Assessment of Secondary Coal Combustion Emissions: The TERESA Study

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EUEC
January 22, 2004
Primary Objective: Determine the toxicity of realistic coal combustion emissions.

Approach:

- Evaluate toxicity of secondary coal combustion emissions at multiple power plants in the U.S. by exposing laboratory rats to a variety of simulated atmospheric scenarios.

- Determine relative toxicity of coal combustion and mobile source emissions, as well as ambient PM$_{2.5}$ (concentrated ambient particles; CAPs).
Study Design

- **Primary Particles and Pollutants**
  - Mobile Chemical Laboratory
    - 2-Chamber Atmospheric Reaction Simulation System
    - Add OH•, NH₃, HC, light
    - Pollutant monitoring
  - Secondary Particles and Pollutants

- **Power Plant Stack**
  - Coal-Fired Power Plants
    - Different coal types
    - Different plant configurations
  - Mobile Toxicological Laboratory
    - Exposure chamber
    - Toxicological assessments (Stages I and II)
    - Pollutant monitoring
Background and Motivation

• **Key issue**: increase our understanding of the *sources* and *components* of air pollution responsible for health effects.

• Two sources of information exist on the health effects of coal-fired power plant PM:
  • Studies examining the health effects of *components* of coal combustion emissions (e.g., sulfate, sulfuric acid).
  • Studies examining the health effects of *coal fly ash*.
Coal Fly Ash (CFA)

- Mostly intratracheal instillation studies:
  - Reductions in antibody-forming cells in rats (Dogra et al., 1995), and total/vital capacity in guinea pigs (Chen et al., 1990), changes in lung histopathology in hamsters (Wehrer et al., 1979, 1980).
  - 2, 10, and 50 mg of CFA instilled in rats: minor differences between CFA and TiO$_2$ (negative control) groups (Arts, 1993).

- \textit{In vitro} studies: acellular OH generation and cytotoxicity in rat epithelial cells (van Maaenen et al., 1999); decreased phagocytic activity in mouse AM (Fisher and Wilson, 1980); little effect on DNA (Prahalad et al., 2000, 2001), effect seemed to be V- and Ni-mediated; some studies do show genotoxic effects.

- Few inhalation studies:
  - MacFarland et al. (1971) and Alarie et al. (1975) in monkeys and rodents: no unique biological effects from CFA exposure.
  - Rats exposed to CFA (0.6 mg/m$^3$, 4.25 mg/m$^3$) 8 h/day for up to 180 days: no effect in the low exposure group and only minor effects related to BAL macrophages in the high exposure group (Raabe et al. 1982).
  - Hamsters exposed to 2 mg/m$^3$ CFA (inhalation exposures) for 180 days: no change in surfactant properties (Nishimura and Negishi, 1995).
Coal Fly Ash (CFA): Effect of Size and Composition

• Using eastern bituminous coal, PM<2.5 was more cytotoxic and mutagenic than larger fractions, and particle size was inversely related to metal content of the ash (Mumford and Lewtas, 1982).

• CFA from bituminous coals appears to be more toxic than lignite coals (Smith et al., 2000).

• Mice exposed to CFA samples with the highest levels of metals showed the greatest effect on enhanced susceptibility to infection (Hatch et al., 1985).

• Higher metal sulfate ultrafine aerosols from a bituminous coal induced greater effects on pulmonary function in guinea pigs than a lower sulfur coal (Chen et al., 1990).

• Importance of ultrafine fraction??
Elemental Analysis of Ultrafine, Fine, and Coarse Coal Fly Ash (Gilmour et al., in press)

