Evaluation of the Emission, Transport, and Deposition of Mercury, Fine Particulate Matter, and Arsenic from Coal-Based Power Plants in the Ohio River Valley Region

Semi-Annual Technical Progress Report for the Period April 3, 2005–October 2, 2005

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Ohio University
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PROJECT ABSTRACT

Ohio University, in collaboration with CONSOL Energy, Advanced Technology Systems, Inc (ATS) and Atmospheric and Environmental Research, Inc. (AER) as subcontractors, is evaluating the impact of emissions from coal-fired power plants in the Ohio River Valley region as they relate to the transport and deposition of mercury, arsenic, and associated fine particulate matter. This evaluation will involve two interrelated areas of effort: ambient air monitoring and regional-scale modeling analysis.

The scope of work for the ambient air monitoring will include the deployment of a surface air monitoring (SAM) station in southeastern Ohio. The SAM station will contain sampling equipment to collect and measure mercury (including speciated forms of mercury and wet and dry deposited mercury), arsenic, particulate matter (PM) mass, PM composition, and gaseous criteria pollutants (CO, NOx, SO_2, O_3, etc.). Laboratory analysis of time-integrated samples will be used to obtain chemical speciation of ambient PM composition and mercury in precipitation. Near-real-time measurements will be used to measure the ambient concentrations of PM mass and all gaseous species including Hg^0 and RGM. Approximately of 18 months of field data will be collected at the SAM site to validate the proposed regional model simulations for episodic and seasonal model runs. The ambient air quality data will also provide mercury, arsenic, and fine particulate matter data that can be used by Ohio Valley industries to assess performance on multi-pollutant control systems.

The scope of work for the modeling analysis will include (1) development of updated inventories of mercury and arsenic emissions from coal plants and other important sources in the modeled domain; (2) adapting an existing 3-D atmospheric chemical transport model to incorporate recent advancements in the understanding of mercury transformations in the atmosphere; (3) analyses of the flux of Hg0, RGM, arsenic, and fine particulate matter in the different sectors of the study region to identify key transport mechanisms; (4) comparison of cross correlations between species from the model results to observations in order to evaluate characteristics of specific air masses associated with long-range transport from a specified source region; and (5) evaluation of the sensitivity of these correlations to emissions from regions along the transport path. This will be accomplished by multiple model runs with emissions simulations switched on and off from the various source regions.

To the greatest extent possible, model results will also be compared to field data collected at other air monitoring sites in the Ohio Valley region, operated independently of this project. These sites may include (1) the DOE National Energy Technologies Laboratory's monitoring site at its suburban Pittsburgh, PA facility; (2) sites in Pittsburgh (Lawrenceville) PA and Holbrook, PA operated by ATS; (3) sites in Steubenville, OH and Pittsburgh, PA operated by U.S. EPA and/or its contractors; and (4) sites operated by State or local air regulatory agencies. Field verification of model results and predictions will provide critical information for the development of cost effective air pollution control strategies by the coal-fired power plants in the Ohio River Valley region.

EXECUTIVE SUMMARY

Ohio University is performing a Cooperative Agreement with the U.S. Department of Energy's National Energy Technology Laboratory (DOE-NETL) to conduct regional-scale modeling analysis and ambient air monitoring that will provide critical information for the development of relevant and cost effective control strategies by the coal-fired power plants in the Ohio River Valley region.

The regional modeling studies will develop a comprehensive budget of arsenic, elemental mercury (Hg^0) reactive gaseous mercury (RGM), and fine particulate matter across the Ohio Valley region, including sources, sinks, atmospheric lifetimes, burdens, and advective fluxes. Updated emissions inventories for mercury and arsenic within the region will be developed to support the regional modeling studies. A comprehensive surface air monitoring (SAM) site is being developed and operated in southeastern Ohio to provide field data against which the model results can be compared. The SAM has the capability to monitor mercury speciation in ambient air and in precipitation, and it contains a full range of instrumentation for measuring the composition of fine particulate matter and co-pollutant gases. Short-term and seasonal simulations with the refined model will be compared to field measurements from the monitoring site, and the results will be used to develop a decision-support tool. A supplemental objective of the analysis is to evaluate the impacts of long-range transport from regions outside the Ohio Valley as well as biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury concentration levels in the Ohio Valley region.

The Cooperative Agreement began in April of 2003. A six month no cost extension to the original 27 month performance period has been approved. This extends the project through December of 2005. The effort has been broken down into seven separate tasks as follows:

Task 1 consists of establishing and operating the SAM site in southeastern Ohio. The SAM site has been set up and routine sampling was initiated on March 1, 2004; data collection will occur over the following 18 months.

Task 2 consists of the selection and evaluation of a 3-D regional-scale chemical transport model (CTM) for an application focused on the Ohio River Valley region. The Chemical Transport Model CMAQ (Community Multiscale Air Quality) model has been set up and is operational. A one-year base-case simulation has been completed for North America for the year 1996. The results from this assessment were presented in the last report (refer to Semi-Annual Technical Report # 4).

Task 3 involves the refinement and update of emission inventories (EIs) for sources of mercury and arsenic within and upwind of the modeled domain. The Institute for Sustainable Energy and the Environment (ISEE) plans to collect and process that emissions information into the model structure throughout the modeling effort.

Task 4 consists of short-period model runs to be made for comparison with field data. The summer of 2001 has been used for initial comparisons because of the extensive field data on particulate matter, and co pollutants available from the DOE sponsored Pittsburgh Air Quality Study. The ambient monitoring fine particulate data (PM sulfate and PM nitrate) from the Pittsburgh site and other EPA-sponsored air quality sites have been used to calibrate the short-

term atmospheric chemistry model (refer to Semi-Annual Technical Report # 3). Short-term model runs for comparison with the speciated mercury and arsenic data collected at the SAM for the 2004 sampling periods will follow these initial comparisons.

Task 5 involves seasonal-scale simulations focusing on the identification of significant sources and source regions contributing to the deposition of mercury and ambient concentrations of arsenic and fine particulate matter over periods of several months or more. To complete this task, the project team is conducting seasonal photochemical modeling simulations for the summer of 2004. This is the time period during which the SAM site in Athens became operational. The quality and availability of these data are important in both the decision-making processes and the accuracy of the results arising from the air quality modeling applications. The meteorological modeling simulations are one of the most significant components of this task since the simulated meteorological variables are an essential part to the photochemical model. The research team has been conducting meteorological model simulations for the months including July through September, 2004. The results from this model evaluation have been presented in Section 5. The modeling will also examine the efficacy of emission reduction strategies specifically for coal-fired power plants. In addition, researchers will conduct an analysis of long-range transport from regions outside the Ohio Valley and biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury in the Ohio Valley region.

Task 6 consists of the development of Web-based model interface technologies to provide industry and government agencies with a user-friendly decision-support tool to facilitate the evaluation of source-receptor relationships and the efficacy of emission reduction strategies. The framework for the Web-based GIS interface has been developed. Work on this task will continue throughout the remainder of this project.

Task 7 consists of project management, data analysis, and reporting functions.

Accomplishments and tasks completed during this reporting period include: (1) the conduction of meteorological simulations and analysis for 2004; (2) the continuation of refining and updating mercury and arsenic emission inventories for 2004; (3) the operation of a surface air monitoring station (SAM) at Athens, Ohio which uses sampling equipment for collecting and measuring mercury, arsenic, $PM_{2.5}$, pollutant gases, and weather data over the project period; (4) the development of a GIS Web-base interface for the decision support tool.

I. INTRODUCTION

Ohio University is performing a Cooperative Agreement with the U.S. Department of Energy's National Energy Technology Laboratory (DOE-NETL) to conduct regional-scale modeling analysis and ambient air monitoring that will provide critical information for the development of relevant and cost effective control strategies by the coal-fired power plants in the Ohio River Valley Region.

Coal flue gas contains a variety of hazardous air pollutants (HAPs), including organic and inorganic chemical compounds. Among the latter, the metals mercury and arsenic are of particular concern because of their toxicity to humans and animals. An understanding of the chemistry of these elements should be the basis of proposed legislation to regulate mercury and arsenic emissions since specific chemical species will account for differences in human toxicity, rate of transport through the ecosystem, and the design variations in possible emission control schemes. An additional layer of complexity results from the fact that these elements may or may not be associated with fine particulate matter ($PM_{2.5}$ and PM_{10}) during or after emission from a stack. In general, the less volatile species such as arsenic and oxidized mercury are likely to be associated with fine particulate matter while the more volatile moieties such as elemental or reduced mercury tend to be emitted as non-associated gases. Thus, it will be necessary to determine the chemical forms of mercury and arsenic present at the stack and at designated receptor sites, and to determine the fractions of these species bound to fine particulate matter.

Mercury, fine particulate matter, and arsenic can be transported over large distances due to their minimal rate of sedimentation. In particular, mercury transport must be considered a global problem. Elemental mercury is believed to have a half-life of approximately one year in the atmosphere, and little is known about its cyclic transport between land, water, and air. Biogenic transport and biogenic sources are even less well understood. Therefore, the ISEE will adopt a regional scale approach for adequate evaluation of source-receptor relationships for mercury, fine particulate matter, and arsenic. Our approach in evaluating the impact of arsenic and mercury emissions from coal-fired power plants and other sources is to examine the source-receptor relationship through ambient monitoring and regional scale modeling.

