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EXECUTIVE SUMMARY

Scientific Objective

Particulate matter plays an important role in the formation and transformation of ozone (O₃). Although photooxidation of volatile organic compounds (VOCs) with respect to ozone formation in the gas phase is well understood, many unknowns still exist in heterogeneous mechanisms that process soot, secondary aerosols (both inorganic and organic), and key radical precursors such as formaldehyde (HCHO) and nitrous acid (HONO). This project, H105, aims to investigate the following science questions:

- What are the particle properties in Study of Houston Atmospheric Radical Precursors (SHARP) campaign? What is the role of free radicals in particle formation, particularly secondary aerosol?
- What is the role of free radicals (e.g. hydroxyls) and strong oxidants such as ozone in primary and secondary aerosol formation?
- How do radical precursors such as HONO and HCHO affect aerosol growth and transformation?
- What mechanisms drive the day- and night-time heterogeneous chemistry during ozone and highly reactive hydrocarbons events?

Answers to these questions are needed to understand the effect of PM on O₃ cycling, air quality, and public health in Houston.

The field data collected in the 2009 SHARP study by our group (project H105) at the Moody Tower consist of 1) radiometer data to estimate local photolysis rates, 2) instantaneous Lasair particle size distributions, 3) an archive of single particle samples taken with the TRAC sampler, and 4) hourly organic carbon (OC) and elemental carbon (EC) measurements. The time resolution of the TRAC sampler is 30 minutes for routine measurements, and 15 minutes during identified “events” (usually in the mid-afternoon) of high ozone and secondary organic or sulfate particle formation. The latter events last typically about an hour. Other groups have much time-resolved data on gaseous species and radical precursors that we can correlate with.

Status of Deliverables

The following deliverables are stated in our Statement of Work (SOW) at the inception of this project, H105. The status of each deliverable is reported here.

1. Battelle Northwest Division (Battelle thereafter for brevity) delivered a letter report describing the QA/QC plans for instruments to be deployed prior to the campaign. This plan was submitted to HARC two months before the deployment so as to allow time for discussion and resolution of issues on this important activity.
2. The DRAFT Final Report was turned in 30 days prior to the final report to allow HARC two weeks to review, and Battelle two weeks to complete the Final Report based on comments. The final report contains preliminary time series of OC and EC from the Sunset OCEC field analyzer, particle size distribution from the Lasair, $J(\text{NO}_2)$ and $J(\text{HCHO})$, or $J(\text{HONO})$ from the two Metcon radiometers.
3. Preliminary analysis of several samples (< 5) collected by TRAC during high radical precursor events for the report including particle number concentration, size distribution, and morphology (shape). Detailed chemical analysis of archived particles of interests will have to be conducted in follow-up studies, because they cannot be carried out with the resources requested in this proposal. A couple of samples collected by TRAC were analyzed. Some discussion associated with these samples is reported. The details are seen in the next section.

We successfully deployed a suite of measurements during the SHARP campaign: 1) spectral measurements of $J(\text{NO}_2)$, $J(\text{HCHO})$, and $J(\text{HONO})$ by two Metcon spectrometers; 2) particulate matter characterization including size, composition, morphology, mixing state, hygroscopicity, and reactivity by a Battelle Time-Resolved Aerosol Collector, TRAC, (Laskin et al., 2003). This instrument collects individual aerosol samples for post-campaign analysis using a wide variety of state-of-the-art tools within the Environmental Molecular Sciences Laboratory; 3) semi-continuous organic and elemental carbon, OC and EC, by a Sunset OCEC field analyzer; and 4) continuous particle size distribution by a Lasair system.

Table 1. The Battelle Instruments deployed in the 2009 SHARP Campaign.

Instrument	Quantity measured	Additional information	Location	Sample Resolution	Sample Duration	
$J(\text{NO}_2)$ radiometer	$4\pi J(\text{NO}_2)$	Side-by-side comparison with the $J(\text{NO}_2)$ of UH	Moody Tower	1 s	5/11/09 5/30/09	–
Actinic flux spectrometer	$2\pi J(\text{HCHO}) / 2\pi J(\text{HONO})$	Various locations by the mobile platform	Aerodyne Research Vehicle	2 min	4/22/09 5/29/09	–
Sunset OCEC Analyzer	EC and OC hourly	EC 1 min	Moody Tower	1 hr	4/16/09 5/31/09	–
TRAC	≥ 1 min archived particles	Single particle information for post-campaign analysis. 30 min	Moody Tower	30 min	4/16/09 5/31/09	–
Lasair	Size distribution, $< 2 \mu\text{m}$	Particle number concentration	Moody Tower	14 s	4/16/09 5/31/09	–

The summary of Battelle Northwest Division (Battelle, hereafter) measurements is listed in Table 1. The operation principles and data quality assurance and control plan is detailed in Appendix A.

