

THE DOE-NETL AIR QUALITY RESEARCH PROGRAM: AIRBORNE FINE PARTICULATE MATTER (PM_{2.5})

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ABSTRACT

In response to growing concerns over fine particulate matter (PM_{2.5}) emitted into the atmosphere from coal-fired power plants, the Department of Energy's National Energy Technology Laboratory (DOE-NETL) is pursuing a major research effort as part of its Innovations for Existing Plants program. The overall goals of the DOE-NETL PM_{2.5} research effort are to: (1) provide the applied science needed to quantitatively relate the emissions from energy production to ambient PM_{2.5} concentrations and composition at downwind receptors; and (2) inform decision-makers about management options applicable to coal-fired power generation to achieve the national standards for PM_{2.5} and regional haze. Special emphasis is given to Pittsburgh, PA and the surrounding upper Ohio River valley region because, on many occasions during the year, this region is downwind of major coal-fired power plants and other industrial sources of air emissions and upwind of the Boston-Washington corridor, the largest regional complex of urban areas in the United States. The upper Ohio River valley region also has its own set of coal-fired power plants and mobile/industrial pollution sources. The DOE-NETL PM_{2.5} program is organized into four components: (1) Ambient Sampling and Analysis; (2) Characterization of Emissions and Plumes; (3) Predictive Modeling and Evaluation; and (4) Emissions Control Technology R&D. The early focus of the program has been on ambient sampling and analysis, because it provides the foundation for the other three components. Greater emphasis is now being placed on the interpretation and application of the ambient air data, acquisition and characterization of emissions data, and analysis of all the information via advanced modeling studies. Several DOE-NETL projects contain direct links to companion projects that are evaluating human exposure and health effects of PM_{2.5}. In emissions control technology, DOE-NETL is focusing on several technologies that can be used to replace or enhance the efficiency of existing electrostatic precipitators. The development of new emission control technology options for PM_{2.5} and its gaseous precursors under the DOE-NETL program will be modified, expanded or reduced as necessary to meet the needs identified by ongoing health-effects research and predictive modeling studies.

INTRODUCTION

Epidemiology studies have often shown positive statistical correlations between ambient mass concentrations of fine particulate matter (PM_{2.5}) and adverse respiratory and cardiopulmonary effects in humans. As a result, PM_{2.5} was specified as a "criteria pollutant" in revisions to the National Ambient Air Quality Standards (NAAQS) promulgated by the U.S. EPA in 1997. Attainment of the PM_{2.5} NAAQS requires an annual average mass concentration of less than 15µg/m³ and a daily maximum concentration of less than 65µg/m³.

EPA and the States are now in the process of identifying specific areas that are and are not in attainment of the PM_{2.5} NAAQS. Ambient PM_{2.5} has also been found to contribute significantly to the impairment of long-range visibility (regional haze) in many areas of the United States. EPA's 1999 Regional Haze Rule has established goals for reducing regional haze in areas of the U.S. where long-range visibility has been determined to have exceptional value (Class I areas) and has outlined methods for achieving those goals.

It is generally recognized that coal-fired power plants can be important contributors to ambient PM_{2.5} mass concentrations and regional haze. Therefore, it is very likely that EPA and/or State and local air pollution control agencies will require additional restrictions of coal power plant emissions over the 2005 - 2008 time frame as they develop State Implementation Plans (SIPs) for achieving and/or maintaining compliance with the PM_{2.5} NAAQS and Regional Haze Rule. However, specific requirements as to the types of pollutants to be reduced, and the timing, magnitude, and locations of these emissions restrictions have yet to be determined.

A great deal of research is now being performed with respect to the chemical composition of ambient PM_{2.5}, its relationship to emission sources, its relationship to human exposure, and its overall impact on human health. The results of this ongoing research will serve to shape future policy decisions with respect to the PM_{2.5} NAAQS. The PM_{2.5} research effort at DOE-NETL is designed to help resolve existing uncertainties with respect to the effects of emissions from coal-fired power plants on ambient PM_{2.5}, identify areas where improvements in technology for controlling the emissions of PM_{2.5} and its precursors may be needed, and assist in the development of these technologies. These efforts are part of DOE-NETL's Innovations for Existing Plants program, a broad effort to address critical environmental issues such as mercury, NO_x, coal utilization byproducts, and the quality and availability of water at electric generating facilities.

ISSUES AFFECTING COAL POWER PLANTS AND PM_{2.5}

Primary Emissions

According to EPA estimates¹, primary PM_{2.5} emissions (fine particles emitted in solid or liquid form) from coal combustion at electric generating facilities constitute less than 2% of anthropogenic primary PM_{2.5} emissions nationwide. Many other source categories produce far more primary PM_{2.5} than coal plants (Table 1). This suggests that existing particulate control devices (e.g., electrostatic precipitators and fabric filters) at electric generating facilities are doing a reasonably good job in preventing the emission of fly ash.

Since fly ash from pulverized coal boilers consists primarily of calcium and iron aluminosilicates, fly ash would appear as a "crustal" and/or "trace metal" component in bulk analyses of ambient PM_{2.5} samples. Figs. 1 and 2 show that these two components typically constitute only around 5% or less of ambient PM_{2.5} mass in the upper Ohio River valley, where there are many coal-fired power plants². In addition, preliminary analysis of PM_{2.5} samples from this region using scanning electron microscopy³ suggest that spherical

aluminosilicate particles (i.e., fly ash) typically account for less than 10% of the “crustal” component. Therefore, it is reasonable to estimate that the total contribution of fly ash to PM_{2.5} mass in the upper Ohio River valley region is on the order of 0.5% or less. Since the PM_{2.5} NAAQS are based strictly on fine particle mass, additional reductions of primary fine particle emissions from coal-fired power plants in and upwind of this region are unlikely to be of much value in achieving or maintaining compliance with these standards.

Table 1. U. S. Primary PM_{2.5} Emissions, 1999

Source Category	Emissions, tons/1000	Percent of Total
Coal-fired power plants	102	1.5
Residential wood combustion	374	5.5
Mobile sources	640	9.4
Wildfires, managed burning	872	12.9
Agriculture & Forestry	948	14.0
Other stationary anthropogenic	1203	17.8
Fugitive dust (roads, construction)	2631	38.8
All sources	6773	100.0

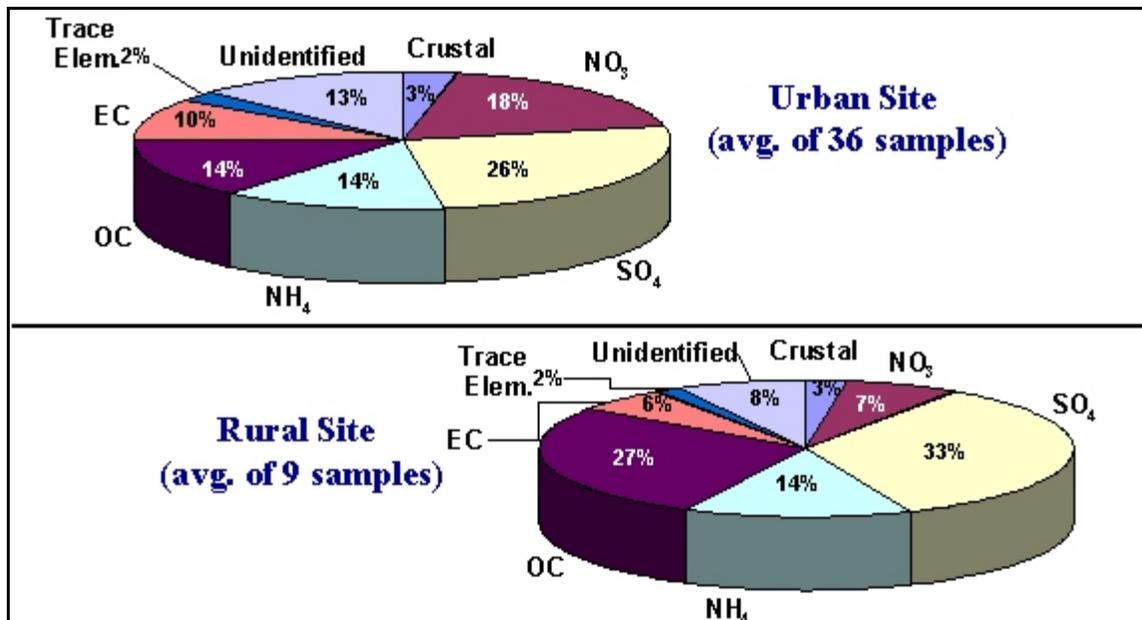


Fig. 1. Chemical speciation of PM_{2.5} in the upper Ohio River Valley, Winter 1999

Source: *National Air Pollution Emission Trends Report, 1999*; EPA-454/R-01-0049-80-009

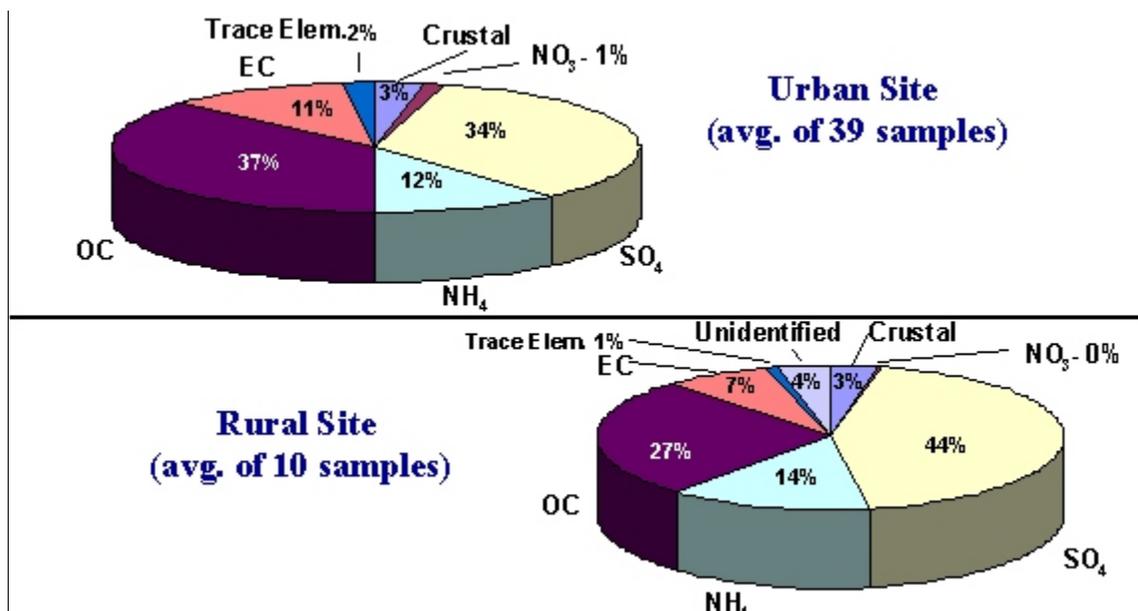


Fig. 2. Chemical Speciation of PM_{2.5} in the Upper Ohio River Valley, Summer 1999

The low percentage contribution of fly ash to ambient PM_{2.5} mass in the upper Ohio River valley can be attributed, in part, to the fact that the contribution of sulfate is quite high. In regions where coal is burned with proportionally less emission of SO₂ than in the upper Ohio River valley, the fly ash contribution to ambient PM_{2.5} would be expected to be somewhat higher. The fly ash contribution to PM_{2.5} mass may also increase if nationwide emissions of SO₂ and NO_x from coal power plants continue to decrease without additional reductions in fly ash emissions. However, given the very small current contribution of fly ash toward total PM_{2.5}, very large reductions in the sulfate, nitrate, and carbonaceous components from all sources will have to occur before the fly ash contribution becomes significant. If such large reductions in these other components do occur, it is doubtful that the remaining PM_{2.5} mass will cause widespread exceedence of the NAAQS, thereby obviating the need for additional reductions in fly ash emissions.