<table>
<thead>
<tr>
<th>Element</th>
<th>MT UF µg/g ash</th>
<th>MT &lt;2.5µm µg/g ash</th>
<th>MT&gt;2.5 µm µg/g ash</th>
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<tbody>
<tr>
<td>Si</td>
<td>28,500</td>
<td>156,742</td>
<td>222,875</td>
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<tr>
<td>Al</td>
<td>93,780</td>
<td>103,979</td>
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<tr>
<td>Ca</td>
<td>82,900</td>
<td>89,858</td>
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<tr>
<td>Fe</td>
<td>6,920</td>
<td>53,929</td>
<td>30,350</td>
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<tr>
<td>S</td>
<td>39,400</td>
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<tr>
<td>Mg</td>
<td>14,600</td>
<td>27,721</td>
<td>31,300</td>
</tr>
<tr>
<td>Ti</td>
<td>1845</td>
<td>6353</td>
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<tr>
<td>K</td>
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<td>5580</td>
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<tr>
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<td>2298</td>
<td>1843</td>
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<tr>
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<tr>
<td>Sr</td>
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<td>3426</td>
<td>3858</td>
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<tr>
<td>V</td>
<td>712</td>
<td>208</td>
<td>108</td>
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<tr>
<td>Ni</td>
<td>330</td>
<td>347</td>
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</tr>
<tr>
<td>Nb</td>
<td>910</td>
<td>176</td>
<td>22</td>
</tr>
<tr>
<td>Mn</td>
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<td>1048</td>
<td>907</td>
</tr>
<tr>
<td>Cd</td>
<td>1620</td>
<td>463</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>565</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>460</td>
<td>83</td>
<td>27</td>
</tr>
<tr>
<td>Cu</td>
<td>420</td>
<td>320</td>
<td>77</td>
</tr>
<tr>
<td>Elements %</td>
<td>22.5</td>
<td>47</td>
<td>54</td>
</tr>
<tr>
<td>Oxygen %</td>
<td>16.5</td>
<td>44.5</td>
<td>45</td>
</tr>
<tr>
<td>Carbon %</td>
<td>unknown</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Effect of Coal Fly Ash Instillation on PMN Numbers in Mouse Lungs

![Graph showing the effect of different types of particles on neutrophil (PMN) numbers](image-url)

- **Total Cell Number (x10^3)**
- **Type of Particle**
  - Saline
  - M. Coar
  - M. Fine
  - M. UF
  - WK Coar
  - WK Fine
  - Endotoxin

- **Graph Legend**
  - 25 µg
  - 100 µg

- **Statistical Notations**
  - *: Significant difference
  - **: Highly significant difference
Limitations of Coal Fly Ash Studies

• Studies using collected primary CFA (from ESPs or pilot combustors):
  • Low quantities of primary CFA are emitted from U.S. power plants
  • Populations are exposed to secondary PM.
  • Possible differences between collected particles and those that penetrate the ESPs into the ambient environment.
  • Instillation and *in vitro* studies tend to involve very high doses.
  • Possible changes in PM characteristics during storage.

• Inhalation exposure studies:
  • All studies have used pilot combustors: emissions from pilot combustors may differ from full-scale plants due to differences in surface area/volume ratios and therefore time-temperature histories.
Knowledge Gaps

- No information on the toxicity of secondary particles formed through $\text{SO}_2$ conversion in the atmosphere.
- No assessment of the toxicity of actual plant emissions.
TERESA Objectives

Primary Goal:
• Investigate and clarify the impact of the sources and components of PM$_{2.5}$ on human health via a set of realistic animal exposure experiments.

Specific Objectives:
• Investigate the relative toxicity of coal combustion emissions and mobile source emissions, their secondary products, and ambient particles.
• Assess the effect of atmospheric conditions on the formation/toxicity of secondary particles from coal combustion and mobile source emissions.
• Evaluate the impact of coal type and pollution control technologies on emissions toxicity.
• Increase understanding of toxicological mechanisms of PM-induced effects.
Plant Selection

Program currently includes 3 coal-fired plants (with additional plants planned):


2. Southeast: low sulfur (<1%) eastern bituminous coal, no scrubber for post-combustion \( \text{SO}_2 \) removal, with or without selective catalytic reduction (SCR) for NOx removal.

3. Medium-to-high sulfur (>2-3%) eastern bituminous coal, scrubbed unit, with or without SCR.
Atmospheric Reaction Simulation System

• Critical component of TERESA.
Technical Requirements

• Large, stable, and reproducible aerosol mass concentrations for animal exposures.
• Consistent size distribution across exposures.
• Sufficient flow of aerosol for exposure and characterization.
• Stable output in a short period of time.
• Secondary particles generated using typical atmospheric pathways and conditions (temperature, pressure and RH), without incorporation of compounds not present in the atmosphere.
• Aerosol components (SOA, sulfate, metals) in ratios consistent with typical average values in an aged plume.
• Low concentrations of unreacted gases (SO₂, NOx, O₃) during animal exposures.
• Small photochemical chamber for use in mobile laboratory installed in a refurbished bus.
• Minimal particle losses.
Atmospheric Reaction Simulation System

- Two-chamber design.
- Add atmospheric oxidants (OH radicals) to convert SO$_2$ and NOx in stack gas to sulfuric acid and nitric acid.