Daily updates of preliminary data series of Sunset OCEC field analyzer and Lasair were provided for comparison with other participants during the SHARP campaign. These data traces are summarized and reported in the preliminary results section. The preliminary photolysis rates of $J(\text{NO}_2)$, $J(\text{O}^1\text{D})$, $J(\text{NO}_3)$, $J(\text{HONO})$, $J(\text{H}_2\text{O}_2)$, and $J(\text{HCHO})$ collected in the campaign are also presented. More in-depth analysis is warranted to gain understanding of photolysis of free radical precursors such as formaldehyde and HONO and its role in the formation of ozone and particulate matter.

Relevance to the Future Investigations Determined by the Science Advisory Committee

This project (H105) is clearly identified as one of contributors to solve the science question of **Reactive Nitrogen Reservoirs**, namely, to provide the missing piece of multi-phase chemistry leading to the production of HONO on particulate or urban canopy surfaces in the SIP model. In addition, we can provide scientific insight to issues related to organic nitrates, i.e., studying reactions of VOCs with daytime NO_x or nocturnal NO_3 to see if organic nitrates were produced, which may lead to local or downwind renoxification.

H105 also looks into the **Radical Budget** issue, where laboratory studies can be conducted to study HCHO production from ozonolysis of olefins, and evaluate if this route is underestimated at night. This approach can be coupled with single particle analysis and observations of VOCs and HCHO during the campaign to narrow down the cases of interest and reduce uncertainties.

Moreover, data collected in this project can provide solutions to address questions in the category of **Control Strategy Assessment**. We can provide further analysis of emission and ambient events observed during the SHARP campaign. The TRAC particle analysis is particularly suitable for this application. Since markers of emission sources such as heavy metals can be identified using ESEM/XRD analysis, we can provide insight to the point or area sources, which is needed to reduce both local ozone formation and exports of pollution to downwind areas of East Texas.

Preliminary Analysis Results

The preliminary photolysis rates of $J(\text{NO}_2)$, $J(\text{O}^1\text{D})$, $J(\text{NO}_3)$, $J(\text{HONO})$, $J(\text{H}_2\text{O}_2)$, and $J(\text{HCHO})$ collected in the campaign are also presented. More in-depth analysis is warranted to gain understanding of photolysis of free radical precursors such as formaldehyde (HCHO) and nitrous acid (HONO) and its role in the formation of ozone and particulate matter.

- The averages and ranges of OC, EC, and TC are comparable to earlier observations in the early 2000s (Allen, 2004).
- The ratio of OC to EC (OC:EC) can be used to analyze secondary vs. primary organic carbon aerosols. The preliminary analysis of the OCEC data suggests the average OC:EC is 6.9, which indicates that secondary organic aerosols are a component in the carbonaceous aerosols observed in Houston.
- When compared with ozone measurements, OC usually peaked at the same time when an ozone event took place. An ozone event is defined when ozone exceeds 75 ppb according to the new Environmental Protection Agency's (EPA) State Implementation Plan (SIP).
- Five ozone days were identified by the Texas Consortium of Environmental Quality (TCEQ) between April 15, 2009 and May 31, 2009: April 21, 2009, May 4, 2009, May 20, 2009, May 29, 2009, and May 30, 2009. All our measurements were operating during these events. Of particular interests are those particulate samples collected by our TRAC sampler during these peak ozone hours, as they can provide insights to the heterogeneous reactions driven by photoactivity and strong oxidants including hydroxyl radicals and ozone.
- The average EC is fairly low over the whole sampling period. This is also comparable with previous observations (Allen, 2004). The 1min EC data for most of the sampling time can also be provided by our measurements. This can be very useful information to investigate how elemental carbon acts as reaction medium for free radical formation such as HONO, which can potentially be an avenue to increase ozone production, therefore important in the overall SIP attainment strategy.
- The Lasair particle spectrometer was used to determine particle size distribution in 0.1 – 0.2 μm , 0.2 - 0.3 μm , 0.3 – 0.4 μm , 0.4 – 0.5 μm , 0.5 – 0.7 μm , 0.7 – 1.0 μm , 1.0 – 2.0 μm , and > 2.0 μm . Particle mass loadings of each size can be derived assuming particle density and geometry. This data set provides almost complete coverage of particle size measurements over the campaign. One of the items to ensure data quality is that we will look into the data between May 8 and May 12 especially for the larger sizes. The mass loadings seem to be markedly low compared to the rest of the campaign.
- Preliminary analysis of photolysis rates of $J(\text{NO}_2)$, $J(\text{O}^1\text{D})$, $J(\text{NO}_3)$, $J(\text{HONO})$, $J(\text{H}_2\text{O}_2)$, and $J(\text{HCHO})$ indicate that these measurements were conducted properly. Distinctive diurnal patterns were observed. Follow up analysis in relation to ozone production and secondary particulate matter formation will provide more insights to free radical sources and sinks.
- Based on SEM/EDS analysis, the primary particles seem to contain sulfate or ammoniated sulfate salts, i.e., ammonium bisulfate or ammonium sulfate. Sulfate particles sometimes are also mixed with sodium or titanium, the latter are possibly from dust. Sea salts are major contributors of these particles. However, these sea salt particles do not appear to have the same mixing state. These particles tend to be larger, i.e. > 1 μm . Although we generally call these sea salt particles, they differ in their shapes and compositions. For