Prior studies⁴ have shown that primary fine particle emissions from coal plants can contain toxic trace metal constituents such as arsenic, chromium, and cobalt. However, the only "air toxic" from coal plants that is currently of significant nationwide concern is mercury, which is released mostly in gaseous form. Despite this, the continued scrutiny of air toxics in the future may eventually result in greater public pressure for additional control of all potential sources of air toxics, including coal plants. This is especially true in the case of trace metals, which tend to be preferentially concentrated in sub-micron particles which are collected less efficiently by today's electrostatic precipitators. In addition, older electrostatic precipitators and fabric filters may not perform as efficiently as their newer counterparts. If very stringent nationwide restrictions on air toxics emissions are eventually mandated, further reductions in primary PM_{2.5} emissions from coal plants may be required, even if these reductions are not needed to achieve compliance with the PM_{2.5} NAAQS.

What about “Soot”?

Many articles in the popular press tend to incorrectly use the word “soot” as a synonym for fine particulate matter, when in fact soot – a black carbonaceous residue of incomplete combustion of fuel – is rarely the dominant component of ambient PM_{2.5} mass. By definition, soot would be identified as carbon (probably elemental but perhaps organic) in bulk analyses of PM_{2.5} samples. Figs. 1 and 2 shows that in the upper Ohio River Valley, organic and elemental carbon together comprise 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 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. Since fly ash is already recognized as only a very minor component of ambient PM_{2.5} mass, it is likely that the carbon in fly ash constitutes only a minuscule portion of the total carbon in PM_{2.5}. It is therefore likely that sources other than coal plants, such as wood burning and diesel exhaust, will have to be targeted if a significant reduction in the “soot” component of PM_{2.5} is to be achieved.

Secondary Emissions

Figs. 1 and 2 show that about half of the ambient PM_{2.5} mass in the upper Ohio River valley is in the form of ammonium sulfate, and, to a lesser extent, ammonium nitrate. These “secondary particles” are formed from atmospheric oxidation of gaseous sulfur dioxide (SO₂) and nitrogen oxides (NOx), and their subsequent chemical reaction with ammonia to form ammonium sulfate or nitrate salts. Coal power plants account for over 60% of the total nationwide emissions of SO₂ and about one-fifth of NOx emissions (Table 2). Strategies for bringing non-attainment areas into compliance with the PM_{2.5} NAAQS are therefore almost certain to include reductions of SO₂ and perhaps NOx emissions from existing coal-fired utility boilers. Given the well-documented link between airborne sulfate particles and light scattering, which impairs long-range visibility, SIPs for reducing regional haze can also be expected to center on the reduction of SO₂ emissions from coal plants. Therefore, the major “PM_{2.5} problem” associated with coal-fired power plants stems from their emissions of SO₂ and NOx, rather than emissions of fly ash.

Table 2. U. S. Emissions of PM_{2.5} Precursor Gases, 1999

PM_{2.5} Precursor	Coal plant emissions, tons/1000	Total emissions, tons/1000	% Contribution of coal plants
Sulfur dioxide	11,856	18,867	62.8
Nitrogen oxides	4,935	25,393	19.4
Volatile Organic Compounds	29	18,145	0.2
Carbon Monoxide	239	97,441	0.2

Source: *National Air Pollution Emission Trends Report, 1999*; EPA-454/R-01-0049-80-009

Although the reduction of SO₂ and NO_x emissions from coal-burning power plants appears to be a logical step toward reducing ambient PM_{2.5} mass concentrations, the amount of particle mass reduction that can be achieved via such controls is still far from certain. For example, lower SO₂ emissions from coal plants may be beneficial in reducing regional haze, but may not, on their own, achieve significant reductions in ambient PM_{2.5} mass. Studies of atmospheric chemical reactions⁵ suggest that lowering the concentration of atmospheric sulfate particles, without concurrently reducing the concentration of nitrates, will result in the increased production of ammonium nitrate particles to offset the reductions in ammonium sulfate. While this may support the mandatory simultaneous reduction of SO₂ and NO_x emissions from coal plants, the situation is complicated by the fact that the contribution of coal plants to ambient nitrate concentrations is often less than that of motor vehicles and other sources, especially in Eastern urban areas. Therefore, even if SO₂ and NO_x emissions from coal plants are reduced, there may be enough nitrate left in the atmosphere to negate much of the benefit that would otherwise be expected. Also, the production of atmospheric sulfate and nitrate particles from their gaseous precursors is highly dependent on atmospheric conditions such as temperature, sunlight, clouds, and humidity. Moreover, some atmospheric chemistry models⁶ suggest that reductions in the concentrations of atmospheric ammonium would be far more effective in reducing ambient fine particle mass than reductions of sulfate or nitrate. Agricultural activity is suspected of being the primary source of atmospheric ammonia (coal plants and vehicles release almost no ammonia), but the issue of mandatory reduction of ammonia releases is rarely considered. Therefore, even if both SO₂ and NO_x emissions from coal plants are reduced, the accompanying reduction in sulfate and nitrate particles and the reduction in total PM_{2.5} mass will most likely be proportionally less than the reduction in SO₂ and NO_x emissions.

Acid Gases

Gases such as sulfuric acid (H₂SO₄), hydrochloric acid (HCl), and hydrofluoric acid (HF) are also produced by coal-fired power plants. These gases condense rapidly after they are released to form fine acid aerosols, so they can be viewed technically as a form of PM_{2.5}. They are reported as toxic releases under EPA's Toxic Release Inventory (TRI) requirements, but they do not contribute significantly to ambient PM_{2.5} mass concentrations, and do not generally constitute a toxic inhalation hazard because they become diluted and neutralized long before they reach any human receptors.

However, acid aerosols, especially sulfuric acid, can cause problems in the form of plumes that violate Federal, state, and/or local standards for opacity. When coal is burned, most of the sulfur is converted to SO₂, but a small percentage is converted to sulfur trioxide (SO₃), which combines with moisture in the flue gas to form sulfuric acid vapor. When the vapor is quenched rapidly, as in the inlet to a wet scrubber for SO₂ control, it condenses to form a sub-micron acid mist that passes through the scrubber, and increases the opacity of the scrubber stack exhaust. Under some adverse weather conditions (e.g., inversions), plumes containing elevated concentrations of sulfuric acid can "touch down" in nearby communities, causing respiratory irritation. The problem of SO₃ and sulfuric acid vapor can be exacerbated by the installation of post-combustion selective catalytic reduction (SCR) devices for NO_x control.

Although the catalyst reduces the nitrogen, some of the SO₂ can oxidize to SO₃ as the flue gas passes through the SCR device. Recent studies⁷ have shown that the amount of SO₃ formed across an SCR can be approximately equivalent to the amount produced in the furnace when burning high-sulfur coal. Therefore, as more coal plants install SCRs and wet scrubbers as a means of controlling NO_x and SO₂, the incidence of problems related to acid gases may also increase.

Overlapping Regulatory and Legislative Drivers

In order to develop an efficient, coherent plan for reducing emissions from coal power plants to achieve compliance with the PM_{2.5} NAAQS and Regional Haze Rule, it should be recognized that emissions of the same key pollutants – SO₂, NO_x, and primary fine particles – are also governed by other Federal, State, and local regulatory programs. Emissions of these pollutants are expected to decrease significantly in the future under the provisions of these other programs. For example, emissions of NO_x will be greatly reduced at many power plants in response to the 22-state SIP call issued by EPA to help northeastern states achieve compliance with the NAAQS for ozone. Significant reductions in emissions of SO₂ and NO_x are also expected to occur as the power generating industry responds to Phase II of the Title IV (acid rain) provisions of the 1990 Clean Air Act Amendments. As older coal plants are retired and replaced with new generating capacity, the new facilities will be subject to stringent new source performance standards for SO₂, NO_x, and primary PM. In addition, many state and local air regulatory bodies have adopted emission standards that are more stringent than Federal standards, especially with respect to plume opacity. These opacity restrictions will almost certainly reduce the overall emissions of primary PM and acid gases in the future. In cases where overlapping regulatory provisions exist, the provision that results in the lowest pollutant emission levels for a specific facility will almost certainly prevail. In some cases, the mandatory emission reductions achieved under existing regulatory programs may be enough to achieve compliance with the PM_{2.5} NAAQS and/or “reasonable progress” toward visibility goals; in other cases, additional restrictions on power plant emissions may have to be implemented.

The regulatory landscape for SO₂ and NO_x emissions may be greatly impacted by possible nationwide “multi-pollutant” legislation for power plants. President Bush’s “Clear Skies Initiative” calls for nationwide emissions of SO₂ from power plants to be cut from current levels (Table 2) to 4.5 million tons per year (tpy) by 2010 and to 3 million tpy by 2018; for NO_x, emissions would be cut to 2.1 million tpy in 2008 and 1.7 million tpy by 2018. Nationwide trading programs for both pollutants, similar to those set up under Title IV of the Clean Air Act Amendments, would be employed to implement the emissions reductions. Another legislative action, Senate bill S.556, calls for greater reductions of SO₂ and NO_x over a quicker time schedule; it also calls for mandatory reductions of greenhouse gases such as CO₂, which could have profound impacts on the operation of all coal power plants. No matter what its final form, there is a general consensus that such multi-pollutant legislation will provide important benefits for meeting the PM_{2.5} NAAQS and regional haze targets, and will greatly affect any SIPs developed under these two existing regulatory programs.

Health Effects

The epidemiology studies that led to the promulgation of the 1997 PM_{2.5} NAAQS showed a consistent statistical correlation between elevated concentrations of ambient PM_{2.5} mass and adverse human health effects, primarily cardiopulmonary and respiratory problems. Recent epidemiological studies and re-analysis of previous research have generally supported the earlier findings. However, after one of the most influential epidemiological studies (the NMMAPS study)⁸ was re-analyzed to correct problems discovered with the statistical package used to perform the analysis, about one-third of the localities examined in the study showed a negative association between premature mortality and ambient PM mass concentrations (in this case, PM₁₀, and by extension, PM_{2.5}). In other words, the study results implied that in some locations increased exposure to PM is harmful, but in other locations, increased exposure is beneficial to health. This counterintuitive result suggests that different constituents of PM do not yield similar health impacts. No conclusive explanation for this “heterogeneity” of results has yet been found.

To date, epidemiology studies have not identified a clear, consistent causal link between specific components of PM_{2.5} (e.g., sulfates, carbon, metals) and the observed adverse health endpoints. For the PM_{2.5} components most closely linked to coal power plant emissions, (sulfates, nitrates, and fly ash), the research findings have been mixed. Some epidemiology studies have shown statistically significant correlations between elevated ambient PM_{2.5} sulfate concentrations and adverse health effects⁹, including lung cancer.¹⁰ Conversely, the results of a recent study in Atlanta, which examined more chemical constituents of PM_{2.5} than any study to date, suggested that organic and/or elemental carbon were the components of PM_{2.5} most closely associated with adverse health effects.¹¹ Furthermore, whenever PM_{2.5} in Atlanta showed a statistically significant association with a health impact, sulfates and nitrates did not. These contradictory results suggest that additional studies and better understanding of the health impact of specific subspecies of PM_{2.5} are needed.

