

Final Technical Report

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Center Name: University of Rochester–EPA PM Center

Center Director: Gunter Oberdorster

Title: Characterization of the Chemical Composition of Atmospheric Ultrafine Particles

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Project Period: June 1, 1999–May 31, 2005 (no-cost extension to May 31, 2006)

Period Covered by the Report: June 1, 1999–May 31, 2006

RFA: Airborne Particulate Matter (PM) Centers (1999)

Research Category: Particulate Matter

Objective(s) of the Research Project: The objectives of this Core were to provide an improved understanding of the chemical and physical nature of the ultrafine ambient aerosol. In 1999, there was relatively little data available that provides distinct information on the chemical and physical characteristic of particles in the size range <100 nm. Because of the relatively small concentrations of particle mass in this size range, sampling and chemical analysis is extremely difficult. However, such physical and chemical data provide critical information to the epidemiological and toxicological research to help guide their studies of the relationships of the ultrafine particles and adverse health effects. Initially, the focus of this Core was the development of effective methods to sample and analyze ultrafine particles. Subsequently, these methods were applied to characterize the ultrafine aerosol in a number of locations across the country to assess the variations that exist in the nature of the ultrafine particles.

Summary of Findings: In the early stage of this project, the state of knowledge of the composition of ultrafine particles was summarized by Cass, et al. (2000). The Cass/Dillner group collected ultrafine particle samples in field experiments in a south central U.S. city (Houston, TX) and in a west coast city (Riverside, CA). A cluster analysis was applied by Dillner, et al., (2005) using data from two sites in Houston, TX; one site surrounded by refineries, chemical plants, and vehicular and commercial shipping traffic, and the other site, 25 miles inland surrounded by residences, light industrial facilities, and vehicular traffic. Twenty-four hour size-segregated ($0.056 \mu\text{m} < D_p$ (particle diameter) $<1.8 \mu\text{m}$) particulate matter samples were collected during five days in August 2000. Inductively coupled plasma mass spectrometry (ICPMS) was used to quantify 32 elements with concentrations as low as a few picograms per cubic meter. Concentrations of particulate matter mass, sulfate, and organic carbon at the two sites were often not significantly different from each other and had smooth unimodal size distributions indicating the regional nature of these species. Element concentrations varied widely across events and sites and often showed sharp peaks at particle diameters between 0.1 and $0.3 \mu\text{m}$ and in the ultrafine mode ($D_p <0.1 \mu\text{m}$) that suggested the sources of these elements were local, high temperature processes. Elements were clustered to provide normalized size distributions of all elements and to yield groups of elements with similar

size distributions that were attributed to sources such as automobile catalysts, fluid catalytic cracking unit catalysts, fuel oil burning, a coal-fired power plant, and high-temperature metal working. The clustered elements were generally attributed to different sources at the two sites during each sampling day indicating the diversity of local sources that impact heavy metals concentrations in the areas around the sampling sites.

Su, et al. (2004) described the development of an improved aerosol time of flight mass spectrometry (ATOFMS) instrument to measure the chemical composition of single atmospheric particles smaller than 100 nm in particle diameter. An ultrafine particle aerosol time of flight mass spectrometry instrument has been constructed incorporating an aerodynamic lens system that allows transmission of ultrafine particles into the instrument. An effective method for detecting ultrafine particles in the systems has been developed and used in a number of ambient aerosol characterization studies including studies supported by the Center and many others. Thus, the development effort supported under this Core has led to a significant advance in ultrafine particle characterization that has broadened our understanding of their chemical composition.

To further support the field studies, Spencer and Prather (2006) used laboratory generated ultrafine particles to demonstrate the ability to quantify the amount of organic carbon (OC) on elemental carbon (EC) particles. They coated generated EC particles and developed a calibration curve that permitted the quantification of the amount of OC on EC particles. This resulting calibration curve was used to calculate the OC/EC mass fraction for particles in lab studies; field studies in Boston, San Diego, and Atlanta; and two source studies (gasoline and diesel vehicles). In addition, this calibration curve was used to show that 30% of the additional OC coating observed in particles produced by an ultrafine concentrator were being added to ultrafine particles in the concentrator (Su, et al., 2006). This change was attributed to additional gas-particle partitioning in the humidified growth region.