A. Project Goal and Objectives

The overall objective of the project is to quantitatively evaluate the emission, transport, and deposition of mercury, fine particulate matter (PM), and air toxics (arsenic) in the Ohio River Valley region. This evaluation involves two interrelated areas of effort: regional-scale modeling analysis and ambient air monitoring.

The objective of the regional modeling studies is to develop a comprehensive budget of arsenic, elemental mercury (Hg^0) and reactive gaseous mercury (RGM), and fine particulate matter including sources, sinks, atmospheric lifetimes, burdens, and advective fluxes across the Ohio Valley region. To support this objective, project researchers will develop updated emissions inventories for mercury and arsenic within the region. The second objective is to develop an air-monitoring site in Athens, Ohio to provide the capability to monitor mercury in ambient air and in precipitation. Researchers will compare the refined model's short-term and seasonal simulations to field measurements from the monitoring site and use the results to develop a decision-support tool. A supplemental objective of the analysis is to evaluate the impacts of long-range transport from regions outside the Ohio Valley as well as biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury concentration levels in the Ohio Valley region.

B. Project Development (Tasks)

Seven separate tasks will be completed over a 33-month performance period. A six month no cost extension to the original 27 month performance period has been requested. The following project schedule is based on a project start date of April 3, 2003. Table 1 on page 3 presents a progress summary for each task. Section II Experimental Design is a detailed description of each task and the progress achieved toward its completion as of April 2, 2005.

Project Schedule

- Task 1 consists of establishing and operating a Stationary Ambient Monitoring (SAM) site in Athens, Ohio. Routine sampling was initiated on March 1, 2004. Data collection will occur over the following 18 months.

Tasks 2–6 comprises the modeling process, which will continue throughout the first 30 months of the project. Throughout Tasks 2–6, the project team will keep abreast of ongoing research and newly published literature pertaining to the atmospheric behavior of mercury. Whenever possible, new findings concerning mercury speciation and transport will be incorporated into the model algorithms.

- Task 2 consists of the selection and evaluation of a 3-D regional-scale chemical transport model (CTM) for an application focused on the Ohio River Valley region. The project team has completed the setup and development of the CTM grid system and a one-year base-case simulation for the year 1996 has been conducted for North America.

- Task 3 involves the refinement and update of emission inventories (EIs) for sources of mercury and arsenic within and upwind of the modeled domain. It is anticipated that information on emissions will continue to be collected and processed into the model structure throughout the modeling effort.

- Task 4 consists of conducting short-period model runs for comparison with field data. A short-term modeling run has been completed for July 2001 for the eastern United States. The model run was conducted with the photochemical model CMAQ. The project team used particulate sulfate and nitrate data collected during the summer of 2001 from the DOE funded Pittsburgh Air Quality Study for initial comparisons. In addition short-term model runs for comparison with the speciated mercury and arsenic data collected at the Athens SAM for the 2004 sampling periods will be conducted.

- Task 5 involves seasonal-scale simulations that focus on the identification of significant sources and source regions contributing to the deposition of mercury and ambient concentrations of arsenic and fine particulate matter over periods of several months or more.

As a part of this ongoing process, the project team has set up a meteorological model MM5 model simulations for the summer of 2004. The results from the assessment of model simulations are presented in section 5. The modeling will also examine the efficacy of emission reduction strategies specific to coal-fired power plants. In addition, researchers will analyze the long-range transport from regions outside the Ohio Valley and the biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury in the Ohio Valley Region.

- Task 6 consists of the development of Web-based model interface technologies to provide industry and government agencies with a user-friendly decision-support tool to facilitate the evaluation of source-receptor relationships and the efficacy of emission reduction strategies. The frame work for the GIS Web interface has been completed. The development of the Web-based system will continue through the remainder of this project.

- Task 7 consists of project management, data analysis, and reporting functions.

Table 1 below is a progress summary for each task.

Table 1. Progress summary

Task #	Description	Planned % Completed	Actual % Completed
1	SAM	100	90
2	Base Case Simulation	100	100
3	Emission Inventories	100	70
4	Model Comparison	100	50
5	Seasonal Scale Simulations	100	40
6	Development of Support Tool	100	30
7	Project Management	100	65

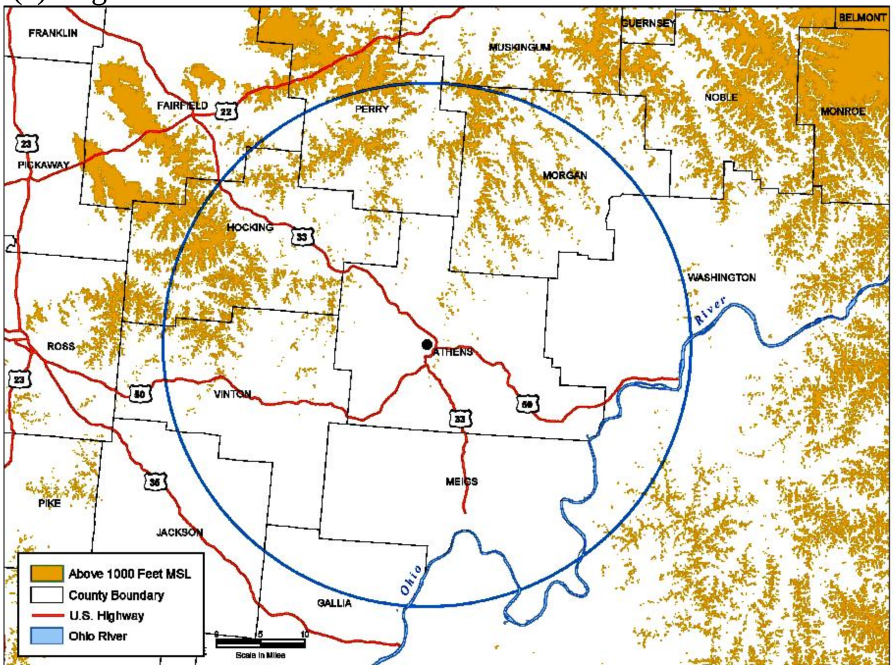
II. EXPERIMENTAL DESIGN

In this section, the description of each task is presented as it was proposed in the funding application. Following the description is a discussion of the progress made toward completing the task.

Task 1 - Establish and operate a (SAM) station in Athens, Ohio

The proposal for this project designated that the ISEE would establish a SAM station in Steubenville, Ohio. However, prior to April 3, 2003 the Environmental Protection Agency set up a SAM station in Steubenville that has the capacity to monitor for mercury. Consequently, the ISEE was able to select another site for the SAM station proposed for this project. The project staff located an optimal site south of Athens, Ohio in the heart of the Ohio River Valley. At an elevation of 950 feet, the site is the highest point within a 100-mile radius to the east, south, and west (Figure 1, page 4). It is an excellent site from which to capture the transport of pollutants into and out of the valley.

(a) Regional



(b) Local

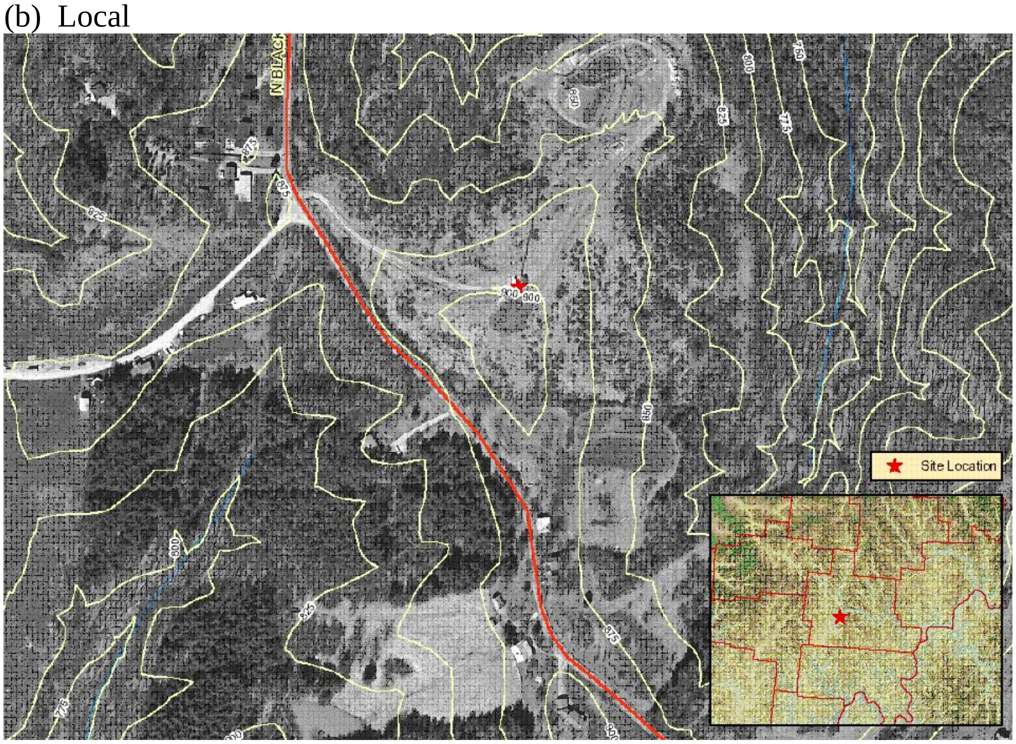


Figure 1. Topographical map of the Athens site: (a) regional and (b) local

The Athens site utilizes air-monitoring equipment from the Steubenville Comprehensive Air Monitoring Project (SCAMP), sponsored by DOE-NETL under Cooperative Agreement DE-FC26-00NT40771. In addition, the site includes sampling equipment to collect and measure mercury, including total, elemental, reactive, particulate, and wet/dry deposition.