Likewise, toxicology studies have not yet revealed any biologically plausible mechanism by which exposure to PM_{2.5} generated by power plants could induce the cardiopulmonary or carcinogenic effects implied by the results of epidemiology studies. Surprisingly, there has been very little research directed specifically toward understanding the toxicology of sulfates and nitrates, specifically the ammonium sulfates and nitrates which constitute such a large percentage of PM_{2.5} mass in many areas. Exposure to residual oil fly ash (ROFA) particles was found to mediate cardiopulmonary injury in laboratory animals, but the problematic effects were attributed to the bioavailable transition metals in the ROFA rather than to its sulfate component¹². Moreover, the dosage of metals that led to toxic effects were much larger than the dosage that humans would be exposed to in ambient air. It should also be noted that fly ash produced by pulverized coal boilers is fundamentally different than ROFA in its composition and structure because most of the transition metals in coal fly ash are part of the essentially inert spherical aluminosilicate matrix of the fly ash particle, and hence are not readily bioavailable. The relatively non-toxic nature of coal fly ash compared to other fly ashes has also been documented in other studies¹³.

The definitive identification of the specific components of PM_{2.5} that are causing the greatest health problems is extremely important from a public policy standpoint. For example, if secondary sulfates and nitrates are not the components of PM_{2.5} that are causing the observed adverse health effects, policies that rely on the reduction of SO₂ and NO_x emissions from power plants as a means of reducing PM_{2.5} mass will not have the desired beneficial effects on public health. Although research has shown conclusively that reducing the ambient concentrations of sulfates and nitrates will be beneficial in terms of improving visibility, the public health benefits of these reduced concentrations are much less certain. Resolving this uncertainty will allow more accurate estimates of the benefits associated with reduced SO₂ and NO_x emissions, and will provide the public with more realistic expectations concerning what these reductions will achieve. DOE's Office of Fossil Energy has recently recommended that "it would be useful for EPA to conduct a limited set of more sharply focused studies, ... to clarify the issues related to the contributions of certain subcategories of PM_{2.5}¹⁴." If the most problematic components of PM_{2.5} are found to be something other than sulfates or nitrates, additional pollution controls at power plants and other emission sources may be required, at a cost over and above that of SO₂ and NO_x controls.

NETL PROGRAM OVERVIEW

The U. S. Department of Energy's National Energy Technology Laboratory (DOE-NETL) is pursuing a major research program - the Innovations for Existing Plants (IEP) Program - to improve the environmental performance of the current fleet of coal-fired electric utility boilers. As part of the IEP program, DOE-NETL is conducting a research effort to clarify the current understanding of how energy production sources, especially coal-fired power plants, contribute to PM_{2.5} concentrations and composition at ambient receptor sites. The DOE-NETL PM_{2.5} research effort is designed to help resolve the uncertainties regarding the magnitude and location of potential coal plant emission restrictions that may be sought by State and Federal agencies in the process of complying with the PM_{2.5} NAAQS and Regional Haze Rule. The overall goals of the DOE-NETL PM_{2.5} program are to: (1) provide the applied science needed to quantitatively relate the emissions from energy production to ambient PM_{2.5} concentrations and composition at downwind receptors; and (2) inform decision-makers about management approaches applicable to coal-fired power generation to achieve the national standards for PM_{2.5} and regional haze.

The DOE-NETL PM_{2.5} program is organized into four components: (1) ambient sampling and analysis; (2) characterization of emissions and plumes; (3) predictive modeling and evaluation; and (4) emissions control technology R&D. The early focus of the program has been on ambient sampling and analysis, because this provides the foundation for the other three components. Greater emphasis is now being placed on the interpretation and application of the ambient air data, acquisition and characterization of emissions data, and analysis of all the information via advanced modeling studies. The first three components of the program are highly integrated because the knowledge gained under each project can be utilized directly by the other projects in the program. The development of new emission control technology options for PM_{2.5} and its gaseous precursors under the fourth program component

can also be modified, expanded or reduced as necessary to meet the needs identified by ongoing health-effects research and predictive modeling studies. Primary funding for the DOE-NETL PM_{2.5} research comes from DOE's Office of Fossil Energy, and most of the projects involve significant levels of cost-sharing by industry, State and other Federal Government agencies, and/or the participating research institutions.

The DOE-NETL PM_{2.5} program, especially the first three components, has placed special emphasis on Pittsburgh, PA and the surrounding upper Ohio River valley region. Air quality in this region had not been as well-characterized as other regions prior to the DOE-NETL program, but coal power plant emissions could be expected to have a greater impact on Pittsburgh than on almost any other major metropolitan area in the U. S. The city of Pittsburgh is almost completely surrounded by coal-fired power plants (Fig. 3); on many occasions during the year, the region is also directly downwind of other major coal-fired power plants to the southwest. The upper Ohio River valley also has a reasonable share of mobile and industrial pollution sources within its boundaries (steel mills, coke plants, etc.) and receives additional mobile/industrial pollution from upwind sources. The region is also upwind of the largest regional complex of urban areas in the United States (the Boston-Washington corridor). Since air pollution from the Ohio River valley has been implicated in many of the air quality problems in the Boston-Washington corridor, these problems ought to be more readily apparent in Pittsburgh. Other reasons for choosing the upper Ohio River valley for study were: (1) opportunities existed to collaborate with several different State and local air management agencies in establishing monitoring sites and resolving interstate pollution transport issues; (2) the unique topography, with rolling hills interspersed with deep and sometimes heavily urbanized river valleys, represented a difficult challenge for air quality prediction; (3) the relatively high percentage of elderly people in the region represented a population that may be more susceptible to adverse health effects of air pollution; and (4) a world-class medical research/university system is also located in the region, which will facilitate the subsequent use of the air quality data in studies of PM_{2.5} health effects.

Although its emphasis is on the upper Ohio River valley, the DOE-NETL program also includes several projects in the southeastern U.S., which also is greatly affected by coal-burning power plants. An Interagency Agreement with the Tennessee Valley Authority, one of the largest electric power producers in the area, has served as the catalyst for much of the DOE-NETL effort in this region. Projects in the southeast are represented under all four components of the DOE-NETL PM_{2.5} program. Many of the results of the projects conducted in the southeast are directly transferrable to the upper Ohio River valley and other coal-burning regions.

The current program was designed with the presumption that the PM_{2.5} NAAQS would continue to be based exclusively on fine particle mass concentrations, at least for the next 5 - 8 years. Studies examining the relationship between PM_{2.5} components and human health are not currently included in the program; however, several DOE-NETL projects contain direct links to companion projects, funded by other entities, that are evaluating human exposure and health effects of PM_{2.5}. It is also expected that the results of the DOE-NETL

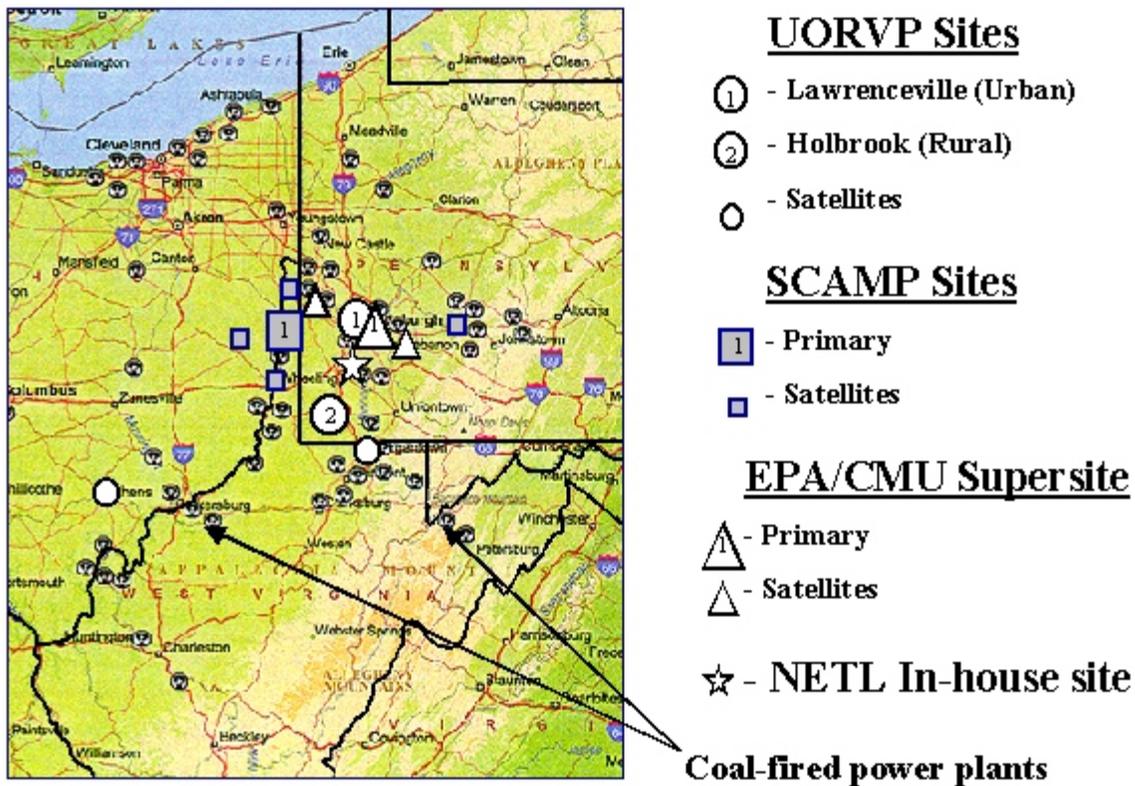


Fig. 3. DOE-sponsored ambient air monitoring sites in the upper Ohio River valley

program will eventually be used by other entities to examine $PM_{2.5}$ health effects. As the program evolves, the need for additional or expanded DOE-NETL involvement in health-based research related to $PM_{2.5}$ will be re-evaluated.

Ambient Sampling and Analysis

The Upper Ohio River Valley Project (UORVP)

The Upper Ohio River Valley Project (UORVP), performed by Advanced Technology Systems, Inc., was the first major project initiated under the DOE-NETL $PM_{2.5}$ program. By establishing a network for monitoring and characterizing $PM_{2.5}$ in the upper Ohio River valley, the UORVP has formed the core around which the remainder of the program was developed. The UORVP includes two urban and two rural monitoring sites (see Fig. 3) that were part of existing local and/or state air quality programs. The primary urban site, located in the Lawrenceville section of Pittsburgh, PA, is an air quality monitoring station operated by the Allegheny County Health Department. The primary rural site is co-located with the Pennsylvania Department of Environmental Protection on a remote hilltop near Holbrook, Greene County, PA. The Lawrenceville and Holbrook sites both contain several types of filter-based PM monitoring equipment for determining $PM_{2.5}$ (and PM_{10}) mass and chemical speciation, continuous samplers for $PM_{2.5}$ mass and co-polluting gases (CO , SO_2 , NO_x , NH_3 , etc.), and surface meteorological stations. Chemical speciation sampling at Lawrenceville

and Holbrook has consisted of one 24-hour filter sample every sixth day throughout the year, supplemented by “intensive” sampling periods during the summer and winter, each lasting about one month. During the intensive sampling periods, four filter samples are collected daily at Lawrenceville and one sample daily at Holbrook. The purpose of the intensive sampling is to obtain the tightly-spaced chemical speciation data needed by epidemiologists to assess the acute health effects of human exposure to the components of $PM_{2.5}$, while the one-in-six sampling regimen allows broad seasonal comparisons to be made between the urban and rural sites and between the various sampling devices being used at each site. A "satellite" urban monitoring station at the Morgantown, WV and a satellite rural site in Gifford State Forest near Athens, OH each collect one 24-hr $PM_{2.5}$ filter sample every sixth day to supplement the measurements at Lawrenceville and Holbrook. Measurements under the UORVP began in early 1999 and have included six intensive sampling periods (3 summer and 3 winter). Initial data analysis under the UORVP has yielded the following results and observations²:

