Executive Summary

The City of Houston, Harris County, and surrounding areas have a long history of air quality issues because of their large population, extensive industrial activity, and sub-tropical climate. These issues predominantly have been manifested through ozone (O_3) mixing ratios that exceed the National Ambient Air Quality Standards (NAAQS) established by the United States Environmental Protection Agency. However, recent measurements indicate that Harris County barely achieves compliance with the NAAQS that have been established for particulate matter (PM), specifically for particles with diameters less than or equal to 2.5 micrometers ($PM_{2.5}$).

In recent years, the National Aeronautics and Space Administration (NASA) has placed considerable emphasis on the use of satellite remote sensing in the measurement of species such as O_3 and PM that constitute air pollution. However, additional data are needed to aid in the development of methods to distinguish between low-level and high-level concentrations in these column measurements. To that end, NASA established a program titled Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ). DISCOVER-AQ began in summer 2011 with work in the Mid-Atlantic Coast region that featured satellite, airborne, and ground-based sampling; similar work was performed in California in 2012. The DISCOVER-AQ program conducted operations in and near Houston in September 2013 and in and near Denver in 2014.

During the Houston operations of DISCOVER-AQ, there was a need for ground-based measurement support. A previous project supported by this program filled that need by providing quantitative measurements of sub-micron particle size and composition and mixing ratios of photochemically relevant gases such as O_3 and oxides of nitrogen (NO_x). The instrumentation for these measurements was deployed using the University of Houston/Rice University mobile air quality laboratory. Data quality assurance/control and preliminary data analyses were performed as part of the original project.

More advanced data analyses have been performed as part of the current project, and results from these analyses are included in this report. These analyses focused on source-specific quantification of PM emissions in a size- and chemically resolved manner, identification of large but short-lived PM events, assessment of the diurnal and spatial distribution of PM in Houston, estimation of the relative oxidation state of organic PM, investigation of the secondary processes that influence PM in Houston, determination of the roles that biogenic volatile organic compounds play in Houston air quality, comparison of *in situ* surface and column airplane and satellite nitrogen dioxide measurement techniques, and photochemical zero-dimensional modeling of O_3 and radical production.

Key findings of this project include the following:

- Motor vehicular emissions distributed between light-duty, heavy-duty, and gasoline vehicles cause enhancements in organic PM of up to 70 $\mu g \ m^{-3}$ based on emission factors that range from 0.14 to 13.74 grams per mile driven. This PM tends to be relatively chemically reduced;
- Biomass burning events lead to enhancements of organic PM up to 100 $\mu g \ m^{-3}$;

this material also is relatively chemically reduced;
- Petrochemical facilities, in contrast (at least those sampled here) lead to increases in sulfate aerosol;
- The amplitudes and exact timing of PM constituent diurnal profiles vary by location. Nitrate increases at night, sulfate and ammonium co-vary, and organic PM increases significantly during rush hour and only moderately in the afternoon;
- When averaged spatially across the sampling domain, the relative importance (on a mass basis) of specific PM constituents decreases in the following order: organic PM, sulfate, ammonium, nitrate, and chloride.
- With respect to extent of oxidation, organic PM upwind of the city tends to be the most relatively oxidized and that near downtown the least. Downwind oxidation levels are intermediate between the two extremes despite having the highest apparent levels of secondary organic aerosol.
- Sulfate aerosol appears to be driven by regional, as opposed to local, processes, with ammonium concentrations appearing to be driven by those of sulfate;
- Local organic PM processes appear to be governed by nitrate radical oxidation of monoterpenes without the need for liquid water to take up products;
- Isoprene chemistry impacts significantly O_3 formation, which is driven by nitric oxide reactions with (in order) hydroperoxy radicals, non-methyl organic peroxy radicals, and methyl organic peroxy radicals; O_3 termination is driven by the formation of nitric acid; and
- The quality of nitrogen dioxide column and *in situ* measurement comparisons varies depending on selection of spatial resolution and vertical mixing parameters.