Task 1: Ambient monitoring accomplishments from April 3, 2005 to October 2, 2005:

There were three primary objectives during this period:

- Maintain instrument operation
- Enhance data QA/QC recovery
- Disseminate preliminary data by attending conferences and preparing publications

Accomplishments by month:

April

- A site audit was scheduled with the Mercury Deposition Network (MDN) auditors to examine if the Athens monitoring site complied with network requirements and if Ohio University personnel were following specified sampling procedures. The audit was conducted on April 5, 2005. The auditors determined the Athens site was in compliance and there were no major problems. Procedures and equipment were in line with network guidelines and only a minor comment was logged in which a recommendation was made that the precipitation collector filter be changed and that tape be added to the rain channel.

- The $PM_{2.5}$ speciation sampler broke during the first week of April 2005. After numerous attempts to solve the problem, it was determined that components on some of the boards were destroyed and beyond repair. Several of the boards had evidence of melting. The cause was undetermined, but electrical problems or water damage was suspected. Thermo was unable to locate replacement parts. Manufacturing of this version of the sampler was discontinued shortly after purchase in 2000 and replacement parts were depleted. A back-up speciation sampler was supplied by the in-house DOE-NETL monitoring group. The sampler was transported to the Athens monitoring site in June 2005. However, this unit needed several repairs before being calibrated and placed into operation. The back-up speciation sampler resumed sampling on July 30.

- The gas analyzers operated properly all 30 days in April. Maintenance included the replacement of the savillex filters on April 7, 16, and 28. The performance of the analyzers was continuously checked every two days by comparing the calibration drift to the acceptable limits. This procedure continued throughout this reporting period. MFC Calibrations (1 and 2) occurred on April 5 and 6. All analyzers were then calibrated on April 6.

- The Tekran and ammonia sampler did well during the month. Regular maintenance and calibrations were performed according to the weekly and monthly schedules. Pump flow difficulties were experienced with the Tekran from April 6-8, but this situation was resolved with only minor data losses.

- There were no problems with the TEOM during the entire April – September reporting period. Filter changes occurred when necessary.

May

- As detailed in the previous report, the Federal Reference Method $PM_{2.5}$ sampler broke in late February 2005. From that time to early May 2005, the vendor, Thermo, was unable to resolve the problems via telephone support. As a result, a back-up FRM sampler was supplied by CONSOL and transported to the Athens monitoring site. The unit was calibrated and operational by late May 2005. The broken (primary) sampler was shipped back to Thermo for repair.

- All other instruments performed well during May 2005. Tekran voltage was too high on May 3, resulting in one day loss of data. Voltage was corrected. Gas analyzer filters changed on May 2, 11, and 25. All data was present.

June

- The back-up $PM_{2.5}$ speciation sampler was transported from CONSOL Energy in Pittsburgh to the Athens monitoring site in June. The original speciation sampler remains onsite and parts from it continue to be useful for the back-up unit.

- Materials including fan filters and aluminum tape were received from Frontier Geosciences to assist in correction of minor problems with the wet deposition collector. In addition, the Belfort rain gauge was mounted securely on a platform and level within one vertical foot of the opening of the wet deposition collector. The instrumentation is now fully in compliance with recommendations made during the April 2005 site audit. The Athens wet deposition site is now a formal site (OH-02) with the national mercury deposition network (MDN).

- Tekran, TEOM, and gases did well.

July

- The $PM_{2.5}$ Speciation unit needed several minor repairs before being calibrated and placed into operation. The back-up speciation sampler resumed sampling on July 30, 2005.

- Inspection at Thermo determined that the FRM $PM_{2.5}$ sampler was suffering from numerous operational and mechanical problems including a bent drive shaft of the carousel mechanism. The sampler was repaired by Thermo and returned to the site in July 2005. Currently two operational FRM samplers are available for use.

- A multi-point calibration was performed on the NO_x analyzer on July 6^{th} and on O_3 on July 25th. Changed savillex filters on the 6^{th} and 21^{st}. Instruments in good repair.

August

- On behalf of the research team, Steve Winter met with Don Martello and Natalie Pekney of DOE-NETL to explore preparing a joint publication. The focus of the publication would be examining spatial variability of ambient mercury in the Ohio Valley Region. The discussion centered on locating a time period in which DOE-NETL and Ohio University were both operating their Tekran sampling systems at the same time, in Pittsburgh and Athens, respectively. There existed only one month of data to examine, September 2004, and some of the DOE data were considered invalid. Although the outcome was not as anticipated, Natalie Pekney did agree to contact Yatavelli Reddy at a later date, to share and collaborate on mercury data issues and source apportionment techniques. It was agreed that this would be beneficial for both research groups.

- Routine maintenance occurred on Tekran, with proper operations observed.

- Calibrated SO_2 on August 18. Changed savillex filters on the 4^{th} and 17^{th}. All gas analyzer data was present.

September

- A problem began on September 3 involving the calibration on the O_3 analyzer. The analyzer would not allow itself to be calibrated. API advised there may be a leak in the system. However, no leak was found. API was scheduled to visit Athens in October and the O_3 would be one of the analyzers that they would repair and return to the laboratory for work if necessary. Therefore, valid O_3 data was collected on just 6 days in September. All other gas analyzers worked. Calibrations occurred for the NO_x analyzer on September 23. Calibrations for the CO and SO_2 analyzers occurred on September 27 and 28^{th} respectively.

- Steve Winter and Dan Connell made a site visit to Athens in late September to meet with Ohio University personnel. The meeting focused on data analysis, plume hit detection techniques, and measurement issues. In addition, comments were provided on Yatavelli Reddy's manuscript *Mercury, $PM_{2.5}$ and Gaseous Co-Pollutants in the Ohio River Valley Region: Preliminary Results from the Athens Supersite*, which will be submitted to the journal Atmospheric Environment.

- Dan Connell provided Ohio University with an examination of potential mercury plume hits originating from the PPG Natrium Plant. The analysis will be explored further by the research team for possible inclusion in a future publication dealing with detection of mercury plumes from sources in the Ohio Valley.

- On September 1, a problem with the pump flow rate developed in the Tekran system and blockage was removed from the sample path. In addition, lamp voltage went out of range. The situation was resolved with one day of data lost.

Additional Items

- Focused efforts by Ohio University and CONSOL Energy R&D reduced almost all of the sampling data (Tekran, TEOM, gases, meteorological, mercury deposition, FRM, and Speciation through the end of July 2005. This brings the majority of the data validation and data reduction phases current (Kevin: not sure what this means).

- As of the end of September 2005, analytical activities completed were as follows:
  - 50 denuders have been coated for mercury sampling.
  - Approximately 960 filters have been pre- and post-weighed for PM sampling.
  - 300 quartz filters were analyzed for carbon species.
  - 110 Teflon filters were extracted and analyzed for ions.
  - 20 filters were analyzed for trace elements. Resuming analysis is planned for early 2006, once a few method issues are resolved.

- Thermo provided little useful technical support with the $PM_{2.5}$ samplers. Numerous complaints and follow-ups were logged with Martin Abbott, the Ambient Products Group National Sales and Service manager. It is strongly recommended in the future to ship the sampler back to Thermo to repair rather than using phone support. This may help contain data losses to a minimum. These instruments are currently discontinued and replacement parts hard to find.

- A meeting was held among CONSOL Energy R&D staff to try to reduce background blank concentrations relative to the Athens sample concentrations for trace elements. Based on a very limited data set (~ 20), the concentration of trace elements in Athens appear to be much lower, about 1/3, of what was measured in Steubenville making the blank more significant. An action plan was formalized in the meeting. The plan includes comparing the use of Optima ultra-pure nitric acid versus trace grade, reducing the concentration of the standards used for calibration, minimizing any exposure to metallic components by preparing samples and standards in dedicated polypropylene hoods, and further optimizing the ICP-MS DRC gas parameters.

<u>Task 2 - Evaluate and Select a 3-D Regional-Scale Atmospheric Chemical Transport Model (CTM) and Conduct a Base-Case Simulation</u>

Several 3-D regional-scale CTMs with the ability to simulate tropospheric ozone, visibility, and fine particulate matter are appropriate for application to the Ohio River Valley region to evaluate total fine particulate matter mass and the arsenic component of fine particulate matter. The ISEE and Atmospheric and Environmental Research (AER) have established the 3-D modeling framework. AER completed a base-case model simulation for the year 1996.