- The continuous PM mass monitoring equipment (TEOM) has performed as well as the Federal Reference Method (FRM) and sequential filter samplers (SFS) in accounting for ambient $PM_{2.5}$ levels; however, the FRM-obtained masses were consistently lower than those of the TEOM and SFS;
- The trending in the $PM_{2.5}$ mass concentrations was similar for Lawrenceville and Holbrook, which represent an urban and a rural site sixty-five miles apart (Fig. 4) This implies that the $PM_{2.5}$ levels appear to be impacted more by regional than by local effects;
- The median $PM_{2.5}$ mass concentrations were slightly higher for Lawrenceville than for Holbrook (Fig. 4), implying that local urban contributions in Pittsburgh had a minor but measurable effect on total $PM_{2.5}$ mass;
- $PM_{2.5}$ and PM_{10} mass concentration levels were consistently higher in summer than in winter, with intermediate levels observed in the spring and fall;
- Sulfate was the dominant chemical species at both the Holbrook and the Lawrenceville sites during winter and summer intensive sampling. Sulfates at Holbrook were higher than those at Lawrenceville regardless of the season;

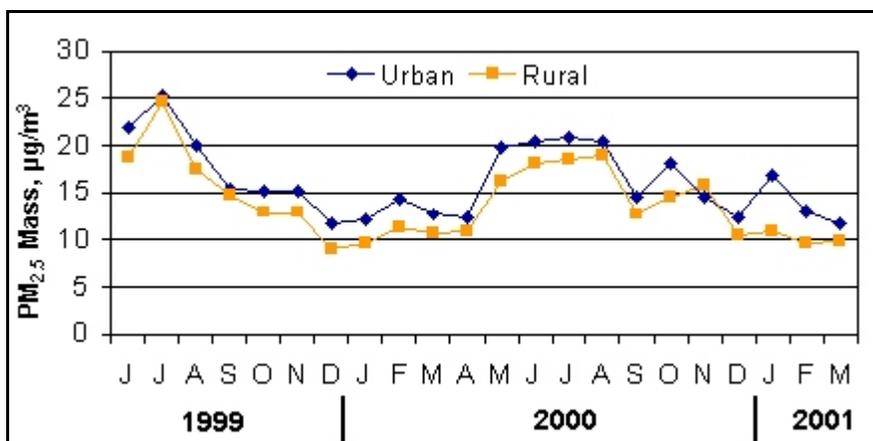


Fig. 4. Monthly average $PM_{2.5}$ mass (TEOM measurements) for urban and rural sites in the upper Ohio River valley.

- Ammonium levels remained relatively constant between seasons and between sites;
- Nitrate levels at Lawrenceville were higher than those at Holbrook during winter intensive sampling. Nitrate levels measured during the summer intensive period were found to be very low at both locations (Figs. 1 and 2); and
- Most of the high PM_{2.5} episodes occurred when the predominating wind direction was from the southwest.

Continuous monitoring of PM_{2.5} mass (via TEOMs) and co-polluting gases will continue at the Lawrenceville and Holbrook sites through at least the end of 2002. Chemical speciation sampling at the Holbrook site was terminated in January, 2002 because sufficient data had been gathered at this site to perform the desired seasonal and urban/rural comparisons. Chemical speciation sampling will continue at Lawrenceville throughout 2002 to increase the quantity of data available for future epidemiology studies.

Chemical analysis of filter samples collected under the UORVP is being performed by Desert Research Institute (DRI). In order to optimize project resources, not all filter samples will be chemically analyzed under the UORVP; instead, after samples are weighed, they are stored at DRI under refrigeration for later analysis on a prioritized basis. For example, samples collected during very high and very low PM_{2.5} episodes and periods where there are substantial urban/rural mass differences will receive higher priority than other time periods. To date, over 1000 filters have been chemically analyzed by DRI under the UORVP; decisions on the types and amounts of additional analyses will be made after the existing data on PM mass, chemical speciation, co-pollutant gases, and meteorology have been more thoroughly examined.

Steubenville Comprehensive Air Monitoring Project (SCAMP)

The overall objective of the Steubenville Comprehensive Air Monitoring Project (SCAMP) is to measure the concentrations of PM_{2.5} and other potential air pollutants at ambient monitoring stations in and around Steubenville, OH, and relate them to the pollutant concentrations actually breathed by persons living in the area. SCAMP consists of complementary “outdoor” and “indoor” activities. The outdoor activities are co-funded by DOE-NETL and EPA, and comprise the sampling and analysis of ambient air quality at three types of locations: (1) a central monitoring station in Steubenville, Ohio; (2) satellite sites to the east, west, north, and south of Steubenville; and (3) outside the homes of persons in Steubenville who have agreed to participate in the study. The indoor activities are funded through the Ohio Department of Development’s Coal Development Office (OCDO) with support by a coalition of industry sources. The indoor portion of SCAMP involves the sampling of air quality inside the homes of project participants and via personal sampling devices worn by these participants. CONSOL Energy has overall responsibility for all activities related to SCAMP, including the integration of all data collected under the outdoor and indoor monitoring programs.

Ambient air monitoring at the central and satellite sites shown in Fig. 3 was conducted from May 2000 through May 2002. All five sites were equipped to obtain daily, 24-hr PM_{2.5} filter

samples; at each site, one sample in four is being analyzed for chemical composition by CONSOL, while the remainder are weighed for PM_{2.5} mass and stored under refrigeration for later reference. The Steubenville central site contained additional equipment for measurements of PM_{2.5} and PM₁₀ mass, gases, pollen and mold spores, and surface meteorology.

Preliminary results of the SCAMP outdoor monitoring program at the central and satellite monitoring sites (data analyzed through December 2000)¹⁵ have been consistent with the findings of the UORVP, specifically:

- PM_{2.5} mass concentrations were close to or above the annual standard at all sites, with the Steubenville site generally slightly higher than the satellite sites;
- There were considerable day-to-day variations in PM_{2.5} mass concentrations, but these variations were consistent across all sites;
- The sum of ammonium, sulfate, and nitrate fractions of PM_{2.5} consistently ranged from 45% to 55% of total mass at all sites (carbon analysis not yet completed);
- The sulfate fraction decreased and nitrate fraction increased from summer to winter at all sites;
- There were no strong correlations between PM_{2.5} and surface weather data (back trajectory analysis has not yet been performed); and
- Pollen and mold spore concentrations were not correlated with PM_{2.5}

Although the data from the central and satellite monitoring sites provide the regional context needed to interpret air quality variations, the greatest value of SCAMP stems from the integration of these data with outdoor, indoor, and personal air quality data collected within the city of Steubenville. Fig. 5 shows the locations of these monitoring sites, which were located inside and outside the residences of individuals who agreed to participate in the study. While monitoring at the central site was conducted continuously, monitoring inside and outside the residences occurred in the form of discrete panel studies of “susceptible” individuals, each lasting approximately 12 weeks. These panel studies were designed and performed primarily by the Harvard School of Public Health. The first panel study involved approximately 30 “older adults” (ages 55+), and was conducted in two sessions during the summer and fall of 2000. Most of the older adults had previously reported heart or lung problems. The second panel involved children (ages approx. 10-13); again, two monitoring sessions with children were conducted, one each during the winter and summer of 2001.

In each panel monitoring session, measurements were made with personal exposure monitors (PEMs) designed by Harvard. Each PEM was capable of obtaining multiple 24-hr filter samples that allowed analysis of total PM_{2.5} mass and its sulfate, organic carbon, and elemental carbon fractions. The PEMs also obtained 24-hr average measurements of NO₂, SO₂, and O₃ gases. Fig. 6 shows how the PEMs were typically deployed during outdoor, indoor, and personal monitoring sessions. Although the participants could not wear the PEMs for the entire 24-hr sampling period, the PEMs remained as close as possible to the individual throughout that time. Each participant kept an activity log to assist in interpreting the results from the personal sampling sessions.

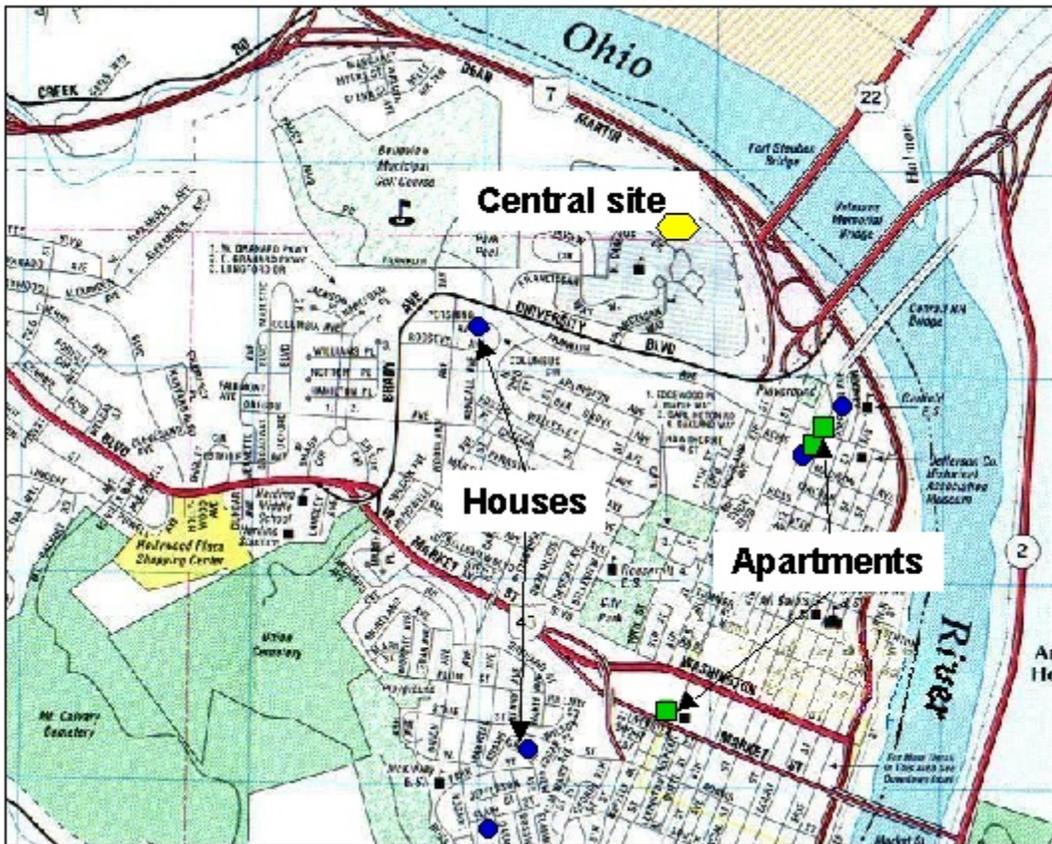


Fig. 5. Locations of SCAMP outdoor, indoor and personal monitoring sites (map courtesy of Harvard School of Public Health)

