PROGRAM facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

**Environmental & Water Resources**

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# NETL AIR QUALITY RESEARCH PROGRAM

## *Identifying the Atmospheric Behavior and Implications of Coal Plant Emissions*

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## AIR QUALITY RESEARCH PROGRAM WEBSITE

http://www.netl.doe.gov/coal/E&WR/air_q/

## NETL WEBSITE

http://www.netl.doe.gov

## Background

The NETL Air Quality Research program is part of the DOE Office of Fossil Energy's Innovations for Existing Plants (IEP) R&D program. Although much of the IEP program focuses on the development of low-cost technology options for reducing emissions of air pollutants from today's coal power plants and gasification systems, it also seeks to generate scientific information that identifies the specific types and levels of emission controls for existing plants that will be most beneficial to the public. Currently, a great deal of uncertainty surrounds the role of coal power plants with respect to two types of air pollutants of great concern to environmentalists – fine particulate matter ($PM_{2.5}$) and mercury. Much of this uncertainty exists because complex atmospheric and meteorological processes play a critical role in the formation, chemical reaction, and transport of $PM_{2.5}$ and mercury after they are emitted from power plant stacks but before they are deposited at ambient receptor sites. Important questions also remain with regard to the human health impacts of these transported and transformed pollutants. The NETL Air Quality Research program is attempting to resolve some of these current uncertainties.

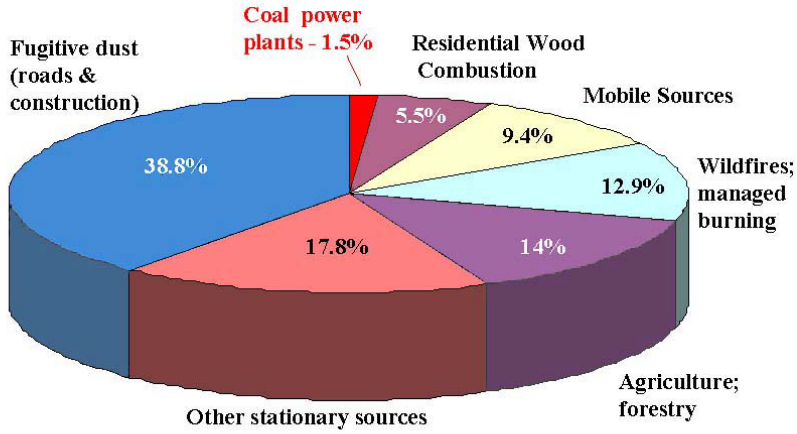
## $PM_{2.5}$ – A Complex Mixture

The current National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$, promulgated by the U.S. Environmental Protection Agency (EPA) in 1997, were based largely on epidemiology studies that showed statistical correlations between elevated $PM_{2.5}$ mass concentrations and adverse human health effects. Although coal-fired power plants are important contributors to ambient $PM_{2.5}$ mass in the Eastern U.S., "primary" $PM_{2.5}$ (fly ash) from coal plants accounts for only a minuscule proportion of the total mass. Therefore, reductions in primary $PM_{2.5}$ emissions from coal plants will not help compliance with mass-based standards. Most of the $PM_{2.5}$ related to coal plants results from the release of gaseous sulfur dioxide, which oxidizes and reacts with water and ammonia in the atmosphere to form very fine sulfuric acid and ammonium sulfate particles. Analogous but less-prevalent atmospheric reactions occur when nitrogen oxides are released from coal plants and other combustion sources and react to form nitric acid and ammonium nitrate particles.