The project team chose the Community Multi-Scale Air Quality (CMAQ) model for air-pollution studies on a regional scale for this study. The EPA and its collaborators (Byun & Ching, 1999) developed the CMAQ, which uses non-hydrostatic Penn State/NCAR mesoscale model (MM5) V3-derived dynamics for transport.

Task 2 accomplishments through October 2, 2005

- Conducted an annual simulation for 1996 using the modified CMAQ-Hg code with the MEBI chemistry solver. The modeling year was divided into four 3-month periods (Jan-Mar, Apr-Jun, Jul-Sep, Oct-Dec) and 3-month simulations were conducted on different processors to speed up the overall completion of the annual simulation. A 10-day spin-up cycle was used for each 3-month simulation period. Each simulation day requires about 3 hours of CPU time.
- The seasonal boundary conditions from the global mercury chemistry transport model were applied as follows for the 3-month simulation periods:
  - Winter boundary conditions: January, February, and December
  - Spring boundary conditions: March, April, and May
  - Summer boundary conditions: June, July, and August
  - Fall boundary conditions: September, October, and November
- The version of the CMAQ-Hg code used in these simulations also included modifications to calculate and save the daily cumulative dry and wet deposition amounts and daily average concentrations of Hg (the default model only saves the hourly values).

The results from the model evaluation of CMAQ-Hg for 1996 annual simulations were presented in the last DOE report. The appraisal of the model was done solely on the basis of the wet deposition flux, and those observations were obtained from the mercury wet deposition sites.

The project team plans to carry out further air quality modeling simulations for the summer of 2004. The output from this CMAQ-Hg model run will be measured additionally against observations of elemental, reactive and particulate mercury from the DOE-NETL sponsored observational sites at Athens and Steubenville. This would give the project team the ability to understand whether the model can reasonably quantify the atmospheric mercury levels in addition to adequately estimating the deposition fluxes.

The emissions input to the new CMAQ-Hg runs for 2004 would include an enhanced global emissions inventory consisting of a new emissions inventory of mercury for China, which supposedly emits high levels of mercury. The China inventory, coupled with an innovative global model, will provide a fresh assessment of the relative contributions of local and distant sources to mercury deposition in Ohio.

Finally a new version of CMAQ-Hg will be used for the 2004 modeling simulations. Five new natural sources of mercury emissions have been added to the modified Community Multiscale Air Quality-Mercury (CMAQ-Hg) modeling system. An annual deposition of mercury from a previous CMAQ simulation was used to develop an annual inventory for “recycled” oceanic and land-mercury emissions. These two inventories were likewise scaled based on solar radiation and temperature. Code was developed to create model-ready emissions for these four sources. This new version of CMAQ-Hg will become operational in 2006.

Task 3 – Refine and Update Emission Inventories (EI's)

Advanced Technology Systems, Inc. (ATS) is enhancing the mercury and arsenic emission inventories.

Task 3 accomplishments from April 3, 2005 to October 2, 2005:

- Continued the refinement of the mercury emissions. ATS is currently working with Ohio University to integrate the updated mercury emissions into the emission inventories for CMAQ simulations.
- In addition we are currently working with David Streets at Argonne National Laboratory, under a separate project, to incorporate updated China emissions for the global model.

Task 4 - Perform Short-Period Model Runs for Comparison with Field Data

ISEE will conduct a series of model runs to evaluate the system against field observations. The model run will correspond to the NETL-sponsored intensive sampling campaigns centered in Pittsburgh, Pennsylvania. Researchers will combine the extensive datasets collected during this campaign with other relevant datasets in this region. Meteorological input data for these simulations will be derived diagnostically using MM5 V3. The model evaluations will involve short-time-period runs for the field-intensive periods, storing hourly averaged fluxes and production-and-loss rates for ozone, hydrocarbons, arsenic, Hg^0, and RGM for direct comparison with field data. In addition, long-range transport events will be identified from the short-term CTM runs and evaluated with the observational data set.

In addition to the model evaluations conducted from field observations obtained from the 2001 NETL-sponsored sampling campaigns, the model will be set up and evaluated against the observational data sets, including the speciated mercury and arsenic data collected at the Athens SAM for the 2004 sampling period. These simulations will be vital for model verification because the Athens SAM will be one of the few sites providing measurements on individual mercury species and arsenic. The model evaluations will involve short-time-period runs for the field-intensive periods, storing hourly averaged fluxes and production-and-loss rates for ozone, hydrocarbons, arsenic, Hg^0, and RGM for direct comparison with field data. In addition, long-range transport events will be identified from the short-term CTM runs and evaluated with the observational data set.

Task 4 accomplishments through October 2, 2005:

- Work is underway to perform regional and urban modeling simulations for 36-, 12-, and 4-km-grid resolutions for the year 2004. The 36-km grid will cover most of Eastern

United States, whereas the 4-km domain will cover all the power plants in the Ohio River Valley region.

- The chemical transport model CMAQ has been evaluated using hourly and mean particulate sulfate and nitrate observations for the time period of July 2001. The hourly sulfate and nitrate observational data were obtained from the DOE-sponsored super site at Pittsburgh and the mean sulfate and nitrate data were obtained from EPA sponsored air quality sites in and around the Pittsburgh region.
- The meteorological inputs were obtained from EPA's 2001 MM5 simulations and the processed emission inputs were based on EPA's 2001 National Emissions Inventory. The spatially and temporally varying lateral boundary conditions for each day of the modeling simulation were obtained from EPA. These boundary conditions were generated by EPA using a global atmospheric model.

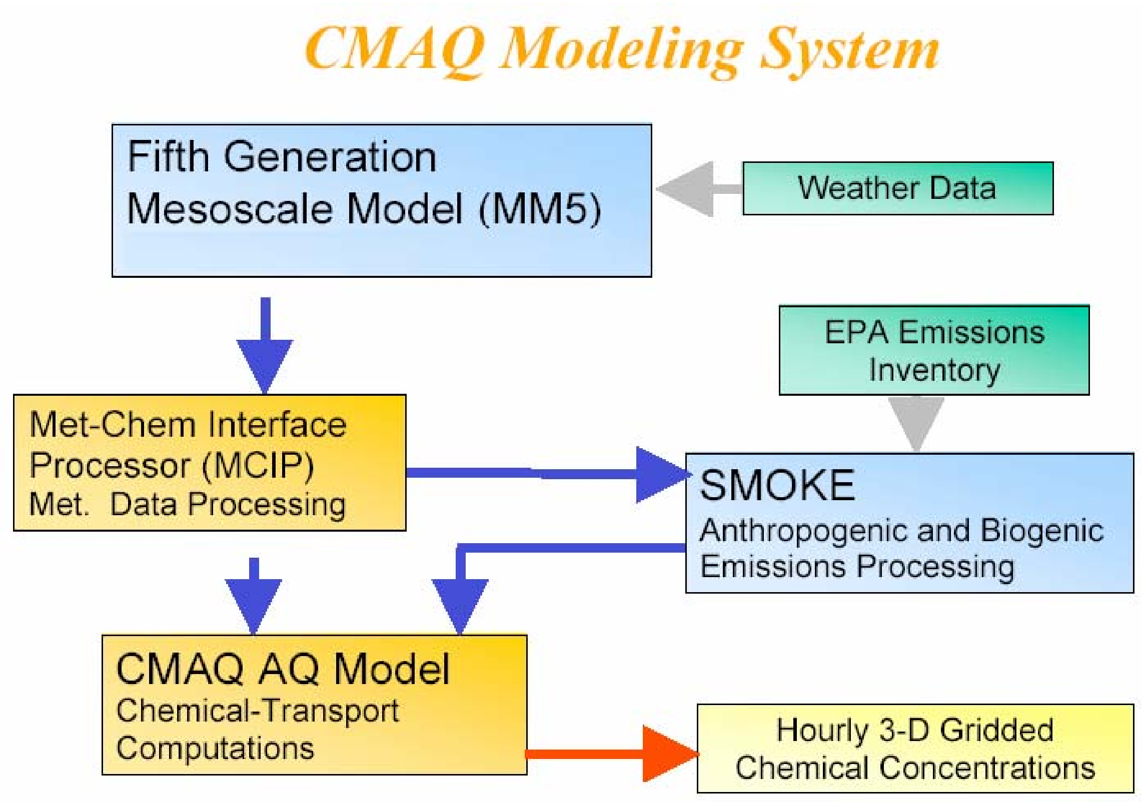
<u>Task 5 - Seasonal Scale Simulations</u>

A major focus of the modeling effort is to identify significant sources and source regions contributing to the deposition of mercury and ambient concentrations of arsenic and fine particulate matter. The modeling will also examine the efficacy of reduction strategies specifically for coal-fired power plants. In addition, researchers will conduct an analysis of the long-range transport from regions outside the Ohio Valley and the biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury in the Ohio Valley Region.