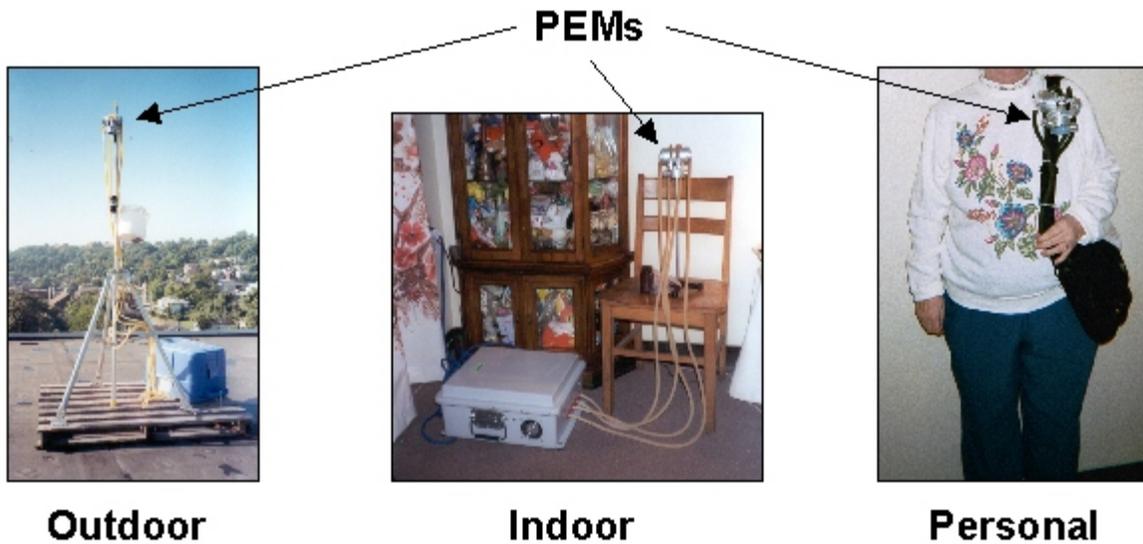


Fig. 6. Harvard multi-pollutant sampler deployed in SCAMP project (photos courtesy of Harvard School of Public Health)

The only data now available from the outdoor-indoor-personal panel studies are for PM_{2.5} mass from the summer and fall 2000 (older adult) panel. All remaining data are still being analyzed and interpreted by Harvard. Preliminary findings from the available data suggest that PM_{2.5} mass was nearly identical at all outside locations (central site and outside residences). Outdoor PM_{2.5} mass concentrations were, in general, slightly higher than indoor and personal concentrations; however, on selected occasions, the indoor/personal PM_{2.5} mass greatly exceeded the outside concentrations. The reasons for these “spikes” in indoor and personal PM_{2.5} mass, and their significance, are currently being investigated.

EPA-CMU “PM Supersite” in Pittsburgh

The ambient sampling and analysis effort conducted by Carnegie-Mellon University (CMU) at its EPA-funded “PM Supersite” in Pittsburgh, PA is part of a larger DOE-sponsored effort that also includes the detailed characterization of source emissions affecting the Pittsburgh region and extensive modeling efforts to identify source contributions and predict the impact of various emission reduction strategies on the region. The ambient sampling and analysis component of the CMU project is described in this section; the other components are described later in this paper.

The measurement campaign at the Pittsburgh PM supersite, located in an urban setting next to the CMU campus (see Fig. 3), began in May 2001 and will continue through October 2002. It consists of baseline (daily or more frequent) measurements of aerosol mass and composition using a variety of filter-based and continuous techniques, supplemented by three "intensive" measurement periods. The first two intensive periods were completed during July 2001 and January 2002, and the third intensive period is tentatively scheduled for September 2002. During the intensive measurement periods, the daily measurement campaign at the central Supersite is extended to other sites upwind and downwind of Pittsburgh. In addition, several advanced technologies for measuring aerosol properties are being employed at the Pittsburgh site to achieve the most detailed possible characterization of particulate matter. These advanced techniques include instrumentation for near-real-time measurement of organic carbon, elemental carbon, and metals in particulate matter, detailed speciation of organic material in aerosols, and three different techniques for measuring the chemical composition of individual particles (as opposed to batches of particles as is done via existing technology).

Preliminary analysis of data obtained from August 2001 through January 2002¹⁶ yielded results similar to those of the SCAMP and UORVP described above. The average daily mass concentration of PM_{2.5} at the central PM Supersite was 17.4 µg/m³ during this period, with higher concentrations during July, August and September (average 21.3 µg/m³) than in October, November and December (average 12.6 µg/m³). The major chemical components of PM_{2.5} are sulfate and organic material throughout the year, with nitrate making a significant contribution during the winter. For the period of July through November, the mass measured with the FRM filter samplers was greater than the sum of chemical components, possibly resulting from water retained on the Teflon filters.

Comparison of data collected at satellite sites indicate that there was relatively little spatial variation in the PM_{2.5} levels around Pittsburgh during July 2001. This suggests that PM_{2.5} was determined mostly by the same sources, namely regional sources upwind of the study area. The total particle number concentration and ultrafine particle levels at the central monitoring site appear dominated by nucleation bursts. Evidence of nucleation bursts can be seen on approximately 50% of the days. The frequency and intensity of these nucleation bursts make them the single biggest factor in determining the number concentration of particles at the sampling site in Schenley Park, followed by traffic intensity, other local combustion, and regional transport as contributing factors.

NETL In-House Monitoring Station

Personnel from the DOE-NETL Office of Science and Technology (OST) operate an extensive ambient air monitoring station at DOE-NETL's suburban Pittsburgh facility (Fig. 3). Unlike the Lawrenceville and CMU central monitoring stations, the DOE-NETL-OST facility is not located near any major roadways or industrial emission sources. Although a small coal boiler for steam heating is located about 600 meters from the monitoring site, it is in the dominant downwind direction from the site (east-southeast) and does not contribute greatly to overall PM_{2.5} levels. Monitoring at the DOE-NETL-OST facility began in summer 1999 and is expected to continue at least through 2003. Equipment at the site includes continuous monitors for PM_{2.5} mass and its sulfate, nitrate, and carbon components; filter samplers for determining PM_{2.5} mass and chemical composition; continuous monitors for criteria pollutant gases and meteorology; and, at times, special instruments to determine the contribution of semivolatile organics and nitrates to overall PM_{2.5}. A key topic of interest at the DOE-NETL-OST site is the use of scanning electron microscopy (SEM) and proton-induced X-ray emission (PIXE) analysis to determine the contribution of specific emission sources to the overall PM_{2.5} mix.

Detailed analysis of data collected at the DOE-NETL-OST site during the "high PM season" (July and August 2000)¹⁷ yielded the following observations and conclusions:

- During high-pressure conditions, mass concentrations of PM_{2.5} were the lowest (average 13 µg/m³) and the composition is dominated by carbonaceous material (approx. 70%), including semivolatile organic material that was lost in varying degrees from the filter samplers. Under these meteorological conditions, the PM_{2.5} originated mainly from local transportation sources and some coal-fired boiler emissions.
- High concentrations of PM_{2.5} were always associated with transport of pollutants to the DOE-NETL-OST site with the passage of a frontal system after a period of high pressure. Analysis of meteorological and back-trajectory data suggested that the pollutants were emitted to the west and southwest of the site during the high-pressure periods and were subsequently transported to the site. When the air mass originated from the west or southwest, the concentrations averaged 31 µg/m³ and ammonium sulfate averaged 54% of the PM_{2.5} mass.
- Limited SEM and PIXE results suggested that when transport was from the west, the

emissions originated from both coal-fired boilers and the coke and steel processing facilities to the west of the DOE-NETL site. When the pollutants were transported to the DOE-NETL site from the southwest, markers for emissions from the iron industries are not present; therefore, coal combustion along the Ohio River valley to the southwest may have been the most important contributor to the PM_{2.5} mass.

Cost-shared Ambient Monitoring Projects in the Southeastern U. S.

Since air quality in the southeastern U. S. is also significantly impacted by emissions from coal-fired power plants, the DOE-NETL PM_{2.5} program has also provided cost-sharing support to ambient air sampling and analysis activities initiated by industries and other Government agencies in the southeast. The largest of these efforts is being performed by Southern Research Institute (SRI) to establish and operate a research station in North Birmingham, AL. The North Birmingham site is part of EPA's nationwide PM_{2.5} chemical speciation network and is also one of eight SEARCH (Southeastern Aerosol Research and Characterization) project sites in a regional monitoring network supported by EPRI, Southern Company, and other industry sponsors. Under the DOE-sponsored project, SRI has augmented the North Birmingham site with an instrument package that provides for the near-continuous characterization of PM_{2.5} chemical composition, along with surface meteorology. Particle properties that are monitored continuously include size distribution (0.2 to 10 microns), organic and elemental carbon, ammonium, nitrate, and sulfate. The detailed database of near-continuous measurements will be used to support studies of source attribution, time/transport properties, and management strategies for fine PM in the region.

In another cost-sharing effort, DOE-NETL and the Tennessee Valley Authority (TVA) are participating in an Interagency Agreement to collect and interpret air quality data in the Great Smoky Mountains National Park. As with the SRI-North Birmingham site, the DOE contribution was used to install and operate several types of continuous monitoring instruments for PM_{2.5} and its constituents at TVA-operated sites in the Great Smokies to supplement the filter-based samplers and gas monitoring equipment already at the sites. As part of the analysis component of this task, investigations will be performed to resolve apparent contradictions among the results of various ambient air quality sampling programs performed to date. For example, data collected by the Clean Air Status and Trends Network (CASTNet) indicates that sulfur levels have declined in many areas of the eastern U.S. since about 1988. Much of this decline is thought to be due to decreases in sulfur dioxide emissions from fossil-fuel-fired utility boilers. However, some data collected under the Interagency Monitoring of Protected Visual Environments (IMPROVE) program suggest that PM_{2.5} sulfate levels have been increasing over parts of the southern Appalachian region. This apparent discrepancy is being investigated further under the TVA Interagency Agreement.

Emissions and Plume Characterization

To accurately assess the effect of any emission source on ambient air quality, it is first necessary to identify, as completely as possible, the chemical characteristics of all emission sources that could be affecting the ambient receptors of interest. The emissions

characterization component of the DOE-NETL 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 condensibles, 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 an updated emissions inventory for the region is also included under this component of the program.

Advanced Low-NOx Burner Emissions Characterization

The goal of this work was to develop a comprehensive, high-quality database characterizing PM_{2.5} emissions from utility plants firing high sulfur coals. The specific objectives were to develop and test an ultra low-NOx pulverized coal burner for plug-in retrofit applications, and to assess the impact of low-NOx burner operation on NOx and PM_{2.5} emissions. The work was performed by McDermott Technologies, Inc. (MTI) at its Clean Environment Development Facility (CEDF), a 100 million Btu/hr near-full-scale facility located in Alliance, OH¹⁸. Co-funding for this project was provided by the Ohio Coal Development Office.

Size classified fly ash samples representative of commercial low-NOx and ultra low-NOx combustion of high-volatile bituminous (Pittsburgh 8) coal were collected at the inlet and outlet of the electrostatic precipitator (ESP) at the CEDF. The mass of size classified fly ash at the ESP outlet was sufficient to evaluate the particle size distribution, but was of insufficient size to permit reliable chemical analysis. The size classified fly ash from the inlet of the ESP was used for detailed chemical analyses. Chemical analyses of the fly ash samples from the ESP outlet using a high volume sampler were performed for comparison to the size classified results at the inlet.

For all test conditions the particulate removal efficiency of the ESP exceeded 99.3% and emissions were less than the NSPS limits of ~48 mg/dscm. With constant combustion conditions, the removal efficiency of the ESP increased as the ESP voltage and Specific Collection Area (SCA) increased. The associated decrease in particle emissions occurred in size fractions both larger and smaller than 2.5 microns. For constant ESP voltage and SCA, the overall particle removal efficiency for the ultra low-NOx combustion condition (99.4 – 99.6%) was only slightly less than for the low-NOx combustion condition (99.7%). The decrease in removal efficiency was mostly in the size fraction greater than 2.5 microns, indicating particle re-entrainment rather than impairment of the ability to collect PM_{2.5}. These results may be specific to the coal tested in this program.