## Coal Plants Don't Produce "Soot"

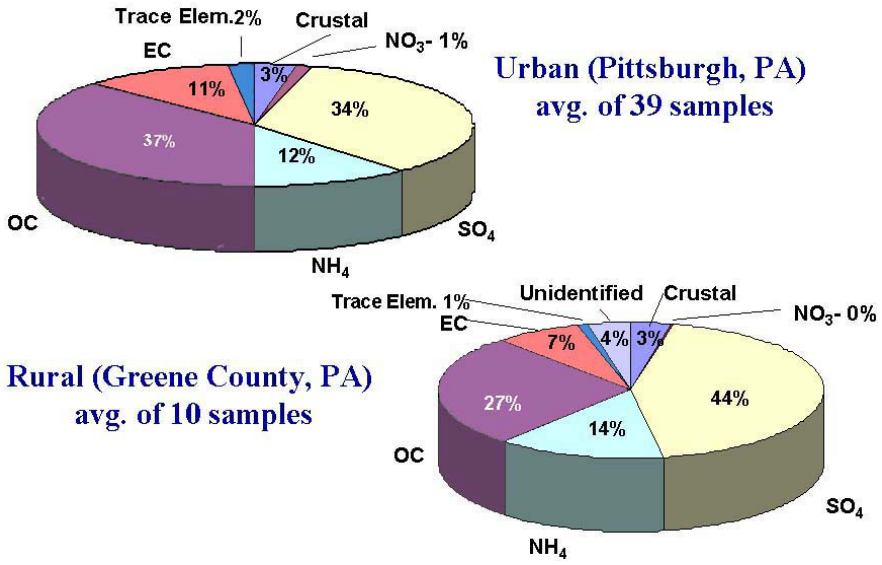
Many articles in the popular press incorrectly use the word "soot" as a synonym for fine particulate matter, when in fact soot – defined as a black carbonaceous residue of incomplete combustion of fuel – is rarely the dominant component of ambient $PM_{2.5}$ mass. In bulk analyses of $PM_{2.5}$ samples, which typically identify carbon as being "organic" or "elemental," soot would most likely be identified as "elemental" carbon. Although soot and other elemental carbon particles may indeed be important from a health standpoint, elemental carbon usually comprises a much smaller fraction of $PM_{2.5}$ mass than organic carbon.

In the upper Ohio River Valley, an area whose $PM_{2.5}$ is considered to be dominated by coal plant emissions, total carbon (organic plus elemental) comprises roughly the same proportion of ambient $PM_{2.5}$ mass as ammonium sulfate and nitrate. However, modern pulverized coal boilers release almost no organic carbon, and elemental carbon in coal fly ash is typically less than 10% by weight. Even with newer low-NOx burners, which typically leave more unburned carbon in fly ash than older burners, the carbon fraction of fly ash rarely exceeds 20 percent. Moreover, high-efficiency particulate collection devices at modern coal plants typically remove over 99.5% of the fly ash from the emission stack. As a result, fly ash typically comprises less than 1% of ambient $PM_{2.5}$ mass, and the "soot" contribution from coal plants is negligible. Although atmospheric reactions involving acid gas emissions from coal plants and organic vapor releases from other sources may affect the organic carbon component of ambient $PM_{2.5}$, such reactions would have no effect on "soot."




Source: National Air Pollution Emission Trends, 1999 (EPA-454/R-01-0049-80-009, March 2001)

*Primary $PM_{2.5}$ emissions in the U. S., 1999*




*Typical $PM_{2.5}$ Composition in Western Pennsylvania*

Because of the complexity of these atmospheric reactions and their dependence on meteorological conditions, sophisticated models are required to assess the effect of future coal plant emission reductions on ambient $PM_{2.5}$ concentrations and composition. To further complicate the issue, it is unlikely that all components of $PM_{2.5}$ are equally harmful to human health; in fact, a fairly large body of toxicological literature suggests that secondary inorganic particles such as ammonium sulfates, on their own, have little biological potency in humans and animals at environmentally relevant levels. Consequently, there is still considerable uncertainty regarding the health benefits that will actually result from reductions in coal plant emissions.