Initially, researchers will set up a seasonal scale simulation for the entire North American continent on a coarse grid (36 km x 36 km), with a nested grid of 12 km over the Midwestern region of the United States and 4 km over the Ohio Valley Region. They will use the NCEP-4D assimilation data set to drive the regional-scale meteorology model (MM5 V3) to develop dynamic inputs for the CTM. The model analysis will be completed for the seasonal run to establish a 'base-case' simulation or the most likely current-day simulation for the season. Uncertainty ranges will be developed for critical parameters in the model, such as emissions and deposition rates. Additional seasonal scale simulations will be performed to develop an 'uncertainty envelope' of the model-generated estimates of deposition rates and fluxes.

Task 5 accomplishments from April 3, 2005 to October 2, 2005:

- The research team is currently preparing for the 2004 sensitivity evaluations. The schematic for the evaluations is depicted below:



- The project team has set up and is executing meteorological model simulations for the months of July, August and September 2004 the preliminary results from these model runs have been represented in this section.

5.1. Background

The Fifth Generation Pennsylvania State University/National Center for Atmospheric Research (PSU/NCAR) Mesoscale Model (MM5) is used to provide hourly three-dimensional meteorological input fields to CMAQ. The model is supported by several pre- and post-processing programs, which are referred to collectively as the MM5 modeling system. The MM5 applications were performed on a Linux cluster installed Redhat7.3 with kernel version 2.4, and the compiler is PGI FORTRAN compiler supported by the Portland Group, Inc with version 5.2-4.

The ultimate goal of MM5 model study is to attempt an improvement in the meteorological inputs which drive advection, transport, diffusion, and chemical rates in the CMAQ photochemical model. The hypothesis is that MM5 performance problems primarily stem from a combination of errors associated with model inputs and the choice of internal algorithms. This effectively means that different kinds of data input and different physics schemes selected in MM5 can cause the variations in the model performance. The model may be constrained during the simulation to relax toward observed temperature, wind and humidity observations through the use of four dimensional data assimilation, known as FDDA. FDDA amounts to adding an additional term to the prognostic equations that serves to “nudge” the model solution toward objective analysis fields and/or individual observations. This has been shown to significantly reduce drift in the solution for simulations of several days or more. Drift may be caused by (among other effects) inaccuracies in the initial conditions, the effects of discretization, or errors in the formulation of various parameterizations.

5.2. Model set up

The MM5 modeling domain for the 2004 modeling simulations is shown in Figure 2. The model has been set up in the Lambert Conformal projection with the domain center at (-97, 40) and the standard parallels located at 33 and 45 degrees. The innermost nest is the 4km domain which is focused on the Ohio River Valley region as shown in the figure. The coarse domain which is the outermost nest covers most of continental United States. The 12-km domain covers several states in the eastern United State, including Pennsylvania, New York, West Virginia, Indiana, Kentucky and Michigan. The number of coarse domain grid cell in the outermost nest (36 km) is 129 (north-south) by 165 (east-west)

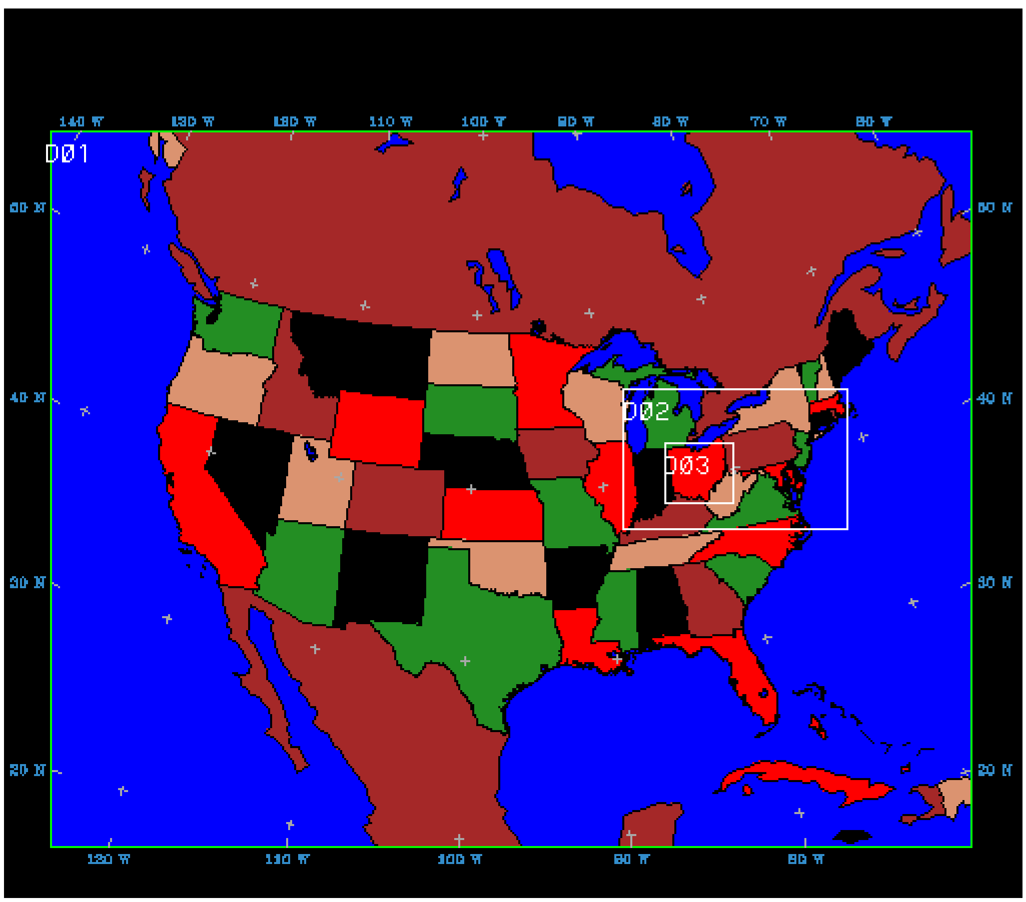


Figure 2: Nested Modeling Domain for MM5

5.3. Model Input data and Model Execution

The MM5 requires gridded analysis and observational data for its preprocessors and gridded analysis nudging. There are many analysis data available. For the July, 2004 time period, we used NCEP Eta data (DS609.2) in the preprocessor to be mapped into MM5. NCEP Eta produces regional analysis fields archived at about 40 km resolution every 3 hours in ADP format. For surface nudging of meteorological parameters NCEP ADP surface observations (DS464.0) and NCEP ADP upper air observations (DS353.4) were chosen.

MM5 was executed in 5 day blocks (7200 minute simulation) with a 90 second time step. Model results are output every 60 minutes and the model output files are written out (i.e. split) every 24 hours to accommodate post-processing utilities. The start and end times are 0Z. Only 4 days from each block will be used for input to a photochemical model since the first 24 hours of the MM5 simulation are ramp-up. This is being done to reduce error propagation through modeling simulations.

The 2004 summer simulation was initiated at 0Z July 1, 2004 and will run through 0Z October 1, 2004.

5.4. Performance metrics

Meteorological inputs required by CMAQ include hourly estimates of surface pressure and clouds; the three-dimensional distribution of winds, temperatures, and mixing ratio; and other physical parameters or diagnosed quantities. Therefore, the objective of the MM5 performance evaluation is to assess the adequacy of this surface and aloft meteorological fields. In this study METSTAT, a widely-used software package designed to examine the MM5 model output and is able to compare and display the differences between the MM5 estimates and observation, was used. The statistics used to quantify model performance include: bias error, gross error, root mean square error (including systematic and unsystematic components), and index of agreement. The definitions for these metrics are as follows:

$$Bias = \frac{1}{N}\sum_{i=1}^{N}\left(V_i^s - V_i^o\right)$$

$$RMSE = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(V_i^s - V_i^o\right)^2}$$

$$GrossError = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\left|V_i^s - V_i^o\right|}{V_i^o}\right)$$

$$IOA = 1 - \frac{\sum_{i=1}^{N} \left| V_i^s - V_i^o \right|^2}{\sum_{i=1}^{N} \left(\left| V_i^s - \frac{\sum_{i=1}^{N} V_i^o}{N} \right| + \left| V_i^o - \frac{\sum_{i=1}^{N} V_i^o}{N} \right| \right)^2}$$

where V_i^s refers to the model values, V_i^o refers to the observed values, and N refers to the number of pairs of model and observation values.

The *bias error* (bias) is the degree of correspondence between the mean prediction and the mean observation, with lower numbers indicative of better performance. Values less than 0 specify under-prediction.

The *gross error*, or mean absolute error, is the mean of the absolute value of the residuals from a fitted statistical model. Lower numbers indicate better model performance.

Root Mean Square Error (RMSE) is a good overall measure of model performance.

Index of Agreement is a relative measure of the degree of which predictions are error-free. The denominator accounts for the model's deviation from the mean of the observations as well as to the observations deviation from their mean. It does not provide information regarding systematic and unsystematic errors. The index of agreement approaches one when model performance is best.