There was an overall increase in unburned carbon in the fly ash when moving from the low-NOx to ultra-low-NOx burner configurations. Although the increase in unburned carbon was quite small on an average basis, it was strongly dependent on particle size. While the carbon

content of PM greater than 10 microns increased from about 1% to 4%, the carbon content of the PM_{2.5} size fraction increased from about 7% to 45%. In general, the concentration of inorganic elements and trace species in the fly ash was dependent on the particle size fraction. The smallest particles tended to have higher concentrations of species/elements than larger particles. This trend was strongly dependent on the volatility of the element or species. The concentration of the least volatile elements tended to be depleted in the smallest particles while the concentration of the most volatile elements/species tended to be enriched.

Dilution Sampler Development

The main objectives of this project, Conducted by Carnegie-Mellon University (CMU), were to characterize the emissions of primary PM_{2.5} from coal-fired utility boilers, study the formation of fine organic aerosols from these sources, and quantify sampling artifacts due to water and vaporization/condensation of semivolatile compounds. A state-of-the-art dilution sampler (Fig. 7) was developed to simulate the dilution and cooling processes that coal combustion products undergo in the atmosphere. Unlike traditional exhaust stack sampling methods, the dilution sampler allows the investigation of processes such as nucleation, condensation, and coagulation, which affect the size distribution and composition of the emissions. This characterization will theoretically allow PM_{2.5} emissions to be tracked from their sources -- in this case, coal-fired boilers -- to ambient air monitoring sites.

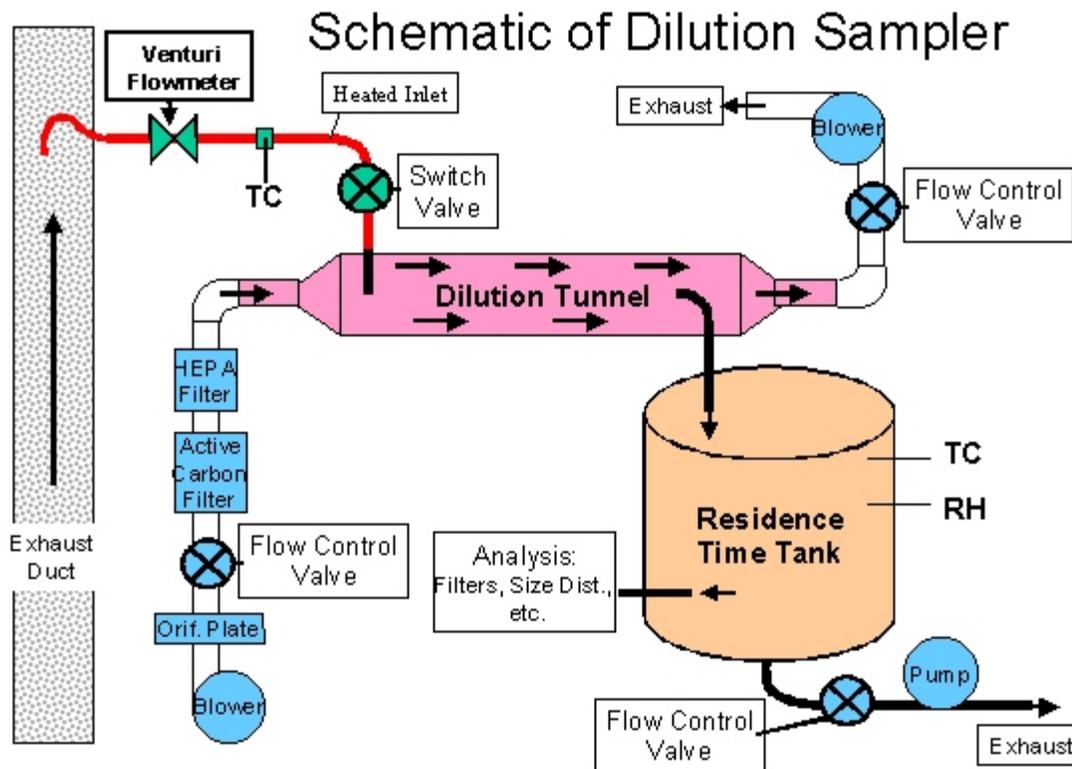


Fig. 7. Dilution sampler developed by Carnegie-Mellon University (as deployed at NETL CERF)

The dilution sampler was tested at DOE-NETL's Combustion Environmental Research Facility (CERF). Flue gases from the CERF experimental furnace are sampled through a cyclone with a 2.5 μ m cut point to prevent larger particles than from depositing downstream in the dilution system. Next, the combustion products flow through a heated sampling probe, past a flow meter, and into the dilution tunnel. In the dilution tunnel, the sample is mixed under turbulent conditions with clean air that has been treated by activated carbon and HEPA filters to remove all contaminants. Temperature and humidity of the air are controlled by passing the dilution air through a chiller and humidification system prior to mixing. The sampler is designed to operate at variable dilution ratios of up to 200:1.

A fraction of the diluted sample is pulled from the dilution chamber and stored in a residence time tank. This chamber provides up to several minutes of residence time, allowing condensation and nucleation to occur, thus enabling a study of the formation of semivolatile aerosols from coal combustion products. Diluted source particulate matter is then captured by a variety of aerosol classification equipment to determine the particle composition, size distribution and other pertinent information about the aerosol. Experiments are being conducted to determine the rates of PM_{2.5} emission as a function of dilution rate, temperature, and relative humidity. The dilution sampler is intended to be fully portable to allow for transportation to individual power plants for emissions characterization experiments.

Using the dilution sampler, size distributions were measured for various dilution ratios and residence tank times. Thus far, concentration data, normalized on a unit volume basis, show higher concentrations of particles of less than 0.01mm when the dilution ratio is increased. These concentrations were found to decrease with longer sample residence times, due to increased coagulation. Additional data analysis is being performed to further investigate the effects of coagulation, as well as the differences between dilution sampling and direct-stack sampling on concentrations of trace species.¹⁹ After the effects of the various sampling parameters have been investigated at the CERF, the dilution sampler will be used to perform detailed sampling on full-scale coal boilers and other major industrial point sources.

Characterization of Source Emissions Affecting the Pittsburgh Region

In conjunction with its ambient sampling and analysis efforts, CMU is also performing detailed sampling of individual pollution sources using some of the same state-of-the-art instrumentation as at the EPA Pittsburgh PM Supersite. Source characterization is planned for major point sources in the Pittsburgh area such as coal-fired boilers, a coke plant, a steel mill, and an industrial manufacturing facility. Mobile source emissions are being characterized by conducting a tunnel study, and dust samples are being collected and analyzed from various locations around western Pennsylvania. For sources such as steel mills and coke plants that do not have a single well-defined emissions point, fence line monitoring is being performed to develop an integrated fingerprint for the source.

To support subsequent modeling activities, CMU is performing a comprehensive survey of existing emissions information for the sources of primary PM and PM precursors for the

Pittsburgh region. The existing fingerprints for the source categories of greatest potential importance to the Pittsburgh region are being reviewed, and sources whose emissions appear to require additional characterization are being identified. The activity data (i.e., quantities of emissions) for all known sources are being compiled for several time periods, with particular emphasis on the Supersite's intensive sampling periods.

Cumberland Power Plant Plume Study

As part of its Interagency Agreement with DOE-NETL, TVA has performed an assessment of the impact of the installation of high-efficiency wet flue gas desulfurization (FGD) and NO_x control technology on primary and secondary fine particulate formation at its Cumberland power plant in Cumberland City, TN. Data were collected using an instrumented helicopter that flew through the Cumberland plant plume at various downwind distances before and after the installation of FGD and NO_x controls, measuring the changes (and rates of changes where possible) in total mass, size distributions, and chemical composition of in-plume fine particles. Additional data on concentrations of gaseous species in the Cumberland plant plume were also collected. Results of the study²⁰ showed that the rate of conversion of SO₂ to SO₄⁻², a key factor in the production of secondary particles, was about 0.04 hr⁻¹ both before and after the installation of FGD. This similarity suggests that the reduction in SO₂ emissions resulting from FGD at the Cumberland plant has likely been accompanied by a roughly proportional reduction in the amount of SO₄⁻² formation during plume dispersion.

Predictive Modeling and Evaluation

It is likely that most or all State Implementation Plans pertaining to PM_{2.5} will be developed with the aid of some type of atmospheric modeling to predict the reductions in PM_{2.5} attainable via reductions in various source emissions. The accuracy of such predictions depends on how accurately the models represent the actual emissions and atmospheric chemistry/transport phenomena. Modeling studies supported by the DOE-NETL program include: (1) receptor-based (source apportionment) modeling pertinent to electric power sources; (2) model evaluation using ambient PM mass measurements; (3) methods for estimating the lifetime and transport distances of primary and secondary PM; (4) quantifying the relationships between PM (nitric acid and sulfate) and NO_x and SO₂ emissions in the modeling domain; and (5) quantifying the contribution of primary and secondary organic aerosol emissions from power sources to observed organic PM.

The emphasis of the modeling work under the DOE-NETL program will be in the application of existing models to examine the effects of various emission reduction strategies, especially those involving coal-fired power plants, on PM levels at regional ambient receptors. Basic research to identify individual atmospheric reactions and rates embodied in the modeling systems is being supported by other DOE Offices (specifically, the Office of Science), EPA, and others. However, it is anticipated that refinements to existing models will be made under DOE-NETL-sponsored projects to incorporate the most recent advancements in atmospheric science. It is expected that the outcome of the modeling studies will be an improved description of the relative contribution of coal-fired power plants to ambient PM levels, and a

set of general guidelines that inform decision-makers of what to expect if emission reductions on coal-fired power plants in the modeled region are implemented.

Pittsburgh Regional Source-Receptor Modeling Study

As part of its Cooperative Agreement with DOE-NETL, Carnegie-Mellon University will employ receptor modeling and chemical transport modeling techniques to identify the sources of particulate matter collected at the Pittsburgh monitoring site and predict the concentrations and composition of particulate matter that are likely to occur in Pittsburgh in the future.

Receptor modeling will involve several forms of factor analysis to identify the composition and contributions of the sources. Potential Source Contribution Function analysis as well as Residence Time Weighted Concentration analysis will be applied to the determination of the locations of the likely major contributing sources. The results will be compared with those obtained utilizing the back-trajectory-based methods. Using the single particle measurements developed in its ambient sampling program, the likely source of the particle nuclei and the secondary species contributions may be identifiable on a particle-by-particle basis. The availability of highly time-resolved data for both the ambient aerosols and the potential contributing sources should permit greater source resolution.

The second type of modeling will use the updated source emissions information as input to an updated version of a publicly-available chemical transport model (CTM) that simulates atmospheric processes at multiple spatial scales. Given the emissions inputs and prevailing meteorology conditions, the CTM simulates the aerosol size-composition distribution for approximately 100 species (e.g., sulfate, nitrate, chloride, sodium, ammonium, elemental carbon, primary and secondary organic carbon, crustal elements, H⁺, and water) throughout the model domain. After the model is verified by comparing its results with field measurements, it can be used to predict the changes in PM concentrations and composition resulting from various power plant emission scenarios, focusing on the changes that may occur in ambient PM in the upper Ohio River valley. The model is also coupled to a sensitivity analysis module so it can calculate directly the sensitivities of PM concentrations to source strength.