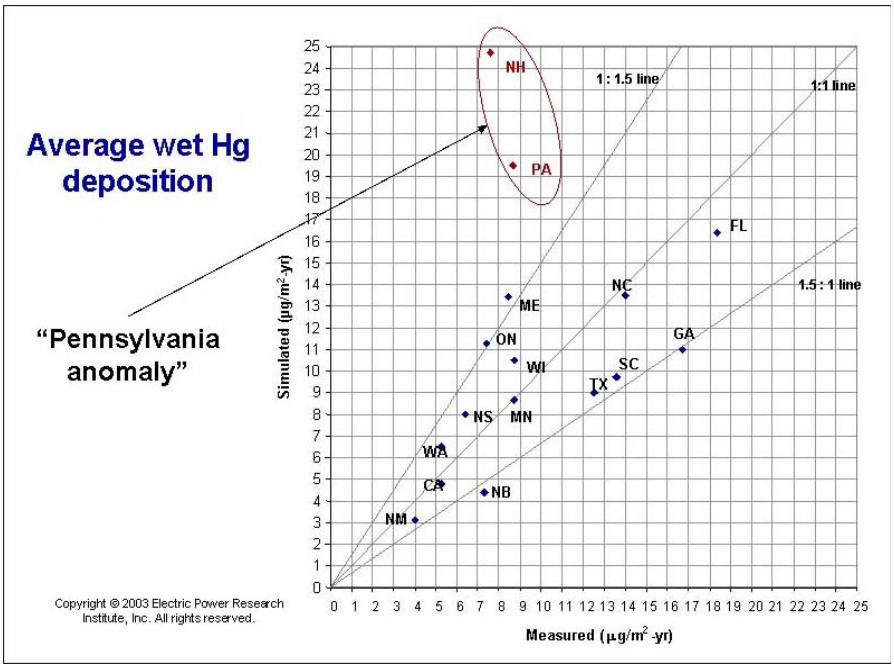
## Why are atmospheric mercury transformations important?

Coal-fired power plants have been identified as the anthropogenic source category that produces the largest air emissions of mercury in the U.S. – approximately 48 tons per year. Unlike other pollutants associated with power plant emissions (e.g., $PM_{2.5}$ and ozone), concentrations of mercury in ambient air are generally far too low to constitute a health or environmental hazard. However, because mercury tends to leave the atmosphere and convert to toxic methylmercury in terrestrial and aquatic environments, it can bioaccumulate in food chains and expose humans to potentially harmful doses of Hg via food consumption.

Depending on the coal type and combustion process, mercury can be released into the atmosphere from coal power plants in one of three basic forms: (1) gaseous elemental mercury ($Hg^0$), which is relatively unreactive and can persist in the atmosphere for periods of months to years; (2) gaseous oxidized mercury ($Hg^{2+}$), which reacts and returns to the earth's surface relatively quickly via wet or dry deposition; and (3) particulate-bound mercury, which is already in a relatively stable chemical form upon release. Virtually all of the particulate-bound mercury is removed at the plant via high-efficiency particulate collection devices; therefore, the type and location of environmental impacts associated with mercury releases from coal plants will be determined partly by relative proportions of $Hg^0$ to $Hg^{2+}$ in the stack exhaust. Atmospheric reactions that cause the mercury speciation profile to change after it is released, and other atmospheric processes governing cloud formation, precipitation, and particle deposition can also play an important role in the environmental impacts associated with mercury.

Questions regarding mercury speciation in power plant plumes could have important implications for U. S. policy regarding the control of mercury emissions from the electric utility industry. From a control technology standpoint, $Hg^{2+}$ is easier to remove from power plant flue gases than $Hg^0$; however, nationwide mercury trading programs for power plants will be much more viable if power plant mercury releases are primarily in the elemental form, or if atmospheric processes cause mercury to convert from $Hg^{2+}$ to $Hg^0$ shortly after release. Conversely, if the mercury released from the stack is in the oxidized form or converts to the oxidized form within the power plant plume, nationwide trading would be less desirable because of the potential for local "hot spots" of mercury deposition and subsequent bioaccumulation immediately downwind of each plant.