5.5. Model performance

5.5.a. Basic Meteorological Parameters

The figures (Figure 3a, Figure 3b and Figure 3c) show daily basic MM5 model output at 4km resolution for the month of July 2004. Figure 3a depicts the qualitative comparison of model wind speed and wind direction with respect to observations. Figure 3b shows temperatures while figure 3c represents humidity. As can be perceived from the figures the MM5 modeled output for the basic meteorological parameters compare well with observations. Similar statistical plots were plotted for the 36 km and 12 km domains (not shown). It is seen that the model output on 36km and 12 km grid resolutions perform comparably with observations as in the case of 4km grid resolution with no significant differences arising due to the different grid resolutions. This is further reinforced by the values of the performance metrics in Table 2 on all three grid resolutions.

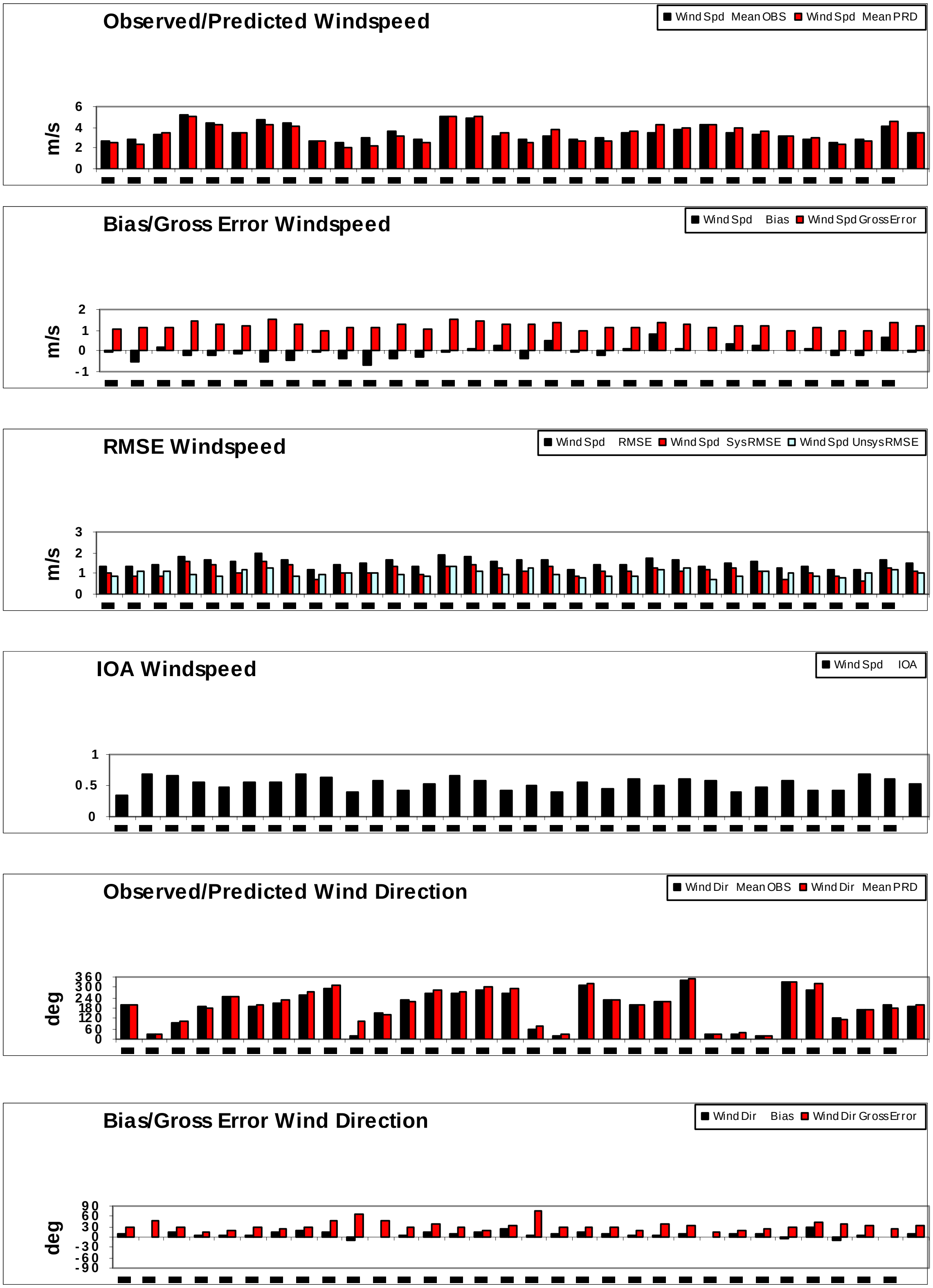


Figure 3a. METSTAT daily wind speed and wind direction statistics for 4km domain

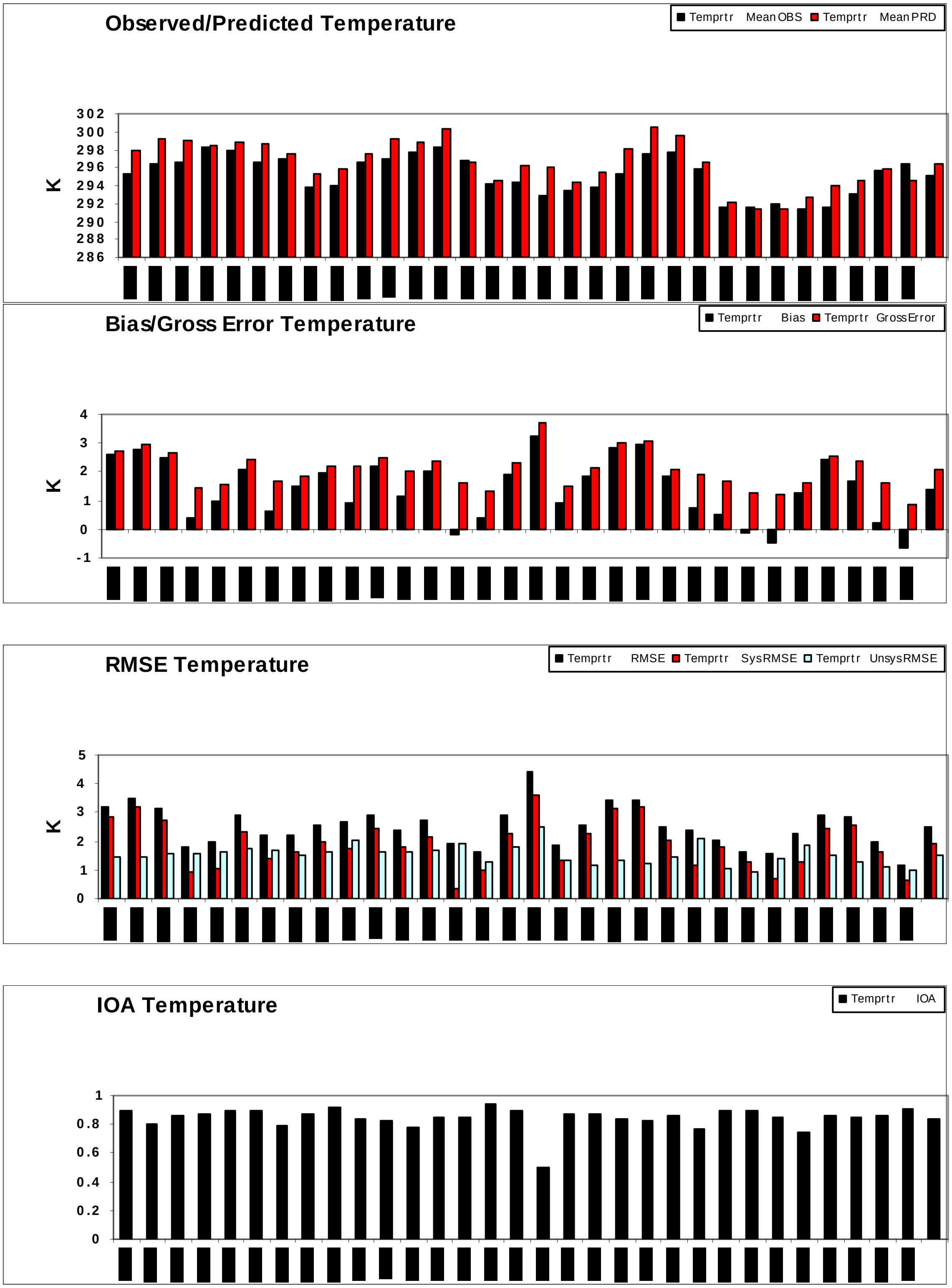


Figure 3b METSTAT daily temperature statistics for 4km domain

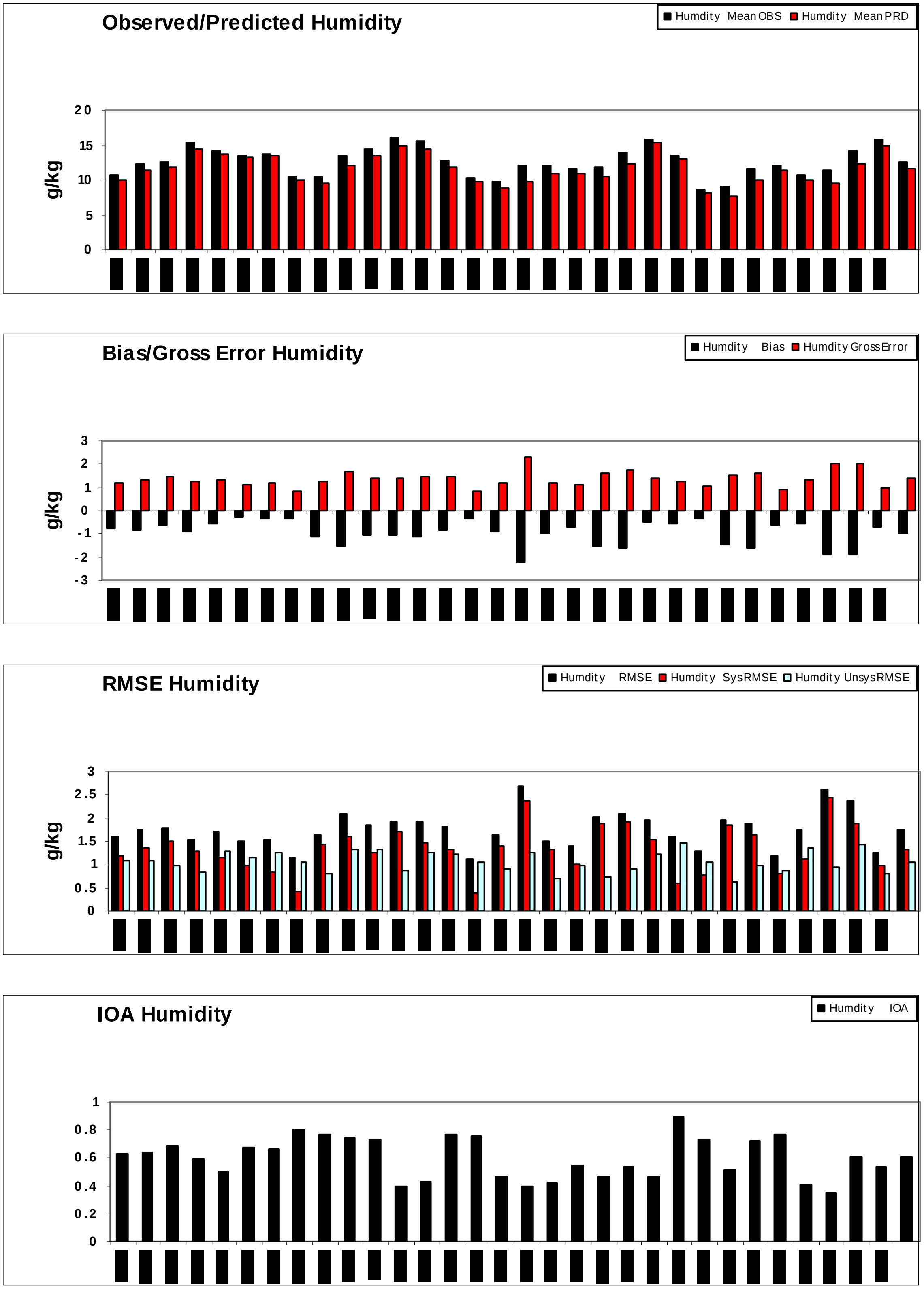


Figure 3c METSTAT daily humidity statistics for 4km domain

		36km	12km	4km
Wind Spd	Bias	-0.08	-0.09	-0.04
Wind Spd	Gross Error	1.21	1.2	1.21
Wind Spd	RMSE	1.51	1.5	1.52
Wind Spd	IOA	0.53	0.53	0.53
Wind Dir	Bias	8.12	8.19	7.78
Wind Dir	Gross Error	31.24	32.06	32.61
Temprtr	Bias	1.12	1.31	1.39
Temprtr	Gross Error	2.02	2.06	2.08
Temprtr	RMSE	2.44	2.49	2.5
Temprtr	IOA	0.84	0.84	0.84
Humdity	Bias	-0.94	-0.96	-0.96
Humdity	Gross Error	1.33	1.36	1.37
Humdity	RMSE	1.69	1.73	1.75
Humdity	IOA	0.61	0.61	0.6

Table 2 Daily statistical measures

5.5.b. Precipitation

The final objective of this study is the accurate assessment of mercury concentrations in the Ohio River Valley region in order to implement effective emission control strategies. Wet deposition fluxes form from the influence of local/regional sources (e.g., in the Northeast) or high precipitation (e.g., in Florida). This important removal mechanism of mercury concentrations is influenced significantly by precipitation. Hence precipitation evaluation plays a crucial role in the overall MM5 system assessment.

The most important physics option for precipitation in MM5 is cumulus parameterization. Two different schemes, Grell and Kain-Fritsch 2 are chosen in the three sensitivity runs. The Grell scheme is based on rate of destabilization or quasi-equilibrium. It is a simple, single-cloud scheme with updraft and downdraft fluxes and compensating motion determining heating/moistening profile. Kain-Frisch 2 is a new version of the Kain-Fritsch scheme that includes shallow convection. It uses a sophisticated cloud-mixing technique to determine entrainment/detrainment, and