To date, modeling efforts under this project have consisted of refining the atmospheric chemistry components of existing of the aerosol modeling tools, incorporating them in 2 three-dimensional chemical transport models (URM and CAMx-AERO), and evaluating them against available data sets. The Trajectory-Grid (T-G) approach has been incorporated in the CMU Hybrid Aerosol Module and the results have been compared to the currently used approach (Adams method in the LSOE package) in a one-dimensional Lagrangian trajectory model. The performance of the T-G method was excellent, decreasing the CPU cost by an order of magnitude without sacrificing any accuracy. The CMU aerosol modules (Equilibrium, Dynamics-MADM, and Hybrid) have been added to CAMx and have been used to simulate a 1995 pollution episode in Southern California. The performance of the model was very good both in terms of accuracy and computational efficiency. CMU is currently setting up the models for simulations in the Eastern United States domain using

meteorological and emissions fields from the NARSTO 1995 campaigns. After this testing, CMU will focus on the simulations for the July 2001 intensive sampling period.

Ozone/PM_{2.5} Formation & Transport Model Comparison

TVA is an active participant in a modeling assessment (using the URM model) for the Southern Appalachian Mountains Initiative (SAMI) as part of its integrated assessment in the southeastern United States. Under its Interagency Agreement with DOE-NETL, results from the episodic and sensitivity runs of URM will be analyzed by TVA to provide DOE with information on how different air quality parameters, including PM_{2.5}, vary with changes in different source sectors (e.g., large point sources, low-level area sources, mobile sources, etc.) This modeling will examine large-scale changes, thereby giving a scope to the results that will be applicable to a large part of the eastern U.S. In addition, SAMI will use actual and future-year emissions data as part of its analysis, giving information that is relevant to current and anticipated future emission scenarios.

In order to build upon the SAMI modeling effort, the regional air quality model recently developed by EPA (Models-3) will also be evaluated. Models-3 and URM will each be run for one or two base cases (depending on the feasibility of converting the existing SAMI data to the Models-3 format), and the predicted PM_{2.5} and ozone levels from the two models in the eastern U.S. would be compared. Several emission control strategies proposed by SAMI will be simulated for the base case(s) and the consistency between the two models will be evaluated.

PM Emission Control Technology

This component of the DOE-NETL program seeks to develop cost-effective control technology for: primary fine particulates, gaseous precursors that form secondary fine particles, and acid gases that can create visible plumes and are reportable under the Toxic Release Inventory^a. DOE-NETL's efforts in PM control technology R&D have been based on the performance capabilities of currently-available technology and regulatory requirements, and are closely coordinated with other three components of the DOE-NETL PM_{2.5} program to ensure that the research focuses on the pollutants of most concern.

Primary PM Emissions

As discussed earlier in this paper, additional reductions in primary PM emissions from coal plants are likely to result in only minimal reductions in ambient PM_{2.5}. In addition, state-of-the-art, commercially-available electrostatic precipitators and fabric filters can usually achieve reductions in primary PM emissions of 99.5% or greater. However, older particulate

^aNETL's extensive efforts in mercury control technology are managed as a separate program because mercury is emitted primarily as a gas rather than as a particle and does not contribute significantly to ambient PM_{2.5} mass.

control devices may not perform as efficiently as their newer counterparts, and local concerns over stack opacity can occur even when primary PM emissions are below new source performance standards. In the future, additional concern over air toxics in fine particles may result in additional regulations to control primary PM from coal plants. Therefore, the DOE-NETL program contains several projects that focus on developing improved technology for primary fine particle control.

Advanced Hybrid Particulate Collector (AHPC). The University of North Dakota Energy and Environmental Research Center (UNDEERC) has developed a new concept in particulate control called the advanced hybrid particulate collector (AHPC). The AHPC utilizes both electrostatic collection and filtration in a unique geometric configuration (Fig. 8) that achieves ultrahigh particle collection with much less collection area than conventional particulate control devices. Instead of placing the ESP and fabric filter sections in series (as is done with other dual-mode particulate collection devices), the filter bags are placed directly between the ESP collection plates. The collection plates are perforated (45% open area) to allow dust to reach the bags; however, because the particles become charged before they pass through the plates, over 90% of the particulate mass is collected on the plates before it ever reaches the bags. When pulses of air are used to clean the filter bag surfaces, the dislodged particles are thrown back into the ESP fields where they have another opportunity to be collected on the plates. The AHPC has less than half the normal number of ESP components and 65%-75% fewer bags than a conventional fabric filter. This translates into an overall smaller system size. Operating experience suggests that the bags will not need to be cleaned as often as in typical baghouses and will provide excellent performance over a long operating life. This leads to low operating costs since filter bag replacement is a key cost component.

A slipstream demonstration unit has been operational since July 1999, filtering 15,000

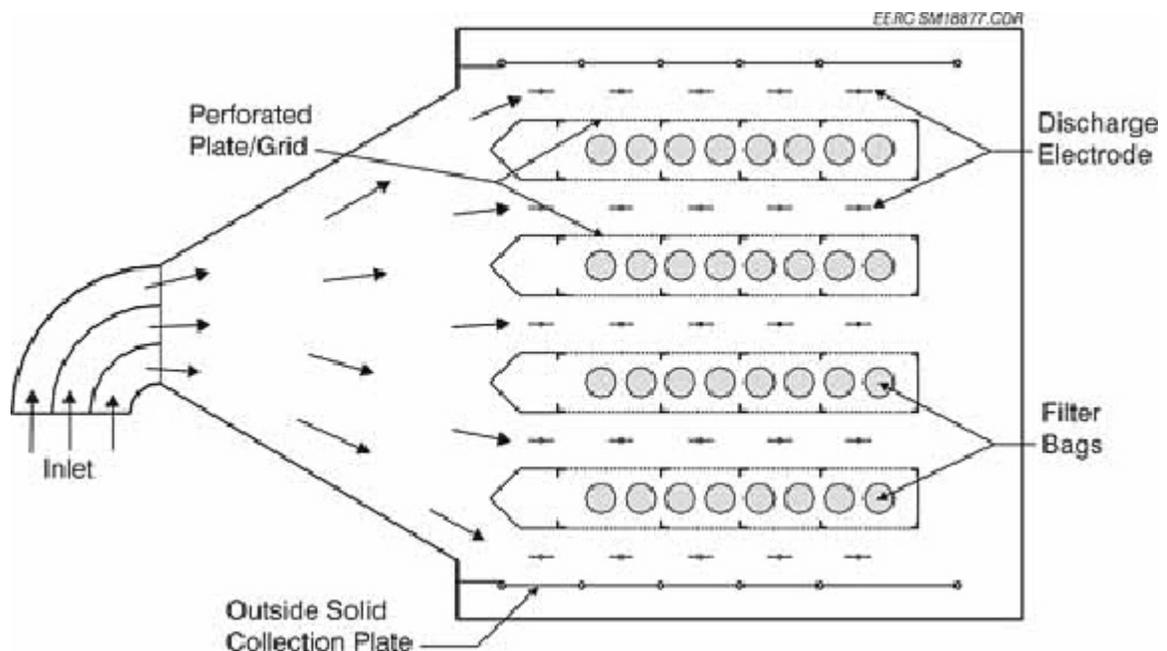


Fig 8. Design features of advanced hybrid particulate collector (Advanced Hybrid™).

m³/hour of flue gas from the Otter Tail Power's Big Stone (South Dakota) coal-fired power plant. The cyclone-fired boiler at Big Stone burns Powder River Basin Coal, whose fly ash has traditionally been found to be difficult to collect with ESP's because of its high resistivity. The pilot AHPC unit has exhibited very stable operating levels while maintaining low energy consumption during continuous operation, with on-line bag cleaning. Tests to date²¹ show that the AHPC provides over 99.99% particulate collection efficiency for all particle sizes, at a cost that is competitive with or lower than existing technologies. This patented technology is now being marketed by one of the project's co-funders (W. L. Gore & Associates, Inc.) as the Advanced Hybrid™, and it will soon be demonstrated at full scale (450 MWe) at the Big Stone Plant in a project sponsored under DOE's Power Plant Improvement Initiative.

Electrocore Separator. LSR Technologies is testing the Advanced ElectroCore system on a 1.5MWe slipstream of the Alabama Power Company's Gaston Steam Plant. The ElectroCore is a polishing device for under-performing electrostatic precipitators (ESPs), that also has multi-pollutant control capabilities. The system consists of a conventional upstream ESP, a dry SO₂ scrubber, a particle pre-charger and an Advanced ElectroCore separator. In initial tests during late 2001 - early 2002, the system collected up to 95 percent of particulate matter that passed through the existing hot-side ESP at the plant; combined particulate removal efficiency (ESP with Electrocore system) was nominally 99.99 percent, with emissions well below 0.01lb/million BTU. Also, a 90 percent decrease in total mercury was achieved when an activated carbon sorbent was injected upstream of the system at a low sorbent feed rate.

Advanced Flue Gas Conditioning. ADA Environmental Systems is developing and testing a family of cohesivity modifying flue gas conditioning agents that can be commercialized to provide utilities with a cost-effective means of complying with particulate emission and opacity regulations. Improving the cohesivity and agglomeration of fly ash particles via flue gas conditioning is a proven means of increasing the collection efficiency of an ESP. However, a new class of additives is needed because currently available agglomerating aids on the market require the storage and handling of large quantities of ammonia, which under recent legislation has been classified as extremely hazardous and necessitates extensive risk assessment and emergency response plans. There are also operating conditions and coals where the ammonia-based technologies are not as effective and the treated ash treated is difficult to dispose of because of the odor produced by ammonia. While ammonia has certain applications, in SCR for example, for plants that can operate without the storage of unnecessary hazardous chemicals, ammonia alternatives are highly desirable. Initial tests of one of the new conditioning agents at a PacifiCorp plant showed significant reductions in plume opacity with no detrimental impacts on fly ash, which allowed the plant to continue the beneficial reuse of the ash. Tests at this site are continuing into 2002 to fully assess the flue gas conditioning product.

Secondary PM Precursors

The secondary PM precursors of greatest relevance to coal-fired power plants are SO₂ and NO_x. Development of technology for improving the efficiency of SO₂ control at power

plants is not currently being pursued by DOE-NETL because previous regulatory drivers (Title IV acid rain regulations) have led to significant private-sector investment in advanced SO₂ control technology. Technology for controlling SO₂ at efficiencies of 95% or greater is already commercially available, and the existing fleet of scrubbed boilers emits less than 15% of the total SO₂ emissions from coal plants. At this time, it is uncertain whether greater efficiencies for existing scrubbers will be required because substantial reductions in ambient PM_{2.5} sulfate concentrations can be achieved simply by employing existing SO₂ removal technology on currently uncontrolled plants. Also, incremental efficiency improvements for existing scrubbers at larger, "dirtier" plants may be achievable using existing technology, but would most likely require case-by-case analysis of operating parameters. The need for DOE research to improve SO₂ scrubbing efficiency may be re-examined in the future if it is determined that currently-available private-sector technology will be insufficient to meet the desired national goals with respect to PM_{2.5} and regional haze.

By contrast, an extensive program to develop advanced NO_x control technology for coal-fired boilers is being performed under the DOE-NETL Innovations for Existing Plants program. However, the NO_x control research is not reviewed as part of this paper. The DOE-NETL NO_x control R&D program is focused primarily on systems capable of achieving low-level NO_x emissions at a cost significantly below that of current state-of-the-art technology. Five projects are focused on the development of technology capable of achieving the limit of 0.15 lbs NO_x/million Btu, while achieving a levelized cost savings of at least 25% over SCR. These technologies are to be ready for commercial-scale demonstration by 2004. An overview of the DOE-NETL advanced NO_x control technology development program can be found on the web at <http://www.netl.doe.gov/coalpower/environment/nox/>.

