

Carnegie Mellon University

**Ultrafine Particles in the Atmosphere:  
Formation, Emissions and Growth**

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by

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## **Abstract**

Despite progress in controlling air pollution in the United States over the past thirty years, airborne particulate matter remains an important focus area for the public health, engineering, and scientific communities. The reason for this concern is the continuing influence of particulate matter (PM) in human health, visibility, and climate. While many aspects of particulate matter are well understood, several important areas are not. This work addresses: (1) in-situ nucleation as an important source of ultrafine (<100 nm) aerosol in the Eastern United States; (2) the formation of secondary organic aerosol; and (3) the role of relative humidity in determining aerosol size and mass. The field-based investigations were performed as part of the Pittsburgh Air Quality Study, a multi-investigator, two-year sampling study focused on characterizing particulate matter, quantifying sources, and developing and evaluating advanced aerosol monitoring techniques.

New particle formation from homogeneous nucleation is an important process in shaping the ambient aerosol size distribution. Prior research on new particle formation mainly focused on its occurrence in clean (non-urban) atmospheres. However, during the Pittsburgh Air Quality Study, new particle formation was observed on over 30% of the study days using Scanning Mobility Particle Sizers (SMPS). The field observations lead to (1) demonstration of the role of photochemical sulfuric acid in nucleation; (2) demonstration of the wide geographic scope of new particle formation; and (3) quantification of the impact of new particle formation on the regional aerosol size distribution.

An automated system to measure the amount of aerosol water at given atmospheric conditions was developed and deployed during the Pittsburgh Air Quality Study. Algorithms for data reduction were developed, including an algorithm for merging aerodynamic diameter number distributions from the Aerosol Particle Sizer with mobility number distributions from Scanning Mobility Particle Sizers. Results from this system showed observations of the water content of ambient aerosols not predicted by thermodynamic partitioning models. Specifically, during the Pittsburgh Air Quality Study, summer aerosols were almost always hydrated, even at relative humidities below 40%, while winter aerosols were not hydrated (up to relative humidities of 60%). The field results were compared with detailed equilibrium thermodynamic calculations based on measured aerosol chemistry.

Currently, our ability to accurately model the formation of secondary organic aerosol and its impact on air quality is limited by our understanding of its chemistry, gas-aerosol partitioning, and hygroscopic properties. Historically, secondary organic aerosol yields (the fraction of reacting organic precursor gas that forms aerosol) have been measured in chamber studies with temperatures from 30-35 °C and reactant concentrations from 20-500 ppb. In many locations and regions of the atmosphere, lower temperatures and reactant concentrations prevail, and parameters for these conditions are calculated by extrapolation, leading to inaccurate model calculations. Novel techniques were developed to extend the temperature range of chamber experiments beyond the typical range of 30 – 35 °C to a broader range from 15 – 40 °C. The methods rely on perturbing

laboratory generated aerosol by heating, and then measuring the rate and equilibrium extent of growth or shrinkage of the particles. Methods were demonstrated using ozone oxidation of monoterpenes such as  $\alpha$ -pinene,  $\beta$ -pinene and  $\Delta$ -carene.