removes all available buoyant energy in the relaxation time. Both of the models consider shear effects on precipitation efficiency. Observational precipitation data was obtained from the NCDC climate data (DS3240) from 42 sites in the state of Ohio, which were used in comparison with the modeled output. The grid resolution used for the sensitivity runs was 4km. The different physics options used in the three sensitivity runs have been depicted in Table 3 below.

Physics Option	Selection	Configure.user
Moisture	Warm rain	IMPHYS=3 (MPHYSTBL=0)
Cumulus	Grell	ICUPA=3
Planetary Boundary Layer	MRF	IBLTYP=5
Radiation	cloud	FRAD=2
Land Surface Model	Five-Layer Soil model	ISOIL=1
Shallow Convection	No	ISHALLO=0
Nudging (Sfc and Grid)	Sfc=Yes Analysis=Yes	FDDAGD=1

Table 3-a Physics Option in Run 1

Physics Option	Selection	Configure.user
Moisture	Warm rain	IMPHYS=3 (MPHYSTBL=0)
Cumulus	KF2	ICUPA=8
Planetary Boundary Layer	MRF	IBLTYP=5
Radiation	Cloud	FRAD=2
Land Surface Model	Noah Land-Surface Model	ISOIL=2
Shallow Convection	No	ISHALLO=0
Nudging (Sfc and Grid)	Sfc=Yes Analysis=Yes	FDDAGD=1

Table 3-b Physics Option in Run 2

Physics Option	Selection	Configure.user
Moisture	Warm rain	IMPHYS=3 (MPHYSTBL=0)
Cumulus	KF2	ICUPA=8
Planetary Boundary Layer	MRF	IBLTYP=5
Radiation	cloud	FRAD=2
Land Surface Model	Five-Layer Soil model	ISOIL=1
Shallow Convection	No	ISHALLO=0
Nudging (Sfc and Grid)	Sfc=Yes Analysis=Yes	FDDAGD=1

Table 3-c Physics Option in Run 3

Figure 4 reveals the model output from the three sensitivity runs in comparison with observed precipitation data for 5 days in July 2004. Although all the three model simulations largely over predict precipitation during the run time, run 3 performs better compared to the other two. The time period picked for the sensitivity runs are July 20- July 24, 2004. Results from the sensitivity runs indicate model performance improvement through inclusion of KF2 cumulus parameterization.

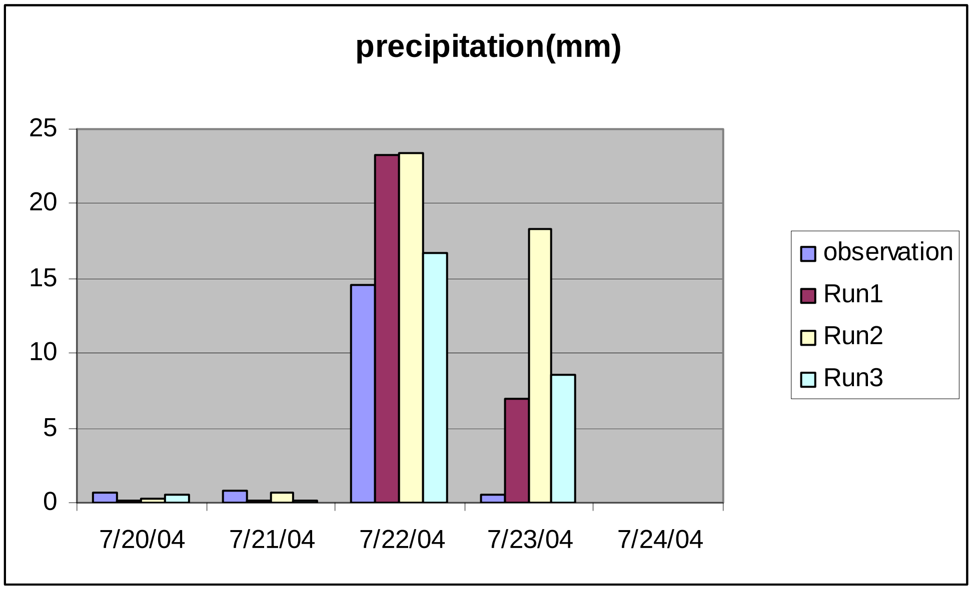


Figure 4. Precipitation from the three sensitivity runs

Figure 5 illustrates the spatial depiction of total precipitation from model output with respect to observations for a few days in July. Gridded observational data are provided by Climate Prediction Center at 0.25 degree x 0.25 degree grid resolution over the whole of United States, with which we can compare MM5 precipitation output over 36 km grid resolution. The 36 km grid resolution is used since it covers most of continental United States and would allow a greater spatial representation. The projection used in both the maps is the Lambert Conformal Projection. It is seen that the model depicts the regions of high and low precipitation with a reasonable degree of accuracy although there are differences in magnitude between the observations and model output.