  **Chamber 1:** Designed to oxidize 20-35% of SO$_2$ to sulfuric acid with a 60-minute residence time using O$_3$ photolysis as a source of OH radicals. For some exposure scenarios, NH$_3$(gas) will be added to partially neutralize acidic sulfate particle strong acidity.

  **Chamber 2:** Designed to coat particles with SOA through addition of VOCs ($\alpha$-pinene) and ozone. Simulates the formation of SOA from the plume mixing with biogenic emissions.

- Sequential approach simplifies chemistry and avoids complex photochemical oxidation of organics.

- Novel “gas-cleaning system” (nonspecific denuder) uses a gas-permeable membrane to removal excess SO$_2$, NOx, ozone, and other pollutant gases while maintaining the secondary particles.
Dual Chamber System

Chamber 1
- UV 313 Lights
- Denuder 1
- Room Fluorescent Lights

Chamber 2
- Denuder 2
- Room Fluorescent Lights
- Dilution
- Animal Exposure

UV 313 Lights
## Exposure Scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Composition</th>
<th>Simulated Atmospheric Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gas- and particle-free air</td>
<td>Sham exposure</td>
</tr>
<tr>
<td>2</td>
<td>Primary (un-aged) emissions diluted to the range of 50 µg/m³ SO₂ using clean air (same dilution as for 3, 4, and 5 below)</td>
<td>Primary stack emissions</td>
</tr>
<tr>
<td>3</td>
<td>Primary emissions + hydroxyl radicals</td>
<td>Aged plume, oxidized stack emissions, sulfate aerosol formation from nucleation</td>
</tr>
<tr>
<td>4</td>
<td>Primary emissions + hydroxyl radicals + ammonia</td>
<td>Aged plume, sulfate aerosol partially neutralized by ammonia</td>
</tr>
<tr>
<td>5</td>
<td>Primary emissions + hydroxyl radicals + ammonia + VOCs</td>
<td>Aged plume, mixture of neutralized sulfate and secondary organic aerosol derived from biogenic emissions</td>
</tr>
</tbody>
</table>

Plus additional Control Scenario: atmospheric components only, no emissions
Exposure Characterization

- PM mass, number, size distribution (including ultrafines)
- PM components:
  - Sulfate, nitrate
  - EC/OC
  - Ammonium
  - Metals
  - Particle strong acidity
  - Selected organics (eg. PAHs)
- Gaseous pollutants:
  - CO
  - NO₂
  - SO₂
  - Ozone
  - NH₃
  - Formaldehyde
Animal Exposure and Toxicological Assessment

- Conducted in separate mobile toxicological laboratory.
- 4-hour exposures, with 1-hour baseline and recovery periods (room air).

**Stage I Assessment** (normal rats):
- Pulmonary function/breathing pattern
- *In vivo* oxidative stress via chemiluminescence
- Blood cytology (CBC/differential)
- Bronchoalveolar lavage (LDH, βNAG, total protein)
- Pulmonary histopathology

**Stage II Assessment** (rat MI model; Wellenius *et al.*, 2002):
- Telemetry: cardiac function (ECG, HR, HRV), BP, temperature
- Blood chemistry (endothelin-1, CRP, IL-1, IL-6, TNFα)
- Pulmonary function/breathing pattern
Mobile Source and CAPs Assessment

- Mobile source assessment:
  - Sample diesel and/or gasoline engines (specific age and type TBD).
  - Methods for atmospheric simulation, animal exposure, and toxicological assessment will be completely analogous to the methods used for coal combustion emissions.

- Concentrated ambient particles (CAPs):
  - Use existing data from the Harvard School of Public Health laboratory.

- Compare toxicities of the three particle sources/types.
Status and Schedule

• Laboratory/methods development work almost complete.
• Outfitting of mobile laboratories almost complete.
• Fieldwork at first plant scheduled for early March.