Spatial and temporal resolution of primary and secondary particulate matter in Houston during Deriving Information on Surface conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality (DISCOVER-AQ)

Executive Summary

This project builds on a previously-funded Air Quality Research Program (AQRP) project which characterized initial elemental carbon (EC) and organic carbon (OC) particulate matter (PM) during DISCOVER-AQ (Deriving Information on Surface conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality) Houston Texas 2013 (AQRP 12-032). The overall goals of the current project were to quantify the strength of PM formation and PM emission sources across the Houston metropolitan area. This was accomplished using samples collected over the DISCOVER-AQ sampling period at two primary sites in Houston: Moody Tower (downtown; urban) and Manvel Croix (southern; suburb); and two auxiliary sites: Conroe (far north; suburb) and La Porte (east; urban industrial). The detailed chemical characterization included elemental carbon (EC) and organic carbon (OC), radiocarbon, water soluable OC (WSOC), organic and elemental tracers and inorganic ions. A majority of the analysis focused on samples collected during 9/21/13-9/28/13 at the two primary and two auxiliary sites, which included a period of high ozone concentrations (9/25/13).

For the OC and EC, there were several trends for the September 2013 campaign. The maximum OC concentration for all four sites occurred between 9/24-9/26, which coincided with the peak ozone concentration on 9/25 in Houston. The maximum EC concentration at Conroe and La Porte was also 9/25-9/26. However, the maximum EC concentration at Moody Tower and Manvel Croix was 9/12-9/13. OC had higher correlation among sites than EC when comparing within the Baylor sites and between Baylor and TCEQ monitoring sites. For the remaining bulk species (WSOC and inorganic ions) there were the following trends during the September 2013 campaign. WSOC concentrations were strongly correlated with OC for all four sites with r^2 near 0.9. Conroe had the highest fraction of WSOC ranging from 40-80%. Manvel Croix and Moody Tower were lower with a range of 30-70%, while La Porte had the lowest fraction at 30-55%. Of Moody Tower, Manvel Croix, and Conroe, the highest consistent concentrations of sulfate were measured at Conroe for September 2013. Trace metals were measured at Moody Tower with 24 h samples. A few metals had consistent detectability, including Fe, which had a monthly average of 0.11 +/- 0.09 $\mu g/m^3$, Zn, which had a monthly average of 0.11 +/- 0.14 $\mu g/m^3$, and Na, which had a monthly average of 1.6 +/- 1.25 $\mu g/m^3$. A number of non-combustion based organic tracers were detected in PM samples from all four sites including current-use pesticides, flame retardants, and plasticizers. For example, Permethrin, a commonly used mosquitocide, was detected in 100% of PM samples analyzed at all four sites (week of September 21-

28) with concentrations ranging from 0.025 to 60 ng/m^3. In addition four current-use pesticides, malathion, bifenthrin, λ-cyhalothrin, and chlorothalonil were frequently detected at all four sites. Organophosphate ester (OPEs), an emerging contaminant, were detected at all four sites. ΣOPEs atmospheric concentrations ranged from 160 pg/m^3 to 3400 pg/m^3.

Source apportionment of PM during the week of 9/21-9/28 was accomplished used radiocarbon combined with organic tracer-based chemical mass balance modeling (CMB). The radiocarbon apportionment effectively constrained the CMB results to provide estimation of both primary and secondary contributions to total organic carbon (TOC). The end results indicated that Moody Tower (a site indicative of urban Houston) had a consistent primary motor vehicle exhaust contribution (18-27%) and a fossil secondary organic aerosol (SOA) contribution that varied from 5-33% depending on atmospheric condition. Conroe (a site indicative of aged urban aerosol combined with biogenic contributions) had a lower contribution of motor vehicle exhaust (5-10%) and a similarly variable fraction of fossil SOA (4-25%). Manvel Croix (a site indicative of residential Houston area) had an interim motor vehicle contribution (9-15%) with a variable fossil SOA (5-30%). For contemporary OC, there was minimal wood smoke contribution during the examined week (0-9% at all sites) except one La Porte total suspended particulate matter (TSP) sample which had 16% wood smoke contribution. This indicates that wood smoke is an event-based contribution for summer in Houston at the urban sites. However, the biogenic SOA was a large contributor at all sites; this ranged from 40-75% at Moody Tower, 56-81% at Manvel Croix and 60-79% at Conroe. In summary, the motor vehicle contribution was consistent at each site during the analysis week, the biogenic SOA was consistently high, while the fossil SOA showed the most variability and dependence on atmospheric conditions.