

## Executive Summary

The objective of this research project was to quantify the spatial distribution of the size-resolved concentration and hygroscopicity of particulates in the Houston area. Three identical instruments were operated at the Aldine, Deer Park, and Bayland Park TCEQ monitoring sites. These measurements were coordinated with those of an array of gas and particulate properties made by other researchers supported by HARC. Specifically, the research group from Pacific Northwest National Laboratory led by Carl Berkowitz measured size-resolve particulate composition and the concentrations of gas phase  $O_3$ ,  $NO_x$ ,  $CO$ , and a range of organics, while Renyi Zhang and his research group used a proton transfer reaction mass spectrometer to make high time resolution measurements of several organic compounds. The sampling period extended from September 7th through 27th. Beyond characterization of the spatial variability and evolution of particulate concentration and properties, these measurements provide details of the liquid water content present in that particulate population, which is needed to estimate the conversion rate of  $N_2O_5$  to  $HNO_3$ , both of which were concurrently measured.

Tandem differential mobility analyzers (TDMAs) similar to those used to examine particle size distributions and hygroscopicity in the Houston area during a number of prior studies (e.g., Gasparini et al., 2004) were operated continuously at the three sites identified above. Over a period of 30-45 minutes, these instruments cycle through a fixed sequence of measurements. Each of the instruments was automatically calibrated every night and more extensive calibrations were conducted prior to, once during, and following the experiment. Confidence in the accuracy of the dataset was gained through comparison of hourly-averaged mass concentrations calculated from the size distributions measured with the TDMA and directly measured by TCEQ using TEOMS. As is evident from the measurement time series provided in this report, data collection was largely uninterrupted during the project. All measured distributions and generated products are provided graphically and in ascii format through a user-friendly project website at the URL identified in the report. The following are several salient findings from the project:

- Variability among the sites in size-resolved properties was rather limited despite the significant differences in local emissions sources. The size-dependent trend in hygroscopicity observed at each of the locations suggests the aerosol is largely an external mixture (multiple particle types present) with the more hygroscopic, sulfate-dominated, mode reaching a peak fractional contribution at roughly  $0.2 \mu m$ .
- The hygroscopicity of the  $0.05$  to  $0.4 \mu m$  diameter particles appears to vary over longer timescales, sometimes exceeding a day, while that of the smaller particles exhibits little day-to-day variability, but instead has a pronounced diurnal pattern that reflects increased importance of sulfuric acid condensation during the afternoon and of secondary organic aerosol at night.
- The impact of mobile emissions of primary aerosols during morning rush hour is evident in the size distributions of the insoluble component of the particulates determined for all three sites. The insoluble particulate concentrations then decrease during the afternoon as the boundary layer depth increases.
- Peak concentrations in the size distributions of the soluble component of the particulates are observed in mid-afternoon during peak photochemical activity. Production of secondary sulfates during this time is pronounced in the number size distributions, but has a relatively modest impact on the resulting mass concentrations.

- There is strong evidence that sea salt contributed as much as  $15 \mu\text{g}/\text{m}^3$  to the total  $\text{PM}_{2.5}$  during a multi-day episode in August, which emphasizes the importance of this often overlooked particle type in coastal regions.
- At each of the three sites, the hygroscopicity of the dominant  $0.2 \mu\text{m}$  diameter particle population was greater when the sampled air came from the south than when from the east, and greater when from the east than from the north. This variation in hygroscopicity likely reflects the organic fraction of these larger particles.
- Hygroscopic growth factor distributions for the  $0.6 \mu\text{m}$  particles indicate a significant and only weakly origin-dependent contribution of dust or some other primary particle type.

These measurements must be evaluated together with the complementary datasets generated during the TexAQS-II study period. Assessment of the ability of current air quality models to reproduce the particulate concentration and inferred composition will aid in evaluating emissions reductions needed to reduce area  $\text{PM}_{2.5}$  if Houston becomes non-compliant. Among the analyses that could improve modeling accuracy, and subsequently SIP effectiveness, are testing model predictive skill at the following:

Model prediction	Calculated from measured size and hygroscopicity distributions
Primary particulate concentration	Primary particle-only size distribution determined as product of size-resolved fraction of particles in non-hygroscopic modes from TDMA distributions and size-resolved particle concentration from DMA distributions
Contribution of sea salt to $\text{PM}_{2.5}$	Sea salt-only size distribution determined as product of size-resolved fraction of particles in very hygroscopic modes from TDMA distributions and size-resolved particle concentration from DMA distributions
Impact of condensation of secondary inorganics (primarily sulfate) and organics on particle size distribution and overall $\text{PM}_{2.5}$	Rate at which median diameter of size distribution modes increase, coupled with rate at which hygroscopicity of the particles in those modes changes
Flux of $\text{PM}_{2.5}$ across Houston metropolitan boundary	Lidar retrieved vertical $\text{PM}_{2.5}$ as determined using CALIPSO backscattering profiles and $\text{PM}_{2.5}$ to backscattering ratio calculated using size and hygroscopicity distributions