A study was conducted in Riverside, CA during the summer and fall of 2005. This was a large field study focused on PM_{2.5} organic aerosols. In addition to standard gas, aerosol, and PM measurements, as part of this project, ultrafine particles were measured using a UF-ATOFMS for 3 weeks during both of these studies. In addition to standard ambient sampling and characterization, ambient particles were size selected using a Scanning Mobility Particle Sizer (SMPS). The aerodynamic sizes of these particles were measured in the ATOFMS. These two sizes could be used to determine the density and shape of ambient EC particles. It was determined that most of the particles in the summer had different densities on different days and times of the day. These densities were strongly dependent on the atmospheric water content. The higher the water content, the lower the particle density. This result suggested the Riverside summer aerosol was highly processed, allowing significant uptake of water (Spencer and Prather, 2007). Spencer, et al. (2006) reported the development of a procedure to make diesel lubricating oil particles and showed how similar their ATOFMS spectra were to ambient particles from diesel vehicles.

Beginning at the end of November 2001, the number concentrations of ultrafine particles have been measured at the NYS Department of Environmental Conservation (DEC) monitoring site on the central fire station in downtown Rochester, NY. Particle size distributions are being

measured using an SMPS comprised of a differential mobility analyzer (DMA) and a condensation particle counter (CPC). In the diameter range of 10 to 500 nm, ambient particles are classified by a DMA (TSI 3071) and counted with a CPC (TSI 3010) every five minutes. This work was originally supported by the New York State Energy Research and Development Authority, but at the end of that support, we have continued this work with Center support. We have 1.5 years of data providing information on the number distributions of particles between 10 and 500 nm. In addition, the DEC site monitors SO₂, CO, PM_{2.5}, and meteorological variables. The results of this monitoring have been reported by Jeong, et al. (2004a; 2006). More than 70% of measured total number concentration was associated with ultrafine particles (UFP, 0.011-0.050 μm). Morning nucleation events typically peaking UFP number concentrations at around 8:00 were apparent in winter months with CO increases. These particles appear to be formed following direct emissions from motor vehicles during morning rush hour. There were also often observed increases in this smaller sized range particles in the late afternoon during the afternoon rush hour particularly in winter when the mixing heights remain lower than in summer. Strong afternoon nucleation events (> 30,000 cm⁻³) peaking at around 13:00 were more likely to occur in spring and summer months. During the prominent nucleation events, peaks of SO₂ were strongly associated with the number concentrations of UFP, whereas there were no significant correlations between these events and PM_{2.5} and CO. Increased SO₂ concentrations were observed when the wind direction was northwesterly where three SO₂ sources were located. It is hypothesized that UFP formed during the events are sulfuric acid and water from the oxidation of SO₂. There was also a more limited number of nucleation events followed by particle growth up to approximately 0.1 μm over periods of up to 18 hours. The nucleation and growth events tended to be common in spring months especially in April.

As part of the Core's effort to characterize the nature of PM_{2.5}, measurements of particle composition were made in Rochester, Philadelphia, and New York City that have been reported by Jeong, et al. (2004b,c) and Venkatachari, et al. (2006a,b). A major contribution of this Core has been the initiation of study of particle-bound reactive oxygen species (ROS). There is currently very limited information available on particle-bound ROS and thus, measurements in Rubidoux, CA (Venkatachari, et al., 2005) and New York City (Venkatachari, et al., 2007) suggest that there can be significant concentrations of oxidant on fine particle surfaces. Studies of the effects of the particle-bound ROS are planned for the future at the University of Rochester.

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Supplemental Keywords: NA

Relevant Web Sites: <http://www2.envmed.rochester.edu/envmed/PMC/indexPMC.html>