**Title:** **Individual Particle Analysis of Ambient $PM_{2.5}$ Using Advanced Electron Microscopy Techniques**

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## OBJECTIVE

Several epidemiological studies have shown associations between elevated mass concentrations of ambient fine particulate matter (mean aerodynamic diameter <2.5 µm; $PM_{2.5}$) and adverse health effects including respiratory and cardiovascular diseases. In particular, fossil fuel combustion has been hypothesized as the source of atmospheric $PM_{2.5}$ believed to be responsible for the observed health effects. As a result, recent studies have been focusing on the use of multiple analytical techniques to characterize particulate matter to better understand the relationship between anthropogenic emission sources and ambient $PM_{2.5}$. However, analytical techniques used to identify individual particles are currently limited, hindering determination of specific sources.

The overall goal of this project is to demonstrate a combination of advanced electron microscopy techniques that can be effectively used to identify and characterize individual particles and their sources. Specific techniques to be used include high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), STEM energy dispersive X-ray spectrometry (EDX), and energy-filtered TEM (EFTEM). These techniques enable us to provide information on the size, morphology, crystalline structure, and elemental composition of individual nano-scale particles. Although these individual techniques have not been used widely in the environmental field, their combined use results in greatly expanded utility, especially when applied to samples of low concentration.

## ACCOMPLISHMENTS TO DATE

During summer of 2005, a series of ambient $PM_{2.5}$ samples was collected in communities in southwestern Detroit, MI (close to multiple combustion sources including motor vehicle/diesel, incinerators, and oil and coal combustion sources) and Steubenville, OH (close to several coal-fired utility boilers) utilizing a recently built, state-of-the-art mobile laboratory. Gaseous air pollutants were measured continuously, including ozone ($O_3$), sulfur dioxide ($SO_2$), nitric oxides (NOx), and carbon monoxide (CO). Meteorological parameters including temperature, relative humidity, precipitation, wind speed and direction were measured to assess the day-to-day variability in local transport pathways and emission source influences.

Daily ambient $PM_{2.5}$ mass concentrations were determined from gravimetric analysis. Then, the collected samples were extracted and analyzed for a suite of trace elements using inductively coupled plasma-mass spectrometry (ICP-MS) (ELEMENT2, Thermo Finnigan, San Jose, CA). The bulk chemical composition of the samples combined with the meteorological data helped determine which sample captured any pollution episode and which major sources were likely to have impacted the sampling site.

Next, a combination of advanced electron microscopy techniques including high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), STEM energy dispersive X-ray spectrometry (EDX), and energy-filtered TEM (EFTEM) were utilized to obtain detailed information on the size, morphology, structure, and elemental composition of individual particles collected in Detroit and in Steubenville. Numerous nano-metal particles including transition metals were detected and examined in detail. HRTEM-imaging showed a series of nanocrystals, and the elemental distributions were mapped at the nanoscale. To date, fine and nano-particles with Al, Fe, Ti, Ca, U, V, Cr, Si, Ba, Mn, Ni, K and S were observed and characterized from the samples from Detroit. Among the identified nano-particles, combinations of Al, Fe, Si, Ca and Ti nano-particles embedded in carbonaceous particles were observed frequently. These particles showed very similar characteristics of ultrafine coal fly ash particles that were previously reported. Therefore, the combination of advanced electron microscopy techniques is a promising approach to obtain unique chemical signatures for source categories.

**FUTURE WORK**

For future studies, we would like to propose to couple the combination of advanced electron microscopy techniques with a recently developed Semi-Continuous Aerosol Sampling System (SEAS) for the analysis of $PM_{2.5}$. The SEAS method uses dynamic aerosol preconcentration and provides greater temporal resolution of elemental concentration in ambient air. In the semi-continuous (30 minutes) sampling intervals, enough slurry is collected to permit us to perform the individual particle analysis. Additionally, we would like to propose to collect a greater mass of nano-particles during a shorter sampling period using a recently developed Versatile Aerosol Concentration Enrichment System (VACES). The use of the particle concentrator enables us to investigate real-life ambient nano-particles at an increased level. This will help characterize the temporal chemical variability and potential sources of nano-particles in various locations.

**CONFERENCE PRESENTATIONS**

Masako Morishita, Gerald J. Keeler, James G. Wagner, Ali S. Kamal, Jack R. Harkema and Annette C. Rohr. “Associations of Chemical Composition of Ambient $PM_{2.5}$with Heart Rate Variability in Spontaneous Hypertensive Rats” To be presented at International Aerosol Conference 2006, September 10-15, 2006.