The best current models for atmospheric transport and deposition of mercury greatly overestimate the actual, measured mercury deposition in critical areas directly downwind of power plants, such as Pennsylvania. Therefore, in order to allow accurate modeling of the mercury cycling process, a much better understanding of the transport, transformation and environmental fate of mercury released into the atmosphere is needed.




*EPRI Hg deposition model – Predictions vs. measurements*

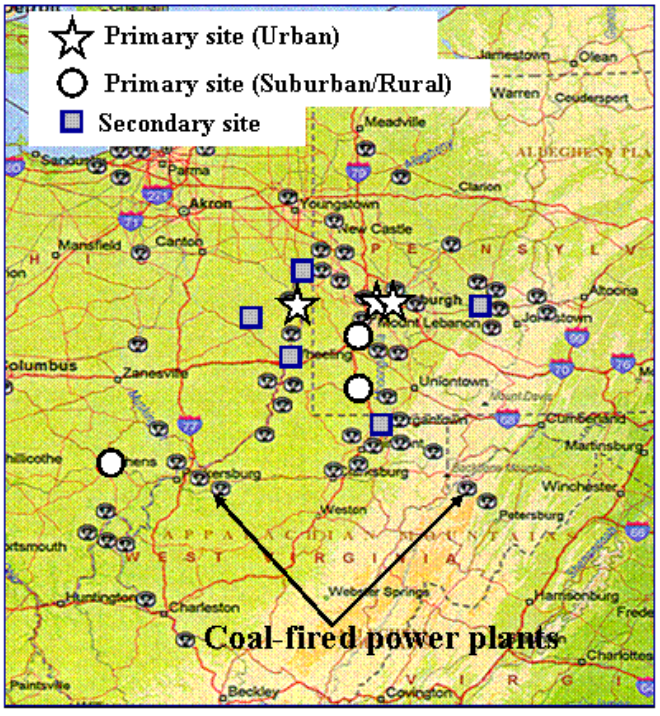
## NETL In-House Air Quality Research

As part of the NETL Air Quality Research Program, the Office of Science & Technology (OST) conducts an ambient air monitoring program that builds upon NETL core capabilities and competencies in both organic and inorganic analyses and instrumentation. The primary site of the in-house program is a fine particulate/air toxics sampling station at the NETL Pittsburgh facility. This air monitoring station includes a 715 $ft^2$ indoor facility housing equipment to continuously monitor gaseous pollutants $O_3$, $SO_2$, NOx, CO, and $PM_{2.5}$ containing carbon, polyaromatic hydrocarbons, nitrate and sulfate. A complete system for measuring concentrations and speciation of atmospheric mercury was added to the monitoring facility in 2003. Two in-house laboratories have been completely renovated to support the analysis of $PM_{2.5}$ / air toxics samples, including the installation of a Kratos MS50 high-resolution mass spectrometer for detailed characterization of organic compounds. NETL-OST personnel also collaborate closely with the Air Quality Research Program's external partners to evaluate the performance of air monitoring equipment, analyze data, and prepare publications for scientific journals. Through 2003, the NETL-OST research team has authored or co-authored over 20 conference presentations and four manuscripts for publication in peer-reviewed journals.

