Executive Summary

The new annual National Ambient Air Quality Standard (NAAQS) for particulate matter smaller than 2.5 micrometers in diameter ($PM_{2.5}$) brings the Houston region to near non-attainment for $PM_{2.5}$, underlining the importance of understanding the composition and sources of $PM_{2.5}$ in Houston. Over half of fine PM in the Houston region is composed of organic material including primary organic aerosol (POA), which are compounds that are emitted as particles and have not reacted in the atmosphere and secondary organic aerosol (SOA), which is formed when gas-phase compounds undergo one or more chemical transformations in the gas phase, forming less volatile compounds that then partition between the gas and particle phases. Understanding the sources and formation of organic aerosol is therefore very complex, and significant uncertainties remain. In this work laboratory experiments, ambient measurements and a photochemical model were combined to better understand the sources of organic particulate matter in the Houston region.

Sixteen laboratory chamber experiments were conducted to form SOA from the oxidation of different intermediate volatility organic compounds (IVOCs). Out of the six IVOCs studied (n-pentadecane, 2,6,10-trimethyldodecane, 2-methylnapthalene, butyl CARBITOL[TM], Texanol[TM], and mineral spirits), all but Texanol[TM] formed secondary organic aerosol. SOA mass yields of 2-methylnapthalene measured in this study agreed well with literature data. A novel contribution of this work is quantification of the SOA yield from butyl CARBITOL[TM], a glycol ether used in surface coatings. The SOA yields from this compound were similar to yields from 2-methylnapthalene. The vapor pressure of SOA formed from n-pentadecane, 2,6,10-trimethyldodecane and mineral spirits was analyzed using a thermodenuder developed as part of this work. The SOA formed from mineral spirits was more volatile than the SOA formed from n-pentadecane and 2,6,10-trimethyldodecane (a branched pentadecane).

Ambient data collected during an ambient measurement campaign in Houston, TX termed Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ, http://discover-aq.larc.nasa.gov/) were analyzed focusing on the concentrations and composition of fine particulate matter. The data were obtained at an air quality monitoring ground site in Conroe, TX (30.350278°N, 95.425000°W) located approximately 60 km north-northwest from the Houston, TX urban center and approximately 125 km northwest of the nearest coastline. On average 65% of the mass of non-refractory particulate matter smaller than 1 micrometer in diameter (PM_1) was due to organic material (including organic nitrates), highlighting the importance of organics in controlling fine PM mass in the Houston region. Positive matrix factorization analysis (PMF) was applied to the organic aerosol mass spectra measured by aerosol chemical speciation monitor (ACSM). The data were best represented by two factors of oxygenated organic aerosol (OOA), a more oxidized OOA (MO- OOA) and a less oxidized OOA (LO-OOA), as well as a fresher factor representative of hydrocarbon like organic aerosol (HOA) and biomass burning organic aerosol (BBOA). According to this analysis on average 85% of the organic aerosol sampled at

Conroe consisted of oxygenated organic aerosol, highlighting the importance of atmospheric processing in influencing concentrations of organic particulate matter in the Houston region.

The Comprehensive Air quality Model with Extensions (CAMx) utilizing the 1.5 dimensional volatility basis set (1.5-D VBS) was applied to simulate organic aerosol formation in the Houston region during the 2013 DISCOVER-AQ campaign. Emissions of IVOC from major combustion sources were added using IVOC fractions of total non-methane organic gas (NMOG) emissions estimated from environmental chamber studies. The model results were evaluated against $PM_{2.5}$ filter measurements at Conroe, Moody Tower and Manvel Croix and PM_1 ACSM measurements at Conroe. The base model generally underpredicts the observed total organic carbon (OC) concentrations and PMF-estimated OOA fractions. The radio carbon analysis indicates that the base model underestimates contemporary carbon fractions while the modeled fossil carbon mass is comparable to observations.

Several improvements were made to the base model: a basis set for cooking-influenced organic aerosol was added, the organic aerosol mass yields from the reactions of monoterpenes and NO_3 were updated, the organic aerosol mass yields of IVOC precursors were adjusted, an error in the emissions of primary organic aerosol from biomass burning area sources was corrected and the formation of secondary organic aerosol from long alkane precursors (8-11 carbons) was added. The base case scenario was simulated again with the revised model. The results show that the revised model gives much better agreement than the base model with the measured OC concentrations, PMF-based OOA fractions, and contemporary carbon fractions by radiocarbon analysis.
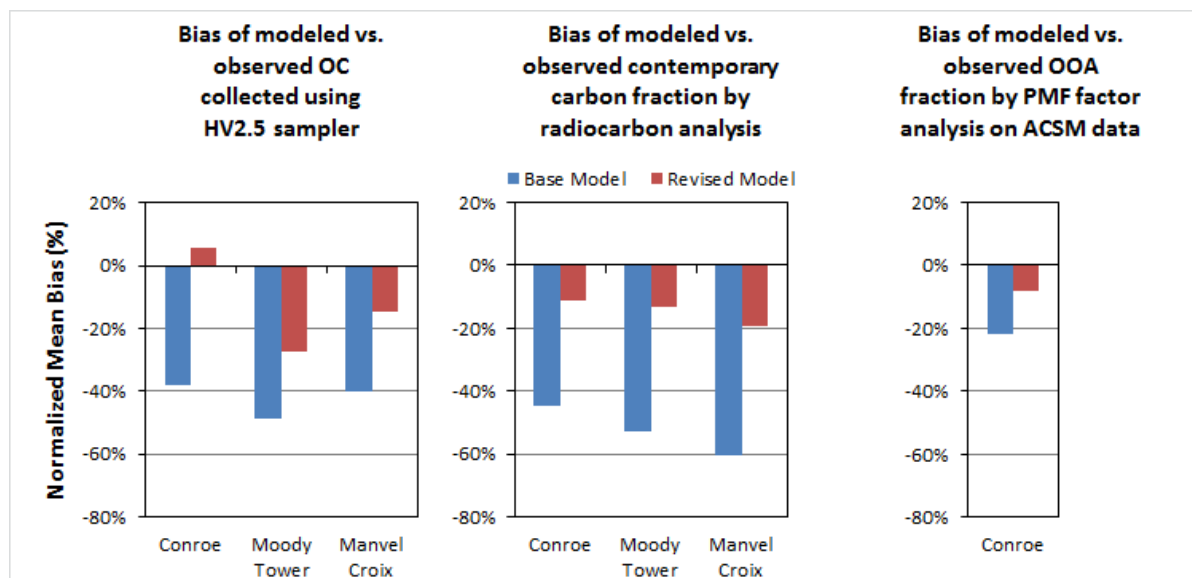
The supplemental measurements in the evaluation database (including filter OC and radiocarbon analysis data, ACSM measurements and PMF analysis) were very useful in guiding model improvements and providing a more informative evaluation. This project greatly benefited from the AQRP projects 14-024 and 14-029 that collected these data.