Additional analysis of rainfall will be done on a monthly basis and for the whole summer season of 2004.

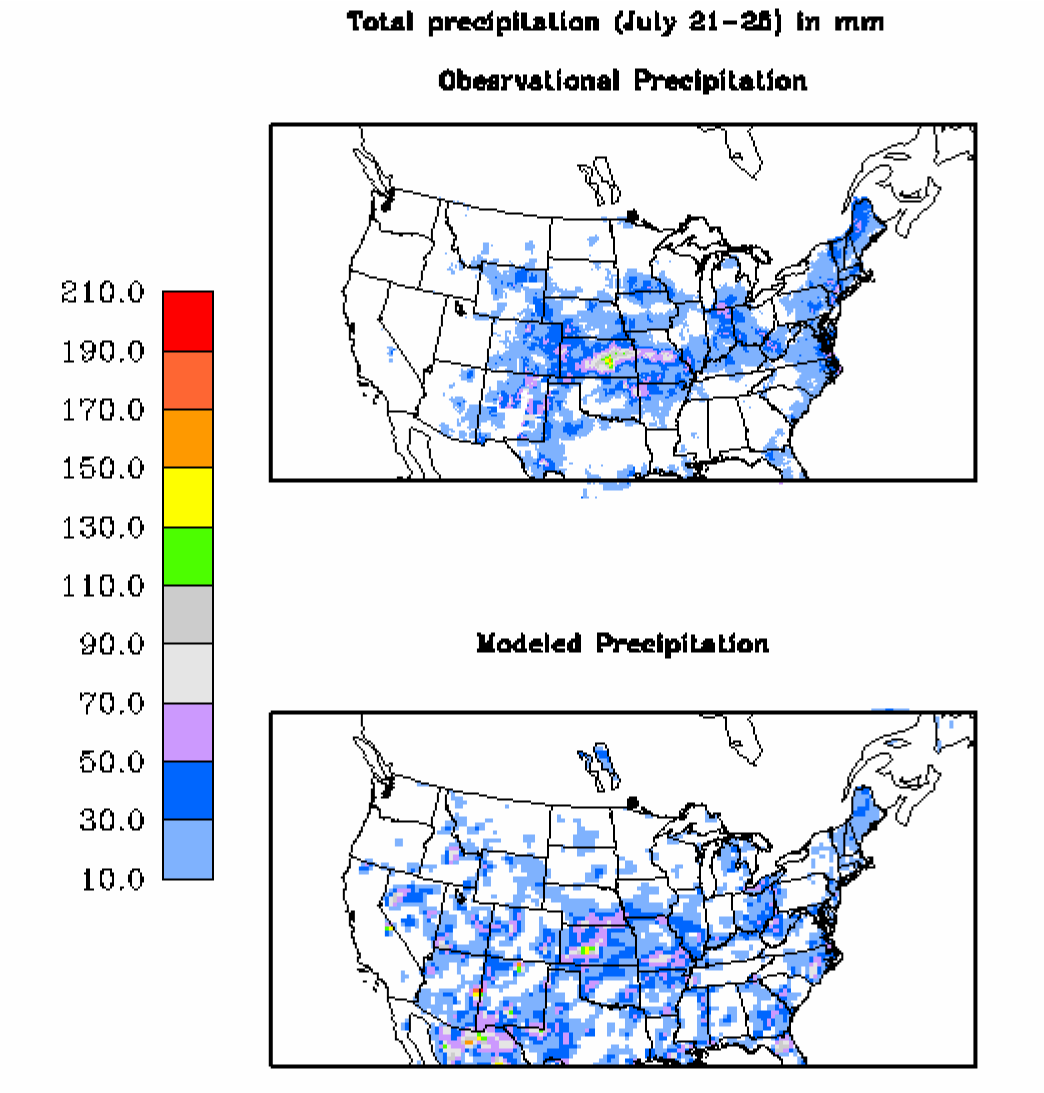


Figure 5. Spatial analysis of total precipitation

5.6. *Post Processing for photochemical models*

The meteorological fields output by MM5 for the summer of 2004 will be prepared for use by the photochemical model with processing utilities. These programs translate certain meteorological parameters from the MM5 grid to the photochemical grid. Additionally, these processors must estimate parameters that are not specific output by MM5. Cloud cover is not a direct output by MM5 and must be diagnosed based on moisture ratios. Vertical mixing is based on vertical diffusivity coefficients.

Task 6 - Development of a Decision-Support Tool

ISEE will conduct a series of model runs to perform a matrix analysis of the sensitivity of point sources to deposition patterns in the region. The analysis will also include selective emission reduction scenarios for these point sources. The team will couple this matrix with a GIS and the emission pre-processor to provide a detailed spatial analysis of the source–receptor relationships. In addition, this entire system will be supported by Web-based technologies to provide industry and government agencies with a user-friendly decision-support tool that will evaluate source-receptor relationships and the efficacy of emission reduction strategies.

Task 6 accomplishments through October 2, 2005:

The frame work for the web-based support tool has been completed. An interactive web based GIS interface linking sources with a data base which will contain the results from the matrix analysis was developed. The Web-based system will provide a user-friendly interface linking specified source reductions with the associated impact on receptor sites.

Task 7 - Project Management, Data Analysis, and Reporting

This task involves all communication between the project team members, DOE-NETL, and external collaborating parties and includes all meetings, presentations, and DOE-required reports pertaining to the project. To facilitate data analysis, the data from the SAM and the results of the model runs will be archived into a user-friendly database that will provide functionality to help calculate final mercury, arsenic, and fine particulate matter mass and composition concentrations. It will also allow the delineation of basic trends and the evaluation of variables. To the greatest extent possible, the data from the SAM site will be incorporated into the ambient air quality database being compiled for DOE-NETL by ATS and Ohio University under project DE-FC26-02NT41476. However, the primary function of the database will be to reduce data efficiently for evaluation of the proposed model simulations. At the conclusion of the project, Ohio University will submit the database containing the SAM information, results of model runs, and comparison statistics to DOE-NETL along with a comprehensive final report.

Task 7 accomplishments from April 3, 2004 to October 2, 2005:

- Steve Winter gave the presentation, *Preliminary Results from a Mercury and PM2.5 Ambient Air Monitoring Program in Athens, Ohio* at the Air Quality V Conference in Washington D.C in September 2005. In addition, a proceedings paper was submitted to the conference organizers, EERC. Presentation slides and the proceedings paper were sent to Ohio University.

- Ohio University and CONSOL tentatively agreed to extend the sampling program by two additional months through November 2005. This would help supplement data recovery that was lost during a 3.5 month period in which the particulate samplers were down for repairs.

- Ohio University and Consol R&D submitted a paper, detailing the initial phase of sampling, to Atmospheric Environment.

III. SUMMARY OF RESULTS

The ISEE researchers chose the CMAQ model developed for air-pollution studies on a regional scale by the EPA and its collaborators. AER has accomplished the 1-year run for the 36-km-grid domain for 1996 using CMAQ. Model performance for the 1996 simulation was conducted by comparing predicted annual wet deposition fluxes with 1996 data from the Mercury Deposition Network.

ATS is continuing to upgrading the mercury and arsenic emission inventory files. The focus of their efforts is to develop a comprehensive and accurate emission inventory utilizing current research on emissions data from coal-fired power plants. The ISEE has initiated work on the short-scale simulations for 2004 and developed a GIS interface for the decision support tool.

Argonne National Laboratory is currently engaged in developing an enhanced global emissions inventory for mercury which will include a recently completed DOE/NETL inventory of emissions in China which was funded under a separate project and will be utilized in this study.

The research team from the Air Quality Center at Ohio University has presented preliminary results from a month of MM5 simulation (July, 2004). The model predicts temperatures, winds and humidity with reasonable accuracy but over-predicts precipitation to a large extent. Sensitivity runs were also carried out for short time periods to determine the cumulus parameterization scheme best equipped to simulate precipitation for this particular modeling simulation.

IV. CONCLUSIONS

The initial phase of the project was delayed by approximately three months due to contract negotiations with the subcontractors. However, the monitoring efforts and the modeling efforts have been initiated and are proceeding as expected.

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