## Program Description

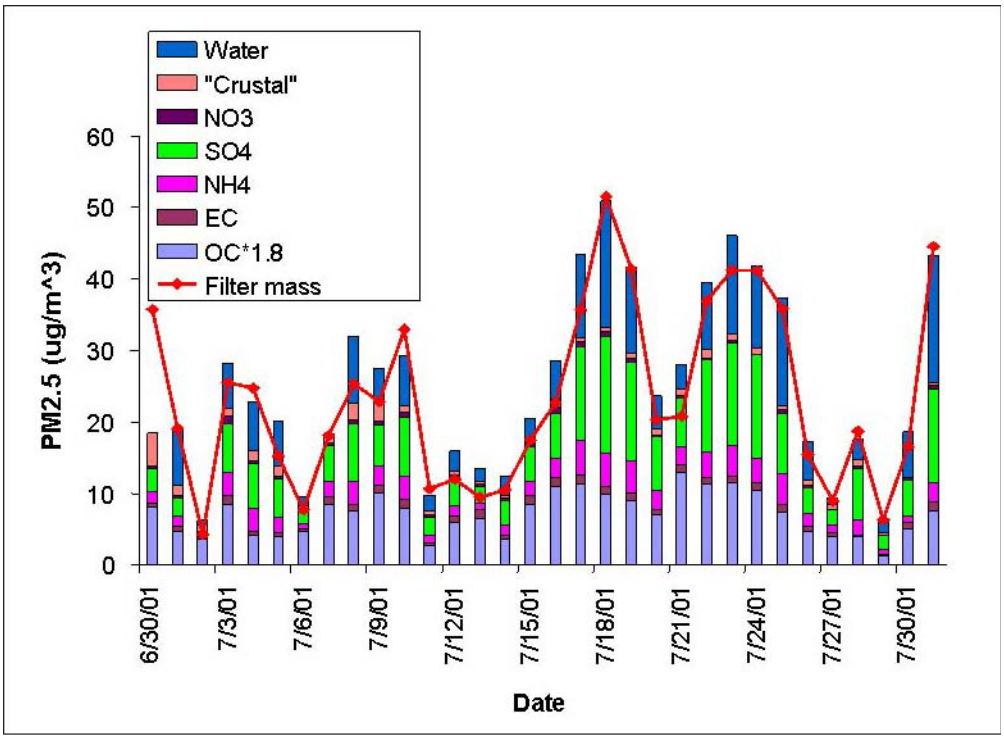
The NETL Air Quality Research program is designed to resolve the scientific uncertainties associated with the atmospheric formation, distribution, and chemical transformation of pollutant emissions from today's coal-fired power plants, and to obtain a realistic assessment of the human health impacts of these emissions. Results of this research will help the DOE Office of Fossil Energy address policy questions regarding coal plant emissions and provide guidance for future R&D programs to control these emissions. The NETL Air Quality Research program is subdivided into four components: (1) Ambient Monitoring & Analysis; (2) Emissions Characterization; (3) Predictive Modeling and Evaluation; and (4) Health Effects of Coal Plant $PM_{2.5}$, as described below.

**Ambient Monitoring & Analysis.** This component of the program is designed to support the goal of obtaining a clearer understanding of how coal-fired power plants contribute to ambient $PM_{2.5}$, regional haze, mercury deposition, and human exposure. NETL has chosen to focus on the upper Ohio River valley as the region of primary interest because of its high concentration of large coal-fired power plants whose emissions are intermingled with significant amounts of emissions from urban traffic and industrial sources. This region represents an ideal field laboratory to apply advanced methods for establishing a combination of local and regional source-receptor relationships, providing a severe "stress test" for these methods. From 1999 through 2002, large amounts of ambient air quality data were collected at monitoring sites in Pittsburgh, PA (two urban sites), Holbrook, PA (rural site), South Park, PA (suburban site), and Steubenville, OH, with a focus on evaluating the spatial and temporal variations in $PM_{2.5}$. To supplement these sites, less-extensive monitoring stations were operated in five other locations in PA, OH and WV. In 2003, the emphasis of the ambient monitoring component of the program shifted to mercury; a new monitoring site in Athens, OH was established to measure atmospheric concentrations, speciation and wet deposition of mercury, and the South Park, PA site was also equipped for this purpose.