instance, among the particles identified as sea salt, a variety of other chemical components are seen. These include, sodium chloride (NaCl) mixed with silicon oxide (SiO₂), NaCl mixed with magnesium chloride (MgCl₂), NaCl mixed with sulfate (SO₄²⁻), NaCl mixed with MgCl₂ and SO₄²⁻, NaCl mixed with SiO₂ and SO₄²⁻, NaCl mixed with MgCl₂ and SiO₂, and NaCl mixed with MgCl₂, SiO₂, and SO₄²⁻. Silicon oxide based particles are another group of particles observed quite frequently in Houston. These include pure SiO₂, SiO₂ mixed with aluminum oxide (Al₂O₃), SiO₂ mixed with magnesium oxide (MgO), SiO₂ mixed with magnesium and sulfate, SiO₂ mixed with sodium and magnesium, SiO₂ mixed with NaCl and MgCl₂. In addition, we have observed potassium particles. Potassium (K) is considered a marker of biomass burning.

- Based on the limited initial TEM/EDS analysis reported above, five types of particles are observed including 1) sulfate (primary and secondary); 2) mineral dust; 3) soot; 4) sea salt; and 5) mixed sulfate and sea salt. However, as we have already learned from the SEM/EDS analysis, these particles in each type are not the same. They vary in their composition, size, shape, morphology, and mixing state.
- We observed primary sulfate and secondary sulfate particles. The composition of primary sulfate is much simpler compared to that of secondary sulfate. Primary sulfate particles are usually smaller in size, and their shape is also cylindrical. Their chemical compositions may be sulfate or sulfate with inclusion of other metal elements. Silicon, sodium, magnesium, potassium, calcium are all seen to occur with these smaller sulfate particles. In contrast, secondary sulfate has a wide range of shape, size, and morphology. In addition to sulfate, secondary aerosols contain silicon, iron, cobalt, aluminum, potassium, molybdenum, lead, cadmium, zinc, chromium, gold, sodium, magnesium, and calcium.
- We have also observed mineral dust type of particles, where little or no sulfur exists. They have diverse shape, size, and morphology. Their chemical compositions may include iron, aluminum, gold, molybdenum, sodium, magnesium, calcium, potassium, silicon, titanium, chromium, molybdenum, and gold. Some lighter elements are also seen including oxygen, sulfur, chlorine, and phosphor.
- As to soot particles, they may exist on its own or coexist with sulfate or other particles as an inclusion. Sometimes they appear as a cluster of spheres, yet with a wide range of shape and morphology. Their chemical composition differs. In addition to carbon, silicon, aluminum, potassium, or molybdenum is also seen.
- As to sea salt particles, many of them retained their cubic shape to certain extent. They tend to be bigger particles, i.e. > 1 μm. Other components are often accompanying including potassium, iron, magnesium, aluminum, iron, gold, molybdenum, silicon, or calcium.
- In addition, we have observed mixed sea salt and sulfate particles. These may be not well-mixed or well-mixed. They differ significantly in their shape, size, and morphology. Other than sulfate and sodium chloride, other observed components are magnesium, potassium, calcium and silicon.