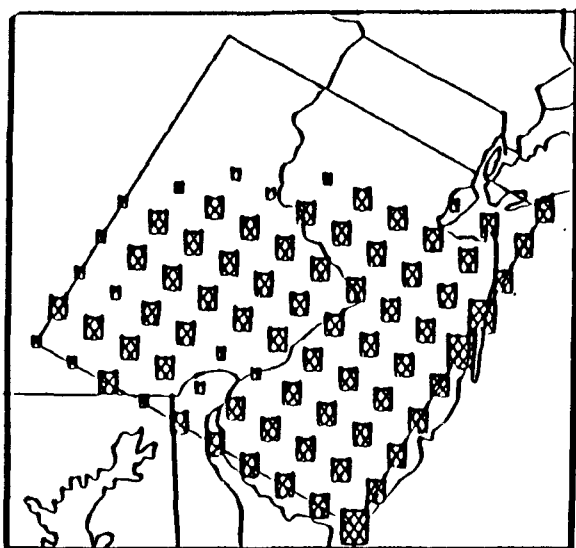


Figure 13. Total 18 hour wet deposition amounts of H_2O_2 (top) and H^+ (bottom) predicted by the fine grid simulation.

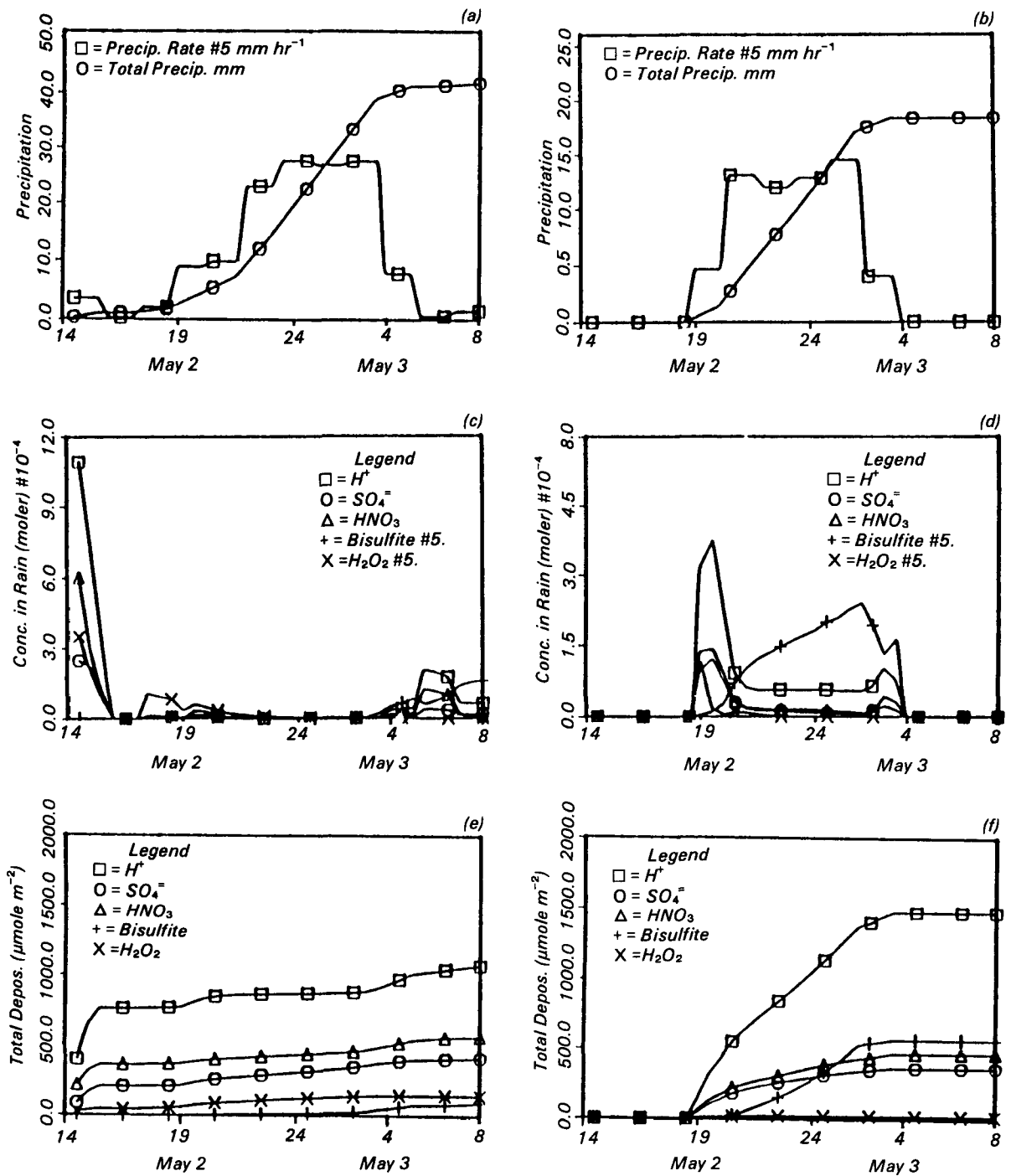


Figure 14. (a) Precipitation field at grid (8,2), (b) precipitation field at grid (4,8), (c) rain water concentrations at grid (8,2), (d) rain water concentrations at grid (4,8), (e) cumulative deposition at grid (8,2), and (f) cumulative deposition at grid (4,8).