*NETL ambient air quality monitoring sites in the Upper Ohio River Valley*

During all seasons, concentrations and composition of $PM_{2.5}$ at urban sites were similar to those at upwind and downwind sites, suggesting that regional sources (as opposed to local sources) were the dominant contributors. A noteworthy finding was that up to 25% of the $PM_{2.5}$ mass at an urban Pittsburgh site consisted of particle-bound water on warm summer days, when the total $PM_{2.5}$ mass was the highest. Data collected at these sites are currently being analyzed in detail, and numerous manuscripts based on the data are being prepared and submitted for publication in various scientific journals. In addition, all data collected at these sites are being compiled into a single database, and a suite of web-based analytical tools are being developed to facilitate the further analysis of the data by air quality scientists, epidemiologists, and regulators.




*$PM_{2.5}$ mass and composition in Pittsburgh, July 2001*

**Emissions Characterization.** The emissions characterization component of the DOE-NETL air quality research program is designed to obtain detailed information on fine particulate emissions from fossil-fuel-based power systems, both in-stack and in the resultant plume. Research efforts include the collection and analysis of primary particles, acid gases and other condensables, and the study of the formation and transport of secondary particulate matter from power plant sources and other sources (e.g. automobiles, steel mills coke ovens, wood smoke) that are likely to be affecting ambient air quality in the Upper Ohio River valley region. The results of these efforts will provide source "signatures" that could be used in source-receptor assessments, and may be valuable in related human-exposure studies. Development of updated $PM_{2.5}$ and mercury emissions inventories for the region for use in predictive models is also included under this component of the program.

Although there are several methods applicable for measuring total $PM_{2.5}$ emitted from stacks, no direct method for measuring all individual components of $PM_{2.5}$ currently exists. Further, existing stack methods do not always adequately account for the in-plume and atmospheric chemical transformations experienced by $PM_{2.5}$ and mercury after their release from the stack. Therefore, the continued development and evaluation of new fine particulate and mercury emissions sampling methods, such as advanced single-particle composition analyzers and dilution samplers, is included in the emissions characterization component of the program.

## PARTNERS

**U. S. Environmental Protection Agency**
Research Triangle Park, NC

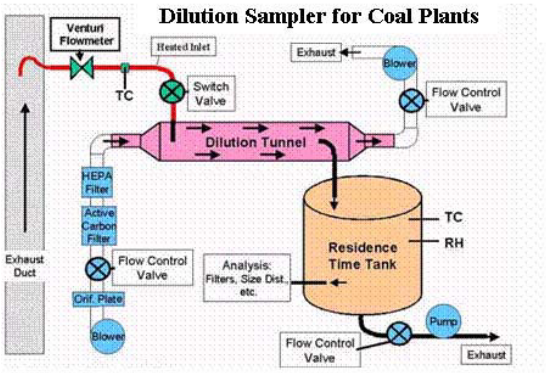
**Allegheny County Health Department**
Pittsburgh, PA

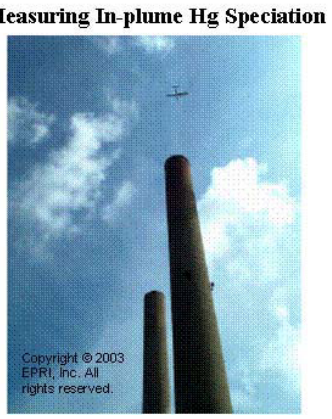
**Ohio Air Quality Development Authority Coal Development Office**
Columbus, OH