Acid Gases

Although coal plants release several types of acid gases (e.g., H₂SO₄, HF, and HCl), sulfuric acid and its precursor, sulfur trioxide (SO₃), is currently the acid gas of most interest because it is produced in the greatest quantities and is perceived to be the most amenable to control via near-term technological advancements. Besides being a Toxic Release Inventory substance and a potential precursor to visible plumes at some plants, sulfuric acid in the flue gas can lead to internal plant maintenance problems such as boiler air heater plugging and fouling. However, small amounts of SO₃ in the flue gas are helpful because it makes the fly ash less resistive to electrical charging, and thereby easier to collect in electrostatic precipitators. In fact, some western power plants that burn very low-sulfur coals have systems for injecting SO₃ into the flue gas to decrease the fly ash resistivity and improve ESP performance. The DOE-NETL PM_{2.5} research program has therefore included a project to develop improved technology for controlling the production and release of sulfuric acid.

Furnace Injection of Alkaline Sorbents. This project, performed by URS Group, Inc., tested the effectiveness of alkaline reagents injected into the furnaces of coal-fired boilers at controlling sulfuric acid emissions²². The project was co-funded by EPRI, FirstEnergy Corporation, the Tennessee Valley Authority, American Electric Power (AEP) and Carmeuse

NA. The advantage of injecting the reagents into the upper levels of the furnace rather than in the flue gas stream was the possibility of “conditioning” the boiler to reduce slag buildup and/or prevent SO₃ formation in addition to neutralizing the SO₃ that had already formed.

Two month-long sorbent injection tests were conducted, one on Unit 3 at FirstEnergy's Bruce Mansfield Plant (BMP) and one on Unit 1 at AEP's Gavin Plant. Noticeable improvements in scrubber exhaust plume opacity were observed at both plants during the tests. The alkaline slurries tested included a byproduct magnesium hydroxide slurry (at both Gavin and BMP) and a commercially available magnesium hydroxide slurry (Gavin only). The tests showed that injecting either the commercial or the byproduct magnesium hydroxide slurry could achieve up to 70-75% overall sulfuric acid removal with minimal negative impacts on other plant operations. At BMP, greater overall removal of SO₃ (over 90%) was achieved over the short term, but such high levels of SO₃ removal increased the resistivity of the fly ash and adversely affected the ESP performance. Control at the 70-75% level was found to be optimum to avoid adverse ESP effects. At Gavin Plant, the furnace-injected sorbents were very effective in removing SO₃ formed in the furnace, but were much less effective in removing SO₃ formed across the SCR system, thereby limiting the overall SO₃ removal efficiency. No adverse effects on ESP performance were noted at Gavin.

INTEGRATION OF CURRENT AND FUTURE RESEARCH IN PM_{2.5} AND RELATED AIR QUALITY ISSUES

It is apparent that the issues pertinent to PM_{2.5} and coal power plants overlap a wide range of interrelated scientific, regulatory, and control technology development activities. For this reason, the DOE Innovations for Existing Plants (IEP) Program incorporates the current PM_{2.5} research effort as part of a much broader program designed to supply key scientific and technical data on emerging environmental regulatory and policy issues, and to develop environmental control technologies for near-term application to power plants. Fig. 9 illustrates how the current PM_{2.5} research effort is integrated with the broader IEP program. For example, the NETL activities in ambient sampling, emissions characterization, and atmospheric modeling, while currently focusing on PM_{2.5}, can be viewed as the basis for a broader research program to address the impacts of other power plant emissions (e.g., mercury) on ambient air quality. Since air pollutants can eventually have adverse impacts on water quality, the modeling activities currently conducted as part of the DOE-NETL PM_{2.5} effort can assist the portion of the IEP program that addresses the impacts of power plant emissions on watershed science and policy. Furthermore, while the PM/acid gas emission control technology component of the DOE-NETL PM_{2.5} effort can be viewed separately from similar efforts for mercury and NO_x under the current IEP program, the continued emphasis on “multi-pollutant” control legislation is causing R&D attention to shift from single-pollutant to multi-pollutant control technologies. As a result, new technologies for power plant emissions control can be expected to incorporate integrated approaches for controlling all air pollutants of concern. A complete discussion of current and future activities under the IEP program is beyond the scope of this paper; however, a few of the near-term future activities in the area of air quality research are discussed below.

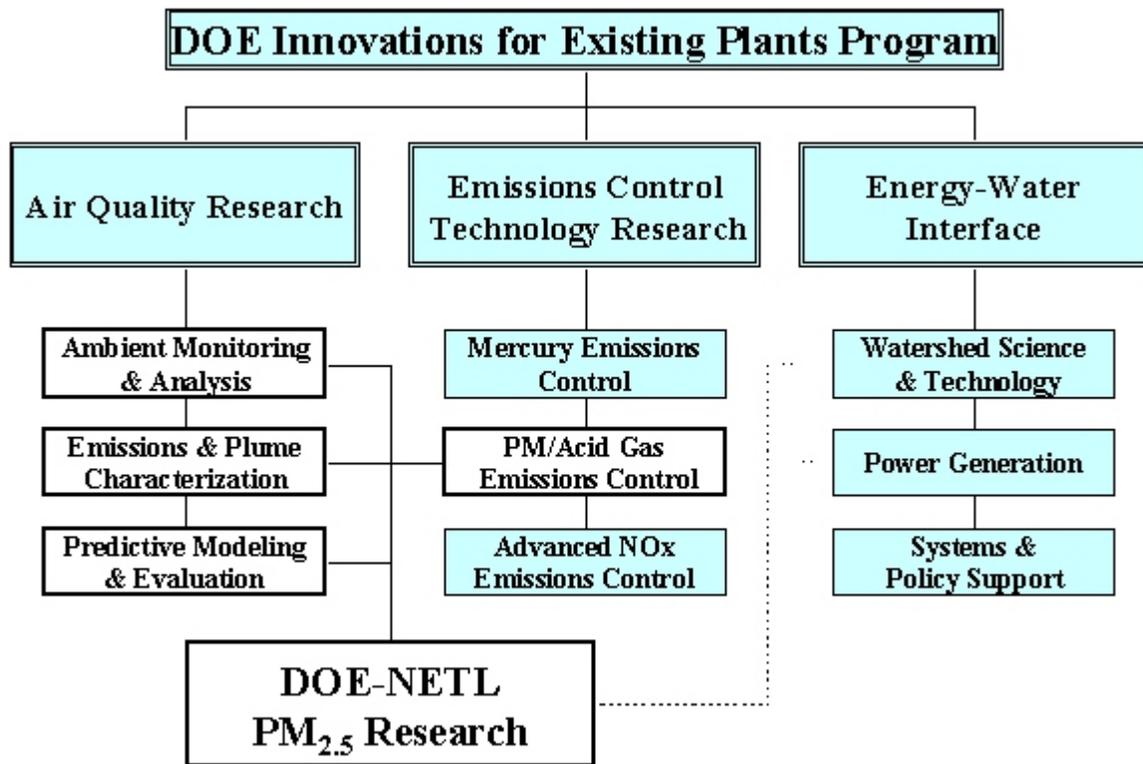


Fig. 9. Integration of PM_{2.5} Research with DOE Innovations for Existing Plants Program

Database and Analytical Tool for Air Quality in the Upper Ohio River Valley

Beginning in August 2002, Advanced Technology Systems, Inc. with Ohio University and Texas A&M University - Kingsville as subcontractors, will develop a state-of-the-art, scalable and robust computer application for DOE-NETL to manage the extensive data sets resulting from the DOE-sponsored ambient air monitoring programs in the upper Ohio River valley region. Efforts will be made to include, to the greatest extent possible, ambient air data collected by other agencies in the upper Ohio River valley region, such as U.S. EPA, Pennsylvania Department of Environmental Protection (PA-DEP), West Virginia Division of Environmental Protection (WV-DEP), Ohio EPA, and the Allegheny County Health Department (ACHD). Although emphasis will be placed on data collected in the upper Ohio River valley region, the computer application developed under this Agreement will be designed, to the greatest extent possible, to access data collected at DOE-NETL-sponsored ambient air monitoring sites outside the region, such as the TVA site in the Great Smoky Mountains and SRI's North Birmingham site described earlier in this paper. The data base and analytical tool development effort will also be coordinated, to the greatest extent possible, with similar tools being developed for use by U.S. EPA. This will ensure that the database and analytical tools compiled under this Agreement will be readily accessible to a wide variety of stakeholders.

The data management system will include a web-based user interface that will allow easy access to the data by the scientific community, policy-makers, and other stakeholders while providing detailed information on sampling, analytical and quality control parameters. In addition, the system will provide graphical tools for displaying, analyzing and interpreting the air quality data, multiple report generation capabilities, and easy-to-understand visualization formats that can be utilized by the media and public outreach/educational institutions.

Study of Mercury Speciation in Power Plant Plumes and Air Quality Models

Although currently-available air quality models include provisions for simulating the emission of mercury from power plants and its eventual atmospheric fate, there is considerable debate as to the adequacy of these models for decision-making purposes. For example, models currently being used by EPA predict substantial wet deposition of mercury in selected areas such as Pennsylvania; however, field measurements show substantially less deposition than predicted. One potential reason for this discrepancy may be the incomplete understanding of how mercury behaves in power plant plumes. Specifically, the current models predict (and stack gas measurements confirm) that much of the mercury released from power plants burning high-sulfur eastern bituminous coals is in the oxidized (Hg^{+2}) form. Oxidized mercury tends to react and become deposited relatively close to the emission source, whereas elemental mercury (Hg^0) is relatively unreactive and can remain in the atmosphere for long periods (~1yr or more). However, there is some evidence to suggest that conversion from Hg^{+2} to Hg^0 may occur within the power plant plume; this may be responsible for some of the errors in current predictive models. Understanding mercury speciation in power plant emissions is important from a policy standpoint because mercury emissions trading strategies will be more environmentally effective if the mercury is released in elemental rather than oxidized form.

In order to investigate the changes in mercury speciation that may be occurring within power plant plumes, DOE and TVA will jointly participate in a project with EPRI to be completed at Georgia Power's Plant Bowen in northern Georgia. TVA scientists will fly an airplane through the power plant plume at various downwind distances (up to 50 km) and collect speciated mercury data within the plume. Stack gases will be monitored concurrently for mercury speciation. These measurements will help determine whether mercury speciation is changing within the plume, and provide insight regarding mercury reactions embodied in predictive models. DOE-NETL will also attempt to augment its current air quality modeling efforts to include mercury as well. As with $\text{PM}_{2.5}$, initial DOE-NETL efforts in mercury deposition modeling are expected to center on the upper Ohio River Valley, where current models predict significant amounts of mercury deposition.

PM Epidemiology Studies

To date, DOE-NETL has not included PM health-related research as part of its portfolio; however, the need for further information on the relative effects of PM constituents on human health, coupled with the availability of a vast amount of ambient air data from ongoing programs, is causing DOE-NETL to re-evaluate this position. At the conclusion of

the ongoing ambient sampling and analysis projects described in this paper, it is likely that enough data will be available to perform retrospective epidemiology studies in Pittsburgh, and perhaps Steubenville. It is envisioned that an epidemiology study similar to those recently completed in Atlanta¹¹ may be possible, focusing on the contribution of various PM_{2.5} constituents to human mortality and morbidity. The availability of all DOE-NETL's data in a common database and analytical tool (described earlier in this section) may greatly facilitate the performance of such a study. Over the next year, DOE-NETL will continue to evaluate the suitability of these data for use in epidemiology studies and will determine whether a solicitation to perform such a study is warranted.

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