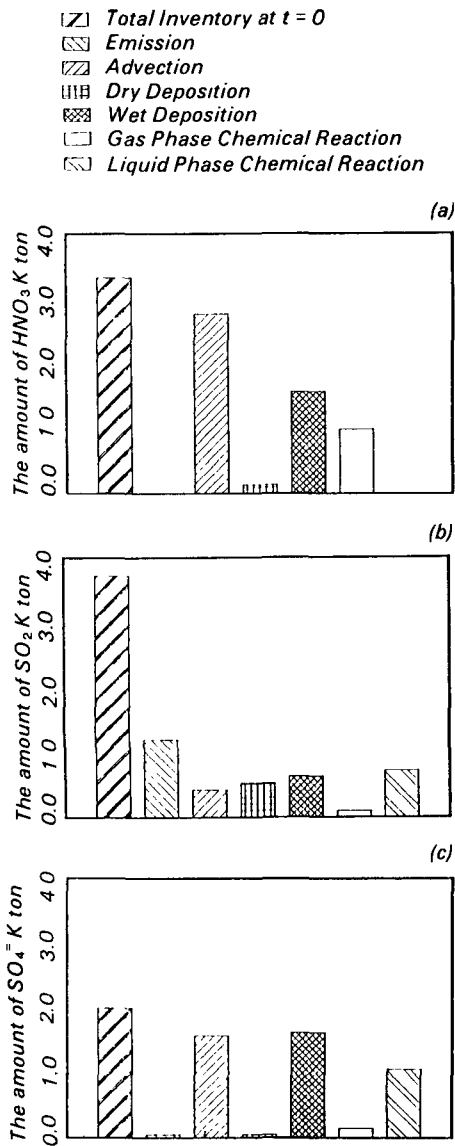


Figure 15. Budget calculations for (a) HNO₃, (b) sulfate and (c) SO₂

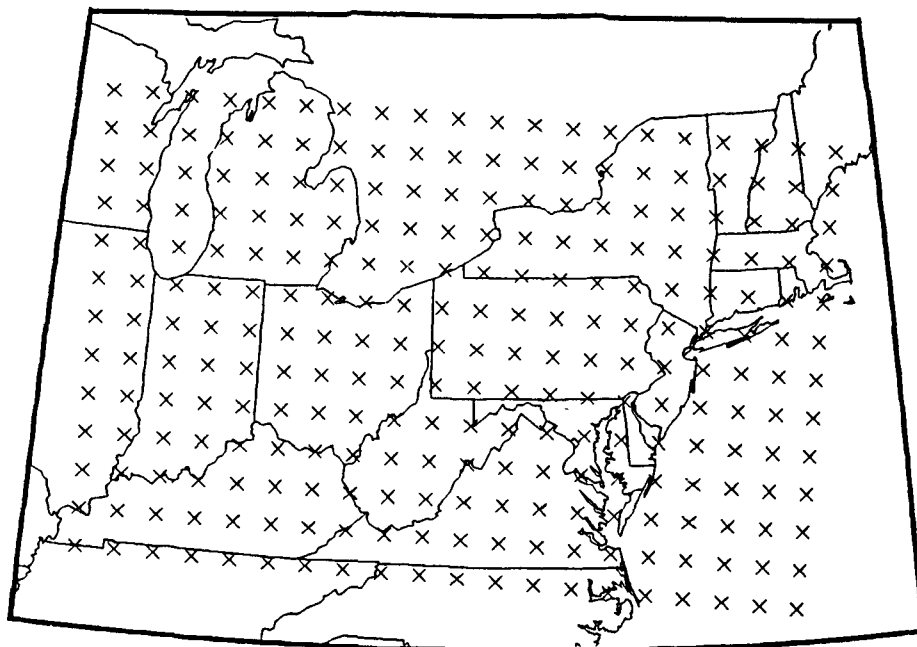


Figure 16. Grid systems for the regional scale simulation.

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The complete report, entitled "A Mesoscale Acid Deposition Model: Preliminary Applications and a Guide for User Interface," (Order No. PB 87-227 658/AS; Cost: \$18.95, subject to change) will be available only from:

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