**Ohio Environmental Protection Agency**
Columbus, OH

**Pennsylvania Department of Environmental Protection**
Harrisburg, PA

**Tennessee Valley Authority**
Chattanooga, TN

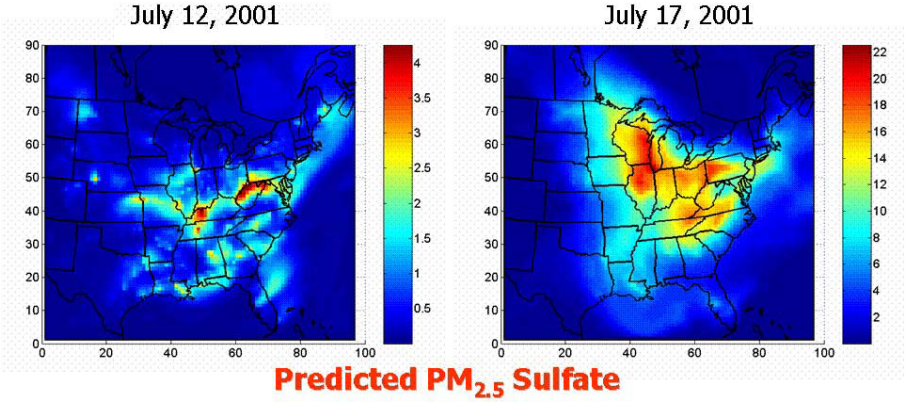



*NETL Emissions Characterization projects*

Part of the reason for the inaccuracy of current mercury deposition models may be a rapid chemical change from $Hg^{2+}$ to $Hg^{0}$ within the plume structure. Preliminary laboratory studies and field observations at ambient air monitoring sites suggest this conversion may be occurring, but direct evidence of within-plume mercury speciation changes is lacking. Additional research and field measurements via specially-instrumented aircraft are being supported by NETL to determine the chemical speciation of mercury into elemental and oxidized forms and the changes of gas/particle fractionation as the material is transported downwind of the plant.

**Predictive Modeling & Evaluation.** Using the detailed measurements obtained under the ambient monitoring and emissions characterization components of the program, advanced receptor modeling and chemical transport modeling (CTM) techniques are being employed to determine the likely sources of the particle nuclei and the secondary species contributions on a particle-by-particle basis. Updated versions of publicly-available chemical transport model (CTMs) are being used to simulate atmospheric processes affecting $PM_{2.5}$ and mercury at multiple spatial scales. Given the updated emissions inputs and prevailing meteorology conditions, the CTMs simulate the aerosol size-composition distribution for approximately 100 chemical species throughout the model domain. After the models are verified by comparing its results with field measurements, they can be used to predict the changes in $PM_{2.5}$ and mercury concentrations, composition, and deposition resulting from various power plant emission scenarios, focusing on the changes that may occur in the upper Ohio River valley in response to current and future EPA regulatory requirements.




*CTM results for regional $PM_{2.5}$ "episode" in July 2001*

**Health Effects of Coal Plant $PM_{2.5}$.** This component of NETL's Air Quality Research Program was initiated in 2003 in an attempt to enhance the body of scientific evidence relating the health effects of $PM_{2.5}$ from coal plant emissions to the health effects of $PM_{2.5}$ from other emission sources. As long as source-specific health effects of $PM_{2.5}$ remain uncertain, regulatory agencies will continue to adopt a default position that treats all components of $PM_{2.5}$ (and as a result, all emission source classes) as being equally harmful to health. If, however, some components of $PM_{2.5}$ are actually significantly less harmful to human health than other components, this default regulatory position may neglect sources emitting the "more harmful" components and/or unduly penalize sources emitting the "less harmful" components of $PM_{2.5}$.

Recent epidemiologic research has yielded somewhat contradictory results with regard to the human health effects of secondary inorganic components of $PM_{2.5}$ (ammonium sulfates and nitrates) that have traditionally been linked to coal plants. Several well-publicized epidemiology studies conducted over the past 10 years have suggested that sulfate particles were positively correlated with adverse health effects such as respiratory disease, cardiovascular disease, and lung cancer. However, in these studies, particulate sulfate concentrations were very highly correlated with total $PM_{2.5}$ mass concentrations; many other key components of $PM_{2.5}$, notably carbon species, were not measured. If one or more of the unmeasured $PM_{2.5}$ components were actually the problematic constituent(s), and were also closely correlated with total $PM_{2.5}$ mass, the statistical association between particulate sulfate and adverse health effects would exist even if sulfates were not a causative factor.

Results from a recent set of well-controlled, short-term epidemiology studies in Atlanta, GA, in which a vast array of $PM_{2.5}$ components were measured, suggested that adverse health effects were most closely associated with carbon monoxide and/or the carbonaceous fraction of $PM_{2.5}$. These carbonaceous species are related primarily to emission sources other than power plants (e.g., motor vehicles, wood burning). Importantly, the sulfate and nitrate components of $PM_{2.5}$ were never positively correlated with adverse health outcomes in the Atlanta studies.

Initial efforts under this component of the NETL Air Quality research program include a project involving the exposure of exposing laboratory animals to actual plant emissions that have been "aged" and converted to reaction products in a mobile reaction chamber that simulates the conditions and dilution levels experienced by coal power plant plumes en route to ambient receptor sites. The project thus simulates the exposures to $PM_{2.5}$ from coal-fired power plant emissions in a much more realistic manner than previous experiments that used "fresh" coal combustion products. NETL has also co-sponsored a workshop to help develop a plan for using a laboratory setting to generate meaningful, reproducible, repeated inhalation exposures of sufficient numbers of animals for a sufficient time to characterize health hazards of $PM_{2.5}$ from coal combustion, and to manipulate the exposure variables modifying those hazards. In 2004, NETL issued a new Funding Opportunity Announcement to perform new epidemiology and toxicology studies that will improve our current understanding of the link between power plant emissions, $PM_{2.5}$, and human health.

## PARTNERS

**Electric Power Research Institute**
Palo Alto, CA

**Consol Energy**
Pittsburgh, PA

**Carnegie-Mellon University**
Pittsburgh, PA

**Ohio University**
Athens, OH

**Advanced Technology Systems, Inc.**
Pittsburgh, PA

**Harvard School of Public Health**
Cambridge, MA

**University of North Dakota Energy and Environmental Research Center**
Grand Forks, ND

## Project Information

Detailed information on all projects being performed under the NETL Air Quality Research Program can be obtained on the NETL web site. This information includes Fact Sheets on individual projects, technical progress reports, presentations and manuscripts submitted to conferences and journals, and other publications and presentations related to specific projects. The following key projects, along with other supporting projects, are represented on the NETL web site:

| Program Component | Project Title | Primary Performer |
|---|---|---|
| Ambient Monitoring | Upper Ohio River Valley Project | Advanced Technology Systems, Inc. |
| Ambient Monitoring | Steubenville Comprehensive Air Monitoring Project (SCAMP) | CONSOL Energy |
| Ambient Monitoring | Ambient $PM_{2.5}$ Monitoring "Supersite" | Carnegie-Mellon University |
| Ambient Monitoring | Air Quality Database and Analytical Tools | Advanced Technology Systems, Inc. |
| Emissions Characterization | Advanced Low-NOx Burner Emissions Characterization | McDermott Technologies, Inc. |
| Emissions Characterization | Source Emissions Characterization Study | Carnegie-Mellon University |
| Emissions Characterization | Direct Measurement of Mercury Reactions in Coal Power Plant Plumes | Electric Power Research Institute |
| Predictive Modeling | Regional Source-Receptor Modeling Study | Carnegie-Mellon University |
| Predictive Modeling | $PM_{2.5}$ Formation & Transport Model Comparison | Tennessee Valley Authority |
| Predictive Modeling | Emission, Transport, and Deposition of Mercury from Coal Plants in the Ohio River Valley Region | Ohio University |
| Health Effects | TERESA: Toxicological Evaluation of Realistic Emissions of Source Aerosols | Electric Power Research Institute |
| Health Effects | Laboratory Generation of Coal Combustion Atmospheres | Lovelace Respiratory Research Institute |

To obtain project-specific information from the NETL web site, follow these instructions:

1. Enter the URL in your browser: http://www.netl.doe.gov/coalpower/environment/air_q/
2. Click on the title of the program component: Ambient Monitoring, Emissions Characterization, Predictive Modeling, or Health Effects; a U.S. map with project titles should appear.
3. Click on the project title.